

SEMAINE D'ETUDE
SUR
LES FORCES MOLECULAIRES

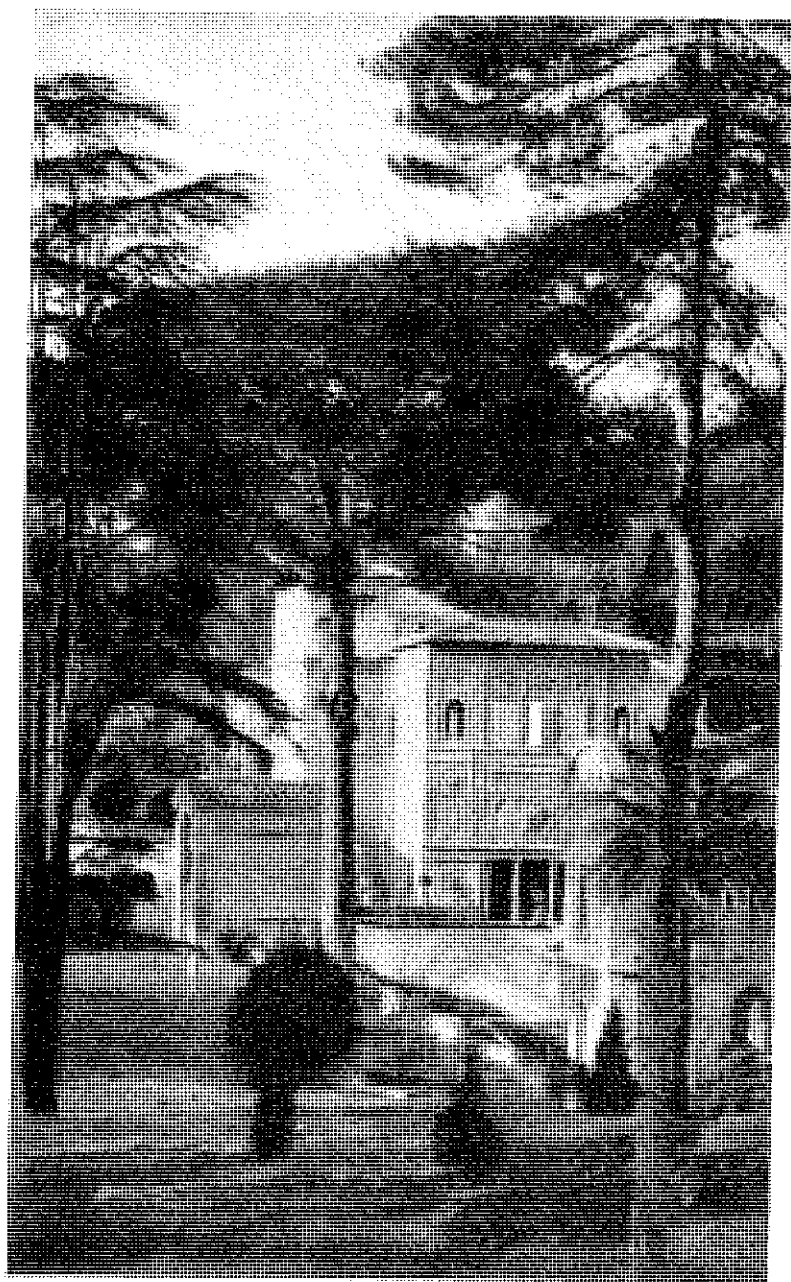
18-23 avril 1966



PONTIFICIA
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MCMLXVII



STUDY WEEK
ON
MOLECULAR FORCES

april 18-23, 1966



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MIA SCIENTIARVM - CITTÀ DEL VATICANO

LES FORCES MOLECULAIRES

On est généralement d'accord sur le fait que les forces entre molécules sont d'origine électromagnétiques, qui entourent les molécules mêmes, dans leur interaction avec les charges dans chacune d'elles et provoquant ainsi une distortion dans leur distribution.

Il est clair aussi que les interactions doivent être décrites en suivant les règles de la mécanique ondulatoire.

En retenant ce point comme point de départ général, au cours de la Semaine d'Etudes sur « Les forces moléculaires », on a discuté la détermination expérimentale des moments de la distribution des charges qui sont responsables du champ électromagnétique entourant une molécule aussi bien que les preuves expérimentales de la nécessité de la mécanique ondulatoire pour une description de l'interaction des molécules dans les faisceaux moléculaires.

Ensuite on a considéré les plus récents développements de la théorie de l'interaction, c'est-à-dire on a examiné la généralisation de la théorie bien connue de London, surtout en ce qui concerne les interactions du type magnétique et relativistique.

Sur le même sujet, une discussion a suivi sur les problèmes des forces macroscopiques de van der Waals à grandes distances, de l'ordre de la longueur d'onde de la lumière visible et au sujet de l'effet dû au retard comme résultat de la vitesse limitée de propagation de la radiation électromagnétique.

La discussion théorique étant ainsi terminée, on a examiné les résultats expérimentaux au sujet des forces de van der Waals entre plaques à distance de l'ordre de la longueur d'onde de la lumière visible, et d'autres preuves expérimentales d'un autre type mais sur le même sujet.

Entre autres, on a discuté l'équilibre en films liquides très minces comme moyen pour étudier les forces de van der Waals à distances raccourcies; l'importance des interactions de van der Waals dans la chimie des colloïdes. La compréhension de la stabilité ou instabilité des suspensions colloïdales a été aussi soulignée.

Finalement on a fait une analyse des forces moléculaires dans l'état cristallin solide.

Au cours des dernières années, on a prêté beaucoup d'attention à la compréhension de la structure des liquides et surtout aux effets particuliers qui se présentent près du point critique.

Dans ce domaine on a examiné les preuves expérimentales concernant la diffusion de la lumière et des rayons X près du point critique; tandis que les corrélations de « range » remarquablement long ainsi que leur corrélation avec les forces moléculaires de « range » court ont été discutées du point de vue théorique.

L'état liquide même et sa constitution, surtout dans les liquides à molécules simples, ont été discutés d'un point de vue théorique et en soulignant le comportement aux alentours du point critique.

La discussion sur les forces moléculaires et la distortion de la structure des molécules par « absorption », qui a une importance tout à fait fondamentale pour la chimie de la catalyse hétérogène, a été introduite du point de vue expérimental.

Il a été important dans ce domaine d'écouter autant d'opinions diverses sur le sujet qu'il y a d'écoles nationales.

En même temps beaucoup de problèmes se présentent en ce qui concerne notre compréhension de l'origine des forces moléculaires dans les sciences biologiques.

La présence d'éminentes personnalités qui sont des experts dans le domaine, a apporté sans doute une contribution essentielle au sujet même.

Dans ce domaine il y a donc eu une revue expérimentale de l'influence de la configuration et de l'interaction moléculaires dans certains problèmes en biologie; une discussion sur l'importance de la liaison hydrogène en biologie d'un point de vue uniquement théorique et une revue sur plus large base des forces moléculaires dans les systèmes biologiques.

PIETRO SALVIUCCI

Chancelier de l'Académie

LA SEMAINE D'ETUDE
SUR
LES FORCES MOLECULAIRES

Le but des « Semaines d'Etude » de l'Académie Pontificale des Sciences a été ainsi défini par son premier Président, S.E. le Rév.me Père AGOSTINO GEMELLI O.F.M.

« Tandis qu'on fixait, après sa fondation, les travaux de l'Académie, un problème se présenta bien vite avec évidence: les sciences posent chaque jour des problèmes nouveaux qui donnent lieu d'ordinaire à divers essais de solution, souvent contradictoires. Il arrive ainsi constamment que parmi les représentants les plus autorisés d'une science et, en particulier, entre ceux qui se sont consacrés à l'étude d'une même question, on rencontre des opinions opposées. De pareilles divergences se maintiennent parfois pendant de longues périodes et constituent à la fois une grave difficulté pour l'enseignement des sciences et fréquemment aussi un obstacle considérable à leur développement. D'ailleurs, l'expérience montre que les méthodes actuellement pratiquées dans la discussion des problèmes scientifiques, n'ont qu'une efficacité limitée au point de vue de l'établissement d'une unité de doctrine. Il serait hautement souhaitable de promouvoir tout ce qui pourrait favoriser une entente sur les points en discussion.

« Un tel procédé semble devoir être particulièrement utile sous ce rapport: savoir établir des contacts personnels prolongés entre quelques représentants d'opinions différentes au sujet d'une question déterminée ».

Dans ce but, l'Académie Pontificale des Sciences a réalisé une nouvelle « Semaine d'Etude » ayant pour titre: « Les forces moléculaires » (1).

Bien que ces derniers temps un travail intense ait été fourni sur les divers aspects de ce problème, il restait cependant quelques questions de détail à résoudre, et de nouvelles questions s'étaient de plus posées pendant ces dernières années.

Etant donné qu'on n'avait pas encore provoqué un débat approfondi à ce sujet et que le moment semblait propice pour le faire, l'Académie Pontificale des Sciences s'est proposée de réunir un nombre restreint de savants spécialistes de la question. Son but était de recueillir, au cours d'une discussion approfondie, les synthèses des nombreuses recherches effectuées dans ce domaine; de formuler clairement l'état des différents problèmes qui s'y rapportent; et par là de pouvoir fixer les directives de recherche les plus logiques, les plus persuasives et les plus prometteuses, étant donné l'état actuel de la science.

(1) Cette « Semaine d'Etude » sur « Les forces moléculaires » est la neuvième de la série.

La première « Semaine d'Etude » a eu lieu du 6 au 13 juin 1940; elle a été dédiée au « Problème biologique du Cancer », et a été présidée par l'Académicien Pontifical S.E. PIETRO RONDONI, Professeur de Pathologie Générale et expérimentale à l'Université de Milan; y ont participé personnellement 15 savants tandis que 3 autres ont envoyé des mémoires. Les comptes-rendus de la « Semaine d'Etude » ont été publiés dans le 7ème volume des « Scripta Varia » de l'Académie; ils représentent un volume de 364 pages.

La deuxième « Semaine d'Etude » a eu lieu du 19 au 26 novembre 1951; elle a été dédiée au « Problème des Microséismes », et a été présidée par l'Académicien Pontifical S.E. FRANCESCO VERCELLI, Directeur de l'Institut Thalassographique et de l'Observatoire Géophysique de Trieste; y ont participé personnellement 15 savants tandis que 4 autres ont envoyé des mémoires. Les comptes-rendus de la « Semaine d'Etude » ont été publiés dans le 12ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 466 pages.

La troisième « Semaine d'Etude » a eu lieu du 24 avril au 2 mai 1955; elle a été dédiée au « Problème des Oligoéléments dans la vie végétale et animale », et a été présidée par l'Académicien Pontifical S.E. JOSÉ MARIA ALBAREDA HERRERA, Directeur de l'Institut de Pédologie et de Physiologie

A cet effet ont été invités par l'Académie des experts qualifiés en physique, en physico-chimie, en géodesie, en chimie-théorique et en leurs différentes applications, qui, grâce à ces études spécifiques, ont contribué à la connaissance des plus récents développements sur le problème des forces moléculaires.

La présidence de cette « Semaine d'Étude » sur « Les forces moléculaires » a été confiée par le Président de l'Académie Pontificale des Sciences, S.E. le Rév.me Monseigneur GEORGES LEMAÎTRE, à l'Académicien Pontifical S.E. PIETER DEBYE, Président du Department of Chemistry de la Cornell University de Ithaca, N.Y., et l'organisation générale au Chancelier de l'Académie Pontificale des Sciences Dr. PIETRO SALVIUCCI.

Malheureusement l'Académicien PIETER DEBYE n'ayant pu être présent en raison de son état de santé, la Semaine d'Étude a été

végétale de l'Université de Madrid, Secrétaire Général du Conseil Supérieur des Recherches Scientifiques d'Espagne; y ont participé personnellement 19 savants tandis qu'un autre a envoyé un mémoire. Les comptes-rendus de la « Semaine d'Étude » ont été publiés dans le 14ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 630 pages.

La quatrième « Semaine d'Étude » a eu lieu, du 20 au 28 mai 1957; elle a été dédiée au « Problème des Populations stellaires », et a été présidée par l'Académicien Pontifical Surnuméraire le Rev.me Père DANIEL J. K. O'CONNELL, Directeur de la « Specola Vaticana » de Castelgandolfo; y ont participé personnellement 21 savants. Les comptes-rendus de la « Semaine d'Étude » ont été publiés dans le 16ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 615 pages.

La cinquième « Semaine d'Étude » a eu lieu du 23 au 31 octobre 1961; elle a été dédiée au « Problème des macromolécules d'intérêt biologique avec référence spéciale aux nucléoprotéides », et a été présidée par l'Académicien Pontifical S.E. ARNE TISELIUS, Professeur de Biochimie à l'Université de Uppsala; y ont participé personnellement 28 savants. Les comptes-rendus de la « Semaine d'Étude » ont été publiés dans le 22ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 544 pages.

La sixième « Semaine d'Étude » a eu lieu du 1 au 6 octobre 1962; elle a été dédiée au « Problème du rayonnement cosmique dans l'espace inter-planétaire », et devait être présidée par l'Académicien Pontifical S.E. VICTOR FRANCIS HESS, Professeur émérite de Physique à l'Université Fordham

présidée par l'Académicien Pontifical S.E. SAN-ICHIRO MIZUSHIMA, Professeur émérite de Chimie à l'Université de Tokyo et Directeur de l'Institut des Recherches scientifiques « Yawata ».

Ont été invités à la réunion les savants suivants:

Prof. Dr. RICHARD BARRY BERNSTEIN, Professeur de Chimie physique à l'Université de Wisconsin, Président de la Section de Chimie Physique de l'Américan Chemical Society. - *Madison, Wisc. (U.S.A.)*.

S.E. Prof. Dr. GIOVANNI BATTISTA BONINO, Académicien Pontifical, Professeur titulaire de Chimie à l'Université de Gènes. - *Gènes (Italie)*.

de New York; malheureusement l'Académicien VICTOR FRANCIS HESS n'a pas pu, en raison de son état de santé, être présent et la « Semaine d'Etude » a été présidée par l'Académicien Pontifical S.E. GEORGES LEMAITRE, Professeur de Mécanique et de Méthodologie mathématique à l'Université de Louvain et Président de l'Académie. Y ont participé personnellement 24 savants. Les comptes-rendus de la « Semaine d'Etude » ont été publiés dans le 25ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 574 pages.

La septième « Semaine d'Etude » a eu lieu du 7 au 13 octobre 1963; elle a été dédiée à « Le rôle de l'analyse économétrique dans la formulation de plans de développement », et a été présidée par l'Académicien Pontifical S.E. MARCELLO BOLDRINI, Professeur de Statistique à l'Université de Rome; y ont participé personnellement 18 savants. Les comptes-rendus de la « Semaine d'Etude » ont été publiés dans le 28ème volume des « Scripta Varia » de l'Académie; ils forment une oeuvre de 1260 pages en deux volumes.

La huitième « Semaine d'Etude » a eu lieu du 28 septembre au 3 octobre 1964; elle a été dédiée au « Cerveau et expérience consciente », et a été présidée par l'Académicien Pontifical S.E. Sir JOHN CAREW ECCLES, Professeur de Physiologie à l'Université de Canberra; y ont participé personnellement 18 savants. Les comptes-rendus de la « Semaine d'Etude » ont été publiés dans le 30ème volume des « Scripta Varia » de l'Académie; ils forment un volume de 885 pages.

L'organisation générale de chaque « Semaine d'Etude » a été confiée au Chancelier de l'Académie Pontificale des Sciences, le Dr. PIETRO SALVIUCCI. Toutes les réunions se sont tenues au Siège de l'Académie à la « Casina di Pio IV » dans le Jardins du Vatican.

Prof. Dr. FRANK PHILIP BOWDEN, Professeur de Physique de Surface au Cavendish Laboratory de Cambridge, Professorial Fellow au Gonville and Caius College de Cambridge. - *Cambridge* (Grande-Bretagne).

Prof. Dr. AMYAND DAVID BUCKINGHAM, Professeur de Chimie Théorique à l'Université de Bristol. - *Bristol* (Grande-Bretagne).

Prof. Dr. HENDRIK BRUGT GERHARD CASIMIR, Professeur extraordinaire de Physique à l'Université de Leyde, Membre du Conseil de Direction de la N. V. Philips's Gloeilampenfabrieken. - *Eindhoven* (Pays-Bas).

S.E. Prof. Dr. CARLOS CHAGAS, Académicien Pontifical, Professeur de Biophysique à la Faculté de Médecine et Directeur de l'Institut de Biophysique de l'Université du Brésil. - *Rio de Janeiro* (Brésil).

Prof. Dr. BENJAMIN THOMAS PENG NIEN CHU, Professeur Associé de Chimie au Département de Chimie de l'Université de Kansas. - *Lawrence, Kansas* (U.S.A.).

S.E. Prof. Dr. PIETER JOSEF WILLIAM DEBYE, Académicien Pontifical, Président du Department of Chemistry de la Cornell University. - *Ithaca, N.Y.* (U.S.A.).

Prof. Dr. MARSHALL FIXMAN, Professeur de Chimie au Département de Chimie de la Yale University. - *New Haven, Connecticut* (U.S.A.).

Prof. Dr. JUAN FRANCISCO GARCÍA DE LA BANDA, Chercheur scientifique du Conseil Supérieur de Recherche scientifique (C.S.I.C.) d'Espagne, Directeur du Laboratoire de Catalyse à l'Institut de Chimie Physique « Rocasolano ». - *Madrid* (Espagne).

S.E. Prof. Dr. GIORDANO GIACOMELLO, Académicien Pontifical, Professeur de Chimie pharmaceutique et Directeur de l'Institut de Chimie pharmaceutique et toxicologique à l'Université de Rome. - *Rome* (Italie).

Prof. Dr. THOMAS BURTON GRIMLEY, Maître Doyen des conférences au Département de Chimie inorganique, physique et industrielle à l'Université de Liverpool. - *Liverpool* (Grande-Bretagne).

S.E. Prof. Dr. WEIKKO ALEKSANTERI HEISKANEN, Académicien Pontifical, Directeur de l'Institut de Géodésie de l'Université de l'Etat d'Ohio. - *Columbus, Ohio* (U.S.A.).

S.E. Prof. Dr. GERHARD HERZBERG, Académicien Pontifical, Directeur du Département de Physique pure au Conseil National des Recherches du Canada. - *Ottawa* (Canada).

Prof. Dr. JOSEPH GARLAND HIRSCHFELDER, Directeur de l'Institut de Chimie Théorique de l'Université de Wisconsin et Professeur Homer D. Adkins de Chimie. - *Madison, Wisconsin* (U.S.A.).

Prof. Dr. PER-OLOW LÖWDIN, Professeur de Chimie des Quanta, Chef du Département de la Chimie des Quanta à l'Université d'Uppsala (Suède), Directeur des Summer and Winter Institutes in Quantum Chemistry, Solid-State Physics and Quantum Biology. - *Gainesville, Florida* (U.S.A.).

Prof. Dr. JOHANNES LYKLEMA, Professeur de Chimie physique et de Chimie des colloïdes à la Landbouwhogeschool (École Supérieure d'Agriculture) à Wageningen. - *Wageningen* (Pays-Bas).

S.E. Prof. Dr. SAN-ICHIRO MIZUSHIMA, Académicien Pontifical, Directeur de l'Institut des Recherches scientifiques « Yawata » de l'Université de Tokyo et Professeur émérite de Chimie à cette même Université. - *Tokyo* (Japon).

Prof. Dr. JAN THEODOR GERARD OVERBEEK, Professeur de Chimie physique à l'Université d'Utrecht. - *Utrecht* (Pays-Bas).

Prof. Dr. MARCEL PRETTRE, Professeur titulaire de la chaire de Chimie industrielle à la Faculté des Sciences de Lyon (promu à la classe exceptionnelle en 1967). - *Lyon* (France).

Prof. Dr. FRANCESCO PAOLO RICCI, Chargé de cours en Physique appliquée des solides à l'Université de Rome, maître de recherches à l'Institut de Physique de la même Université. - *Rome* (Italie).

S.E. Prof. Dr. MANUEL SANDOVAL VALLARTA, Académicien Pontifical, Professeur de Physique théorique au Colegio Nacional et à l'Université de Mexico, Chargé de la recherche scientifique à la Commission Nationale de l'Energie nucléaire du Mexique. - *Ciudad de México* (Mexique).

Prof. Dr. GEORG-MARIA SCHWAB, Professeur titulaire de Chimie physique à l'Université de Munich. - *Munich* (Allemagne).

Prof. Dr. EVERT JOHANNES WILLEM VERWEY, Directeur des Laboratoires de Recherches Philips (Philips Research Laboratories). - *Eindhoven* (Pays-Bas).

Prof. Dr. BENJAMIN WIDOM, Professeur de Chimie à la Cornell University. - *Ithaca, N.Y.* (U.S.A.).

Le « Règlement des Semaines d'Etude » prescrivant que le nombre des Participants doit être rigoureusement limité, a malheureusement empêché d'inviter d'autres illustres savants.

Ont aussi participé à la réunion: en qualité d'interprète et chef de Secrétariat Mme VALENTINE PRÉOBRAJENSKI; en qualité de sténographes polyglottes de séance Mlle MAURA BALOCCO, Mlle WENDY FIELD et Mlle MURIEL SADLIE et Mlle PAMELA SUTTON; en qualité de sténo-dactylographes polyglottes chargées des Procès-verbaux: Mlle JOSÉPHINE LUCAS, Mlle RITA MAURO, Mme PAULETTE ROSSALDI, Mlle EDNA RYAN; en qualité de technicien pour l'enregistrement et la projection, Mr. MAURO ERCOLE, assisté par des opérateurs de Radio-Vatican. Le Bureau de Presse était confié au Dr. FRANCESCO SALVIUCCI, Coadjuteur du Chancelier de l'Académie.

Le Comité de Réception pour les Dames était ainsi composé: les Comtesses ISABELLA et KARINA CALVI DI COENZO, Mme GIOVANNA AMBROSINI et Mlle DANIELLA PERSIA.

L'après-midi du dimanche 17, à l'occasion d'une rencontre amicale prévue par le Chancelier de l'Académie afin que tout le monde puisse se donner la bienvenue, se connaître l'un l'autre, et prendre les premiers contacts avant de commencer le travail scientifique, ce qui devait avoir lieu le lendemain, est arrivé le télégramme suivant:

« Dr. PIETRO SALVIUCCI, Chancellor Pontifical Sciences Academy - Vatican City. — Please confer to the members of the Study Week my good wishes for a period of blessed and fruitful discussions together with sincere apologies to you and the participants for not being able to be present personally. — PIETER DEBYE ».

Le matin du lundi 18, au commencement des travaux scientifiques de la Semaine d'Etude, S.E. MARCELLO BOLDRINI, Président

f.f., s'adressa aux Participants dans les termes suivants d'ouverture :

« Your Excellencies, Gentlemen,

« My name is MARCELLO BOLDRINI, and I am the senior member present of the Council of the Academy.

« On behalf of the president H.E. GEORGES LEMAÎTRE, who for health reasons has been prevented from coming to Rome, I have the honour of welcoming the distinguished scientists attending the Academic Study Week of this year.

« And I have the same honour on behalf of H.E. Pontifical Academician professor PIETER DEBYE who, also due to illness, cannot preside over the Study Week. The chair will be taken instead by H.E. Pontifical Academician professor SAN-ICHIRO MIZUSHIMA.

« The Pontifical Academy of Sciences is a very special learned body. Because of its international character and the strictly limited number of members, it is impossible to hold weekly or monthly sessions, as happens with most national academies. Therefore, the annual ordinary meetings are supplemented by an extraordinary study week for the discussion of particularly controversial matters of the day.

« The subject of the present week is "Molecular Forces".

« I regret that I personally am neither a chemist nor a physicist, I am not qualified to make a contribution to your work, but I do not feel myself alien to your problems because they tend to solve some epistemological questions useful to the interpretation of nature.

« The English expression "as like as two peas" corresponds to the Italian phrase "rassomigliare come due gocce d'acqua" (to be as like as two drops of water).

« The Italian expression was true in the past, but day by day it becomes less and less satisfactory. The discovery of three isotopes for hydrogen and of two for oxygen tells us that there are thirty different molecular combinations of water.

« But the proportion of isotopes varies as was demonstrated by the analysis of the water of Lake Michigan and the air above it. Therefore, two drops of water may contain the thirty possible molecular combinations with an unlimited number of percentages.

« But now comes into account one of your specific branches of knowledge, because the knowledges about the molecular forces tell us that the number of the thirty molecular forms is merely an abstraction and this makes the two drops of water not less unlike than two peas.

« Let me conclude by saying that every fact in science is changing and only the effort demanded of its students is constant.

« May I express the hope that your study week will be a success, giving you through good results some reward for your labours. Thank you. »

En outre, S.E. MARCELLO BOLDRINI, Président f.f., envoya à S.E. Monseigneur GEORGES LEMAÎTRE, qui a été empêché le télégramme suivant :

« Excellence Monseigneur GEORGES LEMAÎTRE, Président Académie Pontificale Sciences - 5, Avenue Roi Albert - Louvain. — Ayant pris parole à ouverture Semaine Étude ai communiqué Assemblée expression vos sentiments. Stop. Suis prié vous transmettre sentiments respectueux Participants. Stop. Personnellement souhaite votre prochain retour au travail commun. Stop. Salutations très cordiales. — MARCELLO BOLDRINI ».

Aussitôt que les travaux de la « Semaine » furent commencés, S.E. SAN-ICHIRO MIZUSHIMA, qui avait pris le place de S.E. PIETER DEBYE, malade, envoya à son illustre collègue le télégramme suivant :

His Excellency PIETER DEBYE, Pontifical Academician - Highgate Road, 104 - Ithaca, New York 14850, USA. — « All Parti-

cipants send you best wishes. Stop. The meeting is going very well along the lines you suggested. Stop. Wishing you a speedy recovery kind regards. — SAN-ICHIRO MIZUSHIMA ».

Le samedi 23 avril tous les Participants ont été reçus en Audience Solennelle par le Souverain Pontife qui leur adressa un discours et après l'Audience a eu lieu, au Siège de l'Académie Pontificale des Sciences, une séance extraordinaire de l'Académie, à laquelle ont été invités également les Participants à la « Semaine d'Etude ».

La chronique de l'Audience et le discours du Saint-Père sont imprimés dans les pages suivantes.

Pendant la Semaine, qui se déroula jusqu'au samedi 23, les travaux scientifiques se poursuivirent sans interruption. Les discussions des différents rapports se déroulèrent groupées selon l'affinité des sujets.

Les séances se tenaient deux fois par jour, le matin de 9 h. 30 à 12 h. 30 et l'après midi de 16 h. à 19 h.; chaque séance était présidée par l'un des Participants à la réunion.

La réussite de la « Semaine d'Etude » a pleinement satisfait les illustres Participants, qui, à la fin de leurs travaux, ont tenu à exprimer au Saint Père leur profonde gratitude et leur très sincère admiration pour cette manifestation scientifique si réussie, en envoyant à l'Auguste Pontife, animateur et mécène de l'Académie, le télégramme suivant :

« Sa Sainteté le Souverain Pontife PAUL VI - Cité du Vatican. — Les Participants à la Semaine d'Etude sur les Forces Moléculaires Vous prient daigner d'accepter l'expression de leur admiration et de leur profonde gratitude pour leur avoir donné la possibilité de travailler dans les conditions les meilleures à l'étude des problèmes des forces moléculaires et d'échanger leurs idées en pleine liberté.

Ils Vous expriment leur sincère reconnaissance pour l'honneur que Sa Sainteté a bien voulu leur accorder en leur permettant de travailler sous les auspices de Son Académie. — BERNSTEIN, BOWDEN, BUCKINGHAM, CASIMIR, CHAGAS, CHU, FIXMAN, GARCÍA DE LA BANDA, GIACOMELLO, GRIMLEY, HEISKANEN, HERZBERG, HIRSCHFELDER, LÖWDIN, LYKLEMA, MIZUSHIMA, OVERBEEK, PRETTRE, RICCI, SCHWAB, VERWEY, WIDOM ».

A ce télégramme d'hommage et de remerciement, le Saint Père a daigné répondre par le message suivant, signé par Son Eminence le Cardinal Secrétaire d'Etat :

« Professeur PIETRO SALVIUCCI, Chancelier Académie Pontificale des Sciences - Casina di Pio IV - Città del Vaticano. — Sa Sainteté très touchée déférent télégramme participants Semaine d'Etude Académie Pontificale des Sciences sur Forces Moléculaires remercie vivement tous signataires invoquant sur leurs personnes et continuation travaux abondance bénédictions divines. — Cardinale CICOGNANI ».

Dans les pages qui suivent, après le compte-rendu de l'Audience du Saint-Père et du « Règlement des Semaines d'Etude », sont imprimés les rapports originaux présentés à la Réunion, et les discussions qui les ont suivis.

Les « Conclusions » de la « Semaine d'Etude » se trouvent à la fin du présent volume.

Pendant la Semaine les Participants ont visité les Musées Pio-Clementino, Chiaramonti, Etrusque, Egyptien; le Braccio Nuovo; les Galeries des tapisseries, des cartes géographiques; les Chambres

et les Loggia de Raphaël, la Chapelle de Fra Angelico, la Chapelle Sixtine, l'Appartement Borgia et la Pinacothèque Vaticane avec l'assistance du Prof. Gr. Off. FILIPPO MAGI et du Dr. DEOCLECIO REDIG DE CAMPOS de la Direction Générale des Monuments de la Cité du Vatican.

Les Participants ont aussi visité la Bibliothèque Apostolique Vaticane et les Archives Secrètes Vaticanes sous la conduite des Rév.mes Préfets Mons. MARTINO GIUSTI et Père ALPHONSE RAES, S.I. et la Station de Radio-Vatican qui leur fut présentée par le Directeur, le Rév.me Père ANTONIO STEFANIZZI, S.I.

Enfin, le soir du samedi 23 avril, un dîner d'adieu a été offert par l'Académie, selon la coutume, aux savants participant à la « Semaine d'Etudes ».

L'AUDIENCE
ET
LE DISCOURS DU SAINT-PERE

Le matin du samedi 23 avril, le Saint Père a accordé dans la Salle du Consistoire du Palais Apostolique Vatican, une Audience Solennelle à l'Académie Pontificale des Sciences à l'occasion de la « Semaine d'Etude » sur « Les Forces Moléculaires » tenue par l'Académie. Ont participé aussi à l'Audience de nombreux hautes personnalités.

Etaient présents Leurs Eminences les Cardinaux: PIZZARDO et CICOGNANI, Académiciens Pontificaux honoraires, DA COSTA NUNES, FORNI, SLIPYI, DANTE et BROWNE.

De nombreux Académiciens Pontificaux sont intervenus, et spécialement Leurs Excellences: MARCELLO BOLDRINI, Président f.f., HERMAN ALEXANDER BRÜCK, CARLOS CHAGAS, GUSTAVO COLONNETTI, EDWARD JOSEPH CONWAY, EDUARDO CRUZ-COKE, ANTONIO DE ALMEIDA, GEORGE CHARLES DE HEVESY, JOSÉ GARCÍA SIÑERIZ, GIORDANO GIACOMELLO, WEIKKO ALEKSANTERI HEISKANEN, GERHARD HERZBERG, CORNEILLE HEYMANS, SVEN HÖRSTADIUS, BERNARDO ALBERTO HOUSSAY, ALBERTO HURTADO, JEAN LECOMTE, LOUIS LEPRINCE RINGUET, MANUEL LORA TAMAYO, SAN-ICHIRO PAULO MIZUSHIMA, DANIEL JOSEF KELLY O'CONNELL, JAN HENDRIK OORT, SALIMUZZAMAN SIDDIQUI, HUGH STOTT TAYLOR, le Chancelier de l'Académie Prof. Dr. PIETRO SALVIUCCI et le Coadjuteur du Chancelier Dr. FRANCESCO SALVIUCCI.

Parmi le groupe des Académiciens assistaient les savants spécialistes « Participants » à la Semaine d'Etude sur « Les Forces Molé-

culaires » MM. les Professeurs: RICHARD BARRY BERNSTEIN, FRANK PHILIP BOWDEN, AMYAND DAVID BUCKINGHAM, HENDRIK BRUGT GERHARD CASIMIR, BENJAMIN THOMAS PENG NIEN CHU, MARSHALL FIXMAN, JUAN FRANCISCO GARCÍA DE LA BANDA, THOMAS BURTON GRIMLEY, JOSEPH OAKLAND HIRSHFELDER, PER-OLOW LÖWDIN, JOHANNES LYKLEMA, JAN THEODOR GERARD OWERBEEK, MARCEL PRETTRE, FRANCESCO PAOLO RICCI, GEORG-MARIA SCHWAB, EVERT JOHANNES WILLEM VERWEY, BENJAMIN WIDOM.

Etaient également présents: Son Excellence Rév.me Monseigneur ANTONIO SAMORÉ, Secrétaire de la Sacrée Congrégation des Affaires Extraordinaires, Son Excellence Rév.me Monseigneur ANGELO DELL'ACQUA Substitut de la Secrétairerie d'Etat, le Rév.me Monseigneur ANTONIO MAURO Chef du Protocole, le Rév.me Monseigneur ERNESTO CAMAGNI Chancelier des Brefs Apostoliques, et autres personnalités de la Curie et de l'Etat de la Cité du Vatican.

Au complet le Corps Diplomatique accrédité près le Saint Siège, dont les Membres étaient reçus par le Gr. Uff. Dr. MARIO BELARDO.

Le Saint Père a fait son entrée dans la Salle du Consistoire à 12 h. 45, accompagné par sa Noble Antichambre avec LL.EE. Nosseigneurs FEDERICO CALLORI DI VIGNALE Majordome et MARIO NASALLI ROCCA DI CORNELIANO Maître de Chambre, ses Camériers Secrets Participants et sa Garde Noble.

Une déferente manifestation d'hommage a accueilli l'arrivée du Saint Père.

Après avoir gagné le trône, le Saint Père donna son assentiment à l'Académicien S.E. MARCELLO BOLDRINI, Président f.f. qui s'adressa alors au Souverain Pontife en ces termes :

« Très Saint Père, cette journée faste est aussi la dernière de la principale session annuelle de l'Académie Pontificale des Sciences. Au cours des journées précédentes, le Conseil a tenu ses réunions de travail, les Académiciens se sont réunis en séances plénières et un groupe international de savants éminents, physiciens, chimistes et biologistes, s'est penché durant une semaine sur les problèmes concernant les forces moléculaires.

« Aujourd'hui, l'Académie assiste avec une foi respectueuse à la remise par Votre Sainteté de la médaille PIE XI au jeune astronome ALLAN REX SANDAGE, en reconnaissance de la valeur de ses recherches concernant les amas stellaires.

« Ce n'est point à moi, simple membre du Conseil académique, qu'aurait dû échoir l'honneur de présenter à Votre Sainteté, en plus de mon très respectueux hommage filial, celui des Académiciens présents, des savants ayant participé à la Semaine d'Etude et, enfin, du Docteur SANDAGE; mais leur état de santé a retenu chez eux notre illustre Président Mgr GEORGES LEMAÎTRE et notre collègue Monsieur PIETER DEBYE qui a organisé la Semaine d'Etude.

« Que Votre Sainteté daigne accepter que je lui exprime, au nom des deux absents, la dévotion de l'Académie et que j'ajoute à ceux du monde entier, nos sentiments de profonde admiration pour Celui qui — appelé à guider l'Eglise du Christ — rappelle chaque jour à l'humanité, par la parole et par l'exemple, la nécessité de rétablir la fraternité de tous les enfants de Dieu.

« Le travail coordonné accompli au cours de la Semaine d'Etude par les savants illustres appartenant à diverses disciplines, provenant des pays les plus lointains et qui se trouvent réunis autour du trône de Votre Sainteté, préfigure en quelque sorte sur le plan de la science, les possibilités de traduire en action de bien l'utilisation conjointe des meilleures énergies de l'intelligence humaine.

« C'est vers un tel idéal que vient heureusement concourir la conscience qui s'affirme au sujet du rôle des sciences, qui doit être limité aux phénomènes du monde matériel, ainsi que le refus des théories philosophiques antérieures, qui voulaient ramener au domaine de la science les problèmes suprêmes de l'homme et de la vie.

« Nous croyons que la science est un système clos, comme la logique et la mathématique, et qu'elle trouve son critère de vérité dans la cohérence rigoureuse des problèmes et de leurs solutions, cohérence qui s'exprime au moyen de langages conventionnels et de l'emploi d'une syntaxe rigoureuse. Ceci ouvre à chaque savant, fidèle à ses études, une voie qui mène à d'autres certitudes supérieures, dérivant de la révélation, de l'enseignement de l'Eglise et de la méditation métaphysique.

« Il semble donc que soit surmonté, ou du moins réduit, le péril dénoncé par la "Constitution pastorale sur l'Eglise dans le monde contemporain", que la méthode dont font usage les sciences "soit élevée au rang de norme suprême d'une vérité totale", alors que le seul objectif immédiat de la science demeure celui d'une "fidélité rigoureuse à la vérité" (pars II, sectio II, 57).

« Une récompense d'un prix inestimable attend l'homme d'étude qui obéit à sa vocation avec un cœur pur et une raison sans détour.

« Après avoir cité une sentence de Saint JÉRÔME, "Non gloriatur sapiens in sapientia sua", Saint THOMAS D'AQUIN distingue deux béatitudes: la première est promise à celui qui travaille au service de la science profane, mais elle est imparfaite parce qu'elle "non attingit sed participat quandam particularem beatitudinis similitudinem"; la deuxième, au contraire, est parfaite parce qu'elle est au dessus de la science même et qu'elle "attingit ad veram beatitudinis rationem" (*Summa Theol.* I-II, 3, 6).

« Rendons donc grâce à Dieu pour ces récompenses qui justifient et sanctifient le travail de tout savant fidèle ».

Le Saint Père daigna répondre par le discours que nous reproduisons plus loin.

A la fin de l'Audience le Souverain Pontife daignait remettre au Prof. ALLAN REX SANDAGE, Astronome des Observatoires du Mont Wilson et Palomar, la grande médaille d'or qui porte le nom auguste de Pie XI, Fondateur de l'Académie Pontificale, et adressait au Prof. SANDAGE, qui était accompagné du Président f.f. et du Chancelier de l'Académie, des paroles de satisfaction et de félicitations.

Le Saint-Père s'entretint ensuite, après avoir reçu l'hommage des Cardinaux, avec l'Académicien S.E. MARCELLO BOLDRINI, Président f.f., les Académiciens Pontificaux, le Chancelier PIETRO SALVIUCCI et les savants « Participants » à la « Semaine d'Etude », trouvant pour chacun d'aimables paroles de félicitations et de souhaits, pour eux, leurs familles et leur activité scientifique.

L'assistance exprima enfin ses remerciements au Saint-Père, sa reconnaissance émue et sa profonde gratitude, et le plus chaleureux hommage se manifesta de nouveau au moment où, l'Audience terminée, le Souverain Pontife quitta la Salle du Consistoire.

Chers Messieurs,

En vous accueillant, Messieurs, au terme de votre semaine d'étude sur les Forces moléculaires, Notre intention n'est pas — vous vous en doutez — de Nous hasarder à pénétrer sur le terrain scientifique qui est le vôtre, mais bien plutôt de vous dire l'estime que l'Église professe envers vos personnes, l'intérêt avec lequel elle suit vos travaux, le désir qui l'anime de faire tout ce qui dépend d'elle pour favoriser l'heureux déroulement et le constant progrès de vos recherches au sein de l'Académie Pontificale des Sciences.

Dear Gentlemen,

In welcoming you, Gentlemen, at the close of your study week on *Molecular Forces*, it is not Our intention — as you may imagine — to venture into the scientific field which is yours. We prefer to speak to you of the Church's esteem for you, of the interest with which she follows your activities, the desire which animates her to do all in her power to encourage the happy development and constant progress of your researches within the Pontifical Academy of Sciences.

The eminent founder of this Academy, the great Pope Pius XI, as you are aware, was deeply interested in this activity. So also

Ce souci était, vous le savez, celui de l'éminent fondateur de cette Académie, le grand Pape Pie XI. Il fut celui de ses deux successeurs, et Nous n'avons pas à vous rappeler ici les discours magistraux par lesquels, au cours de son long et glorieux pontifical, Notre prédécesseur Pie XII tint à illustrer chacune de vos sessions.

Avec l'avènement du Pape Jean XXIII, dont Nous avons recueilli la lourde succession, un élément assez nouveau — on peut le dire — est intervenu dans les rapports de l'Autorité ecclésiastique avec le monde scientifique.

Ce n'est plus seulement le chef visible de l'Eglise, dans des discours isolés, c'est l'épiscopat mondial, réuni en Concile, qui a eu à se prononcer sur l'attitude de l'Eglise dans le monde d'aujourd'hui, et notamment en présence des développements modernes de la culture et à l'égard de ce qui fait l'objet des travaux auxquels vos vies sont si noblement consacrées: la recherche scientifique.

were his two successors, and it is unnecessary to remind you here of the masterly addresses by which, in the course of his long and glorious pontificate, Our predecessor, Pius XII, desired to honour each of your sessions.

With the accession of Pope John XXIII, from whom We have inherited the heavy burden of office, it may be said that quite a new element entered into relations between ecclesiastical authority and the scientific world.

It is no longer merely the visible head of the Church in isolated addresses, but the bishops of the whole world assembled in Council, who have been obliged to express their opinion as to the Church's attitude in the modern world, more particularly in view of modern

Les conclusions de ce vaste « examen de conscience » de l'Eglise en ce domaine ont été consignées dans un document qui mérite, pensons-Nous, toute votre attention, et dont plusieurs d'entre vous ont sans doute déjà pris connaissance: la constitution pastorale sur l'Eglise dans le monde d'aujourd'hui.

Envisageant dans sa seconde partie, un certain nombre de problèmes concrets qui se posent à l'Eglise de notre temps, cet important document aborde le domaine de la culture. Il salue d'abord l'essor de celle-ci et l'avènement de ce qu'on peut appeler un « nouvel humanisme ». Mais il signale aussitôt la complexité des problèmes qui en sont la conséquence, celui-ci notamment, qui Nous semble avoir pour vous un intérêt tout spécial: « Comment — y est-il dit — comment l'émiettement si rapide et croissant des disciplines spécialisées peut-il se concilier avec la nécessité d'en faire la synthèse et avec le devoir de sauvegarder dans l'humanité les

cultural developments and in regard to the object of those labours to which your lives are so nobly devoted, namely, scientific research.

The results of this vast « examination of conscience » on the part of the Church in this field have been recorded in a document which, We believe, is worthy of your attention and with which many of you are no doubt already familiar, namely, the Pastoral Constitution on the Church in the Modern World.

Contemplating in its second section a certain number of real problems with which the Church is faced in our day, this important document deals with the domain of culture. It hails the progress of culture, in the first place, and the advent of what may be called a « new humanism. » But it points out immediately the complexity of the consequent problems, more particularly the one which seems

puissances de contemplation et d'admiration qui conduisent à la sagesse? » (V, 56, § 4).

On peut dire que ce bref paragraphe situe parfaitement, l'un en face de l'autre, le point de vue du savant spécialisé — le vôtre — et celui de l'Eglise. Vous êtes — et c'est votre honneur — soucieux avant tout de faire progresser le savoir humain, d'assurer continuellement de nouvelles acquisitions dans chacune de ses branches: il s'ensuit, par la force des choses, cet « émiettement rapide et croissant » dont parle le document conciliaire. L'Eglise, elle, est avant tout soucieuse de synthèse, car elle a pour mission de sauvegarder l'harmonie et l'équilibre de la créature raisonnable, de l'aider à s'élever jusqu'à cette « sagesse » supérieure, découlant de la révélation divine dont elle est la dépositaire.

Elle voit les risques d'une trop grande spécialisation et les obstacles que celle-ci peut apporter à l'élan de l'âme vers le spirituel.

to Us to be of special interest to you: « *As special branches of knowledge continue to shoot out so rapidly — it states — how can the necessary synthesis of them be worked out, and how can men preserve the ability to contemplate and to wonder from which wisdom comes?* » (No. 56, § 4).

It can be said that this brief paragraph places perfectly face to face the point of view of the specialized scientist — your own — and that of the Church. You are concerned — and this does you honour — before all else about the progress of human knowledge, to ensure fresh acquisitions continually in each of its branches. There follows, by force of circumstances, this continued « shooting out so rapidly » of which the conciliar document speaks. The Church herself is before all else solicitous for synthesis, for her

Dans l'intérêt de l'homme, l'Eglise veut à tout prix sauver ces « puissances de contemplation et d'admiration » dont une civilisation purement technique risquerait de faire bon marché. Elle craint surtout, comme une mère soucieuse du véritable bien de ses enfants, « que l'homme, se fiant trop aux découvertes actuelles, ne vienne à penser qu'il se suffit à lui-même et qu'il n'a plus à chercher de valeurs plus hautes » (ibid. n. 57, § 5). Ce sont encore les propres termes de la Constitution sur l'Eglise dans le monde d'aujourd'hui, et ils nous introduisent au coeur du débat entre l'Eglise et la science. L'Eglise interroge: que vaut exactement, demande-t-elle, la recherche scientifique? Jusqu'où arrive-t-elle? Epuise-t-elle toute la réalité, ou plutôt n'en est-elle qu'un segment, celui des vérités qui peuvent être atteintes par les procédés scientifiques? Et ces vérités elles-mêmes, si justement chères à l'homme de science, sont-

mission is to safeguard the harmony and balance of the rational creature, to aid him to ascend to this higher « wisdom » stemming from the divine revelation of which she is the depositary.

The Church is aware of the dangers involved in excessive specialization and of the obstacles which the latter can place in the way of the soul's impulse towards what is spiritual.

In man's own interests, the Church desires at all costs to save that « ability to contemplate and to wonder » to which a purely technical civilization would be in danger of attaching little value. Above all does she fear, like a mother solicitous for the true good of her children, « that man, confiding too much in modern discoveries, may even think that he is sufficient unto himself and no longer seek any higher realities » (ibid., No. 57, § 5). These are again the very words of the Constitution on the Church in the

elles au moins définitives? ou ne seront-elles pas détrônées demain par quelque nouvelle découverte? Que de leçons nous donne là-dessus l'histoire des sciences!

Et puis, cette étude du chercheur spécialisé, si admirable, si approfondie qu'elle soit, donne-t-elle, à la fin, la raison des choses qu'elle découvre? Que d'étoiles dans le ciel! Certes. Mais comment et pourquoi? Que de merveilles dans l'anatomie et la physiologie du corps humain! Sans doute. Mais pourquoi le corps humain? Mais pourquoi l'homme? Ici, la science est muette, et elle doit l'être, sous peine de sortir de son domaine. Elle s'arrête au seuil des questions décisives: qui sommes-nous? d'où venons-nous? où allons-nous?

Ne croyez pas, Messieurs, qu'en soulevant ces interrogations, Nous voulions le moins du monde mettre en doute la valeur de la

Modern World and they introduce us into the heart of the debate between the Church and science. The Church enquires. What exactly, she asks, is the value of scientific research? Just how far does it go? Does it exhaust the whole of reality, or is it not rather a mere segment, the one pertaining to the truths that can be reached by scientific processes? And these truths themselves, so justifiably dear to the man of science, are they at least final, or are they not to be dethroned tomorrow by some new discovery. How many lessons do we receive on this point from the history of the sciences!

Besides, this study of the specialized researchers, however admirable and profound it may be, does it in the end supply the reason for the things it discovers? How many stars there are in the sky! Certainly, but how and why? How many marvels there are in the anatomy and physiology of the human body! Undoubt-

méthode scientifique. Plus que quiconque, l'Eglise se réjouit de toute véritable acquisition de l'esprit humain, dans quelque domaine que ce soit. Elle reconnaît et apprécie grandement l'importance des découvertes scientifiques.

L'effort d'intelligence et d'organisation nécessaire pour aboutir à de nouveaux résultats en ce domaine est, de sa part, objet d'encouragement et d'admiration. Car elle n'y voit pas seulement l'emploi magnifique de l'intelligence: elle y découvre aussi l'exercice de hautes vertus morales, qui confèrent au savant l'aspect et le mérite d'un ascète, parfois d'un héros, auquel l'humanité doit payer un large tribut de louange et de reconnaissance.

Dans son dialogue avec le monde de la science, l'Eglise ne se borne pas à assigner à la recherche scientifique sa place exacte dans l'univers de la connaissance, à en préciser les limites et à en re-

edly, but why does the human body exist? Why does man exist? Science is mute at this stage, and must be so, under pain of departing from its own domain. It stops on the threshold of the decisive questions: who are we? whence have we come? where are we going?

Do not think, Gentlemen, that in bringing up these questions We have even the slightest intention of calling in question the value of the scientific method. More than anyone else the Church rejoices at every true acquisition of the human spirit, in any field whatsoever. She recognizes and keenly appreciates the importance of scientific discoveries. The effort of intelligence and organization necessary to reach new results in this domain is, as far as she is concerned, the object of encouragement and admiration. For she does not see here merely the magnificent use of the intellect. She

connaître les mérites. Elle a encore une parole à dire à l'homme de science sur sa mission dans l'univers créé par Dieu.

Il est trop évident que la science ne se suffit pas à elle-même: elle ne saurait être à elle-même sa propre fin. La science n'existe que par et pour l'homme; elle doit sortir du cercle de sa recherche et déboucher sur l'homme, et par là sur la société et sur l'histoire tout entière.

La science est reine dans son domaine. Qui songerait à le nier? Mais elle est servante par rapport à l'homme, roi de la création. Si elle refusait de servir, si elle ne visait plus au bien et au progrès de l'humanité, elle deviendrait stérile, inutile, et, disons-le, nuisible.

Les conséquences de cette mission de service sont incalculables, et il faudrait aborder ici — mais les trop courts instants dont Nous disposons ne Nous le permettent pas — l'immense problème de la

discovers also the exercise of high moral values which confer on the scientist the aspect and the merit of an ascetic, at times of a hero, to whom mankind must pay an ample tribute of praise and gratitude.

In her dialogue with the world of science, the Church does not limit herself to assigning to scientific research its exact place in the universe of knowledge, to stating precisely its limits and recognizing its results. She has a further word to say to the man of science concerning his mission in the universe created by God.

It is only too evident that science does not suffice in itself, is unable of itself to be its own end. Science does not exist except through and for man; it must leave the circle of research and pour itself out on man, and hence on society and history as a whole.

Science is a queen in her own domain. Who would dream of

moralité des applications de la science. Qu'il s'agisse de génétique, de biologie, d'emploi de l'énergie atomique, et de tant d'autres domaines qui touchent à ce qu'il y a d'essentiel dans l'homme, le savant loyal ne peut pas ne pas s'interroger devant l'incidence de ses découvertes sur ce complexe psycho-physiologique qui est en définitive une personne humaine. Tout est-il permis? La science appliquée peut-elle faire abstraction d'une norme de moralité, peut-elle aller sans frein « au delà du bien et du mal »? Qui ne voit à quelles aberrations certains pourraient se livrer au nom de la science?

Mais l'Eglise n'attend pas seulement de la science qu'elle ne porte pas atteinte à la moralité, au bien profond de l'être humain. Elle attend d'elle un service positif, ce qu'on pourrait appeler la « charité du savoir ». Vous êtes, Messieurs, ceux qui détiennent les clés de la plus haute culture. Nous osons Nous faire en ce moment

denying it? But it is a servant in relation to man, who is king of creation. If it were to refuse to serve, if it no longer aimed at the good and the progress of humanity, it would become sterile, useless and, let us say so, harmful.

The consequences of this mission of service are incalculable, and here we ought to face — but the too brief moments at our disposal do not allow of this — the immense problem of the morality of the applications of science. Whether it is a question of genetics, of biology, of the employment of atomic energy, of many other fields which affect what is essential in man, the upright scientist cannot but question himself as to the bearing of his discoveries on this psycho-physiological complex which is, in a world, a human person. Is everything permissible? Can applied science dispense with a norm of morality, can it proceed unchecked

auprès de vous l'avocat des masses innombrables auxquelles n'arrivent que de loin et rarement quelques gouttes, quelques miettes de ce vaste savoir humain.

Permettez que Nous vous disions en leur nom: cultivez la recherche, mais afin qu'elle profite aux autres, afin que la lumière de la vérité découverte se répande, afin que le genre humain en soit instruit, amélioré, perfectionné; que l'économie politique des peuples y puise des directives conduisant plus sûrement au véritable bien des hommes. Tel est l'immense panorama qui se découvre à l'homme de science lorsque, sortant de son laboratoire pour jeter les yeux autour de lui, il perçoit quelque chose de l'attente des hommes: attente qui soulève les coeurs et les ouvre à l'espérance et à la joie, non sans laisser place parfois, il faut bien le dire, à un sentiment d'inquiétude et d'anxiété.

« beyond good and evil »? Who can fail to see the aberrations in which some could indulge in the name of science?

But the Church expects from science not merely that it may not injure morality or the profound welfare of the human being. She expects from it a positive service, what might be termed the « charity of knowledge. » You, Gentlemen, are the ones who hold the keys of highest learning. We venture to assume towards you at this moment the office of advocate on behalf of the innumerable masses who receive only from a distance and rarely, a few drops, a few morsels of this vast human knowledge.

Allow Us to ask you on their behalf to cultivate research, but in order that it may be of use to others, that the light of discovered truth may be spread abroad, that the human race may be enlightened by it, improved and perfected; so that the political economy

Cette inquiétude, cette anxiété, seront dissipées le jour où l'humanité saura et sentira que l'homme de science est animé envers elle d'un sincère esprit de service, qu'il ne désire rien tant que l'éclairer, la soulager, assurer son progrès et son bonheur.

Vous vous souvenez sans doute, Messieurs, de ce « message aux hommes de la pensée et de la science » qui fut proclamé le jour de la clôture du Concile. Avant de se disperser, l'imposante assemblée se tournait vers vous pour vous laisser cette instante exhortation: « Continuez à chercher sans vous lasser, sans désespérer jamais de la vérité... Cherchez la lumière de demain avec la lumière d'aujourd'hui, jusqu'à la plénitude de la lumière! ». Et les Pères du Concile ajoutaient: « Nous sommes les amis de votre vocation de chercheurs, les alliés de vos fatigues, les admirateurs de vos con-

of the nations may draw from it directives which will lead more surely to the true welfare of mankind. This is the immense panorama which is unfolded before the scientist when, issuing forth from his laboratory to look around him, he perceives something of man's expectation; an expectation which stirs men's hearts and opens them up to hope and joy, although leaving room at times it must indeed be said, for a feeling of uneasiness and anxiety.

This uneasiness and anxiety will be dissipated on the day on which men will become aware and will feel that the scientist is animated by a sincere spirit of service towards humanity, that he desires nothing so much as to enlighten men, to assist them, to ensure their progress and happiness.

You will no doubt recall, Gentlemen, this « message to men of thought and science » which was proclaimed on the closing day of

quêtes, et, s'il le faut, les consolateurs de vos découragements, et de vos échecs ».

Cette dernière phrase a pu vous étonner: la recherche scientifique n'apporte-t-elle pas avec elle sa récompense? Le savant n'est-il pas payé de sa peine par les hautes satisfactions d'ordre intellectuel attachées à son travail?

L'Eglise pourtant nous apporte une sagesse supérieure, source de joies incomparablement plus hautes encore. Votre vie de savants se passe, peut-on dire, à lire dans le grand livre de la nature. Nous avons, nous, un autre livre, celui qui nous communique les pensées de Dieu sur le monde: le livre inspiré, le livre saint. Ce livre-là donne les réponses décisives que la science ne peut pas donner.

Permettez-Nous, Messieurs, d'ouvrir devant vous, en terminant, une page de ce livre: celle où l'auteur inspiré décrit l'ivresse qu'il

the Council. Before dispersing, the imposing assembly turned to you to leave you this urgent exhortation: « *Continue your search without tiring and without ever despairing of the truth... Seek the light of tomorrow with the light of today until you reach the fullness of light!* » And the Council Fathers added: « *We are the friends of your vocation as searchers, companions in your fatigues, admirers of your successes, and, if necessary, consolers in your discouragement and your failures.* »

This latter phrase may have astonished you. Does not scientific research bring its own reward? Is the scientist not repaid for his trouble by the deep intellectual satisfactions attached to his work?

The Church nevertheless brings a higher wisdom, the source of incomparably greater joys. It may be said that your life as scientists is spent in reading from the great book of nature. We have another

ressentit dans son âme lorsqu'il lui fut donné d'accéder à cette sagesse, supérieure à toute connaissance humaine, que vous avez entendu le Concile évoquer tout à l'heure.

« J'ai prié, dit-il, et la prudence m'a été donnée; j'ai invoqué, et l'esprit de sagesse est venu en moi. Je l'ai préférée aux sceptres et aux couronnes, et j'ai estimé de nul prix les richesses auprès d'elle... Tout l'or du monde n'est, comparé à elle, qu'un peu de sable, et l'argent, à côté d'elle, sera estimé pour de la boue. Je l'ai aimée, plus que la santé et la beauté; j'ai préféré la posséder plutôt que la lumière, car son flambeau ne s'éteint jamais. Avec elle me sont venus tous les biens... Je l'ai apprise sans arrière-pensée, je la communique sans envie... Elle est pour les hommes un trésor inépuisable: ceux qui l'acquièrent s'attirent l'amitié de Dieu » (Livre de la Sagesse, VII, 7-14).

book, one which communicates to us the thoughts of God concerning the world, the inspired book, the holy book. This book gives us the decisive answers that science cannot give.

Allow Us, Gentlemen, in concluding, to open before you a page of this book, the page in which the inspired author describes the rapture of his soul when he is given access to this wisdom, higher than all human knowledge, which you have heard the Council evoke just now.

« I prayed and prudence was given me; to God I prayed and the spirit of wisdom came upon me. This I valued more than kingdom or throne; I thought nothing of my riches in comparison... All my treasures of gold were a handful of dust beside it, my silver seemed but base clay in presence of it. I treasured wisdom more than health or beauty, preferred her to the light of day, for hers is a

Que cette sagesse soit votre compagne fidèle dans vos labours ardu, Messieurs. C'est Notre désir et Notre souhait, tandis que Nous invoquons de Dieu sur vos personnes, vos familles et vos travaux, les bénédictions les plus abondantes.

flame which never dies down. Together with her all blessings came to me... The lessons she taught me are riches honestly won, shared without stint, openly proclaimed... She is a treasure men will find incorruptible; those who enjoy it are honoured with God's friendship » (Book of Wisdom, 7, 7-14).

May this wisdom be the faithful companion of your arduous labours, Gentlemen. This is Our wish and Our hope, as We invoke from God upon yourselves, your families and your activities, most abundant blessings.

LES « SEMAINES D'ETUDE »

ET

LEUR REGLEMENT

Lorsque l'Académie Pontificale des Sciences fut fondée par le Souverain Pontife Pie XI, de vénérée mémoire, par son « Motu Proprio » du 28 octobre 1936 « In multis solaciis », cette initiative suscita dans les milieux scientifiques un mouvement général de sympathie et d'admiration. Cette institution unique au monde, qui groupait en une même assemblée des représentants de toutes les Nations civilisées, était appelée, en effet, à de hautes destinées dans le développement de la pensée scientifique.

D'autre part, cette oeuvre de coopération fut accueillie avec un véritable soulagement par tous ceux que plongeait dans le désarroi le plus profond la période qui suivit la guerre 1914-18. On voyait, en effet, s'altérer profondément les caractères d'objectivité et de

A general movement of sympathy and admiration was aroused in scientific circles when, in 1936, the Pontifical Academy of Sciences was founded by His Holiness Pope Pius XI, of venerable memory, by means of his « Motu Proprio » of October 28, « In multis solaciis ». This institution, the only one of its kind in the world, which brought the representatives of all civilized nations into touch with each other, was, in fact, called upon to play a leading role in the development of scientific thought.

This work of cooperation was, moreover, welcomed with a sense of real relief by all those who were plunged in a deep state of confusion in the period following the 1914-18 war.

Signs of drastic changes were, in fact, discernible in the objective and disinterested nature of scientific work and even a tendency to make science subject to pragmatic aims.

In his immortal « Motu Proprio » of October 28, 1936, Pope Pius XI,

désintéressement propres au travail scientifique, et s'affirmer même une tendance à asservir la science à des fins pragmatiques.

Tout au contraire, dans l'immortel « Motu Proprio » du 28 octobre 1936, le Pape Pie XI proclamait solennellement la dignité de la recherche de la vérité pour elle-même, et, élevant sa pensée au-dessus de toute préoccupation utilitaire, affirmait qu'il ne demandait rien d'autre aux nouveaux « Académiciens Pontificaux » que de se consacrer, avec une ferveur toujours plus grande, au progrès de la science et, par là, au culte de la vérité: « C'est Notre souhait ardent et Notre ferme espérance: que par cet Institut, à la fois Nôtre et leur, les "Académiciens Pontificaux" contribuent toujours plus et mieux au progrès des sciences. Nous ne leur demandons pas autre chose; car en ce dessein généreux et ce noble labeur consiste le service, qu'en faveur de la vérité, nous attendons de leur part » (*).

(*) « Nobis autem in votis expectationeque est, fore ut "Pontificii Academici" vel per hoc Nostrum suumque studiorum Institutum, ad scientiarum progressionem fovendam amplius excelsiusque procedant; ac nihil praeterea aliud petimus, quandoquidem hoc eximio praeclaroque labore famulatus ille nititur servientium veritati, quem ab iisdem postulamus ».

on the contrary, solemnly proclaimed the dignity of the search for truth for its own sake and, raising his thoughts above all preoccupations of an utilitarian nature, asserted that all be asked of the new « Pontifical Academy » and its members was that they should dedicate themselves, with increasing fervour, to the furthering of the progress of science and, consequently, to the cult of truth: « It is Our ardent wish and firm hope that, by means of this Institute, which is both Ours and theirs, the "Pontifical Academicians" will contribute to an increasingly great extent to the progress of science. We ask nothing more than that from them because the service in favour of truth that We expect from them consists in this generous intention and noble work » (*).

(*) « Nobis autem in votis expectationeque est, fore ut "Pontificii Academici" vel per hoc Nostrum suumque studiorum Institutum, ad scientiarum progressionem fovendam amplius excelsiusque procedant; ac nihil praeterea aliud petimus, quandoquidem hoc eximio praeclaroque labore famulatus ille nititur servientium veritati, quem ab iisdem postulamus ».

La consécration pratique de cette idée, par la nomination d'un certain nombre de non-catholiques parmi les nouveaux Académiciens Pontificaux a fait une profonde impression sur beaucoup d'esprits, comme l'ont montré les réactions de la presse internationale de l'époque et de nombreux témoignages individuels d'hommes de science et des plus grands savants du monde.

Beaucoup de préjugés à l'égard de l'Eglise ont été fortement ébranlés par ce geste du Souverain Pontife qui a obligé à reconnaître la place éminente réservée aux valeurs purement intellectuelles dans l'Eglise Catholique.

Pour toutes ces raisons, la fondation de l'Académie Pontificale des Sciences a été hautement appréciée dans le monde scientifique et y a fait naître de grands espoirs quant aux possibilités d'action d'une institution si opportune.

Elle est placée sous la dépendance directe du Souverain Pontife et composée de soixante-dix « Académiciens Pontificaux » nommés par le Pape sur proposition du Corps Académique et choisis sans

By including a certain number of non-Catholics amongst the new Pontifical Academicians, the practical application of this idea made a deep impression on many persons, as is proved by the reaction of the international press of the time and by the innumerable individual tributes paid by scientists and by the greatest scholars of the world.

Many prejudices against the Church were very deeply shaken by this gesture on the part of the Sovereign Pontiff, since it called attention to the lofty place reserved for purely intellectual values in the Catholic Church.

For all these reasons, the foundation of the Pontifical Academy of Sciences was greatly appreciated by the scientific world and aroused high hopes as to the prospects open to such a timely institution.

The Academy is directly subject to the Sovereign Pontiff, and it is composed of seventy « Pontifical Academicians », nominated by the Holy Father himself, proposed by the Academical Body and chosen

aucune discrimination parmi le plus insignes spécialistes des sciences mathématiques et expérimentales de tout pays.

L'Académie Pontificale des Sciences est actuellement unique en son genre, étant la seule Académie scientifique à caractère supranational et à classe unique existant dans le monde.

Elle a pour but d'honorer la science pure, où qu'elle se trouve, d'en assurer la liberté, d'en favoriser les recherches qui constituent la base indispensable du progrès des sciences appliquées.

Le Saint-Père Pie XII, qui avait collaboré avec son Prédécesseur au projet et à la fondation de l'Académie et qui l'avait représenté comme Légat personnel lors de l'inauguration solennelle, ne se borna pas à maintenir à son égard ses sentiments de haute estime par sa présence à de solennelles séances académiques, où il daigna prononcer ses discours d'une haute portée scientifique; il a tenu en outre à lui donner un nouveau témoignage de son auguste satisfaction en accordant à ses membres le titre d'Excellence par le Bref Apostolique du 25 novembre 1940.

without any discrimination from amongst the most famous experts in mathematical and experimental sciences in all countries.

At the present time the Pontifical Academy of Sciences is unique, in the sense that it is the only Academy of Sciences in the world which is super-national and which has only one class amongst its Members.

It has for its purpose to pay honour to pure science wherever it exists to ensure its liberty and to further its researches, which are the necessary basis for the progress of applied sciences.

His Holiness Pope Pius XII, who had helped his predecessor to draw up the plan and to found the Academy, and who had represented him as his personal Legate at the time of its solemn inauguration, did not confine himself to the expression of lofty sentiments when attending solemn academic gatherings, where he deigned to make speeches of great scientific importance, but he also afforded proof of his august satisfaction by granting the title of Excellency to the members of the Academy, by an Apostolic Brief of November 25, 1940.

* * *

Les sciences posent chaque jour des problèmes nouveaux qui donnent lieu d'ordinaire à divers essais de solution, souvent contradictoires. Il arrive ainsi constamment que, parmi les représentants les plus autorisés d'une science, et en particulier parmi ceux qui se sont consacrés à l'étude d'une même question, on rencontre des opinions opposées. Pareilles divergences se maintiennent parfois durant de longues périodes et constituent à la fois une grave difficulté pour l'enseignement des sciences et fréquemment aussi un obstacle considérable à leur développement.

Par ailleurs, l'expérience montre que les méthodes actuellement pratiquées dans la discussion des problèmes scientifiques n'ont qu'une efficacité limitée au point de vue de l'établissement d'une unité de doctrine.

Il serait dès lors hautement souhaitable de promouvoir tout ce qui pourrait favoriser un accord sur les points en discussion.

Un procédé semble devoir être particulièrement utile sous ce rapport: à savoir, l'établissement de contacts personnels prolongés

* * *

Every day science raises new problems, which usually give rise to various, and often contradictory, solutions. Consequently it often happens that amongst the most authoritative representatives of a given branch of science, and particularly amongst those who are engaged in studying the same question, one meets with contrasting opinions. Divergences of this kind often exist over long periods of time and are a serious obstacle not only to the teaching of science but also to its development.

Experience shows, moreover, that the methods at present in use in the discussion of scientific problems have only a limited efficacy in so far as concerns doctrinal unity.

It would, therefore, be highly desirable if everything that could favour agreement on controversial points were to be promoted.

One process that would seem to be particularly useful from this point of view would be the establishment of prolonged personal contacts

entre quelques représentants d'opinions différentes au sujet d'une question déterminée.

En effet, le contact personnel entre hommes de science constitue, sans aucun doute, le moyen le plus efficace de résoudre les controverses scientifiques.

Dans ce but, l'Académie Pontificale des Sciences a décidé de convoquer de pareilles rencontres. Pour la partie scientifique ces rencontres seront présidées par un Académicien Pontifical versé dans la même discipline tandis que l'organisation générale en sera réalisée par le Chancelier de l'Académie.

Ces rencontres, qu'on a appelées « Semaine d'Etude » ont été réglées de la manière suivante :

RÈGLEMENT DES SEMAINES D'ÉTUDE

1. - L'Académie invite quelques illustres savants, parmi ceux qui, ayant étudié spécialement une question déterminée, sont arrivés à des conclusions différentes, à se rencontrer à Rome, à son siège, la

between some of the representatives of different trends of thought on a given subject.

Personal contacts amongst scientists are, in fact, the most efficacious means of solving scientific controversies.

With this aim in mind, the Pontifical Academy of Sciences decided to organize meetings of this description. These meetings, for the scientific part, will be presided by an Academician versed in the same discipline while the general organization of these will be realized by the Chancellor of the Academy.

These meetings, known as « Study Weeks », were planned on the following lines :

STANDING RULES FOR « STUDY WEEKS »

1. - The Academy invites a number of illustrious scholars — comprising those who have especially studied a given question and have

« Casina di Pio IV », à l'intérieur de l'Etat de la Cité du Vatican, afin d'y procéder en commun, en dehors de toute autre préoccupation, à un examen général de toutes les données du problème.

2. - Le but essentiel de ces discussions est de chercher à formuler de façon précise les raisons qui sont à la base de la divergence des opinions. Les savants conviés aux réunions s'engageraient d'avance à concentrer leurs efforts dans cette direction.

3. - Un examen critique de ces raisons aboutira soit à un accord sur une solution déterminée, soit à la constatation qu'à l'état actuel des connaissances, il est impossible d'établir une unité de doctrine au sujet du problème envisagé.

Dans ce dernier cas, les savants invités auront pour tâche :

a) de préciser les motifs pour lesquels un accord s'avère pratiquement irréalisable;

arrived at different conclusions — to meet in Rome at its headquarters, the « Casina di Pio IV », situated in the Vatican City, so as to make a joint examination, free from all other preoccupations, of all data concerning the problem.

2. - The chief aim of these discussions is to endeavour to formulate precisely the reasons which are at the root of the differences of opinion. The scholars invited to these meetings undertake in advance to concentrate their efforts on this.

3. - A critical examination of these reasons should lead, either to agreement on a given solution or else to the conclusion that, on the basis of the information actually available, it is impossible to establish doctrinal unity on the problem envisaged.

In the latter event the scholars concerned will be called upon :

a) to define the reasons why agreement appears to be impossible for the present;

b) de définir le genre de recherches qu'il serait souhaitable d'entreprendre en vue de résoudre la question.

4. - L'invitation ne sera adressée par l'Académie qu'à un très petit nombre de représentants de chaque science: ceux-ci seront choisis exclusivement parmi les spécialistes de la question considérée, qu'ils soient membres ou non de l'Académie.

5. - Les discussions auront un caractère strictement privé; elles prendront la forme de conversations particulières.

Des interprètes polyglottes, des sténographes, des rapporteurs, etc., seront mis à la disposition des savants réunis.

6. - Les « Conclusions » des discussions seront publiées sous la forme d'une « Note Collective Finale » (à laquelle pourront éventuellement être jointes des annotations individuelles), mentionnant:

a) les points sur lesquels un accord aurait été réalisé;

b) to specify the kind of research work it would be desirable to undertake with a view to solving the problem.

4. - The invitation will be addressed by the Academy to only a small number of representatives of each branch of science: those will be exclusively selected from amongst the specialists of the question being considered, either members of the Academy or no.

5. - The debates will be strictly private and will take the form of personal talks.

Polyglot interpreters, stenographers, reporters, etc. will be placed at the disposal of the participants.

6. - The « Conclusions » arrived at will be published in the form of a « Collective Note » (to which may eventually be added individual notes) mentioning:

a) the points on which agreement was reached;

- b) les points sur lesquels un accord n'aurait pas paru réalisable;
- c) les raisons pour lesquelles l'accord n'aurait pu être réalisé;
- d) des suggestions relatives aux recherches paraissant les plus aptes à résoudre les difficultés.

7. - Les « Conclusions » seront aussitôt imprimées et communiquées, par les soins de l'Académie Pontificale des Sciences, à tous les centres scientifiques qu'elles seraient de nature à intéresser.

8. - L'Académie préparera, donc, la publication d'un volume officiel des Actes de la Semaine d'Étude contenant la chronique des journées, les rapports des participants avec les discussions correspondantes et la Note Collective Finale.

Le volume fera partie des publications officielles de l'Académie: il sera envoyé aux Institutions Scientifiques avec lesquelles l'Académie même entretient des relations d'échange et toute personne pourra se le procurer.

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- b) the points on which it was impossible to reach agreement;
 - c) the reasons why it was not possible to reach agreement;
 - d) suggestions regarding the research work which appears most suitable for arriving at a solution of the difficulties.

7. - The « Conclusions » reached will be immediately printed and transmitted, by the Pontifical Academy of Sciences, to all the scientific centres which might be interested therein.

8. - The Academy will publish an official volume of the Proceedings of the Study Week, containing an account of the sessions, the papers presented by the participants, together with the relevant discussions, and the final « Collective Note ».

This volume will form part of the official publications of the Academy and will be sent to the scientific institutions with which the Academy maintains exchanges. It can be acquired by anyone.

En vue d'étendre sa diffusion, le volume pourra aussi être confié à une organisation éditoriale pour être mis en vente, la Copyright demeurant toujours réservé à l'Académie.

9. - Toutefois, chaque participant reste libre de faire imprimer son propre rapport partout où il le juge convenable et à n'importe quel moment.

10. - L'Académie offrira en hommage à chaque participant une copie du volume officiel des Actes de la Semaine d'Étude, et des Extraits de son propre rapport suivant le nombre de copies qu'il souhaiterait avoir.

11. - Toutes les frais de voyage et de séjour à Rome des personnalités invitées seront à la charge de l'Académie Pontificale des Sciences. L'hospitalité sera assurée dans l'un des principaux hôtels de Rome.

The volume may also be entrusted to a publisher, with a view to ensuring a wider distribution, but the Copyright will always be reserved to the Academy.

9. - Each participant remains free to print his own contribution wherever and whenever he thinks fit.

10. - The Academy will present to each participant a copy of the official volume of the Proceedings of the Study Week, as well as such number of reprints of his own communication as he may desire.

11. - All travelling expenses, and accommodation in one of the best hotels in Rome, of the persons invited to the meetings will be borne by the Pontifical Academy of Sciences.

L'Académie se fera un plaisir d'offrir la même hospitalité aux épouses des savants invités, à l'exclusion toutefois des frais de voyage.

12. - La participation à la Semaine d'Étude comporte de la part de chacun l'acceptation de toutes les clauses du présent Règlement.

The Academy will be pleased to offer similar accommodation to the wives of the scholars who are invited, but not their travelling expenses.

12. Participation in the Study Week implies on the part of each member the acceptance of all the clauses in these regulations.

TRAVAUX SCIENTIFIQUES
ET
DISCUSSIONS

SESSION PREMIERE

SOUS LA PRÉSIDENCE DU

Prof. Dr. J.O. HIRSCHFELDER

THE NATURE OF INTERMOLECULAR FORCES

J.O. HIRSCHFELDER

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We want to thank the Pontifical Academy for making these wonderful arrangements and giving us the opportunity of being here on this very special occasion. This is an excellent time to hold a symposium on intermolecular forces. It really marks a renaissance of interest in this field. Up to now we have been very much lacking in precise experimental data and this resulted in a lack of development of the theory. The situation is now changing very rapidly, as we shall see this morning from the papers of BUCKINGHAM and BERNSTEIN, and the papers of other people throughout the meeting. Many new types of experiments have been devised for determining very accurately intermolecular forces. On this account there is renewed interest by theoreticians in developing all accurate theoretical treatment of the intermolecular forces. The subject is so complicated that the theory and the experiment must work together: neither the experiment alone nor the theory alone could cope with the complexity of the subject. What I mean when I say that there was a lack of the interest among the theoreticians can be illustrated by the following example. About 25 years ago, MARGENAU calculated the energy of interaction of two hydrogen molecules and found that they were dependent on the relative angles between the two molecules. Later DE BOER made other calculations of the angle dependence of the forces between two hydrogen molecules and obtained results which were entire-

ely different from those of MARGENAU. Yet no one could say which one was better than the other. Nine years ago BRITTON and BEAN made new calculations of the energy of interaction of two hydrogen molecules and found that it is almost independent of angle. Even at the present time we do not know what the angle dependence of the intermolecular forces between the two hydrogen molecules really is. Experimental colleagues, however, I am sure, will soon provide us with the answer.

I want to illustrate how complex the subject of intermolecular forces really is. And so this morning I thought I would write on the blackboard an expression for the long range intermolecular forces between two hydrogen atoms in their ground states which represents the current status of the theory:

ENERGY OF TWO HYDROGEN ATOMS IN THEIR $1s$ GROUND STATES

$$(R \text{ in } a_0, E \text{ in } e^2/a_0, \alpha = 1/137)$$

$$\chi_0 = (\alpha \Delta E)^{-1} = 365 a_0$$

INTERMEDIATE SEPARATION, $10 < R < 230 = 0.6 \chi_0$

$$\begin{aligned} E_{H-H} = \dots & - \frac{3.28 \times 10^{12}}{R^{20}} - \frac{3.24 \times 10^{10}}{R^{18}} - \frac{3.94 \times 10^8}{R^{16}} \\ & - \frac{6.060 \times 10^5}{R^{14}} - \frac{1.215 \times 10^5}{R^{12}} - \frac{1135 + 2151}{R^{10}} \\ & - \frac{124.4}{R^8} - \frac{6.499}{R^6} + \frac{0.4628 \alpha^2}{R^4} \\ & + \frac{A \alpha^2 - 0.3714 \alpha^3}{R^3} + \dots \end{aligned}$$

$$\begin{aligned}
 \text{Here } A &= 0 && \text{for } {}^1\Sigma \\
 &= +1 && \text{for } {}^3\Sigma (M_s=0) \\
 &= -\frac{1}{2} && \text{for } {}^3\Sigma (M_s=\pm 1)
 \end{aligned}$$

However, at separations greater than $10 a_0$, we must consider the hyperfine splittings of the potential energy curves. The electronic spins of the atom-pair become uncoupled and the designation of electronic singlets or triplets is no longer appropriate. Instead, we must consider sixteen hyperfine states (ten of which are doubly degenerate). The corresponding values of A lie between $-1/2$ and $+1$.

LARGE SEPARATIONS, $\lambda^0 = 1800 < R$

$$E_{H-H} = \frac{A\alpha^2}{R^3} - \frac{37}{\alpha R^7} + \frac{1228}{\alpha^3 R^9}$$

The leading term at intermediate separations is the usual London dipole-dipole dispersion energy, $-6.499/R^6$. The coefficient 6.499 was calculated accurately, first by PAULING and BEACH, and later by HIRSCHFELDER, and LÖWDIN, CHAN and DALGARNO, BELL, etc. The $1/R^8$ term corresponds to dipole-quadrupole dispersion; the $1/R^{10}$ is due to both quadrupole-quadrupole and dipole-octopole dispersion; the $1/R^{12}$, $1/R^{14}$, $1/R^{16}$, ... terms arise from higher multipole dispersion interactions. The α^2/R^4 and α^3/R^3 terms come from CASIMIR and POLDER's quantum electrodynamical consideration of the dipole-

dipole interactions of the two atoms. Actually, the α^2/R^4 term can also be obtained as mixed second order perturbation using the Breit-Pauli Hamiltonian (first order with respect to the electrostatic dipole-dipole and first order with respect to current-current interactions). MEATH has recently obtained the $A \alpha^2/R^3$ term as the result of the spin-spin interaction.

In the long range region of separations, relativistic retardation plays a major role. The $(\alpha R^7)^{-1}$ and $(\alpha^3 R^9)^{-1}$ term come from CASIMIR and POLDER's quantum electrodynamical treatment of the dipole-dipole interactions. It is interesting to note that *if* the spin-spin interactions were not affected by retardation, then the $A \alpha^2/R^3$ term would be dominant. I think it is almost sure that the spin-spin interaction term is modified by retardation, but at the present time no one knows what this modification should be.

This afternoon I will try to summarize the present theories for the intermolecular forces between small molecules. It is high time we were finishing off the atom-atom interactions and turning our attention to the much more interesting problems of the poly-atomic molecules where there are angle dependencies and so forth which we have to determine theoretically in order to help our experimental friends to unravel their difficulties of interpretation.

PERMANENT AND INDUCED MOLECULAR MULTIPOLE MOMENTS

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The first thing I want to do is to express my gratitude to the Pontifical Academy of Science for convening this Study Week on Molecular Forces and for permitting me to participate in it. I also want particularly to thank Professor DEBYE and to wish him well.

INTRODUCTION

It is now generally agreed that the forces between atoms and molecules have an electric origin. It is true that there may be other sources, such as magnetic and gravitational interactions, but these are normally negligible. When the interacting molecules are far apart, the separation being large compared to the dimensions of the molecule, the interaction energy is determined by the permanent electric moments, and these give rise to what is called electrostatic energy. Also the permanent moments may distort the electronic structure of neighbouring molecules, thereby leading to an additional interaction energy which is always associated with an attractive intermolecular force and is called the induction energy. Both

the electrostatic and induction energies are determined by the properties of the free molecules, so a knowledge of these properties is essential for a full understanding of intermolecular forces. In addition, the dispersion energy may be approximately related to the polarisabilities describing the distortion of the free molecules by external fields. My paper is concerned with the determination of the permanent moments of free molecules and also those induced by external electric fields and field-gradients.

The Hamiltonian describing a molecule interacting with fixed external charges is

$$(1) \quad H = H^{(0)} - \boldsymbol{\mu} \cdot \mathbf{F} - \frac{1}{3} \Theta : \mathbf{F}' - \dots$$

where $\boldsymbol{\mu} = \sum_i e_i \mathbf{r}_i$ and $\Theta = \frac{1}{2} \sum_i e_i \{3\mathbf{r}_i \mathbf{r}_i - r_i^2 \mathbf{1}\}$ are the dipole and quadrupole moments operators; e_i is the i th element of charge at the point $\mathbf{r}_i$ relative to an origin fixed at some point in the molecule. $\mathbf{F}$ and $\mathbf{F}'$ are the field and field-gradient at the origin due to the fixed external charges. If the molecule is in the quantum state Ψ its energy is

(2)

$$E = \langle \Psi | H | \Psi \rangle$$

$$\begin{aligned} &= \mathcal{U}^{(0)} - \boldsymbol{\mu}^{(0)} \cdot \mathbf{F} - \frac{1}{2} \boldsymbol{\alpha} : \mathbf{F}^2 - \frac{1}{6} \boldsymbol{\beta} : \mathbf{F}^3 - \frac{1}{24} \boldsymbol{\gamma} : \mathbf{F}^4 \\ &- \frac{1}{3} \Theta^{(0)} : \mathbf{F}' - \frac{1}{3} \mathbf{A} : \mathbf{F} \mathbf{F}' - \frac{1}{6} \mathbf{B} : \mathbf{F}^2 \mathbf{F}' - \frac{1}{6} \mathbf{C} : (\mathbf{F}')^2 - \dots \end{aligned}$$

where $\mu^{(0)} = \langle \Psi^{(0)} | \mu | \Psi^{(0)} \rangle$ and $\Theta^{(0)} = \langle \Psi^{(0)} | \Theta | \Psi^{(0)} \rangle$ are the permanent dipole and quadrupole moments of the molecule, $\Psi^{(0)}$ being the unperturbed wave function (i.e. $H^{(0)}\Psi^{(0)} = \epsilon^{(0)}\Psi^{(0)}$); α , β , γ , and $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, are molecular polarisabilities describing the distortion of the molecule by the external electric field and field-gradient.

The total dipole and quadrupole moments of the molecule in the state Ψ are

$$(3) \quad \mu = - \frac{\partial \epsilon}{\partial \mathbf{F}} = \mu^{(0)} + \alpha \cdot \mathbf{F} + \frac{1}{2} \beta : \mathbf{F}^2 + \frac{1}{6} \gamma :: \mathbf{F}^3 + \\ + \frac{1}{3} \mathbf{A} : \mathbf{F}' + \frac{1}{3} \mathbf{B} : \mathbf{F} \mathbf{F}' + \dots$$

$$(4) \quad \Theta = - 3 \frac{\partial \epsilon}{\partial \mathbf{F}'} = \Theta^{(0)} + \mathbf{A} \cdot \mathbf{F} + \frac{1}{2} \mathbf{B} : \mathbf{F}^2 + \mathbf{C} : \mathbf{F}' + \dots$$

The second rank tensor α is the well-known polarisability, and β and γ are « hyperpolarisabilities » describing the deviations from a linear polarisation law. The tensor $\mathbf{A}$ determines both the dipole induced by a field-gradient, and the quadrupole induced by a uniform field. The tensors β and $\mathbf{A}$ are of the third rank, and γ and $\mathbf{C}$ of the fourth. In static fields, α , β , γ are symmetric in all suffixes, and $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ in pairs of suffixes.

Measurements of $\mu^{(0)}$ and α have been accurately made for many years — particularly through the classical work of DEBYE [1]. At the present time, all of the molecular constants in equation (2), with the exception of $\mathbf{A}$ and $\mathbf{C}$, are accessible to measurement; this paper is particularly concerned with the determination of $\Theta^{(0)}$, γ and β through experiments in which

the optical anisotropy induced in the gas by an external field or field-gradient is measured. The polarisability tensor of a molecule in an external field is conveniently written as π , where

$$(5) \quad \pi = \frac{\partial \mu}{\partial \mathbf{F}} = \alpha + \beta \cdot \mathbf{F} + \frac{1}{2} \gamma : \mathbf{F}^2 + \frac{1}{3} \mathbf{B} : \mathbf{F}' + \dots$$

so that β , γ , and $\mathbf{B}$ may be regarded as determining the effects of an external field and field-gradient on the polarisability of a molecule. The difference in the refractive index of a gas for light polarised in the x - and y -directions in space is

$$(6) \quad n_x - n_y = 2\pi N(\overline{\pi_{xx}} - \overline{\pi_{yy}})$$

where N is the number of molecules per unit volume and the bars over the polarisabilities denote statistical averages. Thus

$$(7) \quad \overline{\pi} = \frac{\sum_i \langle \Psi_i | \pi | \Psi_i \rangle \exp(-u_i/kT)}{\sum_i \exp(-u_i/kT)}$$

where the summation $\sum_i$ extends over all the quantum states Ψ_i .

It is usual to treat the rotational degrees of freedom classically, and to replace the sum in equation (7) by an integral over all orientations ω :

$$(8) \quad \overline{\pi} = \frac{\int \pi \exp(-u/kT) d\omega}{\int \exp(-u/kT) d\omega}$$

QUADRUPOLE MOMENTS

If two parallel wires are at the same potential relative to a tube outside them, there is an electric field-gradient between the wires, and this interacts with the molecular quadrupole moments of gaseous molecules and partially orients them. This orientation may be measured by observing the double refraction induced in the gas by the field-gradient. For molecules with axial symmetry, with polarisabilities $\alpha_{||}$ and $\alpha_{\perp}$ along and at right-angles to the axis, there is just one quadrupole moment $\Theta^{(0)} = \Theta_{||}^{(0)} = -2\Theta_{\perp}^{(0)}$, and if the field gradient is $F'_{xx} = -F'_{yy}$, $F'_{zz} = 0$, the difference in the refractive indices for light with electric vectors in the x - and y -directions is [2]

$$(9) \quad n_x - n_y = \frac{4 \pi N F'_{xx}}{15} \left\{ \frac{15}{2} B + \frac{(\alpha_{||} - \alpha_{\perp}) \Theta^{(0)}}{kT} \right\}$$

For anisotropic molecules, the quadrupolar term proportional to T^{-1} is normally much larger than that due to the hyperpolarisability B , which describes the effect of the field-gradient on the polarisability π [see equation (5)]. The two terms in equation (9) may therefore be related to a *distortion* of the molecule, inducing a double refraction that is independent of temperature and is present in all species, including isotropically polarisable ones like Ar, CH₄, SF₆, and secondly a partial, temperature-dependent *orientation* through the interaction of the molecular quadrupole moment with the field-gradient. Hence double refraction measurements over a temperature range lead to values for $(\alpha_{||} - \alpha_{\perp})\Theta^{(0)}$ and B . If $(\alpha_{||} - \alpha_{\perp})$ is known from other measurements, and it generally is, through depolarisation studies of the Rayleigh scattering by the gas [3], then the magnitude and sign of $\Theta^{(0)}$ may be derived. The fact that the sign of $\Theta^{(0)}$ may be found contrasts

with the classical Debye-method of determining molecular dipole moments [1], for that gives $(\mu^{(0)})^2$. It could be argued that depolarisation measurements give $(\alpha_{\parallel} - \alpha_{\perp})^2$, thus leaving a sign ambiguity in $(\alpha_{\parallel} - \alpha_{\perp})$; this is strictly true, though experience generally permits us to choose the appropriate sign. In any case, Kerr effect studies of dipolar molecules (see the next Section) give the magnitude and sign of $(\alpha_{\parallel} - \alpha_{\perp})$, as would the frequency dependence of the Kerr constant of non-dipolar molecules.

Some recently determined molecular quadrupole moments are listed in Table I [4, 5].

TABLE I — *Quadrupole moments of simple molecules.*

Gas	CO ₂	N ₂	O ₂	C ₂ H ₆	N ₂ O	CO	H ₂
10 ²⁶ Θ ⁽²⁾ (e.s.u.)	-4.2	-1.5	-0.4	-0.64	-3.0	-2.5	+0.65

The value for H₂, obtained by a very detailed quantum mechanical calculation [6, 7], has been included for comparative purposes.

The equation (9) has been derived on the assumption that the rotation of the molecules is classical. However, in reality the rotational energy is quantized, and strictly it is necessary to determine the effects of the field-gradient on the individual quantum states and then to take the statistical average in equation (7). This detailed theory has been developed for linear molecules in ¹Σ states [8], and it is found that the classical equation (9) has to be replaced by

$$(10) \quad n_x - n_y = \frac{4 \pi N F'_{xx}}{15} \left\{ \frac{15}{2} B + \frac{(\alpha_{\parallel} - \alpha_{\perp}) \Theta^{(0)}}{kT} \left[1 - \frac{hcB_0}{kT} + \frac{8}{15} \left(\frac{hcB_0}{kT} \right)^2 + \dots \right] \right\}$$

where the molecular constants B , $(\alpha_{\parallel} - \alpha_{\perp})$, $\Theta^{(0)}$, and the rotational constant B_0 , refer to the ground vibrational state. It has been assumed in deriving (10) that the excited vibrational states are not significantly populated. Effects due to centrifugal distortion have also been evaluated [8] but are generally smaller than those due to quantization of the rotational motion. For H_2 at room temperature, $hcB_0/kT = 0.29$, and the quadrupolar contribution to the double refraction is reduced to three-quarters of its classical value. Since B_0 for deuterium is half B_0 for hydrogen, the quantum correction is much smaller in deuterium.

Equation (9) has been used to determine B for some molecules in which $\alpha_{\parallel} - \alpha_{\perp}$ and hence $\Theta^{(0)} = 0$. The results are in Table 2 [5]. The calculated value for atomic hydrogen [9] has been included for comparative purposes.

TABLE 2 — *The hyperpolarisability B of atoms and molecules.*

Gas	Ar	CH_4	H
$10^{33} B$ (c.s.u.)	< 0.5	$- 0.3$	$- 0.487$

One further point requires discussion, and that is the question of the origin of the quadrupole moment $\Theta^{(0)}$ of a dipolar molecule as determined by measurement of $n_x - n_y$, as in equation (9). The quadrupole moment of a dipolar molecule is dependent on the origin, and a movement of ϵ along the dipole axis of a linear molecule changes $\Theta^{(0)}$ by $- 2 \mu \epsilon$. A careful analysis [10] of the experiment shows that the appropriate origin for $\Theta^{(0)}$ is not the centre of mass (which changes on isotopic substitution); but if it is possible to say at what point in the light beam the rotating molecule appears

to be, then that point is the origin of the quadrupole moment. Since the observable is the refractive index, the molecule may be considered to be at the point from which the scattered radiation appears to emanate. The quantitative aspects of this problem have not yet been fully explored, and it remains as an intriguing and important question.

THE KERR EFFECT

The anisotropy in the refractive index induced by a uniform electric field is known as the Kerr effect. There are three distinct contributions to the anisotropy: The first is common to all substances and arises from γ in equation (5) — it gives a temperature-independent Kerr constant and is the only non-vanishing term for isotropic molecules. The second is only found in dipolar molecules, and is due to the fact that in a molecule which is partially oriented through the interaction of the dipole and the field, the polarisability $\beta \cdot E$ in equation (5) is significant. Thirdly, for anisotropic molecules, the partial orientation of the molecule through interaction of its permanent and induced dipole moments with the field leads to a difference in the bulk refractive indexes. For axially symmetric molecules, these three effects combine to give

(II)

$$n_x - n_y = \frac{2 \pi N F_x^2}{15} \left\{ 5\gamma + \frac{10 \mu \beta}{3 kT} + \frac{(\alpha_{||} - \alpha_{\perp})}{kT} \left[(\alpha_{||} - \alpha_{\perp})_0 + \frac{\mu^2}{kT} \right] \right\}$$

where $(\alpha_{||} - \alpha_{\perp})_0$ is the static polarisability anisotropy.

For isotropic molecules, measurements of $n_x - n_y$ therefore yield γ ; some recent results [5, 12] are shown in Table 3. The two-electron case of helium is of special theoretical interest, for it is sufficiently simple for accurate

TABLE 3 — *The hyperpolarisabilities of isotropic molecules.*

Gas	He	Ne	Ar	Kr	Xe	CH ₄ *	H
$10^{38} \gamma$ (e.s.u.)	2.6	5.5	63	150	390	260	67.1

quantum mechanical calculations to be performed on it. An analytic treatment [12], in which the electron-electron interaction is treated as a perturbation to the hydrogen atom in the field, has yielded the value 1.57×10^{-38} e.s.u. The calculated α is 0.203×10^{-24} cm³, and the experimental value is 0.2051×10^{-24} .

The Kerr effect does not generally lead to reliable values for the first hyperpolarisability β , for if $\mu \neq 0$, the term in $\mu^2(\alpha_{11} - \alpha_{11})$ is generally dominant. However, in some molecules this dipolar contribution may be small and the β term dominant; such a case is CH₂Cl₂ [13]. But accurate values of β are also available from measurements of second harmonic generation by molecules in intense light beams. From equation (3) it may be seen that β is responsible for the induced dipole proportional to F^2 , and this oscillates at twice the frequency of F , thus leading to frequency doubling. Similarly γ gives rise to third harmonic generation.

(*) From E. KUSS and H.A. STUART, « Phys. Z. », 42, 95 (1941).

CONCLUSIONS

Through measurement of the double refraction induced in gases by the application of an electric field or field-gradient, it is possible to study many of the molecular constants that describe the charge distribution of the free molecules and the way in which this distribution may be perturbed by external fields. The double refraction may be quite small, but with the aid of a gas laser (whose intensity and parallelism permits a large amount of light to traverse the small significant region of the gas — this is particularly valuable in the quadrupole moment work, where the field is non-uniform), and a narrow-band phase-sensitive detector, phase differences as small as 10^{-8} radian can be detected. With a field-gradient of 1000 e.s.u. and a path length of 125 cm, this phase difference would be induced in 0.02 atm of carbon dioxide at room temperature.

Thus the electrostatic and induction energies of interaction of gaseous molecules are quantitatively known in favourable cases. However, while these energies are of importance in determining the long-range part of the intermolecular potential, it should be stressed that they are insufficient to describe the energy at or close to equilibrium, or at short-range.

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DISCUSSION

Chairman: J. HIRSCHFELDER

HIRSCHFELDER

Who would have a question he would like to ask Dr. BUCKINGHAM?

CASIMIR

I have one little remark to make. It's just a simple question of definition. You define very rightly quadrupole moment as R^2 multiplied by the second spherical harmonic. So it becomes $\frac{3}{2}z^2 - \frac{1}{2}R^2$. Now, unfortunately, there is also a lot of work on nuclear quadrupole moments and there one defines the nuclear quadrupole moments as $3z^2 - R^2$ which differs by a factor 2. I am afraid that I am partly to blame for this because I happenend to make some of the first quantitative calculations on quadrupoles. It is not very important but I just thought to remind the audience of this.

BUCKINGHAM

Thank you for doing that. I'm afraid I'm equally to blame, because I used the half.

CASIMIR

Well I think the half is more correct because it is the usual mathematical definition. Another question I wanted to ask is this: If you make the transition from atomic or molecular moments to macroscopic electric properties, it is well-known that the polarization P is not the average of the atomic dipole moment, but contains a correction which is essentially the divergence of the quadrupole moment. I wonder whether such things occur here when you make an interpretation of the refraction of light, going through a medium with quadrupole moments in an inhomogeneous field.

BUCKINGHAM

The symmetry of our system is such that there is a double refraction of light as it traverses our cell, and that we can separate rigorously any orientation that arises from the electric field (rather than the field gradient) because it will depend *quadratically* on the field. It's a fortunate difference. In other words, if the voltage is modulated with a frequency ω , any refraction arising from the field squared will have the frequency 2ω . So in fact we do, I think, achieve a proper separation.

I believe that the contribution to the refractive index due to the quadrupoles induced by the fields of the light wave are negligible.

VERWEY

May I ask a brief question to Dr. BUCKINGHAM? Coming back to molecular forces, I have been asking myself how large is the order of magnitude of the electrostatic contribution to the intermolecular forces, because oxygen has the higher boiling point, but a lower quadrupole moment; so it seems that the second part of the interaction energy, viz. that of the dispersion forces in general is really the predominant part of the interaction.

BUCKINGHAM

In the case of oxygen, there is no dipole moment, and a small quadrupole moment, but the contribution of the electrostatic energy to the binding energy in the liquid is in fact proportional to the square of the electrostatic energy, because the electrostatic energy (including the quadrupole contribution to the electrostatic energy) involves a function of angle, and this function of angle has a zero average. In the solid we can have a very large contribution to the binding arising from electrostatic forces because the orientations are fixed and this function might be unity or some definite number which depends on the structure. In the case of a liquid, however, to a first approximation this averages to 0 and provided this interaction is small compared to kT one can do a classical averaging over rotation and the energy will then come out to be proportional to its square over kT , and it will, therefore, be much smaller. In the case of oxygen, I think the quadrupole contribution to the binding is approximately proportional to the fourth power of the quadrupole, which is very small in any case. So I would agree with your interpretation that the electrostatic contribution to the binding in liquid oxygen is very small.

BERNSTEIN

Can you comment on the importance of molecular collisions in the experiment involving measurement of the anisotropy of the refractive index? Perhaps you can just indicate the pressure levels and give us your interpretation of the influence of collisions on the measurements.

BUCKINGHAM

I think our problem involves an equilibrium measurement so that the dynamics of the collision are unimportant. However, there

are collisions, of course, and these may distort the molecule. We looked for these pressure effects because in the early experiments (which, I want to say, were actually conceived in Prof. HIRSCHFELDER's department in Madison in 1958), we worked at rather high pressures — in fact the highest we could get. The pressure effects in the cases we examined, which were carbon dioxide, nitrogen and oxygen, were really rather small and were on the limits of detectability up to 50 atmospheres of CO_2 , and a good deal more of nitrogen. I think we could pick up these density effects now the experiment is so much more sensitive, but I believe that in the non dipolar systems the effects of interaction are very small.

MOLECULAR BEAM SCATTERING AS A ROUTE TO THE INTERMOLECULAR POTENTIAL

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It has been known for more than thirty years (since the early experiments of RABl and his group [1] and the theoretical analysis by MASSEY and co-workers [2]) that molecular beam scattering cross sections are completely determined by the intermolecular forces. Yet, the problem of « inversion » of experimental measurements of differential and total elastic scattering cross sections to yield the potential [3] has not yet been completely solved in practice, even for an orientation-averaged, spherically symmetrical potential.

We may divide the problem into two parts: first, the deduction of the repulsive, short-range part of the potential from high energy beam scattering measurements, and second, the determination of the attractive well and long-range « tail » of the potential from scattering data at thermal and epithermal energies. The first part of the problem has been thoroughly investigated since 1940 by AMDUR and co-workers [3-b], and, with only a slight reservation, it appears to have been fairly well solved. It is possible to make a one-to-one connection between the classical « impact parameter », b , and the « angle of deflection », θ , so that from experimental data on the energy

dependence of the classical, low-resolution cross section one can obtain uniquely the potential function, $V(r)$, in the region in which it is monotonic. Fig. 1 shows AMDUR's results [3*b*] for the He-He system (curves A and B), compared with $V(r)$ deduced from transport coefficients (curves C and D).

However, the second part of the problem, dealing with the attractive part of the potential, is more difficult (and in some ways more interesting, since the macroscopic properties of

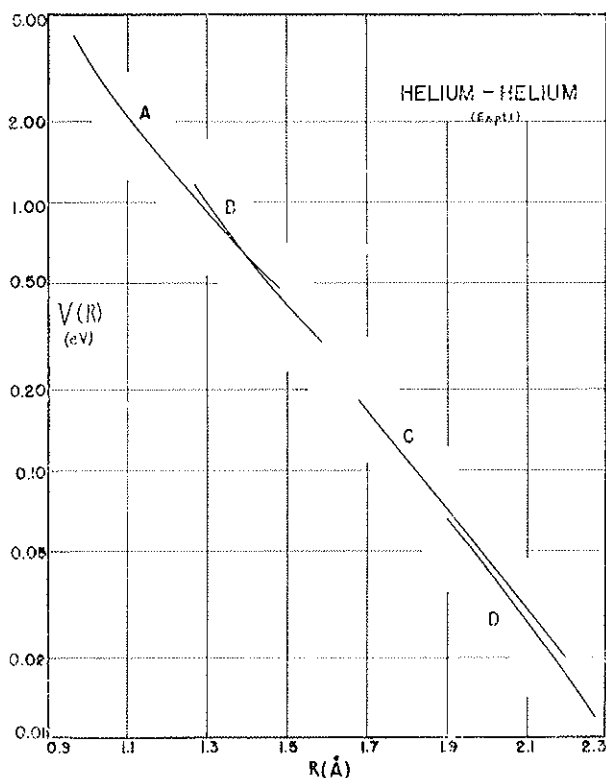


FIG. 1 — He-He repulsive potential [3-*b*]. Curves A, B: from beam data; C, D: from transport properties.

fluids are usually more strongly influenced by the potential well). Fig. 2 shows three suggested potential curves [4] for the He-He well; even for this simple system with a spherically symmetrical potential there is no theoretical unanimity of opinion on the magnitude of the attractive forces, nor is there a well-defined « experimental » potential energy curve yet in existence [5].

It might be of interest to point out that the idea of such potential curves is not new; the Italian Jesuit, ROGER BOSCOVICH (a mathematician at the University of Padova) put forth a number of such curves in his book, published in 1754 in Venezia. We have come a long way since 1754 but we are not yet in a position where we know a single intermolecular

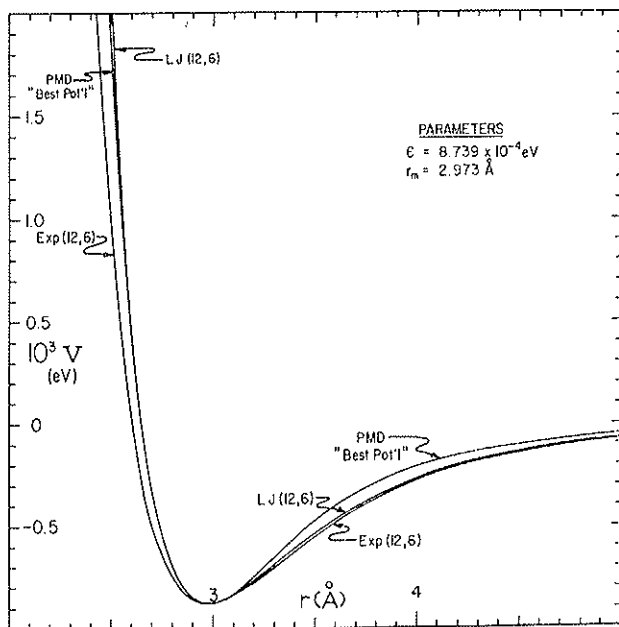


FIG. 2 — He-He attractive potential [4].

potential curve, either experimentally and theoretically, over a sufficient range and with sufficient accuracy to make reliable predictions of all the macroscopic properties.

The main reason for the difficulty in carrying out the inversion of experimental scattering data is the fact that the *non-monotonic* potential function produces an angular deflection function with a minimum, so that the $\theta(b)$ relationship is not single-valued [6]. Fig. 3 (upper) shows a typical calculated [3c] deflection function for a Lennard-Jones (12,6) potential, for a relative collision energy 1.6 times the well-depth. The abscissa is the impact parameter in units of the

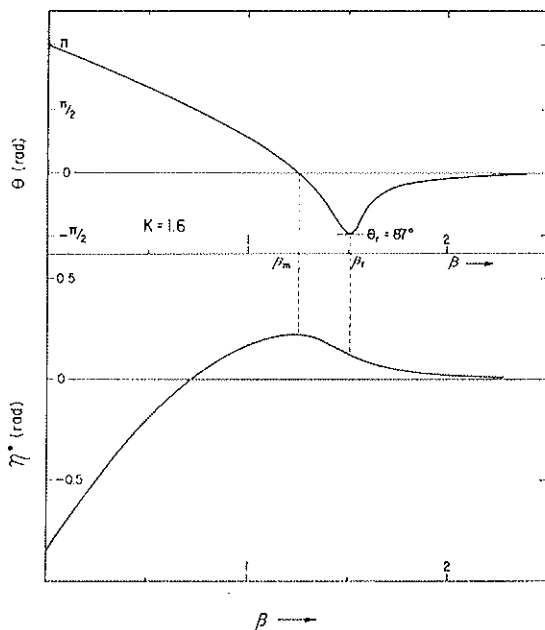


FIG. 3 — Upper: Dependence [3-c] of the deflection function upon the reduced impact parameter for an L.-J. (12,6) potential Lower: Corresponding dependence [3-c] of the reduced phase shift upon the reduced angular momentum.

« collision diameter », σ . The minimum in the deflection function produces, classically [7], an infinity in the differential cross section at the critical angle θ_c ; quantum mechanically one expects [8] (and experimentally one observes [9]) a so-called « rainbow maximum » near θ_r , the « rainbow angle ». The quantum-mechanical analog of the classical problem of the several « contributing branches » of the deflection function (i.e., the differential cross section as a sum $\frac{d\sigma(\theta)}{d\Omega} = \sum_i \frac{b_i db_i}{\sin \theta d\theta}$) is the following. The differential cross section or intensity function $I(\theta)$ is the absolute square of the amplitude $f(\theta)$, which is [10], in turn, a sum over all orbital angular momentum quantum numbers l of a function of the partial-wave phase shifts η_l :

$$(1) \quad f(\theta) = \frac{1}{2ik} \sum_l (2l+1) (e^{2i\eta_l} - 1) P_l(\cos \theta) \quad .$$

The phase shifts are determined by the potential function *via* the radial Schrödinger equation:

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{2\mu}{\hbar^2} V(r) - \frac{l(l+1)}{r^2} \right] G_l(r) = 0$$

with $G_l(0)=0$ and $G_l(r) \sim \sin(kr - l\pi/2 + \eta_l)$, asymptotically. Fig. 4 shows a calculated curve [3c] of the radial wave function for a typical situation: one compares the radial function with a spherical Bessel function of the same order and obtains the asymptotic phase shift at a specified wave number $k=\mu v/\hbar$ (where μ is the reduced mass and v the relative velocity; i.e. the collision energy $E=\frac{1}{2} \mu v^2$). Fig. 3 (bottom) shows a typical curve [3c] of the dependence of the phase shift upon the

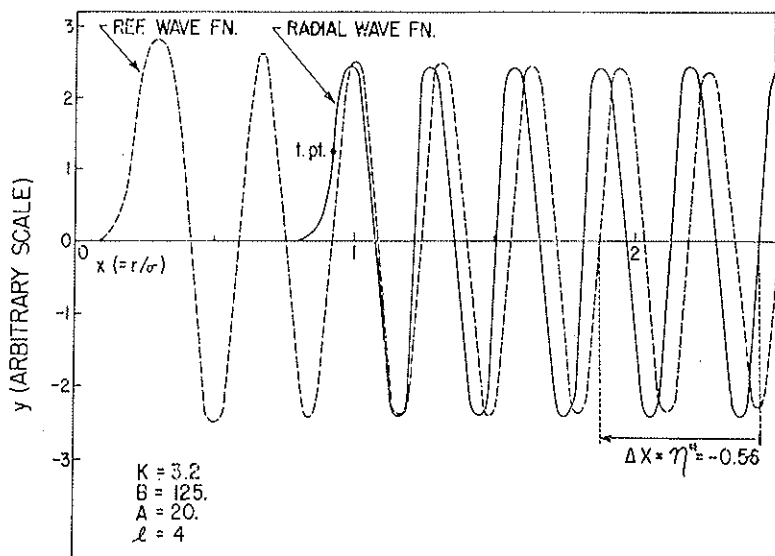


FIG. 4 — Typical radial wave function [3-c] $y(x) \propto G_l(x)$ for L.-J. (12,6) potential, at specified values of parameters. Dashed curve is the « reference » wave function, a spherical Bessel function.

« reduced orbital angular momentum », here represented by $\beta = (l + \frac{1}{2})/k\sigma$. (According to the semiclassical theory, the equivalence relation between the classical impact parameter and the orbital quantum number l is $b = (l + \frac{1}{2})/k$; in addition, one has $\Theta = 2 \, d\eta_l/dl$). Note that at low angular momentum the phase shifts are negative (dominated by the repulsion) while at high angular momentum they are positive (attraction predominates). The maximum in η_l leads to a phenomenon known as « glory scattering », to be discussed shortly.

For a monotonic phase shift curve, it can be shown by the method of stationary phase that the main contribution to the sum in Eq. 1 at any angle θ is from the few partial waves for which $l \approx k \, b(\theta)$. For the case when there are three branches

of the deflection function, there are three classical contributions to the differential cross section:

$$\left[\frac{d^2\sigma(\theta)}{d\Omega} \right]_{cl} = I_{cl}(\theta) = I_a(\theta) + I_b(\theta) + I_c(\theta),$$

where a , b and c represent the three impact parameters associated with the given θ (a being the largest one, influenced largely by the long-range attractive part of the potential). For this case the quantum mechanical analog, in terms of the amplitude, is:

$$f(\theta) = f_a(\theta) + f_b(\theta) + f_c(\theta)$$

so that

$$[I(\theta)]_{qu} = |f(\theta)|^2 = |f_a(\theta)|^2 + |f_b(\theta)|^2 + |f_c(\theta)|^2 + \text{interference terms}.$$

Thus $[I(\theta)]_{qu} = [I(\theta)]_{cl} + \text{interference terms}$. Fig. 5 shows a sample calculation [3c] comparing classical and quantum angular distributions of intensity for a physical situation in which the de Broglie wavelength $\lambda = \frac{h}{\mu v}$ is comparable with the characteristic distance σ , the « collision-diameter » of the system, a measure of the « range » of the interaction. For angles smaller than the rainbow angle θ_r , the amplitude of the interferences is appreciable under all circumstances, while for $\theta > \theta_r$, the amplitude decays with angle and with increasing wavenumber k , as will be discussed later.

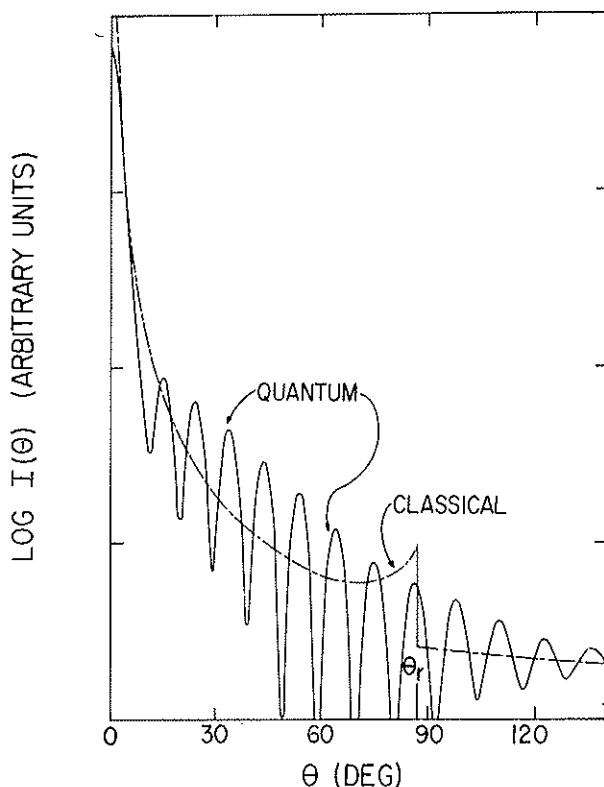


FIG. 5 — Semilog plot [3c] of the angular distribution function $I(\theta)$ for scattering by a L.-J. (12,6) potential, comparing quantum with classical results. The reduced collision energy, $E/\epsilon = 1.6$.

Fig. 6 shows a log-log plot [3c] of the classical differential cross section; for a long-range r^{-6} potential one has, at low angles

$$I(\theta) \propto \theta^{-4/3} \csc \theta \approx \theta^{-7/3}.$$

The graph refers to a L.-J. (12-6) potential with a collision energy 1.6 times the well-depth. Three points are to be men-

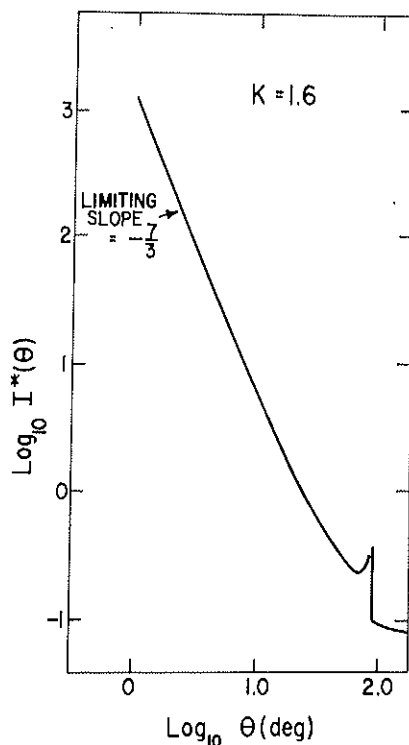


FIG. 6 — Log-log plot [3-c] of the classical curve of Fig. 5. The sharp peak near 87° is the classical rainbow effect.

tioned in connection with this figure. First, the classical divergence at $\theta=0$ (the « forward infinity ») associated with the infinite range of the potential, i.e. $d\theta/db \rightarrow 0$ as $b \rightarrow \infty$, leading to an infinite total (integral) scattering cross section. Second, the previously-mentioned « rainbow infinity » at $\theta=\theta_r$; and third, the fact that the limiting low-angle slope is a function of the power (here, -6) of the long-range part of the potential and so can be used to characterize this functionality. Fig. 7 shows some experimental data [9] confirming the long-range r^{-6} behavior for the K-Hg system. Fig. 8 shows another ex-

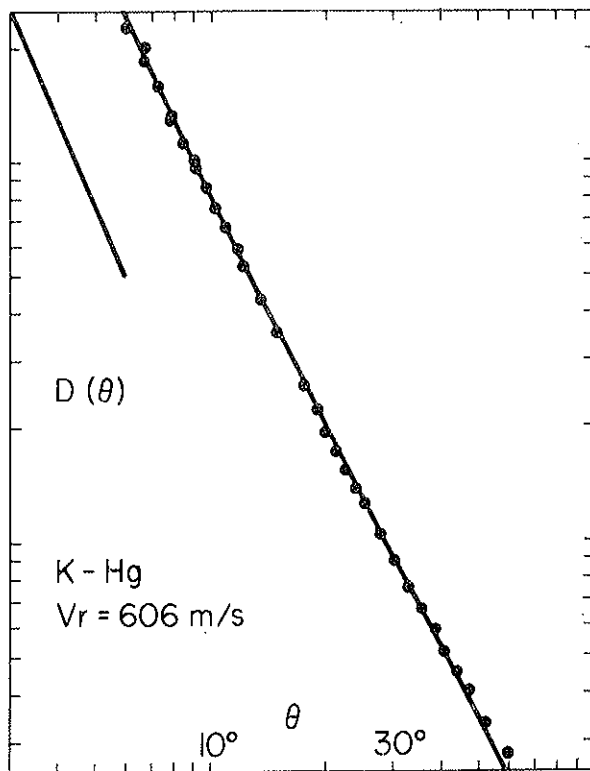


FIG. 7 — Log-log plot [3-d] of experimental data [9] (K-Hg) for comparison with Fig. 6. $D(0)$ is proportional to the differential scattering cross section in the center-of-mass system.

periment [9] at a higher energy; the rainbow peak is clearly resolved. These observations yield only the mean of the rapid oscillations which bunch together in the angular region where the classical rainbow angle is expected. Fig. 9 shows calculated angular distributions [3c] for a L.-J. (12,6) potential for the same relative collision energy as Figs. 5 and 6 but for successively greater values of a parameter $B = \frac{2\mu}{\hbar^2} \epsilon \sigma^2$ (related inversely, to the de Boer parameter Λ^*) which is a measure of

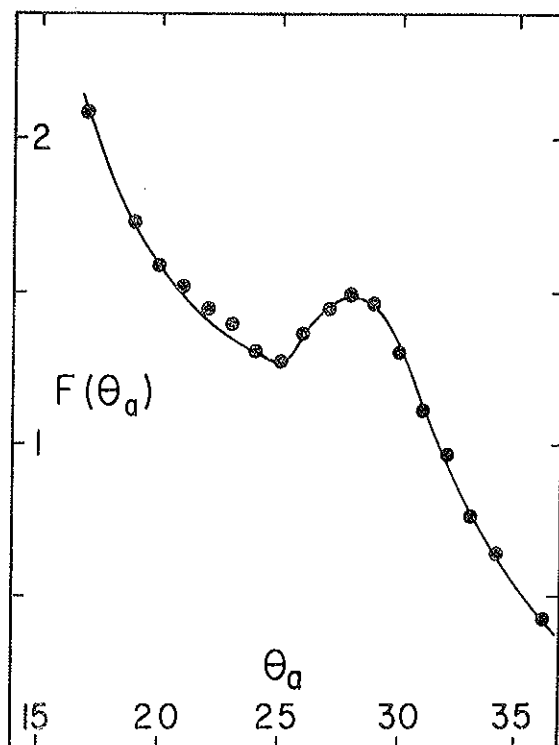


FIG. 8 — Plot [3-d] of derived [9] rainbow maximum (K-Hg) in scattered intensity. $F(\theta_a)$ is the scattered flux at various angles θ_a in the apparatus system.

the « classical character » of the system. The rainbow maximum is accompanied by subsidiary maxima at lower angles. These are illustrated in Fig. 10 for the Na-Hg system, studied by PAULY et al. [11a]. Fig. 11 shows rainbow maxima for the same system; here [11b] the experimental points are compared to the calculated curves based on L.-J. (n , 6) potentials.

Fig. 12 shows the energy dependence of the primary rainbow angle for the Cs-Hg system [9]; the experimental points are compared with the behavior calculated for various

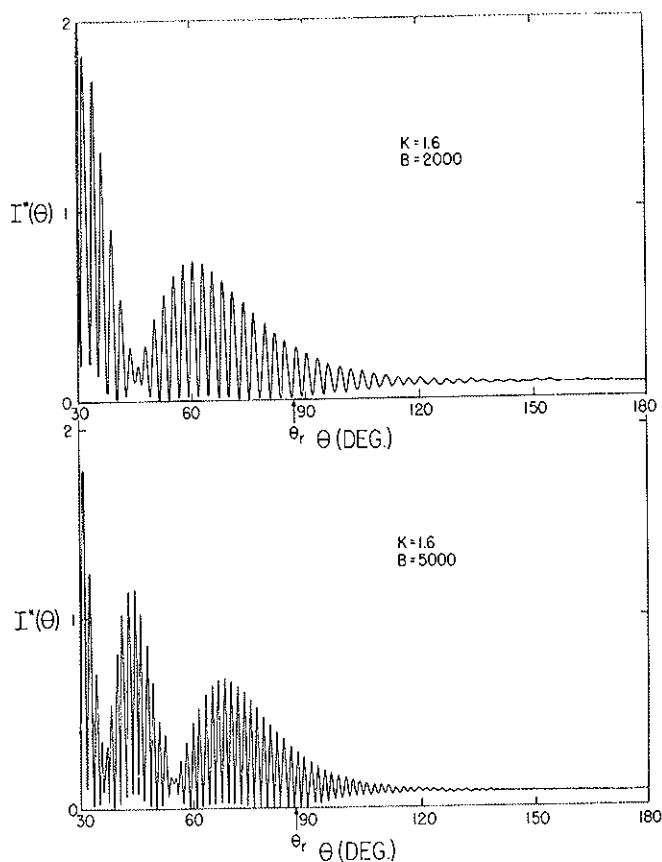


FIG. 9 — Plots of quantum-calculated [3-c] angular distributions for scattering by a L.-J. (12,6) potential at the same (constant) reduced energy of 1.6 as that of Figs. 5 and 6. As the parameter $B = \frac{2\mu}{h^2} \epsilon \sigma^2$ is increased, the system becomes « more classical », and the semiclassical rainbow effects are seen.

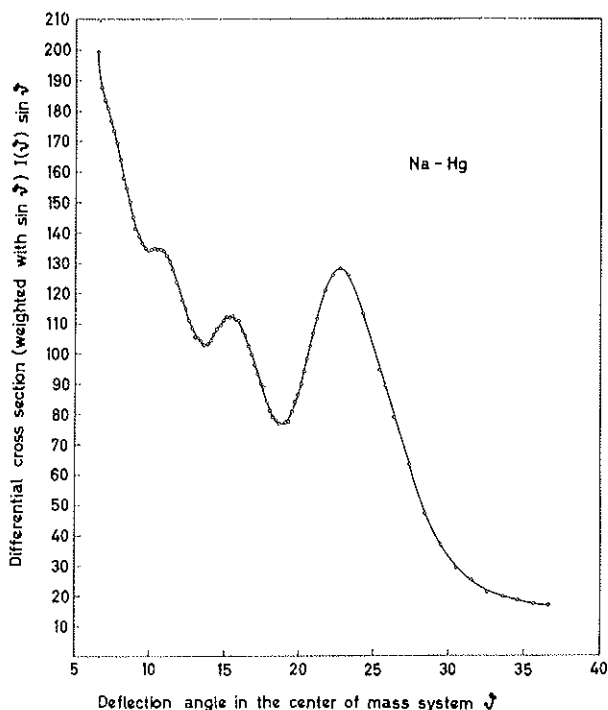


FIG. 10 — Observed rainbow scattering for the Na-Hg [11-a].

potentials but with a given well-depth ϵ . From such data the well depth, and with lesser accuracy, the position of the minimum in $V(r)$, namely r_m , may be estimated. However, it must be noted that the derived potential parameters are somewhat dependent on the functional form assumed for the potential; the basic problem of « inversion » still remains.

Next we consider the classical « forward infinity ». The quantum mechanical treatment yields for an inverse sixth-power long-range potential a very well-behaved angular distribution: $I(\theta) \propto e^{-c\theta^2}$, where c is a combination of angular-

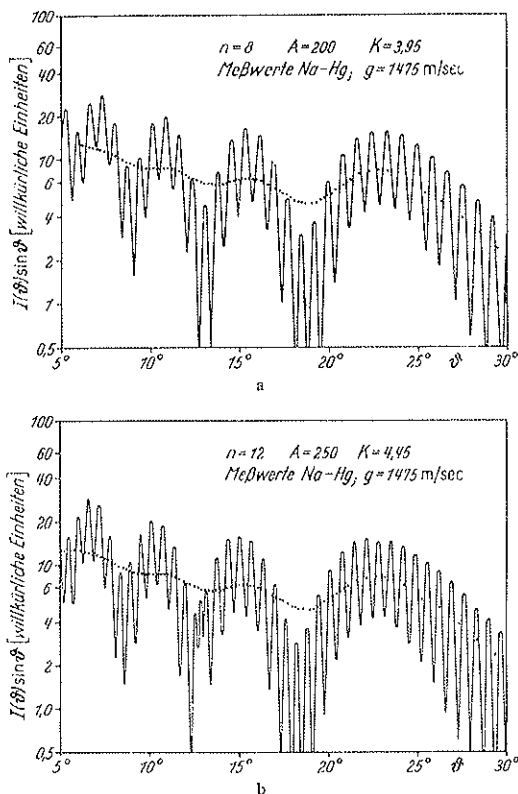


FIG. 11 — Observed vs. calculated rainbow effects for the Na-Hg system [11-b].

independent terms. Fig. 13 shows a typical calculated curve [12a], plotting $\log I$ vs. $\log \theta$ to show better the classical relationship. Fig. 14 illustrates the experimental results [12b] for the K-Xe system plotted in the same way. The solid curve is a calculated fit assuming an r^{-6} potential. These and other measurements of low-angle scattering (and of the influence of angular resolution in total cross section measurements) have

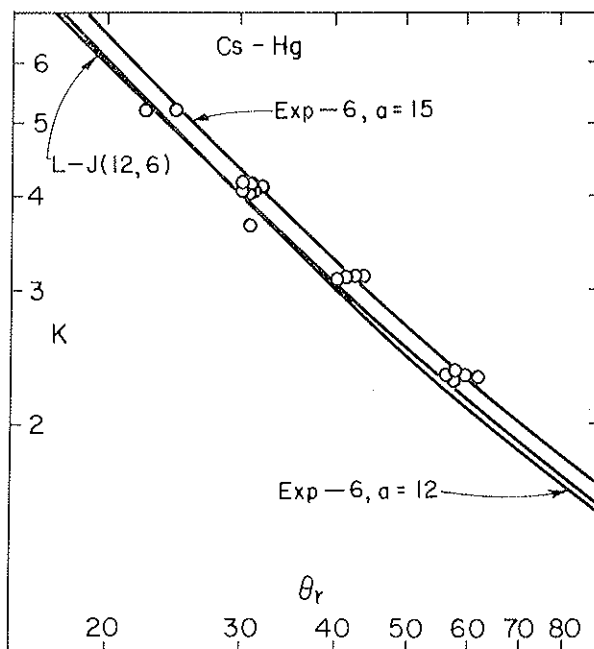


FIG. 12 — Energy dependence of the primary rainbow angle for the Cs-Hg systems [9]. The curves are calculated for the indicated potentials; the points are experimental.

not only verified the functionality of the long-range part of the potential but have justified the very existence of a total

or integral elastic scattering cross section: $Q = 2\pi \int_0^\pi \sin \theta I(\theta) d\theta$.

Since most total cross section measurements are now carried out with angular resolution such that $I(\theta)$ is well in the parabolic region, they are termed « quantum » total cross sections. Using Eq. 1 the quantum cross section is given [2] by the expression:

$$Q = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \eta_l$$

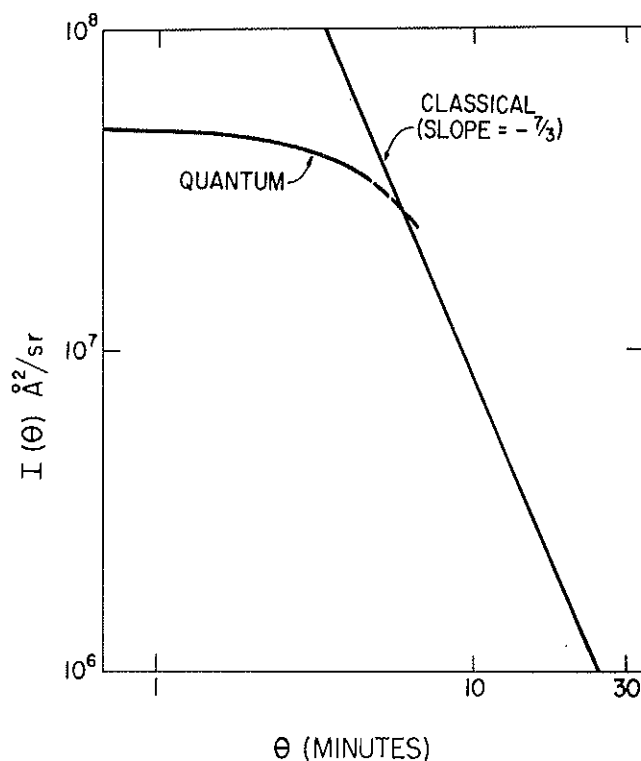


FIG. 13 — Log-log plot [3-c] of $I(\theta)$ at very low angles, calculated [12-a] for the K-Hg system.

The simple random-phase approximation of MASSEY and MOHR [2] predicts the following velocity dependence of the quantum cross section, for a potential $V(r) \sim -C^{(s)}/r^s$,

$$(3) \quad Q = p(s) \left[C^{(s)} / \hbar v \right]^{\frac{2}{s-1}}$$

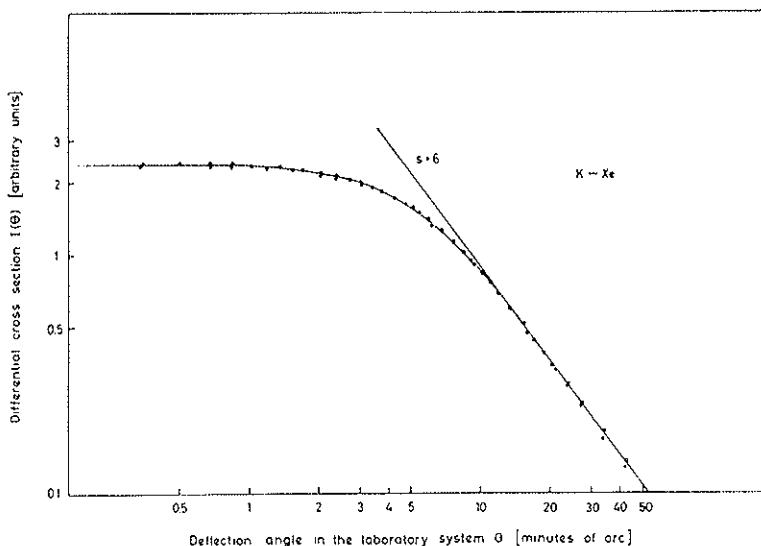


FIG. 14 — Experimental plot [12-b], comparable to Fig. 13, for the K-Xe system. The line designated $s=6$ represents the classical low angle dependence for a long range r^{-6} potential, while the very low angle curve is the limiting quantum behavior.

where $p(s)$ is a known function of s . For a large number of systems the above dependence has been verified experimentally. Fig. 15 shows a log-log plot of data [13] for the K-N₂ system; the line through the experimental points has a slope of $-2/5$, corresponding to $s=6$, while the other lines have slopes appropriate to $s=5$ and 7.

Fig. 16 shows a summary [14] of data for several dozen systems studied in three laboratories. Plotted are observed total cross sections versus estimated value of $C^{(6)}/\bar{v}$; the $C^{(6)}$ constants are calculated by the simple Slater-Kirkwood formula from the polarizability of the interacting atoms (or molecules). We have examined more than one hundred systems and concluded that, within about ± 10 per cent, the observed

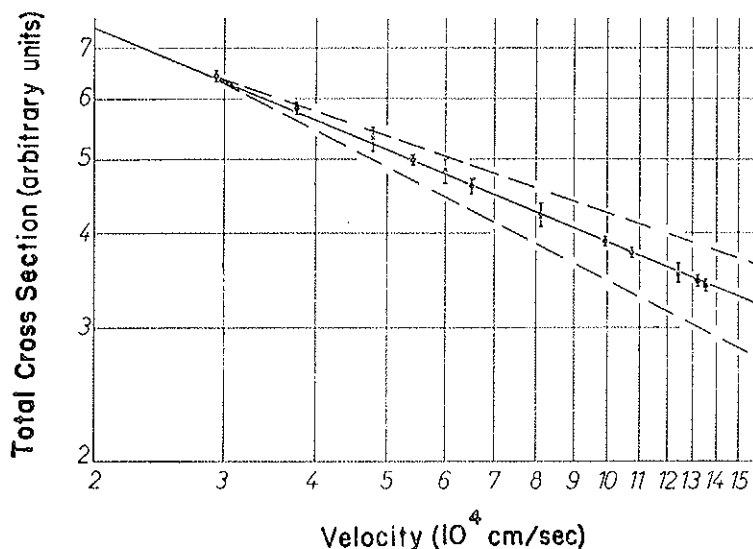


FIG. 15 — Log-log plot [3-d] of the experimental velocity dependence [13] of the total cross section (arbitrary units) for the scattering of K by N_2 . The solid line (slope $= -\frac{2}{5}$) corresponds to an inverse sixth power attraction; the dashed lines, fifth and seventh powers.

cross sections can be reproduced by a simple S-K type estimate of $C^{(6)}$ followed by the use of a slightly improved version of the Massey-Mohr equation, namely, the Schiff-Landau-Lifshitz (SLL) equation.

During the past years it has become possible to measure total cross sections with an absolute accuracy of 5-10 per cent, so that the $C^{(6)}$ constants are now known within 15-25 per cent. For a number of systems accurate theoretical calculations of these constants are now available (e.g., by DALGARNO and others), and the accord between theory and experiment is now within the mutual limits of uncertainty. Thus the « inversion » to obtain the long range part of the potential from the total cross section has been reasonably successful.

A valuable new source of information about the shape of

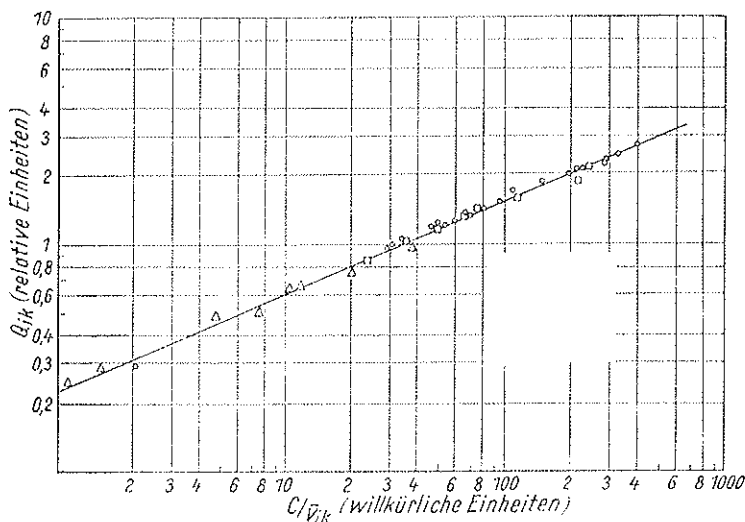


FIG. 16 — Log-log plot [14] summarizing experimental total cross sections vs. $C/\bar{v}$. Here the C values are the Slater-Kirkwood-estimated coefficients of the long-range r^{-6} potential and $\bar{v}$ the average relative velocity. The solid line has the theoretical slope of $2/5$.

the potential well has become available *via* high precision measurements of the velocity dependence of the total cross section. By considering phase shift curves such as Fig. 3 (bottom), at various energies, one notes [3c] that the region near the maximum phase will contribute a non-negligible increment ΔQ to the cross section of Eq. 3 (based on the random-phase approximation). Starting at high energies, where the maximum phase is small ($< \pi/2$), and then reducing the energy, the maximum phase passes successively through $\pi/2$, π , $3\pi/2$, etc, yielding alternate positive and negative « glory » extrema, ΔQ , superimposed on the random-phase-approximated cross section of Eq. 3. The index $N=1$ designates the maximum at highest velocity, due to a maximum phase near $\pi/2$; the other integer indices designate successive maxima at lower

velocities. According to the simple theory the intercept of a plot of N vs. $1/v$ should be $3/8$ and the limiting (high-velocity) slope yields the product $\varepsilon\sigma$ or εr_m .

Fig. 17 shows a calculated curve [3c], $\log Q$ vs. $\log v$, for a L.-J. (12-6) potential with parameters the same as Fig. 5. The two straight lines show the random-phase cross sections

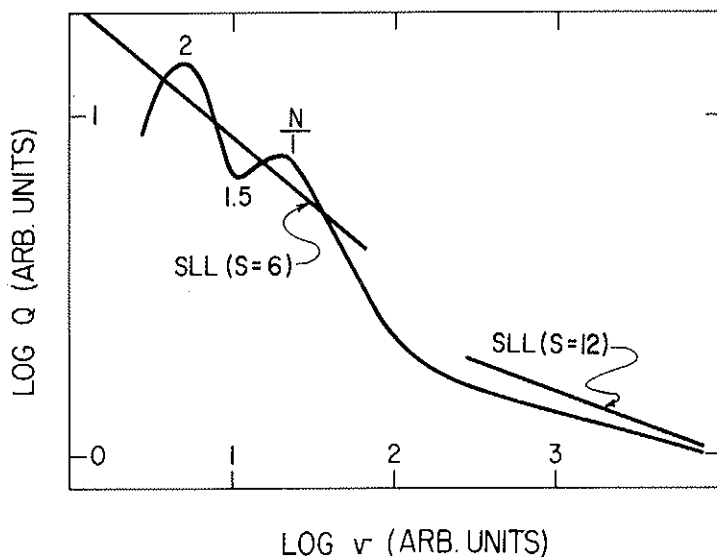


FIG. 17 — Log-log plot [3c] of $Q(v)$ calculated for a L.-J. (12,6) potential. The straight lines represent theoretical approximations for the inverse 6th power attraction and the inverse twelfth power repulsion, separately. The extrema are indexed $N=1, 1.5, 2$ etc. starting from the first maximum at the highest velocity.

(SLL equation) for a pure inverse 6th power attraction, and for an inverse twelfth power repulsion. Fig. 18 plots [3c] (for another case) the deviation function $\Delta Q/Q$ vs. a dimensionless parameter D , proportional to $1/v$.

Fig. 19 shows the first experimental results [15a] (for the Li-Xe system) displaying extrema in the total cross-section-

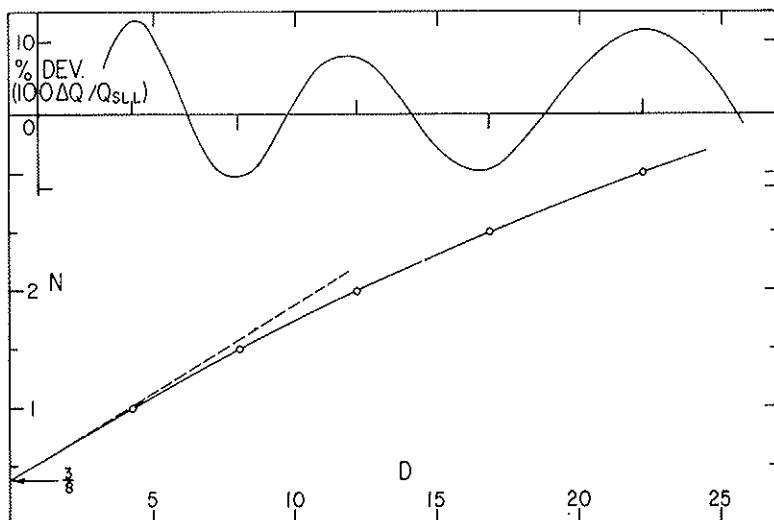


FIG. 18 — Extrema plot [3-c] for a L.-J. (12,6) potential. Upper: deviation function; lower: indexing of extrema. The abscissa is a reduced reciprocal velocity, $D = 2\epsilon\sigma/\hbar v$.

velocity dependence, superimposed on the $s=6$ behavior of Eq. 3. Fig. 20 shows a plot [3d] of the results *vs.* reciprocal velocity with the extrema indexed. Fig. 21 [15b] summarizes the extrema analysis for the Li-Ar, -Kr, and -Xe systems, with the derived values of the product $\epsilon\sigma$, assuming a L.-J. (12,6) potential. Further analysis of the glory-extrema effect shows that one may also estimate the curvature of the potential well at its minimum (i.e. the force constant of the diatom) [17].

Fig. 22 shows some recent data [16] for He-Ne, -Ar, -Kr, and -Xe. The solid curves through the experimental points are calculated for an L.-J. (12,6) potential with optimized parameters. Parenthetically, it should be pointed out that the ordinary « mixing-rules » [$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$ and $\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2)$] are not adequate for these pairs involving helium.

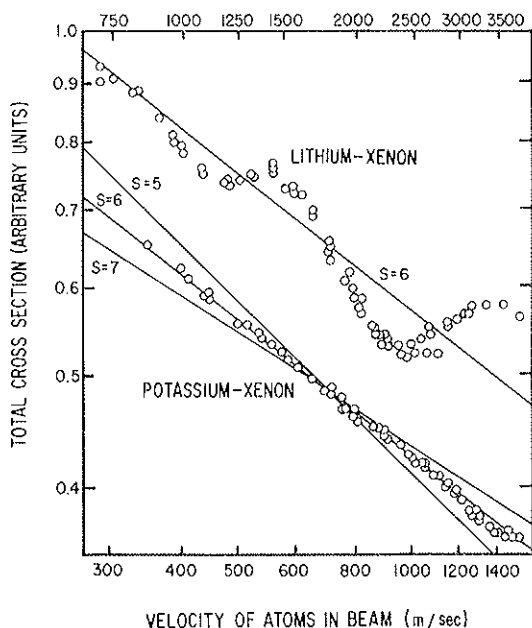


FIG. 19 — Log-log plot [3-d] of observed [15-a] $\sigma(v)$ for Li-Xe and K-Xe. The straight lines have their usual significance.

To summarize, the glory-extrema in the total cross section make possible the characterization of the potential well. Combined with data on rainbow scattering, the parameters ϵ , r_m and even the curvature [17] of the well may be obtained. Thus there is further small progress in the direction of « inversion ».

Next we return to the differential cross section to reconsider the fine interference effects at angles below the rainbow angle. Fig. 23 shows the first such observations [18a] (for the Li-Hg system). A calculated interference pattern for perfectly monochromatic conditions is shown for comparison. Fig. 24 shows more refined and recent measurements [18b, 3d] with the oscillations fully resolved. The velocity dependence of

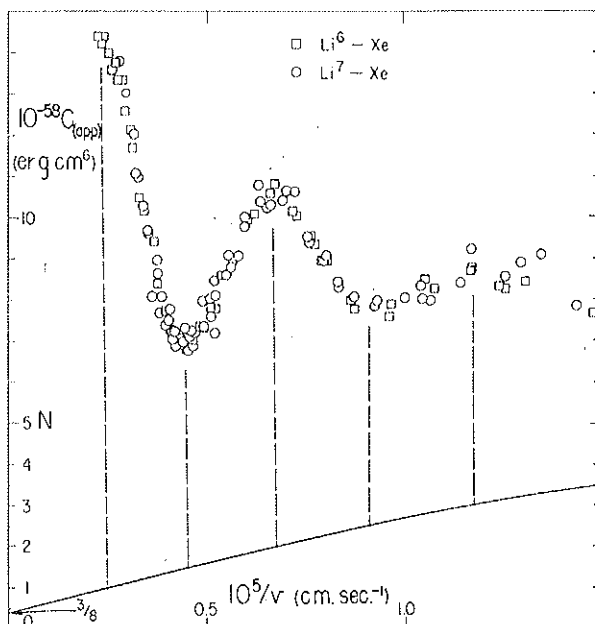


FIG. 20 — Plot [3-d] of an « elastic atom-atom impact spectrum » for the Li^6 - and Li^7 -Xe systems [15]. Upper: « apparent » C constant; lower: indexing of extrema (cf. Fig. 18).

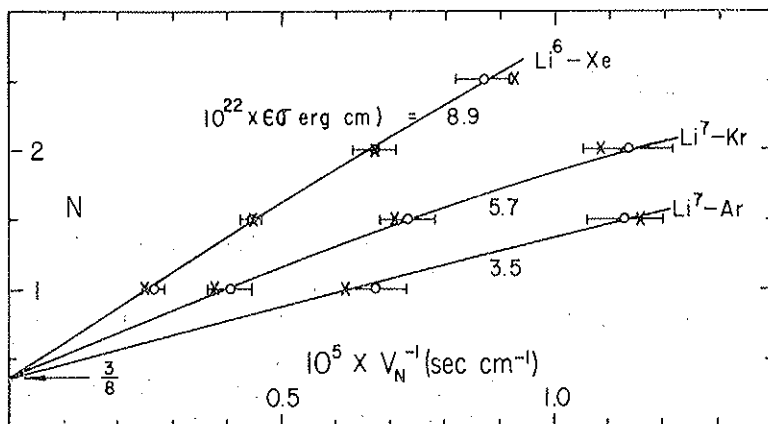


FIG. 21 — Summary plot [3-d] of extrema for Li-Xe, -Kr, and -Ar systems [15-b]. Values of $\epsilon\sigma$ shown refer to an analysis based on a L.-J. (12,6) potential.

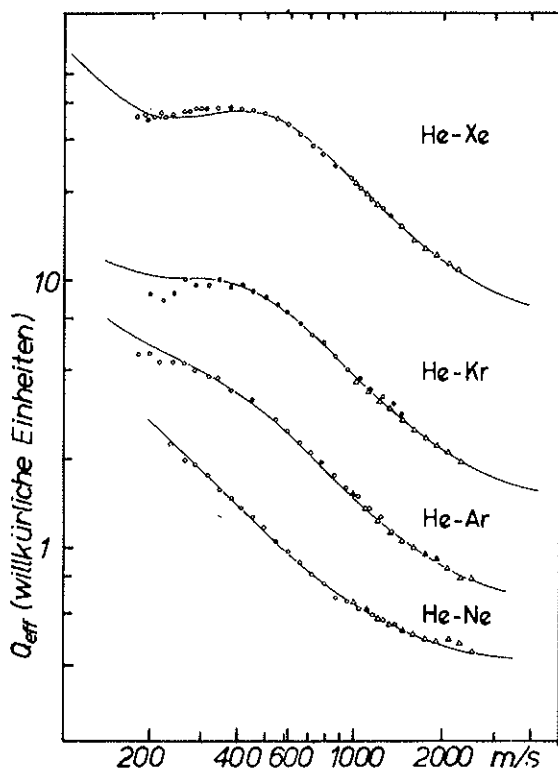


FIG. 22 — Plots of $Q(v)$ for He-rare gas systems [16]. Points are experimental, curves theoretical, assuming a L.-J. (12,6) potential.

the scattering pattern is in the expected direction. Fig. 25 summarizes the entire set of data [18b] for Li^6 - and Li^7 -Hg. The lines are « experimental », as a guide to the calculations. Fig. 26 shows [18b] the fit of calculations based on a L.-J. (12-6) potential to the observed scattering pattern. The vertical positioning establishes the value of the r_m , nearly independent of the functionality of the potential. Figs. 27 and 28 show some recent high-resolution measurements [11b] on Na-Hg

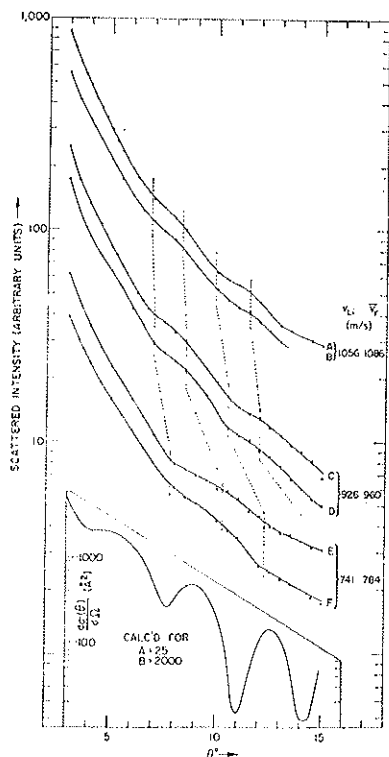


FIG. 23 — Observed [18-a] angular distributions for the scattering of Li by Hg at various relative velocities, showing quantum interferences. Insert: calculated, fully-resolved, angular distribution for a (comparable) L.-J. (12,6) potential.

and Na-Xe. In the latter case the experimental points accord better with calculations based on a L.-J. (8,6) potential rather than a 12,6 function.

A few theoretical investigations of the interference patterns are summarized [3-c] in Figs. 29-31 incl. Fig. 29 shows a « reduced » differential cross section calculated for a given

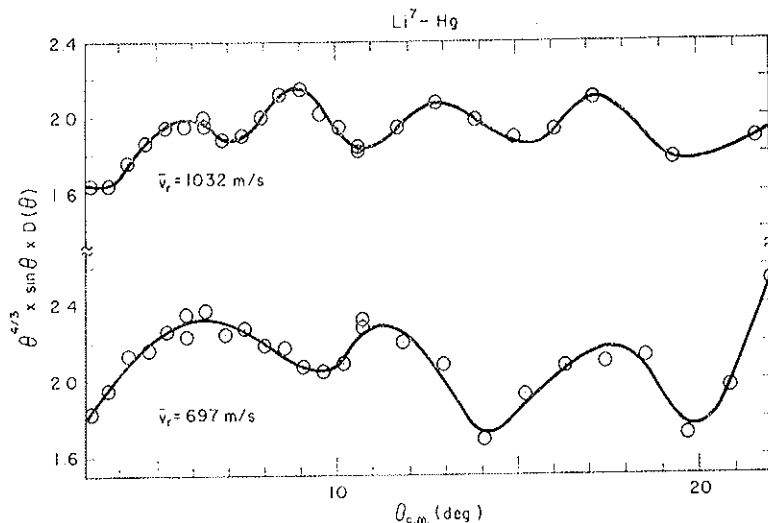


FIG. 24 — Observed [18-b, 3-d] angular distributions for the scattering of Li^7 by Hg, better resolved than Fig. 23; presentation such that the steep « classical » angular dependence is removed.

L.-J. (12-6) potential, where the main low angle ($\theta^{-7/3}$) forward component of the scattering has been removed. The quantum interferences are compared with the smooth classical functionality. Fig. 30 shows the dependence of the interferences on the wave number k at constant reduced energy. Note the nearly constant « average amplitude », but the decreasing periodicity of the oscillations. Fig. 31 summarizes the regularities of the interferences; the points represent computations while the line is calculated on the basis of semiclassical theory. Note that, to a first approximation, the separations or spacings $\Delta\theta$ are inversely proportional to the parameter $\Lambda = k\sigma$. Thus, from observed spacings as a function of k the characteristic distance σ (or r_m) may be obtained directly, as mentioned earlier.

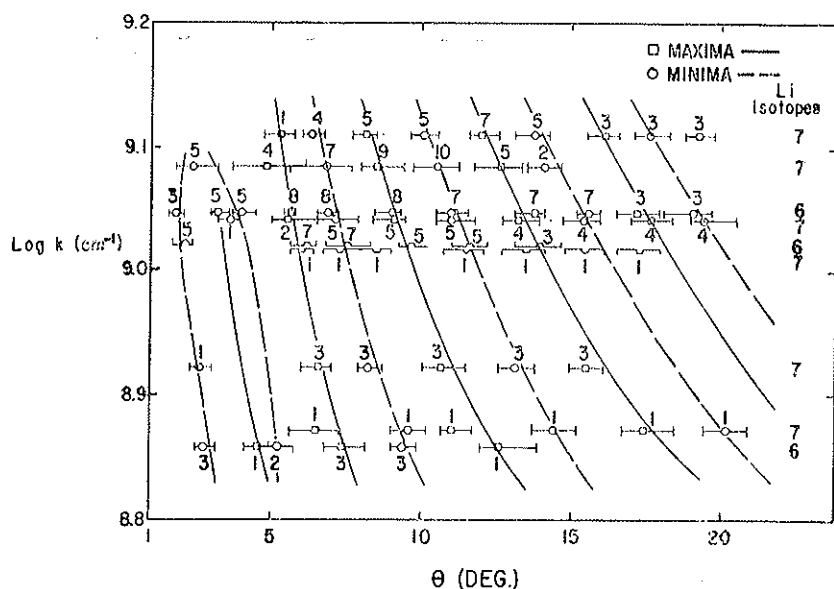


FIG. 25 — Summary of experimental data [18-b] showing the variation of the angular scattering patterns with wavenumber k for the Li-Hg system. The numbers are an indication of the reliability of the observations (10 being best). The solid curves are the best « experimental » ones.

Future experiments may be expected to discriminate among various potential shapes and to yield accurate potential constants. However, it is clear that although one may readily compute from assumed potentials the angular distributions, and then iterate, a true *inversion* from the interference pattern to the potential is not yet possible.

At present, studies are in progress [19] of the Hylleraas inversion procedure [20] which allows the deduction of a non-monotonic potential from experimentally-derived phase shifts as a function of energy. It appears probable that this method can be made practical in the field of molecular beam scattering, but the results are still preliminary and do not warrant reporting at this time.

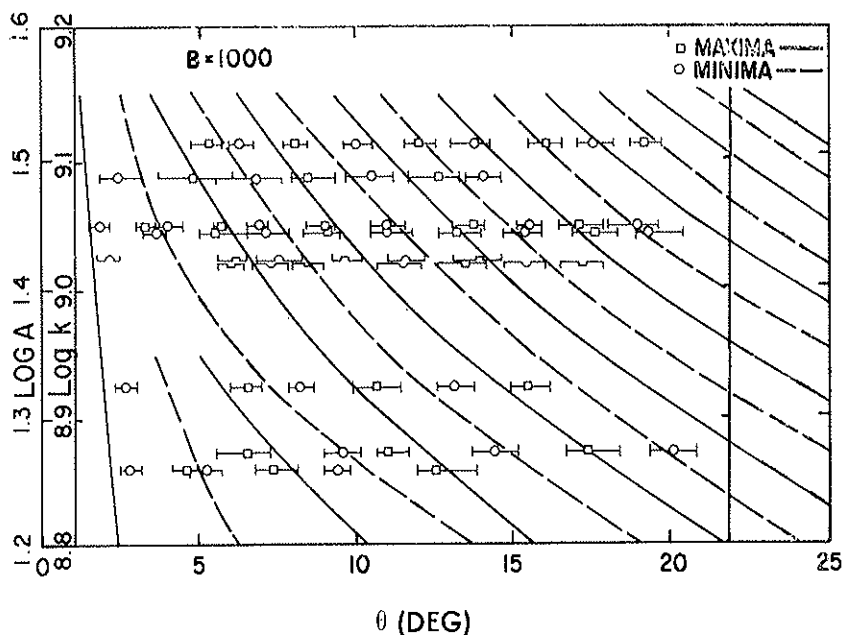


FIG. 26 — Comparison [18-b] of experimental and calculated scattering patterns for the Li-Hg system (cf. Fig. 25). Here the solid curves are calculated, based on a L.-J. (12,6) potential.

This concludes my main presentation. However, I would like to add some remarks which bear on the subject of the determination of intermolecular forces via a somewhat different approach.

We have recently established [21] a connection between the long-range, attractive part of the interatomic potential, the predissociation of the di-atom and resonances in atom-atom scattering. The construct, by HERZBERG [22], of the limiting curve of dissociation (LCD) of a diatomic molecule has been of considerable utility in elucidating the potential energy curve of a predissociating electronic state. In the present

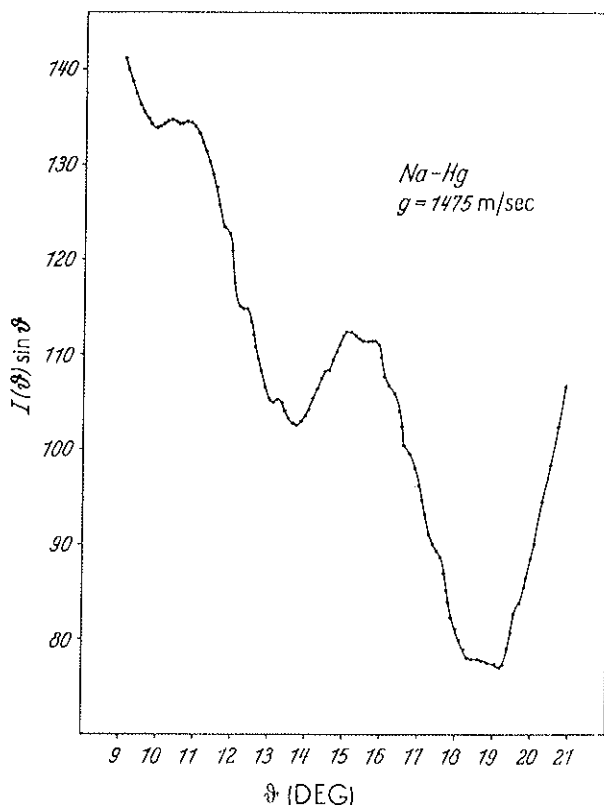


FIG. 27 — Experimental [11-b] angular distribution for the scattering of Na by Hg at the specified relative velocity. The quantum interferences are seen superimposed on the supernumerary rainbow structure.

discussion it is only necessary to note that the shape of the LCD is strongly, if not entirely, governed by the functionality of the *long-range* part of the potential. If this is of the form $V \sim -C_{(n)}r^{-n}$, it can easily be shown that the equation for the LCD is $\Delta E = s_n [j(j+1)]^{\frac{n}{n-2}}$ where the constant s_n is proportional to $[\mu^n C_{(n)}^2]^{\frac{1}{n-2}}$.

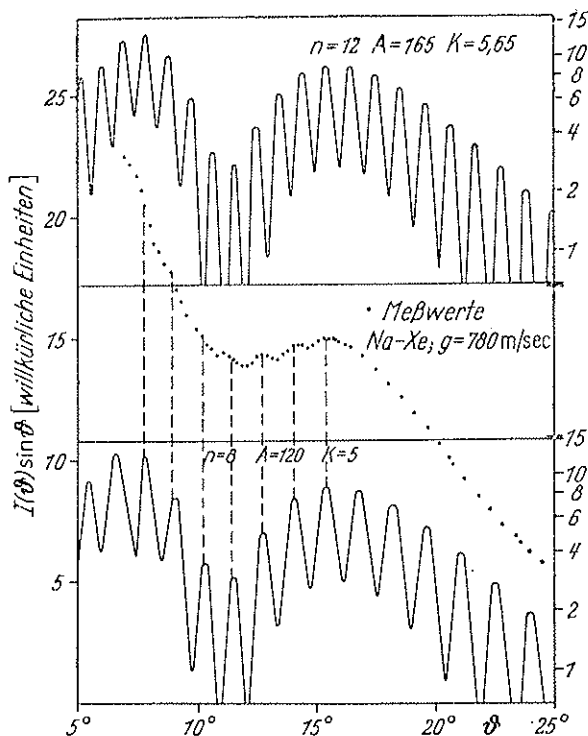


Fig. 28 — Comparison [11-b] of experimental and calculated angular distributions for the scattering of Na by Xe. The upper calculated curve is based on a L.-J. (12,6) potential, the lower one (better fit to the experimental interferences) is for an L.-J. (8,6) function.

Fig. 32 shows a suitable plot [21] of the LCD (the last unpredissociated spectral terms) for the ground electronic state of HgH (and HgD), from the slope of which the long-range $C_{(6)}$ constant can be directly obtained. Fig. 33 shows an alternate presentation [21] of the same data along with similar data for an excited state of N_2 . It is believed that a considerable body of such predissociation data may be available from which long-range interatomic forces may be deduced.

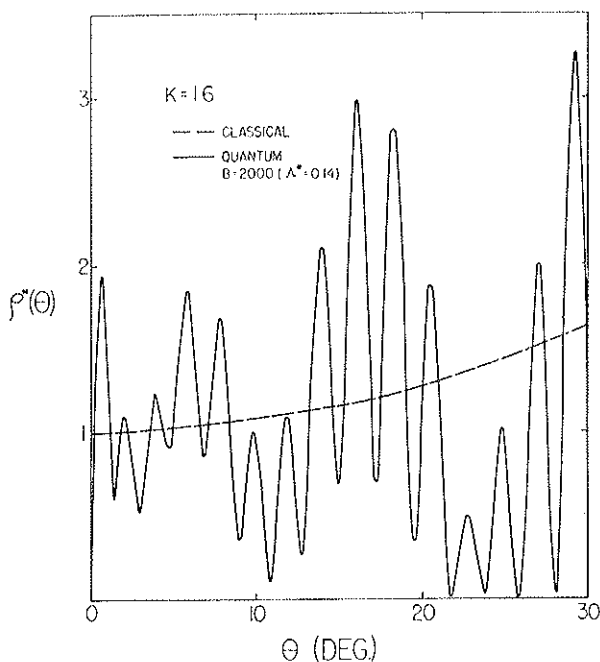


FIG. 29 — Plot [3-c] of a « reduced » angular distribution function, i.e., $\rho^*(\theta) \propto I(\theta) \times \theta^{1/3} \sin \theta$, for a L-J. (12,6) potential, comparing the results of classical and quantum calculations.

The same factors responsible for the line broadening and breaking-off of the diatomic rotational structure (i.e., penetration of the centrifugal barrier) lead to predicted resonance behavior [23] in elastic atom-atom scattering (inverse predissociation). The spectrum of the quasi-bound (virtual) states of positive energy is reflected in the pattern of resonances in the cross section Q . Fig. 33 shows such a predicted resonance pattern, as correlated with the predissociation spectrum, for the H-Hg system. If such patterns can be observed, they would yield data equivalent to the LCD and thus serve to determine the long-range interatomic forces.

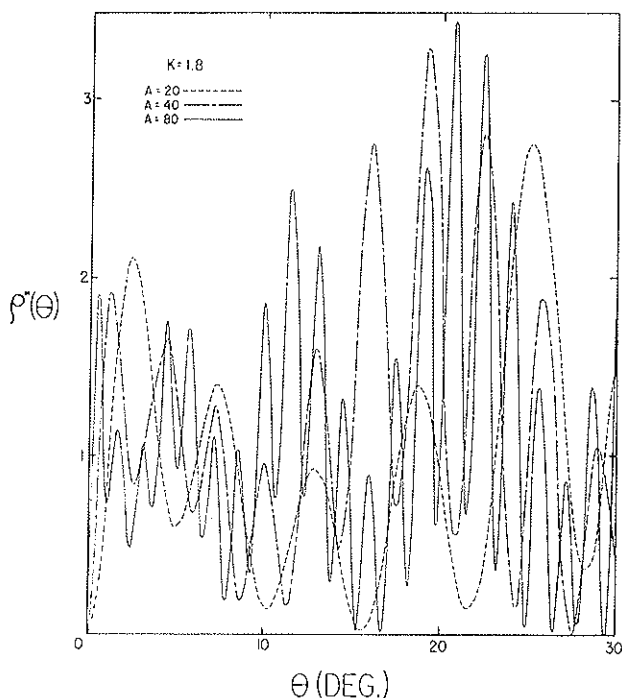


FIG. 30 — Interference patterns calculated [3-c] for scattering by an L.-J. (12,6) potential at constant reduced collision energy but with various values of the reduced wavenumber $A = k\sigma$. Note the decreasing « wavelength » of the oscillations with increasing A (but the insensitivity of the amplitude of the oscillations) as the classical limit is approached.

SUMMARY AND COMMENTARY

From the molecular beam studies of elastic scattering, the following conclusions may be drawn.

1. High energy beam scattering measurements of so-called « classical cross sections » have yielded reliable values of the short-range, repulsive forces for rare gas and simple molecule

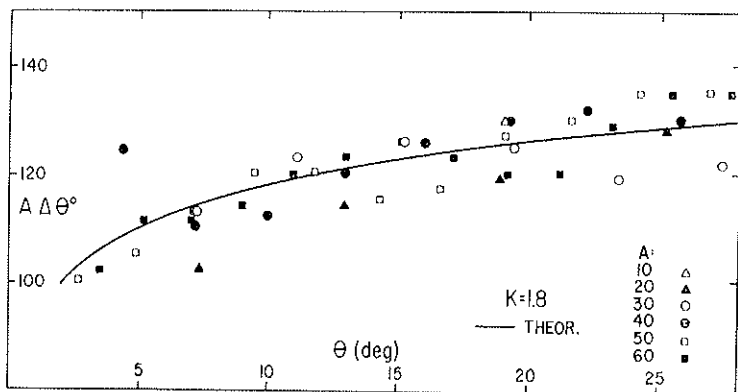


FIG. 31 — Correlation [3-c] of interference spacings ($\Delta\theta_{min}$), calculated points vs. semiclassical theory (the solid line).

systems. Potential energy curves, best represented by an exponential form: $V(R) = A \exp(-BR)$, are obtained with an accuracy of about 10 per cent. With the exception of the He-He system at extremely small separations, the experimental results are in accord both with theoretical calculations and with potentials deduced from high temperature transport property measurements.

2. Thermal energy measurements of so-called « quantum cross sections » have been made for systems involving rare gases, alkali atoms, etc., with an accuracy better than 10 per cent, yielding the long-range attractive R^{-6} potential with an uncertainty of about 25 per cent. The results are consistent with theoretical calculations within the mutual uncertainties.

3. Angular distribution studies of elastic scattering have revealed these features:

a) At very small angles the differential cross section $I(\theta)$ becomes nearly constant, in accord with quantum mechanical

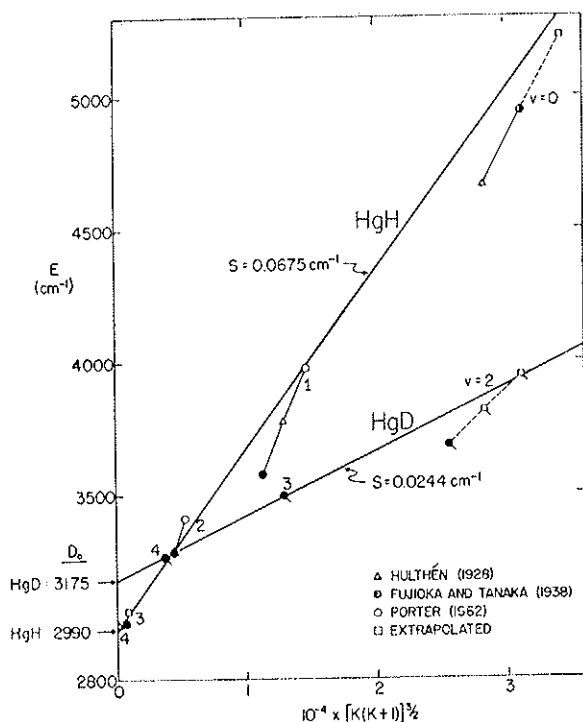


FIG. 32 — Plots $[21]$ of last unpredissociated terms of HgH and HgD ($\chi^2\Sigma^+$); slopes yield the long-range constants $C_{(6)} = 3.0 \times 10^{-59} \text{ erg cm}^6$ (same for both).

expectations, thus justifying the concept of an absolute total cross section Q .

b) At moderately small angles the « smoothed » $I(0)$ is found to vary as $\theta^{-7/3}$, in accord with classical low-angle scattering theory, assuming an R^{-6} long-range potential.

c) So-called « rainbow maxima » are observed, explainable by semiclassical theory. The energy dependence of the rainbow angles θ_r yield the depth of the potential well, ϵ , within

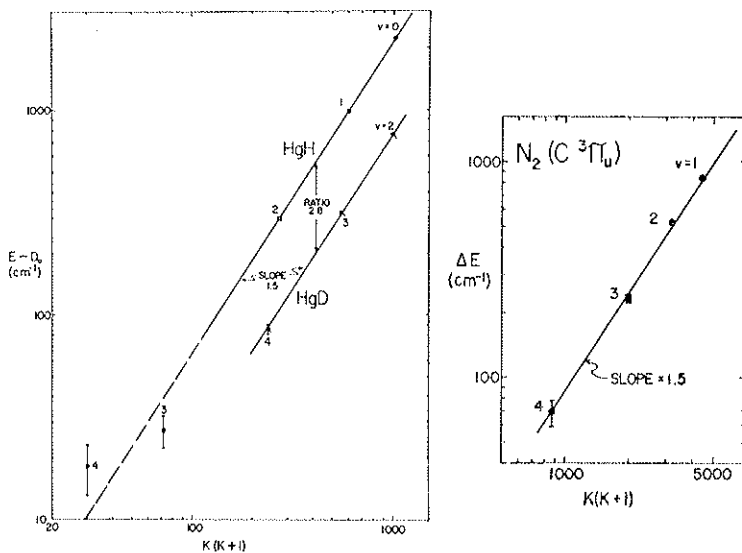


FIG. 33 — Log-log plots [21] of LCD's for HgH, HgD on left (cf. Fig. 32), and $\text{N}_2(\text{C}^3\Pi_u)$ on right. The slopes of $3/2$ imply an R^{-6} long-range inter-atomic potential.

about 10 per cent and the position of the minimum, r_m , within about 15 per cent.

d) With high resolution the angular distribution shows an oscillatory interference pattern (for $\theta < \theta_r$), whose interpretation requires wave mechanics. From an analysis of the pattern and its dependence in velocity, the value of r_m can be determined within about 10 per cent.

4. Extrema in the total cross section Q , as a function of velocity (so-called « glory extrema ») are observed, from which absolute values of certain values of the scattering phase shifts may be deduced. From the extrema-velocities and -amplitudes, the product ϵr_m can be directly determined within about 10

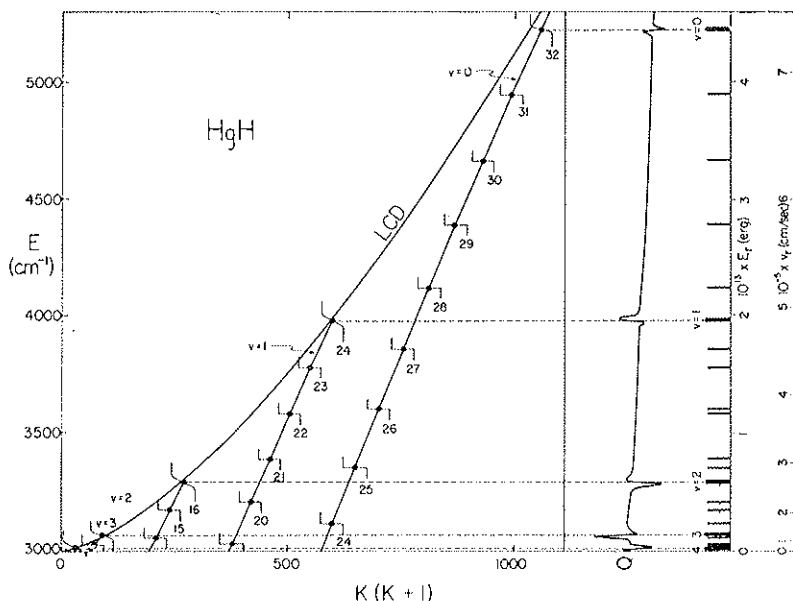


FIG. 34 — Composite LCD and resonance plot [21] for HgH. Left side: unpredissociated terms (indices are K values) with LCD from Fig. 32; right side: spectrum of the quasibound states. $Q(E_r)$ represents the expected appearance of the resonance scattering pattern ($E_r = \frac{1}{2}\mu v_r^2$ is the relative collision energy).

per cent. The « smoothed » $Q(v)$ is found to vary as $v^{-2/5}$ in accord with the quantum mechanical theory, assuming an R^{-6} long-range potential.

At the present time the accuracy of these experiments is not sufficient to distinguish reliably among the different commonly used functional forms for the potential. Since the derived potential constants are slightly dependent on the assumed functionality, the situation is not yet ideal. The problem of strict inversion of the experimental scattering data to yield the potential has not yet been solved in practice. However,

the method of Hylleraas shows promise, provided the initial approximation for the potential is a good one.

Future developments in the field will depend largely upon technical developments, e.g., more sensitive, general detectors and more intense beam sources. With improved velocity - and angular - resolution it should be possible to observe the various interference effects and thus obtain details of the attractive potential well for all the various combinations of rare gases and simple molecules. It is also anticipated that identifiable resonances in atom-atom scattering cross sections (associated with the quasi-bound states) will shortly be observable; that these will be directly correlated with the predissociation data for the diatom; and that such observations will serve as a sensitive probe of the long-range part of the potential for the interaction of both ground state and excited atoms.

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DISCUSSION

Chairman: J. HIRSCHFELDER

HIRSCHFELDER

Do you have any information from predissociation data regarding quadrupole-quadrupole interactions?

BERNSTEIN

There is one predissociation, that of the $b^3\Sigma^+$ state of CO that was studied by SCHMID and GERO in 1935 in which CO dissociates to two P state atoms. According to KNIPP's work of 1938 one should expect an R^{-5} long-range interaction for such a system (two P state atoms); if one interprets the predissociation in this way one can evaluate the C_5 constant. The resulting value is about 35 percent different from Knipp's theoretical prediction for that particular pair of atoms. Thus I think there is evidence for an interaction with a long-range leading term of R^{-5} , but there are not quite enough experimental data to make that certain at the present time.

HIRSCHFELDER

I think it is very important to make clear that this interpretation and utilization of predissociation data is quite independent of the molecular beam scattering implications. This is a second line of attack, but it is really a very powerful approach. Dr. BERNSTEIN, can you tell us whether this method will be useful in telling whether potential curves have a hump, that is, a hump exclusive of the centrifugal barrier?

BERNSTEIN

I think by looking at the dependence of the energy above the dissociation limit of the last unpredissociated level as the function of K (or J , as the case may be), with enough points on the curve (i.e., if there are data for several vibrational states) it should be possible. In the case of BH, for example, such a hump is presumed to exist. Its existence is based upon the functionality relating the last unpredissociated terms and their I values. A re-analysis of the data in the form of a plot of the terms vs. $[J(J+1)]^{3/2}$ suggests the possibility of a normal R^{-6} long range attractive potential. I think that if more experiments were available, one could say definitely whether the hump is there or not. Perhaps Dr. HERZBERG has some thoughts on this question.

HERZBERG

Unfortunately there is at present nothing new to report about the question of the potential maximum for zero rotation in BH. Dr. JOHNS in my laboratory has investigated this problem recently, but certain difficulties have arisen which make it necessary to await the outcome of further experiments. Dr. JOHNS hopes to study

BD as well and in that way we hope that a clear-out answer can be given to the question whether or not there is a potential maximum (*).

WIDOM

I would like to ask Prof. BERNSTEIN a number of small questions. Firstly, I am curious to know what is the present status of the theoretical inversion problem. One knows that there are examples where even measuring something with infinite precision over a range of values of the parameters is not sufficient in principle to allow an inversion to produce a potential function. An example is the second virial coefficient known as a function of temperature, even if over an infinite range and with infinite precision, the potential function is not determined. This presumably is not the case in scattering; knowing the phase shifts with infinite precision would indeed determine the potential function?

BERNSTEIN

For a monotonic potential the answer is yes. For a potential with a minimum it remained for HYLLEBRAND to prove that one could do this inversion. It doesn't require data of infinite precision, but it does require that one abstracts from the angular distributions and their energy dependence a large set of phase shifts. In other words it is a very difficult problem, but in principle he has shown that it is possible. Also, we are favoured by the fact that we know the potential reasonably well to begin with. Measurements, such as the total cross-section give us the long-range $C^{(6)}$ constant; the

(*) *Note added in proof:* Recent experiments by JOHNS, GRIMM and PORTER (J.W.C. JOHNS, F.A. GRIMM and R.F. PORTER, « J. Mol. Spec. » [in press]) in our laboratory have definitely confirmed the presence of a potential maximum in the $A^1\pi$ state of BH, as originally suggested by HERZBERG and MUNDIE (G. HERZBERG and L.G. MUNDIE, « J. Chem. Phys. », 8, 263 [1940]).

extrema measurements give us the product of the depth of the well times the position of the minimum, the high energy scattering yields the slope of the repulsion, and so on. A wild excursion is not really possible, since we are already within 10-20% in $V(R)$ for many of these systems. In fact, for the system potassium-mercury, BECK recently has combined all of these scattering techniques to construct the potential piece-wise. I think the attractive part of the potassium-mercury potential is now known within five or ten percent over the whole range.

WIDOM

My next question is going to be precisely about the potassium-mercury system. I notice in your slides that you compared the slope of the experimental data with the line that was drawn with the theoretical $7/3$ slope and indeed they looked close but they didn't look identical. Now, suppose that you had not started with a notion of what the exponent ought to be and had measured the slope; what would it come out to be?

BERNSTEIN

After reviewing all the data on low angle scattering I would say that there is evidence that the slopes determined independently and without prejudice yield s values a little greater than sixth power, e.g. say 6.1-6.3. There has thus been some indication of the influence of the dipole-quadrupole R^{-8} term, which you see would begin to make this number 6 increase. On the whole the low angle scattering results are in accord with an s which is 6 (between the limits 6.0 and 6.5).

WIDOM

If I may ask my last question: I am a little bit uncertain of the status of the Massey-Mohr formula. The fact that it goes in-

versely with Planck's constant would indicate that this is showing the way the cross-section would become infinite as one approaches the classical limit, am I right in that? There is an alternative expression for the cross-section, with a velocity dependence that goes as the inverse $4/S$ power, is independent of Planck's constant, and is the same in quantum and classical theory. Under what circumstances does the cross-section go as the inverse $2/(S-1)$ power of the velocity, as in the Massey-Mohr formula, and when as the inverse $4/S$ power?

BERNSTEIN

If in the study of the low angle scattering we go out to an angle beyond the parabolic « quantum region », the total cross-section varies with velocity according to the classical equation $Q \propto v^{-2/3}$. It is the low angle feature that introduces the « quantum » velocity dependence, $Q \propto v^{-2/5}$.

HIRSCHFELDER

I am very much interested in the inverse eighth power term which seemed to work quite well. I am not too puzzled over it because it seemed to me that the Lennard-Jones (6-12) potential has a rather sharp minimum whereas I think that the best evidence seems to indicate that the real potential should have more of a soup-bowl shape. The inverse eighth power term tends to broaden the minimum beyond that of the Lennard-Jones (6-12).

BERNSTEIN

We have preferred to talk about the parameters of the potential defined by an ϵ , an r_m and the curvature at the minimum as the

third parameter. I think that when the « repulsive index » is used it is less relevant; the repulsive index which is appropriate to high energy scattering studies might have very little relation to the index which would be important in describing the well shape. I think that what you are saying is reasonable, that the well may be broader, but the way to say that, is probably in terms of the curvature parameter (the force constant). I think that from measurements of the total cross-section extrema we may be able to evaluate that curvature directly. It turns out that the extrema-indexing plot (N versus $1/v$) is not exactly linear. The deviation from linearity of this plot (the amount of deviation from the high velocity behavior) gives us a measure of the curvature of the well. I think that ultimately we can characterise these intermolecular potentials in terms of the depth, the position of the minimum and the curvature and we will forget about the Lennard-Jones or the exponential sixth-formulae. I think those are the three key parameters together with the long range $C^{(6)}$ constant, in which we are most interested.

GRIMLEY

I have one question: the question is, in the circumstances of your experiments is multiple scattering ever a problem? You interpret always on single scattering.

BERNSTEIN

No, multiple scattering is not a problem. The normal vacuum in the apparatus is 10^{-7} mm of mercury and the collision zone is very small; we are working at very low attenuation and we get self-consistent data, such as an attenuation function $\log I_0/I \propto$ proportional to the number of target molecules. There are people who wish to make multiple collision measurements but they are having a bit of trouble finding suitable conditions. In any case, the question of multiple scattering is a separate problem.

RICCI

I would like to ask about the method based on Fourier inversion of X-ray scattering by not very dense gases (P.G. NIKOLAS, C.J. PINGS, « Phys. Rev. Letters », **16**, 4, 1966). They tried in the case of Argon, and the L.J. (6-12) agreed quite well with the experimental results. One has really all the potential curve for low energy values *and they did not find that* the well is too sharp.

BERNSTEIN

I think their work is very significant, and we would like to be able to produce a « band » within which the true potential lies, as they did. They produced this band without putting into the problem any potential function. This is the same goal as in our work in beam scattering. We would like to be able to construct such a band from experimental observations of the angular distribution patterns and total cross-sections.

RICCI

Do you think such a method of X-ray scattering by not dense gases would be comparable with the beam scattering or not?

BERNSTEIN

I think there would be certain similarities in the theory.

INTERMOLECULAR FORCES

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Intermolecular forces are responsible for most of the physical and chemical properties of matter. Although the exact nature of these forces is very complicated, there are no conceptual difficulties. At small separation, the largest forces are due to electron exchange or chemical valence. At larger separation, they arise from the interaction of permanent or induced electric moments. In order to determine intermolecular forces quantitatively, both precise experimentation and theoretical calculations will be required. The determination of properties of the isolated molecules will be useful in predicting the long range interaction. With the use of new types of quantum mechanical techniques and high speed computing machines, it should be possible to calculate the intermolecular force accurately on the basis of accepted laws of physics. Much experimental and theoretical research is required to make our knowledge of intermolecular forces quantitative.

The concept of an intermolecular potential assumes the Born-Oppenheimer separation between the electronic and nuclear motions. For fixed or « clamped » configurations of the nuclei, $\mathbf{R}$, we could, in principle, calculate the complete set of energy levels $E_k(\mathbf{R})$ which are the eigenvalues to the electronic (electrostatic) Hamiltonian H_e which includes the

nuclear-nuclear energy of repulsion. The subscript k represents the electronic quantum numbers for the system of interacting molecules. For fixed values of the quantum numbers k , the E_k give the potential energy surfaces (as functions of $\mathbf{R}$) which determine the nuclear motions of colliding molecules. At least the E_k are the *usual* definition of intermolecular potentials.

Let us consider the sorts of corrections which should be incorporated in the definition of potential energy surfaces:

I. Even assuming the Born-Oppenheimer separation there are additional terms which must be added to the intermolecular potential (¹). The Schrödinger equation for the nuclear motion is

$$-\sum_a \frac{\hbar^2}{2m_a} \Delta_a \chi_k + \frac{\hbar^2}{2M} \sum_{\alpha, \beta} \nabla_\alpha \cdot \nabla_\beta \chi_k + E_k(\mathbf{R}) \chi_k + B_{kk} \chi_k + \\ + \sum_\alpha \mathbf{C}_{k\alpha} \cdot \nabla_\alpha \chi_k = -\frac{\hbar}{i} \frac{\partial \chi_k}{\partial t}$$

where

$$\psi_k(\mathbf{r}, \mathbf{R}) = \chi_k(\mathbf{R}) \phi_k(\mathbf{R}, \mathbf{r})$$

and

$$B_{kk} = -\sum_a \frac{\hbar^2}{2m_a} \langle \psi_k | \Delta_a | \psi_k \rangle$$

$$\mathbf{C}_{kk\alpha} = -\frac{\hbar^2}{m_a} \langle \psi_k | \nabla_\alpha | \psi_k \rangle$$

(¹) J. HIRSCHFELDER, C.F. CURTIS, and R.B. BIRD, *Molecular theory of Gases and Liquids* (John Wiley, New York, second printing, 1964. This treatise will be referred as to MTGL). See Sec. 13.1.

The B and C terms should be incorporated in the intermolecular potential according to BORN. WU and BHATIA [1] found that these diagonal terms are significant in the interaction of hydrogen and also helium atoms. However, DALGARNO and MCCARROLL [2, 3] believe that WU and BHATIA made an error and these terms are only appreciable if the atoms are excited. These terms should become less important for higher nuclear masses. The C term corresponds to a velocity dependent potential.

Deviations from the Born-Oppenheimer separation (and also the velocity dependent C terms) manifest themselves in giving the intermolecular potential a natural « line width » as a function of the nuclear configuration. They also induce transitions from one electronic state to another. When two potential energy surfaces of the same symmetry almost cross, the « line width » becomes very large and there is a large probability of an electronic transition. If there are only a few small regions in the configuration space where the transitions are likely to occur, there are simple formulae of LANDAU, ZENNER, etc. to calculate the transition probability; COULSON and ZALEWSKI [4]. If, on the other hand, there is an appreciable probability of an electronic collision occurring over a large range of configurations, then the concept of intermolecular potential is not significant.

2. In considering interactions of molecules with permanent electric or magnetic moments, at large separations where the interaction are weak, the components of the moments are quantized in the laboratory Z direction. Whereas, at small separations the interaction becomes strong and the quantization refers to the intermolecular axis. This shift in significant reference frame results in most such collisions being non-adiabatic and the concept of intermolecular potential is questionable for the interactions of molecules with permanent electric or magnetic moments; HORNIG and HIRSCHFELDER [5].

3. Of course the intermolecular potentials or potential energy surfaces should be corrected for magnetic or relativistic effects. There are three sorts of terms to be considered:

1) The Breit-Pauli terms which add to the electrostatic Hamiltonian lead to the spin-spin, spin-orbital, and orbital-orbital angular momentum interaction terms which play an important role in atomic structure and spectra and therefore may be expected to play an equally important role in molecular collision phenomena. At large separations the angular momentum interaction terms vary as $1/R^3$ but their magnitude is small since they vary as the second order in the fine-structure constant, $\alpha = 1/137$. There are also magnetic interaction energy terms which vary as $1/R^2$ and add to the centrifugal potential. Such terms are proportional to $g^2 b^2$ where b is the impact parameter and g is the relative velocity of the molecules at the start of their collision when $R = \infty$. DALGARNO and MCCARROLL [2, 3] are wrong in supposing that the $1/R^2$ terms are not zero for head-on collisions where $b = 0$. The Breit-Pauli Hamiltonian gives all of the energy terms correctly which vary as α^2 .

2) The variation of the LAMB shift with change of inter-nuclear configuration may produce a significant effect on the intermolecular potentials. In the case of H_2 , GARCIA [6] found that the Lamb shift reduced the binding energy by 0.22 cm^{-1} . For molecules with nuclei of high atomic number, the LAMB shift may be very large. Indeed, HARTMANN and CLEMENTI [7] have found that the Lamb shift in Argon atoms is many electron volts. Thus, even a small deviation from additivity of the Lamb shift in colliding molecules would change the intermolecular potential.

3) As CASIMIR and POLDER [8] have shown, there is a variety of small quantum electrodynamic corrections to the

intermolecular potentials. At very large separation these corrections arise from « retardation ». But there are other corrections which lead to terms varying as α^2/R^4 , α^3/R^3 , α^4/R^2 , etc. at intermediate separations.

Intermolecular forces are either electrostatic or magneto-relativistic. Electrostatic forces can be further divided into six classes:

(1) direct electrostatic,	long ranged;
(2) polarization or induced,	long ranged;
(3) dispersion or fluctuation,	long ranged;
(4) resonance,	long ranged;
(5) charge transfer,	intermediate ranged;
(6) valence or chemical,	short ranged.

Excluding the magnetic and relativistic interactions, HELLMANN [9] and FEYNMAN [10] have proven (see MTGL, p. 932) that the quantum mechanical forces are just exactly what one would expect on the basis of classical electrostatics for a given configuration of the nuclei and a known electron probability density. In other words, once the distribution of the electron cloud has been determined by solving the Schrödinger equation, the forces on the nuclei are coulombic.

BERLIN [11] dramatized this result (see MTGL, p. 935) by making a diagram showing the region in which an increment of the electron cloud helps to draw the nuclei together, in contrast to other regions where it would tend to pull the nuclei apart. In Figures 1 and 2 the anti-bonding regions are cross-hatched. It is anti-bonding if the increment of electron cloud produces a larger z -component of force on the closer nucleus than on the farther nucleus (where z is the internuclear axis).

Assuming the Born-Oppenheimer approximation, the elect-

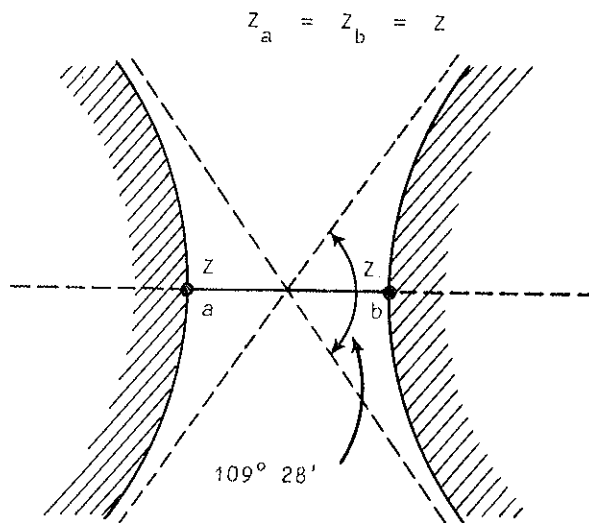


FIG. 1 — Bonding and antibonding regions for a homonuclear molecule.

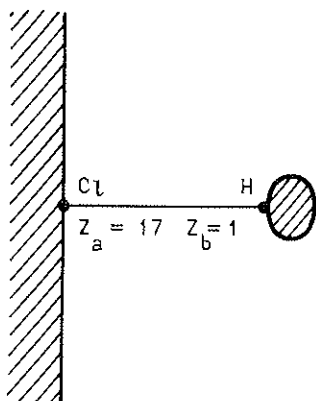


FIG. 2 — Bonding and antibonding regions for hydrogen chloride.

rostatic interaction energy can be obtained by solving the usual electronic Schrödinger equation for the system of two molecules in the appropriate relative configurations. Indeed, the direct solution of the Schrödinger equation is far better than determining each of the six types of electrostatic interaction energies separately and adding them together. In the intermediate separation range, the exchange integrals become important and the contributions of the different types are not additive.

The nature of intermolecular forces is best understood in terms of electron correlation. For example, consider the interaction of two hydrogen atoms with Nuclei A and B separated by a distance R . Let z_{A1} and x_{A1} be the projections of r_{A1} (the distance of Electron 1 from A) along the line of nuclei and in a perpendicular direction, respectively. The corresponding coordinates of Electron 2 are z_{B2} and x_{B2} , measured in the same directions as z_{A1} and x_{A1} but with origin at B. For all values of R , the expectation value of the product $x_{A1}x_{B2}$ is negative, $\langle x_{A1} x_{B2} \rangle < 0$. At large values of R where van der Waals forces are important, the expectation value $\langle z_{A1}z_{B2} \rangle$ is positive. The type of polarization (or a typical instantaneous charge distribution) is

$$R \text{ large:} \quad +^- \quad +^-.$$

For intermediate separations ($R < 2.2 \text{ \AA}$ according to HIRSCHFELDER [12] and HIRSCHFELDER and LINNETT [13], $\langle z_{A1} z_{B2} \rangle$ becomes negative and the typical polarization is

$$R \text{ medium:} \quad +^- \quad -+.$$

At small separations ($R < 0.8 \text{ \AA}$, according to DAVIDSON and JONES [15]) there is an « almost crossing » of potential-energy

curves and in-out correlation becomes more important than left-right correlation. The value of $\langle z_{A1} z_{B2} \rangle$ remains negative but the typical polarization is

$$R \text{ small: } \quad - + + -.$$

According to BUCKINGHAM and DUPARC [16] a similar « almost crossing » of potential-energy curves occurs for the interaction of two ground-state helium atoms at $R=0.15 \text{ \AA}$. The wave-function corresponding to the potential curve at larger separations would tend to approach the excited-state beryllium configuration $(1s)^2 (2p)^2$ as R approaches zero rather than the ground state configuration $(1s)^2 (2s)^2$. This « almost crossing » of potential energy curves at small separations is probably a very general characteristic of molecular interactions.

It would seem logical to apply perturbation techniques (HIRSCHFELDER, BYERS, BROWN, EPSTEIN [14] to the calculation of intermolecular potentials. However, there are a number of difficulties which appear:

(1) For small separations, R is *not* a natural perturbation parameter. The « united-atom » expansion of the energy of interaction of two atoms has the form

$$E_{AB} = Z_A Z_B / R + C_0 + C_2 R^2 + C_3 R^3 + C_4 R^4 \\ + C_5 R^5 + C'_5 R^5 \ln(R) + \dots$$

Here Z_A and Z_B are the nuclear charges of A and B, respectively, and the C 's are constant. As BYERS BROWN and STEINER [77] showed, this expansion contains an $\ln(R)$ term and hence E_{AB} is not an analytic function of R .

(2) For large separations, $1/R$ is *not* a natural perturbation parameter. Overlaps in the wavefunctions lead to exponential energy terms such as $\exp(-aR)$ which are not analytic in powers of $1/R$.

(3) At large separations, the treatment of exchange forces requires considerable care. As HERRING and FLICKER [78] point out, at large separations the Heitler-London energy for the $^3\Sigma$ state resulting from the interaction of two ground-state hydrogen atoms is slightly lower than the corresponding energy for the $^1\Sigma$ state. PRIMAS [79] feels that this illustrates the general need for better quantum mechanical treatment of weakly interacting systems.

One very practical difficulty in calculating intermolecular forces is the large number of potential-energy curves all having the same asymptote at large separations. Twenty or 30 potential-energy curves are not unusual for even simple atom-atom (such as oxygen-oxygen) interactions. These curves « almost cross » and cross in a most complicated fashion and a particular potential may have many maxima and minima. An example of such an unexpected secondary minimum is provided by the first excited $^1\Sigma_g^+$ state of H_2 which has been discussed by DAVIDSON [80].

At very large separations, of the order of 200 Å, retardation effects become important and really should be considered by field theory. According to STEPHEN [17], when R is large compared to the de Broglie wavelength corresponding to an electron excitation, the relative phases of the wavefunctions for the two molecules change with time in such a way as to reduce the electron correlation between the molecules. In resonant collisions, the intermolecular force may be velocity dependent since the residence time of a photon (between annihilation and creation) is an essential parameter at large separations.

At large separations, of the order of $10 \text{ \AA}$, there are still a number of interesting relativistic or magnetic coupling terms. For example, MAVROYANNIS and STEPHEN [18] discovered a $1/R^6$ energy term which applies only to the interaction of optically active molecules. Another example of considerable interest is a $1/R^4$ energy term (MEATH and HIRSCHFELDER [19]), which applies to all molecular interactions including ground-state noble-gas atoms. All of the relativistic or magnetic interaction terms are small by a factor of at least the square of the fine-structure constant, $(1/137)^2$. However, they may be important in producing « forbidden » transitions in collision processes and spectroscopy.

Currently, there is considerable interest in the London dispersion energy, $-C/R^6$. As KINGSTON [20] explains, there is a discrepancy between theory and experiment considerably larger than can be explained in terms of the probable error of either the measurements or the calculations. Reaction field and other techniques which are being developed by MAVROYANNIS and STEPHEN [18], KARPLUS and KOLKER [21], CHAN and DALGARNO [22] et al. will lead to improved calculation of C .

At intermediate separations, near the bottom of the potential curve, the greatest calculational difficulties are encountered. Neither expansions in powers of R or $1/R$ are appropriate. Instead, one should apply the standard techniques for solving molecular problems to the solution of the double-molecule system. Exchange integrals become very important at intermediate separations and the first-order perturbation energy becomes correspondingly large. Exchange integrals also become important in the second-order perturbation energy, a fact which has often been ignored. The possibility of charge transfers or ionic states should always be considered. Donor-acceptor complexes are surprisingly common.

The question is frequently argued whether one should use atomic or molecular orbitals. As NESBET [23] points out, for each orbital there is a critical separation at which the orbital

shifts rather sharply from the atomic orbital at large separations to the molecular orbital at small separations. With the Fisher-Coulson orbital, $a + \lambda b$, this corresponds to a change in the parameter from zero to one.

There are many tricks which may prove useful in the determination of intermolecular forces. However, the proof of the pudding is in the eating. Right now, accurate calculation of the interaction of two helium atoms in their ground states is long overdue!

Let us consider individually each of the different types of interaction energies:

I. DIRECT ELECTROSTATIC INTERACTIONS

Direct electrostatic interactions are long-ranged. At a separation of 562 Å, the energy of interaction between two ions, H^+ and H^+ , is 600 cal/mole (or RT at room temperature). The same energy occurs when a polar molecule (H_2O) approaches an ion (H^+) at a separation of 14.6 Å; or the H_2O approaches another polar molecule (H_2O) at a distance of 5.5 Å.

It is customary to express the large distribution of a molecule in terms of a multipole expansion: charge, dipole, quadrupole, octupole, etc. Then the direct electrostatic interaction between two molecules is the sum of the interactions of their respective multipole moments. However, in order that the multipole-multipole interactions be applicable, it is necessary (see MTGL, p. 844) that the separation R between the two molecules A and B be larger than the sum of the greatest radii of the two molecules. If r_{max} is the greatest distance to the center of the molecule of any element of charge in the molecule, then the requirement for the validity of a multipole-multipole interaction between two molecules is that

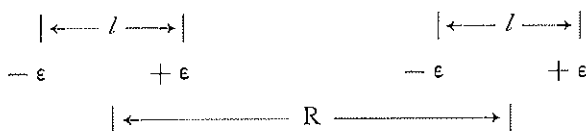
$$(I) \quad R > (r_{max})_A + (r_{max})_B$$

For the interaction of two large biologically active molecules, separations sufficiently large for condition (1) to apply, are seldom of interest.

Thus, I recommend that the electrical charge distribution of a molecule A be idealized by a set of monopoles « i » with charge $\epsilon(A)_i$ located at position $\mathbf{r}(A)_i$. Figure 3 shows such a monopole electrostatic model for the water molecule. The PULLMANS [24] and others very frequently use monopoles to idealize the charge distribution of biologically active molecules. The direct electrostatic interaction energy between two molecules is then given as the sum of a set of coulombic energy terms,

$$(2) \quad E_{AB}^{(\text{direct-elect})} = \sum_{i,j} \frac{\epsilon(A)_i \epsilon(B)_j}{|\mathbf{r}(A)_i - \mathbf{r}(B)_j|}$$

Two monopoles of opposite charges form a « real » dipole. In « real » dipoles, there is a finite separation l between the positive and negative charges ϵ . The dipole moment is $\mu = \epsilon l$. Consider the interaction between two such polar molecules with their dipoles pointed in the same direction along the line of nuclei:



Here, according to Eq. (2),

$$(3) \quad E_{AB}^{(\text{direct-elect})} = \epsilon^2 \left[\frac{2}{R} - \frac{1}{R-l} - \frac{1}{R+l} \right]$$

$$= -\frac{2 \epsilon^2 l^2}{R(R^2 - l^2)} = -\frac{2 \mu^2}{R(R^2 - l^2)}$$

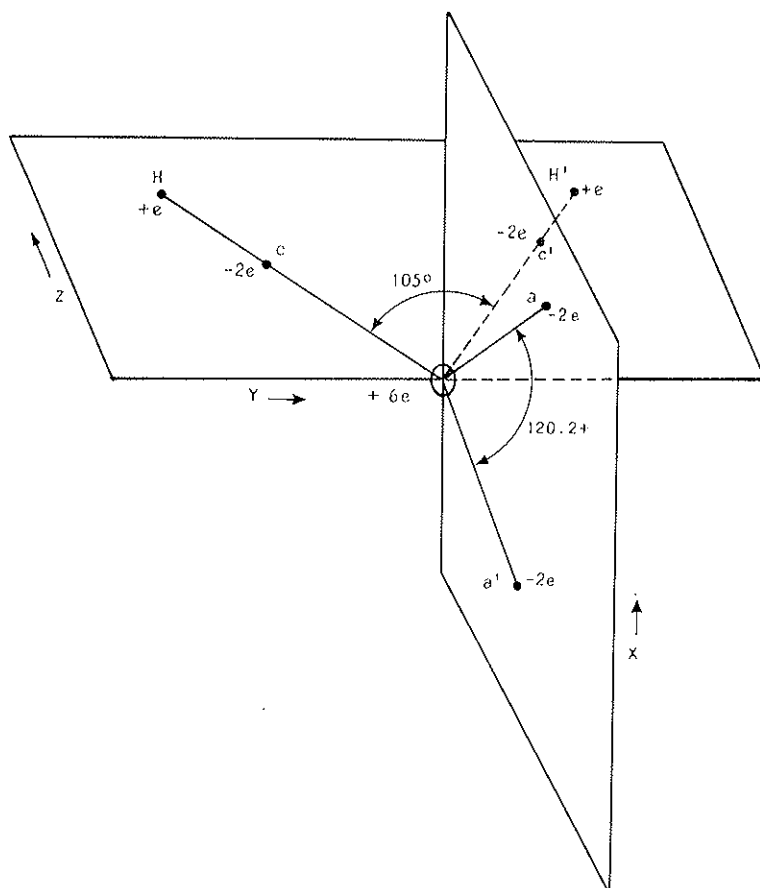


FIG. 3 — Monopole electrostatic model of the water molecule as suggested by DUNCAN and POPLÉ [48'] (see also MTGL, p. 103). Here the water molecule is represented by seven monopoles, one at each of the hydrogen and oxygen atoms, one along each of the OH bonds, and two « lone pair » electron monopoles in the plane perpendicular to the H_2O .

The energy of interaction of two « ideal » dipoles in the same configuration is $-2 \mu^2/R^3$. If the separations R and l are comparable, the energy of interaction of the « real » dipoles can be much larger than for « ideal » dipoles.

The very large binding energy of hydrogen bonds can be explained in terms of a monopole representation. As shown in Figure 4, the partially unshielded proton of one molecule comes very close to the lone pair electrons of the oxygen atom of another molecule.

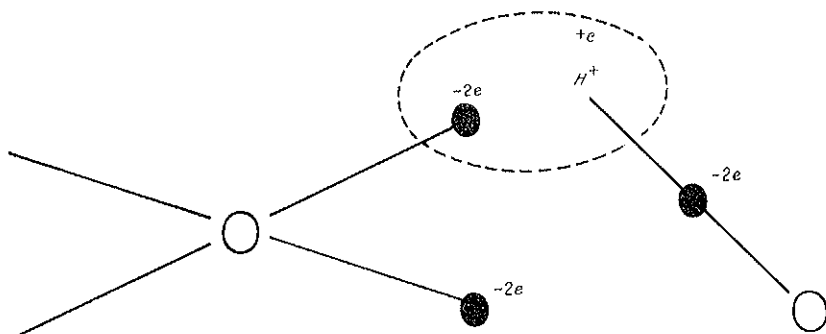


FIG. 4 — Monopole electrostatic model of hydrogen bonding. Here the proton of one molecule comes close to the lone pair electrons of an oxygen atom of a second molecule.

Direct electrostatic interactions are generally dependent on the orientations of the two molecules, as well as on their separations. If the system is at thermal equilibrium, the average energy of interaction of two molecules separated by a distance R is given by the Boltzmann average

$$(4) \quad \bar{E}_{AB} = \frac{\int \int E_{AB} \exp(-E_{AB}/kT) d\omega_A d\omega_B}{\int \int \exp(-E_{AB}/kT) d\omega_A d\omega_B}$$

Here the integrations are taken over all the orientations of A and B corresponding to the solid angles ω_A and ω_B . This Boltzmann averaging has a profound effect on the experimen-

tally observable interaction energies. For example, at very low temperatures where $|E_{AB}| > kT$, two dipoles tend to align so as to give the lowest energy of interaction and $\bar{E}_{AB} = -2 \mu^2/R^3$. But at high temperatures, the Boltzmann average only slightly favors the energetically favorable configurations so that the average energy of interaction between two dipoles is $\bar{E}_{AB} = -(2/3kT)\mu^4/R^6$. The Boltzmann averaged direct electrostatic energy of interaction is always negative, corresponding to a net attraction between the molecules (1). In the remainder of this paper, we shall not consider the Boltzmann averaging. However, statistical averaging over a thermal distribution of energy states is frequently required in connection with experimental problems.

2. POLARIZATION OR INDUCED ELECTROSTATIC INTERACTIONS

Polarization or induced electrostatic forces are usually very small and unimportant. However, in large biologically active molecules there is the possibility of inducing zwitter-ions with very large induced dipole moments. Thus, polarization forces should be carefully considered (see MTGL, p. 29 and p. 984).

If molecule A has the charge C_A , it produces an electric field $\mathcal{E}_A = +C_A/R^2$ at the position of molecule B. This induces

(1) The direct orientational average [Eq. (4) without the Boltzmann factor] of any multipole-multipole interaction energy is zero (MTGL, p. 846). Since the Boltzmann factor favors orientations with negative interaction energy, the Boltzmann averaged multipole-multipole energy is negative. The only exception is the charge-charge coulombic energy in the interaction of two positive or two negative ions.

a dipole moment $\mu^{(\text{ind})} = \alpha_B \mathcal{E}_A$. See Figure 5. The energy of interaction of the induced dipole with the electric field is then

$$(5) \quad E_{AB}^{(\text{polar})} = - \int_0^{\mathcal{E}_A} \mu^{(\text{ind})} d\mathcal{E}_A = - \frac{1}{2} \alpha_B \mathcal{E}_A^2 = - \frac{C_A^2 \alpha_B}{2R^4}$$

Similarly, if molecule A possesses a dipole moment μ_A in a direction θ_A with respect to the internuclear axis, this dipole can induce a dipole moment in molecule B which interacts with the original dipole moment to produce the energy

$$(6) \quad E_{AB}^{(\text{polar})} = \frac{\mu_A^2 \alpha_B (3 \cos^2 \theta_A + 1)}{2R^6}$$

This induction energy was first obtained by DEBYE [25] and FALKENHAGEN [26].

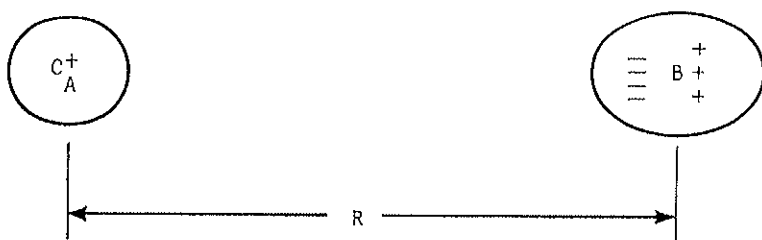


FIG. 5 — Dipole induced in molecule B by a charge C_A^+ on molecule A.

3. DISPERSION OR FLUCTUATION INTERACTION

From quantum mechanical considerations, there are rapid fluctuations in the electronic charge distributions. Thus even a non-polar molecule A has an instantaneous dipole moment $\mu_A^{(instant)}$ which induces a dipole moment in molecule B which interacts with the instantaneous dipole to produce the instantaneous energy, according to Eq. (6),

$$(7) \quad E_{AB}^{(instant)} = \frac{[\mu_A^{(instant)}]^2 \alpha_B [3 \cos^2 \theta_A + 1]}{2R^6}$$

The LONDON dispersion energy (see MTGL, p. 960) results from time-averaging $E_{AB}^{(instant)}$.

$$(8) \quad E_{AB}^{(dispers)} = -\frac{1}{R^6} \sum_{i,j}' \frac{\left[\mu_x(A)_{oi} \mu_x(B)_{oj} + \mu_y(A)_{oi} \mu_y(B)_{oj} \right]^2 - 2 \mu_z(A)_{oi} \mu_z(B)_{oj}}{E(A)_{io} + E(B)_{jo}}$$

$$+ O(1/R^8) + \dots$$

Here, as in most of the remainder of this paper, all distances are given in Bohr radii (a_0) and all energies are in atomic units (e^2/a_0); $E(A)_{io} = E(A)_i - E(A)_o$ is an excitation energy of molecule A; $\mu_x(A)_{oi}$, $\mu_y(A)_{oi}$, and $\mu_z(A)_{oi}$ are the x , y , and z components of the transition dipole moment of molecule A going from « o » to « i »; the z -axis is the line joining the centers of A and B and has the same direction for B as for A.

The prime on the summation excludes transitions for which $E(A)_{io}$ or $E(B)_{jo} = 0$. In addition, those high energy transitions must be excluded for which ⁽¹⁾

$$E(A)_{io} > hc/R \text{ or } E(B)_{jo} > hc/R.$$

For many biologically active molecules, there is either one or only a few important electronic transition bands for which the values of the transition dipole moments are appreciable. In such cases, Eq. (8) may be useful for calculating the dispersion energy from the experimentally observed molecular absorption spectra.

The dispersion energy can also be written in the form

$$(9) \quad E_{AB}^{(\text{dispers})} = - \sum_{i,j} \frac{N_A^2 N_B^2 | \langle 0, 0 | r_{ab}^{-1} | i, j \rangle |^2}{E(A)_{io} + E(B)_{jo}}$$

Here N_A and N_B are the number of electrons in molecules A and B, respectively; r_{ab} is the distance between electron a in molecule A and electron b in molecule B; and the matrix component is

$$\iint \Psi_o(A)^* \Psi_o(B)^* r_{ab}^{-1} \Psi_i(A) \Psi_j(B) d\tau_A d\tau_B$$

⁽¹⁾ M.J. STEPHEN [27] points out that these high energy transitions should be excluded because time changes in the phases of their transition charge density make the induced dipole moment out of phase with the instantaneous dipole. This is a retardation effect.

where the integrations are to be made over the spin and coordinate space of all of the electrons in the two molecules. Eq. (9) has the advantage over Eq. (8) that it is applicable to intermediate as well as very large separations.

Now let us define the transition charge density of A to be

$$(10) \quad \rho_{oi}(a) = N_A \int \Psi_o(A)^* \Psi_i(A) d\tau_{N_A-1}$$

where the integration is over the spin-configuration space of all of the electrons in A except a and over the spin space of a ; $\rho_{oj}(b)$ is similarly defined as the transition charge density of B. Thus

$$(11) \quad N_A N_B < 0, 0 | r_{ab}^{-1} | i, j > = \iint \rho_{oi}(a) r_{ab}^{-1} \rho_{oj}(b) d\tau_a d\tau_b$$

LONDON [28] and HAUGH and HIRSCHFELDER [29] suggested that the transition charge densities might conveniently be approximated by sets of monopoles (see MTGL, p. 971). Thus $\rho_{oi}(a)$ is approximated by the set of charges $\epsilon_{oi}^{(k)}(A)$ at the positions $\mathbf{r}_{oi}^{(k)}(A)$. Similarly, $\rho_{oj}(b)$ is approximated by the set of charges $\epsilon_{oj}^{(l)}(B)$ at the positions $\mathbf{r}_{oj}^{(l)}(B)$. Thus,

$$(12) \quad \iint \rho_{oi}(a) r_{ab}^{-1} \rho_{oj}(b) d\tau_a d\tau_b = \sum_{k,l} \frac{\epsilon_{oi}^{(k)}(A) \epsilon_{oj}^{(l)}(B)}{|\mathbf{r}_{oi}^{(k)}(A) - \mathbf{r}_{oj}^{(l)}(B)|}$$

and

$$(13) \quad E_{AB}^{(dispers)} = - \sum_{i,j}' \left[\frac{\sum_{k,l} \frac{\varepsilon_{oi}^{(k)}(A) \varepsilon_{oj}^{(l)}(B)}{|\mathbf{r}_{oi}^{(k)}(A) - \mathbf{r}_{oj}^{(l)}(B)|}}{E(A)_{i0} + E(B)_{j0}} \right]^2.$$

Equation (13) is particularly useful for calculating the dispersion energy between asymmetric molecules at intermediate separations.

COULSON and DAVIES [30], HAUGH and HIRSCHFELDER [29], and STERNLICHT [31] have obtained rather strange forces in the interaction of conjugate double bond molecules. The energetically best angle between the two molecules is between 60° and 90°, as one would expect from the crystal structure of such molecules. Also, as one molecule is displaced parallel to the other, there is a series of maxima and minima in the interaction energy. In general $E_{AB}^{(dispers)}$ varies as the fifth power of the length of the conjugate double bond system. STERNLICHT [31] using the method of Tomanaga [32, 33] has found that Hückel and free-electron calculations of the $\pi - \pi$ contribution to the polarizability of conjugate double bond molecules is much too large because of the neglect of the mutual repulsion of the electrons within a molecule. In a similar manner, he finds that the Hückel calculations of COULSON and DAVIES [30] and the free-electron calculations of HAUGH and HIRSCHFELDER [29] give too large a $\pi - \pi$ component of $E_{AB}^{(dispers)}$. Thus the $\pi - \pi$ interaction energy dominates at large separations and becomes comparable to the $\sigma - \sigma$ interaction energy at small separations. At close separations, AONO [34, 35, 36] has shown that charge-transfer energies between conjugate double bond molecules become much larger than dispersion energies. Much further work will be required to clarify the conjugate double bond molecule interactions.

Dispersion energies are usually considered on the basis of second-order perturbations, and this leads directly to Eqs. (8) and (9). However, recently LINDER [37, 38]; LINDER and HOERNSCHMEYER [39]; YOS, BADE, and JEHLE [40]; JEHLE, YOS, and BADE [41], YOS [42]; and JEHLE, PARKE, and SALYERS [43] have developed a general type of « reaction-field » technique for considering dispersion energies in terms of fluctuations. Their approach is based on the treatment of LANDAU and LIFSHITZ [44, 45] and of CALLEN and WELTON [46]. See also BROWN [47]. The reaction-field of a molecule A is the field produced on it by the moments of the surrounding molecules which are induced by the moments of molecule A. An idealized model is assumed for the reaction-field response function which connects the reaction field to the moment that has produced the field. This function determines the dielectric susceptibility and the intermolecular free-energy. There are many advantages of the reaction field technique: (1) All types of electrostatic interactions can be considered simultaneously. (2) Forces due to thermal fluctuation of the charge distribution (electron or proton transfers) are also given. (3) The BOLTZMANN averaging of the interaction energies is included in the calculations. (4) The effects of solvents and three-, four-, etc. body forces are obtained in a rigorous manner. JEHLE stresses that the reaction-field technique is particularly well suited to the treatment of biological problems.

4. RESONANCE INTERACTIONS

Resonance occurs (see MTGL, p. 990) whenever the molecular interaction produces a perturbation which removes an energy degeneracy. The wave function for a resonance state corresponds to a dipole or electric moment where classically

such a moment should not occur. Resonance energies can be either positive or negative — the value of the resonance energy vanishes when averaged over all of the quantum states which occur. There are two types of resonance interactions:

(1) *One molecule degeneracy*

EXAMPLE: Collision of a proton with an H-atom in either $2s$ or $2p$ state.

Under the influence of the proton electric field, the zeroth order wave function for the H-atom becomes

$$(14) \quad \Psi = \Psi(2s) + c \Psi(2p_z)$$

As can be seen from Fig. 6, the center of the electronic charge corresponding to Ψ is shifted (the figure shows it shifted towards the right). Therefore the hydrogen atom has a dipole moment! The resulting energy of interaction varies as $1/R^2$ instead of $1/R^4$ as one would expect for a charge-induced dipole energy if no resonance were involved.

(2) *Two molecule degeneracy*

EXAMPLE: Collision between two like molecules, one in the state « 0 », the other in an excited state « 1 » such that the transition $1 \rightarrow 0$ with the emission of a photon is permitted by the selection rules. This example is illustrated in Fig. 7. A photon can be emitted by molecule A and absorbed by B, etc. The large resonance energy can be attributed to this photon exchange. However, the problem can be analyzed without

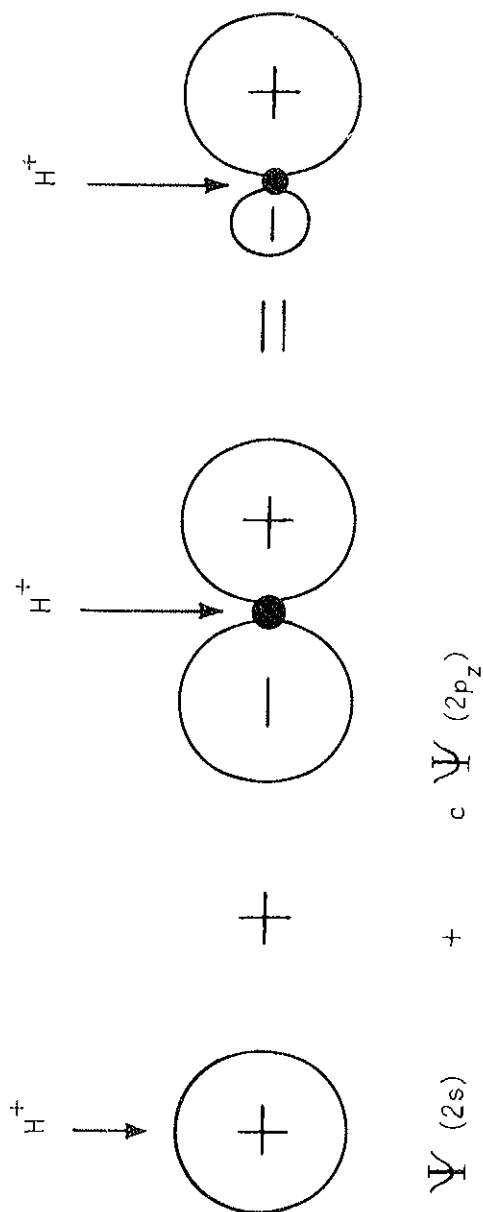


Fig. 6 — H-atom wave function.

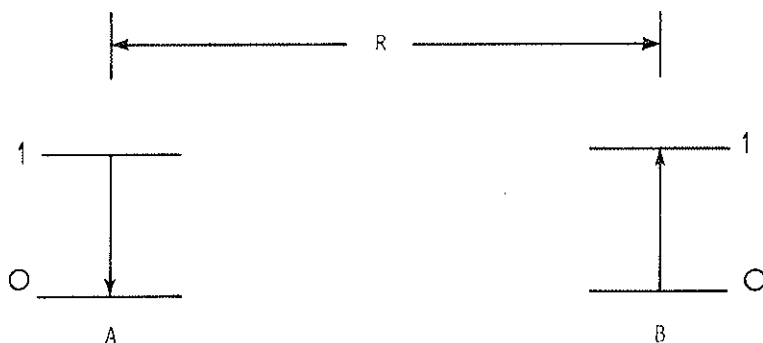


FIG. 7 — Two molecule resonance collision stabilized by photon interchange.

recourse to photons. The wave function for the two molecule system can be written in either the gerade or ungerade forms,

$$(15) \quad \Psi_g = \Psi_0(A)\Psi_1(B) \pm \Psi_1(A)\Psi_0(B)$$

The square of Ψ contains the product $[\Psi_0(A)\Psi_1(A)] [\Psi_0(B)\Psi_1(B)]$. This term behaves as though molecule A and molecule B had dipole moments. The resonance energy is given by the expectation value for the interaction potential. Thus,

$$(16) \quad E_{AB}^{(res)}(g) = -E_{AB}^{(res)}(u) = -\frac{1}{R^3} [|(\mu_x)_{01}|^2 + |(\mu_y)_{01}|^2 - 2 |(\mu_z)_{01}|^2]$$

Here

$$(17) \quad \mu_{01} = \int \Psi_0(A) \mu \Psi_1(A) d\tau = \int \Psi_0(B) \mu \Psi_1(B) d\tau$$

It is equally probable that a collision will result in a gerade or ungerade state. As a result of the resonance, the interaction energy varies as $1/R^3$ instead of $1/R^6$.

STEPHEN [17] has studied the nature of resonance collisions from the standpoint of quantum mechanical field theory. At separations greater than $R = hc/E_{10}(A)$, the problem becomes time dependent rather than stationary. The gerade state, but not the ungerade state, can spontaneously emit a photon to leave both molecules in the « 0 » state. The concept of intermolecular energy as a function of separation may become ill-defined under such conditions.

5. CHARGE EXCHANGE INTERACTIONS

Charge transfer between two molecules may take place at intermediate separations and greatly increase the energy of interaction. Charge transfer is characterized by the (almost) crossing of two potential energy curves, one corresponding to $A+B$, the other corresponding to $A^+ + B^-$. This is shown in Fig. 8. There are many examples of donor-acceptor charge transfer complexes, such as Benzene-Iodine, which behave in this manner. AONO [34, 35, 36] believes that charge transfers are very important in interactions between conjugate double bond molecules. Whenever charge transfer may be important, we should use for the wave function of the two molecule system the form

$$(18) \quad \Psi = \Psi(AB) + c\Psi(A^+B^-)$$

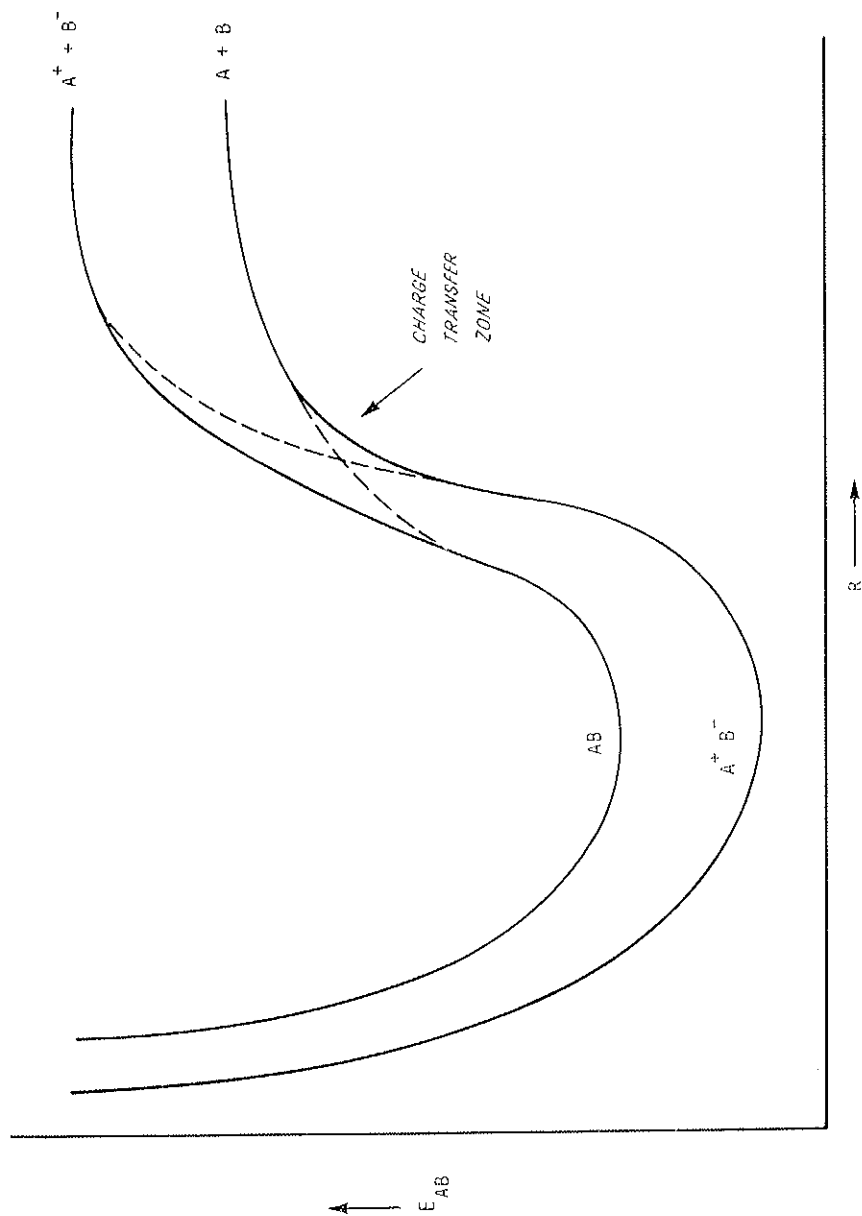


FIG. 8 — Charge transfer between two molecules. Here the charge transfer takes place at an intermediate separation. The two potential energy curves (almost) cross in the charge transfer zone.

so that the contribution of the ionic state A^+B^- can be varied by adjusting the constant c . Ionic states are even important in the interaction of two like molecules.

6. VALENCE OR CHEMICAL INTERACTIONS

These are the chemical forces which are familiar in molecular quantum mechanics. They are responsible for the short-range repulsive forces between molecules. For intermolecular purposes, the first order perturbation « Vector Model » of DIRAC [48], VAN VLECK [49], SERBER [50], KIMBALL and EYRING [51], PAULING [52], and BEAR and EYRING [53] gives an adequate approximation (see VANDERSLICE and MASON [54]; EYRING, WALTER, and KIMBALL [55] HIRSCHFELDER [56]; VAN VLECK and SHERMAN [57]; EYRING [58]; and MTGL, p. 939)

$$(19) \quad E_{AB}^{(val)} = -\frac{1}{2} \sum_{\substack{a,b \\ \text{orbitals} \\ \text{with} \\ \text{randomly} \\ \text{paired spin}}} K_{ab} + \sum_{\substack{a,b \\ \text{orbitals} \\ \text{with} \\ \text{paired} \\ \text{spins}}} K_{ab} - \sum_{\substack{a,b \\ \text{orbitals} \\ \text{with} \\ \text{anti-paired} \\ \text{spins}}} K_{ab}$$

Here the K_{ab} are exchange integrals (usually negative) between an orbital a in A and an orbital b in B. All of the Coulomb, overlap, and multipole exchange integrals are neglected ⁽¹⁾.

⁽¹⁾ The reader is reminded that the total energy of interaction is taken to be the sum of direct electrostatic, dispersion, ..., and valence energies. Therefore, the coulombic interaction terms are not required in Eq. (19); they have been considered separately.

There is a variety of ways in which these exchange integrals can be estimated. They have the approximate functional form

$$(20) \quad K_{ab} = -C_{ab} \exp(-\beta_{ab}R)$$

The constant β_{ab} may be approximated by (see ZENER [42']; and MTGL, p. 26).

$$(21) \quad \beta_{ab} = [2 E_I(a)]^{\frac{1}{2}} + [2 E_I(b)]^{\frac{1}{2}}$$

where $E_I(a)$ and $E_I(b)$ are the ionization potentials of a and b expressed in units of (e^2/a_0) and β_{ab} is given in units of a_0^{-1} . EYRING and POLANYI [59], EYRING [60], and EKSTEIN and POLANYI [61] approximated the exchange integrals from an empirical knowledge of the binding energy of diatomic molecules.

A further clue regarding K_{ab} is given by HIRSCHFELDER and ELIASON [81] who found that the kinetic theory collision diameter (where $K_{ab} = kT$) is equal to $\bar{r}_a + \bar{r}_b + 1.8 \text{ \AA}$. Here $\bar{r}_a$ and $\bar{r}_b$ are the mean values of the radii of the orbitals a and b respectively, calculated with the use of Slater orbitals and Slater screening constants. They also found that the equilibrium separation in a diatomic molecule is $\bar{r}_A + \bar{r}_B$ where $\bar{r}_A$ and $\bar{r}_B$ are calculated for the outermost orbitals.

7. MAGNETIC AND RELATIVISTIC INTERACTIONS

There are two basic types of energies of interaction — electrostatic and magnetic. Until quite recently the magnetic forces have been thought to be small and were generally ignored. However, there are good reasons to suppose that the magnetic interactions may be important in some biological problems. As AMPERE discovered, a moving charged particle or electric current produces a magnetic field. Thus, the ring currents in conjugate double bond molecules behave like small magnetic dipoles. Two such molecules interact with magnetic dipole-magnetic dipole energy (which varies as $1/R^3$). The magnetic interaction terms tend to be smaller than the corresponding electrostatic interactions by a factor of $(1/137)^2$ or the square of the fine-structure constant. However, the larger the molecule, the more important can the magnetic terms become.

In quantum mechanics, the magnetic terms arise from the relativistic corrections to the Schrödinger equation. In addition to the magnetic moments produced by their motion, the electrons and nuclei possess intrinsic magnetic moments called « spins ». The relativistic corrections to the Schrödinger equation may be expressed in powers of $(1/137)$ and involve spin-spin, spin-orbit, and orbit-orbit magnetic interactions as well as terms expressing the time lags in the interactions and relativistic corrections to the kinetic energy. For most purposes, the Breit equation (see BETHE and SALPETER [62]; and MTGL, p. 1044) can be used to obtain the required energy shifts. But for second-order effects, it may be necessary to use photon annihilation-creation operators to obtain the required accuracy. At the present time, we are examining types of magnetic forces which can occur. An understanding of magnetic coupling terms is essential in the understanding of nuclear magnetic resonance experiments.

A very interesting magnetic interaction term was discovered by MAVROYANNIS and STEPHEN [18]. Assuming, in order to simplify the formula, that the molecules are rotating rapidly,

$$(22) \quad E_{AB}^{(opt. act.)} = - \frac{4}{3R^6} \sum_{i,j} \frac{[\mu_{oi}(A) \cdot \mathbf{m}_{io}(A)] [\mu_{oj}(B) \cdot \mathbf{m}_{oj}(B)]}{E_{io}(A) + E_{jo}(B)}$$

Here $\mathbf{m}$ is the magnetic moment operator, $(e/2mc) \sum_k \mathbf{r}_k \times \mathbf{p}_k$.

This energy is different from zero only if both molecules A and B are optically active. If B is replaced by its mirror image, the sign of $E_{AB}^{(opt. act.)}$ is changed. The value of $E_{AB}^{(opt. act.)}$ is usually small relative to $E_{AB}^{(dispers.)}$; however it may be important in causing steric arrangements between neighboring molecules.

MAVROYANNIS and STEPHEN [18] used quantum mechanical field theory to derive Eq. (22). However, if we write the interaction Hamiltonian in the form (see MEATH and HIRSCHFELDER [19])

$$(23) \quad H = H_0 + \frac{1}{R^3} \left[\mu_A \cdot \mu_B - \frac{3 (\mu_A \cdot \mathbf{R}) (\mu_B \cdot \mathbf{R})}{R^2} \right] + \frac{1}{R^3} \left[\mathbf{m}_A \cdot \mathbf{m}_B - \frac{3 (\mathbf{m}_A \cdot \mathbf{R}) (\mathbf{m}_B \cdot \mathbf{R})}{R^2} \right],$$

Eq. (22) is obtained as one of the interaction energy terms by the use of the usual second-order perturbation procedure.

CASIMIR and POLDER [8] showed that the retarded dipole-dipole interaction energy, E_{int} , between two non-degenerate atoms can be expressed exactly in terms of an integral. For

all separations R , this integral can be expressed in closed form (in terms of Sine and Cosine integrals). This result is then expanded both for small and for large value of R/χ_0 . Here the characteristic length is $\chi_0 = (\alpha\Delta\varepsilon)^{-1}$ where α is the fine structure constant and $\Delta\varepsilon$ is the excitation energy corresponding to the transition from the ground state to the first excited atomic state. The « small R » expansion is only accurate for $R/\chi_0 > 5.0$ (see MEATH and HIRSCHFELDER [19]). In between $R/\chi_0 = 0.6$ and $R/\chi_0 = 5.0$, it is necessary to use the exact or closed form. In the « large R » expansion, the interaction energy has the form

$$E_{int} = \alpha^{-1} R^{-7} D + \alpha^{-3} R^{-9} F + \alpha^{-5} R^{-11} G + \dots$$

In the « small R » expansion the interaction energy has the form

$$E_{int} = R^{-6} C_6 + \alpha^2 R^{-4} W + \alpha^3 R^{-3} A + \alpha^4 R^{-2} B + \dots$$

Here $R^{-6}C_6$ is the usual London dispersion energy. The term $\alpha^2 R^{-4}W$ can also be obtained by taking the expectation value of the Breit-Pauli Hamiltonian using the wave function for the two-atom system corrected for the classical electrostatic interactions. Thus, at least in the dipole-dipole approximation, the Breit-Pauli Hamiltonian gives the interaction energy accurate through $o(\alpha^2)$. It does not give accurate results for terms of higher order in α , such as the $\alpha^3 R^{-3}A$ and $\alpha^4 R^{-2}B$. The applicability of the Breit-Pauli Hamiltonian is limited to « small R » with $R < \chi_0$. This restriction has been discussed by POWER and ZIENAU [63] in connection with their quantum electrodynamical treatment of a one-dimensional oscillator model. Indeed, it is well known that the classical analogue

of the Breit-Pauli Hamiltonian (the Darwinian Lagrangian) is only valid for $R < \chi_0$.

CASIMIR and POLDER [8] used quantum field theory in their derivation of the interaction energy. However, AUB, POWER, and ZIENAU [64] obtained the same result as CASIMIR and POLDER by using time-independent quantum mechanical perturbation theory together with the classical electromagnetic interaction Hamiltonian in the dipole approximation. This semi-classical approach is much simpler since it avoids the calculation of the terms which result from a large number of FEYNMAN diagrams.

MCLONE and POWER [65, 66] have used quantum field techniques to calculate the energy of interaction (in the dipole approximation) of two atoms, one in an excited state and the other in the ground state. The results are interesting and may be important with respect to chemical catalysis and enzyme reactions. In the range of « large R », the resonance case (where the two atoms are alike) has a leading term which varies as $1/R$;

$$E_{\text{int}} = - [(\mu_x)_{01}^2 + (\mu_y)_{01}^2] \frac{\cos (R/\chi_0)}{\chi_0^2 R} \\ - [(\mu_x)_{01}^2 + (\mu_y)_{01}^2 - 2 (\mu_z)_{01}^2] \left[\frac{\sin (R/\chi_0)}{\chi_0 R^2} + \frac{\cos (R/\chi_0)}{R^3} \right]$$

The non-resonance case (where the two atoms are different species) has a leading term which varies as $R^{-2} \cos^2(R/\chi_0)$. STEPHEN [17] considered the resonance case and concluded that the very long range energy of interaction should have an exponential cut-off due both to the spontaneous emission of the excited state and to the Doppler effect. STEPHEN warns

that the actual very long range interactions involving excited state molecules should be treated by time-dependent rather than steady state techniques.

Recently, PHILPOTT [67] has obtained the complex energy of interaction between electronically excited molecules separated by a large distance. The real part corresponds to the McLONE and POWER interaction energy, the imaginary part corresponds to the rate of decay of the excited states due to photon emission. Usually, but not always, the energy of interaction is less than the radiative line width and therefore may not have much physical significance. However, the energy of interaction between an excited state molecule and a surface may be large enough to have interesting consequences.

8. SOLVENT EFFECTS

Up to now, we have only considered the interaction energy between an isolated pair of molecules. Let us discuss briefly the non-additivity of pair potentials and the effects of solvents.

Dispersion energy is calculated by perturbation theory. The lead term is the second order term (the usual London van der Waals energy) which varies as $1/R^6$. There are also second order terms varying as $1/R^8$, $1/R^{10}$, etc. which are progressively less important. In addition there are small third order terms which vary as $1/R^9$, $1/R^{10}$, ... All of the second order terms are pair-wise additive. It is only the third order (and higher) terms which lead to 3-body forces. Fourth order terms lead to 4-body forces, etc. Order of magnitude-wise, the ratio of the n -body dispersion energy to the $(n-1)$ st is (α/R^3) , where α is a polarizability and R is a separation.

LAURENS JANSEN [68] calculated the magnitude of the deviations from pair-wise additive dispersion energies. In the

crystalline noble gases these terms are sufficiently large to make the face centered cubic lattice energetically favorable as compared to the hexagonal close packed lattice. However, the three body energies are quite small. Thus, Ne, Ar, Kr, Xe satisfy corresponding states equations of state up to 250,000 atmospheres although their 3-body forces are different.

Thus we conclude that the dispersion energy $E_{AB}^{(dis)}$ between two molecules is essentially unaffected by immersion in a non-polar solvent.

There is very little evidence at the present time regarding the effect of polar solvents on the dispersion energy. KESTNER and SINANOGLU [69], and SINANOGLU, ABDULNAR, and KESTNER [70] use the same type of calculation as JANSEN [68] in which they totally disregard the polar nature of the solvents. They obtain reductions in dispersion energy between two polymers in water up to 15 to 30 per cent. For base-base dispersion energies in water the reduction is only of the order of 5 to 7 per cent. These calculations are very crude. At the present time we do not even know how to calculate the dispersion energy between molecules in the gas phase to within 10 per cent (see KINGSTON [20]).

The effects of solvents on polar molecules are difficult to ascertain. At large separations, the energy of interaction of two polar molecules is reduced by the factor ϵ , the dielectric constant of the solution. However, the more interesting question is what is the energy of interaction of a single polar molecule with the surrounding solvent?

The simplest treatment is due to ONSAGER [71] who regarded the solvent as a continuous medium (see also BONNOR [72] and LINDER [37]). He scooped out of the medium a spherical cavity of radius « a » surrounding the molecule. Here « a » is regarded as the effective radius of the molecule. The local electric field $\mathcal{E}^{(loc)}$ which acts on the molecule is the sum of a field C which would exist in the cavity if our molecule were

absent and a reaction field G which is produced in the dielectric by virtue of the dipole μ of our molecule. On the average, if there is no external field, $C=0$. ONSAGER found that

$$(24) \quad G = g \left[\frac{\mu}{1 - \alpha g} \right]$$

where α is the polarizability of our molecule and

$$(25) \quad g = \left[\frac{2(\epsilon - 1)}{2\epsilon + 1} \right] a^{-3}$$

The work required to produce the spherical cavity in the dielectric is equal to the energy of interaction of the molecule with the dielectric

$$(26) \quad E(\text{solvation}) = -\frac{1}{2} \mu \cdot G = -\frac{1}{2} \left[\frac{\mu^2 g}{1 - \alpha g} \right]$$

Equation (26) gives good agreement with experiment and can therefore be used on an empirical basis.

Rigorously, however, in Eq. (26) μ^2 should *not* be used as μ_{gas}^2 , the square of the molecular dipole moment in the gas. But rather,

$$(27) \quad \mu^2 = \frac{\mu_{gas}}{1 - \alpha g}$$

Substituting Eq. (27) into Eq. (26) gives values for $E^{(solvation)}$ which do *not* agree with experiment. For asymmetrical molecules, WADA [73] generalized the Onsager treatment by scooping out an ellipsoidal cavity. Wada's treatment gives good agreement with experiment.

ONSAGER is extending his rigorous formalism to consider real dielectric liquids with an arbitrary distribution of solvent molecules surrounding the molecule in question. Also, as stated previously, LINDER and JEHL are developing a comparatively simple mathematical procedure which (hopefully) should give results equivalent to Onsager's.

The continuous medium model for the solvent is probably satisfactory for hydrophobic molecules. However, hydrophylic molecules are « wetted » by an aqueous solvent. By « wetted » we really mean that at least part of the molecule is surrounded by rigidly attached water molecules.

Some parts of biologically active molecules are hydrophylic and other parts are hydrophobic. The rigid shell of attached water molecules should be incorporated into any discussion of the molecular properties. Slight changes in Ph, temperature, or concentrations can make a profound difference in the attachment of water molecules. For example, the well known double consolute temperature of nicotinic acid and water solutions has been explained by EYRING as due to a sudden unfreezing of the attached ice layer. Such a change in the nature of solvation is much like a phase transformation. Perhaps such a change in solvation might help to explain the shift from the coiled to the uncoiled structures of DNA, etc. Foam and surface tension studies might reveal a great deal about the nature of the solvation of biologically active molecules. Excellent theoretical work on the hydrophobic stacking of bases and the solvent denaturization of DNA has been done by SINANOGLU and ABDULNAR [74] but there are many difficult problems which have not yet been solved.

And, lest anyone get the impression that solvation problems are easy, I should mention clathrate compounds such as the hydrocarbon hydrates which result from the energetically easy formation of certain types of cavities in the water (see, for example, McKoy and SINANOGLU [75] and ALLEN [76]). The small hydrocarbon (CH_4 or C_2H_6) or gas molecule (O_2 , N_2 , CO_2 , etc.) fills this cavity and is surrounded by a rigid layer of ice. Such clathrate is the very opposite of the continuous medium model of the solvent. From a study of clathrates we learn to appreciate the importance of the detailed molecular geometry of the solvent and its relations to the solute molecules.

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DISCUSSION

Chairman: J. HIRSCHFELDER

HIRSCHFELDER

The most interesting feature of the symposium are the discussions. We hope there will plenty of arguments and controversy. After all, intermolecular forces was chosen as the topic of discussion because it represents a field of controversy.

HEISKANEN

When Dr. HIRSCHFELDER wrote his formulas on the Intermolecular forces, I realized that the formulas were similar with the formulas in the research of earth gravity field, on its irregularities, on geoid undulation and deflections of the verticals. Of course the quantities, symbols, units and meaning were different. Same is the case when we study the solarsystem of the universum. In fact we have good opportunity to study both microcosmos because the mass of a man (80 kg) is as many times bigger of the proton mass as it is smaller than the mass of Sun.

Most important factor is some force: gravity, electricity, magnetism a.s.o. Therefore no wonder that formulas are to some extent similar, regardless we study intermolecular forces or the forces of the earth itself.

If we know the gravity anomalies around the world most geodetic constants of the earth can be computed: size, shape, gravity field with its irregularities caused by the irregular mass distribution in at its surface. It is interesting to know that the famous Cambridge mathematicians: NEWTON, STOKES, GREEN, and AIRY (astronomer, geodesist) and PRATT have given the mathematical fundament for the gravimetric geodesy.

According to the English astronomer EDDINGTON Good, when he created the world, he was more mathematician than engineer. So we need mathematics regardless we study the behavior of the earth molecules or earth itself.

We live now in a periculus of *Renaissance* of Science and Technology, which started about two decades ago, and which we never have had.

The fast progress of the electronic technic, of new sophisticated new equipments, of statistical mathematics and highspeed computers has changed so much the situation that we can speak about *Revolution*.

Because I know best the progress of the gravimetric studies I mention some of them. You others can tell similar cases for the world of the molecules. I am only happy that the molecules and other small particles are so large that the centrifugal force of earth diurnal rotation is unable to destroy earth's atmosphere.

Twenty years ago we measured the gravity by pendulum apparatus of about 2000 kg, continuous observations took 48 hours, accuracy ± 2 mgd. Now we measure the gravity by gravimeters, which weigh 3 kg (« worden cocktail shaker »), measuring time 3-5 min. and accuracy 0.1 mgd, 1000 mgd = 1 gd.

About 20 years ago Austrian PREY needed 16 years to compute by logarithms the constants of the spherical harmonics to 16th degree. Prof. NOTILA in Columbus, Ohio, last year computed by highspeed computer the corresponding constants to 37th degree in some hours and the geoid of the earth also in some hours, the programming, of course, took more times, but that was done by the technician.

It is now relatively easy to be professor, because the computers take care of the computations. He has time for his teaching and research. In many case he has freedom to study almost what he likes. If he makes error, it is not dangerous, because his kind colleagues are ready to correct it.

My slogans to my students during my teaching carrier of 40 years have been these:

1. Bachelor must know, *how*; Master must know, *why*, and Doctors, how to *improve* the problems.
2. Easy problems we solve *today*, difficult problems we solve *tomorrow* and impossible problems we solve *after-to-morrow*.
3. Theory, which can be shown to be wrong, is good, it is still better, if it is right, but if we can not show it be right or wrong, is useless.
4. The students have privilege and duty to develop the science further than his teachers have been able to come.
5. Scientist need 10% intuition, 10% inspiration and 80% perspiration.
6. You must not ask, how much science will give to you, but how much you can give to your science.
7. Ingeniuses, as NEWTON discover naturis laws, but who has created them?

These are not mine, but I have used them.

HIRSCHFELDER

I thank you, I think your remarks are very interesting.

GRIMLEY

I want to make a remark which is perhaps a little provocative. It is this. The notion of force is a classical notion — this notion is foreign to quantum mechanics anyway, and I am wondering how much we are piling up difficulties in retaining such a classical notion. For example, we don't need this notion to interpret the molecular beam experiments of BERNSTEIN. What we are measuring there is a scattering cross section, and BERNSTEIN is really making things rather difficult by trying to go back to a force when the job of the theoretician is to calculate the scattering cross section, and not the force.

HIRSCHFELDER

As you know, ROOTHAAN calculated the energy of the hydrogen molecule without invoking the Born-Oppenheimer separation considering it as a four particle system. In that case one really knows what the errors are in assuming a potential energy. The reason for assuming Born-Oppenheimer separation is a very practical problem, the work is much, much more difficult without it.

BERNSTEIN

I have first comment to make on the last question, and then a question of my own. With regard to the desirability of extracting an intermolecular potential function from scattering data, the goal would be to elucidate the potential and then try to make predictions with that potential of the macroscopic properties of the fluid. In other words it is not enough merely to make « correlations » of cross sections, but if we can interpret the scattering data in terms of a *potential* which is then useful to describe the equilibrium and the non-equilibrium properties of the fluid then we have made

progress. That is the reason why we were spending so much time in going back from the scattering measurements to the potential.

Now I have a question for Prof. BUCKINGHAM. In scattering of polar molecules we have observed many striking effects; for example for the scattering of polar beam molecules by polar target molecules we find very enhanced cross sections (relative to those for non-polar targets), which are strongly temperature dependent. Until recently, we have been using a naïve and very out-of-date treatment. The Keesom type of dipole-dipole interaction, the Debye type induction term and the London dispersion term. Now, in view of other findings in recent years, including the importance of dipole-quadrupole contributions, etc., I wonder if you could help us by writing down an expression for the potential that includes all the important interactions at least at fairly large separations which could be of interest to us interpreting a measurement involving the scattering of polar molecules.

BUCKINGHAM

In answer to that question, I think it is important to consider the nature of the experiment being conducted. As Prof. HIRSCHFELDER said half an hour ago, if we have two molecules which are close relative to their dimensions, then an expansion in a multipole series may be divergent. So one has to take care in writing down the interaction, but if one is sensible in using the series for the appropriate range, it can be very useful. If the molecules are neutral the longest range interaction is the dipole-dipole energy which is a function of angle. There will also be more rapidly decreasing contributions, but if it has a dipole, it will have a point with respect to which the quadrupole is zero.

If we have two molecules, 1 and 2, then the interaction is $\mu_1 \mu_2 R^{-3}$ times an angle dependent function. Then there will be an additional term involving the dipole of one and the quadrupole of two with another function of angle, plus another term in which one and two are interchanged. The magnitude of this term in

relation to that of the dipole-dipole is of the order of magnitude of the quadrupole over the dipole times the separation R ; so that if internal dimensions are small compared to external dimensions, this will be negligible. Provided the distance between molecules 1 and 2 is comparable to molecular distances, this term will not necessarily be small. There is also the possibility of a quadrupole-quadrupole interaction which goes as R^{-5} times another angle dependent function, and this term can be dominant if the molecule has a small dipole. These are the electrostatic forces. Then one has the induction forces. The induction energy is of the form $-\frac{1}{2} \alpha F^2$. This has a central force part, as well as an angle-dependent part. Induction energies are generally small, as Prof. HIRSCHFELDER said. They are often small compared to the dispersion energy, which can be written approximately in terms of the product of the polarizabilities divided by a molecular energy such as the ionization potential as LONDON suggested many years ago; and of course the dispersion energy varies as R^{-6} , as does the dipole induction energy. The square of the field F can also involve terms of the form $\mu_1 \Theta_1$. This is the term which was evaluated by ANDERSON some years ago and in fact he thought this term dominated the pressure broadening of the microwave absorption of ammonia by gases like argon. I believe he may have been wrong in doing so. Then there are other terms, which are associated with higher polarizabilities. The most interesting one of these is the dispersion energy proportional to A_1 instead of α_1 — that is, instead of its being $\alpha_1 \alpha_2$, it is $A_1 \alpha_2$, over some ionization potential, times R^{-7} . And this is a dispersion energy involving a distortion of the system by the interaction. If the molecule lacks a centre of symmetry we can have an angle dependent dispersion energy varying as R^{-7} . As Prof. HIRSCHFELDER mentioned this morning there are also dispersion energies in R^{-8} , R^{-10} etc.; the term in R^{-7} is present when either molecule lacks a centre of symmetry. For methane and argon there is an R^{-7} contribution if we measure the separation from the centers of mass of the two systems, from the carbon to the argon nucleus. This is, I think, the dominant angle dependent

interaction in this case. Its magnitude is rather hard to assess, because we do not know much about A. Turning to Prof. BERNSTEIN's question, the relative magnitudes of these terms are dependent of the system studied. If you have a collision, as Prof. BERNSTEIN has in his beam, and if he finds a cross section which is associated with a very large distance, for example if his cross section is of the order of, say, $500 \text{ \AA}^2$, then I think one could quite safely say that the terms higher than the dipole-dipole are not significant to the scattering. If on the other hand your cross section came out to be of the order of magnitude of $10 \text{ \AA}^2$ — and it may do so in a case where the angle dependence of interaction is rather weak — then you will have to be very careful in applying an expansion in R^{-1} .

HIRSCHFELDER

Dr. BIRNBAUM of North American Aviation Science Center is very much concerned right now about the collision, say, between argon and neon. During the collision, the collision complex has a dipole moment. Which of your terms would represent the collision dipole moment?

BUCKINGHAM

That is another effect again. It is a very interesting point. In a collision between dissimilar molecules, the pair lacks a centre of symmetry, so there is the possibility of a dipole. The long range dipole varies as R^{-7} . But I believe this particular long range dipole is of little importance in determining the absorption of microwaves. At short range there is an important effect that is related to the exchange of charge. In pure argon three atoms are needed to produce a dipole so there could be microwave absorption proportional to the cube of the pressure in this case, though it might be small. Thank you.

LÖWDIN

May I draw attention to some problems concerning first principles where we may not fully agree. We know that all problems concerning intermolecular forces may be treated as time-dependent problems and that even stationary states could be properly studied in this way; in connection with molecular collisions, the dependence comes in very clearly. We also know that the present basis for the theory is the time-dependent Schrödinger equation containing inner and outer electromagnetic potentials, where the Hamiltonian may also contain spin-orbit couplings and spin-spin couplings to take at least some of the relativistic corrections into account to achieve higher accuracy.

The first question I would like to raise is the question of *gauge invariance*. All physical and chemical properties of a system should be invariant under a gauge transformation of the electromagnetic potentials, and this implies that all measurable quantities should be gauge invariant. In the transition from theory to experiment, this invariance requires some attention particularly in connection with the definition of fundamental quantities to be measured by the experimentalists, since the definitions should be independent of any specific choice of gauge. It is well-known that there are considerable difficulties in getting properly gauge-invariant definitions in connection with certain phenomena, for instance diamagnetic susceptibilities, optical rotational powers etc., depending on the fact that it seems hard to achieve gauge-invariance in any finite-order perturbation theory.

I would like to ask Prof. BUCKINGHAM whether it could happen that lack of gauge invariance in the formulation of the multipole expansion has anything to do with the fact that certain basic quantities do not seem welldefined, that higher multipoles depend on the specific choice of origin, etc.?

The next question I would like to ask is not concerning the basic equations, which we all seem to believe that we know with sufficient accuracy, but concerning the *boundary conditions* for these

equations. There is particularly one point which has been emphasized by Prof. CASIMIR in his work with POLDER namely the effect of retardation on the intermolecular forces. We know that we have to introduce the proper electromagnetic potentials in the Schrödinger equation but the question is: should these potentials be retarded potentials, advanced potentials or perhaps the symmetric potentials being the average of the two? The retarded potentials seem natural to us for reasons of « causality », but arguments of this type have become weak after the introduction of the theory of relativity. It is often emphasized that it is essential that the Schrödinger equation itself is invariant under reversal of the time direction. However, if an outer field would be represented by a retarded potential in the Hamiltonian, such a potential would become « advanced » after time reversal, and the only potentials which are invariant under time reversal are actually the symmetric ones. Now comes the question: what type of electromagnetic potentials are we really supposed to introduce into the basic Schrödinger equation, so that the resulting equations do correspond to the boundary conditions of the experimental set-up under considerations. In connection with radiation theory, these problems were discussed 25 years ago by WHEELER and FEYNMAN. Now I would like to ask Prof. CASIMIR whether his studies of these effects in connection with intermolecular forces indicate that the potentials should be retarded, advanced, symmetric or something else?

The third question I have is rather controversial, since it deals with the commonly accepted idea of expanding the intermolecular potential $U(R)$ in inverse powers of R . We have heard a lot today of R^{-6} , R^{-7} , R^{-8} , ... and so on, not to speak of the small powers and the logarithmic terms. We speak about these problems as if the coefficients would be well-defined, and still little is known about the analytical character of $U(R)$ for $R=\infty$ (or $R=0$). There is no question that such an expansion may be highly useful in treating a finite intervall $a \leq R \leq b$, but the coefficients are in such a case determined by the Chebyshev expansions rather than the Lau-

rent series. This also implies that, if the interval is changed, the coefficients of the inverse powers are changed in the expansion of $U(R)$ of most rapid convergence. In comparing theory with experiments, it is of essential importance to make clear what coefficients we are speaking about. The experimentalist is usually carrying out his investigations for a finite interval of R and is likely to refer his results to Chebyshev-type coefficients, in expansions of most rapid convergence, whereas the theoretician is usually thinking of coefficients in the Laurent series for $R=\infty$.

Part of the difficulties with the inverse power expansions come, of course, from the fact that we are using perturbation theory, that we usually have considerable difficulties in collecting all the various terms which contribute to the higher terms, and that we know very little about the « convergence » properties of this asymptotic expansion of $U(R)$. Perturbation theory requires the separation of the Hamiltonian into an unperturbed part H_0 and a perturbation V , but such a separation is by no means trivial in studying intermolecular forces. Another problem is connected with the so-called virtual states, of which a large part is situated in the continuum. Conventional perturbation theory uses the eigenfunctions of H_0 as a basis, but I am not convinced that this was really SCHRÖDINGER's original intention. As we all know, SCHRÖDINGER developed quantum-mechanical perturbation theory in connection with a study of the Stark-effect of the hydrogen atom. As a basis, he did not use the eigenfunctions of H_0 , i.e. the hydrogen functions $1s, 2s, 2p, 3s, 3p, 3d, \dots$ including the continuum; but rather a discrete set $1s, \bar{2}s, \bar{2}p, \bar{3}s, \bar{3}d, \dots$ where the functions are more localized in the region of the unperturbed state $1s$ and hence more suitable for the study of the polarization of this state due to the electric field. The treatment was simple, and the results excellent.

When EISENSCHITZ and LONDON studied the interaction between two hydrogen atoms in the first quantum-mechanical derivation of long-range interatomic forces, perturbation theory in its conventional form was well established, so they used hydrogen-like functions including the continuum as a basis. The contributions from

the continuum are usually neglected as being small by using energy-denominator arguments, and it is hence worthwhile to observe that EISENSCHITZ and LONDON in their very careful study found that more than 40% of the constant C in the potential C/R^6 came from the continuum. In such a study, the virtual states have no direct physical significance, and the inclusion of the continuum states adds considerable mathematical difficulties. A few years ago, Prof. HIRSCHFELDER and I reexamined this problem and, using SCHRÖDINGER's discrete set $1s, 2s, 2p, \dots$ for each atom involved and transforming the final result to natural orbitals, we found that the long-range interaction could be explained by a single orbital $2p$ which would lead to an interaction energy C/R^6 of about the same accuracy as obtained by EISENSCHITZ and LONDON.

It seems to me as if now the time has come to get away from conventional perturbation theory as well as inverse powers expansions in treating intermolecular forces. In the Upsala and Florida projects, we have during the last few years developed a method for solving the SCHRÖDINGER equation called the partitioning technique which is equivalent to infinite-order perturbation theory but has the added feature that it permits the calculation of true upper and lower bounds to the energy eigenvalues; the results have been published in *J. Mol. Spec.*, *J. Math. Phys.*, *J. Chem. Phys.* and *Phys. Rev.* By using this technique we are now trying to get good upper and lower bounds for the intermolecular potential $U(R)$ without using any power-series expansions whatsoever.

Calculations on H_2^+ and H_2 are in progress.

BUCKINGHAM

There's the question of invariance of gauge. It's something I'd not considered; the gauge is something that comes in when one introduces the vector potential, is it not? And it turns out that one can add the gradient of any scalar to your vector potential and leave the electric and magnetic fields unchanged. I'd always

looked upon this as affecting magnetic properties but not electrostatic ones.

LÖWDIN

The gauge transformation is certainly just as important in treating electric as magnetic properties. As you recall, it has the form

$$A' = A - \text{grad } X$$

$$\phi' = \phi + \frac{1}{c} \frac{\partial X}{\partial t}$$

where $X = X(x, y, z, t)$ is the function characteristic for the gauge transformation. In radiation theory, there are people who prefer to work in a gauge where there is no scalar potential whatsoever ($\phi = 0$), and every theoretician is certainly entitled to work in his personal choice of gauge. The difficulty lies in the fact that all measurable properties should be gauge invariant and that, as far as I know, there do not exist any experimental methods to fix a gauge.

BUCKINGHAM

That's true of course. An experimental observation has to be independent of any trace of origin, for example, or gauge in the theory. I was actually discussing a static situation and in that case the perturbation can be written down in terms of a scalar potential, and if it is a uniform field, the dipole times the field is a precise representation of the perturbations, so that is complete in itself. So the question does not have relevance in that particular case of a static field.

HIRSCHFELDER

The polarizability, for example, is not well defined for an excited state where the molecular energy is almost degenerate.

BUCKINGHAM

If the separation of the states is large, then you look upon the states themselves as being meaningful states even in the presence of the perturbation, and you talk about the polarizability without danger. On the other hand if the separation between the states is comparable to or small compared to the perturbation, then you can't usefully talk about the polarizability of one of those states. An example would be the one that Dr. CASIMIR mentioned, the hydrogen atom in an excited state in the electric field; it is not meaningful to talk about a $2s$ hydrogen atom in the electric field. In fact the states you have to think of are combinations of nearly degenerate states, and the appropriate combination is that which diagonalizes the Hamiltonian; then you can talk about the properties of those particular stationary states.

LÖWDIN

Can I make a quick comment? I believe that Prof. BUCKINGHAM comes out very well by specifying that he works in a stationary situation with a fixed electrostatic potential which corresponds to a specific gauge. I feel, however, that the entire question of gauge invariance in the theory of intermolecular forces would gain by a more detailed study.

For the moment, many quantities in the theory of matter based on finite-order perturbation theory are certainly not-gauge invariant. Sometimes it happens that a theoretician may use this fact to improve his results, since he may try to change his gauge until the theoretical result agrees with the corresponding experimental data. However, since he may obtain any result whatsoever, such a procedure is, of course scientifically meaningless, and it should not be necessary to warn against such an approach.

There is another thing about the multipole expansions, which Prof. BUCKINGHAM has emphasized in a very clear way, namely

its limitation to systems containing small molecules at comparatively large distances. Today when the multipole expansions are often applied rather uncritically to the interaction between very large molecules at short distances in biological systems, such a statement is of particular value. I would like to thank Prof. BUCKINGHAM very much for his answer.

CASIMIR

May I say a few words? First of all, as to gauge invariance, in the particular case of the calculation of the retarded form in the London-van der Waals interaction, the equations written down were certainly gauge invariant and the calculations have been repeated by many authors using different gauges but always in a gauge invariant way and finding the same results. So there I feel satisfied there is no difficulty.

The question of retarded and advanced potentials is more complicated. First of all we should remark that after all both Schrödinger's equations and Maxwell's equations have symmetry with respect to time reversal, and if we specify the initial conditions, there is no arbitrary choice to be made between advanced or retarded potential; what you will get depends on the initial conditions you have chosen.

It is a little bit difficult to trace this through the whole of the various calculations and equations. However, I have once amused myself by deriving the retarded expression in a rather elementary way. I start from a stationary state in a cavity containing one molecule; then I introduce another molecule as a perturbation. Now, if you want to study a stationary state of a cavity with, for example, a small sphere inside, then for that stationary state you have to use a sum of retarded and advanced potentials, because there is no energy being lost or created, and in that stationary state as much wave is going in as is going out. Now that calculation gives exactly the same result as all the other quantum mechanical calculations. So although I cannot trace advanced and retarded potentials in

detail through all the calculations that have been performed, I think we can say that the result is independent of the choice.

This follows also from the very first treatment of POLDER and myself which was unsymmetric, and started with a retarded wave coming from one atom, and then interacting with the other atom, so that looked at from the other atom it was advanced. Yet the final result you get is symmetric in the two atoms, which shows that for getting the final formula for the interaction, it should make no difference.

LÖWDIN

I thank Prof. CASIMIR very much for his answer, let me just check, though, on one point. The Schrödinger equation containing an outer electromagnetic potential is, of course, not invariant against time reversal, unless the potential is a symmetric one, since a retarded potential goes over into an advanced potential, and viceversa, under reflection of the time axis.

CASIMIR

If you put in a Schrödinger equation a macroscopic electromagnetic field coming from an outside source, and if you don't do something about time reversal of that outside source then of course it's not, but if I write down a Schrödinger equation for two coupled systems so that the source of the field is part of the system itself then it is,

LÖWDIN

I was most interested to learn that it does not seem to make any difference as to the « retarded » form of the intermolecular forces what type of potential you introduce in the Schrödinger equation.

More than three decades ago, MÖLLER tried to derive the Breit equation for the helium atom by using field theory and, as far as I remember, he had to use a symmetric potential to obtain the correct result.

CASIMIR

I seem to remember, but it is fairly long ago, and I have not looked at it much since that time, that the somewhat surprising thing in Möller's derivation was that, although he used an asymmetrical treatment for the interaction between two particles with a retarded potential with respect to the first particle, the result he got was up to a certain approximation independent of this choice and symmetric in the two particles. That may have something to do with what you get in the van der Waals forces.

FIXMAN

Should like to question Prof. LÖWDIN's insistence that we ask for explicit gauge invariance. I think that such a demand would not allow multipole expansions to be terminated with the dipole or the quadrupole moment. BUCKINGHAM pointed this out. And for the theorist, it's often true that the choice of gauge is a variable, which can make perturbation expansions of an approximate wave functions converge more rapidly just as a proper choice of gauge can make an experimental multipole expansion converge more rapidly. So I think we should feel free to choose the gauge arbitrarily as long as we realize what we are doing.

BUCKINGHAM

I have one remark to make concerning the point you made in your introduction this morning where you wrote down potential

curves for several states of H_2 . You wrote down curves for the 1Σ and for the 3Σ states at very large R . Now at very long range these curves are essentially degenerate. Therefore, the tiniest perturbation may mix these two states, and I'm not sure that it's useful to talk about the singlet and the triplet states at these very large separations. For many experiments it would be more meaningful to talk about two atoms in doublet states. It depends on the time of the experiment, and on the separation of the atoms. If the atoms are far apart, then for most experiments done in a short time it will be more meaningful to look upon them as two doublet atoms.

HIRSCHFELDER

This is a very good point, and this is another example of what I was talking about. At very large distances one has weak interactions and one type of quantization. At shorter distances, you have the strong interaction quantum numbers. Thus there must be some separation at which one switches the quantum descriptions for the super molecule.

VERWEY

I want to make a general remark on behalf of the poor chemists. Listening to the discussions of today (the importance of which I do not deny) I could not avoid thinking that a development of our thoughts along these lines will take several decennia before chemists can start to incorporate the results of this work on intermolecular forces in their attempts to link up in a more systematic way the multitude of facts they are dealing with. Accordingly I would like to stress that there is an urgent need for an approach to intermolecular forces in a more qualitative or semi-quantitative way. Methods should be developed which would enable us to understand

at least roughly the action of intermolecular forces in more complicated systems, including biochemical systems. As an analogy one may refer to the rather successful attempts (up to 40 years ago) of GRIMM, FAJANS, VAN ARKEL and DE BOER, and many others after them, to systematize the facts of inorganic chemistry, with the aid of an approximate theory of interatomic forces (considering electrostatic forces between ions, dipoles etc., polarization forces, Born-Mayer repulsive forces, van der Waals-London forces, etc.). In the more complicated molecular systems as present in biochemistry, it seems that an important part of the interaction can often be approximated by an estimation of the electrostatic energy of the interaction between molecules. This stresses the importance of a better knowledge of the charge distribution in molecules. The interesting considerations as given here today, especially the line of thought given in Dr. BUCKINGHAM's paper, should ultimately give us the tools to make better estimations of the interaction energy in specific cases. I realize that the difficulties involved in such considerations in more complicated systems are considerable and may seem almost insurmountable at the present moment. For a more detailed analysis of some of the problems in biochemical systems I refer to the text of my paper to be presented on Friday morning. I only wanted to point out now that the situation is such that even highly approximative methods could be helpful in bringing some order in the overwhelming amount of facts provided by chemists working, for instance, in the field of catalysis or on the mechanism of chemical processes in the living cell.

HIRSCHFELDER

I think, Dr. VERWEY, that we have to proceed with science at all different levels. When we look through our « GEDENKS » microscope with the highest magnification we see all kinds of hills and valleys, which, then, for many purposes, can be smoothed depending on which particular applications you were thinking of one smooths in different manners. Today we have been trying to look

with the highest degree of magnification which makes the whole subject of intermolecular forces seem excessively complicated. We have been stressing interesting microscopically small terms which we think are interesting as curiosities instead of the main terms which are well known and therefore not particularly of interest apparently to this learned group. It is not that we feel that for practical purposes the intermolecular forces are as complex as it might seem. We are anxious, before proceeding to the big molecules and the biological molecules, to have a sufficient degree of understanding of all of the different terms, some of these terms, which for small molecules appear small, might very well turn out to be large terms in big biological systems. We need lots and lots of practical calculations which do not, at the present, exist. They do not exist because there has not been enough pressure from the experimental people to get that kind of data. If you want practical calculations of intermolecular forces, they can be obtained without difficulty with the high speed computing machines (and the methods are currently available).

HERZBERG

I just thought I should make one remark concerning the physicist's attitude on this problem and that is with regard to the hydrogen molecule. Prof. HIRSCHFELDER mentioned earlier today the fact that the LAMB shift correction is calculated to be about 0.2 cm^{-1} and that the relativistic corrections are of the same order. A few years ago we redetermined the dissociation energy of H_2 and D_2 with much increased precision. The surprising thing is that the recent variational calculations have led to a theoretical value for this quantity which is higher by 5 cm^{-1} . This difference is 10 times greater than our experimental accuracy. Perhaps this strange discrepancy is connected with a lack of gauge invariance in the calculations, as suggested by Prof. LÖWDIN. At any rate it seems to me that this discrepancy must be explained before we can say that we fully understand the forces between two hydrogen atoms.

SESSION DEUXIEME

SOUS LA PRÉSIDENCE DU

Prof. Dr. H.B.G. CASIMIR

VAN DER WAALS FORCES - I

H.B.G. CASIMIR

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It is not my intention to discuss here the theoretical foundations of the formulae for van der Waals interaction or to give details of the derivation. All I want to do by way of introduction is to summarize the results.

I. VAN DER WAALS INTERACTION BETWEEN TWO ATOMS OR MOLECULES AT THE DISTANCE R

Be k an excited state, o the ground state. To each transition $o \rightarrow k$ there corresponds a matrix element of the dipole moment q_{ok} .

The static polarisability of one atom is given by

$$\alpha_{(o)} = \sum \alpha_k = \sum \frac{2}{3} \frac{|q_{ok}|^2}{\hbar \nu_k}$$

where ν_k is the excitation frequency. The London-van der Waals interaction energy is found by a second order perturbation calculus and can be written as

$$(1) \quad \mathcal{U} = -\frac{3}{2} \frac{\hbar c}{R^6} \sum \frac{\alpha_k \alpha_{\nu}}{\lambda_k + \lambda_{\nu}}$$

where the index k refers to the states of the second atom. This theory is due to F. LONDON.

2. VAN DER WAALS INTERACTION WITH RETARDATION

If in one of the terms in equation (1) R becomes comparable with $\lambda_k + \lambda_{\nu}$ then this term has to be multiplied by a correction factor which decreases monotonically with increasing R . If for all the important terms in (1) $R \gg \lambda_k + \lambda_{\nu}$ then a simple limiting formula is found viz.

$$\mathcal{U} = -\frac{23}{8\pi^2} \frac{\hbar c}{R^7} \alpha_{1(0)} \alpha_{2(0)}$$

These corrections to London's theory were first given by CASIMIR and POLDER but have been confirmed by numerous other authors.

3. VAN DER WAALS FORCES BETWEEN BODIES CONSISTING OF MANY ATOMS

As long as we restrict ourselves to the second approximation van der Waals forces are additive. The force between two bodies can be found by summation which in many cases can

be replaced by integration. In this way we obtain for the interaction between two flat plates at the distance d the following expressions.

Nonretarded. If

$$\mathcal{U} = -\frac{c_1}{R^6}$$

is the interaction between two atoms then the interaction between two plates is given by

$$\frac{\mathcal{U}}{S} = -\frac{\pi}{12} n^2 \cdot \frac{c_1}{d^2}$$

where S is the area of the place and n the number of atoms per cm^3 . This was first pointed out by HAMAKER.

Retarded. If

$$\mathcal{U} = -\frac{c_2}{R^7}$$

is the interaction between two atoms then we find

$$\frac{\mathcal{U}}{S} = -\frac{\pi}{30} n^2 \cdot \frac{c_2}{d^3}$$

4. INTERACTION BETWEEN TWO INFINITE CONDUCTING FLAT PLATES

Starting from simple expressions for the zeropoint energy of electromagnetic waves in empty space one arrives at the following formula

$$\frac{\mathcal{U}}{S} = - \frac{\pi}{1440} \cdot \frac{\hbar c}{d^3}$$

This leads to a small but measurable interaction between metal plates at the distance of about 1 micron or so. This equation was first derived by the present author.

5. INTERACTION BETWEEN TWO FLAT DIELECTRIC PLATES

The formulae given above contain already two limiting cases namely that for $\epsilon = \infty$ and that for very small $\epsilon - 1$. We may relate the static polarisability α to the dielectric constant by means of the formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \alpha n$$

This leads to

$$\frac{\mathcal{U}}{S} = - \frac{69}{1280\pi^3} \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^2 \cdot \frac{\hbar c}{d^3}$$

Since this formula is certainly correct for $\epsilon \sim 1$ and differs by no more than 20% from the correct value for $\epsilon \sim \infty$ it may be expected also to give the right order of magnitude for intermediate values of ϵ . An accurate expression for any value of ϵ has been given by LIFSHITZ. Its derivation is based on a more sophisticated form of quantum field theory.

6. TEMPERATURE CORRECTIONS

The expression given above holds for $T=0$. Since the relevant contributions to the interaction energies are given by waves whose wavelength is comparable to the distance, the equations for $T=0$ will also hold for finite temperatures, as long as these waves are not thermal excited. For distances of a few microns and less this condition will be satisfied. Formulae for the cases of higher temperatures were also derived by LIFSHITZ although he made some errors in their final evaluation as was shown by SAUER and by HARGREAVES.

The formulae given above would appear to be well established and should provide an adequate background for to-day's discussions.

VAN DER WAALS FORCES BETWEEN MACROSCOPIC OBJECTS

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INTRODUCTION

The phenomena of adhesion, of aggregation of colloidal particles and certain aspects of adsorption have drawn attention to the cumulative effect of van der Waals forces between large numbers of molecules.

Basing themselves on the strict additivity of the London forces, and replacing a summation of the energies of interaction between all pairs of molecules by an integration over the volumes filled by these molecules, TOMLINSON [1], BRADLEY [2], DE BOER [3] and HAMAKER [4] derived equations for the attraction between parallel plates, separated by a narrow gap, between spheres of equal or different size and between a flat plate and a spherical particle.

Writing for the London energy, U , between two molecules at a distance r

$$(1) \quad U = - \frac{\lambda}{r^6}$$

and introducing the « Hamaker constant » A

$$(2) \quad A = \pi^2 q^2 \lambda$$

where q is the number of molecules per unit volume, the interaction energy V per unit area between two thick flat plates separated by a gap of width H is found to be

$$(3) \quad V = - \frac{A}{12 \pi H^3}$$

and the force of attraction, F , per unit area

$$(4) \quad F = \frac{A}{6 \pi H^3}$$

Later (5, 6, 7, 8) similar equations have been given for the retarded van der Waals forces. If the retarded van der Waals energy between two molecules is written

$$(5) \quad U_{\text{retard}} = - \frac{\mu}{r^7}$$

the energy per unit area of flat plates separated by a gap, H , becomes

$$(6) \quad V_{\text{retard}} = - \frac{B}{3 H^3}$$

and the force

$$(7) \quad F_{\text{retard}} = \frac{B}{H^4}$$

where B , the « retarded van der Waals constant », is equal to

$$(8) \quad B = \frac{\pi q^2 \mu}{10}$$

The interaction between two spheres of radius a_1 and a_2 can also be expressed by simple equations, provided the distance of closest approach H between the spheres is sufficiently small ($H < a_1, 2/1000$). The non-retarded energy and force are given by

$$(9) \quad V_{\text{sphere-sphere}} = -\frac{A}{6} \frac{a_1 a_2}{H a_1 + a_2} = -\frac{A a}{6 H}$$

$$(10) \quad F_{\text{sphere-sphere}} = \frac{A}{6 H^2} \frac{a_1 a_2}{a_1 + a_2} = \frac{A a}{6 H^2}$$

and in the retarded case

$$(11) \quad V_{\text{retarded}} = -\frac{\pi B a}{3 H^3}$$

$$(12) \quad F_{\text{retarded}} = \frac{2 \pi B a}{3 H^3}$$

where a is equal to $a_1 a_2 / (a_1 + a_2)$. The equations (9) through (12) can be easily applied to the case of interaction between two equal spheres (a = half radius of spheres), between a sphere and a flat (a = radius of sphere) or between two crossed cylinders (a = radius of cylinders).

Refinements to the above equations, taking non-additivity of the London-van der Waals forces into account have been discussed in Professor CASIMIR's lecture.

In this lecture we shall concentrate on experiments in which these equations have been tested or from which values of the constants A and B have been derived. One may distinguish two main different types of measurements.

In adhesion experiments the distance between the two bodies is very small, they are essentially « in contact ». The attraction is non-retarded and usually quite strong.

In the second type of experiment the two bodies are kept strictly separated, say, by a distance of 1000 Å or more, the forces are retarded and weak.

We shall not discuss adsorption measurements in which relatively thick layers of liquid are condensed on a flat substrate and which can be interpreted as « adhesion » between the substrate and a layer of liquid of finite thickness.

ATTRACTION AT VERY SMALL DISTANCES, ADHESION

Although numerous measurements of adhesion have been made for obvious practical purposes, they can as a rule not be interpreted quantitatively in terms of van der Waals forces. The microgeometries are not sufficiently well known, and often the influence of moisture, electric charges etc. may be substantial.

Nevertheless some adhesion measurements have been performed with the special purpose of obtaining information on

intermolecular attractions and of these we want to cite the following ones.

In 1928 TOMLINSON [1] determined the force necessary to break the adhesion contact between crossed drawn quartz fibres or between fused glass spheres. In agreement with the theoretical expectation (c.f. equation 10) he found proportionality between force and radius of the spheres and he remarked already that in contact a certain elastic deformation should occur. Later KRUPP and SPERLING [9] remarked that non-elastic deformation, creep, should also be considered. It may increase the adhesion considerably.

Even when the technical conditions of adhesion measurements are irreproachable, the interpretation hurts itself against *surface* roughness, which can make the local radius of curvature at the point (points) of contact much smaller than the macroscopic radius of the particle.

Lack of information on the *distance of closest approach* forms another obstacle. Different authors have chosen as plausible values $3\text{\AA}$, $4\text{\AA}$, $6\text{\AA}$ but as the distance occurs squared in the force equation (10), a change from $3\text{\AA}$ to $4\text{\AA}$ corresponds already to an uncertainty of nearly a factor 2.

The deformation and the size of the area of contact are determined by the *surface hardness* on a *microscale*. This surface hardness is not easily accessible and forms another uncertainty in the interpretation, but KRUPP [10] has shown that in extreme cases (very soft materials, very hard materials) this difficulty can be overcome.

After TOMLINSON other authors have made similar measurements with improved techniques.

BRADLEY [2] measured the force between unequal spheres in contact by mounting one on a quartz spiral spring, the extension of which is determined at the moment the contact between the spheres is broken. He took great care to avoid the effect of moisture and incidentally was the first to give a

derivation of the interaction potential between two unequal spheres.

In 1936 RAYLEIGH [11] determined the force necessary to separate two flat glass plates, which had been pressed together until the distance between their surfaces was about $20\text{\AA}$. A force of 45×10^6 dynes/cm² was needed to separate them.

In 1955 HOWE, BENTON and PUDDINGTON [12] suspended a sphere on a pendulum, allowed it to stick to a flat plate and determined the angle through which the pendulum had to be turned before the contact was broken. They found pronounced effects of contact times and relatively small forces of adhesion.

In 1965 SMITH and GUSSENHOVEN [13] did show that « optical contact » between well polished quartz surfaces, which is usually assumed to be due to the cementing action of moisture, is also established under conditions of ultra high vacuum and is presumably due to van der Waals forces.

BÖHME, KRUPP and coworkers [10, 14, 15, 16, 17, 18, 19] elaborated a new method to determine adhesion between particles in the micron range and a flat substrate by mounting the substrate with adhering particles in an ultracentrifuge and determining the centrifugal field at which the particles fly off. They find a rather broad distribution of adhesional forces which is attributed mainly to the surface roughness of the substrate and to a lesser extent to that of the particles.

Table 1 lists some of the typical results of these adhesion measurements. Van der Waals constants, A , of a few times 10^{-12} ergs are in agreement with the measurements, but the reader should be aware that in all cases the quantitative interpretations contain one or more weak points.

TABLE I — Hamaker-van der Waals constant A derived from adhesion measurements with the following assumptions:
 1. distance of closest approach = 4Å
 2. no permanent deformation, except where mentioned explicitly
 3. macroscopic radii used in the equations, except where mentioned explicitly

Author	Type of system	$\frac{a_1 a_2}{a_1 + a_2}$ in cm	Force measured in dynes	A calculated in ergs	Remarks
Tomlinson (1928)	crossed quartz fibres	0.006	0.68	1.1×10^{-12}	fibre radius = 0.006 cm
Bradley (1932)	glass spheres	0.3	1000	32×10^{-12}	$F \propto a$, effect of moisture probable
	quartz spheres	0.025	10	4×10^{-12}	$F \propto \frac{a_1 a_2}{a_1 + a_2}$
Rayleigh (1936)	$\text{Na}_2\text{B}_4\text{O}_7$ spheres	0.075	66 in vacuo about 20 in air	8.5×10^{-12} 5.25×10^{-12}	corrosion by moisture?
	flat plates glass	∞	45×10^6 dynes/cm ²	7×10^{-12}	distance between plates measured 520Å
	sphere/plate pyrex	0.05	> 1 dyne 0.1 — 0.2	$> 2 \times 10^{-13}$ 10^{-12} (assumed)	in vacuo dist. of close approach 20-30Å. corrosion by mois- ture?
Smith and Gussenhoven (1965)	optic. flats quartz	∞	14×10^6 dynes/cm ²	10^{-12} (assumed)	dist. of close appr. 15Å or 2% of surface in 4Å con- tact
Böhme, Krupp et al. (1962-1966)	sphere/plate Fe	10^{-5}	0.004	4×10^{-12}	effective a calculated from surface rugosities; deforma- tion taken into account
	Au quartz rough	10^{-5}	0.011	7×10^{-12}	
	Au quartz smooth	3×10^{-4}	0.1	2×10^{-12}	
	Au plastic	10^{-5}	0.1-0.25	$1-3 \times 10^{-12}$	

ATTRACTION AT LARGER DISTANCES; RETARDED VAN DER WAALS FORCES

Determinations of the attraction between bodies that are not in contact refer — but for one exception — to separations of 1000Å or more. The one exception is Miss BAILEY's work on split mica [20]. She used the property that mica can be split in such a way that the splitting plane follows the same lattice plane over an area of several cm² and applied TOLANSKY's [21] multiple interference technique to determine the distance between the two splitting planes accurately. A split piece of mica was allowed to recombine at one end, but kept open at the other end. The shape of the mica from the cleavage line to the open end should be that of a transversely loaded beam, but for the molecular attraction, which is particularly strong near the cleavage line. By determining the difference between the actual shape of the mica and the calculated shape for the loaded beam, the magnitude of the intermolecular attraction could be determined. The value found for A is $A \approx 3 \times 10^{-11}$ ergs which is of the correct order of magnitude (see table 1) but on the high side.

Most other measurements in this group are all variations on the same theme. One plate is mounted on the arm of a sensitive balance. A second plate is brought sufficiently close to the first one so that attraction makes itself felt. The distance between the two plates is determined by optical interference, the force of attraction is « weighed » on the balance. Such measurements have been made by four groups of authors, viz. by DERYAGIN and his coworkers [23, 24], by OVERBEEK with SPARNAAY and other collaborators [25, 26], by KITCHENER and PROSSER [27] and by SPARNAAY independently [28]. In all cases either flat plates with an area of about 1 cm² or one flat plate and one plate with a spherical surface were used. The distances varied between 0.1 μ and 1 μ .

The main differences in technique are found in the suspension of the balance, in the method of damping, in the method of carrying out the weighing of the force of interaction and in the method of adjusting the narrow gap between the plates. SPARNAAY and OVERBEEK [25] had the most simple set up. They used the air between the plates for damping. One of the plates was directly suspended on a thin piece of sheet steel (razor blade) which bent a little further under the influence of the attraction between the plates. The deviation of this sheet steel spring from its equilibrium position was determined by means of the change of the capacity of a condensor of which one of the plates was mounted on the spring. The adjustment of the gap was carried out roughly by micrometer screws. The fine adjustment was made by changing the gas pressure in little pots with a flexible lid on which one of the two plates was mounted.

KITCHENER and PROSSER [27] used a similar set up with oil damping, which was later on also used in OVERBEEK's group [26].

SPARNAAY [28] in his measurements of the attraction between metal plates, used a double cantilever system for rough and fine adjustment of the gap and he determined the distance between his plates electrically rather than optically. Moreover he suspended one of his plates on a balance arm, rather than on a metal spring. In order to avoid friction the balance beam was suspended by a sheet metal spring rather than by the conventional knife edge.

BLACK et al. [26] used a combination of SPARNAAY's early [25] and later [28] techniques. A schematic picture of their apparatus is presented in figure 1.

In a recent variation of this technique VAN SILFHOUT [29] used a torsion balance. The weight of the balance arm varies when it carries different plates. This variation is compensated for by floats. The pressure in the pots with flexible lid is transferred by oil rather than by gas.

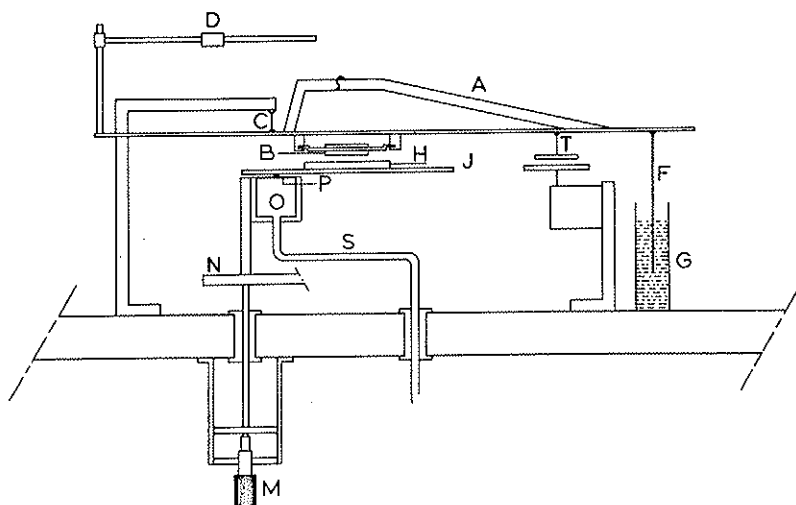


FIG. 1 — Schematic picture of apparatus used by BLACK, DE JONGH, OVERBEEK and SPARNAAY [26].

The balance beam (A) with counter weight (D) is suspended by a metal leafspring (C) and carries the upper quartz plate (B), the upper plate (T) of the condensor and the thin rod (F), dipped in damping oil (G). The lower quartz plate (H) is cemented to a brass table (J) supported on three brass membranes (P) of which only one is shown in the figure. The brass membranes form the lid of brass cylinders (O), inside which the pressure can be changed independently by connecting the three tubes (S) to three independent pressure lines (0.01 — 1 atm.). The cylinders (O) are fixed on a table (N) which in its turn is supported by three micrometer screws (M) for the coarse adjustment.

The whole apparatus is placed in an evacuated (< 0.005 mm of mercury) glass cylinder with stainless steel top and bottom. The optical observations are carried out through glass windows in the steel lid.

DERYAGIN [23, 24] used a very ingenious method, in which he applied a system of negative feedback to stabilize his apparatus against vibrations, to measure the force of attraction and to give the fine adjustment of the gap between the two plates. Fig. 2 gives a schematic picture of the whole arrangement.

about $0.001 - 1$ dyne, and changes very rapidly with the distance. The balance therefore has to be stiff and at the same time very sensitive. Displacements of the ends of the arm of a few Angstrom units have to be measured. In such a sensitive set-up vibrations are extremely disturbing. They have to be avoided as far as possible by special mounting of the whole set-up. VAN SILFHOUT has mounted one of his recent apparatus on floats, suspended in water, which carry the whole weight of approximately 80 kg. This method of suspension allows effective damping, even of vibrations of less than 1 cycle per second.

Electric charges on the plates may cause interactions, which are much stronger than the van der Waals forces and may have a similar dependence on the width of the gap. Several methods have been proposed to suppress these charges. Ultra-violet light, electric discharges, radiation from a radio active source have been used. A very simple device to get rid of surface charges on glass or quartz or similar substances is the admission of water vapour, which is adsorbed and makes the surfaces sufficiently conducting to allow the charges to flow away.

Finally the measurements are hampered by the accidental presence of dust particles and by irregularities on the polished surfaces. A single dust particle with a diameter of 0.5μ between flat plates of 1 cm^2 area prevents valid measurements completely. Therefore extreme care has to be taken to avoid dust and every single measurement has to be checked with respect to the absence of dust. Moreover, even very carefully polished surfaces can rarely be made flatter than $\frac{1}{50}$ of the wavelength of light, so that the surface itself contains hills and valleys of $100\text{\AA}$ or more. Therefore, there are many reasons why this kind of technique does not allow measurements in which the plates are closer than a few hundred Angstrom units. Nevertheless it is still a bit mysterious why in

all the measurements in which this method was used, no valid measurements exist with a gap width below $900\text{\AA}$.

We should also mention here a method developed by SPARNAAÿ and JOCHEMS [30] in which the distance is determined at which the equilibrium between a sphere (radius about 40μ), suspended on a spring and a flat plate just becomes labile, so that the sphere « jumps » to the plate. This distance is directly related to the retarded van der Waals force. The method is very simple and straightforward, although, unfortunately, not very accurate.

RESULTS FOR RETARDED VAN DER WAALS CONSTANTS

In some early measurements, in which electric charges had not been sufficiently removed, rather strong attractions have been found, which were not very reproducible, and in which the force between flat plates varied as an inverse second to third power of their distance. Later, more accurate measurements were all in agreement, that the force between flat plates was inversely proportional to the fourth power of the distance, and that between a flat and a sphere to the cube of the distance. Consequently in all these cases one dealt with retarded van der Waals forces. Good examples are given in figures 3, 4 and 5 taken from KITCHENER and PROSSER [27] for the attraction between pyrex plates, from DERYAGIN and ABRICOSSOVA [24] for Tl-halides and from our own recent work for fused quartz. Especially in fig. 5 the slope of the experimental line comes very close to the theoretical value 3.

Table 2 gives a survey of the measurements published by different authors. Although the order of magnitude found for the constant B is in agreement with theoretical expectations,

TABLE 2 — *Values of the retarded van der Waals constant, B, as derived from measurements by various authors.*

Authors	Materials	Type of system	Radius of sphere	$B \times 10^{19}$ erg. cm.
Deryagin and Abrikosova (1956-1957)	quartz	flat-sphere	10 cm	1.21
		flat-sphere	11.1 cm	0.81
		flat-sphere	25.4 cm	1.37
Tl-halides		flat-sphere	5.2 cm	4.69
		flat-sphere	12.5 cm	3.51
quartz-chromium		flat-sphere	5 cm	3.60
		flat-sphere	10 cm	3.00
borosilicate glass		flat-flat (2.4 cm ²)	—	1.12
		flat-flat (1 cm ²)	—	12
		flat-flat (1 cm ²)	—	12.5
chromiumsteel		sphere-flat	4.10 ⁻³ cm	1-10
		sphere-flat	4.10 ⁻³ cm	1-10
chromium		flat-flat (1 cm ²)	—	2
		flat-flat (1 cm ²)	—	1.15
gold-germanium gold-glass		sphere-flat	715.2 cm.	0.66
		sphere-flat	715.2 cm.	0.74
quartz (fused)		flat-flat (1 cm ²)	715.2 cm.	2.84
		flat-sphere	715.2 cm.	
quartz (fused) quartz (crystal)		flat-sphere	715.2 cm.	
		flat-sphere	715.2 cm.	
quartz-chromium		flat-sphere	715.2 cm.	
		flat-sphere	715.2 cm.	

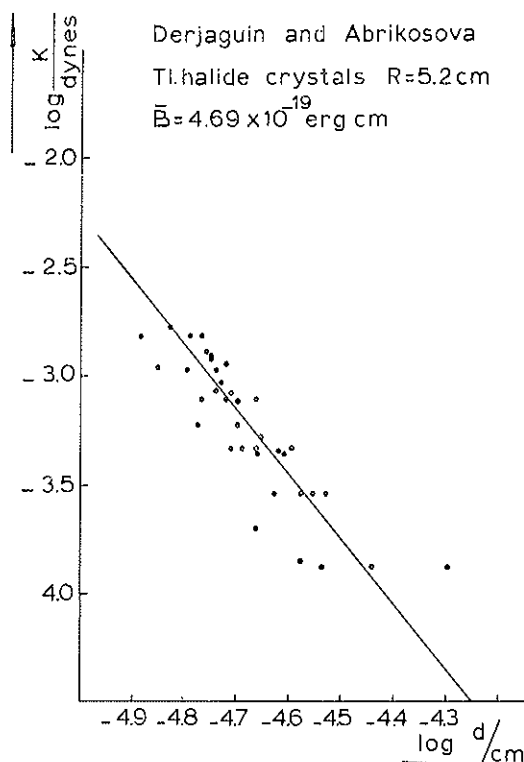


FIG. 3 — Attraction between a flat plate and a sphere (radius=12.5 cm) of the mixed crystal of thallium halides (Tl [Cl, Br]). Deryagin and Abrikosova [24]. The line corresponds to a slope of -3.00 .

it is obvious from the spread in the values found for quartz that the B values are still rather inaccurate. It is believed, that in our recent measurements it has been possible to obtain an accuracy of 10-15% in the value of B , sufficient to distinguish between the values for fused and for crystalline quartz.

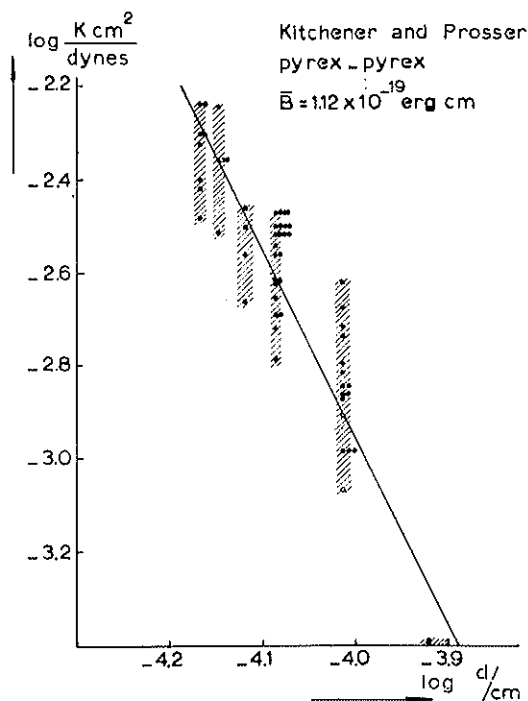


FIG. 4 — Attraction between two flat pyrex plates (area 2.4 cm^2). KITCHENER and PROSSER [27]. The line corresponds to a slope of -4.00 .

THEORETICAL INTERPRETATION

The uncertainty in the experimental values for the non-retarded van der Waals forces is still so high, that further theoretical discussion is not very profitable at this moment. For the retarded van der Waals constant B the situation is more favorable. For the interaction quartz-quartz the constant is known within 10 to 15% and for a number of other cases with an estimated accuracy of 30-50%. The theoretical in-

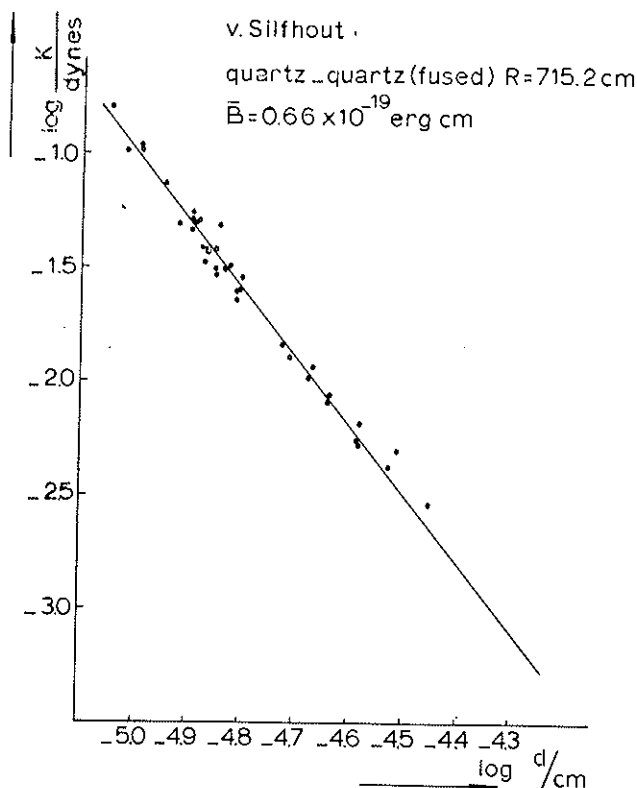


FIG. 5 — Attraction between a flat plate and a sphere (radius=715.2 cm) of fused silica. VAN SILFHOUT [29]. The line corresponds to a slope of -3.00 .

terpretation should be based on Lifshitz's theory [23, 31, 32] for the particular case in which the gap is large as compared to $\lambda/2\pi$, where λ is the wavelength of the first absorption peak in the ultraviolet.

For this case Lifshitz's equation for the force of interaction between parallel plates is

$$(13) \quad F = \frac{\pi \hbar c}{480 H^4} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 1} \right\}^2 \varphi(\epsilon_0)$$

in which h = Planck's constant, c the wavelength of light, ϵ_0 the « static » dielectric constant and $\varphi(\epsilon_0)$ a function of the dielectric constant determined by numerical integration and given in table 3.

TABLE 3. — $\varphi(\epsilon_0)$ as found by numerical integration (33, 34).

ϵ_0	∞	40	10	4	2	1
$\varphi(\epsilon_0)$	1	0.53	0.41	0.37	0.35	0.354

In the static dielectric constant to be used in eq. (13) the contributions of short wavelength adsorption regions have to be taken completely into account, but adsorptions at wavelengths larger than H only give a (negligible) non-retarded contribution to the force of attraction. Consequently the dielectric constant to be used is the square of the refractive index in the visible, extrapolated to long wavelengths.

It is interesting to compare the result from Lifshitz's theory with the interaction calculated from Casimir and Polder's [5] equation for the retarded interaction between two molecules and assuming additivity of these interactions.

The retarded energy of interaction between two atoms of polarizability α at a distance r is given as

$$(14) \quad V = - \frac{23}{8} \frac{hc\alpha^2}{\pi^2 r^7}$$

The energy of interaction between two flat plates is then easily found by integration and is equal to:

$$(15) \quad V = - \frac{23}{240} \frac{hc}{\pi H^3} (\sum_i \alpha_i q_i)^2$$

and the force per unit area

$$(16) \quad F = - \frac{23}{80} \frac{hc}{\pi H^4} (\sum_i \alpha_i q_i)^2$$

when q_i is the number of atoms or molecules of type i per unit volume.

A suitable value for $\sum_i \alpha_i q_i$ can be found from Clausius-Mosotti's equation

$$(17) \quad \frac{\epsilon_0 - 1}{\epsilon_0 + 1} = \frac{4\pi}{3} \sum_i \alpha_i q_i$$

and combination of eqs. (16) and (17) leads to

$$(18) \quad F = - \frac{207}{1280} \frac{hc}{\pi^3 H^4} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \right\}^2$$

This equation might be improved upon by using better approximations than the equation (17) of Clausius-Mosotti, but even then it would still have to be corrected for the non-additivity of the van der Waals forces. It is, however, already in the form (18) quite a useful approximation.

The retarded van der Waals constant, B , can now be expressed explicitly as a function of the dielectric constant, either using Lifshitz's eq. (13) or the Casimir-Polder-Clausius-Mosotti combination (18)

$$(19) \quad B_{\text{Lifshitz}} = \frac{\pi hc}{480} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 1} \right\}^2 \varphi(\epsilon_0)$$

$$\begin{aligned}
 (20) \quad B_{\text{Cas.Pold.Cl.Mos.}} &= \frac{\pi \hbar c}{480} \frac{621}{8 \pi^4} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \right\}^2 \\
 &= \frac{\pi \hbar c}{480} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \right\}^2 \times 0.80
 \end{aligned}$$

Table 4 shows some calculated B values according to the two above equations. It is seen that except for the case of very high dielectric constants the interaction constant is somewhat overestimated if non-additivity is neglected. For $\epsilon \rightarrow \infty$, i.e. metals, the Clausius-Mosotti equation is not really applicable.

TABLE 4 — *Values of the retarded van der Waals constant B for the interaction of flat plates of dielectric constant ϵ_0 .*

ϵ_0	∞	40	10	4	2	1
$10^{19} \times B_{\text{Lifshitz}}$	13.0	6.2	3.6	1.73	0.51	$1.15(\epsilon_0 - 1)^2$
$10^{19} \times B_{\text{Cas.Pold. Cl.Mos.}}$	10.4 (not applicable)	9.0	5.85	2.60	0.65	$1.15(\epsilon_0 - 1)^2$

When the two interacting materials are different the Casimir Polder approach leads to the simple conclusion that the constant B_{12} of interaction between media 1 and 2 is the geometric average between the constants B_{21} and B_{22} , which describe the interaction between two pieces of material 1 or two pieces of material 2 respectively

$$(21) \quad B_{12} = \sqrt{B_{11} \cdot B_{22}}$$

DEVEREUX and DE BRUYN [34, 35] have made numerical calculations on the interaction between different materials, using

Lifshitz's equations. According to their figures the interaction constant B_{12} is consistently smaller than the geometric average of B_{21} and B_{22} , although the difference is smaller than 1% for dielectric constants under 10. For the particular case of interaction between a dielectric (ϵ_0) and a metal ($\epsilon_0 \rightarrow \infty$) they find

$$(22) \quad B_{\epsilon_0, \infty} = \frac{\pi \hbar c}{480} \left\{ \frac{\epsilon_0 - 1}{\epsilon_0 + 1} \right\} \cdot 0.462$$

In table 5 we compare experimental and theoretical values for the retarded interaction constants, B , for the materials mentioned in table 2.

The most recent and accurate measurements of quartz and the measurements on metals are in good agreement with Lifshitz's theory. The older measurements are all somewhat at the high side, but as both surface roughness and electrostatic effect tend to give too high values of the attraction this is not unexpected. It is certainly desirable to extend the measurements and obtain more data on different substances with the accuracy that is presently obtainable.

INTERACTION BETWEEN PARTICLES EMBEDDED IN A MEDIUM

So far, we have only considered the interactions between objects separated by a vacuum or a gas of low density. A major field of application, however, deals with particles suspended in a liquid medium, such as aqueous solutions of electrolytes, liquid hydrocarbons, etc. Measurements of the force of interaction of relatively large objects are very difficult in

TABLE 5 — Comparison between experimental and calculated values for the retarded van der Waals constant, B.

Material	Author	n	$\varepsilon_0 = n^2$	$B \times 10^9$ in erg cm		
				Lifsh.	Cas. Pold.	Exp.
Quartz, fused	Deryagin	1.45	2.10	0.57	0.75	1.21
	»	»	»	»	»	0.81
	»	»	»	»	»	1.37
Black c.s.		»	»	»	»	2.0
	»	»	»	»	»	1.15
Van Silfhout		»	»	»	»	0.67
Quartz, cryst.	Van Silfhout	1.52	2.31	0.72	0.96	0.74
Glass, borosilic.	Kitchener	1.5	2.25	0.68	0.90	1.12
Tl halides	Deryagin	2.27	5.16	2.25	3.5	4.69
	»	»	»	»	»	3.51
Quartz chromium	»	1.45/∞	2.10/∞	2.18	3.1	3.60
	»	»	»	»	»	3.00
Quartz chromium	Van Silfhout	1.52/∞	2.31/∞	2.40	3.5	2.84
Chromiumsteel	Sparnaay	∞	∞	13.0	13.0	12.0
Chromium	»	∞	∞	»	»	12.5
Gold/germanium	»	∞/4.5	∞/20.25	8.3	10.4	1-10
Gold/glass	»	∞/1.5	∞/2.25	2.3	3.4	1-10

this case on account of the high viscous resistances which are encountered. We may recall that in SPARNAAY's early measurements, where air was used as a damping medium, the pressure had nevertheless to be reduced to about 0.1 millibar in order to decrease the viscosity sufficiently.

It is instructive to calculate, how long it takes for two plates to reach an equilibrium position, if the difference between the van der Waals attraction and the force of a spring forms the driving force and the plates are embedded in a fluid medium of viscosity η .

REYNOLDS [36] has derived a relation between the rate at which two parallel circular plates of radius R and distance H , approach one another under the influence of a force F .

$$(23) \quad -\frac{dH}{dt} = \frac{2 FH^3}{3 \pi \eta R^4}$$

Assuming that the retarded van der Waals force drives the plates together against the action of a spring, the rate of approach becomes

$$(24) \quad -\frac{dH}{dt} = \frac{2 H^3}{3 \pi \eta R^4} \left(\frac{\pi R^2 B}{H^4} - P (H_0 - H) \right)$$

where P is the stiffness of the spring and H_0 the position in which the spring is unloaded.

Eq. (24) may be written

$$(25) \quad -\frac{dH}{dt} = \frac{2 B}{3 \eta R^2 H} \left(1 - \frac{H^4 (H_0 - H)}{H_e^4 (H_0 - H_e)} \right)$$

where H_e is the width of the gap at equilibrium.

The time, T , in which H has changed by e.g. $1/10$ of its value, is

$$(26) \quad T \approx \frac{3 \eta R^2 H \cdot H/10}{2B}$$

which for a gap of the order of $1000 \text{ \AA}$, a radius of 0.5 cm , water as the viscous medium and a B value of 10^{-19} erg cm turns out to be about 10^6 sec. , that is about a week; the final approach to equilibrium is even slower than that.

This means that in order to have reasonable times of experimentation, say of 100 or 1000 sec. , the area over which the two objects are in close approach must be very small, consequently the relevant forces are very small too. For non-retarded forces at shorter distances the conclusions are quite similar.

No wonder, therefore, that so far quantitative data on van der Waals interaction across a medium, are very scarce.

DERYAGIN, VOROPAEVA and KABANOV [37, 38] determined the maximum in the repulsion energy between two crossed metal wires in aqueous salt solutions. The wires were polarized, so that their surface potential was sufficiently well known to calculate the repulsion between the electrical double layers. In the maximum of repulsion energy the van der Waals force is equal and opposite to the double layer repulsion and can thus be estimated. For platinum in water A is found to be $2.3 - 4.8 \times 10^{-12} \text{ ergs}$ and for gold in water $A = 14 \times 10^{-12} \text{ ergs}$.

BÖHME et al. [18] determined the adhesion of gold particles to mylar films under water, using the ultracentrifuge technique. Adhesion is diminished to roughly $1/3$ of its value by the admission of water. If the system is immersed before contact is made, the adhesion is very weak and strongly time dependent.

CONCLUSIONS

Retarded van der Waals constants for dielectrics and for metals separated by a vacuum are in good agreement with theory although measurements of more systems and with better accuracy would be welcome.

Non-retarded van der Waals forces in vacuo have only been determined for systems in « contact ». They are in semi-quantitative agreement with the available theories. Measurements at somewhat larger well defined distances between the objects are highly desirable.

The direct determination of van der Waals forces in immersed systems is still in its very early beginning. Since it are just the forces between objects separated by a condensed medium, which are the most important ones for practical applications, further efforts in this direction should be made.

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DISCUSSION

Chairman: H.B.G. CASIMIR

VERWEY

It may be interesting to say a few words about the history of the work discussed today, which, to a considerable extent, was initiated in an industrial laboratory. Before the war HAMAKER and I worked on suspensions in various media, and we had to pay special attention to the problem of stability of these suspensions in connection with their practical applications (mainly electrophoretic deposition of various materials upon an electrically conducting substrate). Accordingly HAMAKER started to calculate the van der Waals-London attraction between the particles, and, later on, OVERBEEK and I started also to consider the repulsion between particles due to the double layers. This led to the DLVO theory to be discussed here by Prof. LYKLEMA.

However, the complete theory (combining attractive and repulsive forces) led to a serious deviation from practical experience for the case of larger particles (as present in suspension), suggesting that the calculated van der Waals-London attraction for larger distances was too large. Then OVERBEEK had the idea that it might be the retardation which had to be taken into account, and CASIMIR and POLDER helped us out of the difficulties by developing their theory, which gave better equations for the interaction of larger

particles. I thought it might be interesting to tell this story here, as an illustration how this theoretical work has been directly stimulated by the actual needs of practice.

FIXMAN

May I ask a further question. Might I ask for a simple explanation, if one is available, why the retardation effects should not depend on the conductivity of the materials which are attracting each other?

CASIMIR

Yes, certainly. Well, in Lifshitz' theory one will find a difference between a perfect conductor and a true metal. The question is that one can derive a limiting formula for a perfectly conducting plate, which is of course an idealization which just means that for electromagnetic waves you assume as a boundary condition that the tangential value of the electric field is zero. Now, of course, these boundary conditions will not hold for real metals. The question, however, is whether they are a sufficiently good approximation. Now in deriving the formula between metal plates you find that the whole effect is really due to a suppression of zeropoint motion of waves that have a wave-length of the same order of magnitude as the distance between the two plates. The question is therefore whether for such waves the boundary condition for perfect conductors is a sufficiently good approximation. Suppose you are working at a distance of the order of a micron or half a micron. The penetration depth of electromagnetic waves of that wave-length into a good conductor is certainly much smaller than one micron. That means that the approximation of a perfect conductor is fairly good. If you would work at 2.000 Å and with a moderately good conductor then it would not hold and you would have to take into account the

specific nature of the metals. The funny thing is that at long distances the whole interaction is determined by geometric factors only, combined with Plank's constant.

BOWDEN

I would like to say first how much I enjoyed the paper which Dr. OVERBEEK gave, not only for the very simple and clear way in which he did it, but also for the account of his own beautiful experiments. Anyone who has done any work with surfaces knows how difficult it is to get repeatable results and when you are dealing with a force of the order of one dyne then it is remarkable that this group of workers have been able to get results as reproducible as they are.

I would like to ask one point. Is Dr. OVERBEEK happy about the experiments where the solids are allowed to touch and the forces to separate them then measured. I agree the experimental results do give a result which may be correct to an order of magnitude. We know that the contact is determined not by the macroscopic shape of the surfaces themselves, but by the shape of the small irregularities present on them. When we put two solids together the area of contact may bear very little relationship indeed to the size of the solids because it is the surface irregularities which determine it. Both the real area of contact and the shape of the surface near them is dominated by these tiny surface irregularities. The second point is that the adhesion between the surfaces (or the friction between them if we slide them) again can be dominated by the strong adhesion of the tiny contact regions, rather than by the long range attraction of the rest of the surface which is separated by a much greater distance. I therefore find it a little surprising that in the early experiments, where solids were pressed together, that he can argue much about the retarded forces between the separated solids. It can be dangerous to calculate the area of contact from the elastic Hertzian

deformation. Although the load is very light, the region of real contact is so small that the pressure often is sufficient to give plastic deformations.

OVERBEEK

Yes, I quite agree with you that the difficulty of interpretation of the experiments where particles or plates have been in contact is very large, and in this respect indeed the early experiments are very dubious as far as their interpretation goes. You may remember that I mentioned Rayleigh's experiment, where he has determined that the distance between two plates in contact was about 20 Angstrom units. Now, this of course, must mean, that on the average the distance was 20 Angstroms but in some spots there was actual contact at a distance of the order of three or four Angstrom units, and therefore we can only expect here something that is a correct order of magnitude. I feel that in the recent experiments of the German Group at the Battelle Institute in Frankfurt the situation is really better because they worked with small particles of the order of one micron which they have investigated very carefully in the electron microscope and have shown that the irregularities on these particles are relatively insignificant and that they may interpret the experiment by using the radius of the particles.

For the substrate the situation is more difficult. The plastic flow which you mentioned comes out rather nicely in some of the experiments these authors have done on iron particles on an iron substrate. If they work in a reducing atmosphere then the plastic deformation is comparatively large and they get fairly large forces; if they work in an oxidizing atmosphere the iron surface is not really iron but it is iron oxide which is a much harder substance. Then the plastic deformation is much smaller and they can interpret their experiments by only taking into account the elastic deformation. But again the uncertainty as far as a value of the van der Waals constant goes remains fairly large. You mentioned for a moment

retarded forces. I don't think that in these experiments where particles or plates are in contact one measures the retarded forces. The distance, even at those places where the particles are separated from each other is still so small, that it is the non retarded force which plays the main role. I would indeed be very much happier if the non retarded van der Waals constant could be determined from experiments with no contact between the plates. Quite apart from the argument you have given, I would like to give two others. When two objects are separated it occurs quite frequently that the electric charge is not distributed evenly between them so that one has an extra coulomb attraction between the plates and the second is that in breaking the contact the forces are so large that one damages the surface to some extent. We have had the experience with nicely polished quartz plates, if we allow them to get into contact once, we spoil the surface to some extent and we cannot do such good experiments as we did before there had been contact.

CASIMIR

I should like to raise one point myself. You spoke about the question of the interaction between bodies immersed in liquids. Now, of course, there may also be some theoretical complications. One has somehow to take into account the dielectric constant of the medium and it is not entirely obvious what value for the dielectric constant one should take and so on, I have seen only one paper really on the theory by MACLACHLAN which was a contribution to the discussions, in Bristol, last year. I do not know whether it has already been published, perhaps it has not. It is a rather tricky theory, if you really want to go to the bottom of things. Of course if the dielectric constant of two flat plates and of the liquid in between were identical then, on the basis of any theory you should get no force at all, so that is at least one limiting case which one knows, and one also knows the case where the dielectric constant in between is equal to unity so one can probably make a fairly good interpolation

between these two extremes. Yet it seems to me to be a slightly complicated state of affairs. I don't know whether OVERBEEK has something to say there.

OVERBEEK

Yes, Mr. Chairman, I would like to go into your first remark about the difficulty about choosing the correct dielectric constant. This difficulty occurs already in the interpretation of experiments such as I have described this morning. According to the Lifshitz theory the retarded force is found, by putting static dielectric constants into the equations, but one has to be a little careful about what the static constant means here. The point that really is important is whether the gap between the plates or the particles is larger or smaller than the absorption wavelength that is responsible for that particular dielectric constant and in the case of quartz or silica there is quite a nice example because the static dielectric constant of fused silica is 3.75, and using Lifshitz' theory with a dielectric constant of 3.75 one finds a B value of 1.6×10^{-19} which is more than twice the value we find experimentally. But the dielectric constant extrapolated from the refractive index for the optical region, but not taking into account the infra red absorption is 2.10. This dielectric constant of 2.10 gives good agreement with the experiments. Here I would say the force is retarded with respect to the absorption region in the far UV. The force is not retarded with respect to the infrared absorption but fortunately this contribution is very small. Now, of course the same kind of difficulties will occur for the medium also. Apart from MACLACHLAN's calculations there is DZYALOSHINSKII's work of the Moscow group on the van der Waals forces with a medium in between, and there is a rather complete calculation of the force between two different bodies by DEVEREUX and DE BRUYN based on Lifshitz' theory. One of the nice and interesting aspects here is that according to, let us say, classical approaches, the interaction constant between two different

bodies A and B is equal to the square root of the products of the interaction constants between two bodies A and two bodies B, that is the approximation that has been used in theories of mixtures quite frequently, because it is simple and often we have no further information. According to the Lifshitz' theory the mixed attraction constant is always somewhat smaller than this square root, so here is a difference from the classical, HAMAKER type approach, which has to be taken into account. But it would certainly be worthwhile if the theoreticians would go a little more deeply into this difficult case of interaction between particles with liquid in between, because that is where the most interesting applications in industry and in biochemistry are to be found.

LYKLEMA

May I ask whether there is any indication for a change in the slope from the third power to a lower one close to the 1,000 Angstrom thickness?

OVERBEEK

We have been looking very carefully for it. We have one or two cases where the experiments have been pushed to 900, or 850 Angstrom distance between the plates and we have not found any good indication of a deviation. There might have been one, but it is still within the limits of errors. So as far our experiments and those of other authors that I have cited this morning go, we must say that all these experiments where there was no contact give a good indication of retarded force but not yet an indication of the non retarded one.

RICCI

The approach time of two bodies in a liquid is just directly proportional to the viscosity. Now, it can be done a very extreme

case in which the viscosity is practically zero. I mean the liquid Helium II. In such a case one must think that the two bodies are collapsing one against the other.

OVERBEEK

This may be quite a difficult experiment to perform but it would certainly be interesting, I may give another example where the viscosity has been very low; that is in all those experiments where there was no medium in between the plates; that is, there was vacuum or a low pressure of air, and in the early experiments by SPARNAAY just the damping action of the viscosity of the air even at a few millimetres of mercury was good enough to eliminate vibrations. The effect of viscosity is really quite extraordinarily strong.

CASIMIR

The idea of combining van der Waals forces with liquid helium 2 is certainly an intriguing one. However, the interpretation might not be entirely straightforward, because of the curious properties of helium films and I do not feel certain that a thin layer of liquid helium does not have some sort of crazy zero point pressure which might influence the result.

But it would be very interesting to study this and it is curious that very little has been done on the relative motion of surfaces separated by thin layers of helium, whereas a lot of work has been done on measurements of motion of films and also on viscosity measurements by means of vibrating discs at somewhat larger distances. I don't know of anyone who has measured, for instance, the friction between two perfectly flat surfaces at distances of $1,000 \text{ \AA}$ in liquid helium 2, and one does not know whether under those circumstances helium 2 behaves as a good high pressure lubricant or whether it does not.

That should be studied together with van der Waals forces and it might well be that interesting work might be done along those lines.

BOWDEN

Dr. CASIMIR mentioned the friction of liquid helium or rather of solids with liquid helium between them. We have not done that, but we have measured the friction of solid krypton sliding on itself. This is an interesting solid, and the friction can be very low. It can resemble the friction of ice under the conditions where you form a very thin liquid layer on the surface of the crystal. If we are going to do this interesting experiment we may be faced with the problem that the inherent friction of solid helium is itself very low. Nevertheless I think this is an interesting point.

HIRSCHFELDER

I would like to ask a question. How closely can the coefficient of friction be related to van der Waals forces?

CASIMIR

Well I don't think there is a direct relation there for the time being.

BOWDEN

Could I comment here? The friction between solids is not usually a true surface effect. We get strong adhesion at the points of contact of the tiny surface irregularities. The van der Waals forces are of

course important in this adhesion, but the subsequent value of the friction is determined mainly by the force required to deform and to shear these regions of contact which are large on an atomic scale. It is their strength properties which are important and we would not expect a direct relation between the friction and the van der Waals forces.

OVERBEEK

Now that the question of friction in these narrow gaps is introduced I hope that LYKLEMA will forgive me if I tell just one of the results that he has obtained for the friction of water between two layers of soap molecules where the result was that the frictional constant has its normal bulk value until at least a distance of at most about $10\text{\AA}$ from the surface, so there is not very much change of the viscosity.

MOLECULAR FORCES AND COLLOIDAL STABILITY

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1) HISTORICAL INTRODUCTION

The first indication that molecular forces are operative between colloidal or suspended particles stems from the work of VON SMOLUCHOWSKI (1916) who studied the rate of aggregation of colloidal particles. He could explain his results only if an attractive force between the particles was postulated.

In 1932 KALLMANN and WILLSTÄTTER [1] recognized the attractive forces, postulated by VON SMOLUCHOWSKI as London-van der Waals forces. Although the London attractions between two atoms are effective only over a very short range (of the order of the atomic dimensions) their additivity in the case of attraction between colloidal particles lends them a much longer range (of the order of the dimensions of colloidal particles, i.e. hundreds to thousands of Å).

During the thirties several attempts have been made to calculate the attractive potential energy quantitatively, a.o. by DE BOER [2] and especially by HAMAKER [3]. The procedure was a summation (or integration) over all atomic interactions, additivity being presupposed. Retardation was not yet considered. Calculations were made for the attraction between

two flat plates, between two spheres, and between a plate and a sphere.

The fact that colloidal particles are usually embedded in a liquid carrier (say water) rather than in vacuum makes the interaction between two particles more complicated because it now includes also the particle-water and water-water contribution. In 1937 HAMAKER [4] showed that the over-all result was always an attraction between the colloidal particles, irrespective whether or not the mutual attraction between the particles outweighs that between the same volumina of water. Carried to the extreme, this means that two gas bubbles in water, like in a foam, attract each other. In other words: a thin liquid lamella between two large gaseous phases experiences a compressive dispersion force. We will revert to the potentialities of thin films for the study of molecular forces in a subsequent paper ⁽¹⁾.

The London-van der Waals attraction is not the only force operating between colloidal particles. Of the other ones the electrostatic repulsion must be mentioned in the first place. The fact that colloidal particles are often electrically charged was discovered as far back as the 19th century mainly by electrokinetic measurements. After experiments had shown that for hydrophobic sols a definite relation existed between stability and electrokinetic potential the following step in the historical development was a series of attempts to treat the stability of hydrophobic colloids quantitatively on the basis of a competition between van der Waals attraction and electrostatic repulsion (BERGMANN, LÖW-BEER and ZOCHER (1938) [5]; DERJAGUIN c.s. (1939-40) [6]; LEVINE c.s. (1939-1942) [7]; CORKILL and ROSENHEAD (1939) [8] and LANGMUIR (1938) [9]). However, the results of these authors were

⁽¹⁾ J. LYKLEMA, *Molecular forces in thin films*. Proceedings Study Week on Intermolecular Forces, Vatican City 1966. Henceforth this paper will be referred to as II.

conflicting, even on essential points like the question of whether or not the interaction of electrical double layers can produce attraction besides repulsion.

The attempts to formulate a quantitative theory for the stability of lyophobic colloids culminated in the theory that is now known as DLVO-theory, developed during the last war independently by DERJAGUIN and LANDAU [10] in Russia and by VERWEY and OVERBEEK [11] in the Netherlands. This theory is now generally accepted as basically sound, although its application to practical systems is not always simple.

2) OUTLINE OF THIS ARTICLE

The existence of the DLVO-theory enables us to proceed in a way different from the procedure employed by the workers during the thirties years: assuming now the electrostatic repulsion to be known, application of the theory leads to a quantitative evaluation of the attractive energy between colloidal particles from stability data. A number of methods to execute this evaluation, together with results available in the literature will be reviewed and discussed below. In order to judge the significance and reliability of the obtained information on van der Waals forces a brief critical discussion of the fundamental principles and basic assumptions of the DLVO-theory must be given first. This is done in Sec. 3. The discussion will be focussed to hydrophobic sols, i.e. sols consisting of particles that are not naturally soluble in water (such sols are called lyophobic if the solvent is any liquid); in hydrophilic (lyophilic) sols the stability is not or not only due to electrostatic repulsion between the particles which makes the DLVO-theory insufficient for these systems. By « stability » is meant stability against aggregation, hence changes

in the properties of the sol that are not due to particle interaction (like e.g. chemical reactions with the solvent or photo-decomposition) are tacitly assumed to be absent.

3) THE DLVO-THEORY

Generally speaking the interaction between colloidal or suspended particles is a very complex phenomenon, which is ultimately reflected in the experimental observable « stability ». Some of the factors that may influence the stability are collected in Table I which also shows the position of the DLVO-theory.

Molecular Forces in Colloidal Stability

<u>Some factors improving stability</u>	<u>Some factors diminishing stability</u>
Double layer repulsion	van der Waals attraction
(a) Steric hindrance	(c) Polyelectrolyte adsorption
(b) Highly viscous adsorbed layers	

Quantitative theory Deryagin - Landau; Verwey-Overbeek (DLVO)
Double layer repulsion and van der Waals attraction only

TABLE I

This table includes three stability influencing factors besides the ones considered in the DLVO-theory but is not exhaustive. Steric Hindrance (*a*) can occur when the two approaching particles are both covered with partly adsorbed long molecules. The loss in configurational entropy due to the steric

hindrance of the free parts of the molecules leads to repulsion as soon as the particles come close. A quantitative estimate of this effect has been given by MACKOR and VAN DER WAALS [12]. Highly viscous adsorbed solvent layers (*b*) could postpone aggregation of the particles simply because the rate of drainage of the solvent from the gap between the particles proceeds very slowly. Polyelectrolytes (*c*) can either promote or diminish the stability, depending on their concentration. At very low concentrations polyelectrolytes can be very effective flocculants, they are used for this reason in waste water purification. At high concentrations they can coat the colloidal particle to give it a hydrophilic protecting jacket. As the precise mechanism of polymer and polyelectrolyte adsorption on solid surfaces is still largely unknown, little quantitative information is available. Summarizing: before the DLVO-theory may be applied it must be verified that no concomitant stability influencing factors are operative besides electrostatic repulsion and van der Waals attraction. If this is not properly done application of the DLVO-theory can lead to erratic conclusions. For example JOHNSON, GOLDFARB and PETHICA [13] recently showed that the interaction between octadecanol or arachidic acid particles certainly contains other factors besides electrostatic repulsion and van der Waals attraction. Another example is found in the work of OTTEWILL *c.s.* The Hamaker constant (measure for van der Waals attraction, see below) between AgI- particles in water as found in 1960 [14] was a factor 2-4 higher than more recent results [15]. According to OTTEWILL [16] the difference is perhaps due to an additional attractive term because of dewetting of the interface between the particles in the older results.

The usual assumptions of the DLVO-theory are summarized in Table 2. The double layer around the colloidal particle is thought to consist of a surface charge (due to adsorbed potential determining ions or dissociation of surface groups) and an equal but opposite countercharge in the solution, consisting of free

Usual assumptions in DLVO-theoryElectrical Double Layer

- (a) POISSON - BOLTZMANN distribution
 - (ions are point charges of negligible dimensions.
 - no specific adsorption
 - invariant dielectric constant etc.)
- (b) Constant surface potential

Von der Waals attraction

- (c) According to HAMAKER and DE BOER
 - (microscopic, non-retarded)

TABLE 2

ions. Because of the thermal motion the countercharge has a more or less diffuse character. The degree to which the diffuse double layer around the particles extends into the solution is of paramount importance for stability questions. The thicker the ionic atmosphere, the larger the distance between the particles at which repulsion is felt, hence the more stable the sol.

The distribution of ions in the diffuse double layer is usually described after GOUY [17] and CHAPMAN [18], that is according to a Poisson-Boltzmann (PB) distribution. Incidentally it can be remarked that the same distribution equation has been used by DEBYE and HÜCKEL in their theory of strong electrolytes [19]. The main assumptions of this picture are mentioned under (a) in Table 2.

The assumed invariance of the dielectric constant is not a serious imperfection. Although the field strengths in the interior part of the double layer (close to the particle) are so high that some saturation must be expected [20] the outer part of the double layer, which is important for double layer overlap and electrostatic repulsion, is certainly saturation free.

More attention requires the neglects of the finite ion size and of specific adsorption. (By specific adsorption is meant

adsorption by other than Coulombic forces). Especially in the inner region of the double layer where the influence of the near-by particle surface is great and where the counterions accumulate strongly the PB distribution breaks down. Some attempts have been published to correct the PB equation for these effects [21, 25]. These theories are attractive because of a certain degree of rigidity. However their application to practical systems is hardly feasible due to the numerous parameters and complicated mathematics. The most practical approach is still the short-cut proposed by STERN as long ago as 1924 [26], STERN proposed to split up the double layer into two regions:

a) an inner part, a few molecular layers thick, adjacent to the particle surface (now known as the Stern layer);

b) an outer part, following exactly the PB distribution (the Gouy layer).

The attractiveness of STERN's picture is that by concentrating all specific effects (notably ion size and specific adsorption) in the non-diffuse Stern layer, the potentials in the remaining part of the double layer drop automatically to values low enough to warrant the applicability of the PB equation. Speaking in terms of electrostatic interaction this means that the DLVO-theory can be applied to the outer part of the double layer. The potential that is determinative for the interaction is not the surface potential (ψ_0) but the potential of the diffuse part of the double layer (ψ_δ).

Three ways can be indicated to estimate ψ_δ :

a) Assuming $\psi_\delta = \zeta$, the electrokinetic potential that under given conditions can be derived from electrokinetic experiments [27]. This is a frequently used procedure. Its results agree at least semi-quantitatively with other evidence, but as the knowledge of shear and slip in the double layer is still very

rudimentary the absolute reliability of this assumption is difficult to assess.

b) From the surface charge (σ_0) if specific adsorption is absent. In that case $-\sigma_0 = \sigma_d$ (σ_d is the charge in the diffuse part of the double layer). Using the Gouy-theory ψ_s can be calculated from σ_d .

c) From σ_0 in the presence of specific adsorption provided the contribution of the specifically adsorbed counterions to the countercharge (σ_m) is known, using $-\sigma_0 = \sigma_d + \sigma_m$, followed by calculation of ψ_s from σ_d .

In connection with the above a few words should be said on the so called lyotropic sequence in the coagulation concentrations. Hydrophobic sols are very sensitive to salts. Addition of salt lowers the stability and leads ultimately to coagulation. The DLVO-theory explains this effect via a compression of the double layer upon salt addition. The concentration of salt required to produce rapid coagulation (C_c , in bmole/L) is called the coagulation concentration (or flocculation concentration). Not all salts are equally effective flocculants. There is in the first place a very strong influence of the valency of the counterion, the so-called SCHULZE-HARDY [28, 29] rule which is satisfactorily accounted for by the DLVO-theory. A secondary but nevertheless not negligible effect is the influence exerted by the nature of the counterion, at given valency. This is called the lyotropic sequence. Some examples are collected in [30]. Being nonspecific, the unmodified Gouy-theory is principally incapable to explain such effects. Hence the DLVO-theory with the unmodified PB-distribution may be applied only when specific effects are absent. If specific stability effects are found they must be accounted for, either by application of a corrected PB-equation or along the lines of Stern's picture.

The greater part of the DLVO-theory has been elaborated

for the case that the double layer potential is independent of the distance between the particle surfaces ((b) in Table 2). In this case the surface charge σ_0 diminishes at the approach of the particles. The other case (σ_0 constant, potential variable) is only incidentally studied. In practical cases a repartition of ions between the Stern- and Gouy layer upon double layer interaction must also be envisaged. The case of constant potential will apply when charge and potential are due to adsorption of potential determining ions, because the potential is now fixed by the chemical potential of the potential determining ion in the solution. If the establishment of thermodynamic equilibrium has a considerable activation energy a certain degree of disequilibrium during rapid particle encounters can occur, which might affect the constancy of the potential. The case of constant charge will apply e.g. when σ_0 is determined by the dissociation of ionogenic surface groups or by isomorphic substitution like in clay particles.

Finally the van der Waals attraction between sol particles is in the DLVO-theory calculated according to HAMAKER and DE BOER [2, 3]. A discussion of the merits and demerits of this approach can be omitted at this point because we will try to work the other way round and find the attraction energy from experimental data (see sec. 6). The neglect of retardation is usually justified because of the rather short distance of interaction. If in incidental cases interaction at larger distances occurs (like « flocculation in the secondary minimum ») retardation corrections could be inevitable [31]. DERYAGIN ⁽¹⁾ and SMILGA [32] showed recently that if the van der Waals forces would be retarded the coagulation concentration becomes less sensitive to the valency of the counterion.

The basic equations for the potential energy of interaction between semi-infinite flat plates and between spheres according

⁽¹⁾ DERYAGIN [32] and DERJAGUIN [6, 10] are the English resp. French transcription of the Russian ДЕРЯГИН.

to the DLVO-theory are collected in Table 3. The symbols as far as not explained before or in the figure are:

V_R = repulsive energy (in erg/cm² for two flat plates, in erg for two spheres)

V_A = attractive energy (same units)

n = number of salt molecules per cm³

kT = thermal energy

$\kappa = \frac{1}{\epsilon kT} \sqrt{4\pi e^2 \sum_i n_i z_i^2}$ = (Debye length)⁻¹

e = elementary charge (4.80×10^{-10} ESU)

n_i = number of ions i per cm³

z_i = valency, sign included

ϵ = dielectric constant

$ze\phi_\delta$ = potential energy of ion with valency z in a place of potential ϕ_δ .

Basic Equations Interaction Potential Energy
(DLVO)

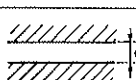
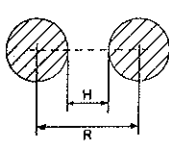
	Repulsion	Attraction
 (semi-infinite) Flat plates d	$V_R = \frac{64nkT}{\kappa} \gamma^2 e^{-\kappa d}$	$V_A = -\frac{A}{12\pi d^2}$
 Spheres. radius a H R	$V_R = \frac{64nkTa}{\kappa^2} \gamma^2 e^{-\kappa H}$ $\gamma = \frac{\exp\left(\frac{ze\phi_\delta}{2kT}\right) - 1}{\exp\left(\frac{ze\phi_\delta}{2kT}\right) + 1}$	$V_A = -\frac{A}{6} \left[\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right]$ short distance: $V_A = -\frac{A}{12} \cdot \frac{a}{H}$ $A = \text{HAMAKER-V.D. WAALS constant}$ $= A_{11} + A_{22} - 2A_{12}$ $A_{11} = \pi^2 q_1^2 \beta_1$

TABLE 3

Our discussion will be focussed on the constant A , which is determinative for the attraction. It is usually called the *Hamaker constant*. Its value can be calculated either via the macroscopy Lifshitz theory [33, 34] or via the microscopic method of Hamaker and de Boer [2, 3]. The first procedure is often unworkable, simply for lack of sufficient optical data. If the summation procedure is applied, additivity must be pre-supposed. In that case the Hamaker constant between two bodies of material 1 in vacuum reads

$$(1) \quad A_{11} = \pi^2 q_1^2 \beta_{11}$$

where q_1 is the number of atoms per unit volume and β the constant in the London equation for attraction between two atoms 1:

$$(2) \quad V_{11} = -\frac{\beta_{11}}{r^6}$$

r is the distance between the two atoms.

The Hamaker constant A between two particles 1 embedded in a medium 2 is related to A_{11} , A_{22} and A_{12} via

$$(3) \quad A = A_{11} + A_{22} - 2A_{12}$$

$$(4) \quad \sim \left(\sqrt{A_{11}} - \sqrt{A_{22}} \right)^2 =$$

$$(5) \quad = \pi^2 (q_1^2 \beta_{11} + q_2^2 \beta_{22} - 2q_1 q_2 \sqrt{\beta_{11} \beta_{22}})$$

The diffuse double layer potential ϕ_δ enters the repulsion energy via the factor γ^2 . For very high potentials $\gamma \rightarrow 1$ and V_R becomes independent of ϕ_δ . The physical reason behind this

fact is that, once ψ_δ is high, any further increase in ψ_δ takes place mainly in the inner part of the double layer, whereas the outer part is dominant for interaction. However in actual sols ψ_δ is usually relatively low, under flocculation conditions often < 50 mV. As at $25^\circ \frac{e\psi_\delta}{kT} \sim 1$ for $\psi_\delta = 25$ mV the exponentials in the expression for γ are then so low that they may be expanded. Retaining only the first two terms:

$$\text{For low } \psi_\delta \quad \gamma = \frac{\frac{ze\psi_\delta}{2kT}}{2 + \frac{ze\psi_\delta}{2kT}}$$

(6)

$$\text{For very low } \psi_\delta \quad \gamma = \frac{ze\psi_\delta}{4kT}$$

Hence V_R becomes proportional to ψ_δ^2 . Thus it is clear that a proper control of this quantity is indispensable. In several of the examples of Sec. 6 the quality of the estimated value for A depends mainly on the degree of precision with which ψ_δ is known.

4) APPLICATION OF THE DLVO-THEORY

Three procedures to elaborate the DLVO-theory with the purpose to find A from stability data are currently in use. They are collected schematically in Table 4.

Ad 1) The determination of A from C_c is easy. One measurement of C_c and one giving ψ_δ suffice (for calculation of γ from ψ_δ see preceding section). A drawback is that there is

Methods to find A from colloid interaction1) From flocculation concentration

$$C_c = f(\epsilon, T) \frac{\gamma^4}{A^2 Z^6} \text{ mMole/L} \quad \text{for water, } 25^\circ : f(\epsilon, T) = 8 \times 10^{-22}$$

2) From rate of flocculation

$$\text{Stability factor } W = 2 \int_2^\infty \exp\left(\frac{V_{tot}}{kT}\right) \frac{ds}{s^2}$$

$$W \text{ and } \frac{d \log W}{d \log C_s} \rightarrow A \text{ and } \gamma$$

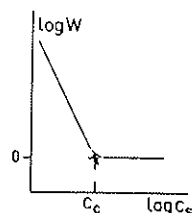
3) From reepitisation

TABLE 4

some ambiguity concerning « the » absolute value of C_c , a problem that will not be discussed here in detail. Suffice it to say that, depending on the stability criterion being applied a variance of at least 50% in C_c can be observed, leading to an inaccuracy of more than 20% in A. In order to check the absence of systematic errors it is advisable to use the pertinent equation at different ϕ_s and for various salts.

Ad 2) This method has been developed by REERINK and OVERBEEK [35]. The underlying thought is, that the rate of coagulation (a measurable quantity, at least in principle) can be correlated to the salt concentration, C_s . The stability factor (or stability ratio) W, plays a central role. W is defined as the rate of rapid coagulation (no potential energy barrier between the particles) over the rate of slow coagulation (positive barrier $V_{tot} = V_A + V_R$). When $\log W$ is plotted against $\log C_s$ a graph should result consisting of two essentially linear

branches. The intersection point may be identified with $C_s = C_c$ because any increase in C_s above this point does not lead to further increase in rate of coagulation. From the two parameters W and $\frac{d \log W}{d \log C_s}$ values for A and γ (i.e. ψ_s) can be derived.

So it is not necessary to know ψ_s in this method. This procedure is perhaps more sophisticated than the former one, but has also its drawbacks. One of them is that W must be determined optically which means that some assumptions must be made with respect to the consumptive and conservative absorption of light by the particles and by aggregates of particles. The theory is apparently not yet perfect because the thus obtained values for A often depend systematically on other variables (e.g. on the particle radius in the experiments of REERINK and OVERBEEK).

Ad 3) Repeptisation is the redispersion of coagulated particles, due to a change in the conditions, usually a lowering of the electrolyte concentration. The rate of repeptisation is a measurable quantity. Theoretically it is correlated to the height of the energy barrier which in the coagulated state prevents the particles from redispersion. This energy barrier is in turn directly related to V_R and V_A , which ultimately enables A to be calculated. As in the coagulated state the particles are very close to each other the specific influence of the nature of the surface is strongly felt. WATILLON and GÉRARD [36] e.g., studying the repeptisation of silica sols found the obtained value of A highly sensitive to the assumed thickness of an adsorbed hydration layer.

Let us finally discuss the range of distances over which A is found by application of any of the methods discussed above. For regular coagulation the critical distances are of the order of several tens of Å that is well within the range of non-retarded forces. These distances lie between the distances covered by adhesion (very short to zero), thin films (100 - 1000 Å) and direct measurement (> 1000 Å), see the contribu-

tions to this congress by BOWDEN, LYKLEMA (II) and VAN SILFHOUT and OVERBEEK respectively. A drawback of the methods based on stability is that it is very difficult to find the attraction as a function of distance, so a straightforward check that the force is indeed non-retarded is almost impossible. In a few experiments where interaction at larger distances occurred retardation corrections were necessary [31].

5) DIGRESSION INTO INTERFACIAL CHEMISTRY

Recently FOWKES [37] has developed a procedure to derive non-retarded Hamaker constants from interfacial tension data. Although the method is only semi-empirical and does not belong to the field of colloidal stability some results of this method will also be included in Sec. 6 for sake of comparison.

FOWKES' starting point is the empirical equation

$$(7) \quad \gamma_{12} = \gamma_1 + \gamma_2 - 2 \sqrt{\gamma_1^d \gamma_2^d}$$

where γ_{12} is the interfacial tension between liquids 1 and 2, γ_1 and γ_2 are the surface tensions of liquids 1 and 2 respectively and γ_1^d and γ_2^d are the dispersion contributions to γ_1 and γ_2 respectively.

The physical picture on which eq (7) is based is as follows: The surface tension γ_1 is a quantity reflecting the intermolecular forces in liquid 1. Part of γ_1 is due to dispersion forces, part to dipole/dipole forces (e.g. in water), part to metallic bond forces (e.g. in mercury) etc. FOWKES assumes that these contributions are additive. When the liquids 1 and 2 meet to form an interface the interfacial tension of this new interface γ_{12} will be equal to the sum of the original surface tensions

$(\gamma_1 + \gamma_2)$ minus a certain reduction term due to the London interaction between the molecules in the surface layer of 1 and the bulk molecules in 2 and vice versa. For this reduction term Fowkes chooses twice the arithmetic mean $2 (\gamma_1^d \gamma_2^d)^{1/2}$. The factor 2 stems from the fact that the reduction term applies both to the molecules in the surface layer of 1 and the molecules in the surface layer of 2. The arithmetic mean is chosen in connection with the success of Hildebrand's solution parameter for solutions of non-electrolytes, as discussed in [38].

Using the fact that for apolar non-metallic liquids like hydrocarbons $\gamma_2 = \gamma_2^d$, it is possible to find γ_1^d . Combination of values for γ^d thus found enables the calculation of new γ_{12} - values, which generally agree quite well with experiment. On the other hand γ_1^d can be calculated from a summation of all dispersion interactions between surface molecular and bulk molecules. According to DE BOER [2]

$$(8) \quad \gamma_1^d = \frac{\pi q_1^2 \beta_{11}}{6 r_{11}^2}$$

where β_{11} is defined through the London equation [2] and r_{11} is the intermolecular distance between molecules 1 in liquid 1. Combination of (8) and (1) gives

$$(9) \quad A_{11} = 6\pi r_{11}^2 \gamma_1^d$$

By the same token A_{22} is found and finally A is calculated from (4).

It is interesting to note that the calculation of A from stability and the calculation from interfacial tension data have one fundamental in common, viz. the summed up dispersion interaction between a large number of molecules. However, the experimental facts that are used to calculate A are totally different.

6) RESULTS AND DISCUSSION

Below some selected results for Hamaker constants A in aqueous solution are given and discussed. For sake of surveyability the material is collected in tables.

Few materials have been studied so extensively that Hamaker constants from various sources are reported in literature. One of the relatively best studied substances is perhaps AgI for which some results are collected in Table 5.

HAMAKER - VAN DER WAALS constant for AgI
in aqueous solution

Authors	Method	A (erg)
REERINK and OVER-BEEK (1954)	Rate of flocculation	4.14×10^{-13} (a)
MATHAI and OTTEWILL (1966)	Ibid, in presence of adsorbed surfactants	$3 - 4 \times 10^{-13}$ (b)
LYKLEMA (1966)	Flocculation above 65°C	$3 - 4 \times 10^{-13}$ (c)
	calculation	$25 - 3 \times 10^{-13}$ (d)

TABLE 5

Ad a) See ref. [35]. The authors studied also the influence of the particle radius (a) on the rate of coagulation and found that $\frac{d \log W}{d \log C_s}$ depended much less on a than theoretically predicted. Consequently there was a systematic variation of A with a . The possibility of such an effect in one of the other

values for A mentioned in Table 5 can not be excluded. The value $4 \pm 4 \times 10^{-13}$ is the average out of 9 values for 5 sols and 3 different counter ions (K^+ , Ba^{++} , La^{+++}).

Ad b) MATHAI and OTTEWILL [15] measured the rate of flocculation in the presence of adsorbed non-ionic surfactants. A was found to depend systematically on the adsorbed amount of surfactant. The authors interpreted this observation via the theory of VOLD [39]. The quoted Hamaker constant applies for $C_{\text{surfactant}} \rightarrow 0$. (In earlier results of OTTEWILL and co-workers [14] higher Hamaker-constants were found see Sec. 3).

Ad c) LYKLEMA [40] found that at elevated temperatures ($\geq 65^\circ\text{C}$) both the differential double layer capacitance and the flocculation concentration become non-specific. Apparently the double layer is purely diffuse at these temperatures. Hence the DLVO-theory may be applied and A is found from C_c (Table 4). Values for A calculated at 65°C and 85°C differ by 25%. It is not yet sure whether this difference is systematic.

Ad d) The calculation was based upon the SLATER-KIRKWOOD equation [41] for β :

$$(10) \quad \beta = \frac{3eh}{8\pi} \sqrt{\frac{N\alpha^3}{m}} = 11,25 \times 10^{-24} N^{\frac{1}{2}} \alpha^{\frac{3}{2}}$$

where N is the number of electrons in the outermost shell of the atoms and α is the polarizability. AgI was considered as consisting of Ag^+ and I^- -ions (i and j). The polarizabilities of these ions are $1,85 \times 10^{-24}$ and $6,28 \times 10^{-24} \text{ cm}^3$ respectively [42]. The following values were found:

$$\beta_i = 1,20 \times 10^{-58} \quad \beta_j = 5,02 \times 10^{-58} \quad \text{and}$$

$$\beta_{ij} = \frac{\beta_i \beta_j}{\beta_i + \beta_j} = 0,97 \times 10^{-58} \text{ erg. cm}^6$$

The Hamaker constant A_{11} for AgI in vacuum can then be calculated from

$$(11) \quad A_{11} = \pi^2 (q_i^2 \beta_i + q_j^2 \beta_j + 2 q_i q_j \beta_{ij})$$

were q_i and q_j are now the numbers of Ag^+ and I^- ions per cm^3 AgI respectively. We found $A_{11} = 1,58 \times 10^{-12}$ erg. The Hamaker constant A for two AgI-particles in water (that is the experimental one) can be calculated from eq (4) as soon as $A_{22} = A_{\text{water}}$ is known. The value calculated according to the method of SLATER and KIRKWOOD [41] as given by OVERBEEK [43] is $A_{22} = 0,6 \times 10^{-12}$ erg. Recently KRUPP [44] calculated the dispersion interaction between two condensed aqueous phases according to the Lifshitz-theory [33], using the spectral data for water vapour. From his work $A_{22} = 0,54 \times 10^{-12}$ erg can be derived. Hence, the microscopic and the macroscopic theory, when applied to water seem to agree within 10%. Finally the tabulated constant for AgI in water is obtained.

From Table 5 we conclude that the various experimental results agree within a factor of 2. The agreement with the theoretical estimate is also good. However, it must be born in mind that the experimental values are still not yet free from systematic errors, whereas the theoretical computation contains some serious approximations, so that future refinements remain desirable.

The results for polystyrene in aqueous solution are much more conflicting than the results for AgI. In Table 6 Hamaker constants from three, entirely different sources are given.

Ad a) See Ref [31]. The calculation was again based upon eq (4). A_{11} was computed, assuming polystyrene to consist of benzene with density $1,05 \text{ gram cm}^{-3}$. The constant β_{11} of the London-equation (2) was taken from MOELWYN-HUGHES [45] as $5,14 \times 10^{-57} \text{ erg. cm}^6 \text{ mol}^{-1}$. This value cor-

HAMAKER - VAN DER WAALS constant for
polystyrene in aqueous solution

Authors	Method	A (erg)
SCHENKEL and KITCHENER (1960)	Calculation	5×10^{13} (a)
FOWKES (1964)	Semi-empiric. from interfacial tension data	5×10^{14} (b)
WATILLON (1966)	Rate of coagulation $\pm \delta = 5$	$0.6 - 1.5 \times 10^{15}$ (c)

TABLE 6

responds well with the value 5.23×10^{-57} erg. cm⁶ mol⁻¹ given by HIRSCHFELDER, CURTISS and BIRD [46]. For A_{11} 3.17×10^{-12} erg is found, which is probably more accurate than DE BOER's value 1.32×10^{-12} erg [2]. For water $A_{22} = 0.77 \times 10^{-12}$ erg was derived, again using the electronic data listed by MOELWYN-HUGHES. This value is somewhat higher than the ones mentioned above in the calculation for AgI. SCHENKEL and KITCHENER finally apply a correction for the reduction of the London-force because of its transmission through a medium of dielectric constant not unity. The reduction factor was estimated as 1.80. If this factor is not applied (like in the computation for AgI) a Hamaker constant of 9×10^{-13} would be obtained.

Ad b) See Sec 5 and Ref. [37].

Ad c) Ref [47].

From Table 6 we conclude that there are definite discrepancies between the experimental results and between experi-

ment and calculation. The computed Hamaker-constant is higher than the experimental ones.

Some results for metals in aqueous solution are collected in Table 7.

HAMAKER - VAN DER WAALS constants
(metals in aqueous solutions)

Material	Authors	Method	A (erg)
Au	TUORILA (1926, 28), reinterp. REERINK-OVERBEEK (1954)	Rate of coagulation	6×10^{-13} (a)
	WESTGREN (1918)-RO (1954)	Ibid	0.8×10^{-13} (a)
	DERYAGIN C.S. (1963)	Direct measurement of force barrier	1.4×10^{-11} (b)
Pt	Ibid.	Ibid	3.3×10^{-12} (b)
Ag	FOWKES (1964)	Semi-empiric, from inter- facial tension data	2.5×10^{-13} (c)
Hg	Ibid.	Ibid	1.3×10^{-12} (c)
Cu	KRUPP (1966)	Calculated LIFSHITS theory + spectral data	$1-2 \times 10^{-12}$ (d)

TABLE 7

Ad a) Hamaker constants were obtained by REERINK and OVERBEEK [35] after reinterpretation of older data on the rate of coagulation by TUORILA [48] and WESTGREN [49].

Ad b) DERYAGIN and collaborators developed a method to measure directly the height of the force barrier opposing contact of two crossed polarized metal wires [50]. As the electrostatic contribution to the force barrier can be calculated with the DLVO-theory the dispersion term can be derived. Two of the thus obtained Hamaker constants are reproduced in Table 7.

DERYAGIN's value for gold is considerably higher than the results of REERINK and OVERBEEK. It is a pity that in all

experiments of these types the distance is a non-controlled variable. This prevents a more penetrating analysis of the obtained results. In connection with Deryagin's experiments one remarkable finding deserves attention. At very high electrolyte concentration where the electrostatic repulsion should be fully suppressed nevertheless a finite repulsion was observed, suggesting that there exists an unknown repulsive force at very high C_s . The authors surmise that adsorbed hydration sheaths are responsible for the repulsion because in carbon tetra chloride no repulsion barrier was observed. However the effect of adsorbed hydration layers on stability, if any, is still very problematic. Anyhow with AgI, where there is some definite evidence for the existence of a structurized water layer around the particles [40] no stability could be detected at very high salt concentration [51].

Ad c) See Sec 5 and Ref. [37].

Ad d) See Ref. [44].

As the results for metals are still scanty it is almost impossible to arrive at this moment at a general conclusion. Further experiments are highly desirable.

Finally in Table 8 some Hamaker constants for non-metals in aqueous solutions are collected.

Ad a) Older data on the rate of coagulation by VAN ARKEL and KRUYT [52] reinterpreted by REERINK and OVERBEEK [35].

Ad b) Ref. [47].

Ad c) Ref. [47]. Calculated from spectroscopic data.

Note that the experimental results for Se agree very well, the calculated value is somewhat higher.

Ad d) See Ref. [36]. The calculated Hamaker constant is very sensitive to the thickness d assumed for the hydration shell around the SiO_2 particles. The quoted value was obtained

HAMAKER - VAN DER WAALS constants
(non-metals in aqueous solution)

Material	Authors	Method	A (erg)
Se	VAN ARKEL-KRUYT(1920,21) reinterpr. REERINK-OVER- BEEK (1954)	Rate of coagulation	2.1×10^{-13} (a)
	WATILLON	Ibid. $\psi_8=5$	2×10^{-13} (b)
	Ibid.	calc.	6×10^{-13} (c)
SiO ₂	WATILLON-GERARD(1964)	Repeptisation	3×10^{-14} (d)
	Ibid.	calc.	$3-9 \times 10^{-14}$ (e)
	FOWKES (1964)	Semi-empirical, from interfacial tension data	6×10^{-13} (f)
Paraffin (wax)	Ibid.	Ibid.	2×10^{-15} (f)
	SRIVASTAVA-HAYDON(1964)	Rate of coagulation ($\psi_8=5$)	1.6×10^{-13} (g)
Arachidic Acid	Ibid.	calc.	2.5×10^{-13} (g)
	OTTEWILL-WILKINS.(1962)	Coagulation concentra- tion	3×10^{-15} (h)
		Rate of coagulation	9×10^{-15} (h)
		calc.	$0.8-3.7 \times 10^{-14}$ (h)

TABLE 8

for $d=1 \text{ \AA}$ because for $d=1 \text{ \AA}$ the Hamaker constants calculated from repeptisation and coagulation agree best.

Ad e) The computed values cover the range obtained by application of any of the following three equations:

i) The London equation (2) with

$$(12) \quad \beta = \frac{3}{4} \alpha^2 h \nu_0$$

where ν_0 is the chief dispersion frequency;

ii) the Slater-Kirkwood equation [10] and

iii) the Neugebauer equation [53]

$$(13) \quad \beta = -2 mc^2 \alpha \chi = -1,62 \times 10^{-6} \alpha \chi$$

in which χ is the diamagnetic susceptibility of the atom under consideration. In this sequence for the Hamaker constant $2,8 \times 10^{-14}$, $6,7 \times 10^{-14}$ and $9,4 \times 10^{-14}$ erg is found respectively. The trend to increase in this direction was already mentioned by VERWEY and OVERBEEK [11, pag. 99]. Again we conclude that the calculated Hamaker constant tends to be slightly larger than the experimental one.

Ad f) See Sec. 5 and Ref. [37]. Note that Fowkes' value for SiO_2 is higher than the one derived from stability whereas for paraffin wax it is lower.

Ad g) Ref. [54]. In this work the coagulation process was studied by counting the particles. The « experimental » Hamaker constant is the one that after insertion in the equation for the attraction energy gives the best fit between the experimental and theoretically predicted rate of aggregation. As flocculation in the secondary minimum took place the formula for the attraction energy (Table 3) had to be corrected for retardation. The « theoretical » Hamaker constant was again calculated using the Slater-Kirkwood [41] expression as modified by MOELWYN-HUGHES [45]. Following FITZER [55] the London-constant β for molecules was obtained from

$$(14) \quad \beta = \frac{3}{4} N^{1/2} h \nu_0 \alpha^2$$

where the symbols have the same meaning as in eq. (10) and (12). As the relevant data for paraffin wax are not available three different approaches have been used. In these it has been assumed that paraffin wax is effectively composed of methane, ethane or methylene groups at the same density as that of the wax ($0,865 \text{ gr cm}^{-3}$) yielding $\beta = 2,53 \times 10^{-58}$, $10,81 \times 10^{-58}$ and $2,123 \times 10^{-58} \text{ erg cm}^6$ respectively. Following BJERRUM [56] for water $\beta = 9,58 \times 10^{-59} \text{ erg cm}^6$ was chosen, which is lower than the Slater-Kirkwood value [31]. Finally, using again (1) and (4) and applying SCHENKEL and KITCHENER's correction for transmission through dielectric medium [31] the following values for A are found: $1,89 \times 10^{-13}$, $3,11 \times 10^{-13}$ and $2,55 \times 10^{-13} \text{ erg}$; the mean of these values is reproduced in Table 8. If Slater-Kirkwood's value for A_w would have been used in stead of BJERRUM's Hamaker constants about twice as high would be obtained. In that case A_{calc} would be higher than A_{exp} , a feature signalized before.

Ad h) See Ref [57]. Arachidic acid = $C_{19}H_{39}COOH$. The rate of coagulation was studied by particle counting. The first mentioned Hamaker constant was obtained from $\log W \rightarrow \log C_s$ plots for $\log W \rightarrow 0$, i.e. virtually from the coagulation-value. The second one was derived from the relation between $\log W$ and ζ , i.e. virtually from the rate of coagulation. This value depends systematically on the valency of the counterion. In the calculation $\beta = 1,49 \times 10^{-56} \text{ erg cm}^6$ was used, based upon a polarizability $\alpha = 3,31 \times 10^{-23} \text{ cm}^3 \text{ mol}^{-1}$ (MOELWYN-HUGHES [45]) and using $v_0 = 2,73 \times 10^{-15} \text{ sec}^{-1}$. For $A_{22} = A_w$ both $0,6 \times 10^{-12} \text{ erg}$ [41] and $0,77 \times 10^{-12} \text{ erg}$ [31] were used. No « screening » correction was applied. If it would be applied along the lines of SCHENKEL and KITCHENER [31] the calculated Hamaker constant would be a factor 1,80 lower. We note that also for arachidic acid the calculated Hamaker constant is larger than the experimental values.

7) CONCLUSION

1) It is possible to obtain information on van der Waals attraction from the interaction between colloidal particles provided all other stability influencing factors are well controlled. The central quantity is the Hamaker-van der Waals constant, A .

2) Few systems have been studied so extensively that three or more A -values obtained from different sources are available in literature. When they *are* reported (like for AgI and Se) they usually agree well.

3) In some cases where a more penetrating study of A was undertaken systematic trends in the obtained values were observed which perhaps means that the interaction is more complicated than considered in the usual approximations of the DLVO-theory.

4) In several cases the calculated A tends to be somewhat higher than the experimental one, although the order of magnitude usually agrees.

5) Noteworthy is DERYAGIN c.s.' finding that at very high salt concentrations, well above the flocculation concentration again repulsion occurs, at least in aqueous solutions.

6) The distances at which the interaction can be studied are usually below 100 Å, i.e. in the non-retarded region. This region lies between the region covered by adhesion and the region covered by thin films.

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DISCUSSION

Chairman: H.B. CASIMIR

OVERBEEK

I would first like to compliment Dr. LYKLEMA on his lecture and on experiments that he has shown; I think it was a particularly good idea to start some of the stability experiments at high temperature and try to get rid of the specificity; although the specificity is of course interesting, it will be easier for us to try to understand what happens when the systems are not specific. Then, I would like to put two questions to Dr. LYKLEMA. The first is: when SCHENKEL and KITCHENER did the work on polystyrene, didn't they also have stability experiments, so that there is not only a calculated value of the van der Waals constant, but also an experimental one? The second question is: at first sight it is rather strange that the van der Waals constant of paraffin wax in water is so much higher than that of arachidic acid in water which is also a largely hydrocarbon substance. Could that be explained by the fact that the carboxyl group in arachidic acid tends to remain hydrated, so that the arachidic acid is more « water-like » and the mixed van der Waals constant between water and arachidic acid is low for that reason?

LYKLEMA

SCHENKEL and KITCHENER first calculated a Hamaker constant and then verified that their experiments could be interpreted on basis of this value. There is no direct evaluation of a Hamaker constant from stability experiments and repulsion theory.

SCHENKEL and KITCHENER constructed potential energy-distance curves for the interaction between their sulphonated polystyrene particles. For the calculation the quoted Hamaker constant was used and retardation was taken into account. From the shape of the thus found curves the authors conclude that flocculation can occur only in the secondary minimum. For KNO_3 the experimentally observed influence of the salt concentration on the rate of aggregation agrees well with this picture (di- and trivalent counterions however show specific effects). Hence it may be concluded that the calculated Hamaker constant agrees with the experimental facts (in KNO_3 solution). The reverse procedure, viz. the calculation of an « experimental » Hamaker constant from stability data was not followed by SCHENKEL and KITCHENER.

The difference in Hamaker constant between paraffine wax and arachidic acid is striking indeed. Hydration might be partly responsible for this fact but a systematic influence of imperfections in the stability theory should not a priori be ruled out. OTTEWILL and WILKINS' results obtained via the « rate of coagulation » method e.g. depend systematically on the valence of the counterion.

VERWEY

I was impressed by Prof. LYKLEMA's talk, especially by the fact that such valuable information can be obtained from relatively simple experiments. I have only a few remarks or questions of minor importance. First of all I prefer to consider AgI as a sub-

stance which is still predominantly polar. If one calculates the lattice energy, including the rather important VAN DER WAALS - LONDON contribution, on the basis of the ionic picture one finds still a reasonable agreement with the experimental value (DE BOER and VERWEY, « Rec. Trav. Chim. », 55, 443 [1936]). Moreover it is known that AgI (especially the high temperature modification) shows an appreciable electrical conductivity and this conductivity is completely ionic.

Secondly I should like to ask whether in the interesting phenomena observed in the presence of butanol a possible shift of the zero point of charge was taken into account.

A third question is: would it not be worth-while to study these phenomena for a completely different class of materials, for instance artificial resins with dissociating groups?

LYKLEMA

Of course, the zero point of charge shifts very much in the presence of butylalcohol but we controlled it. We know the zero point of charge (and hence the surface charge with respect to this shifted zero point of charge). From this new surface charge we derived ϕ_s . We agree with you that it would be very useful to try to do similar experiments with some different materials. In fact nowadays we have some experiments running, with sulphonated polystyrene (like SCHENKEL and KITCHENER) with glass, and with ferric oxide, (hematite and goethite). We have not yet results of any of them but we hope that we can learn something about them in the future.

BOWDEN

Could I ask one question about the structure of the electrical double layer near the surface of a colloidal particle or near an electrode surface. It is customary to make this clear distinction

between the fixed layer and the diffuse layer. It is usually assumed that the fixed layer is of atomic dimensions and the diffuse layer is very much larger; perhaps 10^{-4} cm thick or more. Are we really justified in assuming that there is this clear-cut boundary between the fixed potential and the diffuse potential? Is it not more likely that they shade gradually into one another? Is it realistic to make such precise calculations of the diffuse potential from electrokinetic observations of the movement of the colloidal particles?

Has anyone attempted to examine by direct experiment the distribution of potential throughout the diffuse layer? Since the distance is relatively large (10^{-4} — 10^{-3} cm) and since we can make electrode surfaces which are molecularly flat and probes which are very small (e.g. tiny whiskers) could this perhaps be studied?

LYKLEMA

Yes, with respect to your first question, there is no doubt that you are right. In principle, in the usual picture, the double layer is more or less artificially split up into a diffuse and a nondiffuse part (STERN) but, this is only an approximation. The best thing we can say about it, is that the collected evidence shows that this approximation works very well, and that we run in great mathematical and physical difficulties if we want to improve upon it because it is quite difficult to make a clever guess of what happens close to a surface electrostatically, taking into account polarization, induced moments, the variation of the effective dielectric constant on a molecular scale and so on, and then try to set up a good statistical picture that gives us the potential distribution. Perhaps we can say that if we use STERN's methods to learn something about the specific adsorption potential the method works not so very good.

To your second question I will revert this afternoon. The interaction distance in colloidal stability cannot be controlled. It is

controlled by the repulsive and attractive energy, and therefore we can only assess it using the stability theory. We can say, perhaps, that the distances for bi-valent and mono-valent ions are different. This afternoon I hope to talk about thin films; there it is possible to control the distance but then the control of the potential is not very good.

BUCKINGHAM

I should like to ask if in any of the cases discussed this morning the fluctuation in the charge is a significant contributor to the interaction energy. We know that in the work of KIRKWOOD and SHUMAKER, the fluctuations in the charge can give rise to a potential energy proportional to R^{-2} , just as fluctuations in the dipole give rise to a dispersion energy proportional to R^{-6} . Is there any evidence for this long range force?

LYKLEMA

Do I understand well that you are referring to the work of LEVINE and collaborators who have made a quantitative estimation of the fluctuation potential? With respect to LEVINE's work, I can say that what he discussed is the so-called discreteness of charge effect. One of the results is that the potential ϕ_s as a function of the surface potential should not be a monotonously increasing function, but should pass through a maximum. So, when there is a kind of discreteness of charge effect, this should be found back in the value of ϕ_s and hence in the stability. We have pursued experiments along this line but could not yet find anything. So, if the effect exists on AgI, it is so small that it is not found in the experiments.

SCHWAB

In the region of very concentrated electrolyte solutions we are very far away from the validity of the Debye theory or from the Poisson-Boltzmann statistics. For instance, the activity coefficients in this region tend to become higher with rising concentration. Wouldn't this mean that also the electrostatic repulsion term is quite different from what one would expect from a simpler theory? And perhaps this is the reason for the deviation.

LYKLEMA

Yes, of course, at very high salt content the Poisson-Boltzmann statistics breaks down totally so it must be replaced by something else. I can perhaps add that we did some experiments to find out whether colloidal systems became again stable at very high salt concentrations. We could not find any stability.

OVERBEEK

Dr. BOWDEN has asked if it would be worth while to get the picture of double layer on a surer footing. There I would remind you of the very accurate experiments that have been made in determining the capacity of the electrical double layer at the mercury water interface by direct electrical measurements. Similar measurements have been made for other metals, where the surface area is a little in dispute, and recently also for silver iodide. One can determine this double layer capacity for a range of electrolyte contents and for a charge — or rather a potential on the surface that is rather well controlled. These experiments are quite nicely interpreted by assuming that the total double layer capacity is composed of the Gouy-capacity (the diffuse double layer capacity) in series with a molecular condenser (which may be not just one molecular layer

but a few molecular layers) which is only sensitive to the surface charge and the capacity of which can be determined for one electrolyte content and then used over the whole range. So, there is more information on the double layer and this picture — simple as it is — explains the experiments that we have now remarkably well.

The second remark I would like to make is that in flocculation experiments it would be very important to have systems where all the particles have exactly the same size. Now, it was difficult to prepare isodisperse suspensions of some concentration, until recently the people at Dow Chemical learned to make isodisperse lattices of varying particle diameter with the particle diameters constant within a few % in each sample. At the moment Dr. VANDERHOFF of Dow Chemical is working at my laboratory trying to determine stability with these systems.

The third point is by Dr. BUCKINGHAM about the influence of fluctuations. In most of these colloidal systems the total charge is fairly large, so the fluctuation is relatively not so very important. But on proteins for instance, the total charge can be small enough, so that the fluctuation ought to come in. I have no information on stability experiments, but I have some information on electric conductivity. It is found for instance that a protein (serum albumin) contributes to the electric conductivity in its isoelectric point; which means that some of the molecules have a positive charge and some others have a negative charge, and the charge fluctuation is between about +2 and -2 units (*). So, there are indications that charge fluctuation really exists. But it has not been worked out for the stability problem as far as I know.

CASIMIR

I think we can have two more remarks: Dr. HIRSCHFELDER first and then Dr. LÖWDIN.

(*) G.A.J. VAN OS and W.J.H.M. MÖLLER, « Proc. kon. Nederl. Akad. Wetenschap », B 61, 253 (1959).

W.J.H.M. MÖLLER, G.A.J. VAN OS, and J.Th.G. OVERBEEK, « Trans. Faraday Soc. », 57, 312 (1961).

HIRSCHFELDER

My question is whether it would be of interest to examine the packing of the water molecules and see where the packing of these water molecules in this double layer is different from that in the bulk of the liquid.

LYKLEMA

Thank you for your remark. We have now very convincing evidence that, due to the fact that the silver iodide is structurally speaking very close to ice, it induces a kind of icelike structurized layer around the particle. We think that this is responsible for the mentioned lyotropic specificity. The funny thing is that if one makes the temperature higher, this icelike layer melts and then the system is purely diffuse, so we can get rid of it, and that is what we want in connection with the calculation of A. Of course a closer inspection of structure formation at lower temperature would also give interesting information.

Perhaps I can now revert to Prof. BOWDEN's question. We have the impression that at elevated temperatures the specificity is almost totally lost, except for a few %. We are inclined to think that this small residual specificity is really due to specific effects in the diffuse part of the double layer. (Ion size effects, variation in the dielectric constant and so on).

LÖWDIN

I would like to bring up the question of the additivity and non-additivity of inter-atomic and inter-molecular forces. About 20 years ago in investigating ionic crystals I found that quite a

large part of the cohesive energy was of many-body character, and that the experimental correspondence to this was the failure of the Cauchy relation for the elastic constant. Later, JANSEN has found that the second-order perturbation forces, i.e. the dispersion forces, in the ionic crystals show a fair amount of many-body character. LINDERBERG, in investigating the cohesive properties of solid neon has found a similar many-body character. The question is now how outstanding this many-body character is experimentally. Has the associated non-additivity shown up anywhere in the experiments?

OVERBEEK

Perhaps the only place where it has shown up is in the recent experiments on the interaction between quartz plates and between fused quartz plates which are in better agreement with Lifshitz' theory, which takes the non-additivity into account, than with Casimir and Polder's theory which does not the lack of additivity into account. But I would say that at the moment this is the only indication I have.

MOLECULAR FORCES IN THIN LIQUID FILMS

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1) INTRODUCTION

The study of thin liquid films constitutes a recent development in fundamental colloid chemistry. The main reason to pay attention to this field is that in thin films essentially the same forces are operative as between hydrophobic colloidal particles, hence colloidal stability and thin films yield the same kind of information on molecular forces. (See next section). As compared with the interaction between dispersed colloidal particles, thin liquid films offer the principal advantage that the geometry is well defined with the distance as an important controllable variable.

The phenomenology of isolated soap films and of foams has since long been studied. Well known physicists and chemists, like HOOKE, NEWTON and PLATEAU contributed to this field. Even GIBBS, noted as a theoretical scientist and founder of modern thermodynamics experimented with soap films. A collection of some simple but instructive experiments can be found in a book by BOYS [1] and a bibliography up to 1959 is contained in the monograph by MYSELS, SHINODA and FRANKEL [2].

The most conspicuous feature of soap films is perhaps the pattern of changing interference colours that they display. As every colour corresponds to a given thickness, changes in colour reflect thickness changes. These changes are due to the tendency of most liquid films to thin, either by viscous flow or by the so-called marginal regeneration process [2]. From a thermodynamic viewpoint this thinning should ultimately result in irreversible rupture because films have a very high surface free energy per unit weight as compared to bulk liquid of the same composition. However, in some cases the thinning stops at a given thickness (called the equilibrium thickness) and the film can be kept at this thickness for a long time. This is the same kind of stability that is observed in stable hydrophobic sols: a stable AgI sol can be kept for years but is thermodynamically unstable with respect to the situation (liquid + one big AgI crystal).

Although for pure and applied science the question of drainage and stability are of paramount importance (see e.g. Ref. [3, 6]) in this article we are mainly interested in the behaviour of films as soon as molecular forces become important, i.e. when the films become thinner than about 1000 Å. Such films reflect only little light and appear as greyish or black. Henceforth we will tacitly assume that the film is sufficiently stabilized (usually by a soap) to be studied and that spurious thickness-influencing effects (like evaporation) are absent.

Structurally speaking soap films are sandwiches, consisting of an inner aqueous core, flanked by two monolayers of the surfactant. This is the structure one would intuitively expect but it has also been checked by independent methods. CORRILL c.s. [7] e.g. studied the composition of the film by various techniques (light reflectance, infra-red absorption and radiotracer experiments) and corroborated the sandwich model. LYKLEMA, SCHOLTEN and MYSELS [8], studying the flow in rigid films (films with a high surface shear viscosity) found that

the films consisted of a mobile aqueous core with bulk viscosity and two immobile surface layers, the thickness of which agreed very well with elementary calculations based upon orientation and length of the adsorbed surfactant molecules. The considerations in the following sections will be based upon this sandwich model except if otherwise stated.

2) FORCES IN SOAP FILMS

Several forces are operative in soap films. They can be negative (promote thinning) or positive (help to make the film thicker, or at least oppose thinning).

Like between hydrophobic colloidal particles (see I) ⁽¹⁾ double layer repulsion is the dominant positive force. The double layers arise from dissociation of the adsorbed surfactant molecules. Strictly speaking non-ionic surfactants would produce no double layers at all but practice shows that it is hardly possible to obtain completely charge-free surface layers. Even in soap-free films (assuming they are stable enough to study) a particular distribution of the differently hydrated cations and anions in the surface layer will give rise to some electrostatic repulsion between these surface layers. Some experiments by SCHELUDKO point into this direction [9]. However the surface charge and surface potential are relatively best defined if some ionic surfactant is adsorbed.

Again just like between electrostatically charged colloidal particles the repulsive force can be calculated using the Deryagin-Landau [10], Verwey-Overbeek [11] (DLVO) theory. A discussion of some of the merits and limitations of this theory

⁽¹⁾ I refers to a preceding paper by the same author, discussing the forces between colloidal particles, also published in the Proceedings of this Study Week.

have been discussed in I. For separations larger than twice the double layer thickness κ^{-1} (a condition nearly always fulfilled) the repulsive force or pressure (in dyne. cm^{-2} except if stated otherwise) is given to a very good approximation by

$$(1) \quad P_r = 64 \ n k T \gamma^2 \ e^{-\kappa d_2}$$

In this equation n is the number of salt molecules per unit volume, kT the thermal energy, κ the reciprocal Debye length and d_2 is the distance between the starting points of the diffuse parts of the double layers. d_2 is shorter than the film thickness δ because of the finite thickness Δ of the surfactant surface layers and Stern layers. (For a more detailed discussion of the electrostatic features the reader is referred to I; see also below, Figure 2). The potential of the diffuse part of the double layer ψ_δ enters the equation via the factor γ :

$$(2) \quad \gamma = \frac{\exp \frac{ze\psi_\delta}{2kT} - 1}{\exp \frac{ze\psi_\delta}{2kT} + 1}$$

where z is the valency of the counterion and e the elementary charge. According to [2] γ is proportional to ψ_δ at very low potential but almost independent of ψ_δ and equal to one at very high potential. The latter could be the case for fully ionized monolayers.

The evaluation of ψ_δ is not a simple problem. Assuming full dissociation ψ_δ can be calculated from the surface charge σ_0 by application of the diffuse double layer theory but this procedure breaks down at high salt content, i.e. at short distances, which happen to be particularly interesting for several

reasons. The substitution $\psi_s = \zeta$, often successfully applied in the field of colloid stability could be a useful approximation but as yet little is known on the electrokinetics in soap films [12, 13]. For highly ionized monolayers the problem is not serious because then γ is insensitive to ψ_s .

At 25°C eq. (1) changes into

$$(3) \quad F_r = 1.59 \times 10^9 \, c \gamma^2 \, e^{-\lambda d_1}$$

in which c is the salt concentration in moles/L. The salt concentration enters F_r also via λ . The overall effect is a decrease in pressure with increasing concentration. An interesting feature is that many films are still stable at concentrations higher than the critical coagulation concentration. This means that the interplay of molecular forces in thin films can be studied under circumstances inaccessible in the field of colloidal stability.

Several compressive forces can be mentioned. First an outer pressure can be applied at will. In the second place there exists always a capillary pressure due to the negative curvature in the plateau border (that is the border between film and frame or the border joining different flat films in a foam). It amounts to

$$(4) \quad F_c = - \rho \, g \, h_o$$

$$(5) \quad \text{in which} \quad h_o = \left(\frac{2\gamma}{\rho g} \right)^{1/2}$$

where ρ is the density, g the acceleration of gravity and γ is now the surface tension ⁽¹⁾. In vertical films a hydrostatic pressure

$$(6) \quad F_h = -\rho g h$$

is present. The sum of capillary and hydrostatic pressure,

$$(7) \quad F_c + F_h = -\rho g (h + h_0)$$

is usually small, although not negligible.

Very important is the fact that also van der Waals forces help in compressing the film. This will constitute a central theme of this article. The compressive action of van der Waals forces in thin films can be visualized in several ways. Historically the oldest indication is HAMAKER's conclusion that the van der Waals force between two bodies 1 in a medium 2 is always attractive, irrespective whether or not the density of the dispersed material is higher than that of the dispersing medium [14]. Carried to the extreme, this means that two air bubbles in water attract each other, or in other words: a thin aqueous lamella between two semi-infinite volumes of air experiences a compressive van der Waals force. Another way to look upon it is via the surface energy. The surface energy is due to the fact that surface molecules are attracted inward by intermolecular forces. In thin films the proximity of the two surfaces weakens this inward attraction, i.e. it lowers the free energy of the film and hence acts as a factor favouring further thinning of the film. One may say that, in a way, the

⁽¹⁾ Note that the symbol γ has been used for two different quantities. The difference between them is obvious, though.

absence of molecules (viz. at the other side of the film) causes the van der Waals compressive force.

Although the London force between two atoms has only a very short range, the summed up force between two macroscopic collections of molecules is of much longer range. (See I). In the case of soap films the van der Waals compression becomes significant for film thicknesses around 1000 Å growing progressively more important when the film thickness decreases. The lower limit is usually somewhere around 100 Å. This means that thin films cover a range of distances between the distances usually occurring in colloidal stability and the lower limit of directly measurable forces [15].

Although historically the operativity of van der Waals forces in thin films was established in 1937 [14] it took about 20 years before DE VRIES [16] purposefully treated them as one of the stability determining factors. In an older paper by DERJAGUIN and TITIEVSKAJA [17], perhaps the first paper considering a force balance, van der Waals forces were not yet taken into account. According to DE VRIES the force compressing a film of thickness δ , F_{film} , is exactly equal to the force attracting two semi-infinite layers of the same material, separated by a gap of thickness δ , F_{gap} . For the latter we can write

$$(8) \quad F_{\text{gap}} = F_{\text{vdw}} = \frac{A}{6\pi\delta^3}$$

in which A is the Hamaker-van der Waals constant, a quantity characteristic for the material under consideration. (See I). In the microscopic theory it is given by

$$(9) \quad A = \pi^2 q^2 \beta$$

where β is the London constant for the attraction between two atoms of the material considered and q the number of atoms per unit volume.

Eq. (8) if applied to a film is only approximative. The equivalence of F_{film} and F_{gap} is not corroborated by the macroscopic theory of DZYALOSHINSKIĬ, LIFSHITZ and PITAEV-SKII [18] (an extension of the LIFSHITS theory [19]). SCHELUDKO, PLATIKANOV and MANEV [20] have collected the pertinent equations to show this. The quantitative discrepancy is difficult to assess because of lack of dispersion data. Great discrepancies are not to be expected in view of the fact that the Hamaker constant for water, calculated by the microscopic theory along the lines of Slater and Kirkwood [21] ($0,6 \times 10^{-12}$ erg) agrees within 10% with the corresponding quantity as calculated from the macroscopic theory using optical data for water vapour ($0,54 \times 10^{-12}$, KRUPP, see I).

Eq. (8) for films requires also a correction because the film does not consist of pure water but is virtually a sandwich, the surface layers of which have a Hamaker constant different from that of water. The compressive force for this case has been calculated by DUUVIS [22], it yields

$$(10) \quad F_{\text{vdW}} = -\frac{A_{11}}{6\pi} \left[\frac{1}{d_2^3} - \frac{2}{(\Delta + d_2)^3} + \frac{1}{(2\Delta + d_2)^3} \right] +$$

$$+ 2 \frac{A_{12}}{6\pi} \left[\frac{1}{d_2^3} - \frac{1}{(\Delta + d_2)^3} \right] - \frac{A_{22}}{6\pi} \frac{1}{d_2^3}$$

in which A_{11} is the Hamaker constant of water, A_{22} the same constant for the surface layer and A_{12} the mixed constant (approximately equal to $\sqrt{A_{11} A_{22}}$); d_2 is the thickness of the inner core and Δ the thickness of the surface layers; $d_2 + \Delta = \delta$.

For $\Delta=0$ and $A_{11}=A_{22}=A_{12}$ [10] becomes again identical to (8). The correction increases with increasing difference between Δ and d_2 .

However, the most serious shortcoming of (8) is the neglect of retardation. The retardation of the London force between two atoms has been treated quantitatively by CASIMIR and POLDER [23]. They found that for large distances between the atoms the energy decreases as r^{-7} instead of r^{-6} . This retardation occurs also in the energy or the force between two flat plates. With respect to the force it leads to a gradual change of the δ^{-3} power law of (8) into a δ^{-4} power law. This power change is corroborated by the Lifshitz-theory [18, 19]. The distance stretch over which the transition occurs is determined by the principal London wavelength λ_0 which for water may be estimated as $\sim 1000 \text{ \AA}$. In ref. [24] a function is given to correct the London force between two macroscopic bodies for retardation. Application of this correction to water gives the result of Figure 1. The figure shows that the transition takes place just in the region of thicknesses covered by the thin films. In combination with the fact that the film thickness is a measurable quantity this opens promising new perspectives: soap films are a tool for the study of van der Waals forces in the transition region between retarded and non-retarded forces.

The over-all procedure of the following is analogous to the one adopted in I. The sum of the forces $\sum_i F_i$ is determined experimentally (Section 3). Then F_{vdW} is considered as « unknown », all other forces as « known » (although some discussion on the actual values of some of the parameters might be necessary). Calculation then yields F_{vdW} as a function of δ , allowing the estimation of A and the exponent of the $F_{\text{vdW}}(\delta)$ power law.

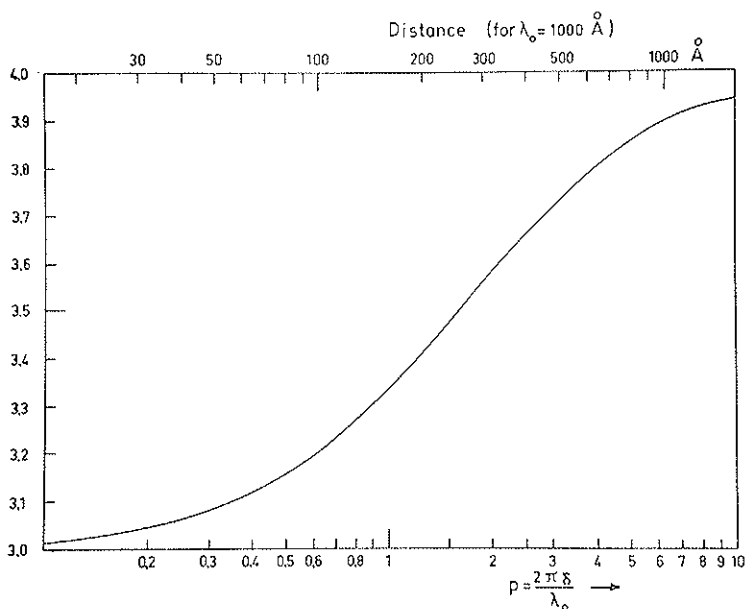


FIG. 1 — Variation of the exponent of the van der Waals pressure-distance relation due to retardation.

3) METHODS TO OBTAIN $\sum_i F_i$

Two principally different approaches are currently used, the *static* and *dynamic* method. In the static method $\sum_i F_i = 0$, the film is in equilibrium and can be kept indefinitely long at the same thickness provided the proper precautions against evaporation, mechanical disturbances etc. are taken. In the dynamic method $\sum_i F_i \neq 0$ and δ changes (usually decreases) with time. $\sum_i F_i$ can be calculated if it can be related to the (measurable) rate of drainage. In both methods the final step is the calculation of F_{vdW} assuming the other forces known.

Film thicknesses can in principle be determined from light reflection. The reflection of monochromatic light by a homogeneous aqueous film is relatively simple. Moreover optically a soap film is at least a three layer system because the surface layers have an index of refraction different from the one of the aqueous core. Perhaps on closer inspection the films are five-layer systems because the Stern layers have again another index of refraction. The result is an intricate composition of multiple reflections. Solutions for this optical problem are available in literature [8, 22, 25]. Experiments with microscopic and macroscopic films have been reported.

As the study of thin films is a relatively recent development not many experimental results have been reported. Equilibrium thickness measurements for free films are a.o. reported in Ref. [17, 22, 26-28]. In the last mentioned paper films having equilibrium thickness were obtained in two different ways: *a*) starting from thick films and letting them drain till no further thinning occurred, and *b*) via the very slow formation of the film. If a thin film is formed by pulling a frame out of a surfactant solution its thickness will generally depend on the rate of pull-out, because the faster it is pulled-out the more liquid is entrained (Frankel's law [2, 8, 29]). However, if formed extremely slowly films cannot become thinner than the equilibrium thickness simply because double layer repulsion opposes further thinning. Consequently very slowly formed soap films possess equilibrium thickness. It was found that the results of methods *a*) and *b*) were indistinguishable which is of course a strong support for the validity of the obtained equilibrium thickness. The procedure to obtain F_{vdw} from the equilibrium thickness is finally summarized in Figure 2.

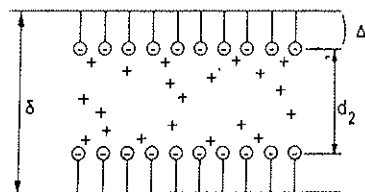
The dynamic method was promoted especially by SCHERER and his school [3, 20, 30]. The Reynolds equation was used to compute $\sum_i F_i$ from the rate of drainage:

$$(11) \quad \frac{d\delta^{-2}}{dt} = \frac{4}{3\eta a^2} \sum_i F_i$$

VAN DER WAALS force from the equilibrium thickness
of free liquid films

At equilibrium:

$$F_{vdW} + F_R + F_{cap.} = 0$$



$$F_R = 64 n k T \gamma^2 e^{-\kappa d_2}$$

$$= 1.59 \times 10^9 c \gamma^2 e^{-\kappa d_2}$$

$$\gamma = \frac{\exp\left(\frac{ze + \delta}{2kT}\right) - 1}{\exp\left(\frac{ze + \delta}{2kT}\right) + 1}$$

FIG. 2

in which η is the viscosity and a the radius of the (circular) film. If the film consists of a viscous aqueous core and rigid surface layers, δ must be replaced by d_2 .

The applicability of (11) is not without doubt. The Reynolds equation applies to viscous flow between two rigid circular plates. The surface of a liquid however is not a rigid disk. Dimpling can occur or irregular outflow through temporarily formed channels [31, 33]. Another restriction is that (11) applies only if viscous flow is the sole thinning mechanism. However, MYSELS and his collaborators [2] have clearly demonstrated that in mobile films (films without a particularly high surface shear viscosity, i.e. the majority of the films) a process called « marginal regeneration » is the major thinning mechanism. Notwithstanding these objections [34] SCHERLUNDKO has produced some interesting results by this method.

4) RESULTS AND DISCUSSION

a) *Equilibrium thickness*. Some recent results on δ as a function of ionic strength are collected in Fig. 3. The general trend is a decrease in δ with increasing c which is due to the decrease in F_r in this direction (3). Some authors did not correct for the deviating optical properties of the surface layers, hence their results might be designated as « equivalent water thicknesses ». The agreement is generally good, perhaps with the exception of the older results of DERJAGUIN and TITIEVSKAJA [17]. For sake of comparison two curves, calculated for two sets of the parameters ($F_h + F_c$) and ψ_δ are also given. F_{vdW} was calculated assuming $A = 5 \times 10^{-13}$ erg; retardation was accounted for along the lines of Sec. 2. The general agreement between theory and experiment is satisfactory, but upon

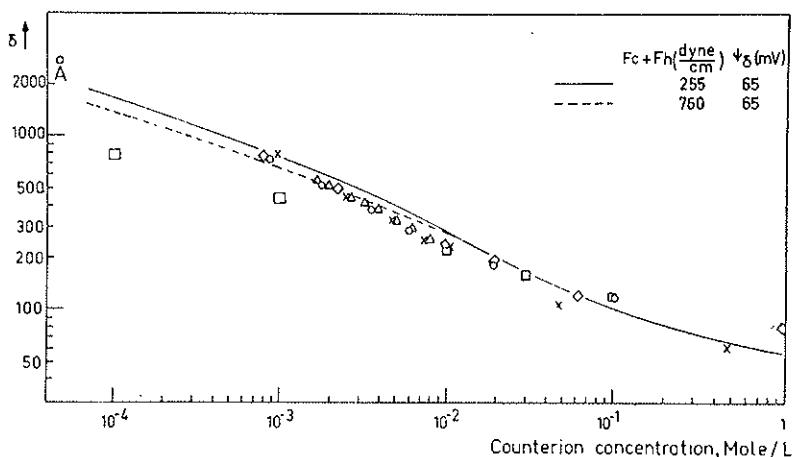


FIG. 3 — Equilibrium thickness of isolated soap films as obtained by different authors. □ DERJAGUIN and TITIEVSKAJA [17], Δ SCHELUDKO and EXEROWA [30], ◇ LYKLEMA and MYSELS [28] mobile films, ○ Ibid, rigid films, × Sonntag [33]. Drawn and broken lines: calculated.

closer inspection some deviations are signalized that deserve more attention.

In the region of thicker films (left in Fig. 3) reasonable agreement exists with the theory for $\psi_s = \text{constant} = 65 \text{ mV}$. However this is an underestimate. ψ_s is higher than 65 mV, at least for ionized surfactants like sodium dodecylsulphate and depends on c [13, 28]. A higher potential means a thicker film. Hence we conclude that at low salt content films tend to be thinner than theoretically predicted. This, in turn implies that either F_{vdW} is higher than expected or F_r is lower.

Just the reverse occurs in the region of thin films (right in Fig. 3). Except for one measuring point by SONNTAG the general trend is that the experimental values are higher than the theoretically predicted ones. The same feature was also observed with aqueous films between oil (in stead of air) by VAN DEN TEMPEL [35]. The reason for this upward deviation is still not yet clear. DERJAGUIN ascribed it to structure formation in the film core, but LYKLEMA, SCHOLTEN and MYSELS [8] found no indication whatsoever for a deviation of the viscosity from its bulk value. One feature that certainly plays a role is the neglect of the finite ion size in the diffuse double layer theory although it is not yet clear whether this effect is solely responsible for the observed deviation [28, 36].

Following the procedure indicated in Sec. 2 we can now work the other way round and calculate F_{vdW} from the experimental equilibrium thicknesses [28] using the force balance of Fig. 2. The result is shown in Fig. 4. This figure shows two curves, designated as « mobile » and « rigid » referring to the mechanical properties of the film. The thicknesses of the surface layers Δ are different for these two types of films. In rigid films the surfactant molecules are assumed to adsorb perpendicularly to the surface with fully extended chains ($\Delta = 16 \text{ \AA}$); in mobile films $\Delta = 8,5 \text{ \AA}$, calculated from a molecular area of $52 \text{ \AA}^2$ [37] and a liquid-like surface layer. The optical reflectance of these types (and hence the equivalent

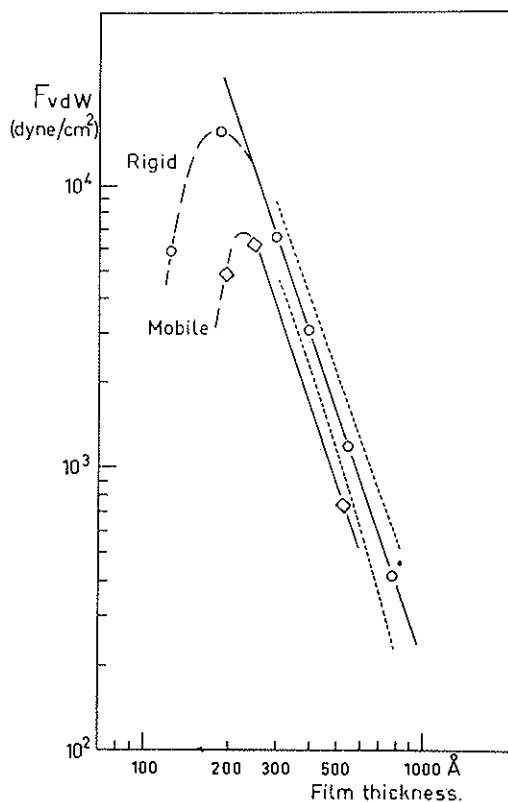


FIG. 4 — Van der Waals pressure, as calculated from experimental data and double layer theory. $\phi_\delta = 100$ mV. Upper dashed line shows the effect of an error of $+25$ mV in ϕ_δ or -5 Å in Δ ; lower dashed line the same errors in opposite direction.

water thickness) is the same. Consequently the difference between these two curves demonstrates very clearly how sensitive the calculated F_{vdw} is to the underlying structural details, the difference between « mobile » and « rigid » films being an upper limit. Recent studies by VAN DEN TEMPEL and collabo-

rators [38] made them believe that the mechanical difference between mobile and rigid films was not due to radical differences in Δ , Δ being $\sim 8,5 \text{ \AA}$ for both types. This would mean that the rigid curve would coincide almost completely with the mobile one. Anyhow, the slopes of the linear parts of both curves are identical, and within a few % equal to 3. SCHELUDKO and EXEROWA [30], covering a much shorter thickness range found also a 3rd power. This is surprising because according to the theory rather a transition between non-retarded and retarded forces (i.e. an exponent between 3 and 4, see Fig. 1) must be expected. Moreover for $\delta > 1000 \text{ \AA}$ the directly measured forces are fully retarded [15]. The reason for this fact is not yet clear. The underlying experimental equilibrium thicknesses [28] are rather beyond doubt as they have been obtained by two different approaches (Sec. 3). The uncertainty in Δ affects A (2×10^{-12} erg for mobile films, $3,5 \times 10^{-12}$ erg for rigid films) but not the slope, although it must be noted that A is about a factor 3 - 5 higher than expected. In order to show the effect of the uncertainty in ψ_s two dashed lines around the linear part of the rigid film curve indicate errors of $\pm 25 \text{ mV}$ in the assumed $\psi_s = 100 \text{ mV}$. From the figure is seen that this does not lead to much difference with respect to the slope. We may note that $\psi_s = 100 \text{ mV}$ is perhaps more realistic than $\psi_s = 65 \text{ mV}$ as applied in Figure 3. If we would have chosen a ψ_s variable with c_{salt} this would have led to a slope even lower than 3. In conclusion: these experiments show a van der Waals force that is non-retarded in the region $200 - 850 \text{ \AA}$ and is about a factor 3 - 5 higher than expected. We may perhaps add, that forces of the Keesom-type would explain these observed results very well. However it is hardly imaginable that the dipolar attractions in water would be effective over a long range without averaging out to zero.

In the discussion given above the downward trend of F_{vdW} at very high salt content (left in Fig. 4) was not further con-

sidered because in this region the diffuse double layer theory breaks down. Hence the calculated F_{vdW} is not free of systematic errors.

Finally, mention should be made of the fact that also the evidence collected from colloidal stability (I) points into the direction of van der Waals forces tending to be higher than the calculated ones.

b) *Dynamic method.* Fig. 5 gives a recent example by SCHELUDKO c.s. [20] for benzene films stabilized with 0.07% silicone oil. Similar results have been obtained with chlorobenzene [20] and aniline [39]. Some results on aqueous films have also been reported [3, 30]. In the benzene film double layer repulsion is virtually absent which facilitates the computation of F_{vdW} . However, the experimental results show a considerable scatter, and it is almost impossible to conclude something on the nature of the $F_{vdW}(\delta)$ power law. Assuming the exponent to be constant, application of the method of least squares yields an exponent close to 4, for all three organic liquids studied. This would mean that the force is fully retarded. For sake of comparison a 3rd power law is also given (broken line); it is clear that in view of the data a transition between 3 and 4 is also possible.

Considering the various uncertainties involved, it is not yet justified to base a penetrating analysis on these results. Nevertheless, the contradiction between the 3rd power for aqueous films (static method) is disturbing. More experimental results preferably by both methods would be very welcome.

5) CONCLUSIONS

1. The study of thin films constitutes an interesting extension of the domain of colloidal stability because in both fields the same forces are dominant.

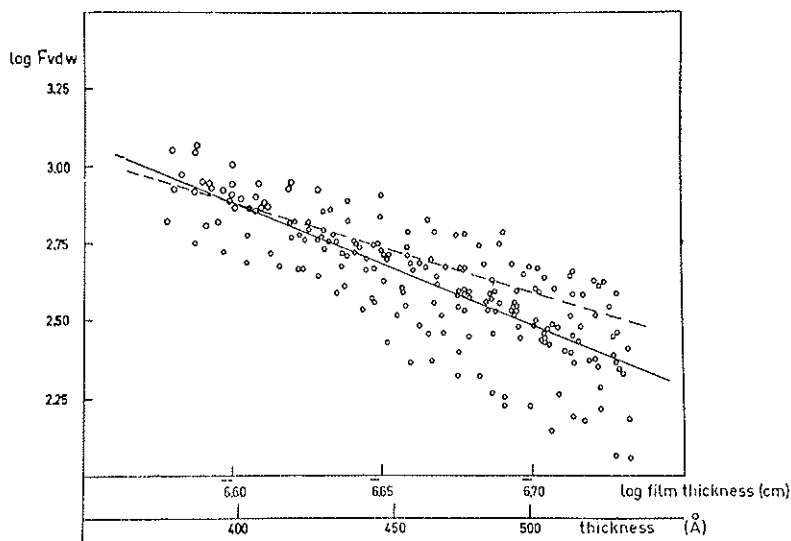


FIG. 5 — Van der Waals force against film thickness for benzene. Dynamic method. $\circ$ Experimental points by SCHELUDKO c.s. [20]. Drawn line 4th power law, broken line 3rd power law.

2. Distances between ~ 100 and $\sim 1000 \text{ \AA}$ can be covered. This stretch lies between the distances important in colloidal stability and those accessible to direct measurement.

3. In principle there are two different approaches for the study of van der Waals forces in thin films, the static (equilibrium) and dynamic method. As yet the static method seems to be the more accurate one.

4. Equilibrium thickness measurements on aqueous films show that between 200 and $800 \text{ \AA}$ the force is non-retarded with a Hamaker constant of $2 - 3.5 \times 10^{-12} \text{ erg}$.

5. Dynamic measurements for benzene, chlorbenzene and auiilue lead to the conclusion that the van der Waals forces are retarded between 400 and $550 \text{ \AA}$.

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DISCUSSION

Chairman: H.B. CASIMIR

FIXMAN

I did not understand what the van der Waals force is between, in these thin films. Perhaps you could back up and explain that point.

LYKLEMA

You mean that you want to have explained that van der Waals force is really trying to help to compress the film?

FIXMAN

My question concerns the relevance of retardation in a thin film where the compressive forces are primarily exerted by molecules on their near neighbors.

LYKLEMA

Yes it is indeed the intermolecular forces between the molecules of the film that are responsible for the compression. There are different ways to look upon this.

One way, due to MYSELS, is to consider the transition between a thick and a thin film, the geometry of the transition region being not specified for the moment. A molecule in this transition region feels a relatively stronger attraction towards the thicker film than towards the thinner one simply because there are more molecules at the side of the thicker film. Consequently there exist a tendency of these molecules to flow towards the thicker film which, macroscopically speaking, means that there is a tendency of the thinner film to grow with respect to the thicker one as a result of the intermolecular attraction between the molecules of the film.

Another way is to consider the surface energy, which exists due to the fact that molecules in a liquid surface are subject to an inward attraction. Now, if the two surfaces of an aqueous film come so close together, that the film thickness becomes of the order of the range of molecular attraction the surface energy will diminish, which thermodynamically means that there is again a tendency to thin as a result of intermolecular forces.

See also this paper, pag. 6.

FIXMAN

I still don't understand something very fundamental. The line of your argument would seem to me to reach the conclusion that the thicker the film the more the retardation, until eventually in a macroscopic body you would find that the major contribution to the van der Waals energy of the body would come from retarded forces. That does not seem right. Most of the interaction will be between molecules close together.

LYKLEMA

The reply to this paradox could be that the thicker the film not only the retardation becomes more important but at the same time the van der Waals energy decreases.

CASIMIR

Yes, but you might say it perhaps in the following way. What you are really studying is an absence of van der Waals attraction. If you have a very thick film you have van der Waals attraction throughout. Now if it is a thinner film you do not have an infinite half space and you have a shortage of van der Waals attraction because below the film on the other side there are just no atoms present. What is taken away from the van der Waals attraction in the thick film is the attraction of rather distant particles. And hence you should get retardation. Is that about right?

OVERBEEK

I have a rather simple picture (see fig. 1) that shows what happens here. We start with two films of the same thickness, and

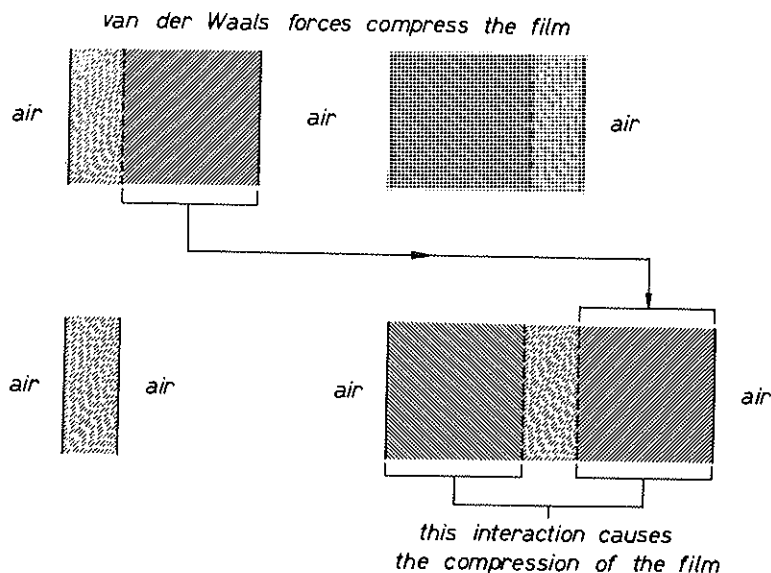


FIG. 1

take away a part of one film and put it at the side of the other film, and now compare all the interaction energies in the two cases. Then in the upper picture we find twice an interaction between a thin layer of liquid and a thick layers, but this gives the same total energy as in the first case. However, in the lower picture we find an additional attraction between two thick layers, and this attraction causes the total energy of the second situation to be lower than that of the first one. This can be interpreted as the result of a force compressing the film and pushing the liquid out to a place where it is more completely surrounded by molecules of the same material.

The actual force can be calculated as if there were two water layers attracting one another across a gap of the same thickness as the remaining film. That's one way of showing that van der Waals forces indeed compress the film.

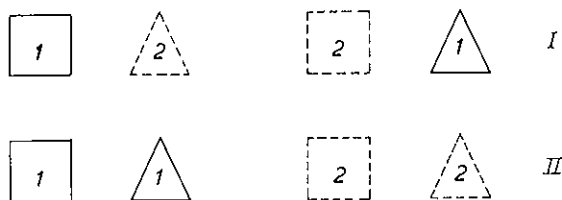


FIG. 2

The other way is a little more sophisticated and shows that two air bubbles in a liquid attract one another. The air bubbles indicated by the index 1 are embedded in a liquid having index 2, as shown in the upper half of fig. 2. If two air bubbles are brought together as in the lower half of fig. 2 at the same time two similar volumes of the liquid have to be brought together as well.

In the two situations of fig. 2 all interactions are the same except those between the drawn volumes. In the upper half there

is twice the interaction between a volume of air and one of liquid, which is negligible. In the lower half there is once the interaction between two volumes of air — again negligible — and once the interaction between two volumes of liquid. Therefore two gas bubbles in a liquid attract one another with exactly the same force that exists between two liquid drops of the same size and distance in a gas.

CASIMIR

That is really what I tried to say - what you notice is the lack of Van der Waals attraction on the other side of the film, because there are no particles present there.

BOWDEN

Could I ask one question. You have in effect a monolayer of long-chain soap-like molecules adsorbed on each side of your water film. Do you know how these molecules are oriented and how they are packed on the water surface? Can you assume that they are always oriented in a direction normal to the surface? Might some of the dimensional changes which you observe be due to a change in the packing arrangement and tilt of these molecules rather than to a running out of the water between them?

LYKLEMA

Starting with your first remark, there is of course always a little uncertainty as to the actual thicknesses of the surface layer (which I have called Δ). For example, VAN DER TEMPEL in the Netherlands thinks that the surface layers on my rigid films are about 4 to 5 Angström units thinner than I presumed. In fact this

accounts also for the difference between mobile and rigid films. In mobile films the surface layer consists only of dodecylsulphate ions, which can be quite mobile; in rigid films the surface is probably built up of Na-dodecylsulphate and dodecylalcohol in a 1:1 relation, in this case the molecules stand perhaps perpendicular or are slightly tilted, to the surface. This does not affect the slope of the van der Waals force vs. thickness curve but gives the Hamaker constant an uncertainty of about 25%.

With respect to your second remark, it is quite possible that, if the liquid effectively drains out so that only the two surface layers are left, a differing configuration is assumed by these soap layers but it is not relevant for our procedure because what we do is extrapolate from higher thicknesses where this effect does not occur.

EXPERIMENTAL STUDIES OF SURFACE TOPOGRAPHY AND THE MEASUREMENT OF THE ATTRACTIVE FORCES BETWEEN MOLECULARLY FLAT SOLIDS

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It is a great pleasure to take part in the discussion held under the auspices of this distinguished Academy and which is taking place in such beautiful surroundings. Professor BERNSTEIN has mentioned that the earliest potential energy curve which he has seen is due to an Italian monk in the 18th century. May I mention an even earlier contribution to the study of surface forces by an Italian who is not unknown to you. This is in a field in which I have been particularly interested — the interaction between two surfaces in contact, and the nature of adhesion and friction. It was LEONARDO DA VINCI [1] who first formulated the two basic laws which govern the frictional behaviour. These are — that friction is proportional to the load, and that it is independent of the area of the sliding surfaces. It seems clear that he investigated them experimentally and in his notebooks he writes « friction produces double the amount of effort if the weight be doubled » and « the friction made by the same weight will be of equal resistance at the beginning of the movement although the contact may

be of different breadths or lengths ». Like so much of his astonishing work it was forgotten and it was not until a couple of hundred years later that these laws were rediscovered.

My discussion may perhaps be regarded as falling into three parts. In the first part I will mention some sensitive physical methods which are now available for determining surface topography and for preparing quite large surfaces which are molecularly flat; the second part will describe an attempt to measure directly the attractive force as a function of distance between solids which are very close to one another (say 10 to 100 Å); the third will deal with the influence of films of adsorbed vapour molecules and of immersion in a liquid on the work required to separate these surfaces.

I. MEASUREMENT OF SURFACE TOPOGRAPHY AND THE PREPARATION OF MOLECULARLY FLAT SURFACES

We may, of course, prepare « smooth » solid surfaces in various ways — by mechanical grinding and polishing, by chemical polishing, by cleavage, by evaporation and condensation or by natural growth. By none of these methods is it easy to prepare surfaces which are perfect. Usually they are not flat on a molecular scale, they may consist of steps or valleys and hills which can be some hundreds of angstroms in height and they will contain imperfections which may vary in magnitude from atomic dislocations to Griffith microcracks or to much larger regions of disorder. In my own laboratory we are using a variety of physical methods to study the geometry of solid surfaces and the irregularities or defects which may be present on them [2, 3]. These include high resolution electron microscopy, scanning and reflection electron microscopy combined with shadowing or with « decoration » techniques, low voltage electron diffraction, moiré

fringe methods and optical multiple beam interferometry. With some of these methods it is possible to detect surface irregularities which may be only a few angstroms in height, so that defects of molecular dimensions can, under appropriate conditions, be observed. Field ion microscopy is also a powerful method since it enables the individual atoms on the surface to be « seen », but it has, of course, limitations in that at present it can only be used on solid surfaces which will withstand very high temperatures or intense electric fields. The two methods which are perhaps most relevant to my present discussion and to the preparation of molecularly flat surfaces are multiple beam interferometry and high resolution electron microscopy combined with shadowing.

Before discussing this we may comment briefly on the nature of metal and glass surfaces which are prepared by mechanical and chemical polishing.

Nature of metal and glass surfaces prepared by mechanical or chemical polishing: The usual method of polishing surfaces is to rub them together first with a fine abrasive powder between them and then to rub them at higher speeds with a polishing pad containing a finer powder such as rouge or alumina. The operation is generally performed in the presence of water or some other liquid. Under the optical microscope the surfaces may appear smooth and flat, but detailed observation by more sensitive methods shows that this is by no means so. They are rough on a molecular scale and their deviation from flatness over any appreciable area may be several hundred angstroms. If we endeavour to place such surfaces close to one another they will be supported on the summits of these irregularities and their behaviour will be dominated by the adhesion and deformation of these small regions of contact [2, 3]. In addition to this the metal on the surface is heavily deformed and, if the polishing has been carried out at high speeds, the surface layer may consist of a smeared mixture

of finely crystalline metal containing oxide and polishing powder. The thickness of this Beilby layer may be several hundred angstroms. Beneath this the metal is grossly deformed to a depth which may extend for a micron or more. Superimposed on the surface will be an oxide layer and also, of course, adsorbed molecules of oxygen, water vapour and other contaminants. With noble metals such as gold and platinum the adsorbed film may not be more than one or two atoms thick. With reactive metals chemical reaction occurs and with most metals a much thicker surface film of metal oxide is formed. A good deal of work has been carried out on the kinetics of growth, the structure and topography of such films but it would not be appropriate to discuss them here in detail. We may note, however, that in some cases the oxide may grow epitaxially with the underlying metal and it may not form a uniform continuous film. Under appropriate conditions the oxide may grow in the form of isolated crystals which are relatively thick; it may also grow in the form of long whiskers which can extend several hundred angstroms or more from the surface. Chemical or electrolytic polishing may also fail to give flat surfaces (see Fig. 1) and it will leave the surface covered with a chemical deposit of some sort.

Quartz or glass surfaces present similar problems. Even if they are prepared smooth by melting they will, on exposure to air or moisture, some become covered with micro-cracks which may readily be revealed by decoration techniques. There is evidence that such surfaces are attacked by water or by water vapour in the air so that the surface structure is grossly changed and « silica gel » may be formed. The cleaning of such surfaces also presents grave problems. Some recent experiments by CROSS and PICKNETT [4] for example have shown that the method of cleaning has a profound effect on the adhesion of small glass spheres to flat glass plates in air containing water vapour. They found that the strongest adhesions were obtained when the glass plates were cleaned with

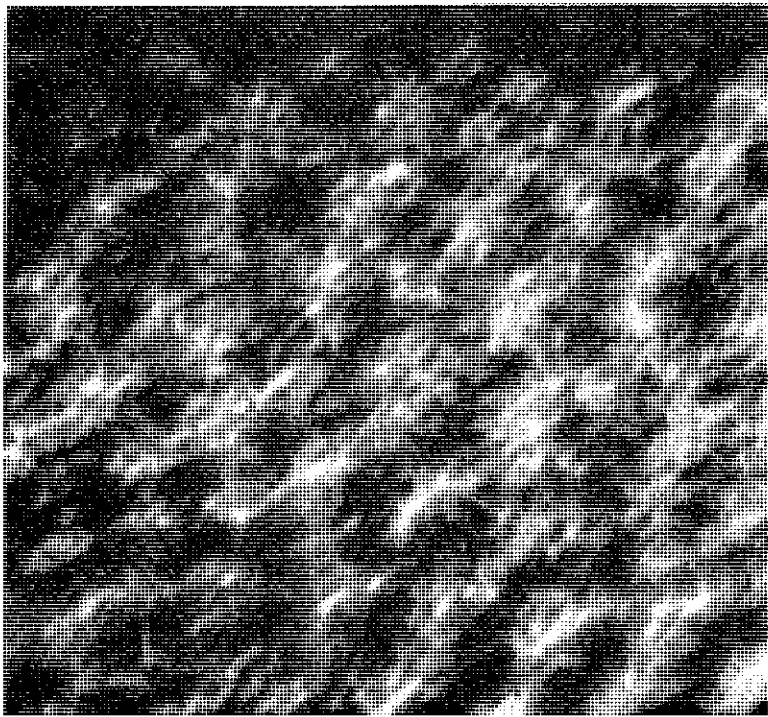
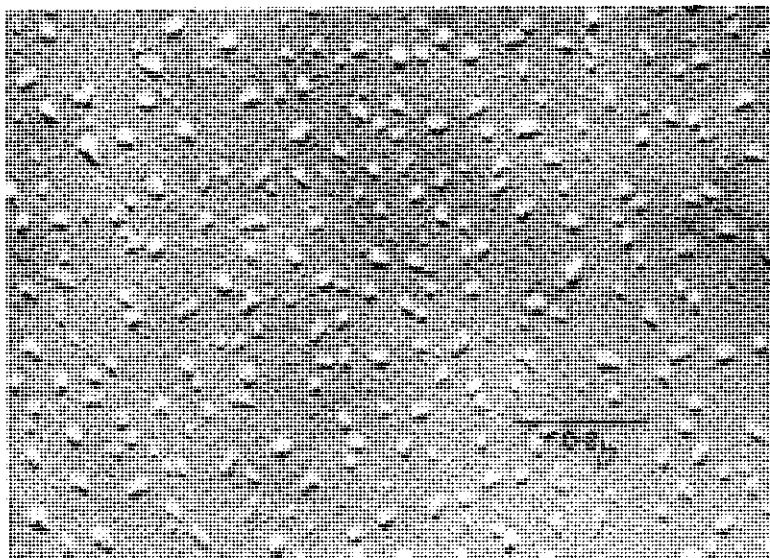


FIG. 1 — Electron Micrograph of electrolytically polished aluminium surface taken in transmission (Formvar replica). The surface irregularities are between 100 and 1.000Å high. Magn. 5,000X.

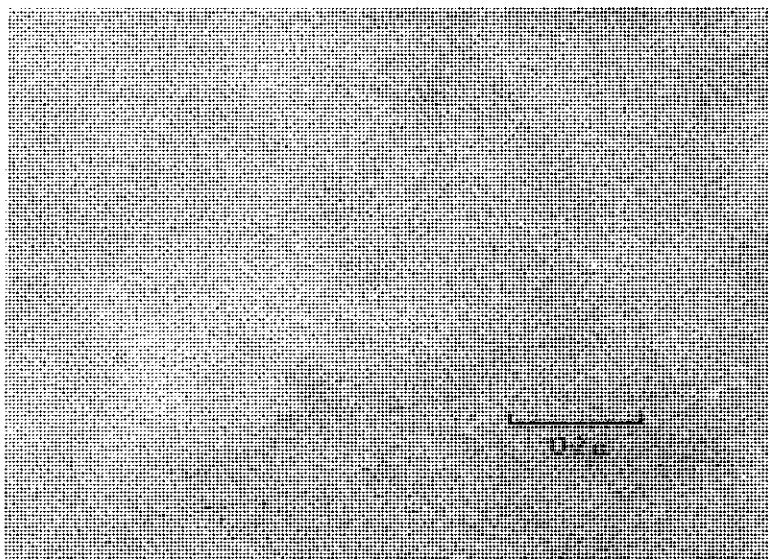
hot concentrated nitric acid followed by thorough rinsing in water and air drying; weak adhesions were obtained when hot concentrated sulphuric acid was followed by benzene. With both cleaning procedure the contact angle between the glass and water was essentially zero, and frequently this is taken as a good criterion for cleanliness. However, electron micrographs showed that the benzene-sulphuric acid treatment had left the plates covered with dome-shaped asperities (Fig. 2 (a)),

whereas the nitric acid treatment had left the plates covered with almost featureless surfaces (Fig. 2 (b)). It is probable that the asperities of Figure 2 (a) arose from the deposition of insoluble impurities formed in the cleaning process. Their average height was about 50Å and their average spacing about 200Å. The weak adhesions obtained following the benzenesulphuric acid treatment can be attributed to the sphere and plate being separated by the height of the asperities. Supporting evidence for the distance separating sphere and plate has been obtained from their adhesion measurements at very high humidity, when the force is almost entirely due to the surface tension of the condensed water that is present in the region of contact. The theory of this surface tension force caused by liquid condensed in the contact regions was established by Dr. DAVID TABOR and Dr. J. MCFARLANE [5]. This has been confirmed and extended by CROSS and PICKNETT [6], and from their observations the average gap between the sphere and the plate can be obtained. For nitric acid cleaned surfaces they found it is about 10Å and for benzenesulphuric acid surfaces about 50Å so that it agrees with the electron microscope observations.

It is clear that the surface layers of metal and of other crystals or solids which are prepared in these ways may be very different from that of the underlying solid, not only in structure, but in composition. These surface layers may be irregular and very thick indeed on a molecular scale. It is unwise to assume that either the physical or the chemical properties of these surfaces are characteristic of the underlying solid. It is also probable that some of the observations which have been published suggesting that tens or even hundreds of molecular layers of a gas or vapour are physically adsorbed to a surface (or that the viscosity of simple liquids may be influenced by a surface to distances of more than a hundred angstroms), may in reality be due to the irregular and complex nature of the surface layers of the solid rather than to a real



(a)



(b)

FIG. 2 — Influence of cleaning on structure of clean glass surfaces.

physical adsorption or to a long distance orientation of the liquid. Some earlier experiments in my own laboratory [7] have shown that the apparent heavy « adsorption » of water vapour on platinum and other surfaces is in fact due to minute amounts of hygroscopic impurities in the surface. If the surfaces are cleaned in vacuo, microbalance experiments and also observations with polarised light, showed that the maximum number of molecular layers of water and of other vapours which were physically adsorbed on the surface was about two. Also Dr. J.S. COURTNEY-PRATT [8] using multiple beam interferometry showed that the number of molecular layers which remained attached to a molecularly flat surface of mica after a drop of liquid fatty acid had retracted from it was only one. It would be interesting to hear from members of the meeting their views on this.

Multiple Beam Interferometry: The ordinary two beam interference method is a useful one for measuring surface contours but it is comparatively insensitive because the Newton fringes are so broad. The width of a 'line' of half maximum intensity is 50% of the spacing of the lines. This means the detail causing a shift of the maximum of less than $1/5$ th of an order is very difficult to detect. If, however, multiple beam interferometry is used the fringes become very sharp and the method becomes very sensitive. This method has been developed in a high degree by TOLANSKY [9]. If the reflective surfaces are coated with a layer of silver having a high reflective coefficient (85-95%) and a significant transmission coefficient, the incident light would be reflected back and forth and the interference pattern will be the resultant of all these beams. The effect (which is analogous to increasing the number of lines on a diffraction grating) is to leave the maxima and minima of intensity as before, but to alter the distribution of in-

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tensity between one maximum and the next. The position of the maxima is given by the usual formula:

$$2 n \lambda = 2 \mu t \cos \theta$$

where λ is the wavelength of the light used;

μ is the refractive index of the material between the silvered surfaces;

t is the thickness of the gap between the silvered surfaces;

θ is the angle of incidence measured from the normal;

and n is an integer for maxima of illumination.

The intensity distribution is similar to that obtained in a Fabry-Perot interferometer — narrow bright lines in a dark field; the width at half-maximum intensity about 2 or 3% of the distance between orders. Fine detail of imperfections of surface finish corresponding to variations of thickness of the film one hundredth of that between successive orders is easily visible so that features in the surface which are 25Å may be observed. Figure 3 (b) illustrates the sharp fringes which may be obtained in this way between the lens and a plate of optical glass. The irregularities seen in the fringes are real and represent scratches and irregularities in the polished glass surfaces which may be 15-100 Å deep. By a modification of the method and the use of white light and a spectrograph to the observed fringes of equal chromatic order, the sensitivity can be increased still further so that steps and small irregularities in the surface as small as 10 or 15Å can easily be detected and their magnitude measured to an accuracy of about 3Å (see Figure 4).

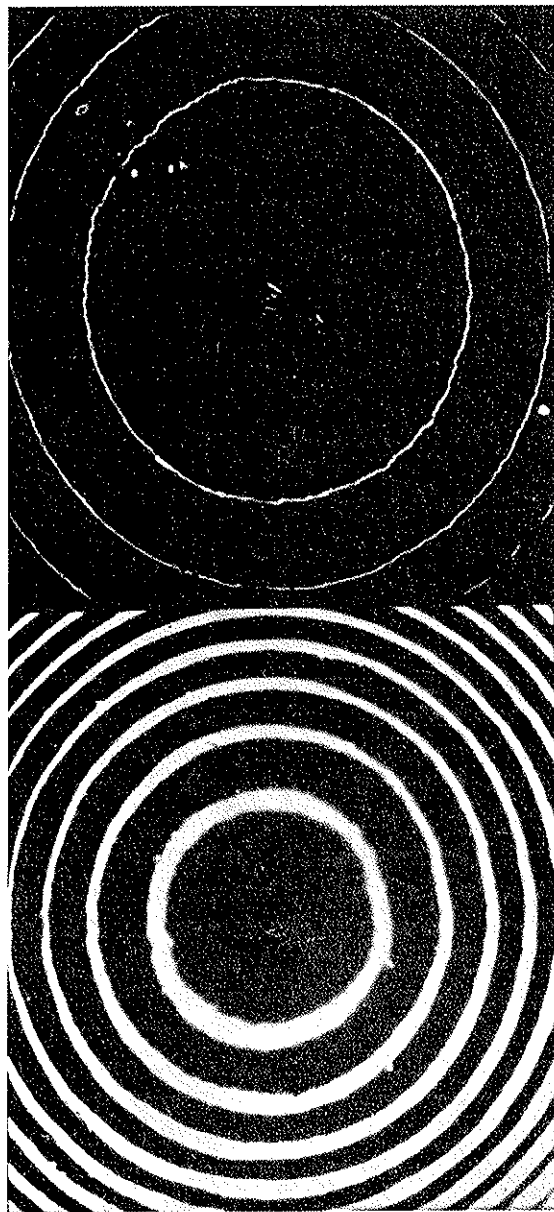


FIG. 3

(a) Newton's rings - two beam interferometric pattern.
Horizontal mag. 10X.

(b) Newton's rings - multiple beam interference pattern.
Horizontal mag. 10X.

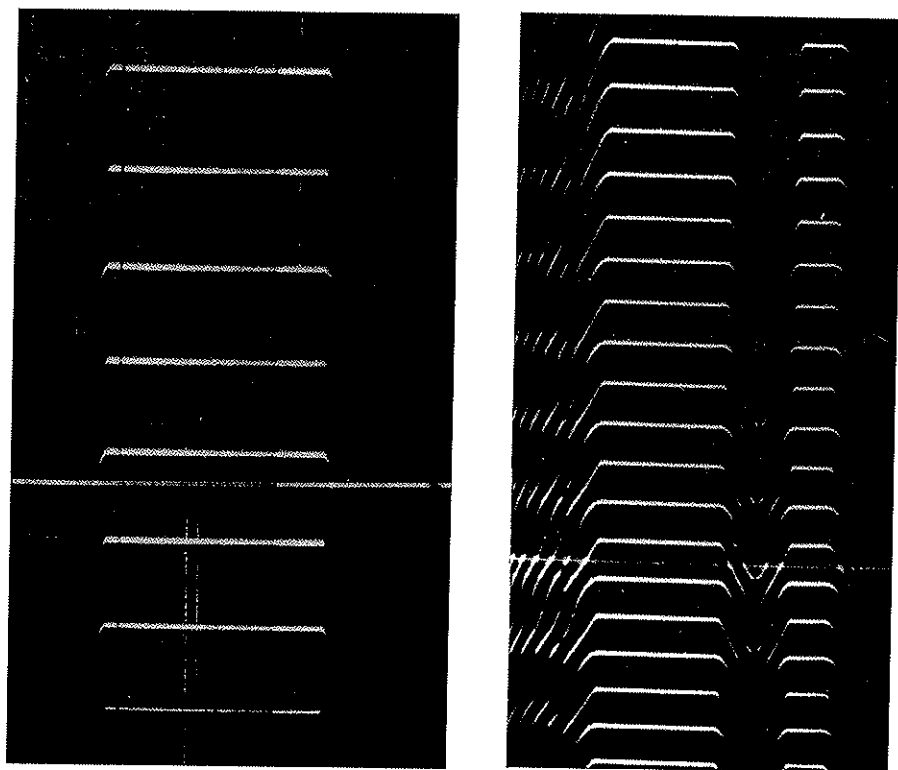


FIG. 4

- (a) Fringes of equal chromatic order between molecularly flat mica surfaces, in contact. (b) Fringes of equal chromatic order for surface separated locally by a small irregularity.

Dr. ANITA BAILEY [10, 11, 12] and Dr. SUSAN KAY [13] have been using this method to study the topography of cleaved mica surfaces and to prepare quite large surfaces which are molecularly flat. Muscovite mica is particularly suitable for this purpose (see Figure 5). In this mica SiO_4 tetrahedra are linked together hexagonally to form a two-dimensional

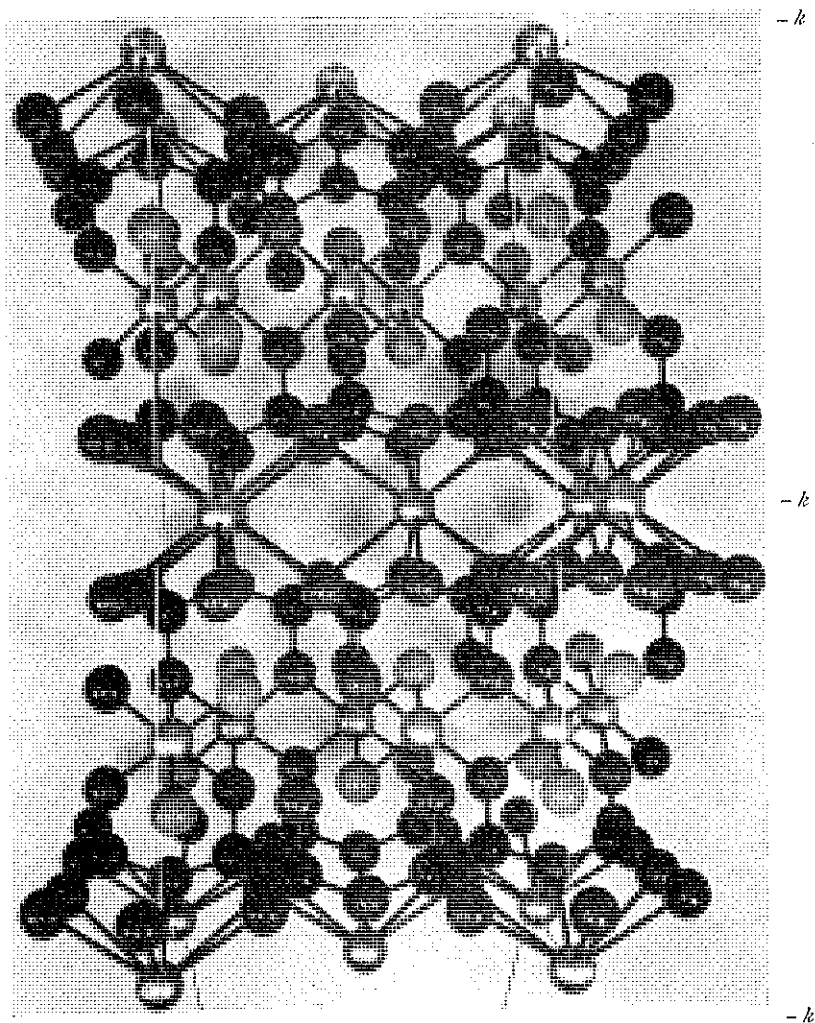


FIG. 5 — Arrangement of atoms in a unit cell of muscovite mica. The cleavage occurs along potassium atoms (*k*).

sheet. These are built up into double layers and linked together covalently by Al atoms. The bonding within each double layer is, therefore, strong. In the ideal structure of muscovite mica, a quarter of the Si atoms are replaced by Al atoms so that the unit gains a single negative charge. To balance this, the layers are ionically linked by potassium ions carrying a single positive charge. Since the K-O bonds are relatively weak, cleavage takes place parallel to the potassium planes (KK) in multiples of half the height of the unit cell (10Å). Over a given facet cleavage takes place between the same potassium planes. By stripping off a sheet of the material, it is possible to obtain facets which are of constant thickness over large areas of the surface. Since these areas contain no steps which are as high as 10Å we are justified in assuming that the surfaces are smooth to a molecular scale.

Transmission Electron Microscopy and Shadowing: Many lamellar crystals may, of course, be cleaved in a similar way to mica. Dr. R. FRINDT and Dr. A. YOFFE [14, 15] also FRINDT have for example prepared very thin flat crystals of molybdenum disulphide in this way which are less than 100 Å thick. Such crystals are mechanically unstable but they can be prepared if they are put onto a flat mica substrate where they are flattened and held to the surface by the attractive forces. The thickness of these crystals can be measured by observing in the electron microscope the width of the shadow cast by its edge onto the mica. Platinum is a suitable shadowing material and a carbon layer about 100 Å thick is then evaporated vertically on top of the platinum layer. The crystal is then floated from the mica surface by immersing it in water and it is examined by transmission in the electron microscope. A typical thin crystal prepared in this way is shown in Figure 6. The shadowing by platinum was done at an angle of 15° and then the approximate estimate of their thickness can be made. The height of the thicker crystal is ca. 25Å and that

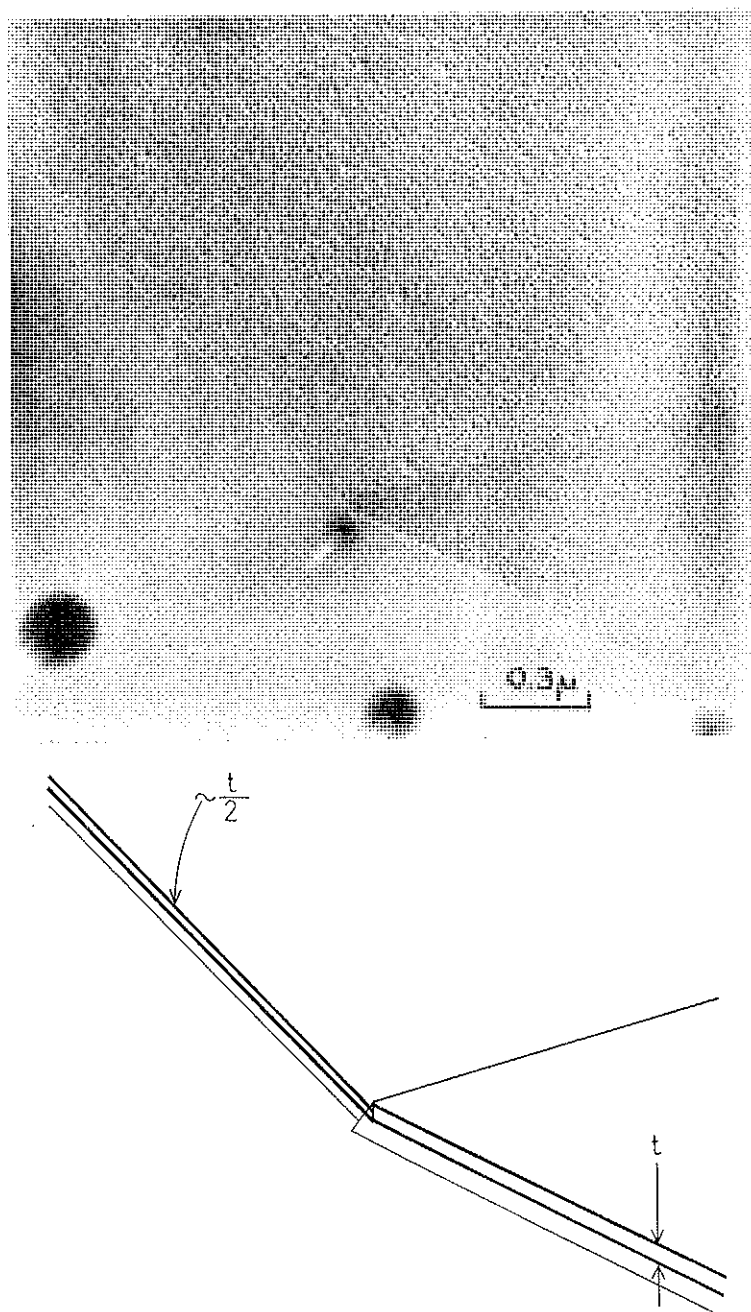


FIG. 6 — Very thin crystals of MoS₂. Thicker crystal is 4 molecular layers thick. Thin crystal may be 2 molecular layer thick.

of the thinner crystal about half this. In molybdenum disulphide the cleavage occurs between the neighbouring planes of sulphur and the thickness of the unit cell is $6.15\text{\AA}$. This suggests that the thicker crystal is about 4 molecular layers thick and the thinner crystal is perhaps two molecular layers thick. Alternatively it may represent a single molecular layer of molybdenum disulphide with a film of gas about $3\text{\AA}$ thick adsorbed on each side. Such crystals are very interesting because they are in effect 'all surface' and a study both of their physical and of their mechanical properties is of considerable interest.

2. THE DIRECT MEASUREMENT OF THE ATTRACTIVE FORCES BETWEEN MOLECULARLY FLAT SURFACES WHICH ARE VERY CLOSE TO ONE ANOTHER

In his introductory paper this morning Professor CASIMIR has given us an admirable account of the theory of the attractive forces between solids. He has, of course, played a major and pioneering part himself [16] in the development of this theoretical treatment. A simple point which emerges here is that for flat solid surfaces which are close (say $25\text{-}100\text{\AA}$) the unretarded van der Waals forces should vary inversely as the cube of the distance between them. For greater separations (say $1000\text{\AA}$) it will be the retarded van der Waals forces which are operative and the attractive forces should appear as the inverse fourth power of the distance. In the following paper Professor OVERBEEK has given a lucid and comprehensive account of the experimental studies which have been made in this field [17]. Most of the experimental studies of the forces at small distances are indirect and there is a considerable scatter in the results. At larger distances, however (ca. $1000\text{\AA}$) he has described delicate experiments by himself and his collaborators, by DERJAGUIN and his colleagues [18, 19] and

by KITCHENER and PROSSER [20]. At these distances the attractive forces are very small of the order of a dyne per square centimetre, but delicate measurements suggest that the force varies as the inverse fourth power. It has not been possible in these experiments to measure the forces at distances appreciably smaller than $1000\text{\AA}$ mainly because the surfaces are not truly flat so that local contact occurs between the solids. Clearly I cannot add anything to these two authoritative papers and what I should like to do is to describe some experimental studies which are being made in my own laboratory in an attempt to measure directly the attractive forces between molecularly flat solids which are much closer, i.e. in the range say $20\text{--}100\text{\AA}$. These studies are being made by Dr. ANITA BAILEY and Dr. SUSAN KAY [13]. For this purpose Dr. BAILEY has been using molecularly flat mica surfaces which are freshly cleaved. (This work has not yet been fully published - for a preliminary account see ref. 21 and for the discussion with DEBYE see ref. 22). The separation may be measured very accurately by multiple beam interferometry which may also be used to reveal the presence of dust particles and other contamination, and to show whether the surfaces are truly flat. The methods is as follows:

A thin sheet of mica is partially cleaved so as to be free from cleavage steps. If a spacer about 0.3 mm in diameter is inserted at the open end the sheets are flexed apart as shown in Figure 7. In the absence of interfacial forces the shape of the sheet near the point of bifurcation will be cubic and may be computed from the geometry of the situation. This is changed by the presence of interfacial forces for the following reasons. The surface forces may be considered as distributed loads which are very large near the point of bifurcation and fall off rapidly as the separation increases. These introduce additional bending moments which cause the point of bifurcation to move in and change the shape of the sheets around this region. The shape may be deduced from the interferometric measurements

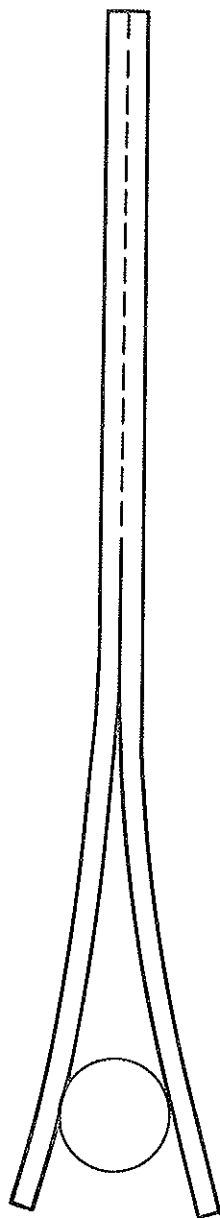


Fig. 7 — Flexing of a bifurcated mica sheet.

and compared with the hypothetical shape. In this way a measure of the interfacial forces may be obtained.

In order to simplify the analysis it is desirable that the two flexed beams should be of identical thickness. To achieve this in practice two sheets of mica are cut from a single facet known to be of constant thickness and molecularly smooth on both faces. These are allowed to adhere to form a single sheet which can then be separated by the cylindrical spacer as described above. The outer surfaces of the cantilever-pair are silvered so that they provide high reflectivity for the interferometric measurements. They are illuminated with collimated white light and fringes of equal chromatic order produced by the system are examined. The part of each fringe which is of constant wavelength corresponds to the regions where the mica

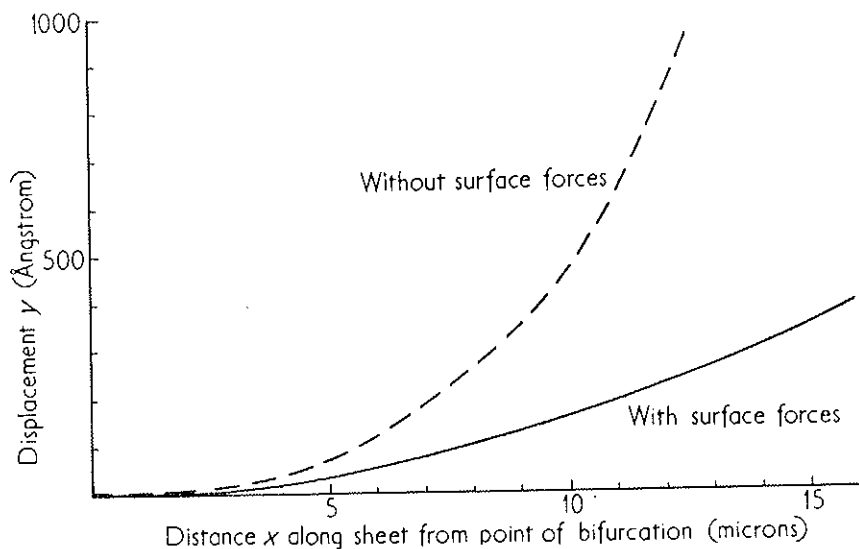


FIG. 8 — Shape of mica sheet as observed interferometrically. Broken line shows approximately the shape of the sheet to be expected if surface forces are absent.

sheets are intimately stuck together, while the part which deviates towards the red end of the spectrum corresponds to the region where the sheets are separated.

The final contour of the mica sheet is shown schematically in Figure 8 while the hypothetical shape assuming no interfacial forces is shown by the broken line. These two curves should of course join again at the point where the sheets touch the cylindrical spacer. It should be possible, from the change of shape of the sheet, to deduce the magnitude of the interfacial forces and so show how they vary in the separation of the surfaces down to distances which approach molecular dimensions. Dr. BAILEY has not yet quite completed these delicate measurements nor the full analyses of the results. It is clear that the attractive forces between the solids at these close distances are very large. Some approximate values, together with the results obtained by other workers at larger distances are summarised in the table.

TABLE I — *Range of Action of Surface Forces - Direct Measurement.*

Separation in Angstroms	Forces dynes/cm ²	
10,000 6,800	0.005 0.0045	KITCHENER and PROSSER [20] (Glass)
2,000 1,000	1.0 10.0	DERJAGUIN and ABRIKOSSOVA [18] (quartz)
100 20	1.5×10^6 300×10^6	BAILEY 1964 (mica)

It will be seen that when the surfaces are close together (20Å to 100Å) the observed attractive forces may be greater by a factor of 10^6 than those observed earlier at the longer distances where the separations were ca. 1000Å to 10,000Å. Typical values (expressed in kg) of the attractive force between mica surfaces in air are 300 kg/cm² at 20Å; and 1.5 kg at 100Å. The last figure is in good agreement with the estimate quoted by DEBYE [22]. These values must be accepted with caution at this stage but it is clear that the van der Waals forces can be extremely large when the surfaces are only a few angstroms apart. However they fall off very rapidly with distance and for separations greater than (say) 1000Å they are reduced to less than a millionth of their value at 20Å.

Variation with distance: In this particular experimental arrangement it appears that once the surfaces are separated by more than about 50Å the forces between the surfaces have comparatively little influence on the shape of the sheet compared with the forces operating at closer distances. It is therefore measuring the shorter range London-van der Waals forces and not the retarded forces predicted by CASIMIR and LIFSHTZ. Although the analysis is not yet complete, Dr. BAILEY's experiments show that with a separation of the two surfaces between 20 and 50Å, the attractive forces between them falls off as the inverse cube of the distance as predicted by the London theory. For separations below 20Å the decreases of the force with distance is certainly less rapid than a third power law and attempts are being made to analyse this interesting region.

The method is a powerful one and attempts are being made to extend it to other solids and also the study of the influence of other media on the attractive forces.

3. INFLUENCE OF ADSORBED VAPOUR MOLECULES AND OF IMMERSION IN A LIQUID ON THE WORK REQUIRED TO SEPARATE SURFACES

Dr. SUSAN KAY [13] working in association with Dr. BAILEY has carried out further work in attempting to measure the influence of adsorbed monolayers and of immersion in a liquid on the work of separation. Again the experiments were done on mica surfaces and they gave a measure of the surface energy of mica under these conditions. The principle of the method is illustrated diagrammatically on Figure 9. Fresh surfaces of mica are produced by cleaving a thin strip of the material. These strips were cut from a larger sheet of constant thickness and cleavage was initiated at the centre. Vertical forces F are applied to the open ends of the strip so it assumes an equilibrium shape shown in the Figure. The cleaved portion of the strip lies horizontally and the two cleaved sheets are equally deflected. The apparatus for performing this experiment is illustrated in Figure 10.

The total energy supplied to the mica sheets during cleavage is expended in two ways, firstly in producing new surfaces and secondly in the elastic deformation of the mica. Since the elastic properties of mica sheets are known, the surface energy of the mica can be determined. The experiments can be carried out in different vapours or liquids or with various adsorbed layers on the surface. The experiments show that the cleavage can take place over surfaces which are atomically smooth. The area of new surface exposed is measured by multiple beam interferometry as before, and a typical picture of the interface fringes between the sheets is shown in Figure 11. Experimental values for the surface energy of mica obtained by her by this methods are given in Table 2.

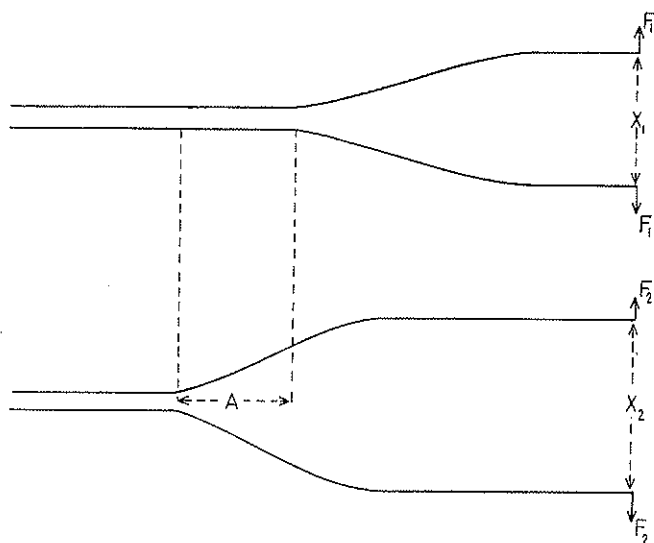
TABLE 2 — *Surface Energies of Mica*

Condition	erg/cm ²
Clean in high vacuum Clean, exposed to air	5000* 300
Adsorbed water vapour Immersed in liquid water	180 110 Difference = 10 = γ of water
Adsorbed hexane vapour Immersed in liquid hexane	271 255 Difference = 16 = γ of hexane
Monolayer of Lauric Acid $C_{11}H_{23}COOH$	37

* OREIMOFF [23], OROWAN [24] and BRYANT [25].

The cleavage plane of mica may be considered to contain an array of positive potassium ions imbedded in a siliceous matrix. When cleavage occurs in vacuum the main forces which have to be overcome arise from Coulombic attraction between the positive potassium ions and the negative holes they leave [26]. This gives the large value of γ 5000 ergs/cm².

If the surface charges are neutralised by exposure to a source of radiation (or simply by leaving in the air) these charges are neutralised. The remaining interfacial forces now arise from van der Waals forces. The experiments described earlier which were done in air give a measurement of such forces modified by the presence of adsorbed surface films of various types. It will be seen that the effect of air containing a small amount of water vapour is to reduce the surface energy to about 300 erg/cm².



$$W = \text{EXTERNAL WORK DONE} = \int_{F_1}^{F_2} F dx$$

= INCREASE IN ELASTIC STRAIN
ENERGY E IN MICA + INCREASE
IN SURFACE ENERGY OF MICA.

$$\underline{W = E + 2A\gamma}$$

FIG. 9

Effect of specified surface films: From the Table 2 we see that for an adsorbed monolayer of water vapour on mica $\gamma = 180$ ergs/cm²; for mica completely covered with water $\gamma = 110$ ergs/cm². The difference is 70 ergs which is the surface energy of water and corresponds to the perfect wetting of the monolayer by the water. Similar agreement is shown for hexane C₆H₁₄. For hexane vapour $\gamma = 270$ ergs/cm², if the surfaces are immersed in liquid hexane $\gamma = 255$ ergs/cm². The

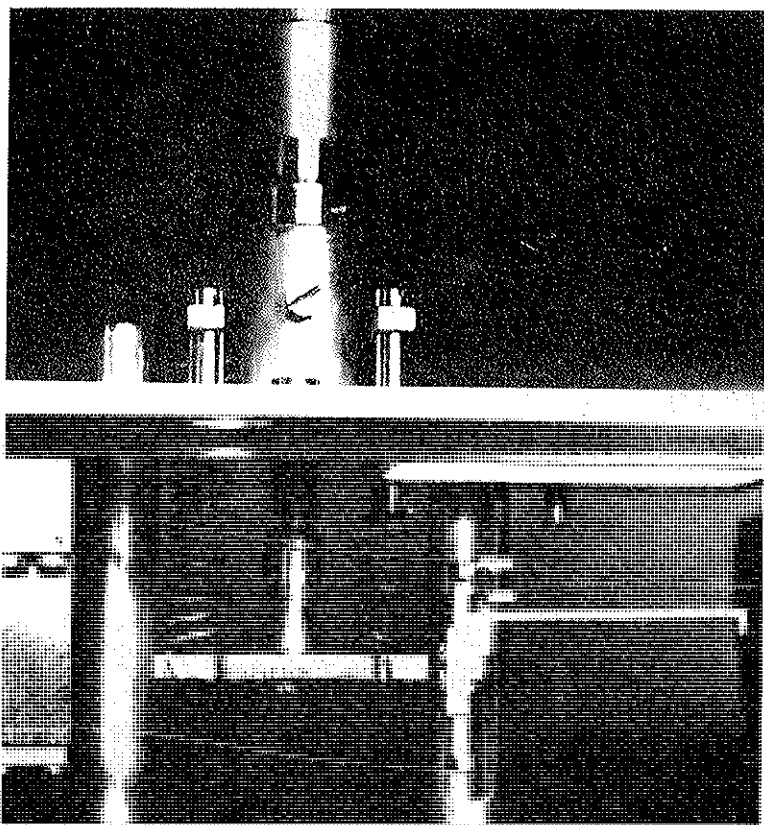


FIG. 10 — Dr. KAY's apparatus for measuring the work required to separate mica surfaces. The opening mica sheets are shown at M.

difference between these two of 16 ergs/cm^2 corresponds to the surface energy of hexane. It is interesting to note that the non-polar liquid like hexane produces a far smaller reduction in the surface energy than a polar liquid like water.

Apart from their relevance to our present discussion these

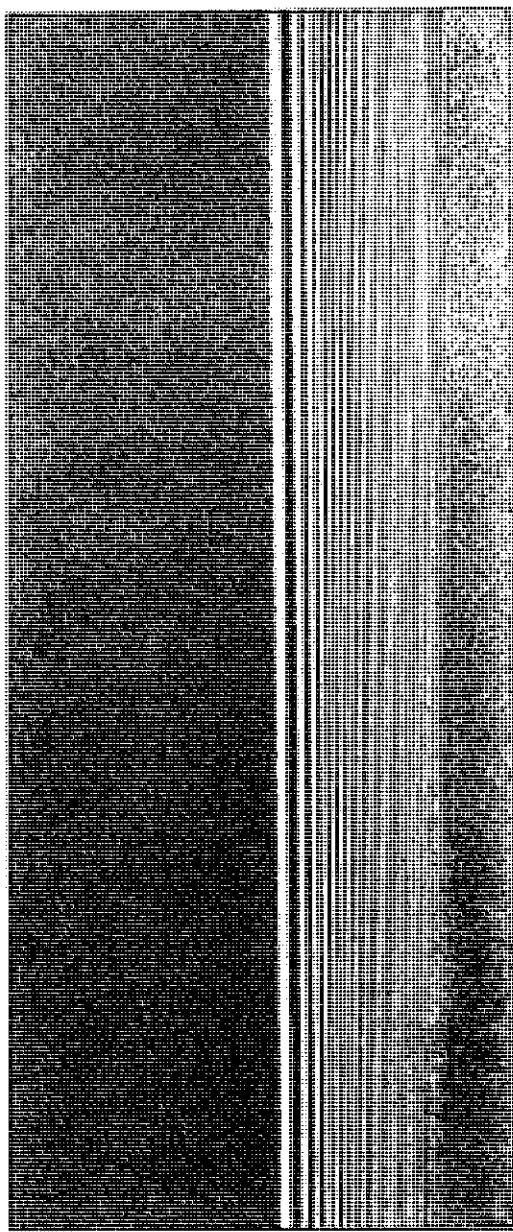


FIG. 11 — Fringes between mica sheets opening at A-B. Uniform dark region represents molecular contact.

observations of Dr. KAY are important because they provide the first direct experimental verification of Young's equation that

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$

where γ_{sv} is the interfacial energy of the solid in contact with saturated vapour of the liquid;

γ_{sl} the interfacial energy between the solid and liquid phases;

γ_{lv} is the interfacial energy of the liquid in equilibrium with its vapour

and θ is the equilibrium contact angle between the solid and liquid surfaces.

Surface energy of a long-chain organic molecule adsorbed on mica: Dr. KAY has also carried out the experiments with mica surfaces on which a molecular layer of a long chain fatty acid was adsorbed. Lauric acid was used (see Figure 12). The surface energy is reduced to a very small value, 37 ergs/cm². This value agrees reasonably well with the observation that the surface is just wetted with liquids of surface tension about 35 erg/cm². In these experiments the mica sheets started by being ca. 30Å apart (assuming the acid is oriented normally to the surface). The force from the mica surfaces themselves will contribute in some measure to the work of separation. It is clear that the attractive forces between the CH₃ groups is small.

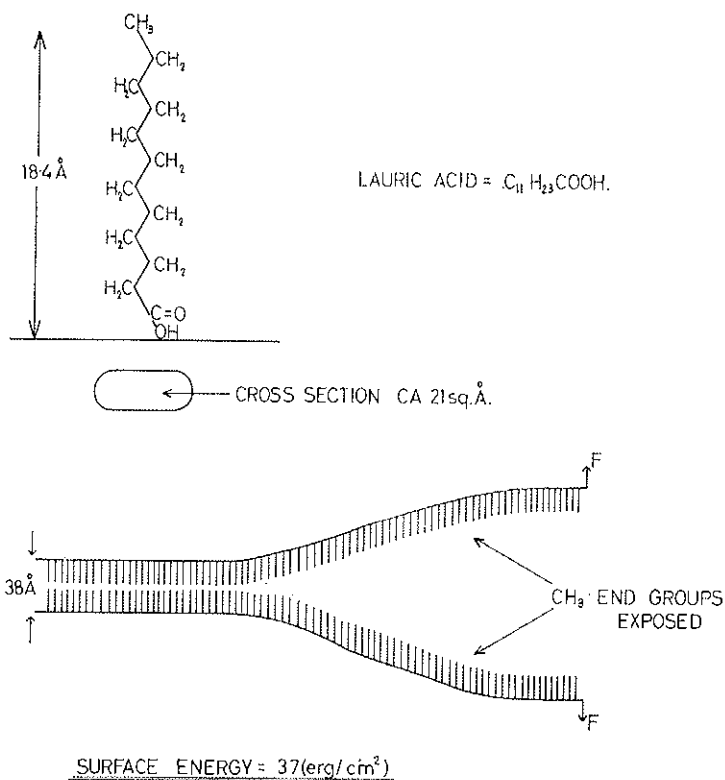
SURFACE ENERGY OF MONOLAYERS OF LAURIC ACID ON MICA

FIG. 12 — Opening of mica sheets covered with monolayer of lauric acid.

CONCLUSION

I think the use of these sensitive physical methods and the preparation of molecularly flat surfaces provides a new and powerful experimental approach to the study of surface forces

and of a number of other surface problems. The work is being extended both to closer and to larger distances and to further studies of the influence of the interposed medium or of adsorbed films on the surface forces.

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DISCUSSION

Chairman: H.B.G. CASIMIR

WIDOM

I would like to ask you Prof. BOWDEN, if anything is known about the electrical nature of a freshly cleaved surface, either what might be left just from the rupture of chemical bonds or any charges that might be captured from the atmosphere or subsequently lost to the atmosphere?

BOWDEN

The evidence is pretty clear that, with muscovite mica, the cleavage occurs across a plane of potassium ions embedded in an aluminosilicate matrix. When cleavage occurs approximately one half of the potassium ions remain in each surface leaving a corresponding number of negative holes in the opposite surface. This process would give a theoretical value for the surface energy of mica cleaved in vacuo of ca. 5000 ergs/cm², and this is in agreement with experiment. The presence of air and of water vapour will neutralise these charges and reduce the surface energy to about 300 ergs/cm². The usual precautions are taken to neutralise any free charge on the surface so that we are concerned primarily with van der Waals forces.

CASIMIR:

I should like to ask: is any-one willing to say something about what to expect for the van der Waals' attraction at very short distances? It is quite logic that it could not go on like $(1/r^3)$ so that indeed you would not be able to pull the mica apart at all and would break it, so it must approach to some constant value. Would any of you have a suggestion what it might look like?

OVERBEEK

I would like to suggest, that in the region of separation of the order of a few angstrom units certainly something like a BORN repulsion should come in, that might be measured as a decrease of the van der Waals force: you find a smaller value than you should find, isn't it? This may be a repulsion by the size of the molecules present, either the mica as such, or perhaps the layer of air that is absorbed on it.

BOWDEN

I agree. As I mentioned Miss BAILEY is attempting to analyse her results in this region of small separation. The van der Waals forces fall off as a much smaller function of the distance than the third power. We must also take into account the fact that there will be an adsorbed layer of gas on each surface of (say) $3\text{\AA}$ in thickness which would make a layer of (say) $6\text{\AA}$ separating the mica surfaces. It is an interesting region.

GRIMLEY

I was just going to mention that in connection with these forces at such short distances, it is going to be very important to know

that you have a clean surface. I also have a question to ask you, in connection with your experiments with mica. You put up a slide which said « clean in high vacuum ». What is high vacuum?

BOWDEN

If we have a vacuum of 10^{-9} to 10^{-10} tor it would take several hours before the number of molecules which could reach the surface would be sufficient to form a monolayer of contaminant. Once on the surface, however, these films are difficult to remove merely by putting the surface in a high vacuum. It is necessary to drive them off by heating or else to expose a fresh surface by cleavage or in some other way.

OVERBEEK

I first want to say how very greatly I admired the beautiful work that has been done in Dr. BOWDEN's Institute, and the clear way it was presented. There are two points on which I would like to make a comment. In the case where, if I understood it correctly, you measured the difference in surface energy of the mica with and without absorbed water or hexane, you find that the differences between the surface energies correspond rather nicely to the surface tensions of these substances. Now, later you talked about the lauric acid and mentioned a surface energy of 37 ergs per cm^2 . Was that also a difference, and if it was not, where has the influence of the attraction between the mica layers themselves disappeared?

BOWDEN

That is a good point. The 37 ergs is probably close to the surface energy of the CH_3 group on the lauric acid molecule but we

have evidence that the mica is still making itself felt at this distance of 18Å. It will be interesting to see the effect of using molecules with much longer chains.

OVERBEEK

The other remark I would like to make is about this layer of liquid in the neighbourhood of a surface which has, let us say, funny properties. There was a recent calculation by STIGTER on a very simple experiment. It concerns the viscosity of a solution with a few percent of micelles of sodium lauryl sulphate and using the Einstein equation (η solution = η solvent $(1 + 2.5 \varphi)$) to derive the effective volume of the micelles. This shows that the micelles are surrounded by layers of water not thicker than one hydration layer around the charge groups. So here is, I think, independent evidence that the water in the neighbourhood of a surface is not changed, at least not in its viscosity properties.

BOWDEN

Could I ask about the hydration layer. How many molecular layers will it be?

OVERBEEK

This is one molecular layer around the charged sulphate groups, so I think four water molecules per sulphate group, and that evens out practically to one molecular layer of water around the hydrocarbon core of the micelle.

BOWDEN

I think this is an interesting and important point, and one of the reasons that I raised it is because it is of interest to the biological

people. I have had a number of discussions with biologists and physiologists, and under many circumstances, they would like to postulate a thick layer of pure water in contact with their biological surfaces which has got properties very different from that of normal water. I have been able to give them small comfort. It seems to me that physicists have very little solid evidence for this, and I am most interested to hear your comments there.

LYKLEMA

May be. I may also comment on the question of the supposed highly viscous layers on surfaces. In my following talk « Molecular forces in thin films », I will mention an example of a direct measurement of the viscosity in a thin liquid film where it was found that the surface layer with higher viscosity, has a zero thickness with an accuracy of 8 Angström units. This is a direct measurement.

In connection with this I looked over the evidence collected in several experiments by DERYAGIN and collaborators and found that at least in one case perhaps an alternative explanation is possible. In this experiment a little slug of water is blown through a narrow capillary by application of a slight pressure difference between the ends of the capillary. The rate of flow can be calculated using the Poiseuille equation, and that agrees very well, with the experiment, which means that the viscosity is normal. However, if the experimentators let it stand for two or three days, and then came back and repeated the measurement they found that the viscosity was a factor higher. After pushing the water forward and back a few times the viscosity retained again its normal value, DERYAGIN c.s. explained this by saying that if one allows the water a certain standing time — say a week-end — then a kind of structure formation takes place in the liquid in that narrow capillary. However it is also possible to explain the observed effect quantitatively by assuming that after standing the receding and advancing contact angles between the liquid and the silica surface

are a little bit different. One needs only a slight difference to have a Laplacian counterpressure which can readily account for the observed effect. After rewetting of the capillary the two contact angles become equal again. Summarizing the experimental evidence I am inclined to agree with OVERBEEK that there is, at least in aqueous systems, at this moment, no positive indication of the existence of thick viscous layers.

BOWDEN

There seems to be one other point in the use of glass and silica surfaces and so on in the presence of a liquid like water. We know very well that they attack the surface and give us a gel on the surface, and my own view is that some of these effects particularly on the earlier experiments, are due to the fact that you have a gelatinous layer of silica gel on the surface, and naturally its viscous properties are not the same as that of water.

FIXMAN

There have been many statistical mechanical calculations on the behaviour of simple liquids near surfaces, especially on the value of density as a function of distance from the surface. Generally speaking these calculations give just what you would expect. At roughly the range of the radial correlation function away from the surface, the density returns to its macroscopic value.

GRIMLEY

At the end of his talk Dr. BOWDEN has this query. How many monolayers are adsorbed on a solid? I want to emphasise that this question is meaningless until we specify what is being adsorbed,

and on what solid. There is always the question of chemical reaction which Dr. BOWDEN himself has mentioned in the case of water on glass. But may I also draw your attention to something rather curious in the system carbon monoxide on tungsten for example. This is a gas-solid system. Workers with the ion microscope have seen patterns which they have interpreted to say that the carbon monoxide is incorporated into tungsten several layers below the surface. Now, I do not say that I necessarily agree with this interpretation, but it has been proposed, and I think one should bear this possibility in mind when we are talking about how many layers are adsorbed on a solid.

BOWDEN

I was interested to hear those comments from Professor GRIMLEY. I would agree that if we have chemical adsorption, i.e. chemical reaction with the surface, then you can build up thick layers (e.g. oxide layers on metals). Also if the gas penetrates the surface then you can have a structure occurring to a considerable depth. I was really asking about physical adsorption on the surface. What evidence have we that it can be more than about two molecular layers? This is a meaningful and real question.

SCHWAB

This situation is very complicated. Besides biologists, there is another group of people who need some comfort in view of your result of the one or two layers which can be absorbed on a flat surface, that is, all those people who determine the internal surface of a porous solid by using the BET equation. They assume that on a surface a first layer is formed with an adsorption energy higher than the energy of evaporation, all the subsequent layers are formed through forces which are equal to the heat of evaporation.

puration. We know very well that this model is not right; it cannot be right because in the theory it is even assumed that second and third layers are formed even at places where the first layer has not yet been formed. However, the funny part is that, on the basis of the evaluation of this BET theory, we get consistent and right values of the internal surface of the porous solid. There is no doubt that in reality what happens is capillary condensation with a concave meniscus in narrow pores which develops a diminished vapor pressure. I find it very surprising that the simple BET theory although it was in contradiction to your experiments and also to logics gives the right value for the surface of a porous solid.

BERNSTEIN

In connection with the forces at short distances between absorbed molecules and surface, about ten to fifteen years ago there was considerable activity in the field called surface-diffusion. Anomalously high mobilities were observed for molecules adsorbed on certain surfaces in the fractional-monolayer range. There were interesting studies on relative mobilities of isotopic molecules as a functional of fractional coverage and there was a good deal of both experimental and theoretical activity. Since I am not in the field I would like to ask whether this type of study has led to any fruitful understanding of the surface forces in the first adsorbed layer. Is this field now active, and has it produced any conclusions of interest to this group studying molecular forces?

SCHWAB

I can safely say that in the beginning it has been shown that this ideal of mobile adsorption can explain the kinetics of chemical reactions on surfaces equally well as the notion of a fixed immobile adsorption, but it appears that chemisorption in most cases is not a mobile adsorption; this comes out also from the entropy

factor of adsorption. So it would appear that this has not really been a fruitful approach, although of course there are examples with a very surprisingly high mobility on the surface, the famous experiment of Volmer for instance, where you have the crystal of benzophenone and mercury dropping on the crystal; a crystal became thinner and thinner, not only where the mercury dropped, but over its whole surface.

BOWDEN

There is of course much evidence that foreign atoms on a surface can be highly mobile. For example PASHLEY's work in the electron microscope has shown not only that metal atoms evaporated into a solid substrate move rapidly to form small crystalline units but that these units themselves can move readily, over the surface to aggregate as larger ones.

CASIMIR

Perhaps I might suggest the following formula $F = \frac{A}{(a+a_0)^3}$. This would account for instance for a case where the surfaces of the mica don't really approach but are kept apart perhaps by very small irregularities of the order of a few Angström. It is a trivial way of approaching this thing but there seems to be some reason in it.

LYKLEMA

Prof. BOWDEN has given a table containing two values for the attractive force, viz. at 20 and 100 Angström units separation. From these forces a Hamaker constant of 3.5×10^{-11} ergs can be calculated. This seems rather high. Does this agree with other results obtained with mica?

VAN DER WAALS FORCES - II

H.B.G. CASIMIR

Philips Research Laboratories
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Before we finish for the day, I should like to make a few concluding remarks. I shall not try to summarize everything that has been said today, for it has been, in my opinion, a rather well-filled day, with a lot of interesting things that have been communicated and discussed.

But perhaps I might try to touch upon a few points.

If we look at the theory many aspects seem to be rather well understood. Although in the interaction between atoms other terms can occur, I think we can safely say that at fairly large distances, let us say at several atomic radii, perhaps 10 or slightly more, at least for neutral and non-magnetic atoms or molecules which have no permanent moments and so on, the van der Waals' force is the largest term by far and there is nothing that could be very much wrong with it. That follows also from experiments. Only at a higher rate of sophistication and precision there are a number of other effects to be considered.

Of course, if we speak about polar molecules, if we speak about excited molecules and what not, a number of other effects might occur which are perhaps not so relevant for the discussions of today.

I think that also the theory of the retarded van der Waals' force for neutral, normal polar atoms or atomic systems is well in hand, and it can be derived formally in many different ways, and therefore I have also decided not to try again to summarize today the theoretical background, because I felt that there were other things of greater interest to be discussed in the course of our meeting.

The next point is the force between solid large scale bodies. There again the theory of attraction between perfectly conducting flat plates and also Lifshitz' theory for attraction between dielectric media is well established, although I would still like personally to see a derivation of Lifshitz' formula on slightly more elementary lines, more like the one I gave for conducting metal plates than the one he has given. However, there again we can be confident that the theory is correct and it is therefore satisfactory that we find in regions where this theory should prevail, as OVERBEEK has shown, a fairly good agreement between theoretical predictions and experimental results.

And there is no reason to doubt, that if one would go even further in increasing the precision of those measurements, further agreement would be reached.

In the intermediate region between isolated atoms and macroscopic bodies, the situation is more complicated, and that is the domain, properly speaking, of the colloid chemist who is dealing with dimensions of perhaps 100 or 1,000 Å units, and where there are many complicated things to be taken into account, which makes the quantitative agreement rather less satisfactory.

Perhaps I might say, as a physicist — to reply to remarks of VERWEY about the chemist — that a physicist feels at ease when he is dealing with one, preferably simple, atom, where he can reach a very high degree of precision in the agreement between theory and experiment. And he also feels at ease with macroscopic measurements where he can measure well-defined macroscopic quantities. In between, in the regions of

some 100 or 1,000 Å units he feels less happy and that is where the chemist starts complicating things, that is the region where such unexpected things like living cells and large molecules occur which for a physicist are always slightly disconcerting.

I think it has been very gratifying to see today that in that very difficult and, of course, extremely important range, the theory is now in much better shape than it was many years ago, and that at least a semi-quantitative picture arises which accounts for many of the phenomena. And although a physicist might like even closer agreement between estimated van der Waals forces and those you need in order to explain the observations, yet on the whole there is at least so much agreement that one can feel that the picture is essentially right.

However, some difficulties have been pointed out which will deserve further attention, especially the possible existence of another mechanism of repulsion at short distances, or a correction to the van der Waals' forces at short distances, or something along those lines.

The very beautiful experiments reported by Dr. BOWDEN on forces between very flat surfaces at close distances should in a way be able to bridge that gap, and might be perhaps regarded as a physicist reaching out a hand from the truly macroscopic domain into the 100 Å region, which is dear to the colloid chemist.

An idea that occurred to me in connection with the thin film work, although I do not really expect that anything will come out of it, is the following point: the way of calculating the forces for material objects by integration of retarded or non-retarded van der Waals' forces, is of course a make-shift procedure, but as was shown by OVERBEEK it happens to give only fairly small errors when applied to the particular case of two dielectrics approaching one another.

Now, although I do not expect that in the case of these liquid films the situation will be far different, yet one should

give some thought to the matter. The notions of Lifshitz' theory, or of the simple theory I gave for the metal plates cannot be applied immediately without modification to this particular case. The situation is slightly different, because you have to change the material inside which the radiation field exists — it is not a question of only changing the geometry inside a cavity by shifting two blocks of dielectrics around. Someone who is really good at such things might take up the calculations and might possibly find that the deviations between the simple integration theory and the exact quantum mechanical theory are greater than they are in the case of two attracting dielectrics. Once more I do not expect it, but it might be worth-while to settle the question. Summarizing I should like to say that we have been confronted with a very impressive series of experimental results which in a rather gratifying way, bridge the gap between large scale macroscopic phenomena and between the theory of atomic forces.

Well, I should now like to close this meeting, thanking once more our speakers of today, and all those who took part in the discussions. Thank you.

DISCUSSION

Chairman: H.B. CASIMIR

CASIMIR:

I could perhaps try to clarify a topic, the question of van der Waals interaction between excited atoms or molecules. I have discussed this question in the meantime with professor HIRSCHFELDER who showed me some relevant papers ⁽¹⁾.

First consider two identical atoms or molecules at such a distance that charge densities do not overlap. Consider the fundamental state O and an excited state I. Now if the first atom is excited and the second is not the wave function can be written as $\Psi_1^{(1)} \Psi_0^{(2)}$.

The state is degenerate with a state where atom 2 is excited and 1 is not, described by $\Psi_1^{(2)} \Psi_0^{(1)}$. The correct wave functions taking in to account interactions are

$$\Psi_{\pm} = \Psi_1^{(1)} \Psi_0^{(2)} \pm \Psi_0^{(1)} \Psi_1^{(2)}$$

Now how about radiative transitions to the ground state? If the distance is small compared with the wavelength and if the individual atoms radiate as dipoles, then the transition $\Psi_{+} \rightarrow \Psi_0$ corresponds to the radiation of two synchronous dipoles, but in the transition

⁽¹⁾ STEPHEN M.J., « J. Chem. Phys. », 40, 669 (1964); PHILPOTT M.R., « Proc. Phys. Soc. », 81, 619 (1966).

$\Psi_- \rightarrow \Psi_0$ the two dipoles are in opposite phase and there will only remain a quadrupole radiation. If $R \ll \lambda$ the life time of this state will be longer by a factor $\left(\frac{R}{\lambda}\right)^2$. In this state the interaction will be of the order q^2/R^3 and definitely not retarded. If on the other hand $R \gg \lambda$ then the life times of Ψ_+ and Ψ_- will not differ very much; this corresponds to the fact that in this case one atom can only intercept a minute fraction of the radiation emitted by the other atom. The interaction should now be proportional to $1/R$. However, as Stephen points out this interaction is always small compared to the natural linewidth and has no physical significance.

We can discuss in a similar way the interaction between an excited atom and a non resonant atom or larger system. If $R \ll \lambda$ there is a slight change of lifetime but considerable interaction between the dipole and the induced dipole. If on the other hand $R \gg \lambda$ then the electric field at a distance R is given by

$$E \sim q/\lambda^2 R$$

This gives rise to a polarisation $\alpha q/\lambda^2 R$ which in turn leads to an induced field

$$E_{ind.} \sim \alpha q/\lambda^4 R^2$$

and an interaction energy

$$\Delta_i. U \sim q^2 \alpha / \lambda^4 R^2$$

On the other hand the natural line width is

$$\Delta_n. U \sim q^2 / \lambda^3$$

and therefore

$$\frac{\Delta_i U}{\Delta_n U} \sim \frac{\alpha}{\lambda R^2}$$

Now we may write $\alpha \sim A^3$ where A is something like the radius of the polarisable system and for any realistic arrangement we must expect $A^3 \ll \lambda R^2$.

For an atom near a perfectly conducting plate we will have

$$\Delta_i U = \frac{q^2}{\lambda^2 R}$$

corresponding to an effective polarisability

$$\alpha \sim \lambda^2 R$$

so even in this case

$$\frac{\Delta_i U}{\Delta_n U} \sim \frac{\lambda}{R} \ll 1$$

The conclusion is that no interesting effects can be expected at distances where retardation is essential.

HIRSCHFELDER

I should like to thank you much for this very clear explanation. These points have been very puzzling to me and I think to many other people. There is one question that I would like to ask you. I am puzzled over the application of your CASIMIR and POLDER retardation formulas to the interaction

of water molecules at very large distances. Water molecules have prominent dipoles so that there are permanent dipole interactions rather than just van der Waals interactions. The Boltzmann averaging of the dipole-dipole interaction should produce an energy of interaction which varies as $1/R^6$.

CASIMIR

I do not think so. The interaction between stationary static dipoles does not show retardation effects. Of course since dipoles are rotating and suffering collisions, there may be some corrections; I think they will be small.

VERWEY

The frequencies of rotations and collisions are much lower than the excitation frequencies of atoms. Therefore retardation will only occur at much larger distances than for van der Waals interaction. This means that there will be no retardation effects at distances that are of any practical interest.

CASIMIR

Yes, I think that answers the question.

HIRSCHFELDER

It is really important to look into the long range interactions between the water molecules, since many practical applications are being made. The thermal averaging of the dipole-dipole forces, of course, produces an R^{-6} energy of interaction. It would be interesting to see whether this changes with distance due to retardation.

OVERBEEK

I want to add to Dr. VERWEY's remarks that the relaxation region where the dielectric constant of water goes over into the value of about 2 is in the order of cm, waves and that would mean that the retardation effect would only come in when the distances are as large as that. The other remark I would like to make is that although the van der Waals constant for bulk water is not yet very well known it is certainly in good agreement with the dielectric constant devised from optical properties, so a dielectric constant of the order of 2, if that is plugged into the Lifshitz equation, but not with a dielectric constant of 80, which seems to point out that the dipole contributions are negligible there. My explanation of this has been that the additivity of the dipole interactions between large numbers of dipole molecules in water are only vectorially additive, so that they cancel out to a very great extent, whereas the dispersion effects are additive to a much larger scale and that is why one can measure them even at distances of the order of 500 or 1000 Å.

BERNSTEIN

I have a few comments to make to Professor OVERBEEK with regard to the measurements of the forces between parallel plates at distances of the order of 1000 Å. He mentioned the difficulty of making the measurements in liquids (for example, in water). I suggest that one consider the use of electroetched glass plates, etched quartz or metal plates are also commercially available now. By a suitable cross-hatched channel structure one could remove only about 50% of the surface area, but so design the channels that there would be a much lower viscous resistance to the flow. Thus one could reach equilibrium in much less than the time of equilibrium (about one week) estimated for flat plates.

OVERBEEK

I feel really rather ashamed that this has to be pointed out to a Dutchman who is used to digging ditches in his meadows to get them drained and that I have not seen that this idea could be applied to the plates. Thank you for this suggestion.

HIRSCHFELDER

In the experiment in films described by Dr. LYKLEMA and in the long range interactions of micelles, it would seem to me that dipole-dipole forces of the Keesom type should be larger and more important than the Casimir-Polder retarded van der Waals interactions. I do not believe that sufficient attention has been given to the possibility of these long range dipole-dipoles being large. From the experimental standpoint, the Keesom energy varies as $1/R^6$ where as the Casimir-Polder energy varies as $1/R^7$. I do not know whether the experiments can distinguish between these different dependencies on separation.

LYKLEMA

It might be easier to distinguish experimentally between a retarded 4th power and a non-retarded 3rd power in the interaction between macroscopic bodies (i.e. after summation or integration over all molecular contributions) than between a 6th and 7th power in the interaction between atoms.

BUCKINGHAM

The long-range dipolar coupling between polar molecules should lead to an attractive central-force potential varying as R^{-6} and

showing retardation effects only when the separation is extremely large where the interaction energy is negligible.

Consider two isolated macroscopic spheres of volume V_1 and V_2 separated by a distance R . If their instantaneous dipole moments are $\mathbf{M}_1$ and $\mathbf{M}_2$, the dipole interaction energy is

$$u = \frac{1}{R^6} \{ R^2 \mathbf{M}_1 \cdot \mathbf{M}_2 - 3 (\mathbf{M}_1 \cdot \mathbf{R}) (\mathbf{M}_2 \cdot \mathbf{R}) \}$$

and this averages to zero if all directions for $\mathbf{M}_1$ and $\mathbf{M}_2$ are equally likely. However, there is a coupling between these dipoles and this leads to a mean interaction energy of the Keesom type:

$$\begin{aligned} u &= \iint u \exp(-u/kT) d\tau_1 d\tau_2 / \iint \exp(-u/kT) d\tau_1 d\tau_2 \\ &= - \langle u^2 \rangle / kT = - \frac{2}{3} \frac{kT}{R^6} \frac{\langle M_1^2 \rangle \langle M_2^2 \rangle}{R^6} \end{aligned}$$

where the brackets $\langle \rangle$ denote unweighted averages. The mean square dipole moments of the spheres can be expressed in terms of their bulk dielectric constants:

$$\frac{4\pi \langle M_1^2 \rangle}{9 kT V_1} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} = \frac{\epsilon_{\infty 1} - 1}{\epsilon_{\infty 1} + 2} = \frac{3(\epsilon_1 - \epsilon_{\infty 1})}{(\epsilon_1 + 2)(\epsilon_{\infty 1} + 2)}$$

where ϵ_1 and $\epsilon_{\infty 1}$ are the static and high-frequency dielectric constants of the material comprising sphere 1. Hence

$$\frac{u}{V_1 V_2} = - \frac{243 kT}{8 \pi^2 R^6} \frac{(\epsilon_1 - \epsilon_{\infty 1})(\epsilon_2 - \epsilon_{\infty 2})}{(\epsilon_1 + 2)(\epsilon_{\infty 1} + 2)(\epsilon_2 + 2)(\epsilon_{\infty 2} + 2)}$$

If the spheres are comprised of highly dipolar materials, $\varepsilon \gg \varepsilon_\infty$ and ε_∞ is normally approximately 2 for a condensed phase. So at room temperature

$$\frac{u}{V_1 V_2} = -10^{-14} R^{-6} \text{ erg cm}^{-6}.$$

The London formula for the dispersion energy is

$$\frac{u_{\text{disp}}}{V_1 V_2} = \frac{3\alpha_1 \alpha_2 u_1 u_2 n_1 n_2}{2(n_1 + n_2) R^6} = -\frac{27 u_1 u_2 R^{-6}}{32 \pi^2 (u_1 + u_2)} \left(\frac{\varepsilon_{\infty 1} - 1}{\varepsilon_{\infty 1} + 2} \right) \left(\frac{\varepsilon_{\infty 2} - 1}{\varepsilon_{\infty 2} + 2} \right)$$

where α_1 and u_1 are molecular polarisabilities and ionisation potentials, and n_1 is the number of molecules per unit volume. Hence $4 \pi n \alpha / 3 = (\varepsilon_\infty - 1) (\varepsilon_\infty + 2)$. Hence for $u_1 = u_2 = 10^{-11}$ erg

$$\frac{u}{u_{\text{disp}}} = 0.4$$

Actually, at large separations the dispersion energy is retarded and varies as R^{-7} , so at these distances u may be dominant.

For spheres in a medium of static dielectric constant ε_0 (see H. FRÖHLICH, *Theory of Dielectrics*, Second Edition 1958, p. 181),

$$\frac{4 \pi \langle M^2 \rangle}{9 k T V} = \frac{(\varepsilon - \varepsilon_\infty) (2 \varepsilon_0 + 1)^2}{3 (\varepsilon + 2 \varepsilon_0) (\varepsilon_\infty + 2 \varepsilon_0)}$$

where $\langle M^2 \rangle$ is now the mean square dipole moment of the sphere in the medium. u has now to be divided by ε_0 , so if both spheres are comprised of the same substance

$$\frac{u}{V_1 V_2} = k \frac{3 k T}{8 \pi^2 \varepsilon_0^2 R^6} \frac{(\varepsilon - \varepsilon_\infty)^2 (2 \varepsilon_0 + 1)^4}{(\varepsilon + 2 \varepsilon_0)^2 (\varepsilon_\infty + 2 \varepsilon_0)^2}$$

For $\epsilon \gg \epsilon_\infty$ and $\epsilon_0 = \epsilon_\infty = 2$, this result is

$$\frac{u}{V_1 V_2} = -0.6 \times 10^{-14} R^{-6} \text{ erg cm}^{-6}.$$

In a pure liquid, $\epsilon_0 = \epsilon$, and if the dielectric between the spheres is presumed to be able to follow the fluctuations in M ,

$$\frac{u}{V_1 V_2} = -\frac{kT (\epsilon - \epsilon_\infty)^2 (2\epsilon + 1)^4}{24 \pi^2 R^6 \epsilon^4 (2\epsilon + \epsilon_\infty)^3} = -0.1 \times 10^{-14} R^{-6} \text{ erg cm}^{-6}.$$

These long-range dipole interactions may be of significance for the dynamics of interactions in emulsions, and also in the experiments on films described by Dr. LYKLEMA.

HIRSCHFELDER

This problem is complicated because the water molecules do not rotate freely and therefore the averaging problem is difficult. There is also the question of what is the appropriate value to use for the dielectric constant.

BERNSTEIN

I would like to mention some of our early experiments (1) on the scattering of beams of polar molecules by polar target molecules. If one assumes a Keesom-type interaction (yielding an R^{-6} average interaction at long distances), then the C constant is expected to be

(1) « J. Chem. Phys. » 33, 584 (1960).

much larger for the polar-polar than for the polar-non-polar case. As an example of the importance of the direct polar-polar interaction, compare the cross section for the scattering of a beam of CsCl (for which the dipole moment μ is 10.4 debyes) by *trans*-dichlorethylene ($\mu=0$) and by *cis*-dichlorethylene ($\mu=1.9$ debyes). Both of those molecules have the same polarizabilities and, when scattering a non-polar beam (e.g. a cesium beam), have nearly identical cross sections (implying the same long-range C constant). However, these isomers show a very great difference in cross section for scattering the polar molecule cesium chloride (a factor of 3 in the cross sections, which leads to a factor of about an order of magnitude in the C constants). This difference can be attributed to a dipole-dipole interaction. To study this, the temperature of the (polar) target gas was varied over a wide range. Plotting the apparent C constant against the (mean) reciprocal temperature (analogous to a DEBYE plot of molar polarization) one found a very large slope, as expected. The experimental slope was within a factor of about 2 of the Keesom value, i.e., $\frac{2}{3}\mu_1^2\mu_2^2/K$, and this can be taken as confirmation of the magnitude and importance of the direct dipole-dipole contribution to the R^{-6} term in the intermolecular potential.

SESSION TROISIEME

SOUS LA PRÉSIDENCE DE

S.E. Prof. Dr. S. MIZUSHIMA

EXPERIMENTS ON ELASTIC AND INELASTIC SCATTERING OF ONE AND TWO COMPONENT SYSTEMS IN THE NEIGHBORHOOD OF CRITICAL POINTS

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I. PURPOSE

When a beam of monochromatic light is passed through a dense, transparent medium exhibiting density fluctuations, some of the light is scattered because the density fluctuations are accompanied by local fluctuations in the refractive index. In the Born approximation, the scattering cross section is expressible in terms of a space-time correlation function [1] which characterizes the fluctuations in a system of interacting particles. If the fluctuations are frozen in, we can replace the time average by a space average and regard our system as stationary in time; then, a three dimensional spatial correlation function is sufficient to describe the fluctuations in the system [2]. However, density fluctuations, such as in a condensed fluid, are often time-dependent so that the scattered intensity has a frequency spectrum characteristic of the time dependence of such fluctuations. Scattering measurements

(*) *Alfred P. Sloan Research Fellow.*

remain one of the best ways to determine the space-time correlation function. In the low frequency limit, it is difficult to determine the frequency spectrum using inelastic neutron scattering [3], whereas it is ideal for inelastic light scattering where the wave length of the electromagnetic radiation is of the order of a few thousand angstroms. In this respect, inelastic light and neutron scattering truly compliment each other, and the basic theory is essentially the same. Consequently, in electromagnetic scattering, an experimentalist is often interested in obtaining the scattered intensity as a function of both the frequency shift (at fixed scattering angles) and the scattering angle (at fixed wave lengths), as represented schematically in Fig. 1.

In the vicinity of the critical point where $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$, as shown in Fig. 2, for a one component system, the compressibility becomes very big, infinite in the critical point itself. Thus, the energy involved in the compression to a given amplitude gets smaller the nearer we approach the critical point. There, the thermal motion can produce strong density fluctuations resulting in very impressive scattering so as to make the medium look turbid. This is the so-called critical opalescence. Near the critical point, conventional measurements on thermodynamic and transport properties, such as isothermal compressibility and thermal conductivity, become very difficult. The angular and spectral distribution of the scattered light provide a unique means of measuring such properties without imposing some type of gradient on the system. From dramatic changes in both thermodynamic and transport properties, we may then expect to obtain useful information about the critical point by means of critical opalescence studies.

We usually design our scattering experiments for a variety of purposes. If we want to test theoretical models which try to relate intermolecular potentials to correlation functions, we

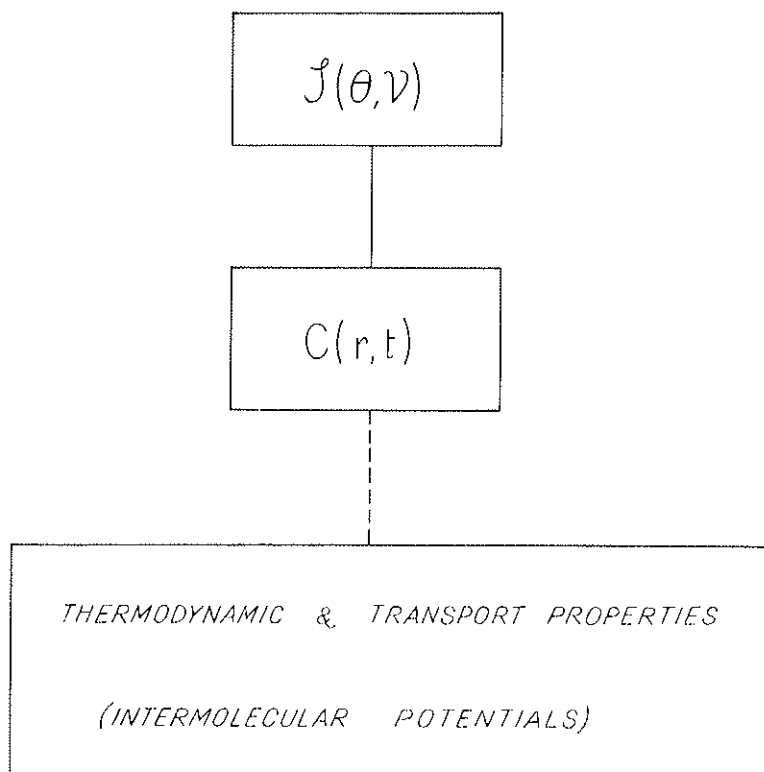


FIG. 1 — Relation between the angular and spectral distribution of the scattered intensity ($\mathcal{J}(\theta, \nu)$), the space-time correlation function ($C(r, t)$) and theoretical models.

would select systems consisting of small simple molecules, preferably a monatomic gas, and try to approach the critical point as close as possible. On the other hand, if we want to obtain information on intermolecular potentials of complex molecules, such as polymer systems, then we would tend to neglect the scattering behavior in the very immediate neighborhood of the critical point and would make our measurements in a region

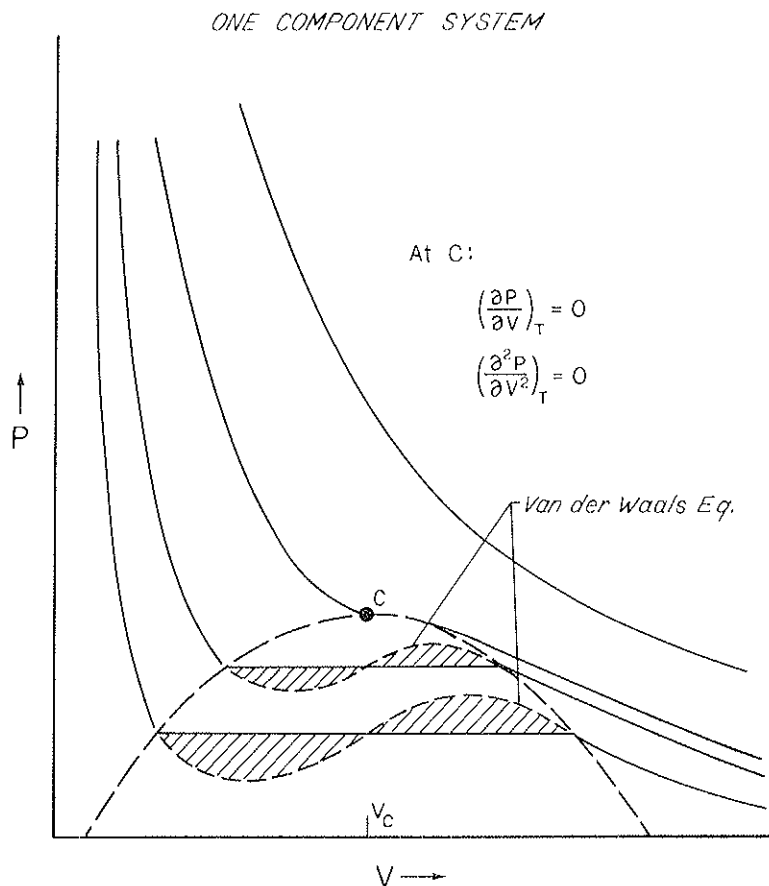


FIG. 2 — Isotherms of a one component system near the critical point.

where theoretical models relating intermolecular potentials and correlation functions remain valid. For example, critical opalescence studies of the polystyrene-cyclohexane system [4-7] can tell us some molecular information about polymer coils in terms of the Debye l -parameter. Such information would be

difficult to obtain by any other means. Yet, the polydispersity certainly excludes this system from any conclusive tests on basic theories. It should also be noted that the connection between the space-time correlation function and the thermodynamic and transport properties of a binary fluid mixture is very complicated when compared with that of a one component system, and for polymer systems, the interpretation of experimental data based on the DEBYE l parameter still require further investigation [7]. Nevertheless, the behavior of a binary fluid mixture which undergoes phase separation is, in many ways, closely analogous to the condensation of a simple fluid. For this reason, seemingly complex binary fluid mixtures (excluding the polymer systems) have been used to test basic theories because of the fact that they are easier to handle experimentally.

2. SCATTERING THEORY

The task for an experimentalists is usually to try to obtain the angular and spectral distribution of the scattered intensity (and its temperature dependence for systems near the critical point) over as large a range as feasible and with the highest possible resolution. Obviously if we want to know what we are looking for, a brief discussion on the connection between the scattering cross section and the space-time correlation function is essential, although details of the theory will be reviewed by Professor M. FIXMAN at the present conference.

A. *Elastic Scattering* (*)

For N small isotropic particles (oscillating dipoles) in volume V excited by an incident unpolarized beam of intensity $\mathcal{I}_0$ the scattered intensity $\mathcal{I}$ is given by

(*) Elastic scattering refers to the classical scattering theory where the scattered intensity has not been resolved into RAYLEIGH (central) and BRILLOUIN components.

$$(1) \quad \frac{\mathcal{I}}{\mathcal{I}_0} = \frac{k_0^4 \alpha^2 n V}{r^2} \left(\frac{1 + \cos^2 \theta}{2} \right)$$

where $k_0 = 2\pi/\lambda_0$, λ_0 is the wave length of light in vacuo, α is the polarizability, $n (=N/V)$ is the number of particles per unit volume, r is the distance from the scattering center to the detector, and θ is the scattering angle. This is the Rayleigh scattering, as shown in Fig. 3. However, for liquids, concentrated solutions, and systems consisting of strongly interacting particles, direct calculations of the effective scattered field of each individual particle become complicated. We then consider the scattering as due to local thermal fluctuations in the density (or concentration) of the system.

The Maxwells equations for a medium with a dielectric constant that fluctuates have the following form:

$$\begin{aligned} ik_0 \mathbf{H} &= -\text{curl } \mathbf{E} & ik_0 (\epsilon_0 + \delta\epsilon) \mathbf{E} &= \text{curl } \mathbf{H} \\ \text{div } \mathbf{H} &= 0 & \text{div } [(\epsilon_0 + \delta\epsilon) \mathbf{E}] &= 0 \end{aligned}$$

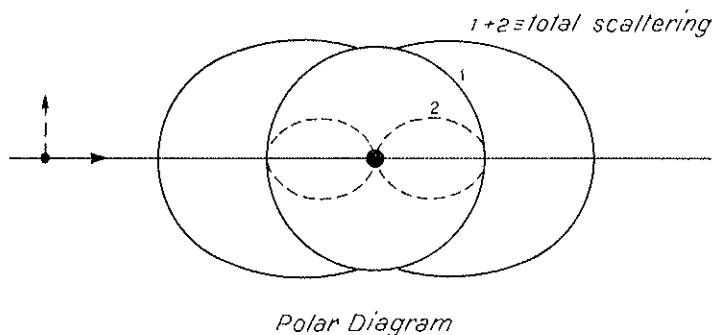
where $\mathbf{E}$ and $\mathbf{H}$ are the electric and the magnetic field vectors, respectively, and ϵ_0 is the average dielectric constant on top of which local fluctuations $\delta\epsilon$ of random character are superimposed. If we let

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 \quad \text{and} \quad \mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1,$$

we obtain

$$\begin{aligned} ik_0 \mathbf{H}_1 &= -\text{curl } \mathbf{E}_1 & ; & \quad ik_0 \epsilon_0 \mathbf{E}_1 + ik_0 \delta\epsilon \mathbf{E}_0 = \text{curl } \mathbf{H}_1 ; \\ \text{div } \mathbf{H}_1 &= 0 & ; & \quad \epsilon_0 \text{div } \mathbf{E}_1 + \text{div } (\delta\epsilon \mathbf{E}_0) = 0. \end{aligned}$$

SINGLE PARTICLE - RAYLEIGH SCATTERING



For $N (\equiv nV)$ particles,

$$\frac{\mathcal{J}}{\mathcal{J}_0} = \frac{k_0^4 \alpha^2 nV}{r^2} \left(\frac{1 + \cos^2 \theta}{2} \right)$$

CONDENSED PHASE - EINSTEIN'S FLUCTUATION THEORY

$$\frac{\mathcal{J}}{\mathcal{J}_0} = \frac{k^4 \left(\frac{\rho}{\epsilon} \frac{d\epsilon}{d\rho} \right)^2 k \beta T V}{16\pi^2 r^2} \left(\frac{1 + \cos^2 \theta}{2} \right)$$

FIG. 3 — Rayleigh scattering and Einstein's fluctuation theory.

Neglecting the time dependence, the electric field created by the fluctuations of the dielectric constant $\delta\epsilon$ is [8]:

$$E = E_0 \frac{e^{-ikR}}{R} \frac{k^2}{4\pi} \sin \theta \int_V \frac{\delta\epsilon}{\epsilon_0} e^{ik(s \cdot r)} d\tau$$

In this relation, $k = \frac{2\pi}{\lambda}$, λ being the wave length of light in the medium. The angle between $\mathbf{E}_0$ and $\mathbf{S}$ is 0; the vector $\mathbf{s} = \mathbf{S} - \mathbf{S}_0$, where $\mathbf{S}$ is a unit vector in the direction of $\mathbf{R}$ and $\mathbf{S}_0$ is a unit vector in the direction of propagation of the incident beam. If θ is the angle between $\mathbf{S}$ and $\mathbf{S}_0$, $s = 2 \sin(\theta/2)$. The vector $\mathbf{r}$ defines the position of the scattering volume element $d\tau$ with respect to an arbitrary center: from it the large distance R is measured. If the fluctuations are frozen in, we can replace the time average by a space average and obtain for the isotropic case [2, 8]:

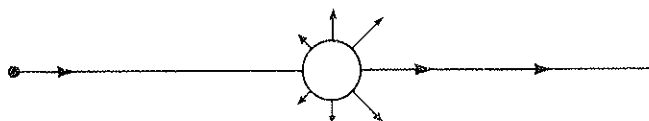
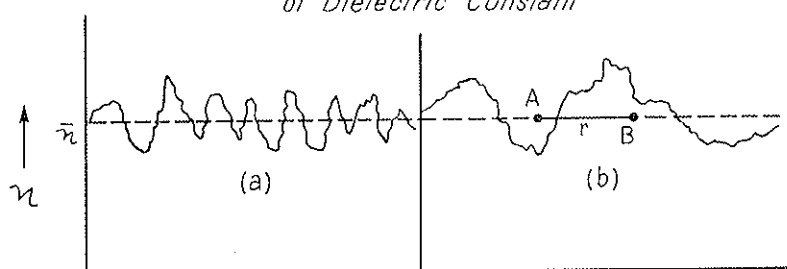
$$(2) \quad \frac{\mathcal{J}}{\mathcal{J}_0} \frac{\sin^2 \theta}{R^2} \frac{k^4}{16\pi^2} < \left(\frac{\delta \epsilon}{\epsilon_0} \right)^2 > V \int C(r) \frac{\sin ksr}{ksr} d\tau$$

where we have introduced a three dimensional spatial correlation function $C(r)$ defined as

$$(2a) \quad < \left(\frac{\delta \epsilon}{\epsilon_0} \right)_A \left(\frac{\delta \epsilon}{\epsilon_0} \right)_B > = C(r) < \left(\frac{\delta \epsilon}{\epsilon_0} \right)^2 >$$

The correlation function is dimensionless; $C(r) = 1$ for $r = 0$, and $C(r)$ tends to zero for large values of r . It is used to characterize the persistence of those fluctuations, as shown in Fig. 4. For small values of s , we may write

$$(3) \quad \frac{\mathcal{J}}{\mathcal{J}_{\max}} = 1 - \frac{k^2 s^2 L^2}{6} + \dots$$

Scattering of Polarized Light by a Large Particle*Scattering of Light by Medium with Irregular Variation of Dielectric Constant**Correlation Function*

$$C(r) = \frac{\langle \Delta_A \Delta_B \rangle}{\langle \Delta^2 \rangle}$$

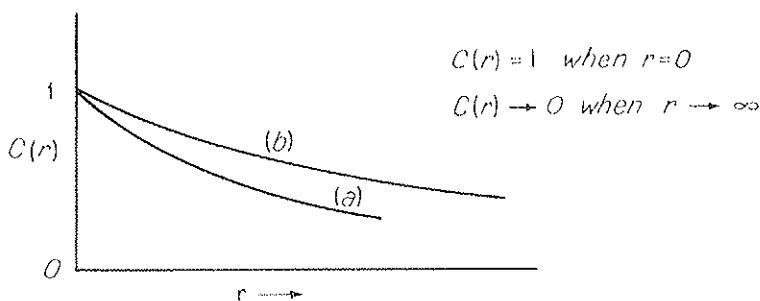


FIG. 4 — Interference and correlation function.

in which $\mathcal{I}_{max}$ is the scattered intensity for $s=0$, and L is the persistence length, defined as

$$L^2 = \frac{\int r^2 C(r) dr}{\int C(r) dr}$$

Eq. (3) tells us that the scattered intensity becomes independent of the scattering angle whenever L becomes very small. In the limit, we have thermal fluctuations independent of one another and obtain Einstein's fluctuation theory [9], as shown in Fig. 3. Furthermore, the appropriate variable is ksL . The higher order terms become increasingly more important as $\frac{k^2 s^2 L^2}{6}$ approaches unity. This implies that we should design our experiments (a) for small values of ks in order to obtain the extrapolated zero angle scattered intensity which is related to thermodynamic properties and to investigate very long range correlations if they exist, (b) over large ranges of ks in order to obtain more information on the shape of the correlation function and (c) over a temperature range so as to determine the temperature dependence of such properties, especially when the changes are dramatic as in critical opalescence.

B. Inelastic Scattering [1, 10-13]

We introduce a space-time correlation function which describes the correlation between the fluctuation in position $\mathbf{r}_A$ at time t_A and that in position $\mathbf{r}_B$ at time t_B when the fluctuations are time dependent. For a stationary and spatially homogeneous random process, the correlation function depends only

on the coordinate differences $\mathbf{r} = \mathbf{r}_B - \mathbf{r}_A$ and the time difference $t = t_B - t_A$, i.e.

$$(4) \quad \langle \Delta_A \Delta_B \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T \Delta_A(\mathbf{r}_A, t) \Delta_B(\mathbf{r}_B, t + \tau) dt$$

We can again make the correlation function dimensionless if we divide Eq. (4) by the mean square fluctuations. Dimensionless correlation functions are sometimes referred to as correlation coefficients [14]. When $\tau=0$, the space-time correlation function reduces to the three dimensional spacial correlation function (Eq. (2a)). In terms of the temporal fluctuations in the scattered field which is related to fluctuations in the dielectric constant, we may write for the spectrum of the scattered light [15]:

$$\mathcal{J}(\mathbf{K}, \omega_f) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mathbf{E}(\mathbf{K}, t + \tau) \cdot \mathbf{E}^*(\mathbf{K}, t) \rangle e^{i\omega_f \tau} d\tau$$

where the space-time correlation function can be expressed in terms of the fluctuations in the dielectric constant

$$\begin{aligned} \langle \mathbf{E}(\mathbf{K}, t + \tau) \cdot \mathbf{E}^*(\mathbf{K}, t) \rangle &\equiv \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T \mathbf{E}(\mathbf{K}, t + \tau) \cdot \mathbf{E}^*(\mathbf{K}, t) dt \\ &\propto \langle \delta\epsilon(\mathbf{K}, t + \tau) \delta\epsilon^*(\mathbf{K}, t) \rangle e^{-i\omega \tau}, \end{aligned}$$

ω_f denotes the angular frequency of the scattered beam, and $K = \frac{2\pi}{\Lambda}$, Λ being the wave length of thermal sound waves. Note a change in notation: τ denotes a relaxation time in inelastic scattering while $d\tau$ is a volume element in elastic scattering.

The model which attempts to depict fluctuations in dielectric constant for a simple fluid has been reviewed elsewhere [12, 13]. Briefly, BRILLOUIN [16] was the first person to investigate theoretically the spectrum of light scattered from a condensed medium. He envisaged light waves being diffracted by thermally excited sound waves, as shown in Fig. 5. The Bragg law gives us

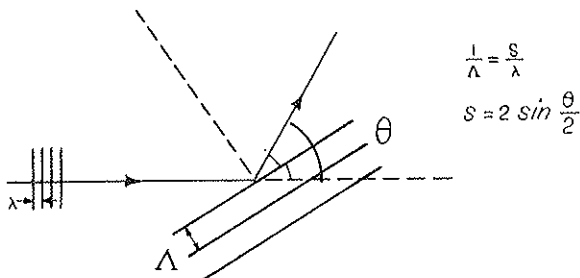
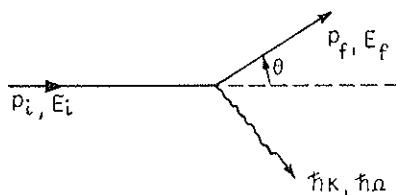
$$(5) \quad \frac{1}{\Lambda} = \frac{s}{\lambda}$$

Quantum mechanically, we may consider Brillouin scattering as inelastic photon-phonon collisions. Since the ratio of the velocity of sound v_s to the velocity of light c is small, one essentially obtains the same result. From statistical physics [17], we may choose that the fluctuations of the entropy (S) and those of the pressure (P) as statistically independent. Then, fluctuations in either the pressure or the entropy will cause fluctuations in the dielectric constant:

$$(6) \quad \delta\epsilon(\mathbf{K}, t) = \left(\frac{\partial \epsilon}{\partial S} \right)_P (\delta S(\mathbf{K}, t))_P + \left(\frac{\partial \epsilon}{\partial P} \right)_S (\delta P(\mathbf{K}, t))_S$$

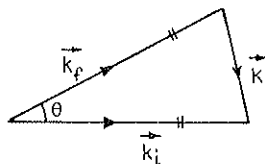
The thermal sound waves are fluctuations in pressure at constant entropy. BRILLOUIN considered the two acoustic modes while LANDAU and PLACZEK [18] explained the presence of

BRILLOUIN SCATTERING

1. Classical Description ($\frac{v_s}{c} \ll 1$)2. Quantum Description ($\frac{v_s}{c} \ll 1$)

Inelastic photon-phonon collision requires

- (a) *Energy conservation* $E_f = E_i \pm \hbar\Omega$ } + "anti-stokes" or phonon annihilation
 (b) *Momentum conservation* $p_f = p_i \pm \hbar k$ } - "stokes" or phonon creation



By Geometry $|k| = 2|k_i| \sin \frac{\theta}{2}$

FIG. 5 — Brillouin scattering.

a heat conduction mode. If we choose the dielectric constant as a function of the density ρ and the temperature T , we would obtain the classical scattering theory of Einstein.

3. TECHNIQUE

A. Preliminary Requirements

Scattering experiments are notoriously difficult to perform near the critical point. Aside from experimental effects, such as multiple scattering, impurities, and temperature fluctuations, we must also realize that scattering measurements are never better than the data used to specify the thermodynamic state of the system. In other words, for critical opalescence studies, we can approach the critical point only as close as we can define it experimentally. For this reason, it becomes important to select appropriate systems before we make extensive scattering studies. One obvious choice would be the rare gas systems if we are interested only in testing basic theories. Unfortunately, it is necessary but difficult to take into account the effect of gravity, in terms of density gradients [19], on one component systems very near the critical point. So, we have decided to begin our investigation on the scattering behavior of two component fluid mixtures where concentration fluctuations are predominant. We look for a two-component system in which both components can be purified by preparative gas chromatography and are stable; has a small refractive index difference between the two components in order to alleviate optical multiple scattering, a large difference in their electron densities in order to enhance the weak small angle X-ray scattering, and a convenient critical solution temperature [20]. Ideally, we should try first to determine very ac-

curately the nature of the coexistence curve, and locate the critical mixing point, in the same spirit as represented by the excellent works of RICE and his coworkers [21], and then, proceed with elastic and inelastic scattering measurements. However, no one has yet been able to achieve this goal.

B. Elastic Scattering

Figure 6 shows a schematic representation of elastic scattering curves in the neighborhood of the critical point for a one

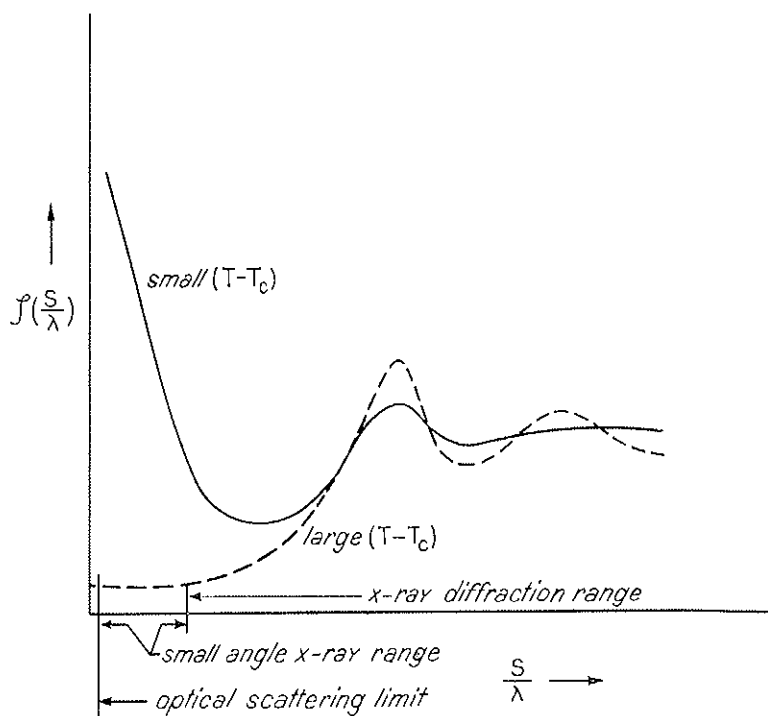


FIG. 6 — Schematic representation of elastic scattering curves in the neighborhood of the critical point.

component system. We use a light scattering photometer [20, 22] for small values of s/λ and a small angle X-ray scattering goniometer [6, 23, 24] with CuK_α radiation for larger values of s/λ . The ranges and some of the limitations in elastic scattering measurements are summarized in Table I. Finally, if the shape of the scattering curve in the optical range is known, we can also measure the temperature dependence of turbidity as a function of wave length and obtain a check for our light scattering data [25, 26].

TABLE I
ELASTIC SCATTERING

	Optical	Small Angle X-Ray
Range (Approx.) $\frac{s}{\lambda} \times 10^4 \text{ \AA}^{-1}$	0.4 - 7.5	3-250
Precision (Approx.)	one per cent	a few per cent
Slit Collimation Correction	no	yes
Multiple Scattering	difficult to avoid	none
Window and Seal	glass; Teflon	mica, aluminium, or beryllium; epoxy, silicon rubber, or metal gasket
Temperature Control	$\pm 0.0005^\circ$	$\pm 0.005^\circ$
$T-T_c$ (Approx.)	$0.002^\circ - 1^\circ$	$0.01^\circ - 10^\circ$
Scattered Intensity	strong	weak

C. Inelastic Scattering

Fig. 7 shows a sketch for a typical frequency spectrum of the scattered light of a dense fluid, such as benzene. The large frequency shifts correspond to Raman (R) vibrational

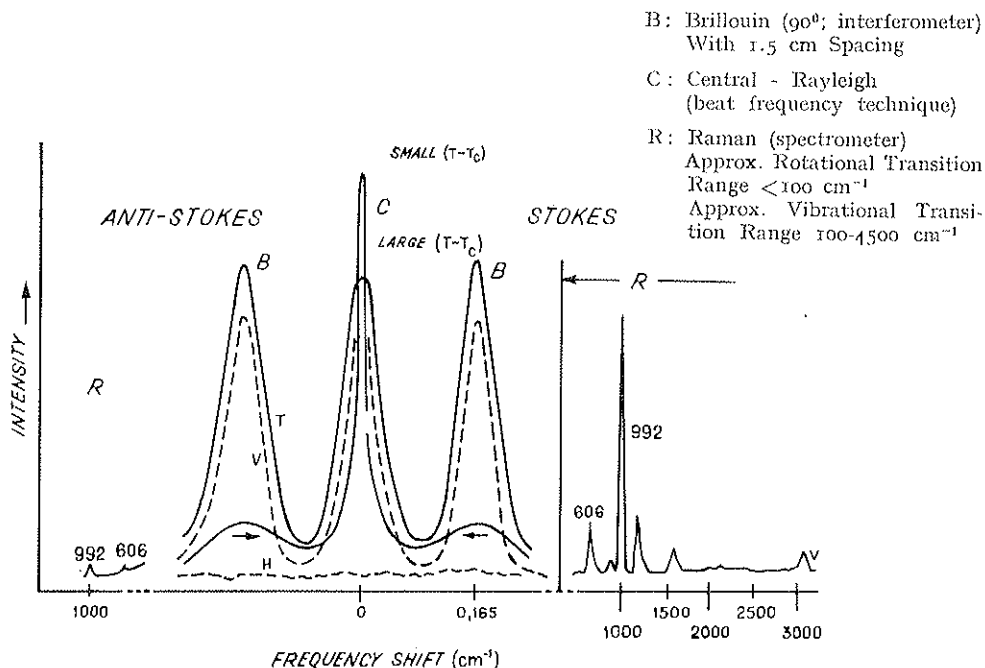


FIG. 7 — Sketch of a benzene spectrum [27, 30].

T $\equiv$ total signal, V $\equiv$ signal polarized perpendicular to the scattering plane.
 H $\equiv$ signal polarized in the scattering plane.

As we approach the critical point the Brillouin doublets should move in toward the center because the adiabatic bulk modulus approaches zero, and the intensity of the Brillouin doublets increases like the adiabatic compressibility. Thus, the curve for small $(T-T_c)$ is not drawn to scale.

transitions [27] and can be resolved using a conventional spectrometer. The two sound modes, or the Brillouin doublets (B), have been resolved using a 12-m focal length grating spectrograph capable of a resolving power of 900,000 [28]. However, it is usually more convenient to take advantage of present day multilayer dielectric coating techniques, and to use a pressure-scanning Fabry-Perot interferometer with photoelectric detectors [29, 30]. The Brillouin lines become

broader and collapse towards the central component while the central component gets narrower as the critical point is approached. This behavior is also sketched in Fig. 7.

Two types of optical beat frequency detection techniques have been used successfully for systems near the critical point where the scattering is very strong. The homodyne spectrometer analyzes the beat between the scattered light and part of the incident light [31-33], while a simple « self-beat » homodyne spectrometer uses a square law detection system [15]. A block diagram of the « self-beat » spectrometer is shown in Fig. 8.

For anisotropic molecules, fluctuations in orientation produce a rotational background which can be considered as highly damped rotational Raman transitions. Depolarization studies, which have usually been neglected would therefore be of interest, as shown by the background H in Fig. 7 [30].

4. SUMMARY OF RESULTS

A. Elastic Scattering

(a) Shape of Scattering Curve: The angular distribution of scattered intensity, by means of both visible light and X-rays, for either one- or two-component systems, has been reviewed and discussed elsewhere [34, 35]. When the temperature distance from the critical point is greater than a few hundredth of a degree, a plot of the reciprocal scattered intensity versus $\left(\frac{s}{\lambda}\right)^2$, which is sometimes referred to as an OZD plot, invariably leads to a straight line in the optical range [20, 35]. This linear behavior persists over large ranges of s/λ and eventually breaks down in the small angle X-ray scattering range as to be expected from Eq. (3) [36, 37]. It is gratifying to note

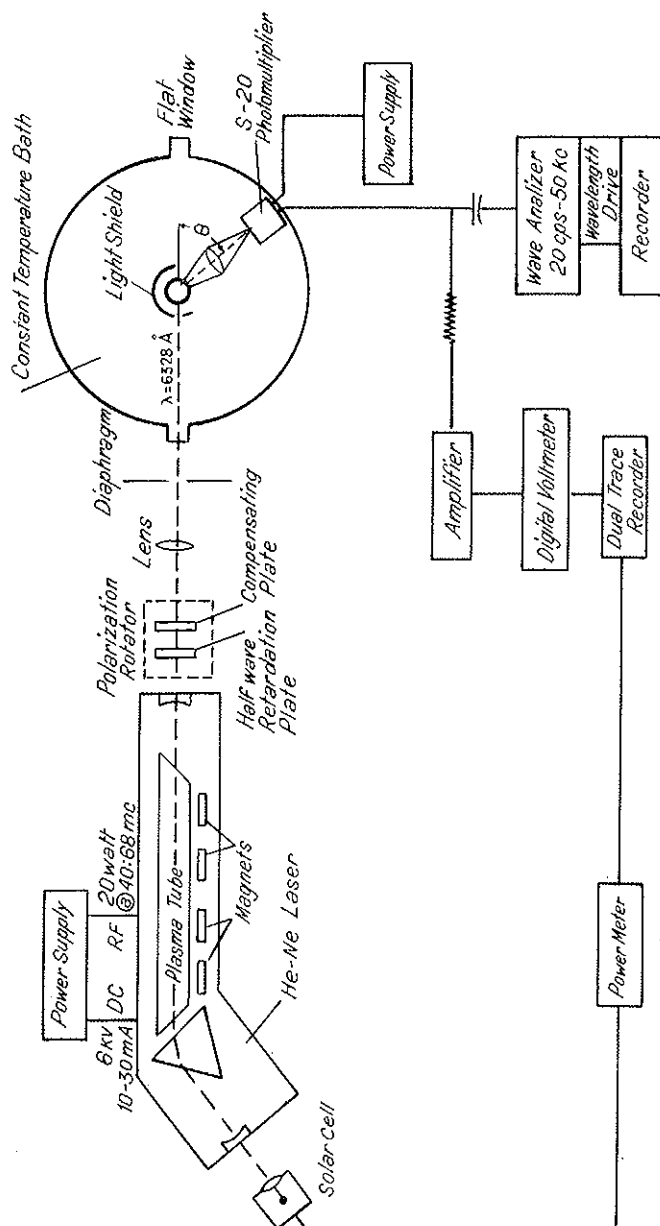


FIG. 8 — Block diagram of a "self-beat" spectrometer.

that the Ornstein-Zernike [38], Debye [2, 39] theory is in excellent agreement with *all* known facts [35, 40] over the intermediate temperature range where most of the deviations have been shown to be experimental effects. We also know that the Debye interaction parameter l has magnitudes of 5, 10-15, 20-60 Å for one component [24], binary fluid mixture [35, 41], and polymer systems [5, 35], respectively. The controversy on the shape of the scattering curve comes from scattering measurements at very small temperature distances (at approximately less than one hundredth of a degree from the critical temperature T_c). There, we are concerned with large fluctuations. So we would emphasize light scattering rather than small angle X-ray scattering measurements. Deviations from the straight line behavior in an OZD plot at small values of s/λ and very close to the critical solution temperature have been detected in some preliminary experiments on a two-component system, normal dodecane and β , β' dichloroethyl ether [42]. We should however note that for the system normal decane and β , β' dichloroethyl ether, the downward curvature is barely observable even when $T-T_c=0.002^\circ$ [43]. Unfortunately, we have also detected a small amount of multiple scattering for the system *n*-decane and β , β' dichloroethyl ether with our present optical systems in the light scattering photometer, as we cannot superimpose the scattering curve measured at $\lambda_0=365$ m μ on that measured at $\lambda_0=436$ m μ , both being at the same temperature distance above the critical solution temperature ($T-T_c<0.01^\circ$). Others [40] have also found that the linear behavior in an OZD plot is obeyed at small temperature distances ($T-T_c=0.002^\circ$). Those measurements, however, were done at one wave length ($\lambda_0=546$ m μ) and over a small angular range ($0<\theta<115^\circ$) so that the gentle curvature if it exists cannot be detected. There have also been some data exhibiting a sharp downward dip, which signifies the existence of very long range correlations, at very small values of s/λ and at very small temperature distances [44]. These data have not yet

been substantiated. Furthermore, in a plot of the reciprocal of the extrapolated zero angle scattered intensity versus $(T-T_c)$ over the intermediate temperature range, one is usually able to extrapolate to within 0.01° from the phase separation temperature. Therefore, the reported sharp downward dip at very small values of s/λ in an OZD plot, if it exists, cannot be large. Secondly, we must realize that although we have drawn the analogy between one component systems and binary fluid mixtures, the complexity of a two component system consisting of organic liquids, such as β , β' dichloroethyl ether, and the presence of three radial distribution functions would always leave a trace of doubt in the final test. So measurements on one component systems have to be performed if we are interested in testing basic theoretical models.

(b) Temperature Dependence of Extrapolated Zero Angle Scattered Intensity: Our interest again centers around observations at small temperature distances from the critical point. It is important to determine γ in an equation of the form: $(\mathcal{I}_0)^{-1} = A(T-T_c)^\gamma$ from a plot of the reciprocal of the extrapolated zero angle scattered intensity versus the temperature distance $(T-T_c)$. Several systems [45] seem to exhibit a very nearly linear behavior in such a plot while others do not [40, 43]. The small deviations at small temperature distances usually appear in the form of a slightly concave upward curvature which tends to extrapolate to a non zero value at T_p . Accurate determinations of this temperature dependence have found to be more difficult than it appears because of density and attenuation corrections [20].

B. Inelastic Scattering

Data on the spectrum of light scattered from either pure fluids or binary fluid mixtures near the critical point have been scarce. Preliminary experiments [10, 15, 28-30, 32, 33, 46-48]

and the theories of Brillouin [16] and of Landau-Placzek [18] and Debye [49] are in reasonable agreement, although modifications of the Landau-Placzek equation have been attempted [50, 51]. In the critical region, the Brillouin doublets are broad, and very weak when compared with the central component. They may be difficult to detect [15] and are of less interest in comparison with the behavior of the central line.

5. CONCLUSION

Scattering measurements indeed offer us a wealth of information. From the extrapolated zero angle scattered intensity we may obtain thermodynamic properties of the system, such as isothermal compressibility, or we can count the number of solute molecules and determine the molecular weight of macromolecules. From the angular distribution of scattered intensity over large ranges of s/λ , we can investigate the geometry, in terms of size and shape, of macromolecules in solution, or the fluctuations in terms of a three dimensional spatial correlation function. From depolarization studies, we can learn something about molecular anisotropy.

It is interesting to note that inelastic light scattering is indeed the low frequency limit for the inelastic scattering of neutrons; yet, at the same time, it is the high frequency limit of the acoustical spectrum, and deals with acoustical phenomena in the gigacycle region which is inaccessible by conventional ultrasonic techniques. For simple fluids, the Brillouin doublet is sharp and it contains several pieces of information. The frequency shift is related to the speed of the thermal sound wave and the adiabatic bulk modulus ($B_s = -V \left(\frac{\partial P}{\partial V} \right)_s$) while the width of these lines is proportional to the sound

absorption coefficient which may provide us a means of determining the bulk viscosity. The width of the central component is proportional to the thermal diffusivity, while the ratio of the intensity of the central component to that of the doublet lines is [18]

$$\frac{\mathcal{I}_c}{2\mathcal{I}_B} = \frac{C_p - C_v}{C_v}$$

in terms of the Landau-Placzek theory.

Furthermore, the absolute Brillouin intensities are related to the electrostrictive coupling constant and the scattered line shapes are related to the time dependence of pressure and entropy correlations. In the latter case, the line shape of the central component is related to slow relaxation times. The interpretations become complex for two component systems. However, I believe that scattering measurements give us a new approach for studying not only molecular configuration but also molecular dynamics of systems, including those of macromolecules. It will indeed become an extremely powerful tool.

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SPACE AND TIME CORRELATIONS IN THE CRITICAL REGION

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I. INTRODUCTION

This paper briefly reviews the correlation of density fluctuations in the one phase region near the gas critical point, and correlations in composition fluctuations near the critical mixing point. The time dependence as well as the spatial dependence of the correlation functions are of interest. And in particular, the long range part of the correlation functions which comes into existence in fluids near the critical point will be of major concern.

We may refer to Figure 2 of Professor CHU's paper, and note that the region lying near the point C, but outside the coexistence curve, is the critical region. A qualitatively identical graph would apply to a binary mixture if the ordinate were taken to be the osmotic pressure and the abscissa were taken to be the volume per mole of one of the components.

The definition of correlation functions and their determination from scattering experiments will be summarized first, and we shall then consider the prediction of these correlation functions according to a quasi-thermodynamic approach, and the errors and probable range of validity of this approach.

2. TIME CORRELATIONS

A time dependent pair correlation function may be defined by [1, 2, 3]

$$F(\mathbf{r}, t) \equiv \frac{1}{\rho^2} \langle \delta\rho(0, 0) \delta\rho(\mathbf{r}, t) \rangle \quad (1)$$

$$\xrightarrow[t \rightarrow 0]{} g(r) = 1 + \delta(r)/\rho$$

where $\delta\rho$ is the fluctuation of number density from the mean number density ρ , and $g(r)$ is the radial distribution function. The average which is required in Eq. (1) is over an equilibrium canonical or grand canonical ensemble, and at zero time the correlation function reduces to a well known form. The number density ρ may be replaced by the concentration of a single species in a binary mixture, to provide a definition of the correlation between composition fluctuations of like species. Of course in a binary mixture there are three different radial distribution functions in principle, but one may plausibly deal with a first approximation in which the mean composition in the vicinity of a fixed molecule varies with position while the total number density stays fixed at its macroscopic value [4]. Then only one independent pair correlation function need be considered.

An electrodynamic wave of amplitude $\mathbf{E}_0$ incident on a sample of the fluid will produce a scattered wave of amplitude $\mathbf{E}'$ given by

$$(2) \quad \mathbf{E}'(t) = K \mathbf{E}_0 e^{-i\omega_0 t} \int \delta \epsilon(\mathbf{r}, t) e^{-i\mathbf{g} \cdot \mathbf{r}} d\mathbf{r}$$

$$\mathbf{g} = \mathbf{k}' - \mathbf{k}$$

where K is a proportionality factor, ω_0 is the incident frequency, $\delta\epsilon$ is the fluctuation in local dielectric constant and $\mathbf{k}$ and $\mathbf{k}'$ are wave vectors in the direction of the incident and scattered waves respectively. The scattered intensity per unit frequency at the frequency ω

$$(3) \quad \omega = \omega_0 + \Delta\omega$$

is then given by

$$(4) \quad I(\Delta\omega) \propto \left(\frac{\partial \epsilon}{\partial \rho}\right)^2 V \iiint F(\mathbf{r}, t) e^{-i\mathbf{g} \cdot \mathbf{r} - i t \Delta\omega} d\mathbf{r} dt$$

We may refer to LANDAU and LIFSHITZ [5], PECORA [3], or VAN HOVE [1] for appropriate derivations of these or closely related formulae.

We see that there is in principle a one to one correspondence between a time dependent pair correlation function and the differential scattering cross section. In practice, the problems of inversion are such that one is limited to a substitution of a predicted $F(\mathbf{r}, t)$, perhaps with a modest number of variational parameters, and a comparison of predicted and observed intensities. In what follows we sketch the derivation of the quasi-thermodynamic approach to $F(\mathbf{r}, t)$, and then return to Eq. (4) to derive the predicted intensities.

III. QUASI-THERMODYNAMIC APPROACH

An application of thermodynamic fluctuation theory typically begins with a division of the macroscopic system of volume V into many equal subvolumes Δ . In the gaseous critical region the i^{th} subvolume is characterized by the number n_i of molecules in it. The set of numbers n_i is designated a configuration $\{n\}$. Each n_i is presumed to be rather large, in part so that it can be treated as a continuous variable, and in part for other reasons which appear later (such as the neglect of interactions between nonadjoining cells, and the neglect of large fluctuations). At the same time the size of the cells can not be too large; in particular the linear dimensions of the cell must be less than the range of the correlation function if anything is to be learned about that function from the behavior of the subdivided system.

$$\begin{aligned}
 M \Delta &= V \\
 \Delta^{\frac{1}{3}} &\ll L \\
 n_i &\gg 1
 \end{aligned}
 \tag{5}$$

An integration over the molecular coordinates and velocities subject to the condition of a constant configuration $\{n\}$, followed by a sum over all configurations must then give the free energy in the form

$$e^{-\beta A} = \sum_{(\sum n_i = N)} \cdots \sum \exp [-\beta A \{n\}]
 \tag{6}$$

where $A\{n\}$ is the conditional Helmholtz free energy, the work required to produce the state $\{n\}$. The qualitative behavior of $A\{n\}$, which is all that matters in the following, can be deduced from crude molecular arguments or from the macroscopic behavior of inhomogeneous systems. To a first approximation in a crude molecular theory, the interaction between molecules in different cells would be treated as negligible, and the conditional free energy would be additive over individual cell free energies. To a next approximation (corresponding to a virial expansion of the free energy of a dilute gas), a pair interaction between cells would arise and the free energy would have the form

$$(7) \quad A\{n\} = \sum_{i=1}^m a_0(n_i) - \sum_{i \neq j} w_{ij} n_i n_j + \dots$$

In the critical region the coefficients w_{ij} , which will of course be temperature dependent, may be presumed positive and favoring a cluster formation, and will certainly be shortranged if calculated according to the suggested scheme. A more illuminating form of Eq. (7) is

$$(8) \quad A\{n\} = \sum_{i=1}^m a(n_i) + \frac{1}{2} \sum_{i \neq j} w_{ij} (n_i - n_j)^2 + \dots$$

which shows that the interaction between cells tends to minimize density gradients if w_{ij} is positive. Moreover, $a(n_i)$ is just the van der Waals free energy per molecule, as a function of the number of molecules per cell. In figure 1 the

function $a(n_i) - \mu n_i$ is graphed against n_i . We may observe that

$$\sum_{i=1}^M \mu n_i = \mu N$$

is independent of configuration and consequently the subtraction of μn_i from $a(n_i)$ will not distort our view of fluctuation probabilities, and indeed forms a more natural measure inasmuch as the cells are in open material contact with each other. At high temperatures the curve of figure 1 shows a single minimum, and at low temperatures it shows two or possibly more minima. If only two, as we shall suppose, they may be made to occur at the same depth by a proper choice of μ . We shall designate the boundary between these two temperature regions by the symbol T_{vw}^c and refer to it as the van der Waals critical temperature. At high temperatures the system has just one locally stable density, the gas density given by $\rho_g = n_g/\Delta$, while at low temperatures the system is locally stable at either of two densities, the vapor density $\rho_v = n_v/\Delta$ or the liquid density $\rho_l = n_l/\Delta$.

Several possible approximations present themselves for use in the summation required in Eq. (6).

I. VAN DER WAALS APPROXIMATION

Here all n_i 's are presumed identical and equal to n , the latter chosen to minimize $A\{n\}$; the contribution from inhomogeneity in Eq. (8) then vanishes. At temperatures less than the Van der Waals critical temperature the system may be unstable

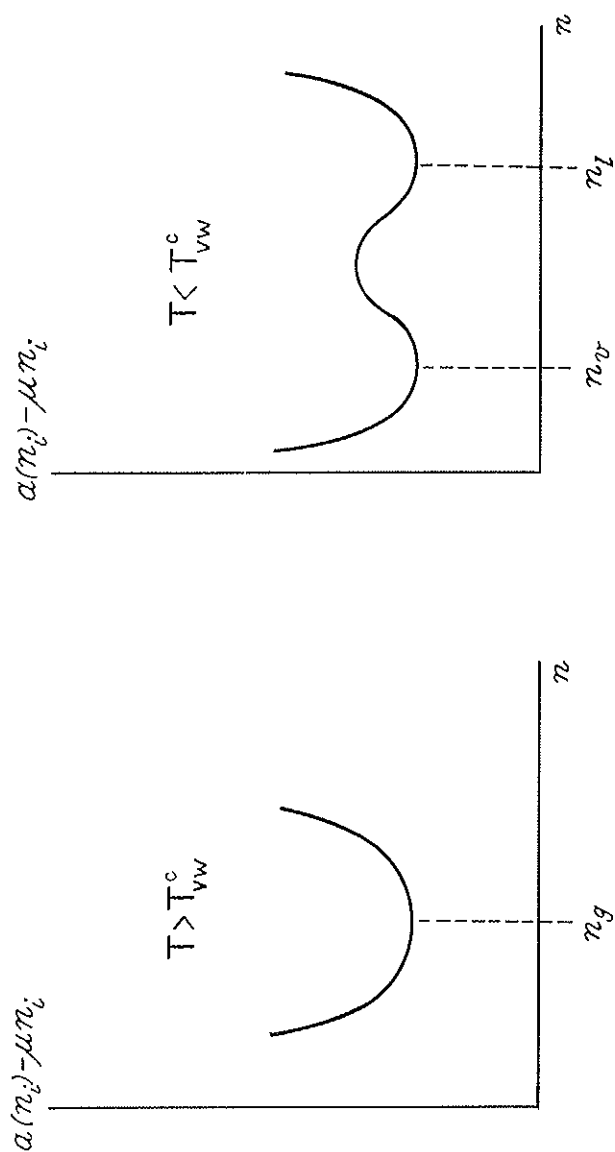


FIG. 1 — Caption : van der Waals free energy curves.

if homogeneous, and one then puts one part of the system at the liquid density ρ_l and another part at the vapour density ρ_v , the contribution of the boundary free energy still being negligible.

It is evident, as may be seen particularly in van Kampen's derivation [6], that the van der Waals approximation picks out the largest single term in the sum required in Eq. (6). Other configurations will have a larger free energy due to the second double sum in Eq. [8], even if not due to the first single sum. But it is equally obvious that the other configurations present in Eq. [6] may, because they are so many, contribute something essential to the free energy which is lost in the van der Waals approximation. We may see this in an alternative approximation, the Ising Analog.

2. THE ISING ANALOG

Here, for temperatures less than the van der Waals critical temperature, we examine the extension of the sum in Eq. (6) to all n_i equal to either n_l or n_v , the favored values in fig. 1. Since the additional contributions to the sum in Eq. (6) are positive, the new free energy is clearly lower than the van der Waals, although still greater than the true free energy. The mathematics of the summation is now identical to that of the Ising model, which has not yet been analytically evaluated for three dimensional systems. But many numerical results are available from the work of DOMB [7], FISHER [8], and others, and may be applied to the theory of liquids through the introduction of temperature and density dependent interactions deduced from Eq. (8).

Because the free energy of the Ising Analog approximation is closer to the true free energy than is the van der Waals

free energy, we may refer to the Ising Analog as a better approximation. We may also say that this better approximation gives a critical temperature lower than T_{vw}^c , since an interaction term in Eq. (8), say $(n_{li} - n_{vj})^2$, would be infinitesimal in an infinitesimal neighborhood of T_{vw}^c . Consequently there is a finite temperature interval below T_{vw}^c in which the Ising Analog model is locally unstable at densities ρ such that $\rho_l > \rho > \rho_v$, but macroscopically stable and homogeneous.

An approximation similar to what we have called the Ising Analog has been investigated by KADANOFF [9] in connection with his investigation of relationships between critical exponents, such as have been conjectured by WIDOM [10] and others. KADANOFF's idea was to group together many adjoining sites of the Ising model, and to assume that each of the resultant domains would have one of just two possible magnetizations. It is clear that this assumption will not change the qualitative nature of the singularities to be expected for the Ising model, but will change the quantitative interpretation of interaction coefficients. Since the quantitative interpretation can be checked when the approximation is applied to the two dimensional Ising model, it is possible that a numerically useful and validated route to the free energy and its derivatives will become available for liquids. Such results would probably be based on Monte Carlo results for small systems combined with the numerical extrapolations for Ising models.

There remains a need for quantitative if inexact models of the growth and decay of long ranged density correlations as the critical point is approached and passed, and also a need for quantitative theories of non-equilibrium phenomena. This additional insight is provided particularly by the work of ORNSTEIN and ZERNIKE [11], LANDAU [12] and DEBYE [13]. The arguments of the last two are based on thermodynamic fluctuation theory.

3. THERMODYNAMIC FLUCTUATION THEORY

In this theory the van der Waals approximation that each phase exists with but a single local density is modified to include the possibility of fluctuations around that local density. It is in practice necessary to assume that the curves of figure 1 are quadratic around whatever local density has been selected. It is evident that the inclusion of additional positive terms in Eq. (6) will lower the free energy, and also clear for $T \ll T_{vw}^c$ that the resultant free energy will still be too large because many of the additional configurations are assigned too great a free energy. For $T \gtrsim T_{vw}^c$ the computed free energy is probably too small, because the quadratic approximation overestimates the probability of large fluctuations. We proceed now to generate some of the consequences of the theory of small fluctuations. We confine ourselves to the theory of the *single phase region*, and begin with the previously mentioned quadratic expansion of the free energy.

$$(9) \quad a(n_i) - \mu n_i = a(n_g) - \mu n_g + \frac{1}{2} a''(n_i - n_g)^2 + \dots$$

$$a'' \rightarrow 0 \text{ as } T, \rho \rightarrow T_{vw}^c, \rho_{vw}^c$$

The second derivative of a is proportional to the inverse compressibility, here evaluated in some approximation which will be qualitatively similar to that of van der Waals. Substitution of this expansion into Eq. (8) and the further approximate representation of n_i as a continuous and differentiable function of position gives

$$(10) \quad A\{n\} = A_{vw}(\rho_g) + \int \left[\frac{1}{2\rho} \left(\frac{\partial \rho}{\partial \rho} \right)_T (\delta \rho(\mathbf{r}))^2 + b |\nabla \delta \rho(\mathbf{r})|^2 \right] d\mathbf{r}$$

where the first term on the right hand side is the van der Waals free energy and the second term represents the free energy density due to fluctuations, integrated over the volume of the system. The derivation shows that the density fluctuation must not be allowed to vary too rapidly with position, a constraint most easily imposed through a cut off at a maximum wave number in a Fourier expansion of the density fluctuation. We may write the free energy density in the form

$$\begin{aligned}
 A\{n\} &= A_{vw}(\rho_g) + \int a(\mathbf{r}) d\mathbf{r} \\
 (11) \quad a(\mathbf{r}) &= \frac{1}{2\rho} \left(\frac{\partial \rho}{\partial \rho} \right)_T [(\delta\rho(\mathbf{r}))^2 + k^{-2} |\nabla \delta\rho(\mathbf{r})|^2] \\
 k^2 &= \frac{1}{2b\rho} \left(\frac{\partial \rho}{\partial \rho} \right)_T
 \end{aligned}$$

from which information about the equilibrium radial distribution function may be inferred as follows.

The equilibrium radial distribution functions is related to the mean density at a distance r from a fixed molecule by the equation

$$(12) \quad \rho[g(r) - 1] = \rho G(r) = \langle \delta\rho(\mathbf{r}) \rangle$$

Since the free energy fluctuation is quadratic in the density fluctuation, the mean and most probable densities at the point $\mathbf{r}$ are identical, and may be obtained by minimization of

$$\int a(\mathbf{r}) d\mathbf{r} + \int \delta\rho(\mathbf{r}) v(r) d\mathbf{r}$$

where $v(r)$ is a short ranged potential. This minimization gives

$$(13) \quad \nabla^2 \langle \delta \rho(\mathbf{r}) \rangle - k^2 \langle \delta \rho(\mathbf{r}) \rangle = 0$$

if r is greater than the range of the potential $v(r)$.

Consequently

$$(14) \quad G(r) \sim e^{-kr}/r$$

the Ornstein-Zernike result. We might observe that a fuller consideration of the equations of motion of the fluid show that the left hand side of Eq. (13), prior to averaging, may be interpreted as an excess pressure [14]

$$(15) \quad \delta p_{loc}(\mathbf{r}) = \left(\frac{\partial p}{\partial \rho} \right)_T [\delta \rho(\mathbf{r}) - k^{-2} \nabla^2 \delta \rho(\mathbf{r})]$$

and consequently Eq. (13) states that the average excess pressure in the neighborhood of a fixed molecule must vanish in equilibrium.

Composition fluctuations near the critical mixing point yield a similar correlation function and this correlation function yields predicted angular dissymmetry of light scattering very close to that observed, as Professor CHU has already noted.

In the next section we consider what modifications must be made to account for the relaxation of fluctuations and for this purpose we go over to a consideration of composition fluctuations in binary mixtures, where the relaxation is diffusion controlled [11] and simpler to describe than density relaxations near the gas critical point [15].

PART IV. — RELAXATION OF COMPOSITION FLUCTUATIONS

With the correspondence $\phi \rightarrow \pi$, $\rho \rightarrow \rho_1$ (species one being the solute), the analog of Eq. (15) is

$$(16) \quad \delta \Pi_{loc} = \left(\frac{\partial \Pi}{\partial \rho_1} \right)_T (\delta \rho_1 - k^{-2} \nabla^2 \delta \rho_1)$$

for the local osmotic pressure. The flux is given by $-D \nabla \delta \Pi_{loc}$ and consequently the conservation equation yields

$$(17) \quad \partial \delta \rho_1 / \partial t = - \nabla \cdot Flux$$

$$(18) \quad \delta = D \left(\frac{\partial \Pi}{\partial \rho_1} \right)_T (\nabla^2 \delta \rho_1 - k^{-2} \nabla^2 \nabla^2 \delta \rho_1)$$

Two comments must immediately be made about Eq. (18). First, if Eq. (18) is to be applied to diffusion in pair space, as part of a generalization of Eq. (12), then the diffusion constant D must be twice the single particle diffusion constant, since both particles in the pair are diffusing. Second, if Eq. (18) is to be applied not to the mean concentration at a fixed distance from a given molecule, but rather to the random composition fluctuations, then Eq. (18) ought to be supplemented by a random diffusional flux, in the manner of LANDAU and LIFSHITZ [16]. For an application of Eq. (18) to Eq. (4), we shall actually use a third interpretation, in which Eq. (18)

determines the mean conditional expectation of the FOURIER component of the composition fluctuation at time t , given the magnitude of the FOURIER component at time 0. Let

$$(19) \quad \delta \rho_1(\mathbf{r}, t) = \int \rho_k(t) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k}$$

and substitute into Eq. (18) to derive

$$(20) \quad \partial \rho_k / \partial t = -D(\partial \Pi / \partial \rho_1)_T k^2 (1 + k^2/k^2) \rho_k$$

the solution of which is

$$(21) \quad \rho_k(t) = \rho_k(0) e^{-|t| \omega_k}$$

where

$$(22) \quad \omega_k = D(\partial \Pi / \partial \rho_1)_T k^2 (1 + k^2/k^2)$$

Substitution from Eqs. (19) and (21) into Eq. (1) gives

$$(23) \quad F(\mathbf{r}, t) = \rho_1^{-2} \int \langle |\rho_k(0)|^2 \rangle e^{-|t| \omega_k + i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k}$$

and therefore the transform required to derive the spectrum from Eq. (4) is given by

$$(24) \int F(\mathbf{r}, t) e^{-i\mathbf{q} \cdot \mathbf{r} - i t \Delta \omega} d\mathbf{r} dt = 2\rho_1^{-2} (2\Pi)^3 < |\rho_s(0)|^2 > \frac{\omega_g}{\omega_g^2 + (\Delta\omega)^2}$$

Consequently the line shape is Lorentzian with half width proportional to ω_g .

Clearly the preceding results are intended to apply only near the critical mixing point where composition fluctuations dominate the light scattering. Far from the critical point, density fluctuations may contribute substantially to the total scattered intensity, and will produce side bands Brillouin scattering) as well as additional contributions to the central bands. The interesting experiments which have begun to emerge [17] are too preliminary to justify comment beyond what Professor CHU has already given.

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 Most of part IV is taken from a letter to Dr. ALPERT based on a preprint report of his work (March, 1965). Prof. DEBYE has given a similar interpretation, without the k^2/k^2 term in Eq. (22), in P. DEBYE, « Phys. Rev. Letters », 14, 783 (1965).

DISCUSSION

Chairman: MIZUSHIMA

FIXMAN

The relaxation time is observed to be proportional to k^2 times the diffusion constant. This much would be derived from purely classical theory assuming that the local osmotic pressure depends only on the local concentration. The remaining term containing k^2 over k^2 is the one that has not been observed but which leads to an equilibrium Ornstein-Zernike correlation.

Note added in proof: preliminary observations of the additional term have been reported by B. CHU and Y. YEH (preprint).

RICCI

Can I ask about the question of elastic scattering? Last year in Washington there was a big discussion about how much the inverse of the elastic scattered intensity versus k^2 must be a slightly bent line and Prof. CHU said something today, but what I am wondering about is, what we mean by elastic scattering. For elastic scattering we can say, scattering in which there must be no energy change in the scattered beam with respect to the incident beam. Now, if this is the case, an experiment like the one in which one is collecting the overall light, at each scattering angle, is not really an elastic scattering.

FIXMAN

I think I should first apologize for using the word elastic so elastically: « elastic scattering » has been used to mean the integrated intensity, that which depends on the equilibrium radial distribution function. The integrated intensity would ordinarily be measured by all but the most refined light scattering techniques.

WIDOM

I would like to ask a question of Prof. CHU and then go on and ask something of Prof. FIXMAN.

Prof. CHU said that in the polystyrene-cyclohexane system one can turn the curved plots into straight-line plots if one makes what he called a « correction for density fluctuations ». Now, am I right in understanding that these are now, quite literally, the density fluctuations that would lead to a turbidity of their own, over and above the turbidity arising from concentration fluctuations at fixed density?

CHU

Yes.

WIDOM

Thank you very much. Now I would like to ask something of Prof. FIXMAN, but first let me make two comments and then ask the question:

The first comment is that one of the possible approximation methods you mention, which you refer to as the Ising Analog Approximation, and that you said has not yet been fully worked

out, looks to me as though it may be the same thing as something which has not yet been published but has been worked out by KADANOFF. These ideas of KADANOFF look on the surface very similar to those that you described in the basic structure of the theory. One takes little cells of dimensions large compared to the intermolecular spacing, small compared to the correlation length, and now Kadanoff's theory assumes that each one of these cells has a magnetization (or, in your language, a density) that is very definitely up or down, that is, very definitely a liquid or a vapour density. What results is that each of these cells now plays the role of a single spin in a now scaled-up Ising model, and from the scaling idea one can then get certain homogeneity properties of the energy and also certain connections between the range of correlation and the compressibility which are identical to others that I had derived in quite other ways, and that one knows are in very good agreement both with experiments and with exact results; so I think, if I am understanding properly what you refer to as the Ising Analog, that this has indeed been worked out and leads to extremely promising results, just as you suspected it would.

The other comment that I wanted to make has to do with the connection between the radial distribution function and the intermolecular potential. You indicated in fact in this equation you have standing here that at very low densities the radial distribution function is just the exponential of minus the intermolecular potential over kT . Now, a point that I want to make is that even at very much higher densities, even with the gases far from ideal, it is still true that at very short distances the radial distribution function is proportional to (not equal to, but proportional to) the exponential of minus $V(r)$ over kT ; so that in the asymptotic limit as r goes to zero, the intermolecular potential curve gives directly the radial distribution function. In some of the most recent and most precise measurements of the radial distribution function by X-ray scattering, one has been able to analyse, or it looks as if one might soon be able to analyse, with sufficient care, the small r behaviour of the radial distribution function, to extract from it directly the

behaviour of the intermolecular potential function. This is something very much in the future. We are very hopeful that by studying the structure of the liquid one might be able to find the potential function. Now, not to monopolize the discussion, but I made two comments, and now the third thing is a question that I want to ask of you.

In your expression between the scattered light intensity and the density fluctuations, you said that you imagined, firstly, that the index of refraction is connected with the density. The light scatters off an index of refraction inhomogeneity, but because of a presumed connection between the index of refraction and the density one can say that the light is scattering off the density inhomogeneity.

Now, any little element of volume, if you imagine some element of volume chosen to concentrate your attention on, in the interior of a large mass of fluid, there is in the volume not only fluctuations of the density but also fluctuations in the energy. Would this mean that, if the index of refraction depended on temperature as sensitively as it does on density, you would have required in your scattering formula additional terms in $d\varepsilon/dT$ as well as in $d\varepsilon/d\rho$?

It is conceivable, of course, that the index of refraction is just not sensitive enough to temperature for these terms to be significant.

FIXMAN

Regarding the last point it is a very good question and the answer must be said to be open. Temperature fluctuation theory is a notoriously difficult subject to comprehend, for me, anyway. Let me say first that where a molecular theory of light scattering has been given, the system studied has been typically something like Argon for which the refractive index is extremely insensitive to temperature and obeys essentially the Lorenz-Lorentz equation. Now, the usual theory of temperature fluctuations assumes these fluctuations to arise from equilibration of a kinetic energy fluctuat-

ion among all degrees of freedom, at constant density. Such an equilibration would not be relevant, I think, to a molecular theory of instantaneous fluctuations in refractive index.

CASIMIR

I should like to go back one moment to the question of temperature fluctuations. It is easier to discuss them in the case of a solid, where you have no fluctuation of the number of atoms or molecules. Then it is not too difficult to work out a theory on the lines of Einstein's old work taking the entropy as a function of temperature for each of the cells and then writing down the probabilities; but such fluctuations are slight. Whether they would lead also to dispersion of light, or scattering of light, would probably depend on the following factors. There is a time-constant of regression of thermal fluctuations and this might be either short or long as compared with the relaxation time between different degrees of freedom. In some cases one would probably have complete equilibrium between the different degrees of freedom; if not you would have to treat the temperature fluctuations of each of the subsystems more or less independently one from the other. On the other hand I don't think specific heat can ever become zero, therefore there cannot exist a critical region with respect to temperature fluctuations. I am not aware of the existence of a phenomenon that might be compared to the scattering of light by density fluctuations and that is related to temperature fluctuations in a solid. Therefore they could hardly play a role in the scattering of light by gases and liquids, or only as a very second order phenomenon.

WIDOM

I think that the conclusion is undoubtedly right, but a part of your argument, about there not being an anomaly in the specific heat that would lead to an enormously large temperature fluctuat-

ion, that is not correct. Now, what you meant to say is that — you said that specific heat is not going to zero — you meant that it is not going to infinity, I presume: but it is. It is the specific heat which is the quantity which determines the temperature fluctuations, in the same sense the compressibility determines the density fluctuations. That specific heat is becoming infinite at the critical point. It's the constant volume specific heat. Now, that point is not shown in a van der Waals equation of state but it has been established independently, both experimentally and by results we have for other theoretical problems.

CASIMIR

One moment, but I am a little bit confused. If the specific heat gets very large, does that mean that you get large temperature fluctuations? I should think it is the other way round.

WIDOM

Yes, it means large energy fluctuations; you see, one could ask, by how much does the energy fluctuate in a fixed volume, in the same way that one could ask, by how much does the total number of molecules fluctuate in a fixed volume; and the compressibility determines the fluctuation of the number of molecules which you could always re-express, if you wanted, as a fluctuation in density; and the specific heat determines how the energy, another extensive quantity, will fluctuate in the given volume. So one could ask, for example, for the index of refraction as a function of number of molecules and total energy content, in a fixed volume, which would be equivalent to asking for it as a function of density and temperature.

CASIMIR

Yes, I agree the energy fluctuation would go up but because specific heat is infinite, the temperature fluctuation, as such, would

go down. (ΔE^2) is proportional to the specific heat, so if you ask for the average value of (ΔT^2) it is proportional to the reciprocal value of the specific heat. So if the specific heat becomes large, the energy fluctuations go up but temperature fluctuations go down. Now unless at the actual point you are referring to the temperature co-efficient of the index of refraction, is getting very high too, as it might if it were really a function not of temperature but of energy, then an infinite value of the specific heat would give no effect. On the other hand, if the specific heat would go to zero, then you would have little energy fluctuations but very high temperature fluctuations which might give more scattering of light.

BUCKINGHAM

Could I make two brief remarks? Firstly about the effect of temperature changes on refractive index: I think there is a considerable body of evidence which shows that refractivity is insensitive to temperature in the visible regions of the spectrum, and for example the polarizability of a water molecule is, I think, 1 or 2% different in steam and in ice. In other words, the polarizability goes through unchanged again, even in a higher polar molecule like water.

And I have a question: You wrote down an expression for the free energy of your fluid in terms of your populations $n_i n_j$. Did that formula assume additivity of the intermolecular potentials?

FIXMAN

I think the answer is no, mainly because I did not define the formula and therefore did not have to make specific assumptions. It would be quite possible to include triplet potentials in the calculation of intra and intercellular interactions and yet to couple only nearest neighbour cells.

GRIMLEY

In your formula for the free energy $A\{n\}$, you only included terms involving the binary product $n_i n_j$. What is the argument which excludes terms in triple products $n_i n_j n_k$?

FIXMAN

That is mainly the assumption that the potential energy of interaction between cells which are far apart is going to be small. An indirect coupling is possible, and it is only a plausible assumption that the indirect coupling will be small for cells containing many molecules, but which are still microscopic in size.

GRIMLEY

I have one question, which I think is directed towards Dr. CHU. I am not too clear about the scattering of electromagnetic radiation from a binary system. There are three correlation functions in a binary system. Which one are we talking about?

CHU

In the case of a binary fluid mixture, the Debye interaction parameter consists of three terms involving 1-1, 2-2 and 1-2 interactions. So the exact physical meaning is somewhat vague although a mathematical expression is available (1).

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·FIXMAN

In a rigorous theory all correlations would be involved, but in a quasi-thermodynamic theory one can say that the compressibility of the liquid mixture is so small that the different radial distribution functions, at least in their long range, are simply related to each other by the criterion that the conditional average density in the neighbourhood of a molecule is the macroscopic density.

INTERMOLECULAR FORCES AND THE NATURE OF THE LIQUID STATE

B. WIDOM

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I wish to discuss the differences in relative importance of the attractive and repulsive components of intermolecular forces in determining the properties of liquids near their critical points and near their triple points. In Fig. 1 is a typical interaction potential $\varphi(r)$ as a function of the distance r between centers of a pair of interacting molecules. It is characterized by a very strong repulsion, of very short range, at small r , and by a much weaker, and much longer ranged, attraction at larger r . In Fig. 2 is the typical pressure (p) — temperature (T) phase diagram of any simple substance, showing the triple point where the solid-liquid, solid-vapor and liquid-vapor equilibrium lines meet, and showing also the critical point at the terminus of the liquid-vapor equilibrium line. The general theme of this paper, and its major thesis, is that to understand the properties of a liquid in the neighborhood of its triple point, and, in particular, to understand the character of the liquid-solid and liquid-vapor equilibria there, it is necessary to know accurately the effects of the repulsive forces, but it is sufficient to treat quite crudely the effects of the attractive forces; and that precisely the opposite is true at the critical point, where,

to understand the properties of the fluid and the character of the liquid-vapor equilibrium, it is necessary to treat with great fidelity the effects of the attractive forces, yet sufficient to take merely nominal account of the presence of repulsive forces.

Where I speak of the necessity to treat accurately the *effects* of the attractive or repulsive forces I do not mean that it is important to know the corresponding part of $\varphi(r)$ with quantitative accuracy. Indeed, even if the $\varphi(r)$ of Fig. 1 were idealized as a square well potential, as in Fig. 3, but the statistical mechanical consequences of such a potential then determined without further approximation, there would undoubtedly result an essentially correct description of all the macroscopic properties of matter throughout a vast region of the

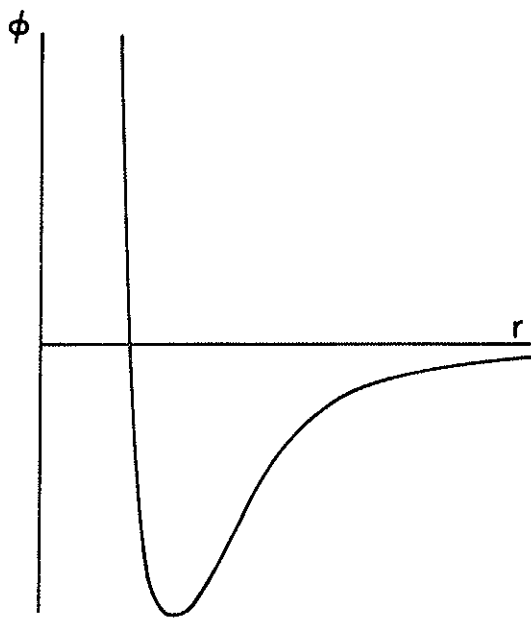


FIG. 1 — Potential energy φ as a function of distance r between centers of a pair of interacting molecules.

p , T plane, including the neighborhoods of the triple and critical points. Thus, what matters is not the quantitative accuracy of the assumed $\varphi(r)$, but rather the *qualitative* accuracy of the resulting *spatial correlations* of molecular positions; and the triple and critical points are distinguished by having the relevant qualitative features of this correlation, and the nature of its propagation through the fluid, determined primarily by the short-range repulsive forces between molecules, or by the longer ranged attractive forces, respectively.

I shall begin by discussing the properties of a fluid near its critical point. The classical description of these properties by the van der Waals equation of state,

$$(1) \quad p = NkT/(V-Nb) - a(N/V)^2,$$

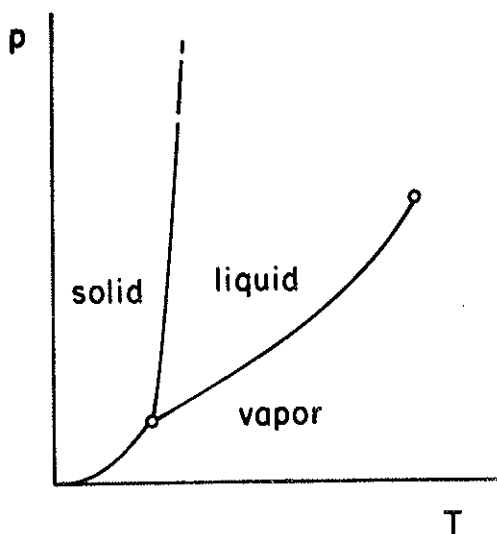


FIG. 2 — Pressure-temperature phase diagram of a simple substance. The circles mark the triple point, where the three equilibrium lines meet, and the critical point, at the terminus of the liquid-vapor line.

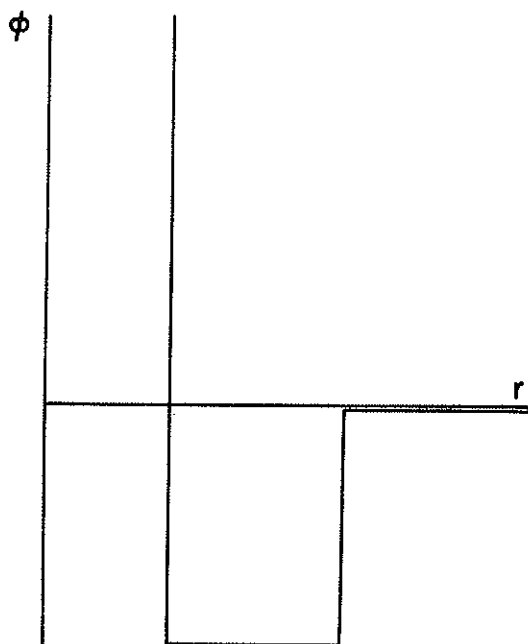


FIG. 3 — The square-well potential, an idealization of the more realistic potential in Fig. 1.

is well known. Here the fluid of volume V consists of N molecules, with a and b characteristic molecular constants and k Boltzmann's constant. The pressure-volume isotherms implied by Eq. (1), near the critical point, are shown in Fig. 4. The highest lying of the three shown is a typical one for a temperature above the critical temperature, $T > T_c$; the next is the critical isotherm, $T = T_c$, characterized by vanishing slope at its point of inflection, which is the critical point; and the lowest of those shown is a typical one for a temperature below the critical temperature, $T < T_c$. The latter, which from

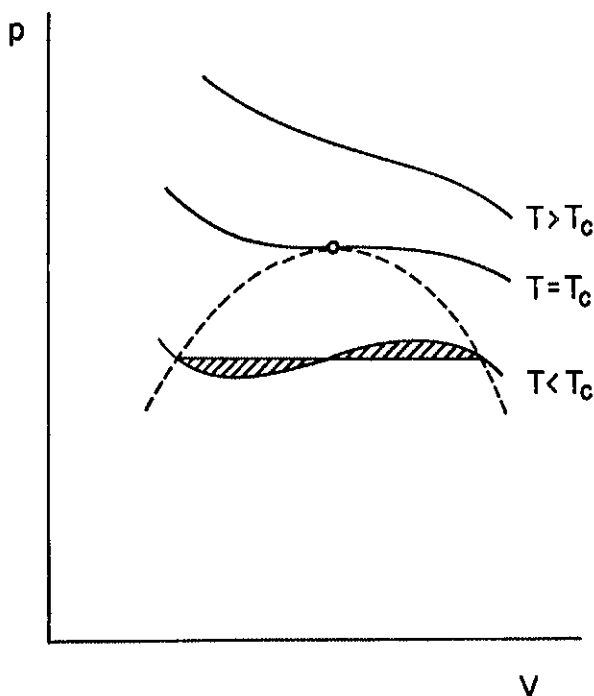


FIG. 4 — Pressure-volume isotherms from the van der Waals equation of state. The horizontal line-segment on the $T < T_c$ isotherm is drawn so as to make the shaded areas equal. The dashed curve is the coexistence curve, which is the locus of the end-points of such horizontal line segments. The circle marks the critical point.

Eq. (1) is a smooth curve with loops, is to be reinterpreted by Maxwell's equal-areas construction, as shown, and the loops then discarded in favor of the horizontal line segment, which represents the behavior of the system when a liquid and a vapor phase are both present. The dashed curve, known as the coexistence curve, is the locus of the end-points of the horizontal line segments, and thus outlines the

two-phase region of the p, V plane. Its maximum is at the critical point, where it is tangent to the critical isotherm.

Of the numerous features which characterize the van der Waals equation, and many other equations of state of that type, I shall call particular attention to three. (i) The critical isotherm is a cubic curve in the neighborhood of the critical point, that is, on the critical isotherm the deviation of p from its value p_c at the critical point is proportional to the cube of the deviation of V from the critical volume V_c ,

$$(2) \quad p - p_c \sim - (V - V_c)^3 ,$$

for small value of $V - V_c$. (ii) The coexistence curve is parabolic in the neighborhood of the critical point, that is, on the coexistence curve the deviation of p from p_c is proportional to the square of the deviation of V from V_c ,

$$(3) \quad p - p_c \sim - (V - V_c)^2 ,$$

for small values of $V - V_c$. (iii) For any fixed volume V , including the critical volume V_c , the constant-volume heat capacity C_v suffers a simple discontinuity when the coexistence curve is crossed. More specifically, as shown in Fig. 5, it increases discontinuously from one finite value to another when the two-phase region is entered from the one-phase region through any point of the coexistence curve, even the critical point. The horizontal axis in the figure could just as well have been labeled with p as with T , and the discontinuity occurs at that value of T (or, equivalently, of p) that corresponds, on the coexistence curve, to the given volume.

Each of these three features, common to almost all approximate equations of state, is in contradiction to the experimental

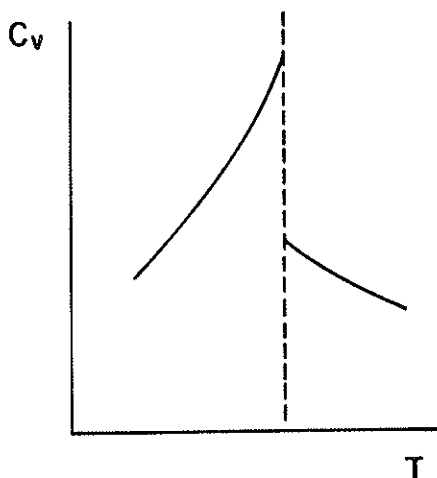


FIG. 5 — Heat capacity C_v as a function of temperature, at a fixed volume, for a fluid satisfying any of the « classical » equations of state of the type of the van der Waals equation. The diagram is qualitatively the same whatever the fixed volume V even if it is the critical volume V_c . The discontinuity occurs at the phase transition temperature that corresponds to the fixed volume in question. For the van der Waals equation itself the high-temperature branch of the curve, representing C_v in the one-phase region, would be horizontal at the constant value $3Nk/2$.

facts [1]. (i) In reality the degree of the critical isotherm in the neighborhood of the critical point surely exceeds 3, probably exceeds 4, and may possibly be as large as 5. Then Eq. (2) should be replaced by

$$(4) \quad p - p_c \sim -(V - V_c)|V - V_c|^{g-1}$$

where g is the algebraic degree in question, which need not be (and very likely is not) an integer, and is in any case greater than 3. (ii) Likewise, the degree of the coexistence curve in

the neighborhood of the critical point is not 2, but is instead very close to 3. Then Eq. (3) should be replaced by

$$(5) \quad p - p_c \sim - |V - V_c|^d$$

where d is the algebraic degree in question, which need not be (and very likely is not) an integer, and is in any case very much closer to 3 than to 2. (iii) Finally, Fig. 5 is a correct qualitative picture of the behavior of C_v only when the fixed volume at which the temperature dependence of C_v is being depicted is far from the critical volume. In a real fluid, the closer V is to V_c the greater are the finite values of C_v between which the discontinuous jump occurs, and these increase without limit as $V \rightarrow V_c$. At $V = V_c$ the dependence of C_v on T is like that shown in Fig. 6. It is well established that the low-temperature branch of this curve (i.e., the behavior of C_v in the two-phase region, with the system as a whole at the critical volume) is given by

$$(6) \quad C_v = A - B \ln |T - T_c|$$

for T close to T_c , with A and B two constants characteristic of the substance; and it is possible, though less certain, that C_v on the high-temperature branch is identical, except for the replacement of A by the smaller constant A' ; so that in $A-A'$ we would have the vestigial remains of a simple discontinuity, now buried beneath the logarithmic infinity. However, the data are also consistent with the possibility that the high-temperature branch of the curve goes to infinity as the inverse of a small fractional power of $T - T_c$ rather than as $\ln (T - T_c)$.

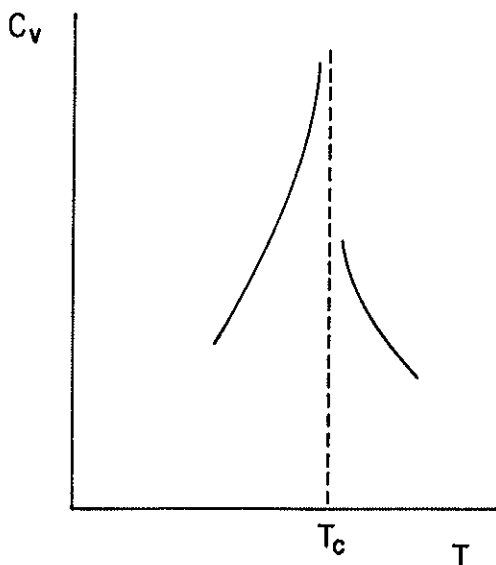


FIG. 6 — Temperature dependence of C_v for a real fluid at its critical volume.

No equation of state of van der Waals type can account for any of these experimental facts. There is, however, a simple fluid model known as the *lattice gas* which has proved to be extraordinarily successful in accounting for the observed critical point properties. The model is a transcription, discovered by YANG and LEE, of the Ising model of ferromagnetism, into language appropriate to a fluid. Suppose, as in Fig. 7, that the fluid volume is divided into a large number of microscopic cells each centered at one site of a lattice. The cells are not imagined to have walls which constrain the molecular motions but are rather imagined merely to provide a coordinate system in terms of which continuous distance variables may be approximated by discrete distance variables; so that the inter-

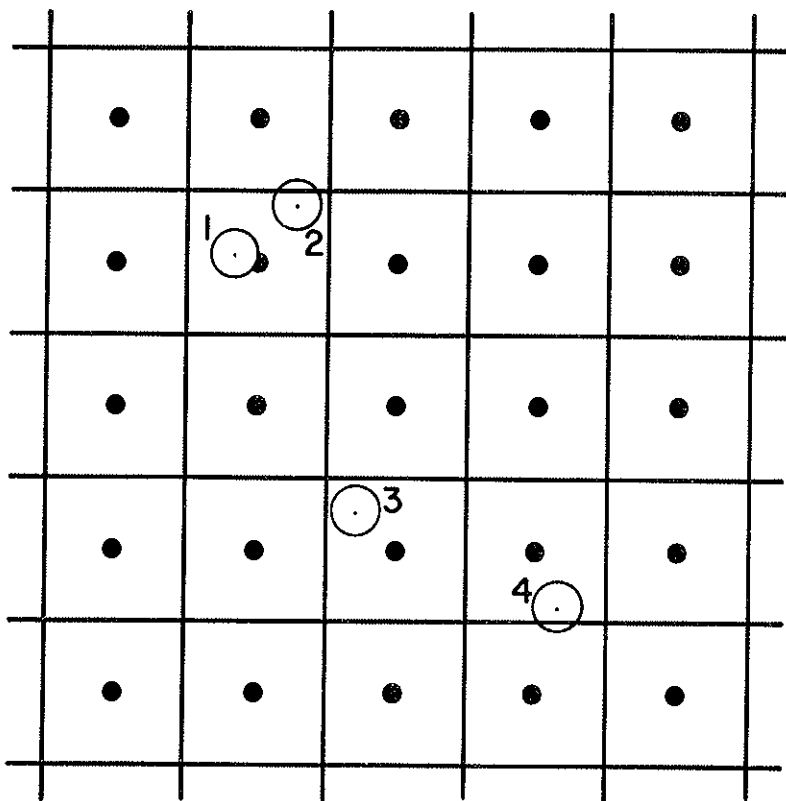


FIG. 7 — The lattice gas model, showing the fluid volume divided into cells, each centered at one site of a lattice. The lattice sites are represented by filled circles. The diagram shows four molecules, represented by open circles and numbered 1, 2, 3, 4. In this configuration the energy of interaction of the pair 1, 2 is $+\infty$, that of the pair 3, 4 is $-\varepsilon$, and that of each of the four remaining pairs (1, 3; 1, 4; 2, 3; 2, 4) is 0.

action potential between a pair of molecules at any instant is taken to depend only on the number of lattice steps separating the cells in which the molecules find themselves at that instant, but not on the precise positions of the molecules within those cells. Specifically, the potential energy of interaction of two

molecules is taken to be $+\infty$ if they are in the same cell; $-\varepsilon$ (with ε a positive constant) if they are in a pair of neighboring cells, one molecule in each; and 0 if the two are neither in the same cell nor in neighboring cells, but are in cells separated by two or more steps on the underlying lattice. In this way one imitates the strong repulsion at small r , weak attraction at intermediate r , and ultimate vanishing as $r \rightarrow \infty$, shown by the more realistic $\varphi(r)$ in Fig. 1. Indeed, this lattice gas interaction appears to resemble closely the idealized $\varphi(r)$ in Fig. 3, but with " r " now discrete, whereas in Fig. 3 it is an ordinary continuous distance variable. In spite of this apparent close resemblance of the lattice gas interaction to an idealized square well interaction in a continuum, the two differ profoundly in their account of the repulsive forces, as we shall later see.

Many of the properties of the lattice gas are known. In two dimensions these properties follow from analytical results derived by ONSAGER and YANG for the corresponding Ising model, and from some later developments; while in three dimensions they are known largely from extensive numerical analysis by the King's College school of DOMB, FISHER, SYKES and their co-workers. The following are properties of the two-dimensional lattice gases: (i) The critical isotherm is of the fifteenth degree, so that $g=15$ in Eq. (4). (ii) The coexistence curve is of the eighth degree, so that $d=8$ in Eq. (5). (iii) When $V=V_c$ the heat capacity C_v has a symmetrical logarithmic infinity at $T=T_c$, so that Eq. (6) holds, but with $A'=A$, that is, there is no finite discontinuity superimposed on the logarithmic singularity. These are, of course, not the experimentally observed properties; but remember that so far we are looking only at a two-dimensional model. Nevertheless, even these results are noteworthy, for they mean that at last a non-van der Waalsian theory has been discovered, a theory which is not inevitably driven to a cubic critical isotherm, a parabolic coexistence curve, and a C_v which is finite, albeit discontinuous,

at the critical point. Furthermore, these results are known to be *exclusively* two-dimensional, so they show, for the first time, that the dimensionality of the system is important in determining the qualitative nature of the critical point. This essential idea was missing from all the earlier theories, which took account, at most, only of certain trivial aspects of dimensionality. We turn, then, to the three-dimensional lattice gas models, with the well-founded expectation that their properties will account for the experimental observations in real fluids; and this hope is fully realized. If there are residual differences between the critical-point behavior of three-dimensional lattice gases and real continuum fluids (and slight differences are indeed indicated), the agreement is in any event very much closer than with any of the classical theories of van der Waals type. (i) The critical isotherm of a three-dimensional lattice gas has a degree close to 5; (ii) the coexistence curve has a degree close to 3; and (iii) when $V=V_c$ the heat capacity C_v in the neighborhood of $T=T_c$ is given by Eq. (6), at least in the two-phase region, though it may become infinite as the inverse of a small fractional power of $T-T_c$, rather than as $\ln(T-T_c)$, on the high-temperature branch.

Granting that the lattice gas model provides an essentially correct description of a fluid in the neighborhood of its critical point, we must now inquire into the different ways that the effects of the repulsive and attractive forces propagate through the model fluid. If ϵ , the magnitude of the attractive interaction potential between molecules in neighboring cells, were 0, there would remain as molecular interaction only the infinite repulsion between molecules in the same cell. In this limiting case, if it is known that a particular cell is occupied then it is certain that no second molecule is in that same cell, but the probability of any other cell in the volume being occupied is simply N/C , where N is the total number of molecules, and C the total number of cells, in the model fluid. Thus, in the lattice gas model, when the attractive component of the inter-

molecular potential vanishes, the equilibrium condition of the fluid is one in which the cells are occupied entirely at random, subject only to the restriction of no multiple occupancy. The repulsive component of the intermolecular potential does not by itself lead to correlations in molecular positions extending beyond a single cell. Any longer ranged correlations in the lattice gas must then be due entirely to the attractive comp-

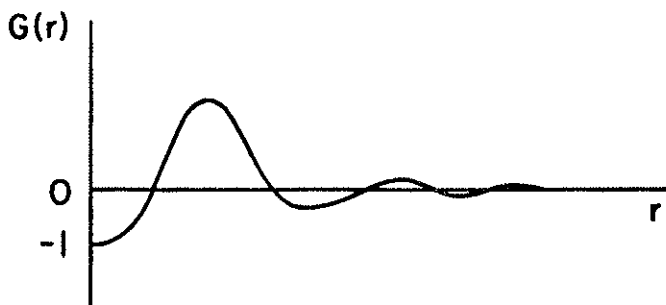


FIG. 8 — A typical pair correlation function in a liquid. It is a measure of the extent to which the average density at a distance r from the center of any molecule deviates from the mean density of the fluid.

onent of the potential. The repulsive component merely establishes a scale of distance, that is, the edge-length of the cell, or the spacing of the underlying lattice, but it is the attractive component which determines through how many multiples of this unit of distance the correlation of molecular positions may propagate.

It is the propagation of such correlations through great distances which is the single most significant feature of the critical point at the molecular level. Turn now from the lattice gas model to a real continuum fluid. Define the radial distribution function $g(r)$ to be that function of distance r which, when

multiplied by the average density ρ of the fluid, yields the average *local* density at a distance r from the center of an arbitrarily chosen molecule in the fluid. Thus, it is the deviation of $g(r)$ from 1 which measures the extent of the correlation between molecular positions:

$$G(r) = g(r) - 1$$

is the pair correlation function, and describes the correlating effect of the presence of any one molecule on the position of any second molecule. A typical $G(r)$ is shown in Fig. 8. At very small distances r the correlation is large and negative because the strong intermolecular repulsion at short distances makes it extremely unlikely that any other molecule will be found so close to the arbitrarily chosen central molecule. At somewhat larger distances $G(r)$ becomes positive, for at such distances from the central molecule there is a greater than average chance of finding another molecule. Such a molecule, in turn, would repel strongly molecules that are near to it, so at still larger distances from the central molecule the local density becomes less than the average density, that is, $G(r)$ again goes negative, etc. At each stage, however, molecular positions are determined only with some probability, not with certainty, so the information about the presence of the central molecule is gradually lost, $G(r)$ decays to 0 at large r , and the local density becomes indistinguishable from the overall average density.

Now by a fundamental theorem of Ornstein and Zernike, the isothermal compressibility χ is closely connected to the integral of the pair correlation function; in a three-dimensional fluid,

$$(7) \quad \rho k T \chi = 1 + 4\pi\rho \int_0^\infty G(r)r^2 dr ,$$

where ρ is the average density measured in number of molecules per unit volume. The integral, as the average of the correlation function, determines the density fluctuations in the fluid, which in turn are related by statistical mechanical theory to the compressibility χ . Equation (7) results from equating those two expressions for the density fluctuations. Near the critical point in the one-phase region the p, V isotherms are almost horizontal (see Fig. 4), and at the critical point itself $(\partial p / \partial V)_T = 0$. The compressibility χ , which is $-V^{-1}(\partial V / \partial p)_T$, is then very large near, and infinite at, the critical point. Therefore the integral in Eq. (7) converges in the one-phase region, but more and more slowly as the critical point is approached, finally diverging at the critical point. The reason is that the effective *range* of the correlations, that is, the distance within which the correlations are still significant but beyond which $G(r)$ decays rapidly, itself becomes infinite at the critical point. Thus, macroscopically a fluid in the neighborhood of its critical point is characterized by a very great compressibility, and this is a manifestation of what we have now seen, at the molecular level, to be a very great correlation range. This correlation length determines the average linear size of the density inhomogeneities, and hence also of the index-of-refraction inhomogeneities, that arise from spontaneous density fluctuations. Sufficiently close to the critical point the correlation length becomes as large as the wave length of visible light, which these inhomogeneities then scatter strongly, thus manifesting themselves in the « critical opalescence », which Professor DEBYE's recent researches have done so much to elucidate.

We may summarize as follows the position we have now reached in our argument: The repulsive forces in the lattice gas model serve merely to establish a unit of distance but do not otherwise contribute to the propagation of correlations through the fluid. This is not a general feature of repulsive forces — quite the contrary, as we shall see — but merely an

artificiality of the model; yet the model is phenomenally successful in accounting for the properties of real fluids near their critical points. It must be, then, that it is fundamentally the propagation of those correlations that are due to the attractive component of the intermolecular interaction, and not of those due to the repulsive component, that determines the character of the critical phenomenon. This was the first half of the thesis I proposed in my introductory remarks. The second half may now be stated thus: It is fundamentally the molecular correlations that are due to the repulsive component of the intermolecular forces, and not those that are due to the attractive component, that determine the properties of a fluid at its triple point; and a model which idealizes the attractive forces in such a way as to ascribe to them no correlating effect whatever, yet treats the correlating effect of the repulsive forces with high accuracy, is just as successful in accounting for the character of the triple point as the lattice gas model is in describing the critical point.

The first clue to the importance of the repulsive forces in determining the nature of liquid-solid equilibrium is provided by the lattice gas model itself, by its utter failure to show any sign of the appearance of a solid phase. A crystalline solid would be characterized by a pair correlation function $G(r)$ which, unlike that in Fig. 8, was not asymptotically zero, but rather approached more and more closely a function which oscillated with undiminished amplitude, and strict periodicity, at large distances r . A solid, then, unlike a fluid, has long-range order. Even at the critical-point of a fluid $G(r)$ is damped to zero - though the damping is then much slower, and of a qualitatively different character, from that in a fluid of finite compressibility. The liquid-solid equilibrium line in Fig. 2 separates sharply those states of the system in which long-range order is absent from those in which it is present. The lattice gas model, however, has only one two-phase equilibrium line in its entire p, T plane, a single analytic curve emerging

from the origin and ending in a critical point. At no finite p , however large, and at no positive T , however small, is there any state of the lattice gas with long-range order. Thus, the lattice gas fails as a model near the triple point as spectacularly as it succeeds near the critical-point. We already know that in that model the attractive forces produce correlations which can propagate beyond the range of the forces themselves, but that the repulsive forces do not; and it is in the latter feature of the model that we must then seek the origin of the failure of the lattice gas to account for crystallization.

If v_o is the volume of one cell in the lattice gas model, then this is the volume from which any one molecule excludes the center of any other. A pair of molecules, one in each of two different cells, excludes the center of any third molecule from a volume $2v_o$. In general, n molecules, whatever their relative positions, exclude an $(n+1)$ th molecule from a total volume nv_o . Thus, the repulsive forces in the lattice gas lead to exclusion volumes which are additive. Contrast this with the exclusions of impenetrable spheres in a continuum, that is, with the exclusions that result from the repulsive portion of a potential such as that in Fig. 3, where r is a continuous distance variable. A hard sphere excludes the *center* of a second identical sphere from a sphere of twice its own diameter, which I shall call the exclusion sphere (see Fig. 9a). While the physical spheres may not overlap, their exclusion spheres may (as in Fig. 9b), with the result that exclusion volumes are not additive: The volume from which two spheres exclude the center of a third may be less than simply twice the volume from which one sphere excludes the center of a second; and the deviation from additivity, that is, the extent of overlap of the exclusion spheres, depends on the molecular configuration. It is through this configuration-dependent deviation from additivity of exclusion volumes that short-range repulsive forces produce longer ranged correlations in molecular positions, so that a continuum fluid of hard spheres has a pair-correlation

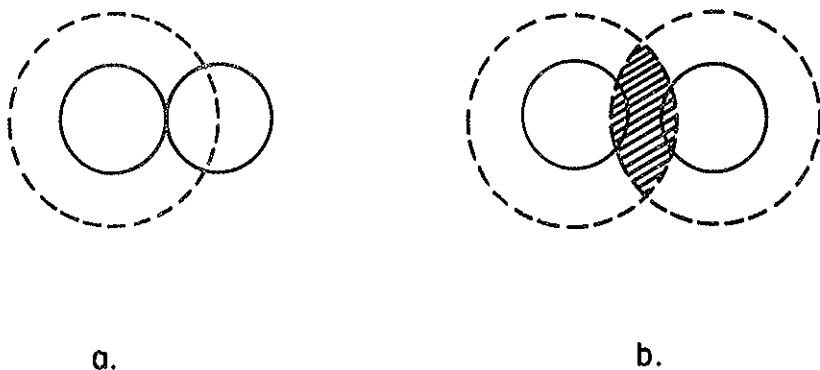


FIG. 9 — *a.* The solid circles represent two hard spheres in contact. The dashed circle is the exclusion sphere of the hard sphere with which it is concentric, that is, it is the sphere from which the center of the second hard sphere is excluded. *b.* Two hard spheres with overlapping exclusion spheres. The region of overlap is shaded.

function $G(r)$ not qualitatively different from that in Fig. 8, but very different indeed from the $G(r)$ of the lattice gas without attraction.

If exclusion volumes were strictly additive, so that n molecules excluded the center of any other from a volume nv_o , with v_o a fixed constant, then in the absence of attractive forces the equation of state of an assembly of N such impenetrable molecules in a volume V would be [2]

$$p = - (kT/v_o) \ln [1 - Nv_o/V] ,$$

whatever the dimensionality of the system. In particular, this is also the equation of state of the lattice gas when $\epsilon=0$. It is an analytic function of density for all densities up to that of

complete filling, $N/V = 1/v_o$, and therefore shows no phase transition. When, as in a continuum fluid of hard spheres, exclusion volumes are not additive, the equation of state depends sensitively on the dimensionality of the system. In one dimension the equation of state of hard spheres (that is, rigid rods) without attraction is

$$(8) \quad p_{h.s.} = NkT/(V-Nb) \quad (\text{one-dimensional})$$

where b is the sphere diameter (rod length). This, too, shows no phase transition. In two and three dimensions the equations of state of hard spheres are not known analytically, but the computer studies of ALDER and WAINWRIGHT and of WOOD and JACOBSON provide strong evidence that in each of these cases there is a first-order phase transition between a less dense phase without crystalline order and a more dense phase with crystalline order [3].

That the attractive forces between molecules are relatively weak and long ranged compared to the very steep repulsive forces suggests that in a fluid as dense as a liquid is at its triple point the attractive forces exerted on any molecule by its neighbors largely cancel, while the negative potentials largely add, so that each molecule in such a liquid may be thought of as a hard sphere in a deep but uniform (that is, gradientless) negative background potential. The depth of this background potential is proportional to the number of molecules contributing to it, and hence to the density of the fluid, so that the total potential energy U in the fluid of N molecules is

$$(9) \quad U = -aN \cdot N/V$$

where a is a positive proportionality constant. Because the background potential has no gradient it leads to no forces on the hard spheres which are immersed in it, and the equilibrium configurations of the latter are identical to what they would be in a fluid of hard spheres at the same density but without a background potential. If $S_{h.s.}$ is the configurational entropy of the latter system, then the configurational entropy S of the model fluid with the background potential is identical:

$$(10) \quad S = S_{h.s.}$$

Then from Eqs. (9) and (10) the equation of state of the model system is

$$(11) \quad p = [\delta(TS-U)/\delta V]_T = p_{h.s.} - a(N/V)^2$$

where $p_{h.s.}$ is the pressure of a hard-sphere fluid without a background potential which is at the same density and temperature as the model fluid. The effect of the uniform negative background potential on the equation of state of the hard sphere system is therefore merely to lower the pressure by an amount proportional to the square of the density [2, 4, 5].

This is now the model which I anticipated earlier. The positional correlations in it are due entirely to the repulsive forces, idealized as those between hard spheres. The attractive forces, which are imagined to give rise merely to a uniform background potential, do not in any way influence the molecular configurations. My original thesis will then be fully established if Eq. (11) proves to account well for the properties of a liquid near its triple point.

It is essential to take $p_{h.s.}$ in Eq. (11) to be the correct pressure of a three-dimensional hard sphere system, just as it was

essential, in the application of the lattice gas model to the study of the critical phenomenon, to evaluate accurately the partition function of the three-dimensional model. If, only for the moment, we identify $p_{h.s.}$ with what we know it to be in one dimension, Eq. (8), then the equation of state of the model, as given by Eq. (11), becomes the van der Waals equation [4, 5], Eq. (1). Thus, except for the fact that we must use the true three-dimensional $p_{h.s.}$, rather than its one-dimensional form, our model fluid is a van der Waals « gas ». An interesting and curious inversion has therefore occurred: The van der Waals equation was originally introduced into physical science to represent the behavior of imperfect gases and to treat liquid-vapor equilibria, in particular the critical phenomenon. Those applications have now been discredited; but I claim that, instead, what is in essence still the van der Waals equation, though with the three-dimensional $p_{h.s.}$ replacing the original one-dimensional $p_{h.s.}$, is the basis of a correct theory of dense liquids and of the liquid-solid equilibrium in the neighborhood of the triple point.

The upper curve in Fig. 10, labeled $a=0$, represents schematically the three-dimensional $p_{h.s.}$ as a function of volume, at a single temperature, as it might be estimated from the computer studies [3] of the hard-sphere system. Because the only forces are then infinitely strong repulsions it follows that at any fixed volume the pressure is necessarily proportional to the absolute temperature, so a $p_{h.s.}$ isotherm at any other temperature would differ from the one shown only by a vertical scale factor. The horizontal portion of the isotherm shows the first-order phase transition occurring between a « liquid » of volume V_2 and a « solid » of volume V_1 . The lower curve, labeled $a>0$, represents schematically the p given by Eq. (11) at the same temperature as that for which the upper curve is drawn; so that it is constructed from the upper curve by subtracting from the latter a quantity inversely proportional to V^2 . Over the range of volumes where the $a=0$ isotherm has its

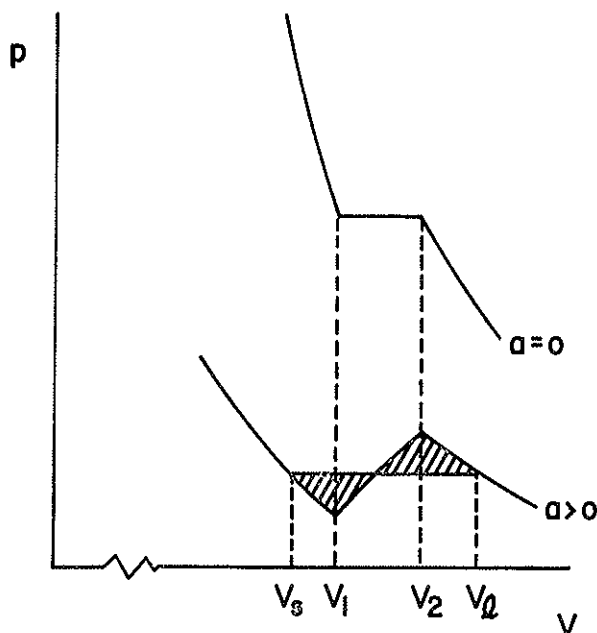


FIG. 10 — A pressure-volume isotherm of a fluid of hard spheres with no background potential ($a=0$), and an isotherm at the same temperature for the same hard sphere fluid with a background potential ($a>0$). The latter has been reinterpreted by an equal-areas construction and shows a first-order phase transition from a solid of volume V_s to a liquid of volume V_l . The phase transition in the former case ($a=0$) occurs between a state of volume V_1 , with crystalline order, and a state of volume V_2 , with no long-range order.

horizontal portion the $a>0$ isotherm is an increasing function of V and so represents mechanically unstable states of the model system. Outside the range $V_1 < V < V_2$ the pressure $p_{h.s.}$ on the upper curve falls sufficiently rapidly with increasing V so that the resulting p on the lower curve also decreases with increasing V outside that range. The $a>0$ isotherm must next be reinterpreted by an equal-areas construction, as shown in the figure, with the result that the model system, at the temp-

erature for which its p , V isotherm is shown, undergoes a phase transition between a crystalline solid of volume V_s and a liquid of volume V_l .

We may read directly from the figure the equilibrium pressure p at the temperature of the depicted isotherm, for it is the value of p at which the horizontal line segment is drawn in the equal-areas construction. Moreover, this may be done at any T , so in this way we derive the solid-liquid equilibrium line in the p , T plane, like that in Fig. 2. Furthermore, applying known thermodynamic formulae to the low-density branch of any isotherm, we may also calculate the common value of the activity z of the liquid and the solid when they are in equilibrium at that temperature. Let z be normalized in such a way as to be asymptotic, say, to the number density $\rho = N/V$ in the ideal gas limit which is approached at low density. Suppose now that at every temperature T the solid-liquid equilibrium pressure p and activity z have been derived in the manner I just outlined, and that p/kT and z are then compared. In general these two quantities will differ, but at one temperature they will be equal to each other, and *that is the triple-point temperature* of the model fluid, which I show as follows: At the triple-point of any liquid to which this theory might reasonably be applied, the vapor which is in equilibrium with the condensed phases is so dilute as to be effectively an ideal gas; therefore, by the stated normalization of the activity z , the equality $p/kT = z$ must hold in this vapor; but at the triple point, p has the same value in all three phases, as do T and z ; so that at the triple-point the equality $p/kT = z$ must hold also in the condensed phases; and, indeed, the condition that this equality *do* hold with the p and z which are the liquid-solid equilibrium p and z for the given T , then uniquely identifies the triple-point.

All the thermodynamic properties of the model have now been derived or are readily accessible; but, so far, they still depend on two parameters, viz., the constant a in Eq. (11)

and the sphere diameter b which is implicit in $p_{h.s.}$. However, if we content ourselves with calculating only dimensionless quantities, and these evaluated only at the triple-point, then the results are invariant characteristics of the model, independent of a and b . In table 1 I quote what amount to the free energy and its first derivatives, in dimensionless form and evaluated at the triple-point. In the first row are the consequences of this model [5, 6] and in the second row are the experimental results for argon [7]. Because only dimensionless quantities appear, the experimental results apply not only to argon but also to any substance which obeys with argon a law of corresponding states, so these experimental results are, with considerable accuracy, the same also for krypton and xenon, and with slightly less accuracy are the same for a very much wider class of substances.

In the first column is the ratio of liquid to solid volume at the triple-point, V_l/V_s . In comparing the theoretical and experimental results for V_l/V_s we must recognize that the 1 preceding the decimal point is a significant figure! The theory is absolute and parameter-less, containing no data beside the single curve giving $p_{h.s.}b^3/kT$ as a function of V/Nb^3 , which is provided by the computer calculations of the equation of state of a three-dimensional hard sphere system. That V_l and V_s are nearly equal, so that 1 precedes the decimal point in V_l/V_s , is therefore a significant (if hardly surprising) result of the theory. In the second column is the logarithm of pV_l/NkT at the triple-point, with V_l/N the volume per molecule in the liquid phase. In the third column is the entropy of fusion per molecule, $\Delta S/N$, in units of Boltzmann's constant k , evaluated at the triple-point, while in the fourth column is the potential energy U_l of the liquid (the negative of the energy of vaporization) in units of NkT , again at the triple-point. The agreement between theory and experiment in table 1 is sufficiently close so that we may conclude that the model of hard spheres in a

uniform background potential provides an essentially correct description of a liquid at its triple-point.

The second and higher derivatives of the free energy, however, are finer probes than are the quantities in table 1, and show the extent to which the model is an oversimplification.

TABLE 1

	V_l/V_s	$\ln(pV_l/NkT)$	$\Delta S/Nk$	U_l/NkT
Model liquid	1.19	-5.86	1.64	-8.6
Argon	1.144	-5.88	1.69	-8.53

Because, in the model, the background potential is independent of the temperature, while the interactions of the hard spheres with each other contribute no potential energy to the system, the model has no configurational specific heat, and C_v is just $3Nk/2$, arising only from the kinetic energy of the spheres. But in a real liquid there is a configurational C_v , of magnitude about half that contributed by the momenta. The other second derivatives of the free energy, viz., the coefficient of thermal expansion α and the isothermal compressibility χ , also reflect the artificialities of the model, though to a somewhat lesser extent. I quote in Table 2 dimensionless forms of these three quantities, all evaluated in the liquid phase at the triple point, both for the model liquid and for argon.

TABLE 2

	$T\alpha$	$NkT\chi/V$	C_v/Nk
Model liquid	0.50	0.058	1.50
Argon	0.366	0.0495	2.33

That in a liquid near its triple-point the correlations due to the short-ranged repulsive forces are more significant than those due to the longer ranged attractive forces, and that in a fluid near its critical point precisely the opposite is true, may be viewed as inevitable consequences of the fact that at the triple-point the density of a liquid is close to that of the corresponding solid, while typically the critical density is only one-third that. Nevertheless, the extreme sharpness with which the distinction appears is most striking and unexpected. I believe it fair to conclude, in any event, that both halves of the thesis are now established, and that we can claim to know, if only in broad outline, the ways in which intermolecular forces manifest themselves in the macroscopic properties of simple liquids.

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DISCUSSION

Chairman: MIZUSHIMA

HIRSCHFELDER

Your equation of state is certainly extremely impressive. I am particularly impressed with the figures that you have on the board for the triple point. It seems to me that if you had used a power law repulsion instead of the square well potential, you would have been able to have adjusted the specific heat to agree with the experiment.

WIDOM

I have no doubt whatever that that's right, because surely by making the change in the potential that you are proposing, one is coming closer to the truth, which can't help but leave the good results good, and to improve the poor results. Of course, it now means that we will not be able to do something that we were able to do when we were working out the details of this model, and that is, to say that we know, to begin with, exactly what the equation of state of our models is.

HIRSCHFELDER

Should we put in our conclusions that it would be very nice if someone would do the Monte Carlo calculations for a simple power law repulsion potential?

WIDOM

Yes indeed, I think that such work would be extremely valuable. Now when you first said power law, I didn't realize that you were referring to a power law repulsive potential, because I don't think that where one does see discrepancies between theoretical and experimental results, the discrepancies are nearly so much due to the idealization of the repulsive forces by hard spheres, as they are due to the idealization of the attractive forces as a uniform background potential. So an improvement in the way the attractive forces are being treated would be more significant.

HIRSCHFELDER

I disagree. I have played around with the equations of state of liquids, and by varying the power law I have been able to vary C_v any way I wanted to.

WIDOM

Yes. So you feel then that it is quite conceivable that the discrepancy in the heat capacity is due at least as much to the repulsive forces as to the attractive?

HIRSCHFELDER

I would bet on it.

WIDOM

That is very interesting. It had not occurred to me as a possibility. I was ascribing it entirely to the treatment of the attractive forces.

CASIMIR

I should first of all like to make a remark. You mentioned that it is somewhat ironical that the van der Waals' equation is only right for the one dimensional case and does not apply to the critical point but to the triple point. Now to add to that, I think the first one to describe the one-dimensional gas was Lord RAYLEIGH in one of his papers, and Prof. ZEEMAN once told me that old VAN DER WAALS for the rest of his life had a poor opinion of Lord RAYLEIGH because he was speaking about weird abstractions like a one-dimensional gas. To learn that this is the only case in which van der Waals' own equation is right, is quite amusing.

I had one question. You have two types of quantities, those for which you get perfect agreement, and those for which the agreement is less good. Now, what is the experimental situation? One might imagine that if you take different gases, let's say argon and neon, and xenon, perhaps, but confining ourselves to noble gases, that the quantities of the first kind would be very close to one another for all these different gases, whereas the experimental values of the second type of quantities might be more different. Is that true?

WIDOM

I am not going to be able myself to give a satisfactory answer to your question. I am going to turn to Prof. HIRSCHFELDER to answer it if he can, but I do want to say that that is a highly ingenious suggestion. On the other hand, I have a feeling that it is not the case. I have a feeling that in so far as there are deviations from corresponding states, they don't show up nearly so strongly in these second derivative quantities, as do these deviations, because you see — suppose we could have worked out the exact statistical mechanical theory with a realistic intermolecular poten-

tial; now under those circumstances, none of the difficulties of assuming uniform background potentials and so on would show up. There can be little doubt that we would arrive at excellent values for the configurational specific heat if we could work out the exact statistical mechanics with a realistic intermolecular potential. And in so far as that intermolecular potential would have only two parameters, the law of corresponding states would be exactly obeyed. So I believe that this situation would be — though I am subject to verification by Prof. HIRSCHFELDER that corresponding states is obeyed almost as well by the second derivative terms as they are by the low order ones.

HIRSCHFELDER

There is quite an argument between MICHELS in Holland and PITZER in the United States regarding the question of whether xenon obeys corresponding states equation of state. The argument was recently resolved in favour of PITZER when RUSSELL DUFF and BERNIE ADLER measured the shock adiabatics of the noble gases running up to pressures of the order of 300,000 atmospheres, and found that indeed argon and xenon, up to 300,000 atmospheres, seem to obey the same equation state very well.

CASIMIR

But my question was also when you have this equation of corresponding states, whether then two different gases are just as equal as far as the second derivatives are concerned, as they are for the first derivatives. I had an idea that perhaps deviations from exact corresponding states might show up more sensitively in the second derivative quantities than in the first derivative quantities.

HIRSCHFELDER

I am sure that you are right that the notion of corresponding states is only a first approximation. The second derivatives provide too sensitive a test.

OVERBEEK

When you combine the hard sphere equation of state with the uniform background energy, there is a parameter (a) in the uniform background. Do you have to adjust it or are your results independent of this parameter?

WIDOM

These numerical results are all independent of that parameter. Had I wanted, for example, to say not just what U_1/NkT is at the triple point, but to be able to say what is the triple point temperature, and what is U_1 at the triple point, I would have had to assign that parameter. But because I am dealing only in dimensionless quantities, the two adjustable parameters in the theory do not appear anywhere in these results. I have never chosen parameters. That is why I was able to speak of this as a parameterless theory, and grant myself the first significant figure in V_1/V_s .

FIXMAN

I received the impression from your talk that the fifteenth power critical isotherm in two dimensions was an analytical result rather than a numerical extrapolation.

The other question concerns the critical isotherm in three dimensions. I understood from your talk that the current numerical

value is the same as the experimental one, whereas I previously thought they were 5.2 and 4.2 respectively.

WIDOM

I will answer your second point first. The best experimental value for the critical isotherm so far is a degree 4.2, and the theoretical value that comes from the analysis of the three-dimensional results is 5.2. So, indeed, there is that discrepancy. Whether this is because the returns are not all in yet on the experimental results, or whether it is because one is here beginning to see some difference between a lattice model and the true continuum fluid, is not known.

Now your first question had to do with the status of the fifteenth power in the critical isotherm of the two-dimensional system. That is almost, but not quite, an analytical result. What it is, is that there is a semi-theory, I should say three or four semi-theories all of which lead to the same result, that say that three quantities, three of these critical point exponents, necessarily are connected by a certain relation; these three being the degree of the critical isotherm, the power of $T-T_c$ with which the compressibility diverges as one approaches the critical point, and the degree of the co-existence curve. And according to that relation, if one takes the analytically known degree of the co-existence curve and analytically known power of $T-T_c$ with which the compressibility diverges, then a fifteenth power critical isotherm comes out, and indeed the first suggestion that the critical isotherm should be of the fifteenth degree was based on that sort of semi-theory, that quasi theory. And then, there followed the numerical evaluation of the critical isotherm by FISHER and ESSAM, and they showed, if we now treat that as an « experimental » result, that the two-dimensional lattice gases have a degree which is $15.00 \pm .08$. So with this being the numerical experiment, and with 15 having already been suggested on theor-

etical grounds, though admittedly not fully rigorous ones, beforehand, that is, the prediction of 15 having been made on other grounds, we can take 15 as certainly beyond doubt.

BERNSTEIN

You mentioned now that the theory is essentially in a dimensional form, and you have eliminated the quantity a . However, it would be of interest to know if the a has a value which is reasonable.

WIDOM

One would want to know if the a , and the b which is the second parameter, do have values that are reasonable, and the answer is yes. And it was GUGGENHEIM who first rewrote the theory, and certain aspects of it that he felt could be done in a more economical way. And secondly, he wanted to satisfy himself that if one did take one experimental datum, for example, let's say this experimental number, 8.53, and use it then to evaluate the a , he wanted to satisfy himself that it was much the same as the a 's that had been gotten in another method, and so on, and indeed, it is. And likewise the b . If you take a second experimental datum and use that to evaluate the b , it turns out to be just about what you would have supposed that it is.

HIRSCHFELDER

I would like to say one more thing about corresponding states. Corresponding states assumes classical dynamics. The corresponding states results if all potential energy curves are similar and differ only in the scale of energy and the scale of distance. However, we

know that as one goes to lower temperatures, the quantum corrections become important. These involve the de Boer parameter which involves the mass of the molecules and destroys the corresponding states.

WIDOM

Yes, that is quite right, and that would mean that in any of these quantities that I have quoted here, where it is not just a value quoted for the liquid, but where it is a value that involves the solids, such as the ratio of liquid to solid densities, and so on, that in those cases these results are not only experimental results for argon, but also closely experimental results for xenon and krypton. They are not the experimental results for neon, and there are quite significant deviations. So that where solids are involved in any of these quantities, let us say the entropy of the phase transition, these numbers that I have quoted here, may be significantly different for neon. Some of these cases are, I am not sure which, but some are significantly different for neon; on the other hand, essentially no difference from argon to krypton and xenon.

HIRSCHFELDER

I am very appreciative of your numbers from the standpoint that if one should write down the same numbers for the Lennard Jones-Devonshire equation of state, or for any of the other free volume type equations of state, one would come out with horrible disagreements with the experimental data. These are very sensitive tests.

WIDOM

I should add that GUGGENHEIM has in addition produced other tests, in the extensions that I spoke of, to the work that LONGUET-

HIGGINS and I did. He, for example, did use one experimental datum, like this, to produce an a ; then, having gotten the value of this parameter, he is now in a position to find things like the ratio of the normal boiling point temperature to the triple point temperature, and so on. That turns out also to be in excellent agreement with experiment.

HIRSCHFELDER

I have used experimental values of the internal energy of liquids to calculate apparent values of the constant a . They seem to differ from the values in the gas by a factor of 1.5 to 2. The internal energy is a linear function of density in both the liquid and the gas. But the two straight lines — one for the liquid and one for the gas, have quite a different slope.

WIDOM

From the point of view of this theory, that is very easy to understand or, that there should be such a discrepancy, is easy to understand, because the theory does not even pretend to look right, to have the right shape, except in a very dense medium. It says nothing whatever about the gas, in fact, disclaims all knowledge of the gas. In that way it differs from the first of the theories we described, which was the lattice gas model of liquid-vapour equilibrium. On the other hand, this does not in any way affect a number of the kind that GUGGENHEIM calculated for the ratio of the normal boiling point to the triple point temperature, because the normal boiling point still occurs at sufficiently low pressure so that the gas is essentially ideal, and therefore even though this theory gives the gas a entirely wrong, the gas a contributes nothing to that ratio.

BOWDEN

I am most intrigued by this talk. I wonder if you could just elaborate a little on your physical picture of the way in which the molecule is condensed on the liquid surface.

WIDOM

Well, the physical picture is that the molecules are on the whole so close to each other, with the attractive fields of so many molecules affecting any central one that you concentrate your attention on, that this molecule sees, so to speak, attractions coming from all directions, so that they cancel out as far as the net force is concerned. On the other hand, it is sitting in what is now a very, very deep potential minimum, due to the fact that all the potential minima of the surrounding molecules have not cancelled, but have added up, so that these molecules see themselves now sitting in an almost uniform background potential, but they have very hard, almost incompressible cores, sitting in this background potential. So they are going to pack the way hard spheres will pack, and their phase transition is going to be dominated by the hard sphere phase transition, except in so far as it is modified by the presence of the background potential.

And now you might want to rephrase your question: how do you account for the phase transition occurring in the hard sphere system? There one can say, of course, why the hard sphere fluid state should have approximately the geometry it does, and why the close packed crystal state should have approximately the geometry that it does, but what one cannot answer, in fact has never yet been able to answer for any phase transition, is why this transition from one kind of configuration to another, should occur *suddenly*, and have associated with it discontinuities in the thermodynamic functions instead of occurring gradually.

In fact, we know many examples of both kinds of behaviour: under what circumstances the transition is first order, and under

what circumstances it is higher order, or not at all a phase transition, but just a gradual change, one does not know. On the other hand, one can begin to get some idea of the magnitudes that are involved if you consider the following.

Suppose we imagine at first hard spheres in a close-packed configuration. Now these things are locked into position. But you can imagine, if you will, that we will hold these things with their centres fixed, but we will shrink the spheres a little, so that they are no longer in contact, and we will ask by how much must we shrink the spheres, how small must we make them, maintaining this geometry in such a way as just finally to free whole lines of molecules to move through the material? That is, what kind of expansion must one make? What is found is that it must be expanded to some point in this region, the region in which the phase transition apparently occurs, in order just to free whole lines of molecules. And correspondingly, in three dimensions, the expansion is that which just frees lines and sheets of molecules for movement. If one maintains the geometry while one shrinks the molecules, that expansion, when translated into a separation of the molecular centres, again is a value which lies just near one end or the other of the region that is apparently the phase transition region. Of course, when the phase transition occurs in reality, it does not occur with maintenance of geometry, that is, one cannot imagine that the geometry remains the same as you increase the spaces between the molecules. The geometry changes at the same time that the spaces increase. That could not be a fully accurate description of the phase transition, but it does give you an idea of the more or less sudden freeing of the molecules. There comes an expansion from the close packed state at which suddenly molecules can make long excursions or, if not a single molecule, long cooperative excursion by whole lines, or whole sheets, of molecules.

So clearly, we have now come to a serious breakdown of the crystal lattice. The only question, the one which I do not think we will ever be able to answer, is why has that transition occurred

suddenly? Why not gradually? In other words, that is a good argument for saying that the equation of state ought to look something like this, but says nothing at all as to whether these corners should be sharp or rounded. It just does not answer that question at all. And I am not sure that we will ever have an answer.

CASIMIR

I have one question about the critical point. When you use this idea of gas lattice with something like an Ising interaction, I can see that you get a phase transition, and below a certain temperature, you get long-range order and so on. I do not quite see how you get co-existence there, how you get another phase appearing.

WIDOM

Well, when in the language of the magnetic case you get long-range order, then that phenomenon translated into the fluid case is the co-existence of two phases. And the reason is this: We have been saying that the radial distribution function $g(r)$, not the correlation function, but the distribution function itself, as a function of r , is asymptotic to unity, that is, that it is something which goes off at very long distances to the value one. If there is to be long-range order, this g would not become asymptotic to unity, it would become asymptotic to something else. Now, when you have two phases in equilibrium, two fluid phases, a liquid and a vapour, it is indeed the case that the g for one fluid phase is asymptotic to unity, and that for the other fluid phase is asymptotic to unity, but that the g for the two-phase system is not. And the reason the g for the two-phase system is not is that g has the significance of being the local density in a little element of volume that is

known to be distant r from some central molecule. Now, suppose that we have two phases present in equilibrium, and I ask, what is $g(r)$. You would say, « Well, we need to find the local density at a point distant r from a molecule that is known to be present at this point ». But if there are two phases present, you may, with a certain probability, depending on the volume fraction of each phase, have chosen your central molecule in one phase, or in the second phase. And the net result is that the $g(r)$ for the two-phase system involves a weighting of the $g(r)$'s for the separate fluid phases that are in equilibrium — this weighting going proportionally to the volume fractions of the two phases that are present. And they represent the probability that the central molecule in the first place will have been a molecule from phase one or a molecule from phase two. And that weighted average $g(r)$, which is the $g(r)$ for the two-phase system, because it has a weighting which depends on the volume fractions of the phases, is not asymptotic to unity, in spite of the fact that the g for each phase separately is asymptotic to unity. And the fact that it is not asymptotic to unity means that there is a resultant long-range order. And it is that way that the long-range order in the two-phase fluid system is a reflection of the long-range order in the magnetic system.

CASIMIR

Does one indicate if you have this long-range order where the liquid and where the gas is, so to say?

WIDOM

You mean where in the volume? No, you can't. All that you can say is, and now not from the Ising model calculations, but just from, so to speak, general principles, all that you can say is that

one of these phases is going to be a droplet floating in the other phase at an arbitrary position, that is, a position which might have its center anywhere with equal probability.

BUCKINGHAM

I have a rather provocative question to ask! You said earlier on that the critical region and the triple-point regions were interesting relative to the region in between. Then you went on to say that the critical behaviour was dominated by the fact that there are attractive forces but is really rather insensitive to the precise nature of these attractive forces. And similarly at the other end you said that the triple point behaviour was dominated by the repulsive forces but was nearly independent of the nature of these forces. Now I think one could say that this is rather *uninteresting* in that every substance seems to behave in a similar way. What is often *interesting* is the behaviour which depends on the region between the extremes of repulsion and attraction.

WIDOM

Fortunately this is not an issue of scientific fact. The difference you just expressed is a difference in personality between you and me and not a matter that is to be settled by scientific argument!

RICCI

Can I ask something about the transport properties? Must one understand that the transport properties are essentially based on the hard sphere fluid model or must there be some change?

WIDOM

Yes, I understand your question. It is an interesting and important one, and I really do not have a satisfactory answer for you. It is known (but, unfortunately, not to me) to what extent the typical transport properties, the diffusion coefficient, the thermal conductivity and so on, are due to the repulsive forces and to what extent they are due to the attractive forces. It is especially in the theory of Rice and Alnatt that these have been clearly separated and appear in quite different ways. But I am afraid I just do not recall what the quantitative split-up is. How much of the transport phenomenon can be said to be due to the one kind of forces and how much to the other. Prof. HIRSCHFELDER would you remember?

HIRSCHFELDER

In order to have diffusion, it is necessary to create an extra amount of space locally. The energy required depends upon the attractive forces and the vapour pressure. On the other hand, the amount of volume which you require depends upon the repulsive forces. Thus both attractive and repulsive forces are involved.

WIDOM

I have no doubt that the numbers, as you present them, are right if you accept to begin with that model of a diffusion process. But I think that it is probably quite inaccurate to suppose that diffusion in a liquid occurs by first creating a hole large enough to accomodate a molecule and then having the molecule flop into it. I think surely the diffusion is a highly cooperative process occurring in a very large number of extremely small steps and it is only little bits of accessible volumes that need to be created at any moment and that occasionally, by a fortunate accident, these little

bits of volume are created all in the same direction, so to speak, and allow the molecule to creep. On those occasion, when it occurs, the molecule has diffused.

RICCI

If this is the case what bothers me is that you must have a clear isotopic effect in the process. Because also if you make vacancy, if you can build up the vacancy by a kind of cooperative free volume change as in the Cohen and Turnbull model, in both cases the molecule goes in the vacancy at a rate proportional to the inverse square root of its mass and gives therefore an isotopic effect.

WIDOM

Your remarks about the isotopic effects on diffusion are very interesting. I have nothing to add to them, though I was interested to hear them.

INTERMOLECULAR FIELD IN SIMPLE LIQUIDS

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In this short communication I would like to stress some experimental results which, in my opinion, point out the important features of the intermolecular field symmetry in the liquid state. With « liquid state » I mean, roughly, the region of the phase diagram of a simple liquid (for example Argon) bounded between the melting line, the vaporization line and a $\rho \geq 2\rho_c$ line, where ρ_c is the critical density.

The theoretical approach, for explaining the liquid state can be divided into two main lines: the first one considers that, in the liquid state, the solid configuration is preserved on a scale of few molecular diameters and we obtain the various lattice theories [1]. The second one is basically the VAN DER WAALS point of view which considers the symmetry of the intermolecular field to be the same in the gas and in the liquid state [2, 3]. On this line considerable efforts have been done on the hard-spheres models which emphasize the importance of the binary encounters.

The experimental results, I would like to examine, are the following:

- A) radial distribution;
- B) diffusion;
- C) collective excitations.

A) *Radial distribution function*

It is well known that we can obtain information about the static structure [4] of a system by means of X-rays diffraction since their exchange with the system is, practically, only momentum exchange; the energy exchange is negligible with respect to the photon energy.

In case of liquids the Fourier transform, with respect to the momentum exchanges, of the scattered intensities gives us the well known radial distribution function $g(r)$ [5] which is an instantaneous flash of the interatomic arrangements. The average involved in the measurements it is just because of the finite dimension of the beam. Therefore we can look at this average as one over many small systems in thermal contact each other. Strictly speaking in the mathematical treatment of the data we do also an average over all the directions since the liquid is macroscopically isotropic, but this means only that we must not pretend to extract anisotropic effects from the $g(r)$ function.

We can evaluate the shape of the $g(r)$ function when we fix the model of the liquid. This has been done many times [1, 6, 7] for the solid-like picture. Since some arbitrary constants are always left in the model, a general agreement of the calculated $g(r)$ functions and of the experimental ones is obtained. However, if one looks carefully, there is always a failure in reproducing the shape of the first peak of the experimental $g(r)$; i.e. the peak given by the next neighbours shell. The calculations give this peak practically symmetric around its maximum whereas the experiments show a strong asymmetry.

In Fig. 1 the experimental result concerning Argon at 84.25°K and 0.7 atm. [8] is shown as an example. If we call a and b the half width at half height, we have $\frac{2(b-a)}{b+a} \simeq 50\%$ to be compared with the value $\simeq 0$ deduced by the lattice models.

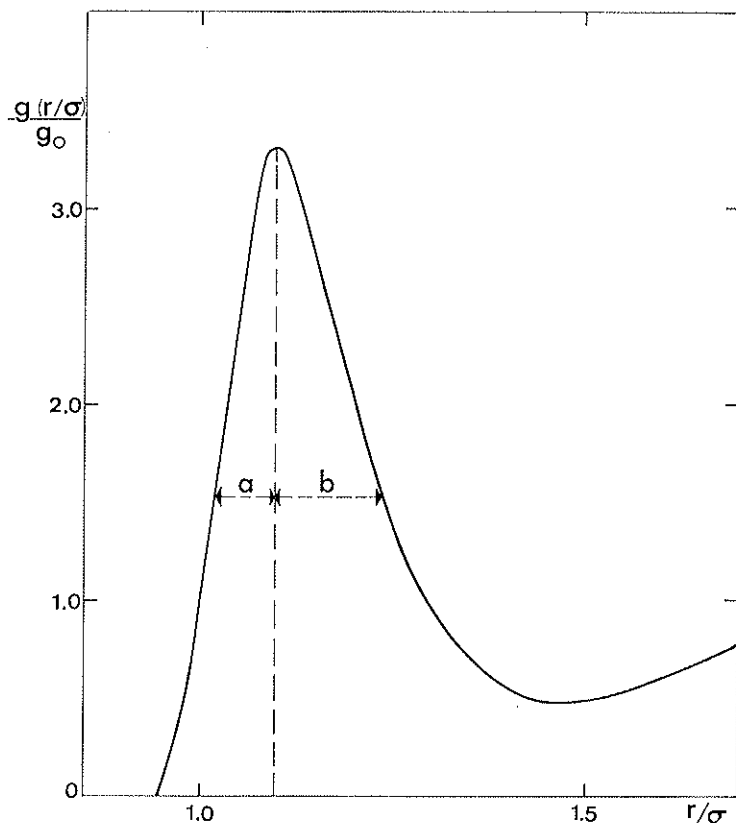


FIG. 1 — The full line is the experimental [8] radial distribution function for Λ_2 at 84.25°K and 0.7 atm. The length is measured in units of molecular diameter ($\sigma=3.41\text{\AA}$) and the $g(r)$ in units of average density g_0 . The symbole a and b are explained in the text.

Moreover up to a distance $r \approx \sigma$ (where σ is the molecular diameter) the $g(r)$ is found to be proportional to $\exp\left(\frac{-V(r)}{KT}\right)$ where $V(r)$ is the usual 6-12 Lennard-Jones intermolecular potential of a pair of molecules. We would like to notice that at this r value the $g(r)$ is yet at a value about half of its maximum.

These *experimental* evidences tell us the equilibrium position (i.e. positions around which the molecules vibrate for times $\gg 10^{-13}$ sec) are not appreciably present in the liquid state. In fact, as we said before, the above measurement is an average over many local configurations (the dimensions of the X-ray beam are practically infinite on the intermolecular distance scale) frozen at a given time. Therefore we find that « equilibrium positions » are practically negligible in determining the structure of the liquid state whereas it turns out to be mainly dictated by the binary encounters. This is also in sharp contraddiction with the « significant structures model » [9] which would predict at this liquid density a strong predominance of the solid-like contributions to the partition function. I would like to stress that the above reported measurement is not affected, as far as the features considered, by the termination error due to the high value of $\frac{\sin \theta}{\lambda}$ up to which the intensity measurements were performed. This can be easily checked, through the convolution, theorem looking the effects on the $g(r)$ obtained after multiplication of the measured intensities by a step function which takes into account the limited range of $\frac{\sin \theta}{\lambda}$ over which informations obtained.

B) *Diffusion*

Transport properties look at the evolution with time of the system structure. Although the macroscopic transport coefficients are mainly connected with the long time behaviour of the distribution functions, anyhow their dependence on the molecular parameters is a usefull test of the proposed models for the dynamic behaviour of the simple liquids.

The diffusion of impurities is the most powerfull source of information. In fact, correlating a great number of experi-

mental results, we can infer some general relationships between the dependence of the diffusion coefficient on the molecular parameters of the impurity, using the corresponding state ideas [11]. For example we can ask if there is some dependence of D on the mass of the impurity. This is a crucial problem since theories [12], which postulate the existence of a time scale over which the only important dynamic event is an hard core collision, would predict a D dependence on $\frac{1}{\sqrt{m_{ij}}}$ ($m_{ij} = \frac{2m_i m_j}{m_i + m_j}$ where i = solute and j = solvent); on the other side models which postulate a short range solid-like configuration for the liquid, and therefore an activated process for diffusion, imply a $\frac{1}{\sqrt{m_i}}$ D 's dependence [13].

We have performed diffusion experiments of various tracers in liquid nitrogen [14] in the range 70-100°K under a constant pressure of 16 atmosphere. We would like to consider mainly the results about diffusion of H_2 , T_2 and Ne . The experimental results are shown in Fig. 2. These three tracers can be considered isotopes as far the effective intermolecular potential in the liquid [15]. The possible influence of quantum effects or molecular shape is negligible and for a more detailed analysis about these points we refer to Ref. 14.

In Fig. 3 the ratios $\frac{D(I-N_2)}{D(H_2-N_2)}$ at 90°K are reported as a function of m_I [I = Hydrogen isotope. The experimental points for $m_I=6$ and $m_I=20$ refer to T_2 and Ne respectively and the behaviour of $D \propto f\left(\frac{1}{m_{ij}}\right)^{\frac{1}{2}}$ or $D \propto f\left(\frac{1}{m_i}\right)^{\frac{1}{2}}$ is also indicated].

The disagreement between the experimental points and the two models is self-explaining. We would like to add that since the temperature dependence of the diffusion of a tracer in a liquid is independent from the tracer's parameters, as it was

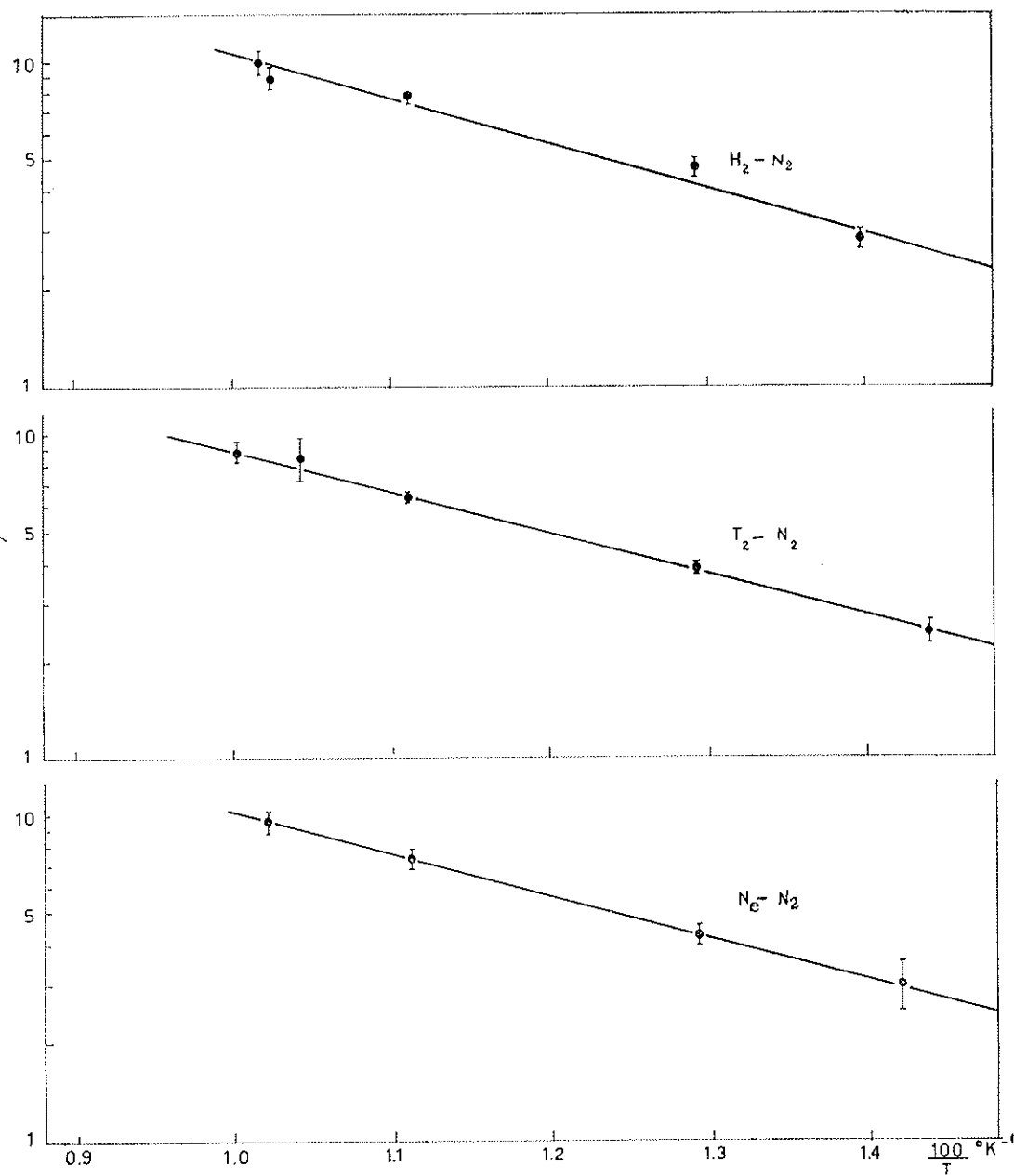


FIG. 2 — Experimental results of diffusion of H_2 , T_2 and Ne in liquid N_2 .

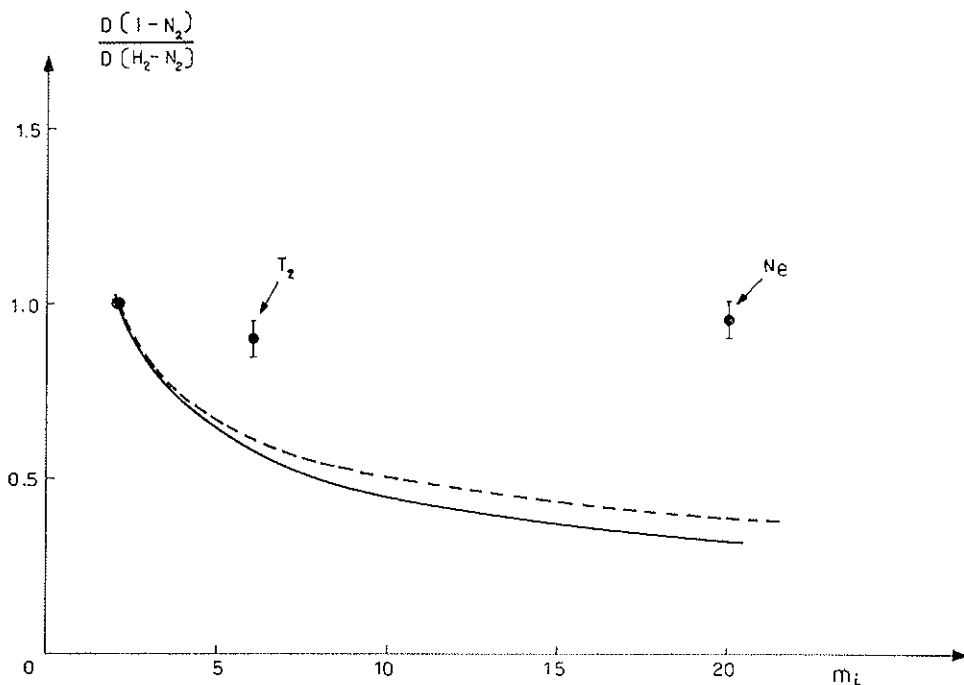


FIG. 3 — Comparison between experimental results and curve: $D \propto \frac{1}{\sqrt{m_i}}$ (-----); $D \propto \frac{1}{m_i}$ (————) showing the absence of isotopic effects in the diffusion process in liquids.

many times stresses [16], there is not ambiguity in Fig. 3 where the various experimental data have been compared at the same temperature; Fig. 3 is temperature independent.

We can conclude that, as far as transport properties are concerned, in the liquid state we cannot speak of binary collisions as well as solid like structure. In other words the collision time is of the same order of magnitude of the life time of the structure of the environment, therefore both these points of view lose their meaning.

C) *Collective excitations*

Finally I would like to comment the problem of the existence of phonons in liquids. Certainly we know that very long wavelength modes are possible but when we speak of phonons I mean modes of wavelength of the same order of magnitude as the interatomic distance. We know that liquid helium II has such excitations up to wavelength of one interatomic distance (rotons region) but the existence of such excitations has been frequently connected with the superfluidity [17].

Above the λ point only the excitations in the roton region broaden so that it is very hard to give them any meaning.

However the branch at lower wavenumber ($K = \frac{2\pi}{\lambda} \leq 0.5 \text{ \AA}^{-1}$) still persist [18]. Therefore we must conclude that such phonons are somehow connected with the general intermolecular field of the liquid state. In fact also in liquid *Al*, liquid *Ar*, and more clearly in liquid *Pb* [19] they have been found. The experiments in all the cases have been performed with neutron scattering. Since a liquid is certainly macroscopically isotropic we are able to impose the conservation of energy and momentum (independently of $2\pi\tau$) if we do scattering around the origin of the reciprocal lattice (Experimentally this means low angle scattering).

We must try to understand what the existence of such modes imply for the structure of the liquids. My opinion is that we have nothing more than a density fluctuations in a region of temperature and pressure where the fluctuations of different momenta are not coupled each other and that the random kinetic motion of individual particles is much smaller than the fluctuation energy. This point has been recently suggested in the case of helium phonons [20] but it can be applied also to the lead case. To fulfill the ERTERS' requirements [20] it is only matter of temperature and compressibility; none

structure parameters enter in these calculations. In analogy with the liquid helium we can say that the dynamical variable connected with the break of symmetry at the melting point, are just the phonons near the zone boundary.

CONCLUSIONS

We can conclude that the experimental evidence tells us the following: in the liquid the short range order idea can only be valid if we mean that each molecule generates an excluded volume and therefore some packing at the higher densities. However this has nothing to do with the lattice order also if we would confine ourselves to a range of one or two interatomic distances. In fact no « equilibrium positions » are present in the sense that we have no vibration around points for times of the same order of magnitude of the DEBEY period.

On the other side, the concept of hard core collisions and therefore the hard spheres point of view is meaningless since the environment life-time is of the same order as the collision time. The intermolecular field in the liquid has certainly the same symmetry as in a less dense gas but we cannot push this idea in the dynamical process where the structure life time is involved. From a dynamical point of view, fluctuations of wavelength of many intermolecular distance are important whereas the short wavelength excitations are strongly damped and goes in diffusion.

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DISCUSSION

Chairman: MIZUSHIMA

WIDOM

I would like to add a comment to something that Prof. Ricci said. He pointed out that scattering results show quite clearly that a liquid is not solid like, and he emphasized the evidence that came from a small R portion of the radial distribution function. He saw a clear difference from what would have been expected on the basis of a local crystalline structure. It is, of course, sure that in an even more fundamental way one can say that the long range behaviour of the radial distribution function shows a clear distinction between a liquid and a solid. That is in the qualitative fact that there is no long range order in the liquid, and there is long range order in solids. Indeed, because of this qualitative question of the existence and the non-existence of long range order (I mean, it is either there or not), it is impossible to conceive of a critical point between a liquid and a solid state. Because if there is to be a critical point, that means that it should be possible to go continuously from one state to the other, and one would have a continuity of states in van der Waals sense. And to go continuously from liquid to solid, would mean to go continuously from a state in which there is a quality of having no long range order to a state in which there is some long range order, and where could that change occur? It is impossible for them to undergo such a qualitative change at the same time as to have a continuous change

from liquid to solid. And it is this non existence of long range order in the liquid that, I think, « defines » the liquid, or defines the difference between a liquid and a crystal. A crystal is by definition a material with long range order. So, it is the long range behaviour of the radial distribution function that distinguishes the liquid and the solid in a fundamental way; though it is not a part that is easily accessible to experiments at the moment. The experiments give with reasonable accuracy the shorter range part only. And there, too, one sees, as Prof. RICCI pointed out, characteristic differences between a typical liquid and a typical solid.

RICCI

The behaviour of the radial distribution function at large values that happens in a liquid, you can find also looking at a very fine powder. This is the main reason, I think, for which people started to think of a liquid like a solid on short range scale. Anyway, this similarity does not hold on the first peak. This is the reason for which I thought it was that part of the radial distribution function which is mainly significant. I agree that this long range order means that the symmetry is really different between a crystal and a fluid, whereas a difference in symmetry between a liquid and a gas has not yet been proved.

HIRSCHFELDER

In line with what Dr. RICCI was telling us, one can see quite easily from the plotting of internal energy as a function of density that a liquid does not have a long range order. The crystal has an internal energy which varies something like a constant times the square of the density minus another constant times the fourth power of the density, whereas a liquid usually has internal energy which is quite accurately proportional to the first power of the density

of the liquid. This means theoretically that the pair distribution function does not change appreciably with density in this region. This implies that a liquid does not have long range order.

FIXMAN

You have stated that the activation energy for tracer diffusion depends only on the solvent species. This is new to me. I wonder if anybody has predicted this or whether it is reconcilable with any theory at all.

RICCI

This has been predicted by COHEN and TURNBULL. They think that the diffusion process can happen just by fluctuation of portions of free volume which are collected together in one place of the liquid. This is, in free volume language a transposition of what RICE did in crystals using normal modes. I think this effect must be inherent in any theory which considers the diffusion process to be connected with relaxation of a large number of molecules. In other words, we can see the diffusion as a really cooperative phenomenon.

INTRAMOLECULAR AND INTERMOLECULAR FORCES

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Ida, Kawasaki-City - Japan

1. INTRODUCTION

Intramolecular forces and intermolecular forces have been discussed from theoretical point of view by many investigators. However, those who are interested in rather complicated molecules and crystals cannot treat the problem on a purely theoretical basis.

One method they follow is to make some specific assumptions about the potential functions and determine the force constants from experimental data, and they will be satisfied, if the values of force constants obtained from independent experimental data (optical, thermal, etc.) agree with one another.

Along this line the author has been working for many years and in this note he plans to report some recent development made in Tokyo University and Tokyo Research Institute of Yawata.

2. INFRARED AND RAMAN SPECTRA

The normal vibrations of a free molecule can be calculated from a secular equation, provided that the force constants of

the potential function are known. However, as stated above it is usually impossible to set up the potential function on a purely theoretical basis. Therefore, we observe the normal frequencies by means of the spectra and determine the force constants from the relation between these constants and frequencies obtained from the secular equation. However, the number of force constants contained in a general potential function is larger than that of the observable frequencies, even if this number is increased by the observation of the spectra of isotopic molecules for which the force constants are the same as those of the original molecule.

One way out of this difficulty is, as mentioned in the Introduction, to make some specific assumptions about the potential function such that the number of force constants is reduced. In our case a refined valence force model of Equation (1) was used. The original form proposed by UREY and BRADLEY [1] contains terms in the change of bond lengths (Δr_i) and bond angles ($\Delta \alpha_i$) and also terms corresponding to the repulsive force between non-bonded atoms.

$$(1) \quad V = \frac{1}{2} \sum_i K_i (\Delta r_i)^2 + \frac{1}{2} \sum_i H_i (\Delta \alpha_i)^2 + \frac{1}{2} \sum_i F_i (\Delta q_i)^2$$

This form is quite acceptable from the view-point of the chemical valence theory and we have studied quite a number of molecules, using this type of potential functions [2, 3].

Recently SHIMANOUCI et al. of my former laboratory took into account the Coriolis coupling, centrifugal distortion etc. and worked out the problem more nicely [4].

In Table 1 are shown the values of the non-bonded H...H interactions calculated by them from spectral data, taking into

TABLE I — *Non-bonded H...H interaction force constants, F and the H...H distances, q.*

Molecule	q(Å)	F(md/Å)		
		SHIMANOUCHI et al.	BUCKINGHAM	DE BOER
H ₂ O	1.52	0.387	0.428	0.704
NH ₃	1.62	0.376	0.362	0.494
CH ₄	1.80	0.288	0.254	0.262
PH ₃	2.07	0.087	0.136	0.101
SiH ₄	2.42	0.058	0.053	0.029

account the Coriolis coupling [5]. These are in good agreement with those calculated from the Buckingham equation [6]:

$$(2) \quad E_3 = R^{-1}(1 + 1.167R + 0.039R^2 + 0.518R^3 + 0.864R^4) \\ \exp(-2.3R)$$

This potential E_3 represents the energy of two hydrogen atoms in the triplet state.

In the last column of the same Table are shown the corresponding values calculated from the empirical equation of DE BOER [7] which are much less satisfactory to compare with the experimental values.

However, at longer distances the situation becomes different. This can be shown by studying the infrared spectra of some molecular crystals. For polyethylene, benzene and naphthalene we considered that the important intermolecular force arises from the interactions between the hydrogen atoms of the different molecules. In the case of polyethylene crystals

intermolecular non-bonded $H\cdots H$ distances less than 3Å were taken into account as shown in the first column of Table 2. (There are four pairs of them). TASUMI and SHIMANOUCI [8] calculated lattice frequencies and the splitting of molecular vibrations with the force constants (shown in the last column) which are approximately equal to those obtainable from de Boer's empirical equation. We see from Table 2 the agreement between the calculated and observed values is satisfactory.

HARADA and SHIMANOUCI made a similar investigation on benzene crystal [9] and found that the observed lattice frequencies and the splitting of molecular vibrations can be explained satisfactorily as in the case of polyethylene crystals. (See Table 3).

Such being the case, SHIMANOUCI and HARADA tried to find a potential function of the Buckingham type:

$$(3) \quad V = -AR^{-6} + B \exp(-CR),$$

which will agree with the numerical values of force constants for both the shorter (or intramolecular) and the longer (or intermolecular) distances.

Assuming $C=3.534$ and using the values of intramolecular non-bonded force constants of H_2O , NH_3 , CH_4 , PH_3 , SiH_4 and intermolecular force constants of polyethylene, benzene, and naphthalene crystals, they obtained the following potential function [10]:

$$(4) \quad \begin{aligned} V &= -0.5831R^{-6} + 22.63 \exp(-3.534R) \quad \text{md} \cdot \text{\AA} \\ d^2V/dR^2 &= -24.49R^{-8} + 282.6 \exp(-3.534R) \quad \text{md}/\text{\AA} \end{aligned}$$

TABLE 2 — *Polyethylene* (TASUMI and SHIMANOUCI).

(a) Shortest intermolecular non-bonded H...H distances and the corresponding force constants

Distance in Å	Force constant in md/Å
$q_1 = 2.943$	0.0045
$q_2 = 2.743$	0.0133
$q_3 = 2.755$	0.0080
$q_4 = 2.575$	0.02 (assumed)

(b) Lattice frequencies in cm^{-1}

B_{1u}	$\nu_{\text{obs}} = 73$	$\nu_{\text{calc}} = 76$

(c) Frequency splitting $\Delta\nu$ of molecular vibration

Frequency of single chain	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
1435	24	17.6
1473	10	9.9
731	11	11.4

TABLE 3 — *Benzene* (HARADA and SHIMANOUCI).

(a) Shortest intermolecular non-bonded H...H distances and the corresponding force constants

Distance in Å	Force constant in md/Å
$q_1 = 2.628$	0.016
$q_2 = 2.698$	0.012
$q_3 = 2.764$	0.010
$q_4 = 2.767$	0.0096
$q_5 = 2.826$	0.0080

(b) Lattice frequencies in cm^{-1} at -3°C

Symmetry species	ν_{obs} in cm^{-1}	ν_{calc} in cm^{-1}
A_g	35	28
	63	57
	—	79
B_{1g}	35	33
	—	70
	105	102
B_{2g}	63	56
	69	69
	—	76
B_{3g}	—	60
	69	72
	105	100

(c) Frequency splitting $\Delta\nu$ in cm^{-1} of molecular vibration

Molecular vibrational frequency	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
707	27	23
410	15	12
987	16	14

If we use the values obtained from Eq. (4) as those of the non-bonded $\text{H}\cdots\text{H}$ interactions, we can explain the observed values of both the intramolecular and lattice frequencies.

It is well known that ethane ($\text{H}_3\text{C}-\text{CH}_3$) exerts intramolecular rotation about the C-C bond as axis [2]. If we calculate the barrier height merely from the non-bonded $\text{H}\cdots\text{H}$ interactions from Eq. (4), we obtain a value of 385 cal./mole which is much lower than the observed value of 2760 cal./mole. (See Fig. 1).

Let us suppose that the difference between these two values, $2760 - 385 = 2375$, is due to an intrinsic lack of cylindrical symmetry of the C-C bond itself as suggested by E.B. WILSON [11]. Furthermore, let us assume this value holds for the C-C axes in *n*-butane $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$. (See Fig. 1). Then the calculated value of the height of the potential barrier between the trans and gauche forms becomes 3770 cal./mole which is in good agreement with the observed value (3300, 3600, 3700 cal./mole). Here the trans form is the one with a center of symmetry in which the two CH_3 -groups are at the farthest distance apart and the gauche form is obtained from the trans form by an internal rotation about the central C-C axis by $\pm 112^\circ$.

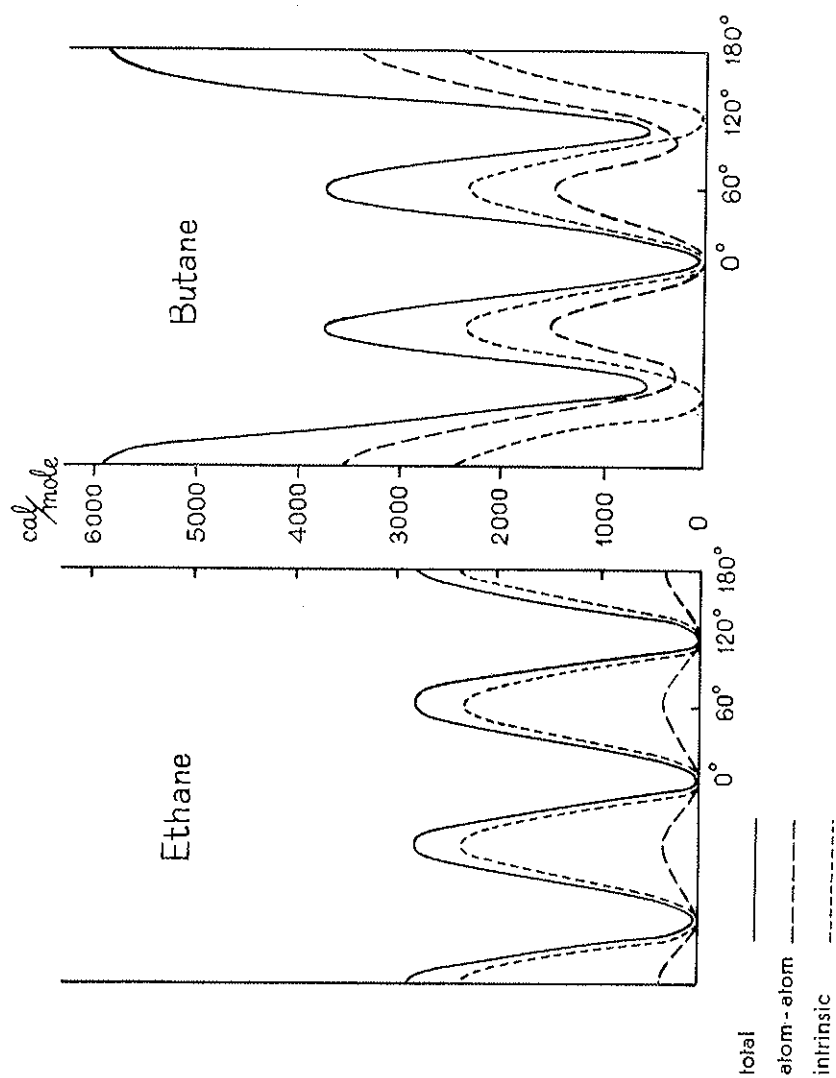


FIG. 1

In this calculation we need the value of the non-bonded C...H interactions which was found to be:

$$(5) \quad V = -1.464R^{-6} + 992.6 \exp(-4.57R) \quad \text{md} \cdot \text{\AA}$$

$$d^2V/dR^2 = -61.47R^{-8} + 2.073 \times 10^4 \exp(-4.57R) \quad \text{md}/\text{\AA}$$

by SHIMANOUCHI and HARADA in the same way as in the case of hydrogen interactions [10].

From the result obtained for *n*-butane we have good reason to believe that the internal rotation of other *n*-hydrocarbons or even polyethylene behaves similarly. In connection with this, it is interesting to see that in the liquid state, *n*-paraffins do not contain extended forms if the chain contains more than ca. 14 C-atoms. (In the solid state all the *n*-paraffin molecules take extended forms, and all the observed infrared and RAMAN frequencies agree well with the result of our normal vibration calculations for these forms) [12]. It seems that the void in the liquid state is not big enough to allow a long molecule to move as a whole, but as a segment (EYRING) [13]. The low potential barrier for the internal rotation of *n*-paraffin molecules conforms to this view [2].

We have here dealt with rather non-bonded atomic interactions which play most important role in the intermolecular forces. However, in our laboratory (Tokyo University) we have now quite a number of reasonable force constants for stretching of bonds and change of bond angles. Evidently these have been obtained from the vibrational frequencies of free molecules. So we may say we know the intramolecular and intermolecular forces fairly well, so far as free molecules and molecular crystals are concerned.

Another group of nonmetallic substances in which the interatomic forces apparently seem to be simple is ionic crystals

of alkali halides. The lattice energy calculated from the electrostatic interaction on the assumption of point charges located at the lattice points is in good agreement with that obtained from the heat of sublimation.

We have measured the infrared absorption of KCl crystal which was found to have a frequency of 141 cm^{-1} . A simple normal vibration calculation yields a force constant of $0.11 \text{ md./\AA}$. Here we have to take into account also the repulsive potential which can be treated simply, because both the K^+ and Cl^- ions have closed shells. However, in the case of FeO which has the same crystal structure as KCl, the situation will be quite different. The Fe atom has an incomplete $3d$ -shell which makes the interatomic forces complicated. This is easily seen from the magnetic properties of FeO in which even the super-exchange force is to be taken into account. We have recently observed an absorption band at 410 cm^{-1} for FeO by infrared measurement (made at Tokyo Research Institute of Yawata). A normal vibration calculation similar to that for KCl yields a force constant of $0.62 \text{ md./\AA}$ which is almost six times as large as that of KCl. This is due to the overlapping of electronic clouds of Fe and O forming the crystal.

3. ELECTRON DIFFRACTION

In the forgoing section we discussed a little bit about iron oxides. It may not be out of place to talk about the work on primary oxide of iron made recently in our laboratory (Tokyo Research Institute of Yawata). This work has been done as a part of our researches on transition elements to understand the nature of interatomic forces of metallic crystals formed by these elements [16].

SAKATA of our laboratory developed a new technique which enables us to prepare an evaporated film of pure iron single crystal [14]. By the analysis of the transmission electron diffraction patterns, we could determine the structure of oxides formed during the first stage of the chemical reaction taking place on the surface of the single metallic crystal (of the thickness of ca. 1000 Å) by a small amount of oxygen left in the bell jar.

The general conclusion of the previous investigators [15] is that at lower temperature spinel-type oxide is formed on the substrate with mutual orientation of the two lattices:

$$(001)_{\text{Fe}} // (001)_{\text{Spinel}}$$

$$[010]_{\text{Fe}} // [110]_{\text{Spinel}}$$

For the samples prepared by us at 10^{-3} mm Hg the same result was obtained as shown in Fig. 2. The mutual orientation mentioned above is shown by the diffraction pattern, in which the diffraction spots of iron are accompanied by the spots due to the secondary diffraction from the oxide. (See the arrows drawn in Fig. 2).

However, for the samples prepared in a higher vacuum ($10^{-5} \sim 10^{-6}$ mm Hg), in addition to the spinel pattern quite a different pattern was observed. (See Fig. 3). This pattern corresponds to neither normal wüstite nor spinel-type oxide but to structures with six-fold symmetry. By tilting the sample by about 50° , the pattern corresponding to these structures turned out to be streak pattern as shown in Fig. 4. In order to confirm the pattern arised from some kind of iron oxide, we deposited carbon on the oxide layer by evaporation and isolated the oxide from the metal which was dissolved by picric

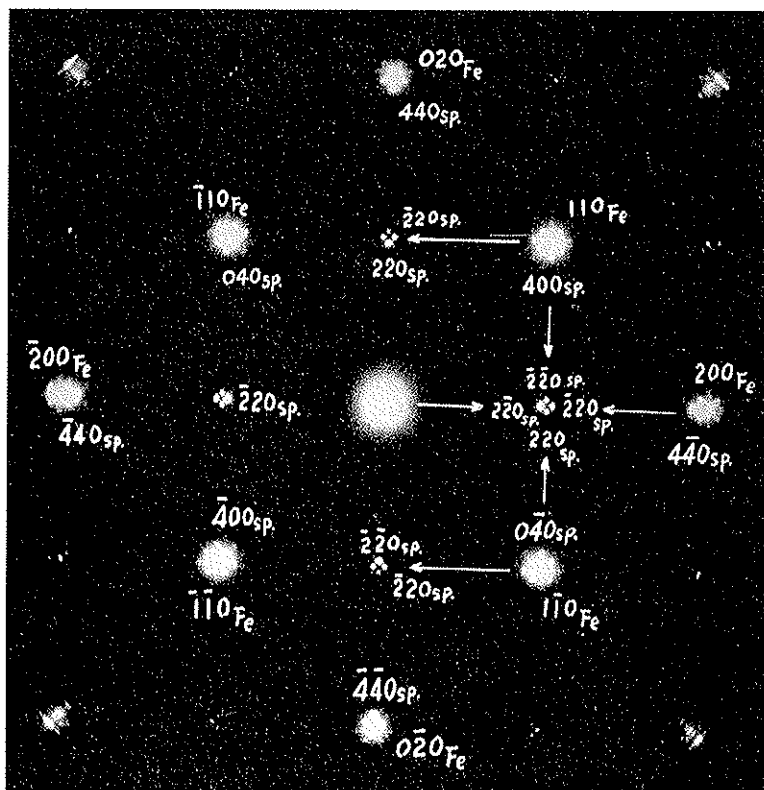


FIG. 2 — Electron diffraction pattern of Fe_3O_4 on single crystal of α Fe prepared at 10^{-3} mm Hg.

acid. Here the carbon deposition served to hold the oxide tightly. The electron diffraction pattern obtained from the oxide is explained as that of the spinel-type crystal and, therefore, the coherent thin oxide turns out to be one of the stable iron oxides, as soon as it is isolated from the substrate.

From the experimental results described above together with some other data not referred to here, we can show that

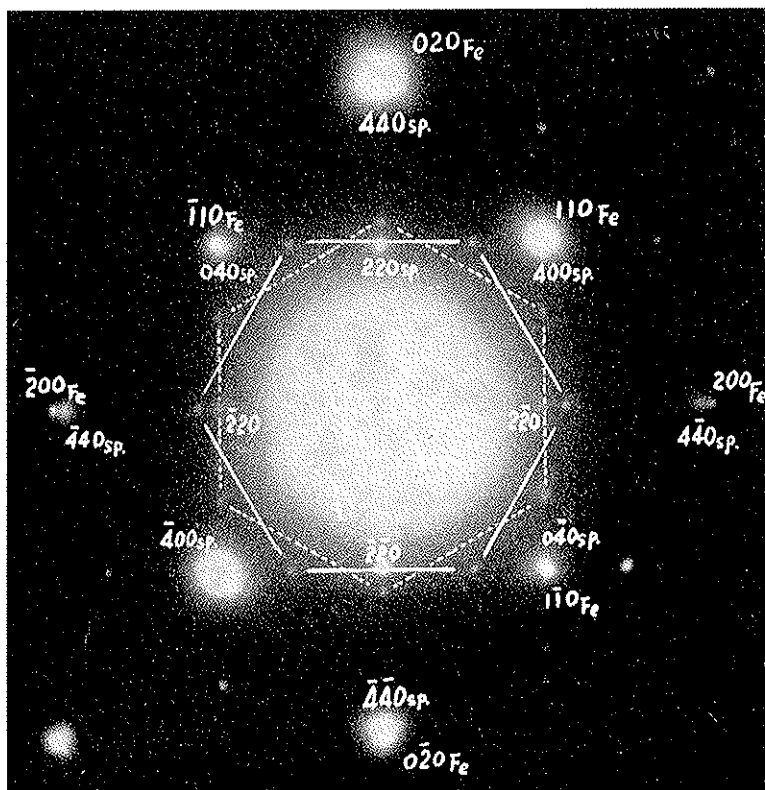


FIG. 3 — Electron diffraction pattern of iron oxides on single crystal of α Fe prepared at 10^{-5} – 10^{-6} mm Hg. (Note the spots other than those of spinel oxide and α Fe).

the oxides with six-fold symmetry are very thin. They are not much different from two dimensional crystal. However, since we have not yet arrived at the understanding of the inter-atomic forces in this case (which is the subject of this Study Week), we will make more detailed discussions in one of our papers to be published in future.

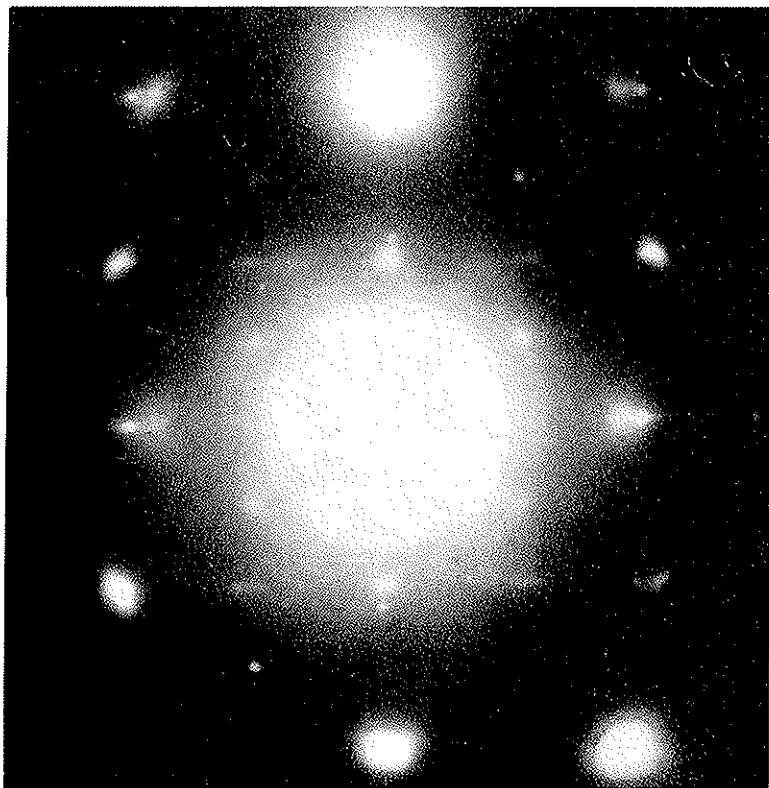


FIG. 4 — Streaks in diffraction pattern.

The paper was presented late in the evening, and we had no time to make discussions on the same day. However, on the following day the author discussed privately with Prof. BOWDEN, Prof. HIRSCHFELDER, Prof. BUCKINGHAM et al. Prof. BOWDEN was interested in the calculation of intermolecular forces of polyfluoroethane and Prof. HIRSCHFELDER in the comparison between his theoretical method and the author's experimental approach to the same problem.

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SESSION QUATRIEME

SOUS LA PRÉSIDENCE DU

Prof. Dr. G.M. SCHWAB

INTERACTION OF MOLECULES WITH SOLID SURFACES

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When a solid is brought into contact with a gas it is usually found, at least at pressure of greater than 10^{-10} Torr, that gas-molecules adhere to the surface of the solid. This phenomenon can be interpreted thermodynamically by ascribing a surface tension respectively a *free surface energy* to the solid and noting that this free surface energy cannot be minimized by diminishing the surface area, as does a liquid, but only by reducing the surface tension. One can, however, also attempt to interpret this phenomenon, called adsorption, by means of a molecular mechanism, in which the question of the nature of the forces between the molecules and the solid is raised.

Experimentally two usually well-defined cases can be distinguished: the first case is that of « physical adsorption » or « physisorption ». The forces operating here are not essentially different from those acting between the molecules of a gas or of a liquid or between the molecules of a liquid and those of an adjoining gas. These forces are dispersion forces for molecules without a dipole and dipole forces for dipole molecules, whereby both permanent and induced dipoles may be operating. This type of adsorption occurs on all solids and is especially conspicuous at low temperatures, where, because

of the exothermal character, it is thermodynamically favoured. The bonding energies of this type are of the order of several kcal/mole. At temperatures higher than room temperature this type is usually negligible. In addition to this another type of adsorption, which apparently is brought about by chemical forces, exists. Generally it becomes appreciable at higher temperatures (« activated adsorption ») and liberates energy in the range of 10-100 kcal/mole. This adsorption is found especially with hydrogen on transition metals and with oxygen on oxydisable metals but also with many other gases, especially if they possess mobile electrons.

The energy liberated by this type of adsorption is mostly dependent on the degree of surface coverage and decreases as this increases. Various explanations for this behaviour must be adopted from case to case; either the surface itself may be inhomogeneous or becomes so through the adsorption or a repulsion among the polarized adsorbed molecules occurs.

In many cases there is evidence that the molecules are not adsorbed as such but as fragments or atoms respectively. This is in particular the case, when, at low degrees of coverage, the adsorbed amount is not proportional to the gas pressure but to its square root.

This is understandable if one considers, that as the chemical forces between the atoms of the solid and those of the molecule cause bonds to be formed, a quantum mechanical effect causes the bonds in the molecule to become weaker.

The reason why this type of adsorption, also called chemisorption, is so interesting, is the fact, that, because of the above-mentioned chemical interactions with the molecules, these are enable to react with one another, a process, which is not present in the absence of the solid. The solid therefore becomes a catalyst.

The investigation of the effect is a challenge to the researchers, not only because of its wide-spread occurrence in the living organism and in the chemical industry, but because it

is as such a natural phenomenon. Aristoteles realized this, as he wrote in his « Meteorology »: « It is obvious that some substances are active, while others are passive. After one has verified this, one must find out, what are the effective forces which cause the active substances to be active and what are the appropriate passive substances ».

From an investigation of catalysis it is hoped to gain more insight as to the nature of the chemical forces prevalent in chemisorption. Nowadays, however, a number of modern experimental methods give a more direct insight into these forces. These results are in agreement with the notions already formed from catalytic investigations. In particular the modern methods of electron spin resonance, field-emission microscopy and infrared spectroscopy should be mentioned in this respect. I will, however, limit myself to information derived from catalytic investigations which probably give the most evident proof of the interaction between solid and gas.

Catalysis is a kinetic phenomenon, that is an alteration in the reaction rate and not in the position of equilibrium. It follows, that a catalyst does not alter the total energy or the free energy of a catalytic reaction but the activation energy.

Apparently, a chemisorbed substance requires a lower activation energy to be brought to the transition state, than does the same substance in the free gaseous state. In other words, the substance in the transition state has a particularly large adsorption energy. The task of research is to investigate these forces, which bond the transition state to the solid. For a long time this was attempted by comparing them with plausible chemical states: it was e.g. easy to understand that substances, which are easily oxidized or reduced, are themselves catalysts for oxidation or reduction reactions. The importance of such elements as iron, manganese, chromium etc. for catalysis is based on this fact.

Further, it was soon noticed that these elements belong to the transition series and this was brought into connection with

another interesting fact, namely, that it was just those elements of the 8th group (i.e. iron and platinum metals), which are particularly often found to have catalytic properties. The fact that these atoms possess incompletely filled *d*-bands was very soon brought in connection with valence changes and with catalysis. It can be simply imagined (BALANDIN) that in order to build the transition state on the one hand bonds inside the molecule are broken and on the other hand bonds must be made between the molecule fragments and the catalyst atoms. From the difference of the necessary or eventually liberated energies for these processes, one can indeed predict very roughly activation energies. Nowadays, this concept should be modified by quantum mechanical considerations, starting from the fact that the intramolecular bonds already begin to loosen during the formation of the chemisorption bonds, exactly as postulated in London's theory of homogeneous activation energy. We have e.g. managed to evaluate satisfactorily the activation energy of the hydrogen-deuterium exchange on a nickel surface by means of a simple calculation on the above basis.

However, the questions, whether covalent chemisorption bonds will be formed and if so which ones, and further, by which catalysts preferentially with which molecules, could only then be answered, if the ionisation energies and electron affinities of all atoms concerned in their appropriate valency states were known. One could then consider, whether electron-transfer bonds, co-ordinate bonds or covalent bonds were to be expected. The data, necessary for such a treatment, is mostly non existent and in any case the London calculation is for purely covalent bonds and even here includes all the deficiencies of a pure L.C.A.O. calculation. A greater insight into the relations between solid and chemisorbed reactant was obtained from the experimental side through the investigation of catalysts. From among the great number of possible chemical reactions there are two groups which in particular led to success. These are, firstly, such reactions in which hydrogen,

carbon monoxide or, in general, an electron donor has to be activated and secondly reactions in which oxygen or some of its compounds, i.e. electron acceptors, must be activated. From this point of view we can distinguish between donor and acceptor reactions.

This distinction becomes extremely useful, when it is correlated with the electronic properties of the catalysing solid. In the case of the metals, we can distinguish between those in which the conduction band (or the overlapping bands responsible for the conductivity) is almost filled and those in which it is almost empty. On the other hand, the semi-conducting catalysts can be divided into those with free conduction electrons, having a Fermi level in the neighbourhood of the conduction band, and those whose conductivity is of the defect electron type, showing that the Fermi level is near the ground band. It is found that metals with few electrons or respectively defect-electron semi-conductors catalyse donor reactions particularly well, while electron rich metals or alloys and electron semi-conductors are for these reactions poor catalysts but are good for acceptor reactions. The following examples show this clearly:

In the system copper-tin formic acid is best decomposed by pure copper. The addition of tin, which increases the electron concentration also increases the activation energy. Of the intermetallic phases of this system, the γ phase is the poorest catalyst, since, in the complicated lattice of this phase, the electron waves may be reflected from so many lattice planes that the electrons can hardly accept additional impulse in any direction. This phase has not only the highest resistance but also the highest activation energy. In the nickel-copper system the alloys rich in nickel, and therefore possessing *d*-holes, are good catalysts for the dehydrogenation of formic acid or methanol, while those rich in copper and so possessing many conductivity electrons, catalyze the hydrogen peroxide decomposition, an acceptor reaction.

Defect electron conducting nickel oxide is a good catalyst for the oxidation of carbon monoxide, which is an electron donor. Increase or decrease of the defect electron concentration by suitable doping increases or decreases respectively the catalytic activity.

Germanium can be prepared in an electron conducting or a defect electron conducting form by doping. It can be clearly shown that hydrogenation of ethylene takes place at room temperature on defect electron conducting germanium whereas on electron conducting germanium it is only possible at temperatures higher than 400°C. The difference in the activation energies between the two types is almost 0.5 eV.

These findings are strengthened by the results of indirect doping; the catalytic activity of a catalyst supported on a catalytically neutral carrier may be influenced by doping not the catalyst itself but the support, so that it becomes electron richer or poorer, or, in the case of a semiconductor, electron or defect-electron conducting. The catalytic activity of the supported catalyst is hereby influenced. This can be understood in terms of the band theory of semiconductivity. In the neighbourhood of the boundary between the two phases, the bands of the semiconducting catalyst are distorted so that the Fermi-level approaches the ground band or the conduction band, in a similar manner as is found in the bulk of a directly doped semiconductor.

Admittedly, all these findings, which could be easily multiplied, do not include the whole field of chemical catalysis. There are many reactions which do not comply with the electronic point of view, while for every reaction special features are found, which are not understandable solely from the above theory. In particular, a « geometrical factor » must be considered. This depends on the spatial arrangement of the adsorbed molecules or atoms and the crystallographic peculiarities of the different crystal faces. The diffraction of slow electrons

shows that the chemisorbed atoms do indeed form two-dimensional lattices on the various crystal planes of the solid.

Be that as it may, the « electronic factor » in catalysis is so clearly evident, that it demands a theoretical interpretation, which eventually could be of general interest. The simplest theoretical picture, which was first made, was that the difference between the potential energy of an electron in a molecule and the Fermi level or Fermi boundary in the catalyst was identified with the activation energy. The formation of the transition state would then be nothing else than the transfer of an electron from a Fermi level to an exchange level in the molecule for an acceptor reaction, vice versa for a donor reaction. There is, therefore, no distinction made between the chemisorbed state and the transition state. The chemisorption is considered to be ionic in nature, donor reactions giving cations and acceptor reactions anions. The greatest objection to such a conception is the fact that for normal chemical reactions one distinguishes the ground from the transition state through a vibrational excitation, the electrons behaving adiabatically. An insurmountable barrier would exist between homogeneous and heterogeneous gas reactions, if the activation energy indeed represented a quantum jump. It soon appeared, therefore, to be much more probable that the bond between catalyst and chemisorbed reactant should be of a covalent nature, in which orbitals of the molecule or the atoms overlap with catalyst states. The difference between donor and acceptor reaction is then, that the electrons to occupy the orbitals come in one case from the molecule and in the other from the catalyst. The more or less covalent chemisorbed state thus formed is converted to an activated chemisorbed state by excitation of thermal vibrations, i.e. activation energy is supplied, whereby the electron movement is so modified that to a greater extent they tend to be found between substrate and catalyst.

If this picture is to be applied to metal catalysts the ques-

tion arises, whether a chemisorption bond, formed by the overlapping of a localized orbital in a molecule and a delocalized conduction state in a lattice, can be quantum mechanically calculated.

I would like to raise this question here, because of its fundamental importance. The development of thought in catalysis (one can scarcely call it a theory of catalysis) has gone in another direction. English workers in particular have pointed out that even in a metal, the electrons are not all and not fully de-localized, but that especially the *d*-orbitals not concerned with lattice cohesion project in certain directions from the surface into space. From this point of view it is those orbitals which overlap with the orbitals of the molecules or atoms and so form the chemisorbed bond. The experimentally observed « electronic factor » can be understood from the above picture: the less electrons a catalyst has internally, the poorer are these orbitals occupied and the easier is a chemisorbed bond formed with a donor molecule. Conversely, an electron-rich lattice causes the projecting orbitals to be filled with electrons, so that chemisorption bonds are formed chiefly with acceptor molecules. The advantage of this view point, which can only be fully exploited in the future, is that it gives an immediate connection between chemisorption and complex chemistry. Both cases then fall into the domain of the ligand field theory. Nowadays, there is experimental evidence that the catalytic activity of surface atoms arises from unsaturated co-ordination complexes; for analogous catalytic results can also be obtained from unsaturated coordination complexes in solution e.g. cobalt complexes.

In the above described experiments the activation energy of the chemical reaction has always been compared with the energy states in the bulk of the catalyst. This is of course only a necessary approximation, since there are very few methods, which would enable us to determine the energy states of the surface. It would, clearly, be necessary to orientate

oneself with respect to the surface states and not to the states and electron terms in the interior of a metal or a semiconductor. We have already done this in two cases: on the one hand we have regarded the distorted bands in boundary layers as being responsible for catalytic activity and on the other hand we have considered the projecting surface orbitals instead of those in the interior of the catalyst.

If we attempt to summarize the knowledge which we now possess over the interaction between solids and molecules during chemisorption, we obtain a qualitatively satisfactory picture: catalysis is no longer the enigma which it was 30 years ago. If, however, we ask, whether the basic quantum mechanical notions with which we represent the system can be concentrated into a theory with which useful forecasts can be made, the answer is unsatisfactory. I have already raised a question in this direction: other questions arise also. What can one theoretically predict over the spatial arrangement and energy of the « projecting orbitals »? What is the influence on each other of bonds to the same atom when they are not purely co-valent but have a polar content? How does the energy of such a bond change with bond distance? Naturally there are many other questions, the answer to which is certainly of prime importance for an understanding of catalysis, but they go beyond the scope of our symposium, which has to restrict itself to the interaction solid-gas. One of them is the question of the nature of the transition state. We have qualitative ideas about this, in as much as the transition state represents a state in which the positions of the atoms are nearer to the final positions in the endproduct than the original positions in the reactant.

We understand also, that thermal energy is necessary to form this transition state. In spite of this we cannot make any quantitative predictions as to the thermodynamic instability of such a state, since we lack an exact model. Research, designed to clarify this problem, has not yet been concluded

even for the simplest homogeneous reaction. We can, therefore, not expect a complete theory of heterogeneous catalysis at present.

But I believe I may say that this is exactly the reason why the investigation of these interactions is so alluring to the experimental worker and also, I hope, for the theorist.

FORCES BETWEEN ADSORBED MOLECULES

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§ 1. INTRODUCTION

Before we can talk about the forces between adsorbed molecules, we must have some idea of the origin of the adsorption force itself. Consider the simple case of a hydrogen atom near the surface of a metal (I shall confine my attention to metals). The energy level diagram (Fig. 1) shows that there will be electron transfer from the metal to the atom. But with two electrons on the atom, their Coulomb repulsion raises the orbital energy so that it lies well above the Fermi level (see Fig. 1). Evidently, only a partial electron transfer takes place so that the orbital energy E of the atomic electrons is raised to somewhere near the Fermi level. In this situation, the occupation numbers $n \uparrow$ and $n \downarrow$ of the atomic level for electrons with « up » and « down » spins are equal, and less than one:

$$(1) \quad n \uparrow = n \downarrow = n < 1.$$

But this is not necessarily the situation of lowest energy. If, for example, we increase $n \uparrow$ and decrease $n \downarrow$, the orbital energy $E \uparrow$ of an electron with spin $\uparrow$ is lowered whereas $E \downarrow$,

the orbital energy of an electron with spin $\downarrow$ is raised. These changes in the orbital energies produce further changes in $n \uparrow$ and $n \downarrow$. Evidently a self-consistent calculation is needed to determine the final situation. It may be that, as a result of such a calculation, we arrive at the situation (1) again, but the possibility that

$$(2) \quad n \uparrow \neq n \downarrow, \quad n \uparrow < 1, \quad n \downarrow < 1,$$

with the consequence that $E \uparrow \neq E \downarrow$, should not be overlooked.

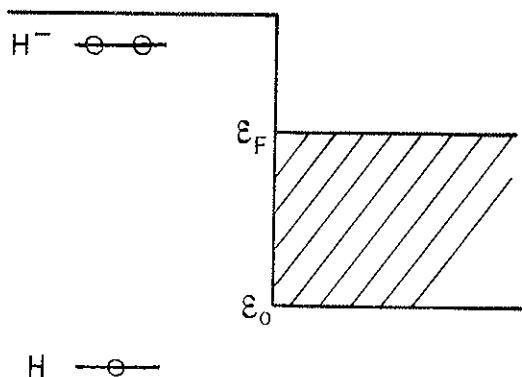


FIG. 1 — Orbital energies of electrons in H and H⁻ in relation to the occupied levels in a metal.

So far I have regarded an atomic level like E , $E \uparrow$ or $E \downarrow$ as a discrete level even though it falls in the continuous spectrum of metallic levels. Of course this is wrong if there is any interaction at all between the atom and the metal.

Instead, the discrete level is destroyed, and one extra level is added to the continuum. This alters the *density of states*. This alteration is most noticeable near the original discrete level where it appears that the discrete level has been broadened by its interaction with the continuum, and this broadened level has been added to the original continuum density of states (see Figs. 2 and 3).

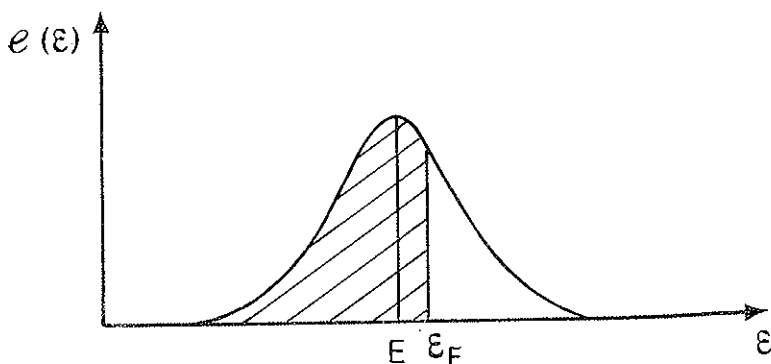


FIG. 2 — A discrete level raised and broadened when $n_{\uparrow} = n_{\downarrow}$.

We can now see that there is an indirect interaction between two adsorbed atoms. One adsorbed atom alters the continuum density of states, and the other adsorbed atom interacts with this alteration in the density.

§ 2. CHEMISORPTION

The simplest Hamiltonian which describes a molecule and a metal in mutual interaction is (the notation of second quantisation is very economical here)

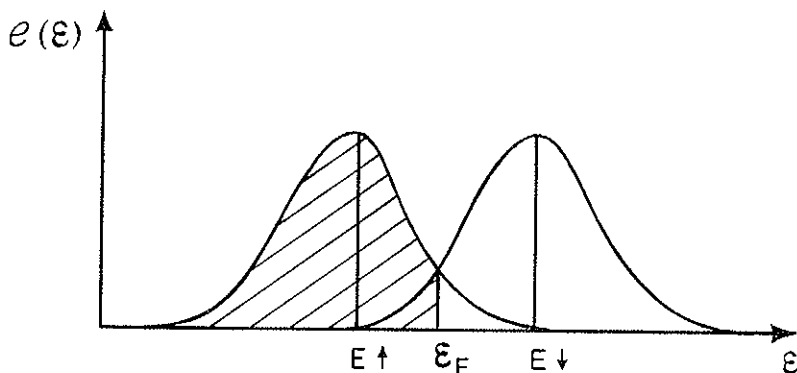


FIG. 3 — The splitting of E into $E\uparrow$ and $E\downarrow$ when $n\uparrow \neq n\downarrow$.

$$\begin{aligned}
 (3) \quad H = & \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma} E_a n_{a\sigma} \\
 & + \sum_{k,\sigma} V_{ak} (c_{a\sigma}^+ c_{k\sigma} + c_{k\sigma}^+ c_{a\sigma}).
 \end{aligned}$$

The first term describes the electrons in the metal, the second term describes electrons in the molecule with orbital energy E_a . This orbital is the one used to form the bond between the molecule and the metal (the surface bond), and consequently the same subscript a appears in the third term in (3) which describes the molecule-metal interaction. $c_{k\sigma}^+$ and $c_{k\sigma}$ are anti-commuting Fermion creation and destruction operators, and $n_{k\sigma} = c_{k\sigma}^+ c_{k\sigma}$ is the operator for the number of electrons in the metal in the orbital state k and with spin σ which is either $\uparrow$ or $\downarrow$. $c_{a\sigma}^+$, $c_{a\sigma}$ and $n_{a\sigma}$ are similarly defined for the state with orbital energy E_a in the molecule.

In writing (3), I have neglected all electron repulsions (there are no four-Fermion terms). This is easier to justify

for electrons in the metal than for those in the molecular level E_a , and we ought therefore to add to (3) the term

$$(4) \quad U n_{a\uparrow} n_{a\downarrow}$$

representing the repulsion between the electrons in the molecular level E_a . Only when this term is included in H is the situation (2) with its attendant orbital splitting a possibility. But if we overlook this possibility for the present, the situation (1) prevails, and in the Hartree-Fock approximation, the term (4) is included in (3) if E_a is changed to

$$(5) \quad E_a + U n ,$$

where n is the expectation value of the number operator $n_{a\sigma}$ in the ground state. I shall therefore continue to use the Hamiltonian (3), but when necessary, I shall interpret E_a as the sum (5).

Although the bilinear form (3) in the Fermion operators can be diagonalised exactly, I first consider the perturbation theory approach. It is natural to regard the first two terms in (3) as the unperturbed Hamiltonian, and the third term as the perturbation;

$$(6) \quad H' = \sum_{k,\sigma} V_{ak} (c_{a\sigma}^+ c_{k\sigma} + c_{k\sigma}^+ c_{a\sigma}) .$$

For definiteness, suppose that $E_a < \varepsilon_F$ (see Fig. 4) so that the unperturbed ground state Φ_0 has

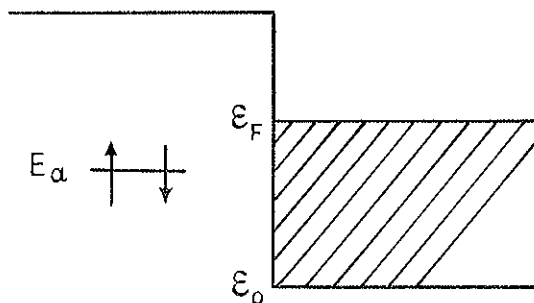


FIG. 4 — The unperturbed ground state of a molecule and a metal.

$$\begin{aligned}
 n_{a\sigma} &= 1 \\
 (7) \quad n_{k\sigma} &= 1, \quad \epsilon_k < \epsilon_F, \\
 n_{k\sigma} &= 0, \quad \epsilon_k > \epsilon_F.
 \end{aligned}$$

It is easy to see that the first order perturbation vanishes, and that $W^{(2)}$, the energy shift in second order, is given by

$$(8) \quad W^{(2)} = 2 \sum_{(k > \epsilon_F)} \frac{|V_{ak}|^2}{E_a - \epsilon_k}.$$

This quantity is an essential part of the heat of chemisorption; it is negative of course.

To analyse higher order terms in the perturbation series, one makes use of diagrams. These diagrams provide a schematic representation of the different virtual processes which contribute to a term in the perturbation series. For example, the

diagram for $W^{(2)}$ is shown in Fig. 5. The two vertices correspond to the two H' 's in the formula for $W^{(2)}$. The initial and final state is Φ_0 , the unperturbed ground state, but intermediate states differ from Φ_0 by the presence of certain holes and additional electrons. These are represented by lines bearing an arrow. If the arrow points to the left, a line represents an electron, otherwise it represents a hole. Reading the diagram in Fig. 5 from right to left we see that in the first

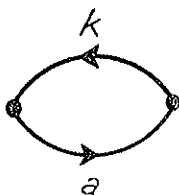


FIG. 5 — Diagram for the second order perturbation $W^{(2)}$.

vertex an electron is transferred from the molecular level E_a to a level in the metal with energy ϵ_k . In the second vertex we return to the ground state.

The third order perturbation vanishes, and the diagrams contributing to $W^{(4)}$ are shown in Fig. 6. Of particular interest is the diagram 6 (i) showing an intermediate state with an electron-hole pair (k, m) in the metal. This is a « dangerous diagram ». The formation energy of such a pair becomes vanishingly small at the Fermi level. Consequently there is a « dangerous » energy denominator in the formula for $W^{(4)}$. It will be better therefore to avoid perturbation theory.

The Hamiltonian (3) describes a system of non-interacting electrons, and each electron is therefore in an eigenstate $|n\sigma\rangle$ say, of some one-electron Hamiltonian F ,

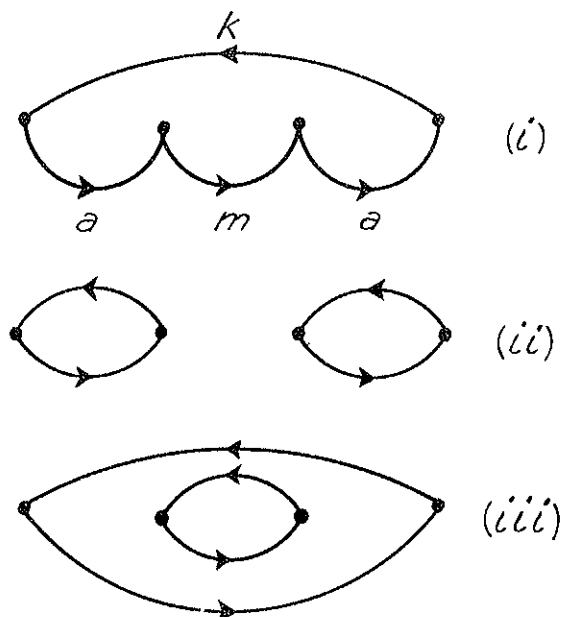


FIG. 6 — Diagrams of terms contributing to the fourth order perturbation.

$$(9) \quad F |n\sigma\rangle = \varepsilon_{n\sigma} |n\sigma\rangle .$$

Consequently, the Green's function operator

$$(10) \quad G(\varepsilon + i\delta) = \frac{I}{\varepsilon + i\delta - F}$$

is diagonal in the representation $n\sigma$ of the exact eigenfunctions of F ;

$$(11) \quad G_{nn} = \langle n\sigma | G | n\sigma \rangle = \frac{I}{\varepsilon + i\delta - \varepsilon_n} .$$

Using the prescription

$$\lim_{s \rightarrow 0} \frac{1}{x + is} = P \frac{1}{x} - i\pi \delta(x),$$

where P denotes principal value, and δ stands for Dirac's δ -function, it follows from (11) that for $s \rightarrow 0$,

$$(12) \quad \text{Im } G_{nn} = -\pi \delta(\varepsilon - \varepsilon_n).$$

Consequently $\rho(\varepsilon)$, the *density of states*, is given by

$$(13) \quad \begin{aligned} \rho(\varepsilon) &= \sum_n \delta(\varepsilon - \varepsilon_n) = -\frac{1}{\pi} \text{Im} \sum_n G_{nn} \\ &= -\frac{1}{\pi} \text{Im } \text{Tr } G, \end{aligned}$$

and W , the ground state energy, by

$$(14) \quad W = 2 \int_{-\infty}^{\varepsilon_F} \rho(\varepsilon) \varepsilon d\varepsilon.$$

Since the trace of an operator is the same in any representation, we can use the representation afforded by the unperturbed eigenfunctions, and write

$$(15) \quad \rho(\varepsilon) = -\frac{1}{\pi} \text{Im} (G_{aa} + \sum_k G_{kk}).$$

Our problem is now solved by calculating G_{aa} and G_{kk} .

The passage from (13) to (15) needs some justification because the states $|k\sigma\rangle$, which include states where the electron is freed from the metal, are a complete set, and consequently the localised molecular state $|a\sigma\rangle$ can be built up from them. The states required to represent $|a\sigma\rangle$ in this way, which will in the main have energies far above the Fermi level, must not therefore be included in the summations over k , either in (3) or elsewhere.

The calculation of G_{aa} and G_{kk} , the diagonal elements of G in the unperturbed function representation, is straightforward. The results are

$$(16) \quad \left\{ \begin{array}{l} G_{aa} = \frac{1}{\epsilon - E_a - A + i\alpha}, \\ G_{kk} = \frac{1}{\epsilon - \epsilon_k} + \frac{|V_{ak}|^2}{(\epsilon - \epsilon_k)^2 (\epsilon - E_a - A + i\alpha)}, \end{array} \right.$$

where

$$(17) \quad A - i\alpha = \lim_{s \rightarrow 0} \sum_k \frac{|V_{ak}|^2}{(\epsilon + is - \epsilon_k)},$$

so that

$$(18) \quad \left\{ \begin{array}{l} A = P \sum_k \frac{|V_{ak}|^2}{\epsilon - \epsilon_k} = P \int_{-\infty}^{+\infty} \frac{|V_a(\epsilon_k)|^2 \rho_M^{(0)}(\epsilon_k) d\epsilon_k}{\epsilon - \epsilon_k}, \\ \alpha = \pi \sum_k |V_{ak}|^2 \delta(\epsilon - \epsilon_k) = \pi |V_a(\epsilon)|^2 \rho_M^{(0)}(\epsilon). \end{array} \right.$$

In (18), $\rho_M^{(0)}(\epsilon)$ is the density of states in the unperturbed metal.

Combining (15) and (16) we can write

$$(19) \quad \rho(\epsilon) = \rho_a(\epsilon) + \rho_M(\epsilon)$$

$$(20) \quad \rho_a(\epsilon) = -\frac{1}{\pi} \text{Im } G_{aa}, \quad \rho_M(\epsilon) = -\frac{1}{\pi} \text{Im } \sum_k G_{kk}.$$

Then

$$(21) \quad \rho_a(\epsilon) = \frac{\alpha}{\pi [(\epsilon - E_a - A)^2 + \alpha^2]}$$

showing how the discrete molecular level E_a is both shifted by an amount A to a new value which is determined by solving

$$(22) \quad \epsilon = E_a + A(\epsilon),$$

and also how it is broadened by its interaction with the continuum of metal states. If the solution of (22) lies in the continuum of metal states, $\epsilon > \epsilon_0$, say, it represents a *virtual state*, otherwise it is a real discrete state. Both cases are illustrated in Fig. 7, and we note that, in the latter case where $\rho_a(\epsilon)$ has a δ -function at the discrete state $\left(\lim_{\alpha \rightarrow 0} \frac{\alpha}{x^2 + \alpha^2} = \delta(x) \right)$, there is still a « tail » in the continuum.

The formula for $\rho_M(\epsilon)$ is obtained from (16) and (20). I shall not however pause to give it here because it turns out

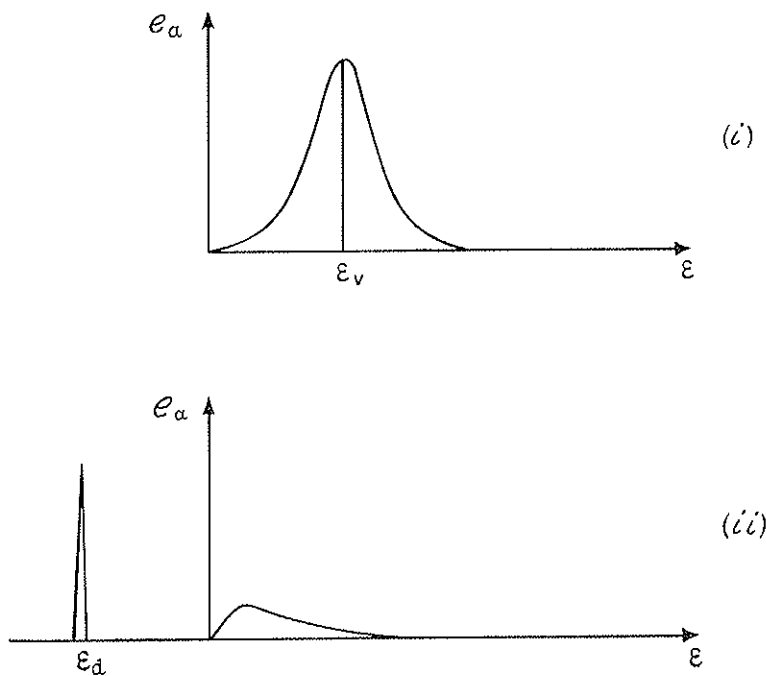


FIG. 7 — The contribution to the density of states for (i) a virtual level at ε_v , (ii) a real discrete level at ε_d .

that, if the unperturbed density of states $\rho_M^{(0)}$ varies only slowly with ε , it is a good approximation to take

$$(23) \quad \rho_M(\varepsilon) = \rho_M^{(0)}(\varepsilon) .$$

Accepting this approximation we have

$$\rho(\varepsilon) = \rho_d(\varepsilon) + \rho_M^{(0)}(\varepsilon) ,$$

so from (14) the ground state energy is

$$(24) \quad W = W_M^{(0)} + 2 \int_{-\infty}^{\varepsilon_F} \rho_a(\varepsilon) \varepsilon d\varepsilon ,$$

where $W_M^{(0)}$ is the unperturbed energy of the electrons in the metal.

§ 3. THE INTERACTION OF TWO CHEMISORBED MOLECULES

The generalisation of the Hamiltonian (3) to describe two molecules, a and b , on the surface of a metal is

$$(25) \quad H = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma} (E_a n_{a\sigma} + E_b n_{b\sigma}) \\ + \sum_{k,\sigma} [V_{ak} (c_{a\sigma}^{\dagger} c_{k\sigma} + c_{k\sigma}^{\dagger} c_{a\sigma}) + V_{bk} (c_{b\sigma}^{\dagger} c_{k\sigma} + c_{k\sigma}^{\dagger} c_{b\sigma})] .$$

Treating the third term in (25) as a perturbation, and assuming [c.f. (7)] that the unperturbed ground state has

$$(26) \quad \left\{ \begin{array}{l} n_{a\sigma} = n_{b\sigma} = 1 , \\ n_{k\sigma} = 1 , \quad \varepsilon_k < \varepsilon_F , \\ n_{k\sigma} = 0 , \quad \varepsilon_k > \varepsilon_F , \end{array} \right.$$

it is easy to see that the first order perturbation vanishes, that the second order perturbation

$$2 \sum_{\substack{k \\ (\epsilon_k > \epsilon_F)}} \left[\frac{|V_{ak}|^2}{E_a - \epsilon_k} + \frac{|V_{bk}|^2}{E_b - \epsilon_k} \right]$$

describes the chemisorption of the two molecules separately, and that the third order perturbation vanishes. In fourth order there is a term which I have represented by the diagram in Fig. 8. The virtual process it describes is the emission of on

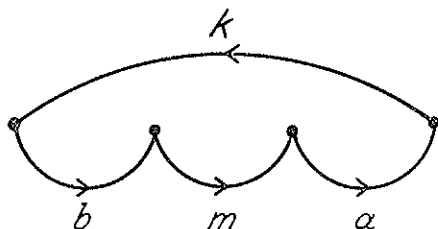


FIG. 8 — The diagram of a term in the fourth order perturbation when two molecules are present.

electron-hole pair (k, m) by the molecule a , and its adsorption by b . This virtual process describes an interaction between the two chemisorbed molecules. Unfortunately, it is represented by a « dangerous » diagram so that the interaction cannot be studied this way. However, an exact expression for the ground state energy of the system can be obtained by a straightforward extension of the argument which led, for the case of one chemisorbed molecule, to equations (14) and (15).

Equation (14) still holds but ρ is now given by

$$(27) \quad \rho(\varepsilon) = -\frac{1}{\pi} \operatorname{Im}(G_{aa} + G_{bb} + \sum_k G_{kk}) .$$

If the molecules a and b are identical,

$$(28) \quad G_{aa} = G_{bb} = \left[\varepsilon - E_a - A + i\alpha - \frac{(C - i\gamma)^2}{\varepsilon - E_a - A + i\alpha} \right]^{-1},$$

where

$$(29) \quad C - i\gamma = \lim_{s \rightarrow 0} \sum_k \frac{V_{ak} V_{kb}}{\varepsilon + is - \varepsilon_k} ,$$

so that

$$(30) \quad \begin{aligned} C &= P \sum_k \frac{V_{ak} V_{kb}}{\varepsilon - \varepsilon_k} = P \int_{-\infty}^{+\infty} \frac{V_a(\varepsilon_k) V_b^*(\varepsilon_k) \rho_M^{(0)}(\varepsilon_k) d\varepsilon_k}{\varepsilon - \varepsilon_k} , \\ \gamma &= \pi \sum_k V_{ak} V_{kb} \delta(\varepsilon - \varepsilon_k) = \pi V_a(\varepsilon) V_b^*(\varepsilon) \rho_M^{(0)}(\varepsilon) . \end{aligned}$$

The formula for G_{kk} is a rather long one, and I shall not give it here because if the unperturbed density of states varies only slowly with energy, it is still a good approximation to take [c.f. eqn. (23)]

$$-\frac{1}{\pi} \operatorname{Im} \sum_k G_{kk} = \rho_M^{(0)}(\varepsilon) .$$

Consequently, (27) becomes

$$(31) \quad \rho(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} (G_{aa} + G_{bb}) + \rho_M^{(0)}(\varepsilon) ,$$

but comparing (28) with (16) it is obvious that, because of the term in (28) involving $C - i\gamma$, the right hand side of (31) is not simply the sum of ρ_a as given by (21), ρ_b (equal to ρ_a for identical molecules a and b), and $\rho_M^{(0)}$. This lack of additivity means that there is an interaction between the two adsorbed molecules; the contribution which one molecule makes to the final density of states is influenced by the presence of the other. This influence, which is expressed mathematically by the term involving $C - i\gamma$ on the right in (28), means that the contribution ρ_a given by (21), which a single adsorbed molecule makes to the density of states, is altered,

$$(32) \quad \rho_a \rightarrow \rho_a + \Delta\rho ,$$

when two such molecules are present. From (14) therefore, the interaction energy U is given by

$$(33) \quad U = 4 \int_{-\infty}^{\varepsilon_F} \Delta\rho(\varepsilon) \varepsilon d\varepsilon .$$

The formula for $\Delta\rho$ is quite complicated so that even the *law of force* described by the potential (33), is not yet known. U depends on $\mathbf{R}$, the vector giving the relative positions of

the two adsorbed molecules, because the product $V_{ak} V_{kb}$ in (30) depends on $\mathbf{R}$. To see how this comes about, we note that V_{ak} and V_{bk} are the matrix elements of a one-electron operator F in the representation afforded by the unperturbed eigenfunctions;

$$(34) \quad \left\{ \begin{array}{l} V_{ak} = \int \Phi_a^*(r) F \psi_k(r) d\mathbf{r} , \\ V_{bk} = \int \Phi_b^*(r) F \psi_k(r) d\mathbf{r} . \end{array} \right.$$

Now ψ_k describes an electron in the *metal with a free surface*, and therefore the usual form of Bloch's theorem does not hold. However, the existence of the free surface does not affect the periodicity of the crystal in directions lying in the surface. This periodicity is described by two fundamental translation vectors $\mathbf{r}_1'$ and $\mathbf{r}_2'$ say, *which depend on the crystal plane exposed*, and which define a two-dimensional sub-space of the usual k -space. If $\mathbf{k}'$ is a vector in this subspace, and $\mathbf{R}$ is a vector in ordinary space, but lying in the crystal surface, then

$$(35) \quad \psi_k(r + \mathbf{R}) = e^{i\mathbf{k}' \cdot \mathbf{R}} \psi_k(\mathbf{r}) .$$

which is the restricted form of BLOCH's theorem applicable to our problem. Consequently, if $\mathbf{R}$ joins a to b , it follows from (34) and (35) that

$$(36) \quad V_{ak} V_{kb} = |V_{ak}|^2 e^{i\mathbf{k}' \cdot \mathbf{R}}$$

The simplest assumption to make about V_{ak} is that it is independent of k and equal to V say. With this assumption it is easy to see that the potential (33) is not isotropic. The interaction is due to the non-vanishing of C and γ in (30), and with the above assumption about V_{ak} we have, on using (36) the following formula for γ ;

$$(37) \quad \gamma = \pi |V|^2 \sum_k e^{ik' \cdot R} \delta(\epsilon - \epsilon_k) .$$

Now the suffix k , which labels the one electron states of the metal, comprises the wave vector $\mathbf{k}'$ and another index k'' say, which is not a wave vector because of the existence of the free surface. Thus

$$\sum_k = \sum_{k''} \sum_{\mathbf{k}'} \rightarrow \int dk'' \int d\mathbf{k}' .$$

The integration over $\mathbf{k}'$ can be carried out in two steps, firstly on a contour of constant energy, and secondly over all such contours. Because of the δ -function in (37) the only finite contribution comes from the contour with energy ϵ . This contribution, which is essentially the mean value of $\cos \mathbf{k}' \cdot \mathbf{R}$ on the contour, *depends on the direction* of $\mathbf{R}$ unless the contours of constant energy in $\mathbf{k}'$ -space are circles i.e., unless we are dealing with free electrons. It is clear therefore that γ (and also C), and hence the potential (33) is not generally isotropic.

§ 4. DISCUSSION

The indirect interaction between two chemisorbed molecules which I have discussed here, stems from the fact that the formation of the surface bond involves a certain sharing of the electrons of the system between the molecule and the solid. Since the electrons in the solid are described by non-localised wave functions, it is clear that the disturbance associated with the chemisorption of a molecule may not be very well localised, and the chemisorption of one molecule therefore influences the chemisorption of another over distances for which the direct interaction between the two molecules would be negligible. This sort of effect is well known in organic chemistry; a substituent affects the reactivities of all the carbon atoms in a conjugated chain. Its existence in chemisorption was, I think, first realised by the Czechoslovakian theoretical chemist, KOUTECKÝ.

I have only discussed here the indirect interaction between two chemisorbed molecules which follows directly from using the Hamiltonian (3) to describe the chemisorption of one molecule. This Hamiltonian contains the notion of bonding by sharing electrons between the molecule and the metal in the simplest possible way. I should mention however that this notion of electron sharing is not an essential prerequisite of an indirect interaction. If we replace the third term on the right in (3) by

$$(38) \quad \sum_{kk' \sigma} a_{kk'} c_{k\sigma}^{\dagger} c_{k'\sigma} \quad ,$$

which describes a certain polarisation of the electrons of the metal by the molecule a on its surface, then this term also gives rise to an indirect interaction between two adsorbed mo-

lecules. The term (38) is similar to the one responsible for the so-called inductive effect in organic chemistry.

Finally I should mention that the treatment of the Hamiltonian (3) given in § 2, follows closely the treatment of a similar Hamiltonian by ANDERSON [« Phys. Rev. », 124, 41 (1961)] in connection with localised magnetic states in metals. The problem can be handled in other ways, but Anderson's method is certainly very elegant.

DISCUSSION

Chairman: G.M. SCHWAB

CASIMIR

In the case of retarded van der Waals forces you get an interaction with an oscillating character and proportional to $1/R^2$ when one atom is excited. This was also mentioned by Prof. HIRSCHFELDER in his introduction. But when both atoms are in their ground state the interaction decreases monotonically to $1/R^7$. In that case only virtual emission of quanta is possible. In the first case there can exist real quanta. I wonder whether you have compared the interaction through the electron gas in any greater detail with the interaction through the radiation field.

GRIMLEY

No, it is too recent to have made the comparison. Of course, your comment is very interesting because you see in the radiation case you have a virtual state, and this is exactly the situation here.

CASIMIR

There would appear to be a rather fundamental difference if in the case of interaction through electrons, a virtual state gives an interaction with $\sin^2 kR/R^2$.

GRIMLEY

I just want to say that I do not have at my fingertips the distinction to be made between the Fermi case and the Bose case. This might be the important point, and this is something I will have to think about.

BUCKINGHAM

Prof. SCHWAB made the point that in some cases there is little difference between the catalytic effect of a free species (I think he mentioned a cobalt cyanide radical), and the catalytic effect of a metal, whereas the effects discussed by Dr. GRIMLEY are peculiar to a metal. Is there a clear difference between the catalytic effects of the type you described and the catalytic effect of a metal?

SCHWAB

Well, there are, of course, many differences because of the system. Besides, in view of these differences it is difficult to state that there is an essential difference in the course of the reaction, but it might be that the two points are very similar between each other and not very similar to the case treated by Dr. GRIMLEY. Of course, we have to do with the active centers of the surface, not with delocalized states.

OVERBEEK

Considering the electronic states in catalysis I was thinking for a moment on biocatalysis where there are a number of cases where it is quite probable that similar things occur. But in those biological catalysts which catalyze hydrolysis, and do not contain any metal ion it is much more difficult to see the relations with electronic states

like they are in metals. Would you mind to give an opinion whether these cases of catalysts should be treated in a different way from the one you have treated now, or are there similarities?

SCHWAB

I am aware of one example and that is a comparison between hydrolases and phosphatases. It appeared that in phosphatases low in the pH region, the interaction is not to be compared with the interaction of a complex molecule. However, in the high pH region it appeared that there is always some metal present, tin or magnesium, and then one actually has had some success in comparing this with complex catalysis.

LYKLEMA

The theory as presented by Dr. GRIMLEY and Dr. SCHWAB pertained essentially to gas adsorption. However, in biochemistry or colloid chemistry adsorption takes place in the presence of a medium. I would like to know if one of the speakers would be willing to comment on whether perhaps an attenuation of the interaction would occur in such medium.

GRIMLEY

Your problems are much more complicated than these, and I would not vouchsafe any comment.

FIXMAN

I have a question for Prof. GRIMLEY, although it is getting somewhat outside my field. This is the question of the applicability

of the free electron model to a problem such as you posed. Although the free electron model works quite well for transport processes, isn't this success due to a screening between the electrons which makes them somewhat independent of each other, and is this not just the kind of screening which would greatly reduce the interaction you have calculated here?

GRIMLEY

Yes, you have a good point, and right from the beginning I said that I had misgivings about the correlation problem that we are facing here. As you say, in dealing with the electronic structure of the bulk metal, you have the long range interaction screened out, and you are left with only a short range interaction between electrons. They are therefore essentially free. The point is that, when you are in a situation of high symmetry as you are in the bulk, this is all right, and this is the point I was trying to make. But we have a much more complicated situation here on the surface, and we would not, I think, be able to make that kind of assumption. However, I have made it only for the sake of getting some sort of answer.

LÖWDIN

I would like to complement Dr. SCHWAB for his excellent talk, and I must say I am completely fascinated by the aspects you have outlined and, particularly, the success of the experimental methods when it comes to the electronic factors. May I comment on a few points. First of all, there are both electronic and geometrical factors involved, and I believe that, as Dr. GRIMLEY pointed out in his paper, present research has pointed to a very useful analogy between certain surface phenomena and the directing powers of substituents on conjugated systems. Conjugated systems

are similar to surfaces in the aspect that they contain mobile electrons and, if you have a substituent coming into a point, it immediately rearranges the electronic distribution on the surface, so that other substituents may more easily attach at other specified points, and in this way one can understand at least part of the geometrical behaviour.

In connection with the electronic factors, I would like to ask Dr. SCHWAB a question whether he believes that today one could understand part of the catalytic of, let us say, the oxidation-reduction enzymes in the respiratory chain through their electron conducting properties. It is true that these enzymes are rather poor « internal » semi-conductors, but they are at the same time excellent pass-ways for external electrons. These proteins are polypeptide-chains stabilized through hydrogen bonds, and they consist of small conjugated systems joined by the « conjugating » power of the protons in the hydrogen bonds, so that a continuous conjugated system reaching from one end to the other of the polypeptide is formed. In conventional biochemistry, the action of such an oxidation-reduction enzyme is often described in terms of standard chemical kinetics: the enzyme is said to lower the activation energy for the process involved or to provide a more convenient reaction pathway with a lower threshold. In terms of quantum mechanics, I would personally prefer a rather different but simple time-dependent description: perhaps the enzyme gets attached to the two molecules involved by means of two hydrogen bonds and then serves essentially as a wave guide or bridge for an electron wave packet going from one partner to the other leading to an oxidation-reduction process; the passage through the enzyme is made possible through the conjugated system mentioned above. After serving as a bridge, the enzyme could become free and move to the next pair of molecules, or it could stay and repeat its purpose indefinitely.

In connection with the quantum mechanics of the surface states, which is certainly very complicated, I would further like to pay my compliments to Dr. GRIMLEY for his attack. What we probably need is entirely new tools, like the Greens-Functions technique,

for treating these phenomena. There is also particularly one type of perturbation theory, which may be very useful, namely the one referring to localized perturbations developed by people like SLATER, KOSTER, and LAX more than ten years ago. Then we also have other variations of perturbation theory like the partitioning technique which I believe has been used by Prof. KOUTECKY in this connection. I think further that one of the main difficulties is that the conventional theory of chemical reactions is very much tied to the stationary states, whereas both in treating surface and ordinary chemical reactions, we need a terminology and a conception as framework which is more based on the time dependent Schrödinger equation and its solution

GRIMLEY

I just want to make a brief reply to the last two remarks of Prof. LÖWDIN. The partitioning technique, for which he is responsible, is used in this treatment in a disguised form. I think he realized this. In the GREENS Function method, when you actually make the calculation, you see that you are doing a partitioning technique. There was something more, but I have now forgotten what it was. Oh yes, the localized perturbation theory. When one tries to make calculations in a surface state problem, one is driven to the localized perturbation theory. One is driven, I think, to make the calculations at least formally in a WANNIER representation.

SCHWAB

May I answer the question of Prof. LÖWDIN concerning enzymes. An enzyme is constituted of an active group and a protein carrier, and it may well be that the specificity of the enzymes is determined by the protein carrier. Now if the protein carrier is a semiconductor in a certain sense, then the substituent effects would have a much

larger range than is provided by the Ingold concepts of induction and so on. So it may well be that this high specificity of the enzymes, which is hereditary, is actually localized in the protein part of the enzyme and is due to its semiconducting character. It would mean that a substituent, far away from the active group, may still have an influence on the active group.

GRIMLEY

I want to disagree with Prof. HIRSCHFELDER on this, if we are speaking about heterogeneous processes. Prof. SCHWAB has talked about catalytic processes on semiconductors. Here you have boundary layers which are regions of charge built up by long range Coulomb forces, and those have a relaxation time, so you might have to do with a time-dependent calculation. Although you have localized states, you definitely have a relaxation time, a double layer relaxation time.

BOWDEN

Prof. SCHWAB has shown, in the admirable paper which he has just given, how it is possible to make clear-cut and important conclusions about the basic mechanism of what is happening on the solid surface during these catalytic reactions. To a physicist who is working outside the field of catalysis, it seems this is not always so. The interpretation of much of the experimental work which is published in this field, is complex and difficult. One of the reasons for this is that the experiments are often carried out, not on a single clean crystal surface of known structure, but on powders or polycrystalline masses of indeterminate surface area and properties. In addition these surfaces are contaminated by extraneous adsorbed films and other surface impurities. Does Prof. SCHWAB think that we should encourage experimental work of a more precise physical

nature? Such work is, of course, being done by a number of scientists but is it too small a proportion of the total body work in this field? Such controlled experiments are not unduly difficult and many new tools are available. Nowadays it is a simple matter in any competent laboratory to get a vacuum of say 10^{-10} torr. In such a vacuum we can get clean surfaces which stay clean for hours and we can study the kinetics of decomposition of one molecular layer from a single crystal which be only 10^{-3} cm² in area. We have been using such methods to study the surface decomposition of azide crystals (WALKER, GANE, BOWDEN, « Proc. Roy. Soc. », A 294, 417 [1966] press). The nature of the decomposition products which come from the surface can be identified by mass ion spectrometry and the changes in the crystal surface by scanning electron microscopy or by low voltage electron diffraction. Such experiments are perhaps a little more difficult to carry out but their interpretation is usually simpler and more certain. Should more work of this kind be done in the study of catalytic mechanisms?

SCHWAB

There are indeed these days many fine techniques available for studying kinetical reactions on really pure surfaces. I would like to mention here for instance, the work of my former collaborator BLOCK, now in Berlin, who has combined a field emission microscope with a mass spectrometer. Here he can observe field desorption and if he pulses his field, he can determine the life-time of an adsorbed molecule on the tip of the electron microscope. So this is a very beautiful technique which probably also deals with a pure crystal. Another point is, of course, the catalytic activities of its different faces. This has been done by SOSNOVSKY some years ago with the decomposition of formic acid, and she actually found that the activation energy of the decomposition varies by an amount of 10 kilocalories going from 111 to 100, 101. BECKEY in Bonn University has also done some work on single crystals in ultra high va-

cuum. This kind of approach is becoming more and more popular, and we look forward to more reliable results than the usual technique where there is a saying that we are always working with dirty surfaces and we are thinking about pure surfaces. On the other side, however, there are also instances in the « dirty » work where we probably have to deal with a pure surface.

I think, for instance, from my experience, that a silver surface in formic acid of one atmosphere is a purer silver surface than you can prepare from quite a high vacuum, because formic acid displaces every other impurity from the surface. What you have to deal with therefore, is a surface covered with formic acid alone.

CASIMIR

We have in some cases been rather successful in studying emission phenomena by cleaving crystals in a ultra-high vacuum. You start with a single crystal and then you make some kind of an arrangement inside a vacuum tube to cleave the crystals inside the high vacuum. I wonder whether the same sort of method could also be used in studies of catalytic reactions. You can be fairly certain that the surface is clean in those cases.

SCHWAB

What I cannot be certain about is the question of whether a cleaved surface has actually the structure one supposes from the crystal lattice of the bulk.

BOWDEN

Fortunately we now have low voltage electron diffraction, high resolution electron microscopy and other sensitive methods — some

of which I have mentioned — which can tell us a great deal about the structure and nature of freshly cleaved crystal surfaces and of surfaces prepared in other ways.

SCHWAB

On the other side, there are cases of many very important technical reactions like isomerisation on alumina and silica or the cracking reaction on alumina-silica catalysts and so on, where one is actually interested in the structure of what we call a dirty surface. We have examples where the question is if on the surface of a silica or alumina catalyst the impurity which is water, is present in the form of oxygen, hydroxy groups or physically adsorbed water molecules. And this has an intrinsic influence on the catalytic activity of alumina. It would be of no use to have a cleaved corundum crystal in an ultra-high vacuum. We will have illustrated these questions by Prof. PRETTE.

BUCKINGHAM

I should like to ask Prof. SCHWAB how one recognizes an activation energy in a case where there are an infinite number of paths from the reactants to the products. Now presumably the Arrhenius equation has not been obeyed, so how does one handle that case?

SCHWAB

The accurate way, of course, is first to illustrate fully the kinetic character of the reaction. One can draw some conclusions. In a favourable case one can say the reaction is zero order and is not inhibited by the product, and then one can be pretty well be sure that one has to do with a homogeneous reaction of a fully-covered layer. In other cases, one may separate the different parts of the reaction,

and one can evaluate the activation energies of these different steps. If this is not possible then, of course, one is in a mess. And I must confess that in many examples I have quoted this morning, we are not entirely sure about the reaction mechanism and the activation energies we are discussing. In part what we call activation energies, are still a mixture of chemical activation and adsorption energies. But even then the influence on adsorption energy and activation energy can sometimes be separated. We have done this in the case of hydrogenation reactions, and we can see that a catalyst giving a high adsorption energy, because it contains positive holes, gives a low activation energy at the same time. And this in the combined apparent activation energy works in the same sense.

LÖWDIN

May I ask the following question? Physicists speaking of activation energies usually think of the barrier in the potential which we would put into the Hamiltonian in the time-dependent problem he is going to investigate in connection with the chemical reaction. An experimentalist, on the other hand, thinks probably of something entirely different. And I wonder if these two concepts of potential energy surfaces, one entering the Hamiltonian and the other being the result of very fine experiments, are really identical, and whether these disagreements between theory and experiment may not lead to a great deal of confusion?

GRIMLEY

Yes, I should think so. You have reminded me of a very simple chemical reaction, that of tunneling. Here you would have a barrier in the Hamiltonian but if you did the experiment, the rate of reaction is much higher with tunneling than without. This is a very serious possibility in catalytic processes involving hydrogen.

WIDOM

I think there are other examples besides tunneling where there might be a discrepancy between the height of the barrier and the activation energy. I think it is very well established, for example, in certain endothermic reactions, such as the dissociation of simple molecules, the dissociation of diatomic molecules into atoms. There the activation energy as defined by the slope of a plot of logarithm of rate constant against reciprocal temperature is quite significantly lower than the independently known, spectroscopically established, dissociation energy. Of course, it is difficult to know exactly what to make of this in a microscopic way. It is possible that one is dealing with a temperature decreasing pre-exponential factor. They reflect certain details of the transition probabilities, but in fact the reaction may have proceeded through this high energy state at the top of the barrier. But still, the activation energy as derived from the usual plot of the experimental data need not be the same thing as the height of the barrier, and many cases are known where it is not.

SOME ASPECTS OF THE ELECTRONIC FACTOR IN CHEMISORPTION ON SEMICONDUCTORS

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INTRODUCTION

This paper does not aim at a complete review, up to date, of all the developments concerning the so called electronic factor in chemisorption and heterogeneous catalysis. The purpose is, rather, to describe the results of experimental and theoretical studies carried out in our Institute on those features which bear more or less directly on the interactions which bind chemisorbed molecules to the surface of the adsorbent, this being the crucial phenomenon in the overall process of heterogeneous catalysis.

This talk is divided in three parts: The first one describes a certain treatment of the statistical thermodynamics of adsorption equilibrium, which yields a formalism for the calculation of adsorption isotherms from first principles. When some partition functions appearing in the analysis are interpreted in terms of parameters related to the strength of the bonds, one obtains explicit formulae for the amounts of chemisorbed species. These can be further specialized for simplifying assumptions (e.g., concerning the physical conditions of the adsorbent).

Following these ideas, the second part describes the interpretation of various experimental results. Our own, using pure chromia (*) as adsorbent (or catalyst), and published data concerning other systems, which we think are relevant to this discussion.

In the third part we consider the changes taking place in the conditions of the surface during the processes of adsorption and catalysis. These changes have a decisive influence on the ability of a given chemisorbed molecule to form different types of bonds with the solid surface.

I. THE THEORETICAL PROBLEM OF CHEMISORPTION

The quantum-mechanical treatment of the adsorbate-adsorbent system, which should be an essential part of any complete theory of chemisorption, is still a difficult and vastly unsolved problem.

Interesting studies have been made of the bonds formed by the chemisorbed species, both from the point of view of basic theory [1] and of possible applications to catalysis [2]. The application of the ideas of crystal field theory apparently opens the way to promising lines of attack. However, the present situation seems to be that one is still far from being able to reach semiquantitative conclusions which might be tested with systems of potential interest as catalysts.

It seems more feasible to start from solid state theory, using appropriate models, and to regard the crystal and the

(*) Instead of chromia we shall sometimes write Cr_2O_3 . This is not meant to imply the quantitative composition indicated by the stoichiometric formula. It only means that we use chromium oxide which, although it is non-stoichiometric, it is pure in the sense that it is not mixed with other oxides. The same applies to zinc oxide, etc.

adsorbed molecule as a single quantum-mechanical system. Although in principle this approach should yield less information on the bond formed at the surface, it is, nevertheless, more popular among practitioners in the field of heterogeneous catalysis. In fact, it has met with a certain measure of success, even in its crudest versions, in the interpretation of results and predictions of new effects.

This approach, which starts from solid state theory, is popularly referred to as the electronic theory of catalysis, although it really is no more than a theory of chemisorption. Its historical precedents are somewhat remote, depending on the historians. Some regard as the first step the work of PIS-SARJEVSKY in 1916 [3] or that of NYROP in 1937 [4]. The modern Russian school has undoubtedly had a great activity in this field, starting with ROGINSKII [5], TÉRÉNINE [6] and LIASCHENKO [7], among others, and culminating with WOLKENSTEIN's school [8].

However, the western contribution is, on the whole, perhaps more important. The boundary layer theory for a metal-semiconductor contact, mostly developed by MOTT [9], SCHOTTKY [10], and MOTT and CABRERA [11], supplemented with further ideas contributed by DOWDEN [12] and then by BOUDART [13], has originated the so called boundary layer theory of chemisorption and catalysis. This was explicitly formulated by WEISZ [14], GERMAIN [15], AIGRAIN [16] and HAUFFE [17].

A few years ago, we observed some unusual results in our study of the catalytic dehydrogenation of isopropyl alcohol on Cr_2O_3 , which prompted us to initiate studies of chemisorption under conditions which differ somewhat from common practice. In an attempt to review our notions on the chemisorption problem GARCÍA-MOLINER [18] and GARCÍA-MOLINER and ESTEVE PASTOR [19] reconsidered the theoretical problems arising in the statistical thermodynamics needed for the electro-

nic theory of chemisorption. Their results, as well as some further elaborations thereof, some of them still unpublished, will be briefly described here.

I a. — *The electrochemical thermodynamics of the boundary layer and the calculation of adsorption isotherms.*

It has been customary in standard boundary layer theory to overemphasize the role of the charge transfer between adsorbate and adsorbent. This can be regarded as a major criticism, as it ignores the fact that a given molecule, on a given solid surface (say, a given semiconductor), may form bonds of different types. This point was stressed by WOLKENSTEIN [20] and is supported by experimental evidence, such as ROMERO ROSSI's work [21] on the chemisorption of oxygen on ZnO.

Another point is that adsorption isotherms have been usually calculated for specific assumptions concerning the physical condition of the solid sample (in the case of oxygen on a semiconductor, for example, GRIMLEY calculated the isotherm for adsorption on an *n*-type semiconductor and then for a *p*-type sample[22]). Besides being frequently restricted to unnecessary simplifications, the calculation has to be done all over again each time. It seemed therefore worthwhile developing a formalism which yields general expressions for the amount of a given adsorbate which is adsorbed in specific forms, the calculation being, to start with, independent of the type of solid on which adsorption takes place. In an abstract fashion, this is equivalent to considering the statistical problem of a system of « traps ». For example, certain « active centers » on the surface are traps for gas molecules. These, in turn, can be adsorbed in states characterized by different amounts of charge transfer. If the transferred charges are always taken to be

electrons, the most positively charged molecule on the surface may be regarded as a trap for electrons, up to a certain number, which corresponds to the other extreme, namely, the most negatively charged molecule on the surface. Now electrons at the same trap are so close to each other that they may interact too strongly for Fermi statistics to be applicable. This point was also taken into consideration in the work presently to be described. Since the main ideas involved in this analysis have been discussed at length in [18] and [19], we shall only give here a brief outline, quickly going over to the discussion of our experimental data.

I. a. 1. — *Trapping statistics.*

Following GUGGENHEIM's suggestion [23] that the concept of absolute activity should be very useful in studying statistical problems in semiconductors, LANDSBERG [24] formulated the statistics of electrons trapped at impurities, etc., using the formalism of grand partition functions, the idea being to regard the traps as open systems, since the number of trapped electrons is variable. This can be extended in two ways:

i) By applying the same methods to problems of surface traps (e.g. active centers trapping gas molecules, or adsorbed molecules trapping electrons).

ii) By including in the analysis the possibility that different species (like molecules and electrons) can be simultaneously trapped at, for example, an active center, and also that different types of traps may act simultaneously.

The statistical treatment of simultaneous trapping runs as follows.

Let A, B, ... be the species which may be trapped; $\lambda_A, \lambda_B, \dots$ their corresponding absolute activities for overall

thermal equilibrium; $a, b, \dots$ the corresponding number of « molecules » trapped at the system of traps and assume at first that there is only one kind of such traps. If $\mathcal{Z}$ is the grand partition function of the system of traps, the average values of $a, b, \dots$ in thermal equilibrium are given by

$$(I) \quad \langle a \rangle = \lambda_A \frac{\delta \ln \mathcal{Z}}{\delta \lambda_A} \dots$$

Now suppose we have R different types of traps (for example, different types of active centers) and r is an index labelling them. Let N_r be the number of traps of type r and assume these can trap up to $M_{A,r}$ « molecules » of species A, $M_{B,r}$ of species B, ... We ask for the thermal equilibrium value of $v_{\alpha, \beta, \dots}^r$, the number of traps of type r with α « molecules » of species A, β of species B, ... For this we should need sufficient information about energy levels, which we might even imagine is obtained from experimental information. The crucial question is how to construct the *total grand partition function*, $\mathcal{Z}_t$, out of the information we have on individual centers. The problem, of course, is that of their mutual influence. What we need here is an extension of the theory of molecular interactions to cases like the interaction between molecules adsorbed on different centers. This area is still widely unexplored.

In what follows we shall assume non-interacting traps. We shall see later that in fact we can include the Coulomb interaction between adsorbed charged molecules. With the assumption of independent trapping $\mathcal{Z}_t$ is easily written as

$$(2) \quad \mathcal{Z}_t = \prod_{r=1}^R \left(\sum_{\alpha=0}^{M_{A,r}} \sum_{\beta=0}^{M_{B,r}} \dots \lambda_A^\alpha \lambda_B^\beta \dots Z_{\alpha, \beta, \dots}^r \right)^{N_r}$$

where $Z'_{\alpha,\beta,\dots}$ is the ordinary partition function of the center of r type with α molecules of A, etc.

From eq. (2) we obtain

$$(3) \quad \nu'_{\alpha,\beta,\dots} = N_r \frac{\lambda_A^\alpha \lambda_B^\beta \dots Z'_{\alpha,\beta,\dots}}{\sum_{\alpha,\beta,\dots} \lambda_A^\alpha \lambda_B^\beta \dots Z'_{\alpha,\beta,\dots}}$$

With this equation we want to calculate chemisorption isotherms.

I. a. 2. — *Model for the calculation of chemisorption isotherms.*

With the only assumption that the total grand partition function can be written as explained, we can now derive general formulae for chemisorption isotherms which are not restricted by further simplifying assumptions concerning either the mechanisms postulated or the nature and physical condition of the solid sample. We can also take account of the possibility that the gas molecules may be chemisorbed in different ways, especially concerning the degree of charge transfer, instead of describing all chemisorbed molecules as charged. Drastic oversimplifications of this kind have led in the past to the erroneous conclusion that there is a definite correspondence between, for example, the n - or p -typeness of the semiconductor and the form of the resulting isotherm. KRUSEMEYER and THOMAS [25] gave a more complete treatment of the simultaneous adsorption of charged and uncharged molecules, but they assumed with no real justification, that the uncharged fraction follows a Langmuir isotherm.

Suppose we consider one type of active centers and one gas species of molecules M which can either be chemisorbed and uncharged (M^0) or else can trap an electron and constitute the charged form M^- . We need not specify the detailed mechanism by which this electron has become trapped. We only have to regard the active centers as traps for two « molecular » species: gas molecules and electrons. Then α and β can take the values 0, 1 with $Z_{1,0}=0$, since we assume the surface site has to first trap the adsorbed molecules and then, if so, the electron. The absolute activity of the gas species can be written as $\lambda_A = p \chi(T)$, where $\chi(T)$ is a function of temperature with parameters which depend on the nature of the adsorbate. For the electrons $\lambda_B = \exp(\zeta/kT)$, ζ being the Fermi energy, i.e., under equilibrium space-charge conditions, the electrochemical potential.

A diagram (Figure 1) will help to clarify conventions about signs and reference energy levels. The electrochemical

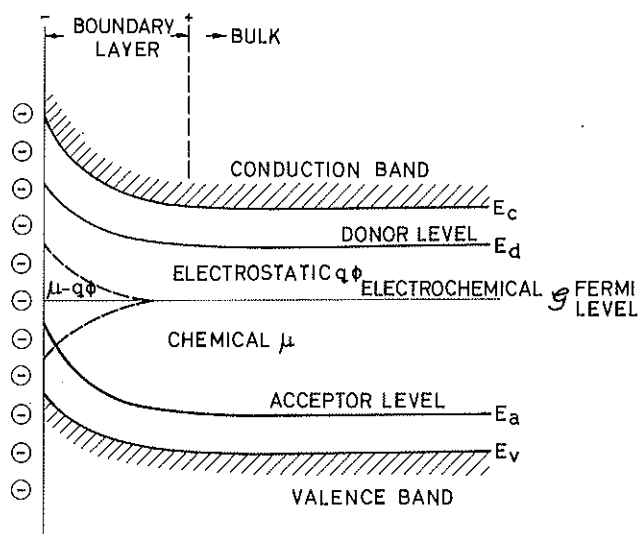


FIG. 1

potential is $\zeta = \mu - q \phi$, if ϕ is the electrostatic potential relative to that of the bulk and q the magnitude of the electronic charge ($q > 0$).

For the case here considered, the general formula (3) gives

$$(4) \quad N^{\circ} = \nu_{10} = N_c \frac{\lambda_A Z_{10}}{Z_{00} + \lambda_A Z_{10} + \lambda_A \lambda_B Z_{11}}$$

and

$$(5) \quad N^{-} = \nu_{11} = N_c \frac{\lambda_A \lambda_B Z_{11}}{Z_{00} + \lambda_A Z_{10} + \lambda_A \lambda_B Z_{11}}$$

N_c being the number of active centers for a given sample and temperature.

Now, the ratios Z_{10}/Z_{00} and Z_{11}/Z_{00} can be interpreted as the partition functions of the uncharged and charged molecules on a surface site, i.e.,

$$(6) \quad \frac{Z_{10}}{Z_{00}} = Z_0 = e^{-\frac{f^0}{kT}}; \quad \frac{Z_{11}}{Z_{00}} = Z_1 = e^{-\frac{f^-}{kT}}$$

where f^0 and f^- denote the corresponding free energies.

We further write $f^- = f_0^- - q \phi_s$, where ϕ_s is the value of ϕ at the surface, and thus take account of the Coulomb interactions by saying that an adsorbed charged molecule sits on top of an electrostatic potential due to the presence of the other charged molecules. In this way the problem is formally reduced to that of independent centers. It will be convenient to introduce the dimensionless quantity

$$(7) \quad u = -q \phi / kT$$

For acceptor adsorption, $u \geq 0$ everywhere. At the surface we shall write

$$(8) \quad f^- = f_0^- + k T u_s$$

and shall call u_s the « surface potential ».

Introducing the fractional coverage degrees θ^0 and θ^- and the overall coverage θ by

$$(9) \quad \theta^0 = \frac{N^0}{N_c}, \quad \theta^- = \frac{N^-}{N_c}, \quad \theta = \theta^0 + \theta^- = \frac{N}{N_c}$$

and the notation

$$(10) \quad a = \chi(T) e^{\frac{-f^0}{kT}}, \quad b = \chi(T) e^{\frac{-(f_0^- - \zeta)}{kT}}$$

formulae (9) and (10) become

$$(11) \quad \theta^0 = \frac{p a}{1 + p(a + b e^{-u_s})}, \quad \theta^- = \frac{p b e^{-u_s}}{1 + p(a + b e^{-u_s})}, \quad \theta = \theta^0 + \theta^-$$

It is seen from here that in general none of the formulae for θ^0 , θ^- or θ is a Langmuir isotherm since the surface potential depends on the coverage, i.e., ultimately on the gas pressure. Sandomirskii and Kogan's formula [26] is the low pressure limit of (11) when $p(a + b e^{-u_s}) \ll 1$.

The electrostatics of the boundary layer can be incorporated in a well-known standard manner. We have to specify the charge density, obey the Poisson equation and use the surface charge given by (11) as a boundary condition. This yields

$$\begin{aligned} 0^- = & (e kT/2 \pi q^2 N_c^2)^{\frac{1}{2}} \{ N_d / n [(1 + G_d e^{u_s}) / (1 + G_d)] - \\ & - N_a / n [(1 + G_a) / (1 + G_a e^{-u_s})] - n_{e_0} (1 - e^{-u_s}) - \\ & - n_{h_0} (1 - e^{u_s}) \}^{\frac{1}{2}} \end{aligned}$$

where:

$$\begin{aligned} N_d &= \text{volume density of donor impurities} \\ N_a &= \text{volume density of acceptor impurities} \\ n_{e_0} &= \text{bulk value of the concentration of free electrons} \\ n_{h_0} &= \text{bulk value of the concentration of holes} \end{aligned}$$

and

$$(13) \quad G_d = g_d^{-1} e^{(E_d - \zeta)/kT}; \quad G_a = g_a^{-1} e^{(\zeta - E_a)/kT}$$

in which g_a and g_d are factors for spin degeneracy of the order of unity.

I. a. 3. — Broad theoretical remarks

With the equations (11) and (12), one has in principle four conditions to determine, θ , θ^- , θ^0 , and u_s as a function of gas pressure. An exact solution for the general case is an imp-

ossible task, but some simplifications can make it tractable. An obvious case is when the surface potential is sufficiently small to justify an expansion in powers of u_s . This corresponds to low gas pressures and, in fact, to an expansion in powers of p . For arbitrary pressures, the simplifications arise from assuming given physical conditions of the solid sample. Essentially the kind of numerical considerations one needs to roughly anticipate the expected effects involve the magnitudes of $|E_d - \zeta|$ (or $|E_a - \zeta|$ and $|u_s|$ compared with kT . Since $|u_s|$ changes along the isotherms, a general rule of thumb is that everything changes. We shall now summarize some of the main conclusions.

i) Low coverage i.e., low pressure limit.

A power series expansion shows that SANDOMIRSKII and KOGAN's results [26] are only valid to first order in p , although they do predict the correct ratio $0^-/0^0$ at all pressures. Depending on the quantity one is interested in, it is easy to evaluate the critical pressure at which the linear approximation ceases to be valid.

ii) Influence of the ionization degree of impurities in the bulk.

This might be very strong at low coverages but it should tend to loose importance at high coverages.

iii) The question of the form of the isotherms.

There is practically no case in which the isotherms can be described by one single tractable function of a recognizable kind, valid at all pressures. At different ranges, which depend very much on the nature of the adsorbate and adsorbent, as well as on temperature, one can obtain standard isotherms (Langmuir, Freundlich-like, etc.) but these change from one to another as coverage progresses. This conclusion, which is quite in line with the general motto of the present communication is definitely against many results previously derived.

iv) The change in the differential adsorption heat.

Here we can only make very crude predictions: a) Because we only attribute the change in free energy to the electrostatic term; b) Because we ignore entropic factors which, as BOUDART has emphasized [27], demand an essential place in the analysis of adsorption heats.

With these reservations, we recover the standard laws for quadratic or logarithmic decrease, etc., as coverage progresses. Again this depends on system and temperature and the same complete function is approximated by different standard laws at different pressure ranges.

I. a. 4. — Possible extension of the formalism

We have illustrated one simple case, but more complicated situations can be handled in the same manner. Thus, for example:

i) Surface heterogeneity. We only have to include different types of trapping centers. The results point to a decrease of differential adsorption heat as coverage increases, because of a preferential tendency for the gas molecules to fill higher surface levels as adsorption proceeds.

ii) Simultaneous adsorption of different gas species. The extension is obvious.

iii) Trapping of electrons at surface states not associated with adsorbed molecules. This case would be very interesting for the physicist. The way to handle it is to introduce the notion of a quantum state (labelled by its quantum numbers) as another type of trap, and otherwise proceed in the same manner.

iv) Multiple charge of the adsorbed molecule. This might correspond in the example discussed above, to letting β take the

values 0, 1, 2. The term $a + b \exp(-u_s)$ is increased by $b_2 \exp(-2u_s)$, where

$$b_2 = \chi(T) \exp\left\{-(f_0^+ - 2\zeta) kT\right\}$$

and the surface charge is given by $0^- + 2 \cdot 0^+$.

I. a. 5. — A speculative model

Consider an adsorbed molecule which can either be donor or acceptor, originating the three forms which we shall call M^+ , M^0 , M^- . We want to study their relative concentrations C^+ , C^0 , C^- in thermal equilibrium. Application of the general formalism gives

$$(14) \quad C^+ = \frac{\lambda^{-1} (Z^+/Z)}{D}, \quad C^0 = \frac{1}{D}, \quad C^- = \frac{\lambda (Z^-/Z)}{D}$$

with

$$D = \lambda^{-1} (Z^+/Z) + 1 + \lambda (Z^-/Z)$$

Then we ask — for a given total number of adsorbed molecules — what are the relative concentrations? Now we are not interested in evaluating the absolute degree of coverage; our attitude is rather to regard the adsorbed molecules themselves as the given traps. In the spirit of the above treatment we shall write for the corresponding free energies.

$$(15) \quad f^+ = f_0^+ - kT u_s, \quad f^0 \quad \text{and} \quad f^- = f_0^- + kT u_s.$$

We expect the quantities

$$(16) \quad kT w \equiv f_+^+ - f_+^0 \text{ and } kT v \equiv f_+^0 - f_+^-$$

to be something like the ionization energy and electroaffinity of an adsorbed molecule (at zero coverage). Define the dimensionless quantities

$$(17) \quad 2m \equiv w + v, \quad 2d \equiv w - v$$

and we find (remember $\eta = \zeta/kT$):

$$\begin{aligned} \frac{e^{-m} \exp(u_s - \eta - d)}{C^+} &= \frac{1}{C^0} = \frac{e^{-m} \exp(-u_s + \eta + d)}{C^-} = \\ &= 1 + 2 e^{-m} \cosh(-u_s + \eta + d) \end{aligned}$$

It is interesting to study the change of these functions with the position of the Fermi level relative to the bands edges. For this purpose, it is convenient to think of equation (15) as written in terms of the reduced chemical potential $\mu' = \mu/kT = \eta - u_s$. The function $\cosh(\mu' + d)$ reaches its minimum value where its argument vanishes. This gives a maximum for C^0 and corresponds to a Fermi level somewhere in the energy gap. Taking as a reference the bottom of the conduction band, for instance, the trend of the curves is illustrated in Figure 2.

It is seen that the position and the sharpness of the maximum depend on the nature of the gas and the solid, inasmuch as this determines the free energy that the adsorbed molecule

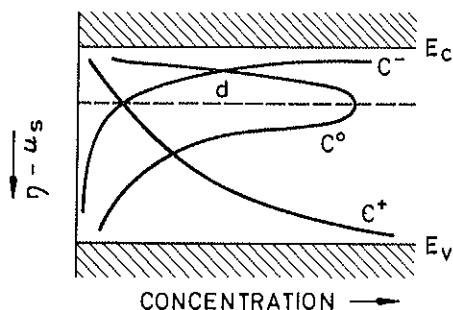


Fig. 2

has in either the forms M^+ or M^- . In fact from equation (16) and (17):

$$d = \frac{f^+ + f^-}{2 kT}; \quad m = \frac{f^+ - f^-}{2 kT}$$

How could we change μ ? By changing either η or u_s . In the first case, we might think of preparing different samples with the Fermi level in different positions. Adsorbing the same total amount of gas, we should obtain varying amounts of surface charge according to the curves of Figure 2. In the second case, we might have, for example, simultaneous adsorption of a second species with appreciable charge transfer. This would alter u_s so that locally (i.e. right at the surface), the molecules M would see a sample of a different type. This should affect the fractions C^0 , C^+ , C^- . We shall come back to this model later.

II. ANALYSIS OF EXPERIMENTAL DATA

We shall first describe the results of our own work on pure chromia and then, as announced, some published data on other systems.

II. a. — Pure chromia

We have studied experimentally the adsorption of hydrogen, oxygen, isopropyl alcohol and acetone on Cr_2O_3 in both its oxidized and reduced forms [28] [29]; the electrical properties of Cr_2O_3 [30-35]; the kinetics of the para-hydrogen conversion on Cr_2O_3 [36] [37] and the dehydrogenation of isopropanol to acetone on the said catalysts [38-41].

These are the data we shall consider here, starting with a brief description of the samples used, their preparation and those of its properties which are relevant to the discussion.

II. a. 1. — Preparation and properties of chromia samples.

The standard method of preparation is abundantly described in the literature [38]. A solution of $\text{Cr}(\text{NO}_3)_3$, BDH Laboratory Reagent in distilled water was partially precipitated with a small amount of Merck analytical grade NH_4OH , in order to eliminate possible traces of iron. The filtrate was heated to about 80°C and the chromium precipitated, with Merck analytical grade NH_4OH , in the form of $\text{Cr}(\text{OH})_3$. The precipitate was washed with boiling distilled water until all NO_3^- ions were eliminated, and then dried at $100-110^\circ\text{C}$ during several hours, following which Cr_2O_3 was obtained by decomposition at 400°C during 4 hours in air.

The Cr_2O_3 obtained was sintered at different temperatures, from 600°C up, during 4 hr in air and then sieved in the 0.074

to 0.053 DIN range. For a part of the work 0.60 cm diameter cylindrical pellets weighing approximately 0.5 g were obtained from sieved Cr_2O_3 powder and sintered in the same way.

Properties of Cr_2O_3 which are relevant to our discussion here have been studied by a number of authors, mainly VOLTZ and WELLER [42] and the Polish group of BIELANSKI, DEREN', HABER and coworkers. It is usually concluded [43-46], that at the surface of Cr_2O_3 prepared from chromic oxide gel (which is the method we have followed) there is excess oxygen which originates Cr^{6+} ions. Under the working conditions the number of Cr^{6+} ions does not depend on the oxygen pressure, while it does depend on the temperature of previous sintering and on the time involved in the sintering process. At 400°C the amount of active oxygen corresponding to Cr^{6+} ions per gram of dehydrated sample depends on the sintering time as figure 3 shows [44].

The fact that $[\text{Cr}^{6+}]$ does not depend on p_{O_2} suggests a saturation of the surface, which is consistent with measurements

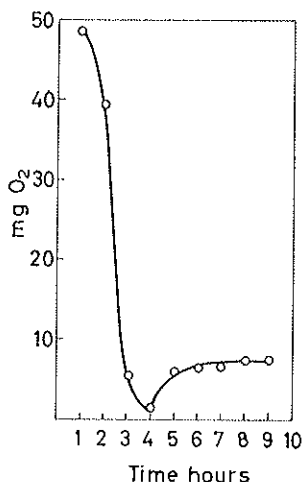


FIG. 3 — Amount of active oxygen corresponding to Cr^{6+} ions per gram of dehydrated sample versus sintering time at 400°C [44].

by PAJARES and SORIA [47] of the dependence of the electrical conductivity of Cr_2O_3 on p_{O_2} .

It is also found that the black colour of the oxydized form gradually changes into green as reduction takes place. However, our latest experimental data indicate that the green colour is not strictly indicative of n -type conduction, but begins to appear as the samples of Cr_2O_3 still maintain some p -type semiconductivity [37]. The general trend, however, is that the decrease in excess chemisorbed oxygen, analogous to the reticular oxygen at the surface, is accompanied by a change in colour from black to green. The correlation between excess oxygen and Cr^{6+} ions is shown in Fig. 4.

Interesting effects have also been found due to carrier and doping, which may help to interpret our results, although we use neither carrier nor doping. In the case of $\text{CrO}_3\text{-Al}_2\text{O}_3$, DEREN, HABER and KOSEK [46] find, using ESR, that, when CrO_3 is dispersed in small nuclei, the carrier stabilizes the existence of Cr^{5+} ions. These ions disappear as the size of the nuclei increases, while the transformation of CrO_3 in Cr_2O_3 originates Cr^{3+} ions.

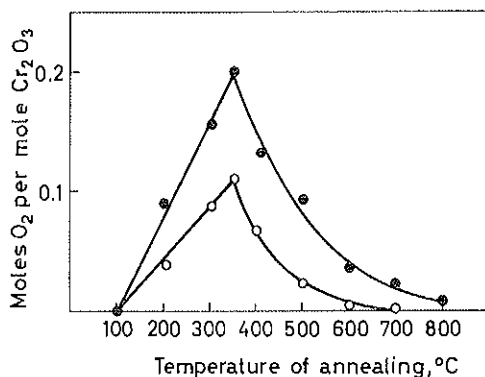


FIG. 4 — Excess surface oxygen (●) and excess oxygen equivalent to Cr^{6+} ions (○), both as function of the temperature of annealing [45].

DEREŇ and HABER [48] have studied the effects of low-temperature doping of chromium oxide with altermvalent ions. It is interesting from our point of view that the O/Cr ratio in the bulk is 1.5 independently of pre-treatments, while adequate conditions may change the surface value of this ratio to 3. Moreover, assuming all Cr^{6+} ions to be due to chemisorbed $\text{O}^=$, they have calculated the amount of $\text{O}^=$ which would be required assuming that the surface is covered by an exagonal close-packed layer of oxygen ions. The results, except for those obtained with samples preheated to 400°C , indicate coverages of less than one monolayer.

The effects of Mg (enhancing adsorption) and of Ti (hindering adsorption), even if they cannot be attributed to substitutions in the lattice, as well as the eventual decrease in the number of excess charges (i.e. decrease in the concentration of Cr^{6+} ions) when the samples are exposed to vacuum, all agree with our experimental evidence.

II. a. 2. — Adsorption of hydrogen and para-hydrogen conversion.

The para-hydrogen conversion reaction can occur in two broadly different ways:

i) At moderate or high temperatures, some chemical mechanism takes place involving the chemisorption of hydrogen as a previous step.

ii) At low temperatures there is at first physical adsorption and then conversion which takes place through a physical mechanism.

Our data [36] indicate that, at temperatures of the order

of 100°C, the orto $\rightleftharpoons$ para conversion of hydrogen on $n\text{-Cr}_2\text{O}_3$ takes place according to the chemical mechanism proposed by BONHOEFFER and FARKAS, which involves the previous dissociation of the H_2 molecules. Thus, the adsorbed species is atomic hydrogen. In the light of the theoretical ideas expounded in Section I, we consider H° and H^+ as the two possible forms in which atomic hydrogen may be chemisorbed.

Our chemisorption experiments [28] do not distinguish between different adsorbed forms. However, we can clearly see that, on the whole, the oxidized samples ($p\text{-Cr}_2\text{O}_3$) adsorbed more hydrogen than the reduced ones ($n\text{-Cr}_2\text{O}_3$). One would feel tempted at first to think of O-H bonds at the Cr_2O_3 surface, which would explain the preferential chemisorption on p -type material. However, it is on n -type samples that we possess evidence in favour of chemisorption of hydrogen with dissociation; $p\text{-Cr}_2\text{O}_3$ has too small a catalytic activity at 100°C and the reaction mechanism has not been determined for this case. It is conceivable that adsorption on $p\text{-Cr}_2\text{O}_3$ may take place without dissociation, in the form of either neutral or charged molecules, like H_2° , H_2^+ , etc., all contributing to increase the total amount of hydrogen adsorbed on a given surface area.

Our measurements of electrical conductivity and thermopower [35] indicate that p - and n -type samples of chromia deviate considerably from the stoichiometric formula Cr_2O_3 and, under the conditions of the experiments, the samples used have large numbers of free charge carriers. It is therefore plausible to think that the forms preferably absorbed are H_2^+ or H^+ on $p\text{-Cr}_2\text{O}_3$ and H° , or even H_2° on $n\text{-Cr}_2\text{O}_3$.

The change from n -type to p -type material may be thought of as doping with oxygen, in such amounts that it does not involve chemical changes. However, the physical and physico-chemical properties of the material are drastically affected as oxygen is added to the surface: the surface value of the Fermi

level is lowered, the catalytic activity for the given chemical mechanism tends to zero and the amount of hydrogen adsorbed per gram of Cr_2O_3 increases.

The above arguments are consistent with the idea that only one of the possible forms of the chemisorbed species constitutes, or is capable of giving rise to, the activated complex of the catalytic reaction, whose rate will therefore depend on the concentration of this chemisorbed species. The situation is further complicated by the fact that the electronic properties of the semiconductor which acts as adsorbent (or catalyst) may be considerably altered as a consequence of its interaction with the adsorbate, thus changing the distribution of adsorbed species as the catalytic reaction takes place: the process affects its own course, until a stationary regime is achieved.

We have set up an experimental technique for the study of the $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion reaction with which, through measurements of electrical resistance, we can control the degree of surface reduction of the Cr_2O_3 which is being used as catalyst. We find that exposing the samples to a vacuum of the order of 10^{-6} mm Hg, at temperatures between 300 and 500°C, we obtain different degrees of surface reduction which are reproducible within tolerable limits. If the time of the treatment and similar factors are fixed, the degree of surface reduction turns out to depend almost exclusively on the temperature used.

Having achieved an approximately constant resistance at the temperature of treatment, we rapidly quench the samples to 80°C and then do the experiments on them. We then find a linear correlation (Figure 5) between R (electrical resistance at 80°C) and the rate constant for para-hydrogen conversion, taking place through a chemical mechanism, at 80°C.

It is also interesting (Figure 6) that the oxidized form (on which a physical mechanism takes place) becomes more active as the temperature is lowered. On the contrary, a decrease in

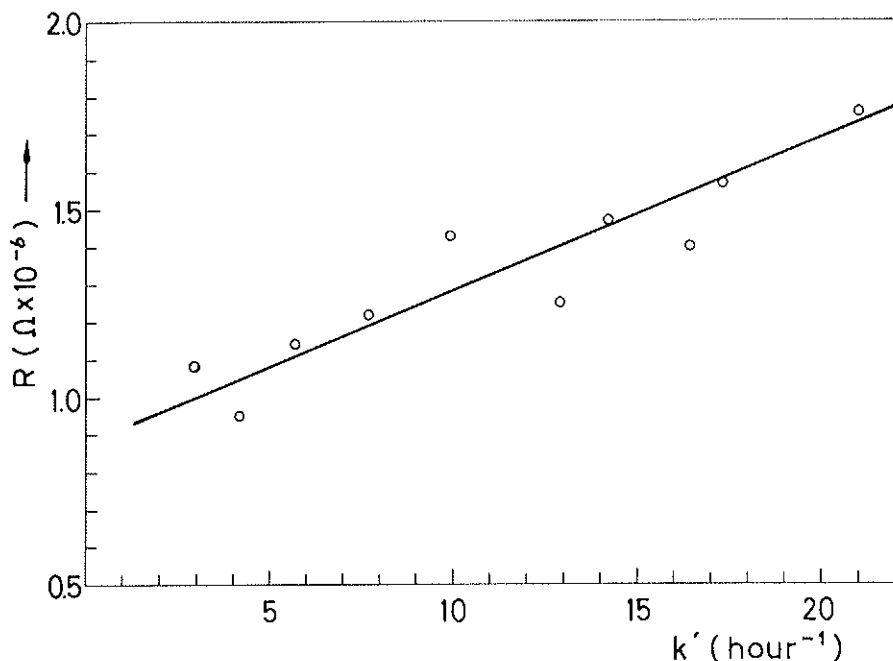


FIG. 5

temperature decreases the activity of the reduced form as is usually the case with chemical reactions.

DERENÍ and coworkers [49], in their study of the decomposition of H_2O_2 on Cr_2O_3 , found a linear correlation between $[\text{Cr}^{6+}]$ and reaction rate constant. Although certain aspects of their treatment are not free from criticism, it is interesting that the observed facts are satisfactorily explained assuming a donor rate determining step, in which a Cr^{6+} ion is the acceptor active centre. According to this, the Cr_2O_3 active centre for reactions involving H_2 could be related, as we shall see later, with donor Cr^{2+} ions which, together with Cr^{3+} , would appear as O^- ions are eliminated from the surface of the oxide.

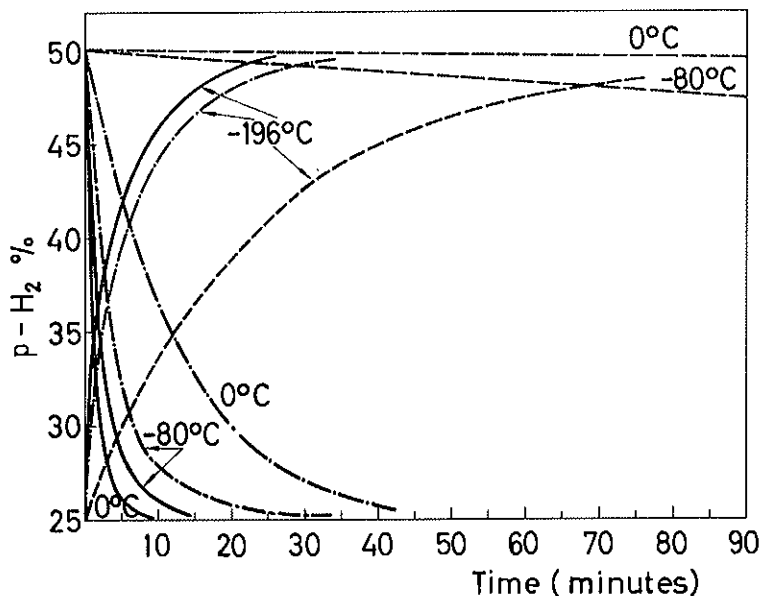
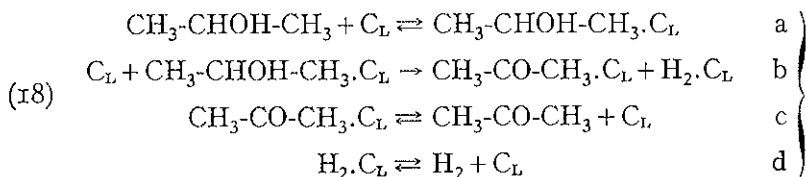


FIG. 6 — $p\text{-H}_2$ conversion on oxidized chromia ———, and on reduced chromia ———.

II. a. 3. — Dehydrogenation of isopropanol.

Kinetic studies of the dehydrogenation of isopropanol into acetone, on ZnO [50, 51], Cr_2O_3 [40, 41] and ZnCr_2O_4 [52] have led us to the conclusion that the apparent mechanism of the catalytic reaction can be described as follows:



Step b, the so called surface reaction, is the rate determining step, and is acceptor of electrons.

The first step (initial adsorption of isopropanol on oxydized Cr_2O_3) is a donor step, as was verified by measurements of electrical conductivity, leading to the formation of $\text{CH}_3\text{-CHOH-CH}_3^+$. The desorptions of both, acetone and hydrogen, are acceptor steps, and the corresponding adsorbed species are therefore $\text{CH}_3\text{-CO-CH}_3^+$ and either H^+ or H_2^+ . Clearly, other possible chemisorbed species will coexist with these, in varying proportions depending on the physical conditions and the degree of surface reduction-oxidation.

The second adsorption of isopropanol, which is included in the overall process described in step b and must be the one leading to the activated complex, is supposed to be acceptor of electrons, so that it should originate either $\text{CH}_3\text{-CHOH-CH}_3^0$ or $\text{CH}_3\text{-CHOH-CH}_3^-$. The later is rather unlikely in view of the observed effect of the desorption on the free carrier concentration. Thus it seems that the activated complex is associated with a molecule of isopropanol bound to the surface by two more or less ionic bonds of opposite polarity. Although the first adsorption of isopropanol is favoured by *p*-type samples, the concentration of activated complex depends, perhaps rather critically, on the possibility of the first adsorbed species accepting electrons, i.e., ultimately on the availability of quasi free electrons. Hence, apart from other possible factors, one expects that, after all, a change to *n*-type character will enhance the catalytic activity of chromium oxyde. This is what actually takes place as more hydrogen is adsorbed when the hydrogen pressure in the atmosphere is increased, which provides the basis for interpreting the data shown in Figure 7 [40].

In the above we have actually assumed that in the total process described by step b (17) the slowest partial process is the second adsorption, which leads to the activated complex. It is also conceivable that the slowest process may be the energetic excitation and subsequent breakup, and this would lead,

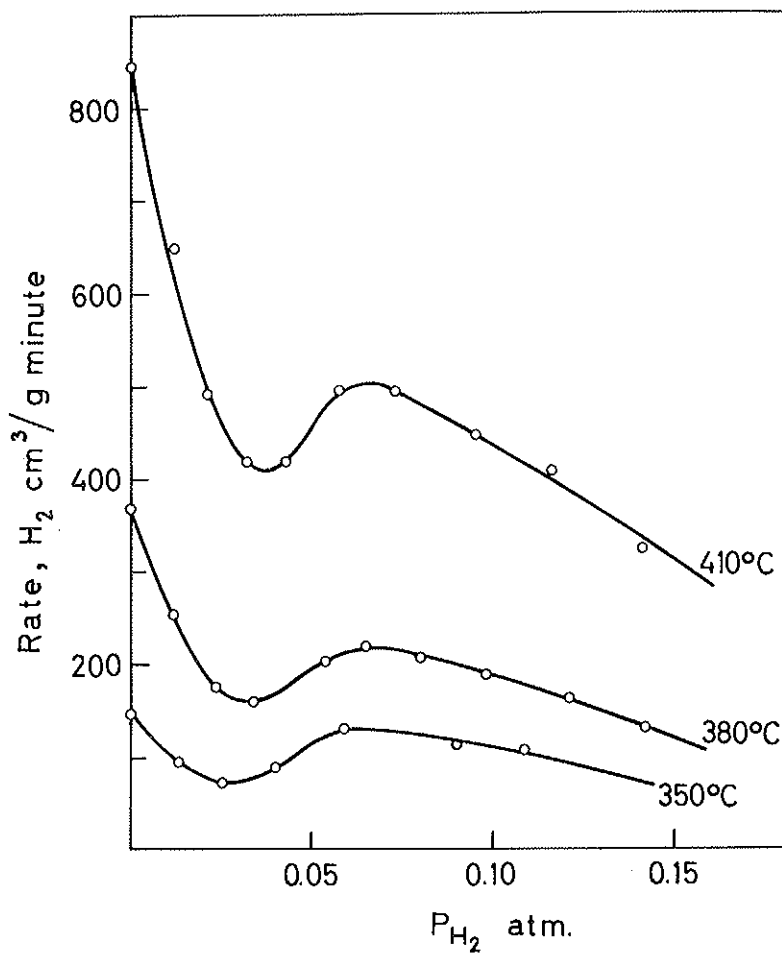


FIG. 7 — Rate of isopropyl alcohol dehydrogenation on Cr_2O_3 versus hydrogen partial pressure in the feed.

qualitatively, to the same type of experimental results, the hump in Figure 7 being then a reflection of the hump in curve C° of Figure 2. However, it is important to stress that under the first assumption the adsorbed species would not be in thermal equilibrium and, in this case, we could not use the equations given in Section I, although clearly they still would indicate the qualitative trend of the results.

The adsorption of isopropanol is more complicated than

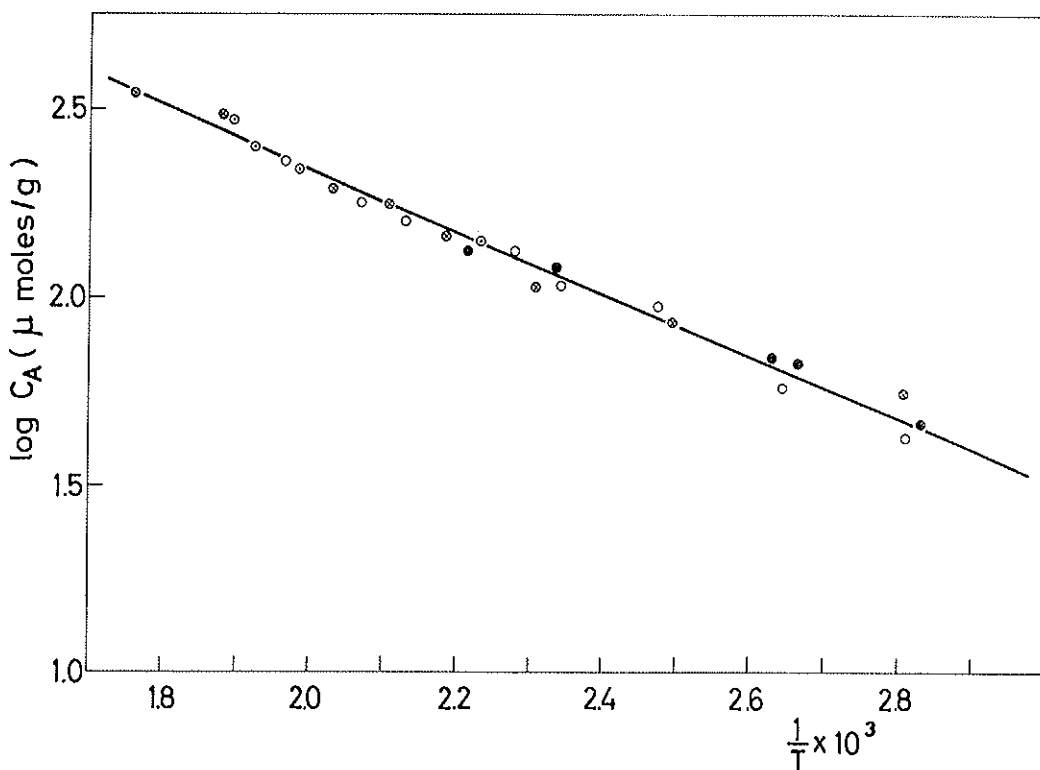


FIG. 8 — Logarithm of the number of μ moles of isopropyl alcohol and acetone adsorbed at saturation on Cr_2O_3 versus $1/T$.

● isopropyl alcohol and ⊙ acetone on oxidized Cr_2O_3 .
 ○ " " " ⊗ " " reduced " " .

that of hydrogen. While hydrogen is preferentially adsorbed on *p*-chromia, rather than *n*-chromia (from 0 to 300°C), the amount of isopropanol adsorbed when the equilibrium has been achieved is independent of the previous degree of oxydation or reduction of the oxide. This can be seen in Figure 8 and has been verified by electrical conductivity measurements. This introduces further complications, namely, the occurrence of oxydation-reduction phenomena during the adsorption and catalytic processes. We shall come back to this point.

II. b. — *Mixed oxides and supported chromia.*

TAYLOR and LIANG [53] have studied the adsorption of hydrogen on mixtures of chromia with zinc oxide and chromia with manganese oxide. Their conclusions are very similar to the ones reached in our studies with pure chromia, which we have described, and with zinc oxide, which we shall mention later.

CLARK, FINCH and ASHE [54], interested in the mechanism of polymerization of ethylene on chromia-alumina-silica mixtures, studied the irreversible adsorption of CO on the catalyst by infrared spectroscopy. They concluded that CO forms a complex with the solid surface, leading to the formation of the carboxylate ion ($\text{-C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O}^- \end{smallmatrix}$), whose presence increases the activity

for polymerization. They also studied the adsorption of formic acid, whose results agree with those obtained for CO as well as the adsorption of the latter at temperatures between -75 and 350°C. Their results are reproduced in Figure 9.

It is interesting to notice that the samples treated at 250°C in CO become active at low temperatures in the polymerization of ethylene. This is clearly related to the appearance of the carboxylate ion, whose presence must be associated with the

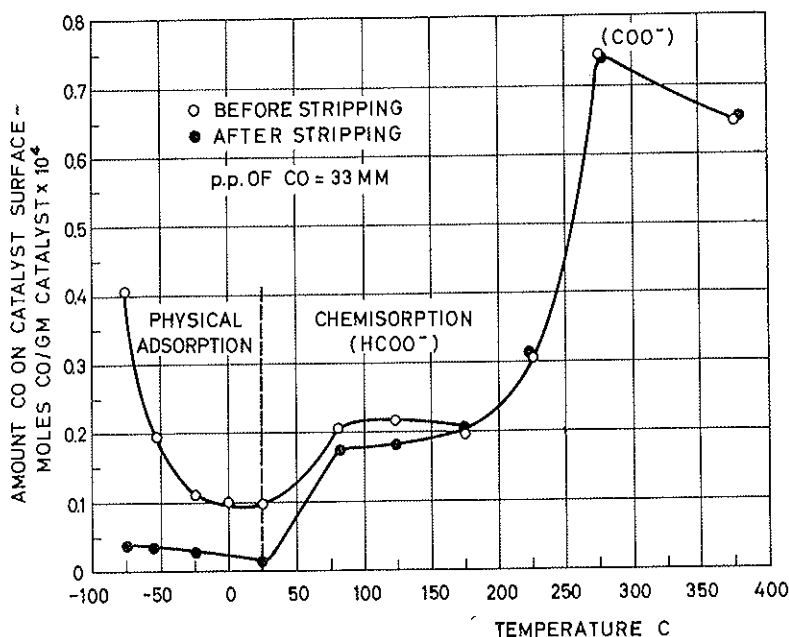


Fig. 9 — Adsorption of carbon monoxide on Cr-Si-Al catalyst (54).

existence of chromia, since no activated adsorption shows up on the carrier at high temperatures.

In short: Two different chemisorbed species are possible. Their relative concentrations vary in the temperature range considered and it is through the appearance of one of them that the system acquires special catalytic properties.

II. c. — Zinc oxide.

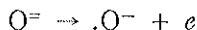
II. c. 1. — Hydrogen chemisorption.

The system H_2 -ZnO is one of the most widely studied and has been most profitable in furnishing experimental information which supports modern viewpoints on chemisorption.

PARRAVANO, FRIEDRICK and BOUDART in a summary of their work on the slow step in chemisorption, published in 1959 [55], say:

« The rates of adsorption of hydrogen and deuterium on a variety of zinc oxide samples are identical over a wide temperature range. It is concluded that the activated complex does not involve the adsorbed species. The slow step in this chemisorption process is associated with the thermal generation of active centers. »

The rate determining step, the formation of active centers in this case, is visualized by these authors in the following manner: Interstitial $Zn^{++} \cdot 2e$ undergo ionization followed by trapping of the conduction electrons by oxygen which approaches the surface and is chemisorbed. As a result of the presence of these charged oxygen surface traps, a space charge and an electric field barrier are set up in the vicinity of the surface. Assuming that oxygen can trap either one or two electrons and that the active form is the $\cdot O^-$ ion-radical, they postulate the following activated process:



since the electron thus originated must overcome a potential barrier before returning to the bulk of the crystal.

These ideas were further discussed by BOUDART [27] who speculated on the potentialities of coordinating kinetic studies of chemisorption with physico-chemical studies of the solid

state, as a possible way of elucidating all these problems consistently.

A number of experiments, old and recent, admit a more natural interpretation if it is kept in mind that the activated process may be the formation of active centers, rather than the chemisorption process itself. For the hydrogen-zinc oxide system we have two types of experiments, namely, those by TAYLOR and LIANG [56] and those by LOW [57].

TAYLOR and LIANG tried to devise a more expeditive way to measure adsorption isobars. They say that « instead, the procedure revealed hitherto unsuspected changes in the extent of adsorption as the working temperatures were changed », which they attributed to surface heterogeneity. One of their typical experimental curves can be seen in Figure 10. Clearly,

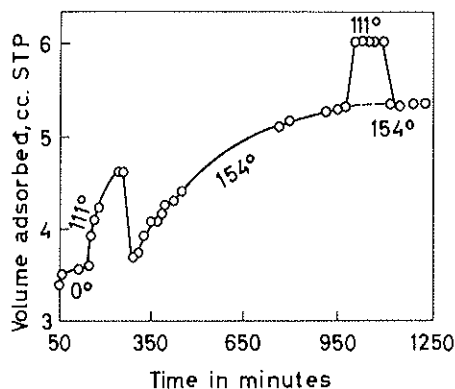


FIG. 10 — Adsorption rate curve on raising and lowering temperature (56).

a more likely alternative than TAYLOR and LIANG's interpretation is simply to think of activated formation of adsorption centers. Thus, on going from 111 to 154°C we can have at first

a quick desorption followed by readsorption as new centers are formed. Changing quickly from 154 to 111°C will result in a higher coverage, hence a larger amount of hydrogen adsorbed. New heating up to 154°C will lead back to the original isotherm (slightly below in fact). Of course, one could say that the creation of new centers as the temperature is raised originates a new surface. In a way this is equivalent to heterogeneity, though not corresponding to the notion of heterogeneity entertained by TAYLOR, although that may also play some role here.

Low [57] studied pressure effects and found experimental curves similar to those of Figure 10, although the changes were brought about by sudden pressure changes (from 379 to 145 mm Hg). He also found that the up and down steps were reproducible. He explained his results by assuming transitions between a weak chemisorption of hydrogen originating as surface species ZnH and OH (W type) and a more strongly bound species (P type). These different species are related to the different types of chemisorption of hydrogen on zinc oxide which were found by infrared spectroscopy and discussed by EISENBERG, PLISKIN and Low [58]. This furnishes new evidence in favour of the existence of different forms of chemisorption for a given adsorbate on a given adsorbent.

II. c. 2. — Carbon monoxide oxidation.

PRATER and CHON [59] carried out Hall effect studies of carbon monoxide oxidation on doped zinc oxide catalyst in the temperature range 200 to 350°C. Their very interesting results may be summarized as follows: i) As oxygen is adsorbed one electron disappears from the conduction band for each one atom of oxygen which has been chemisorbed. ii) The adsorption of CO_2 , which is very intense, does not modify the

concentration of conduction electrons. iii) The adsorption of CO on a surface free from oxygen does not significantly change the concentration of free electrons. iv) When CO is adsorbed on a surface which has oxygen chemisorbed on it, one electron appears in the conduction band for each one molecule of CO which has been chemisorbed.

These facts can be explained assuming that oxygen is chemisorbed in the form O^- and CO and CO_2 in the form CO^0 and CO_2^0 and, furthermore, that CO reacts with the adsorbed species O^- forming CO_2^0 and liberating one free electron.

III. MODIFICATIONS OF THE SOLID BROUGHT BY ITS INTERACTIONS WITH THE GAS

The traditional notion of an adsorbent (or catalyst) would have it remain immutable, a mere witness to the complicated events taking place on its surface. This idea is clearly too rigid and untenable.

Restricting for the moment our attention to the semiconducting oxides, their surface properties depend, among other factors, on temperature and composition of the atmosphere in contact with the surface. This fact has been taken into account, more or less explicitly, in various theories of chemisorption. WOLKENSTEIN, in particular [8] studied the influence that temperature changes could have on adsorption and catalysis as this changes the number of surface defects. The substrate-catalyst interaction in oxidation-reduction processes on oxides and oxygen containing compounds is also well known [60-63].

Strictly speaking, if an adsorbent is defined by the density and distribution law of the bonding energies of its active centers for chemisorption, the same chemical compound should be

regarded as a different physico-chemical entity at different temperatures, and even at the same temperature but different compositions of the atmosphere in equilibrium with the surface.

III. a. — Surface oxidation-reduction phenomena.

A number of compounds, including semiconducting oxides, undergo considerable phenomena of surface reduction-oxidation when exposed to treatments which one would expect to be rather inefficient. Thus, for example, while a temperature of about 1000°C is required for an appreciable bulk reduction of chromia in hydrogen atmosphere of 1 atm [64] appreciable surface reduction of the oxidized form takes place at 250°C in vacuum of 10^{-6} mm Hg.

This, however, is not so surprising if we consider that such changes affect only the small surface region. Very gentle treatments may result indeed in drastic changes in the properties depending on the surface condition. Thus, when we are working with an oxide as adsorbent we must not forget that the adsorbate may cause a reduction of the surface while its own adsorption is taking place. Such reduction creates anion vacancies with up to two electrons possibly trapped at each one, and this may result in « making the semiconductor more *n*-type », via the following mechanism: the anion vacancies with trapped electrons may act as donor impurities if the energy levels of these electrons are near the bottom of the conduction band of the oxide, in which case it is relatively easy for the « impurities » to be ionized. This, incidentally, may be a case in which the power of the formalism described in Section I may be needed to describe the statistics of the traps, since clearly nothing as simple as Fermi statistics could be applicable to this situation. Of course, this is all rather speculative; one might as well inquire whether the anion va-

cancies, being lattice defects and having electrons available in their immediate neighbourhood, might not be themselves plausible candidates as active centers for adsorption of acceptor molecules. In either case the apparent effect would be the same.

We have just seen an example of how, starting from a perfectly ideal surface, exposure to an adsorbate which may either oxidize or reduce it may alter the nature and number of the bonds formed until a final equilibrium is reached for adsorption as well as for the oxidation-reduction process. Now a change in the pressure of the adsorbate, or in the temperature, will alter not only the total amount of gas adsorbed, but also the relative concentrations of the various adsorbed species which may be possible.

This shows that the emphasis which has been frequently put on the dominating role of the Fermi level as a kind of mystical factotum risks overlooking the fact that we cannot ask from a formalism more than we have put into the assumptions constituting the model. By disregarding the complicated interactions between the gas molecules and the solid and by not counting the extra energy levels and mechanisms which this may introduce we may be as wrong as by being inconsistent with the requirements of electrochemical equilibrium. WOLKENSTEIN [65] has vigorously criticised the usual treatments which ignore such complications, although his criticism should not be taken to contradict the legitimate role that the Fermi level does play as the regulating electrochemical potential when different parts of a system are indeed in thermal equilibrium. On the other hand, developping all the equations by following every detail of a series of mechanisms assumed at the start, as WOLKENSTEIN frequently does, is also perhaps unnecessarily explicit and may involve the risks of being restricted to a specific model. It was in this spirit that the formalism described in Section I was developped and advocated as a basically sound procedure within which interesting sug-

gestions, such as are frequently contained in Wolkenstein's models, may be incorporated.

In any case, we believe that any theory of chemisorption on semiconducting oxides is certainly incomplete if it does not take account of surface reduction-oxidation phenomena. Their reality and bearing on chemisorption and catalysis seems to be supported by experimental evidence. In the case of chromia, for example, the appearance of anion vacancies implies the change of Cr^{3+} ions to Cr^{2+} . These ions have been detected by VAN REIJEN [66] and KAZANSKII [67]. Also, experiments carried out by SELWOOD [68] concerning para-hydrogen conversion on powdered synthetic ruby containing 1.1 atomic % chromium fully agree with what we have just put forward. In fact these data were interpreted in terms of oxidation-reduction phenomena involving the transformation of Cr^{2+} in Cr^{3+} and viceversa.

The experimental results just referred to, as well as similar data on other oxides, are in line with the general theoretical ideas sketched, as well as with the conclusions of our own work concerning adsorption and catalysis, the latter with systems involving hydrogen on chromia.

III. b. — The existence of an activation energy for chemisorption.

In the early thirties there was a lively controversy motivated by TAYLOR's suggestion that the chemisorption process requires an activation energy. Phenomenologically, the overall process does present an activation energy, mostly when the adsorbent is a semiconductor, but there is no aprioristic reason to attribute it to the very act of chemisorption itself.

For the sake of argument, let us assume that there is only one type of bond of a molecular species A with a given surface. Let us call C_L the active center for this adsorption, P the entity

which originates C_L and ε a particle which maintains the electrical neutrality and mass conservation. The overall process may be represented by the following scheme:



We thus have two simultaneous, dependent, reactions:



The act of chemisorption itself, described by equation (20), diminishes $[C_L]$. This enhances the progress of reaction (21) to the right which in turn enhances further chemisorption, and so on until a final equilibrium is achieved.

Clearly in many cases, and in particular when hydrogen is adsorbed on chromia, the overall process described by equation (19) exhibits an activation energy. However, it is not obvious whether it should be attributed to step (20) or (21). With the first assumption reaction (21) is in equilibrium; in the other case the chemisorption reaction proceeds very fast and the rate determining step is the formation of active centers.

These considerations were already put forward by TAYLOR and, in 1934, by TAYLOR and PEACE [69], and subsequently taken into account by TAYLOR's school, rather sporadically [70], and by the Russian school, more explicitly. We have analyzed in this light our data concerning chemisorption and catalysis on chromia [71] and concluded that the process res-

possible for the activation energy is the formation of active centers.

This question is of paramount importance in the theory of chemisorption. Both the activation energy and the adsorption heat are experimentally measurable quantities whose knowledge is very useful in ascertaining the nature of the activated complex and in evaluating the binding energy, respectively. Of course, the difficulties of assigning activation energies, from a knowledge of the experimental data, are increased when both processes are activated.

The interpretation of data concerning adsorption heats is also sometimes difficult. Suppose, for example, we have two experimental isotherms determined at two close temperatures. A simple thermodynamical analysis indicates that, if the temperature range is such that the equilibrium of chemisorption prevails, the Clausius-Clapeyron equation can only be used to evaluate the chemisorption heat Q if the system $C_L - A \cdot C_L$ is formed by two phases. This seems not plausible if $[A \cdot C_L] \ll [C_L]$, so that most frequently one should rather use van't Hoff's equation to evaluate Q at low coverages. Even then we have the problem of separating the two contributions coming from reactions (20) and (21), which together determine the experimental data. Such complications are further increased if adsorption can take place simultaneously on different types of active centers, involving different chemisorbed species, kinetics, types and energies of binding, etc.

FINAL REMARKS

We have seen that the chemisorption of a gas species on a solid, i.e., really, the formation of a bond between gas molecules and the solid, is a very complex problem in which one has to consider many possibilities, stemming mainly from two

considerations: *a)* The fact that different types of bonds are possible either as alternatives or simultaneously; *b)* The modifications of the surface itself as adsorption takes place.

As for the first, it is clear that in the chemical bond will participate electrons of the gas molecule and electrons of the solid. The latter may have a variety of origins: they may be found in some sort of localized states, like impurities and other defects near the surface, atomic-like orbitals in certain lattices like transition metal oxides and/or some ionic crystals with strong polaron effects, etc., or else they may be in crystal orbitals of some sort, be it ordinary Bloch states or so-called surface states. This, together with the existence of different types of traps for the electrons of the molecule determines a great variety of ways in which a molecule can be chemisorbed.

The formalism described in Section I was developed precisely for the purpose of being able to treat many different cases within the same formal framework of statistical thermodynamics. In so doing nothing is added to the physics of the problem; this has to be put in the model. A great deal of ingenuity and insight will be required in the years ahead to characterize in sufficient detail all the complicated interactions which may take place in an adsorbate-adsorbent system. What we have done in Section I is to first indicate how the statistical formalism goes on general lines and then illustrate it, somewhat more explicitly, for what we might call a very general model of a standard semiconductor.

We have also touched incidentally on the problem of the interaction between adsorbed molecules and/or between processes taking part on different centers. This calls for an extension of the studies of molecular interactions. The field is vastly unexplored and the challenge is there.

Then, as we have indicated, there are the changes that the solid surface undergoes during chemisorption. As changes of a chemical nature we have those due to the process of chemisorption itself as well as those associated with secondary react-

ions, such as oxidation-reduction. These are very important, as they modify in turn the amounts and fractional distribution of chemisorbed species, thus playing an essential role in the overall catalytic process.

To this one might add the changes of a physical origin, like thermal creation of active centers, or other physical factors which may also affect the ability of the solid to adsorb.

We have seen that a number of experimental data indicate that the above considerations are not merely idle speculations.

It is to be hoped that, as we are becoming increasingly aware of the many complications involved in the chemisorption processes, these will attract more the interest of scientists working in different fields. Their concentrated efforts, coming from different backgrounds, will be necessary to throw more light on the ever more intriguing problem of the interaction between a tiny gas molecule and this sort of huge, complex pseudo-molecule, the solid crystal.

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DISCUSSION

Chairman: G.M. SCHWAB

GARCÍA DE LA BANDA

Before starting the discussion of my paper I would like to make a couple of remarks:

The first one concerns Prof. BUCKINGHAM's question, after Prof. SCHWAB's presentation, on activation energies.

If we accept, which is very likely, that we have a « different catalyst » at each temperature (remember the case of oxides in oxidizing or reducing atmospheres) the activation energy, calculated classically from the Arrhenius plot, is meaningless. Actually it depends on the true activation energies for the different processes involved, for instance the activation energy for the formation of « active centres ».

The second one is related to the comment by Prof. LÖWDIN, also after Prof. SCHWAB's presentation.

I quite agree with Prof. LÖWDIN in his extension of the electronic factor from heterogeneous « inorganic » catalysis to life processes. I would not be surprised if the apparent complexity of enzymes is due mainly to the fact that special electronic properties, in some cases semiconducting properties, are needed in order to be a good catalyst for oxidation-reduction processes.

These aspects of biocatalysis fascinated me and I think the exchange of new ideas between heterogeneous inorganic catalysis and catalysis of living systems would be extremely fruitful.

VERWEY

The previous discussion leads me to the question whether it is possible to make a direct comparison between certain aspects of the mechanism of catalysis at solids and enzymatic action. In this connection it may be interesting to mention the work of COSSEE and ARLMAN on the Ziegler-Natta reaction (polymerization of olefines with catalysts containing a compound of trivalent titanium). They gave a theory for this reaction in which the determining factor is the possibility for the adsorbed molecules to be turned over such an angle that they can easily react, and they consider in detail the type of bonding between the Ti^{+3} and its incompletely filled $3d$ shell and the σ and π -bonding possibilities of the energy pattern as a function of conformation appears to be important, and the same is obviously the case in the action of enzymes, where, in addition, the conformation of the « sites », which are more or less « cages » built up from different parts of the same protein molecule, has to be taken into account.

GRIMLEY

Prof. GARCÍA has mentioned from time to time in his talk, active centres. I should like to ask him if he can give us some idea of how we must picture these centres on semi-conducting catalysts.

GARCÍA DE LA BANDA

Well, I think it is a hard job to try and give a picture of « active centres », Sir HUGH TAYLOR being in this room, but I shall try to do it.

I visualize the active center in this kind of catalysts as — we can say — a peculiar electronic structure, or configuration, in the neighbourhood of some place in the surface (that could be a defect, or any other entity) which allows the molecule to form easily appropriate chemical bonds with the surface. I do not know if this is the kind of answer you want.

SCHWAB

There is some kind of possibility of approach to the nature of active centres with the modern methods mentioned by Prof. BOWDEN before. On the tip of an electron microscope we can see what adsorbed molecules do on different faces of a crystal, and what they do on the edges between these faces, and there is no doubt that the potential of adsorption is different on different surface planes of a crystal. And I visualize active centres as certain kinds of surfaces, perhaps surfaces with high crystallographic indexes which are rarely present in an equilibrium crystal, but which are present in a little particle, which has been prepared by a topochemical reaction at low temperature, and which is not in equilibrium.

GARCÍA DE LA BANDA

I would like to say a few more words in connection with this active center problem.

There are measurements of catalytic activity of chromium dispersed, at very low concentration, on synthetic ruby by Prof. SELWOOD in which it is practically proved that the existence of active centres is associated with one of the oxidation states of chromia.

Also, in connection with the experiment by CLARK that I mentioned before, the existence of the second kind of chemisorption, giving carboxylate ions, must be associated with the presence of chromia.

ETUDE PAR SPECTROSCOPIE INFRAROUGE ET SPECTROSCOPIE HERTZIENNE DE LA NATURE DES INTERACTIONS ENTRE CATALYSEURS ET ESPECES CHIMISORBEES

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INTRODUCTION

Toute tentative d'interprétation du mécanisme d'une réaction de catalyse de contact implique la connaissance aussi précise que possible de la nature des interactions adsorbat-adsorbant dont témoigne la surface du catalyseur. Cela doit concerner tous les constituants du système catalysé ou certains d'entre-eux seulement selon qu'il s'agit d'un mécanisme de Langmuir-Hinshelwood ou d'un mécanisme de Rideal.

Les voies expérimentales susceptibles de fournir des informations plus ou moins complètes sur la nature de ces interactions sont maintenant relativement nombreuses. Les variations, au cours d'une chimisorption, de la fonction de travail, du coefficient d'accommodation, de la conductivité électrique, des propriétés magnétiques, etc. ont apporté dans nombre de cas des informations précieuses. Les méthodes spectroscopiques, des fréquences hertziennes à l'ultraviolet, sont au moins aussi efficaces.

Mais l'emploi de toutes ces techniques se heurtent à certains obstacles. Beaucoup de chimisorptions concernant des substances en cause dans des catalyses importantes ne sont pas accessibles actuellement. Cela est dû le plus souvent soit à ce que la chimisorption est très limitée, soit à ce qu'elle entraîne immédiatement une transformation chimique (dégradation en général) des molécules chimisorbées et parfois même une modification chimique de la surface du catalyseur. Un autre type de difficultés résulte de l'hétérogénéité des propriétés d'adsorption de la surface active. Bien des catalyseurs en effet sont connus pour posséder des sites actifs de nature différente. Dans ce cas, comme le montreront certains des travaux exposés ci-après, les méthodes spectroscopiques présentent sur les autres techniques des avantages certains.

Néanmoins, ces mêmes méthodes spectrales et notamment la spectroscopie infrarouge souffrent de graves limitations qui, dans l'état actuel de nos techniques, diminue la valeur des conclusions dégagées de leur emploi. Les catalyseurs sont le plus souvent des solides peu transparents à l'infrarouge. Il est rarement possible d'étendre l'étude d'un spectre infrarouge d'adsorbat en dessous de 1200, 1000 ou au mieux 700 cm^{-1} . Et même aux fréquences plus grandes, des bandes intenses d'absorption du solide lui-même masquent au moins en partie le spectre de l'adsorbat. Les obstacles ne sont pas moindres en résonance magnétique nucléaire.

Enfin, comme nombre d'autres techniques, les méthodes spectroscopiques peuvent rarement être mises en oeuvre dans les conditions mêmes d'une intervention catalytique d'un « vrai » catalyseur solide. Il est de règle que les masses de contact n'acquiescent l'activité et la sélectivité désirables que dans des conditions opératoires, débit, pression, température, souvent très limitées. Ces conditions sont rarement réalisables dans la cellule d'un spectromètre comme dans la plupart des appareils de mesure d'une propriété physique d'un catalyseur.

Aussi les études des interactions adsorbat-adsorbant sont-

elles le plus souvent faites avec des « catalyseurs » qui ne peuvent présenter que de rares points de similitude avec les catalyseurs industriels, avec des substances n'entrant jamais dans la composition d'un système catalysé et cela, souvent dans des conditions, notamment de température, qui sont plus ou moins éloignées de celles d'une catalyse de contact. Les travaux qui vont être exposés ne sont pas à l'abri de ces critiques.

I. ÉTUDE PAR SPECTROSCOPIE INFRAROUGE DE L'ADSORPTION DE L'AMMONIAC ET DE LA PYRIDINE PAR LA SILICE, L'ALUMINE ET UN CATALYSEUR SILICE-ALUMINE

Il est bien établi que la plupart des propriétés catalytiques des aluminas actifs et des silices-aluminas sont dues à la présence de sites acides à la surface de ces solides, sites acides de Lewis pour les aluminas, sites acides de Lewis et sites acides de Brønsted (protoniques) pour les silices-aluminas. Aussi de nombreux auteurs [1, 2] ont-ils déjà étudié par diverses méthodes, notamment par spectroscopie infrarouge, l'adsorption par ces catalyseurs de l'ammoniac et de la pyridine.

Mais d'autres travaux ont prouvé [3, 4] que les propriétés superficielles de ces catalyseurs sont fonction de la température d'un traitement thermique préalable dont l'effet chimique principal est le départ progressif de l'eau chimiquement liée se trouvant à leur surface et à l'intérieur. Il en résulte que la nature, le nombre et la force moyenne des sites responsables des processus d'adsorption chimique et de catalyse varient avec cette température comme avec la température d'emploi en catalyse. Diverses méthodes, notamment le dosage de l'eau superficielle par hydrolyse ménagée du diborane [5], la mesure par thermogravimétrie de la quantité d'ammoniac chimisorbé irréversiblement à diverses températures [6], le dosage des aci-

dités de Lewis et de Brønsted [6, 7], ont permis de se faire une idée assez précise des variations avec la température des acidités de ces catalyseurs. Mais les diverses méthodes mises ainsi en oeuvre, notamment les deux dernières qui viennent d'être mentionnées, sont loin d'être en accord quantitatif comme le montrent les courbes de la figure 1.

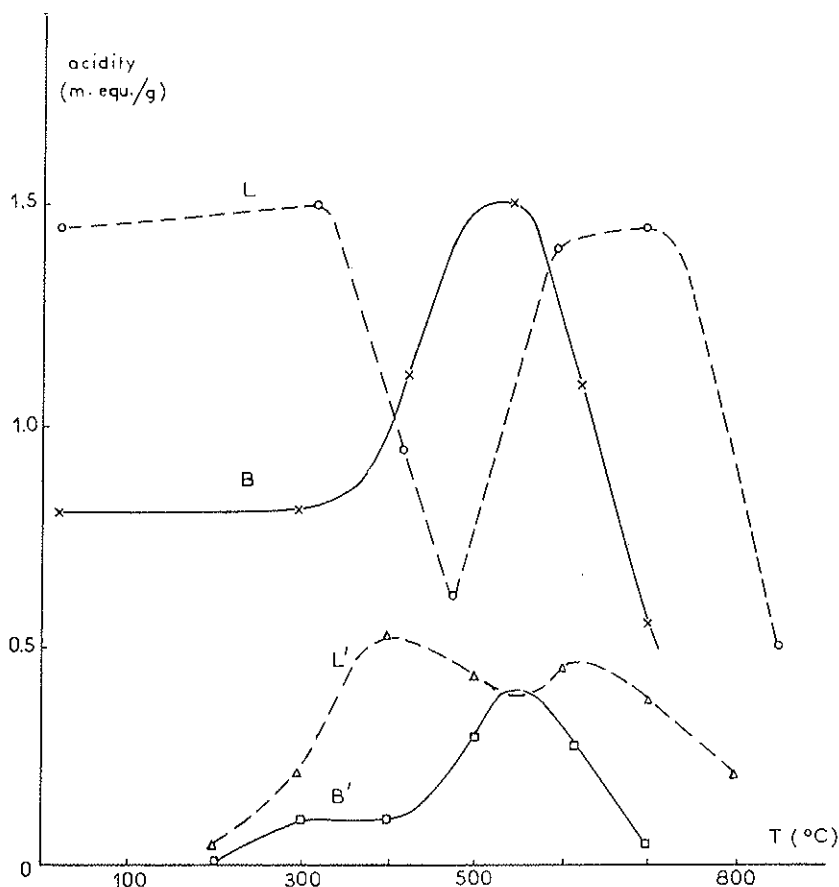


FIG. 1 — Variations avec la température d'un traitement préalable, des acidités de BRÖNSTED (B) et de LEWIS (L) d'un catalyseur silice-alumine. Courbes B et L: acidités mesurées en milieu liquide. Courbes B' et L': acidités mesurées par chimisorption d'ammoniac.

Elles ne permettent guère, d'autre part, d'obtenir des informations valables sur la nature des interactions adsorbat-adsorbant sur ce type de catalyseurs et sur l'influence qu'un traitement thermique préalable est capable d'exercer vis à vis de ces interactions. Il y a lieu de s'attendre à ce que les sites protoniques fixent à l'état d'ions positifs (NH_4^+ ou $\text{C}_5\text{H}_5\text{NH}^+$) l'ammoniac ou la pyridine et que les sites de LEWIS chimisorbent les mêmes bases azotées par liaisons de coordinence. A ces chimisorptions s'ajoute la possibilité de fixation des mêmes espèces soit par forces de van der Waals, soit par liaisons hydrogène avec les groupes OH superficiels que possèdent ces catalyseurs tant qu'une calcination à température élevée ne les a pas totalement déshydratés. Chacune de ces adsorptions se fait en libérant une énergie différente et des désorptions à des températures croissantes doivent permettre d'éliminer successivement chaque type d'adsorbat, donc de différencier les quatre types d'interaction envisagés.

La spectroscopie infrarouge est l'une des méthodes actuelles les plus aptes à déceler la nature de chaque interaction spécifique, liaison par pont hydrogène, liaison de coordinence, échange protonique. Mais il importe de procéder du simple au composé. Pour cette raison, les études spectroscopiques [8] ont concerné successivement une silice amorphe exempte de tout site acide fort, une alumine n'ayant que des sites de LEWIS et un catalyseur silice-alumine possédant les deux types de sites acides. Silice et alumine sont des produits de la firme Degussa: « aerosil » et « aluminiumoxyd P ». Ce sont des solides en grains non poreux de diamètre moyen voisin de 150 Å. Après désorption sous vide à 150° (élimination de l'eau adsorbée physiquement), ils titrent respectivement 3,4 et 7,1 groupes OH par 100 Å². Seul le catalyseur silice-alumine (de marque KETJEN) à 13% d'alumine est poreux.

L'identification des bandes d'absorption infrarouge des adsorbats a été facilitée par l'utilisation d'ammoniac et de pyri-

dine deutériés. En effet la valeur du rapport des nombres d'onde des vibrations (XH) et (XD) doit être un peu inférieur à $1/\sqrt{2}$. De plus l'ammoniac deutérié donne lieu à échange isotopique des hydrogène hydroxyliques, ce qui facilite l'étude des interactions entre adsorbat et ces groupes. La technique expérimentale sera décrite dans un autre mémoire [8].

1. *Adsorption sur silice amorphe.* — L'adsorption de l'ammoniac a été examinée sur des échantillons traités au préalable sous vide pendant 16 à 20 heures (sensiblement jusqu'à poids constant) à 150, 300, 600 et 900°C, celle de la pyridine sur les échantillons traités à 300 et 600°.

La figure 2 reproduit les spectres d'absorption infrarouge dans la région 3000-3900 cm^{-1} de trois de ces échantillons. Celui traité à 150° (courbe a) présente deux bandes intenses, l'une

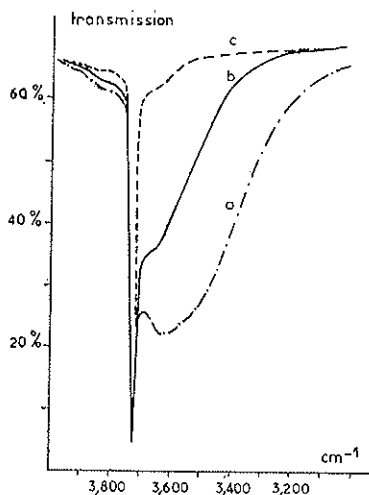


FIG. 2 — Spectres infrarouges d'échantillon de silice aerosil après traitement sous vide:

courbe a — 16 h. à 150°C,
courbe b — 16 h. à 300°C,
courbe c — 20 h. à 600°C.

à 3732 cm^{-1} est celle des groupes OH libres, l'autre, vers 3630 cm^{-1} est celle des groupes OH liés entre eux par un pont hydrogène. Cette seconde bande est très atténuée pour l'échantillon porté à 300° (courbe *b*) et plus encore pour celui calciné à 600° (courbe *c*) pour lequel on n'observe nettement que la bande des groupes Si-OH qui est alors pratiquement symétrique. La connaissance de ces bandes, présentes pour les trois adsorbants faisant l'objet de la présente étude tant qu'ils ne sont pas totalement déshydratés, est indispensable en raison des interactions des groupes OH avec les adsorbats.

Dès que débute l'adsorption d'ammoniac, les deux bandes des vibrations ν_1 et ν_3 apparaissent vers 3320 et 3400 cm^{-1} . Leur intensité augmente avec la pression d'ammoniac. C'est ce que montrent les courbes d'absorption infrarouge de la figure 3

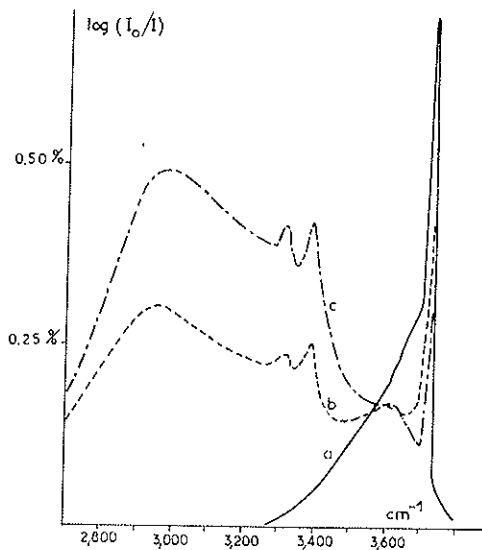


FIG. 3 — Courbes d'absorption infrarouge de l'ammoniac adsorbé sur silice, courbe *a*: silice traitée sous vide 15 h. à 300°C , courbe *b*: ammoniac adsorbé à 25° sous 2,83 mm Hg, courbe *c*: ammoniac adsorbé à 25° sous 9,90 mm Hg.

concernant l'adsorption sur un échantillon partiellement déshydraté sous vide à 300°. Sur la même figure, on voit que la densité optique de la bande d'absorption des groupes OH libres diminue quand augmente la quantité d'ammoniac adsorbée, mais sans s'annuler. L'élargissement de cette bande vers les basses fréquences est remplacé par un nouveau maximum situé à 3620-3640 cm^{-1} et il apparaît dès le début de l'adsorption une nouvelle bande très large dont le maximum est aux environs de 3050 cm^{-1} .

Le tableau I permet d'attribuer les bandes d'absorption de l'ammoniac par comparaison des fréquences observées pour les bandes de l'ammoniac gazeux, liquide et dissous dans CCl_4 . Les variations limitées de fréquence ($\Delta\nu$) entraînées par le passage de l'état gazeux à l'état adsorbé est un indice sérieux de la faiblesse des interactions silice-ammoniac. C'est ce que confirme l'aisance de la désorption réalisable à la température ordinaire. Contrairement à ce que l'on observe pour l'état gazeux, la bande de la vibration ν_1 est moins intense que celle de la vibration ν_3 . C'est aussi le cas de l'ammoniac liquide, solide ou dissous dans CCl_4 . Il se pourrait que cette inversion des intensités soit liée à la mobilité des molécules.

Comme l'avaient déjà signalé TERENIN [9] et KISSELEV et coll. [10], aucun des spectres enregistrés ne présente de maximum d'absorption correspondant à l'ion ammonium. Cela n'est pas pour surprendre, la silice amorphe étant connue pour ne pas avoir d'acidité protonique notable. Par contre, l'influence de l'adsorption d'ammoniac sur les bandes des OH du solide et l'apparition du large maximum centré vers 3050 cm^{-1} (fig. 3) conduisent à conclure à l'existence de *ponts hydrogène entre ces groupes OH et l'atome d'azote de la molécule d'ammoniac* (liaisons OH---N). Mais les spectres montrent qu'après adsorption il subsiste des groupes OH libres (des groupes OD dans le cas de l'adsorption de ND_3) et il a été adsorbé plus de molécules d'ammoniac qu'il n'y a de groupes OH associés à ces molécules. Il y a donc un second processus d'adsorption.

TABLEAU I — Fréquences (cm^{-1}) des bandes d'absorption infrarouge de l'ammoniac (adsorption sur silice amorphe).

Vibration	état de l'ammoniac				$\Delta \nu$		
	gaz	liquide	dissous dans CCl_4	adsorbé sur silice	gaz-adsorbé	gaz-liquide	gaz-solution dans CCl_4
ν_1	3336,2	3285	3315	3320 ± 7	17	51,7	21,7
	3337,2		3313				23,7
ν_3	3443,6	3375	3417	3397 ± 7	47	68,7	26,7
	3443,9		3421				22,7

Comme aucun indice de l'existence de liaisons de type NH--O entre molécules d'ammoniac et atomes superficiels d'oxygène ne peut être trouvé de l'examen des spectres enregistrés, force est de conclure que l'excès d'ammoniac est adsorbé physiquement de manière non spécifique du fait des forces de van der Waals.

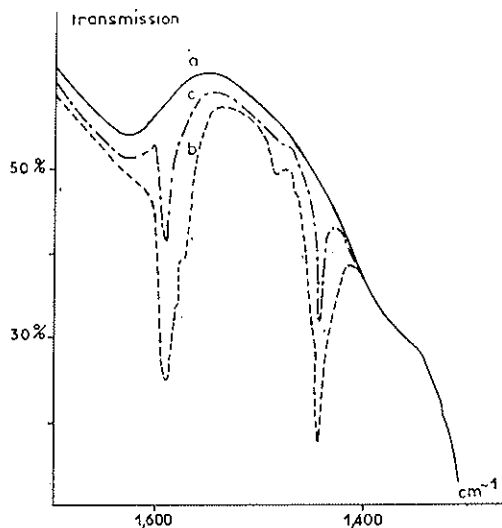


Fig. 4 — Spectres d'absorption infrarouge ($1300-1700\text{ cm}^{-1}$) de la pyridine adsorbée sur la silice,
courbe *a*: silice traitée sous vide 18 h. à 600°C ,
courbe *b*: pyridine adsorbée à 25° sous 25 mm Hg,
courbe *c*: pyridine restant adsorbée après 16 h. de désorption à 25° .

L'adsorption de la pyridine à 25° et sous sa pression de vapeur saturante (25 mm Hg) donne lieu à 4 bandes d'absorption infrarouge, dont deux très intenses, dans la région $1400-1600\text{ cm}^{-1}$ comme le montre la courbe *b* de la figure 4. La courbe *c* prouve que la désorption n'est que très partielle à la

température ambiante. L'examen des courbes de la figure 5 révèle que, dans la région des 3000 cm^{-1} , il est difficile d'observer les bandes d'absorption de la pyridine. Mais l'emploi de pyridine deutériée a permis de discerner plus facilement les fréquences des mêmes modes de vibration qui diffèrent peu de celles de la pyridine liquide. On voit sur la même figure que l'adsorption réduit à très peu de chose la bande des groupes OH libres (ils sont peu nombreux après traitement à 600°) et

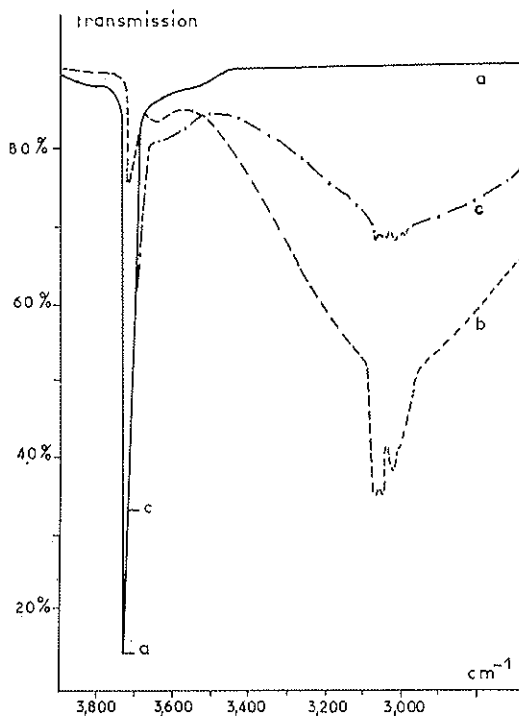


FIG. 5 — Spectres d'absorption infrarouge ($2800\text{--}3800\text{ cm}^{-1}$) de la pyridine adsorbée sur la silice,

courbe *a*: silice traitée sous vide 18 h. à 600°C ,

courbe *b*: pyridine adsorbée à 25° sous 25 mm Hg,

courbe *c*: pyridine restant adsorbée après 16 h. de désorption à 25° .

qu'une désorption à 25° ne restitue pas son intensité initiale à cette bande.

Le tableau II permet de comparer les fréquences et les intensités des bandes d'absorption de la pyridine à l'état liquide, en solution dans l'eau et adsorbée sur la silice. La similitude, (intensités comme nombres d'onde) dans la région 1440-1600 cm^{-1} , des spectres de l'adsorbat et de la pyridine dans un milieu riche en groupes OH ne peut être interprétée que par la formation de ponts hydrogène entre atomes d'azote et groupes OH superficiels du solide, donc comme pour l'ammoniac, par des liaisons OH--N. Mais ces liaisons sont plus fortes dans le cas présent que pour l'adsorption de l'ammoniac puisque la désorption à la température ordinaire est incomplète et doit être poursuivie jusqu'à 150°C.

D'autre part, au cours de la désorption, l'augmentation relative de l'intensité de la bande des groupes OH est bien inférieure à la diminution relative d'intensité des bandes à 1444 et 1593,5 cm^{-1} de la pyridine adsorbée. La désorption élimine donc de la surface des molécules de pyridine qui ne sont pas liées à des groupes OH. Il ne peut s'agir à nouveau que d'une adsorption physique non spécifique due aux forces de van der Waals. Enfin, l'absence de bandes à 1544 et 1638 cm^{-1} , caractéristiques de l'ion pyridinium, interdit d'envisager une chimisorption par échange protonique avec des sites acides de BRÖNSTED.

Par conséquent, la silice amorphe ne donne lieu à aucun processus de chimisorption de l'ammoniac et de la pyridine. Il s'agit uniquement d'adsorption physique qui se fait simultanément selon deux mécanismes, l'un non spécifique dû aux forces de van der Waals, l'autre spécifique dû à la formation de liaisons hydrogène entre une fraction seulement des groupes OH superficiels du solide et l'atome d'azote des deux bases.

2. *Adsorption sur alumine.* — Cette alumine, partiellement amorphe, partiellement cristallisée (variété delta des alu-

TABLEAU II — *Fréquences (cm^{-1}) et intensités des bandes d'absorption infrarouge de la pyridine et de la pyridine deutériée (adsorption sur silice).*

Espèce	Mode de vibration	état de la pyridine		
		liquide	dissoute dans l'eau	adsorbée sur silice
$\text{C}_5\text{H}_5\text{N}$	19b	1439 t.F.	1443-1445	1444 t.F.
	19a	1478 F.	1487-1481	1485 t.f. (large)
	8b	1572 m.		1577 f.
	8a	1579 t.F.	1590-1592	1580 f. 1593,5 t.F.
	1 + 6a	1597 F.		non observée
	8b + 19b	3004 F.	3004-3010	3017
	(7a) (7b)	3029 t.F.	3036	3044
	(2) (13)	3055 F.	3063-3068	3062
	20b	3082 t.F.	3089-3096	3095
	8a + 8b	3148 f.		3157
$\text{C}_5\text{D}_5\text{N}$	19b	1301 F.		1305
	19a	1340 f.		1340 f.
	8a	1530 t.F.		1551 t.F.
	8b	1542 F.		1540 F.
	1 + 6a	1550 m.		1561
	v(CD)	2254 t.F.		2261 t.F.
		2270 F.		2279 F.
		2285 F.		2292 F.
	8b + 18b	2384 f.		2385 f.
	3 + 8b 3.18a	2460 f.		2455 f.

mines de transition), ne possède de groupes OH liés que si le traitement thermique sous vide a été effectué à 400°C au plus. Au delà, il n'y a plus que des OH libres qui sont totalement éliminés dès 750°.

L'adsorption d'ammoniac à la température ambiante entraîne l'apparition de 6 bandes sur les spectres infrarouges.

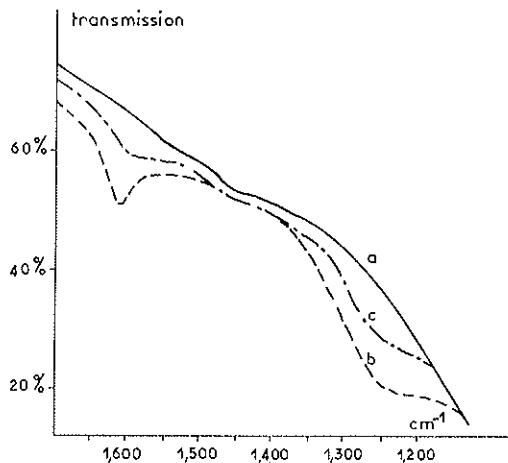


FIG. 6 — Spectres d'absorption infrarouge (1100-1700 cm^{-1}) de l'ammoniac adsorbé sur alumine,

courbe *a*: alumine traitée sous vide 16 h. à 450°C,

courbe *b*: ammoniac restant adsorbé après 2 h. d'adsorption à température ambiante ($p = 22$ mm Hg) et 1 h. de désorption à la même température,

courbe *c*: ammoniac restant adsorbé après 1 h. de désorption à 180°C.

Deux sont situées à 1615 et vers 1270 cm^{-1} comme le montrent les courbes *b* et *c* de la figure 6. Les quatre autres sont situées entre 3100 et 3400 cm^{-1} (fig. 7) respectivement à 3390 (épaulement), 3350, 3265 et 3160 cm^{-1} . La courbe *b* de la figure 7 montre de plus que l'adsorption d'ammoniac atténue beaucoup (cela dès son début) les trois bandes d'absorption des

groupes OH libres. Simultanément apparaît une large bande vers 3560 cm^{-1} . Cinq minutes de désorption à la température ordinaire font réapparaître ces trois bandes des groupes OH,

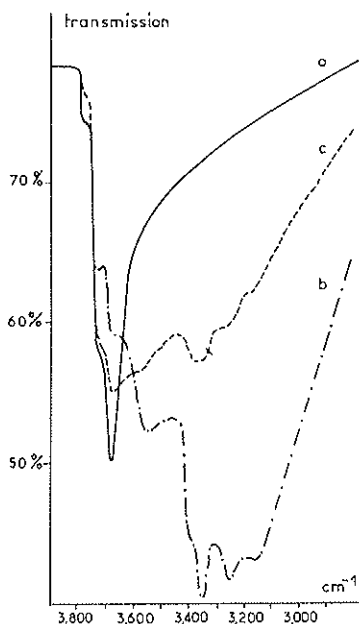


FIG. 7 — Spectres d'absorption infrarouge ($2900\text{--}3800\text{ cm}^{-1}$) de l'ammoniac adsorbé sur alumine,

courbe *a*: alumine traitée sous vide 16 h. à 450°C ,

courbe *b*: ammoniac restant adsorbé après 2 h. d'adsorption à température ambiante ($p=22\text{ mm Hg}$) puis 1 h. de désorption à la même température,

courbe *c*: ammoniac restant adsorbé après 1 h. de désorption à 180°C .

mais leur intensité initiale n'est rétablie qu'après 5 heures de désorption à 250°C .

Par comparaison avec les spectres infrarouges de complexes métalliques amminés, les bandes à 3350, 3265, 1615 et 1270

cm^{-1} sont logiquement attribuées aux modes vibratoires ν_3 , ν_1 , ν_4 et ν_2 . Cette analogie de structure d'une partie de l'ammoniac adsorbé sur l'alumine avec l'ammoniac des complexes amminés conduit à conclure à l'existence de liaisons de coordinence entre atomes d'azote de molécules d'ammoniac et certains sites superficiels de l'alumine. Ces sites ne peuvent être que des sites de Lewis capables d'accepter une paire d'électrons libres de l'atome d'azote. Cette conclusion trouve sa confirmation dans le fait qu'une alumine totalement déshydratée par traitement sous vide à 750°C donne lieu également à chimisorption de ce type.

Mais, pour les échantillons d'alumine incomplètement déshydratés, une partie de l'ammoniac est désorbable dès la température ordinaire en libérant des groupes OH superficiels. Il y a donc aussi adsorption physique spécifique par ponts hydrogène $\text{OH}\cdots\text{N}$, ce que traduit la bande à 3560 cm^{-1} . Et tout laisse à penser que les forces de van der Waals interviennent aussi pour fixer de manière non spécifique et encore plus faiblement d'autres molécules d'ammoniac. Par contre aucune donnée spectrale ne milite en faveur de l'existence d'ions ammonium ni de celle d'ions NH_2^- envisagée cependant par certains auteurs [30].

Le spectre infrarouge de la pyridine adsorbée à 25° sur l'alumine comporte 21 bandes ou épaulements entre 1030 et 3500 cm^{-1} . Comme le précisent les deux dernières colonnes du tableau III, quelques unes de ces bandes disparaissent rapidement par désorption à la même température. D'autres ne disparaissent qu'après deux heures de désorption à 150° et les dernières seulement après 5 heures à 350°C . Cela suffit à confirmer l'existence des trois types d'adsorption déjà décelés dans le cas de l'ammoniac. Les bandes des OH du solide subissent des modifications comparables à celles signalées plus haut pour l'ammoniac. L'attribution de chaque bande à un mode de vibration (1ère colonne du tableau III) s'est révélée délicate. Elle a été facilitée par le recours à la pyridine deutériée.

TABLEAU III — *Fréquences (cm⁻¹) et intensités des bandes d'absorption infrarouge de la pyridine (adsorption sur alumine).*

mode de vibration	état de la pyridine				disparaissant par désorption	
	liquide	complexes métalliques	avec acides de Lewis	adsorbée sur alumine	à	après
12	1031 t.F.	1035-1047	1042-1055	1030 1044	25°C 350°	rapidement 5 h.
18a	1068 F.	1064-1082	1062-1078	1068	350°	5 h.
15	1147 F.	1144-1168	1150-1195	1145	350°	5 h.
9a	1217 F.	1213-1228	1220-1240	1220	350°	5 h.
		1233-1252	1250	1235	350°	5 h.
2. 6b 6a + 11	1296 t.f.		1305	non obs.		
6a + 10b	1357 f.	1353-1362	1355	non obs.		
14	1375 m.	1370-1400	1370	non obs.		
19b	1439 t.F.	1440-1461	1450-1458	1441 1444→1449	25° 350°	rapidement 5 h.
19a	1478 F.	1471-1490	1480-1495	1482 1487→1492	25° 350°	rapidement 5 h.
8b	1572 m.	1562-1575	1560-1575	1576	350°	5 h.
8a	1579 t.F.	1592-1615	1610-1628	1583 1587,5-1590 1606→1620	25° 150° 350°	rapidement 2 h. 5 h.
1 + 6a	1597 F.			non obs.		
6a + 12 1 + 6b	1633 f.	1625-1660	1637	non obs.		
6b + 12	1682 f.			non obs.		
3 + 6b 2. 5	1872 m.			1860		
9a + 11	1923 m.			1920		
2. 1	1987 m.					
8a + 14 2. 19a	2960 m.					
8b + 19b	3004 F.			3004→3014	350°	5 h.
(7a) (7b) (2) , (13)	3029 t.F. 3037 f. 3055 F.		5 bandes entre 2860 et 3285	3032	300°	2 h.
				3057→3062	350°	5 h.
20b	3082 t.F.			3078→3090	350°	5 h.
2. 8b 8a + 8b 2. 8a	3148 f.			3150→3157	350°	5 h.

Il y a donc trois modes d'adsorption de la pyridine comme de l'ammoniac sur l'alumine :

a) les bandes dont les fréquences sont très voisines de la pyridine liquide disparaissent par désorption à la température ordinaire. Elles traduisent une adsorption non spécifique de van der Waals.

b) les bandes éliminées par traitement sous vide à 150° influent sur l'intensité des bandes des groupes OH superficiels de l'alumine et elles n'existent pas sur les spectres des adsorbats d'échantillons d'alumine complètement déshydratés. Elles correspondent donc à une adsorption physique spécifique par liaisons hydrogène OH--N;

c) enfin 9 bandes de la pyridine adsorbée correspondent parfaitement avec 9 bandes des spectres infrarouges de la pyridine liée par coordinence dans des complexes métalliques. Elles ne disparaissent qu'après 5 heures de désorption à 350°C. Elles existent dans les spectres des adsorbats d'échantillons anhydres. Il s'agit alors de chimisorption par coordinence d'atomes d'azote de la base avec des sites de Lewis. L'augmentation de fréquence des modes vibratoires 19b et 8a quand augmente la température de désorption, est un argument de poids en faveur de l'existence de sites de Lewis ayant des forces acides différentes.

Ici encore, aucun spectre ne présente de bandes caractéristiques de l'ion pyridinium. Ce qui est normal, les aluminés actives étant considérées comme exemptes de sites acides de Brønsted.

Par conséquent, aux deux processus d'adsorption physique, l'un non spécifique, l'autre spécifique et résultant de la présence de groupes OH à la surface des échantillons incomplètement déshydratés, processus communs à tous les oxydes adsorbants tels que la silice et l'alumine, s'ajoute, dans le cas de l'alumine étudiée ici comme de toute alumine catalytique, un

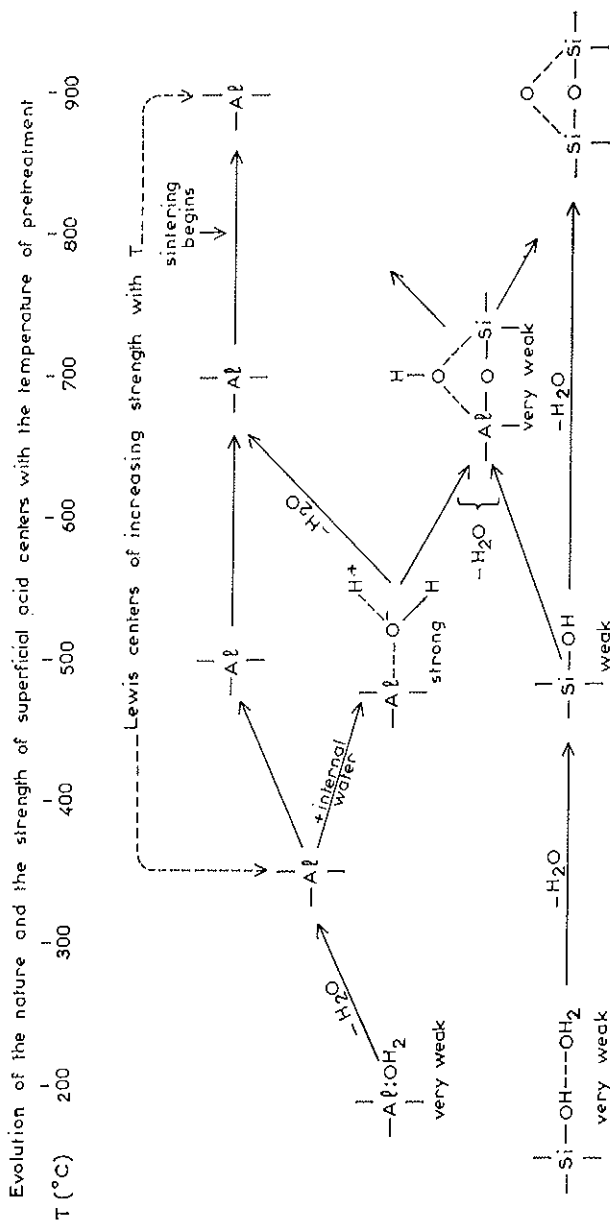
processus d'adsorption chimique par coordinence dû à la présence de sites acides de LEWIS à la surface de ces alumines.

3. *Adsorption sur catalyseur silice-alumine.* — Il est établi qu'au terme d'un traitement thermique convenable, les catalyseurs silice-alumine possèdent à leur surface des sites acides de Lewis et des sites acides de Brönsted (protoniques). Le nombre et la force moyenne de chacun de ces types de sites varie avec la température de ce traitement. L'ensemble des études faites à ce sujet par les méthodes mentionnées plus haut a permis de préciser comme indiqué sur la figure 8 l'évolution des propriétés acides en fonction de la température du traitement et de la déshydratation progressive qu'il entraîne. Il faut donc s'attendre pour ces catalyseurs à une plus grande diversité des interactions adsorbat-adsorbant.

Dès que débute l'adsorption d'ammoniac à la température ordinaire, il apparaît (fig. 9), dans la région des vibrations de déformation, un maximum très intense à 1445 cm^{-1} et un autre maximum à 1615 cm^{-1} qui se superpose à la bande 1635 cm^{-1} de l'harmonique Si-O du catalyseur. La désorption est difficile. Une heure à 180°C n'affaiblit qu'à peine les deux maximums (courbe *b*). Et ils sont encore visibles après une heure de traitement sous vide à 350°C (courbe *c*). L'ammoniac est donc, au moins en partie, bien plus fortement fixé sur ce catalyseur que sur l'alumine.

Dans le domaine $3000\text{--}3800\text{ cm}^{-1}$, il apparaît (fig. 10) une seule bande très large et intense vers 3280 cm^{-1} avec un épaulement à 3350 cm^{-1} . Ici aussi la désorption à 350°C n'entraîne pas la disparition complète de la bande d'absorption. Par contre la bande des groupes OH à 3735 cm^{-1} n'est que peu affaiblie par l'ammoniac restant adsorbé après désorption d'une heure à 180° . Il faut atteindre une pression d'équilibre de plus de 20 mm à 25° pour qu'elle disparaisse et soit remplacée par une bande large à $3570\text{--}3600\text{ cm}^{-1}$.

La bande à 1615 cm^{-1} n'avait pas été observée lors de



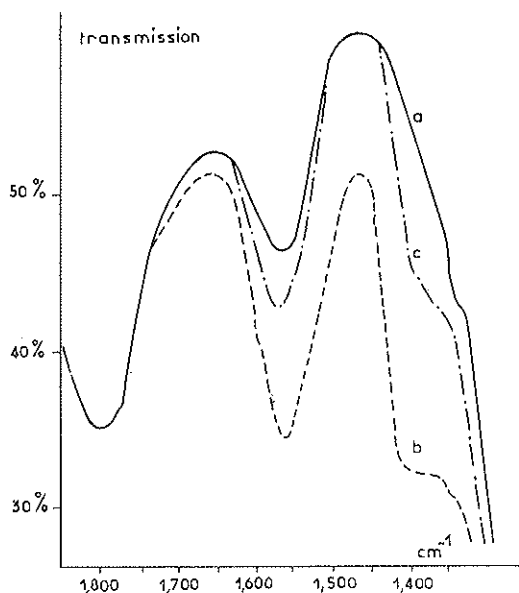


FIG. 9 — Spectres d'absorption infrarouge ($1350-1900\text{ cm}^{-1}$) de l'ammoniac adsorbé sur catalyseur silice-alumine,

courbe *a*: catalyseur traité sous vide 18 h. à 600°C ,
 courbe *b*: ammoniac restant adsorbé après 18 h. d'adsorption à 180° ($p=22\text{ mm Hg}$) puis 1 h. de désorption à la même température,
 courbe *c*: ammoniac restant adsorbé après 1 h. de désorption à 350°C .

l'adsorption d'ammoniac sur la silice et l'alumine. Elle doit être attribuée à la vibration ν_4 de l'ion ammonium. Cela confirme l'existence de sites acides protoniques. Sa forte intensité après désorption à 180° et sa persistance après désorption à 350° suffisent à révéler qu'il s'agit d'une chimisorption forte. Le spectre de l'ammoniac deutérié vient confirmer cette conclusion. Mais d'autres bandes d'absorption infrarouge que celles de l'ion ammonium ne disparaissent également qu'après désorption prolongée à 350° . Il s'agit encore d'une chimisorption forte et, par comparaison avec les spectres d'absorption des

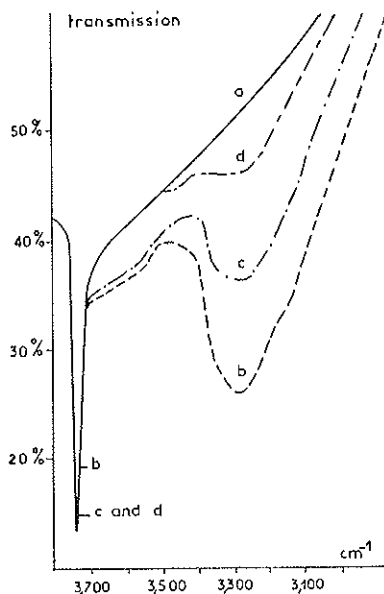


FIG. 10 — Spectres d'absorption infrarouge ($3000-3800\text{ cm}^{-1}$) de l'ammoniac adsorbé sur catalyseur silice-alumine, courbe *a*: catalyseur traité sous vide 18 h. à 600°C , courbe *b*: ammoniac restant adsorbé après 18 h. d'adsorption à 180° ($p=22\text{ mm Hg}$) puis 1 h. de désorption à la même température, courbe *c*: ammoniac restant adsorbé après 1 h. de désorption à 250° , courbe *d*: ammoniac restant adsorbé après 1 h. de désorption à 350°C .

adsorbats d'ammoniac sur alumine, on est en droit de conclure que cette seconde chimisorption résulte de l'établissement de liaisons de coordinence entre l'atome d'azote et un site de Lewis.

Enfin l'adsorption physique spécifique sur les groupes OH par ponts hydrogène $\text{OH}\cdots\text{N}$ est mise en évidence par l'influence de l'adsorption sur la bande des OH du solide. Mais ce n'est que par analogie avec les résultats concernant l'adsorption sur silice et sur alumine, que l'existence d'une adsorption

non spécifique de van der Waals doit logiquement être admise sur un solide dont la majeure partie de la surface est constituée de silice amorphe.

Dans la région $1300-1800\text{ cm}^{-1}$ (fig. 11), les spectres infrarouges de la pyridine adsorbée sur le catalyseur silice-alumine

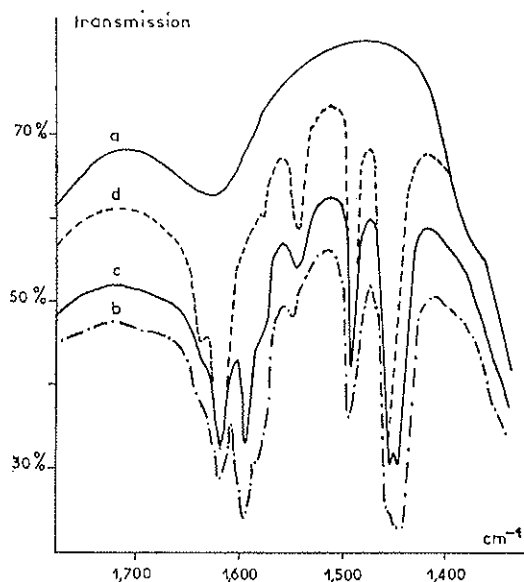


FIG. 11 — Spectres d'absorption infrarouge ($1300-1800\text{ cm}^{-1}$) de la pyridine adsorbée sur catalyseur silice-alumine,

courbe a: catalyseur traité sous vide 18 h. à 410°C ,

courbe b: pyridine adsorbée à 25° sous 25 mm Hg,

courbe c: pyridine restant adsorbée après 3 h. de désorption à 25° ,

courbe d: pyridine restant adsorbée après 1 h. de désorption à 200°C .

présente 12 bandes. Une désorption pendant une heure à 200° ne fait qu'atténuer la plupart d'entre-elles (courbe d). Entre 3000 et 3800 cm^{-1} , 6 autres bandes sont observées (fig. 12). On voit sur cette figure que les groupes OH du solide sont en forte interaction avec la pyridine et que même la désorption à

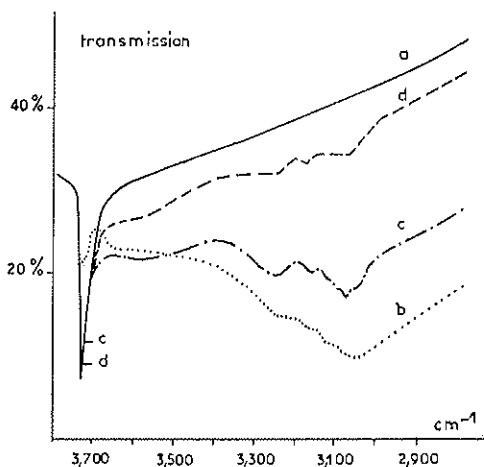


FIG. 12 — Spectres d'absorption infrarouge (2900-3800 cm^{-1}) de la pyridine adsorbée sur catalyseur silice-alumine, courbe *a*: catalyseur traité sous vide 15 h. à 560°C, courbe *b*: pyridine restant adsorbée après adsorption à 25°C puis désorption de 3 h. à la même température, courbe *c*: pyridine restant adsorbée après 1 h. de désorption à 200°, courbe *d*: pyridine restant adsorbée après 3 h. de désorption à 300°C.

300° pendant 3 heures (courbe *d*) ne restitue pas complètement son intensité initiale à la bande 3735 cm^{-1} .

Le tableau IV permet de comparer les bandes du spectre de la pyridine adsorbée à celles de la pyridine liquide et de l'ion pyridinium. Pour certaines de ces bandes, il précise également les conditions de désorption (température et durée) nécessaires à leur disparition. On voit que certaines bandes disparaissent au bout de 3 heures de désorption à la température ordinaire. Leurs nombres d'ondes sont très proches de ceux de bandes de la pyridine liquide. D'autres bandes disparaissent après 2 heures de désorption à 150° et cela entraîne un renforcement de la bande des OH du solide. Un troisième groupe de bandes n'est éliminé qu'après 2 heures de traitement

TABLEAU IV — Fréquences (cm^{-1}), intensités et attributions des bandes d'absorption infrarouge de la pyridine (adsorption sur catalyseur silice-alumine).

mode de vibration	état de la pyridine		attribuée à			disparaissant par désorption	
	liquide	$\text{C}_5\text{H}_5\text{NH}^+$	adsorbée sur catalyseur	adsorption physique v.d. Waals	adsorption chimique sur sites de Lewis Brönsted	à	après
19b	1439 t.F.	1525-1542 F. t.F.	1438-5	x		25°C	3 h.
			1444		x	150°	2 h.
			1451-1455 1544			550°	5 h.
19a	1478 F.	1478-1490 F. t.F.	1482	x		400°	2 h.
			1490-1495		x	25°	3 h.
8b	1572 m.	1600-1613 F. t.F.	1575	x		550°	5 h.
			1620		x		
v8	1579 t.F.	1631-1640 m.-F. t.F.	1582	x		25°	3 h.
			1593		x	150°	2 h.
			1619-1622			550°	5 h.
			1638		x	400°	2 h.
1 + 6a	1597 F.		non obs.				
8b + 19b	3004 F.		3004				
(7a) (7b) (2) (13)	3029 t.F. 3037 f. 3055 F.	une à 5 bandes entre 3042 et 3151	3032 3057				
20b	3083 t.F.		3078-3090				
ν (NH)	—	1 à 4 bandes entre 2375 et 3335	3180 3255				

sous vide à 400° et ces bandes concordent avec certaines de celles du l'ion pyridinium. Enfin, il faut désorber à 550° pour éliminer les dernières bandes qui sont comparables à celles des molécules de pyridine chimisorbées sur alumine.

Par conséquent, il est légitime de conclure sans ambiguïté à quatre types d'interaction pyridine-adsorbant:

a) une adsorption physique non spécifique due aux forces de van der Waals;

b) une adsorption physique spécifique résultant de l'établissement de ponts hydrogène entre atomes d'azote et groupes OH superficiels du solide;

c) une adsorption chimique sur sites protoniques engendrant des ions pyridinium;

d) une adsorption chimique encore plus forte sur sites de Lewis résultant de l'établissement d'une liaison de coordinence entre ces sites et les atomes d'azote de la base.

Selon la température à laquelle les échantillons de catalyseurs ont été préalablement traités sous vide avant adsorption, l'intensité des bandes correspondant aux deux chimisorptions varie. Il est bien connu que le traitement thermique a pour conséquence de faire varier le nombre de sites de Lewis, et celui des sites de Brønsted (cf. fig. 1). Il est donc tentant de chercher à estimer le nombre de chaque type de centres par mesure de l'intensité de certaines des bandes d'absorption de l'ion pyridinium et de la pyridine chimisorbée par coordinence. En fait, le résultat de telles mesures ne peut être qu'approximatif et l'on peut au mieux estimer, pour chaque échantillon, le rapport L/B du nombre de sites de Lewis au nombre de sites de Brønsted.

Cette estimation a été fondée sur la bande à $1451\text{--}1454\text{ cm}^{-1}$ correspondant à la chimisorption par coordinence, et la bande à 1544 cm^{-1} de l'ion pyridinium. Mais la mesure pré-

cise des intensités se heurte à des difficultés sérieuses et de plus la variation du coefficient d'extinction de chaque bande avec le nombre de molécules ou ions adsorbés n'est pas la même d'une bande à l'autre. De ce fait, on ne peut évaluer au mieux que le produit $(L/B).k$, où k est le rapport des coefficients d'extinction, grandeurs non mesurables dans le cas présent, des deux bandes choisies.

La figure 13 donne, en unités arbitraires, les variations du rapport $(L/B).k$ en fonction de la température du traite-

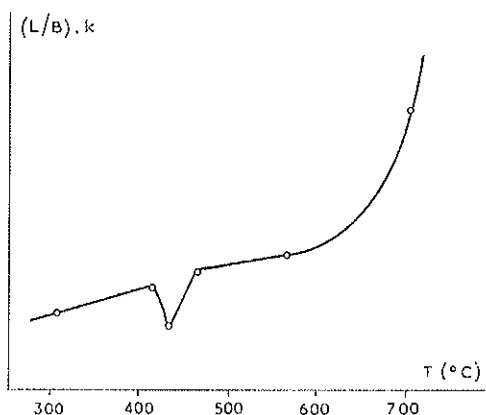


FIG. 13 — Variations approchée du rapport du nombre des sites de LEWIS au nombre des sites de BRÖNSTED (protoniques) en fonction de la température du traitement préalable du catalyseur silice-alumine.

ment thermique préalable sous vide des échantillons du catalyseurs silice-alumine. Les intensités des deux raies ont été mesurées sur les spectres obtenus après désorption partielle de la pyridine à 200° , ce qui élimine toutes les molécules adsorbées physiquement de manière spécifique ou non. La courbe de cette figure montre que l'échantillon traité sous vide à 430°C

est moins riche en sites de Lewis et plus riche en sites protoniques que les échantillons traités quelques 20 ou 30° plus haut ou plus bas. D'autres travaux [6, 7] (cf. fig. 8) avaient permis d'établir que c'est dans un intervalle étroit de température, toujours situé un peu au dessus de 400°, que le catalyseur silice-alumine étudié ici, perd son eau interne de constitution et qu'une partie de cette eau se fixe alors sur certains sites de Lewis, les transformant en sites de Brönsted. La spectroscopie infrarouge apporte une confirmation valable des conclusions de ces travaux.

* * *

L'étude par spectroscopie infrarouge des processus d'adsorption de l'ammoniac et de la pyridine établit donc clairement que les oxydes incomplètement déshydratés que sont les silices amorphes, les aluminas catalytiques et les catalyseurs silice-alumine sont capables d'exercer vis à vis des molécules étudiées des interactions de nature et force très différentes. Du point de vue des interventions en catalyse de contact, seules sont en cause celles de ces interactions qui s'exercent encore aux températures des catalyses, c'est à dire celles décelées et caractérisées dans le présent travail après désorption à environ 300°C.

Pour les aluminas comme pour les silices-aluminas, un type commun d'interaction très forte résulte de l'établissement d'une liaison de coordination entre atome d'azote des deux bases et sites acides de Lewis. Dans le cas des catalyseurs silice-alumine, à ce premier type d'interaction s'ajoute celle exercée par les sites acides protoniques qui, par transfert de leurs protons, fixent les mêmes bases à l'état d'ions ammonium ou pyridinium. Cette seconde chimisorption est moins forte que la précédente.

Il faut également souligner que le déplacement du maximum de certaines bandes au cours d'une désorption en tempé-

rature croissante met en lumière que chacune de ces chimisorptions se fait sur des sites de forces différentes. Il y a donc une hétérogénéité des propriétés de chimisorption aussi bien des sites de Lewis que des sites de Brönsted.

II. ETUDES PAR SPECTROSCOPIE INFRAROUGE DE REACTIONS EN PHASE ADSORBÉE

Deux critiques peuvent être faites aux travaux résumés ci-dessus. Les espèces choisies en vue de déceler la nature des interactions adsorbat-adsorbant ne sont pas comparables aux constituants des systèmes les plus couramment catalysés par l'alumine ou les silices-alumines. D'autre part, si les fortes interactions dues aux deux chimisorptions ont bien été mises en évidence au terme d'adsorptions-désorptions réalisées aux températures d'emploi en catalyse de ces masses de contact, les spectres infrarouges ont été enregistrés après retour des échantillons à la température ordinaire faute de pouvoir le faire à 400 ou 500°C, températures habituelles des procédés catalytiques les plus importants.

Il est donc particulièrement intéressant de conduire des études analogues de phases adsorbées constituées par chacun des constituants, réactifs et produits de réaction, d'un système réactionnel. C'est ce qui a été fait pour deux catalyses, l'oxydation de l'oxyde de carbone au contact de la thorine et la décomposition de l'oxyde nitreux au contact de l'oxyde de nickel. Mais seule cette seconde réaction a pu être étudiée aux températures très modérées, 150 à 200°C, où elle acquiert une vitesse mesurable sur un oxyde de nickel suffisamment divisé. La thorine ne témoignant d'activité catalytique réelle dans les réactions d'oxydation qu'à partir de 350-400°C, les adsorbats n'ont pu être examinés par spectroscopie infrarouge qu'après retour des échantillons à la température ordinaire.

1. *Etude de l'oxydation de l'oxyde de carbone catalysée par la thorine* [11]. — La thorine utilisée est un semiconducteur obtenu par décomposition thermique du nitrate de thorium. Elle présente sur les oxydes étudiés précédemment le grand avantage d'être transparente à l'infrarouge jusque vers 700 cm^{-1} .

L'étude cinétique de la réaction entre 350 et 450°C [12] et celle des processus d'adsorption des oxydes du carbone avait conduit à conclure à un mécanisme en trois étapes:

a) une chimisorption réversible de l'oxyde de carbone sur la thorine ($E=2\text{ kcal/mole}$);

b) l'oxydation de cet adsorbat par l'oxygène gazeux, aucune adsorption d'oxygène n'étant décelable;

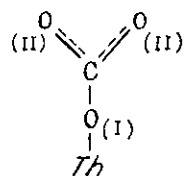
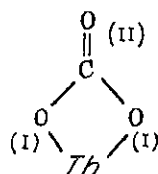
c) une désorption du gaz carbonique formé ($E=1,7\text{ kcal/mole}$). Comme l'énergie apparente d'activation de la réaction est de $17,7\pm0,6\text{ kcal}$, c'est donc la seconde étape qui est la plus lente et dont la vitesse détermine celle de l'évolution globale.

La spectroscopie infrarouge devait avoir pour objectif de confirmer l'existence de ces chimisorptions et de préciser le mécanisme des interactions de la thorine avec les oxydes du carbone. Dans ce but les spectres des adsorbats doivent être comparés à ceux du carbonate et du formiate de thorium. Le tableau V donne les fréquences des bandes d'absorption infrarouge de ces deux sels de thorium. Il est connu que, pour les éléments de transition, l'ion carbonate peut se lier au métal de deux façons: monodenté et bidenté, l'ion ayant alors respectivement les symétries C_s et C_{2v} , cette dernière impliquant un plus grand nombre de vibrations. Les fréquences figurant au tableau V sont celles attribuées aux deux variétés de carbonate de thorium par NAKAMOTO [13].

Les courbes *b* et *c* de la figure 14 reproduisent les spectres d'absorption infrarouge du gaz carbonique adsorbé sur la tho-

TABLEAU V

vibrations	substances		
	carbonates de thorium		formiate de thorium
	monodenté	bidenté	
	fréquences (cm ⁻¹)		
CO(II) asym.	1525	1643-1590	1570
CO(II) sym.	1380		1355
CO(I) asym.		1288-1260	
	1060		
CO(I) sym.		1033-1026	
déformation	840	839-820	
OCO	725	680-670	

monodenté*bidenté*

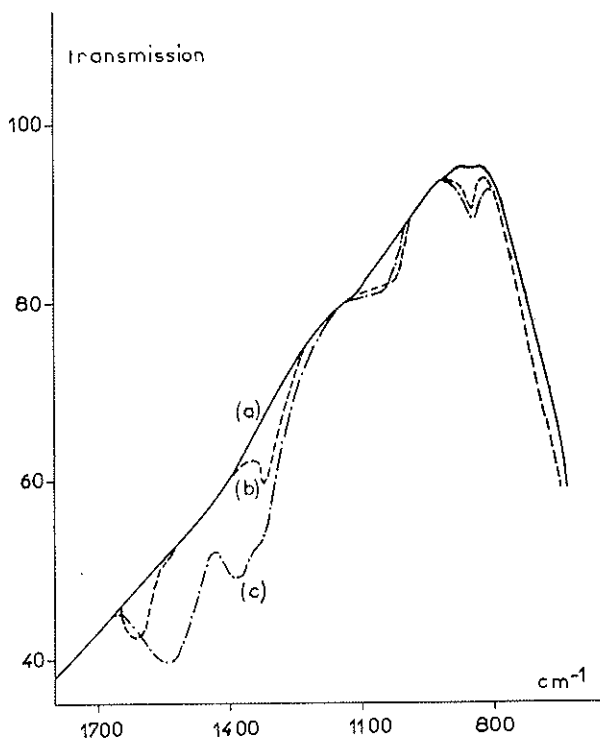


FIG. 14 — Spectres d'absorption infrarouge du gaz carbonique adsorbé sur la thorine,
 courbe *a*: spectre de la thorine avant adsorption,
 courbe *b*: gaz carbonique adsorbé 2 h. à 25°C ($p=83$ mm Hg),
 courbe *c*: gaz carbonique après adsorption 1 h. à 300°C et désorption 1 h. à la même température ($p=83$ mm Hg).

rine, la première à 25°, la seconde à 300°. Les spectres du gaz carbonique adsorbé en dessous de 100° présentent nettement quatre bandes d'absorption à 1610, 1290, 1030 et 840 cm^{-1} . Ces fréquences sont sensiblement celles indiquées au tableau V pour le carbonate de thorium bidenté. Par contre, sur les spectres du même gaz adsorbé au dessus de 150°, les deux pre-

nières bandes sont remplacées par deux autres situées vers 1520 et 1370 cm^{-1} , la troisième étant légèrement déplacée: 1050 cm^{-1} . Elles correspondent à celles du carbonate monodenté. Pour éliminer complètement le gaz carbonique chimisorbé sous cette forme, il faut désorber la thorine entre 500 et 600°C.

La thorine adsorbe donc chimiquement le gaz carbonique selon deux mécanismes distincts suivant que la température est inférieure ou supérieure à 150°C environ. Ce résultat est du reste en accord avec les conclusions que Prrr [14] a dégagé d'une étude thermodynamique de la même adsorption. Cet auteur donne pour variation molaire d'entropie de l'adsorption à température modérée: - 44 ue, ce qui implique la suppression de tous les degrés de liberté de translation et de rotation. La formation d'un complexe bidenté par interaction de la molécule CO_2 avec deux sites voisins Th et O confirme cette immobilité de l'adsorbat.

Au dessus de 250°, Prrr obtient une variation molaire d'entropie bien plus faible, - 7 ue, et il admet que l'adsorbat, bien plus mobile, n'est fixé que par liaison avec un atome superficiel d'oxygène, donnant naissance à un ion carbonate mobile. L'analogie des spectres de l'adsorbat à 150 ou 300°C et du carbonate monodenté ne permet cependant pas de confirmer cette conclusion qui impliquerait la symétrie de l'ion carbonate. Mais la structure monodentée implique évidemment une plus grande « mobilité » de l'adsorbat. C'est évidemment sous cette forme que le gaz carbonique est chimisorbé dans l'oxydation catalytique de l'oxyde de carbone.

Celui-ci ne commence à s'adsorber sur la thorine qu'à partir de 200°C. Son spectre d'absorption infrarouge est reproduit sur la figure 15. On observe deux raies intenses à 1570 et 1360 cm^{-1} qui coïncident avec celles du formiate de thorium. On doit donc conclure à l'établissement d'une liaison entre la molécule CO et un oxygène superficiel engendrant un ion carboxylate. Il faut désorber la thorine au dessus de 350° pour

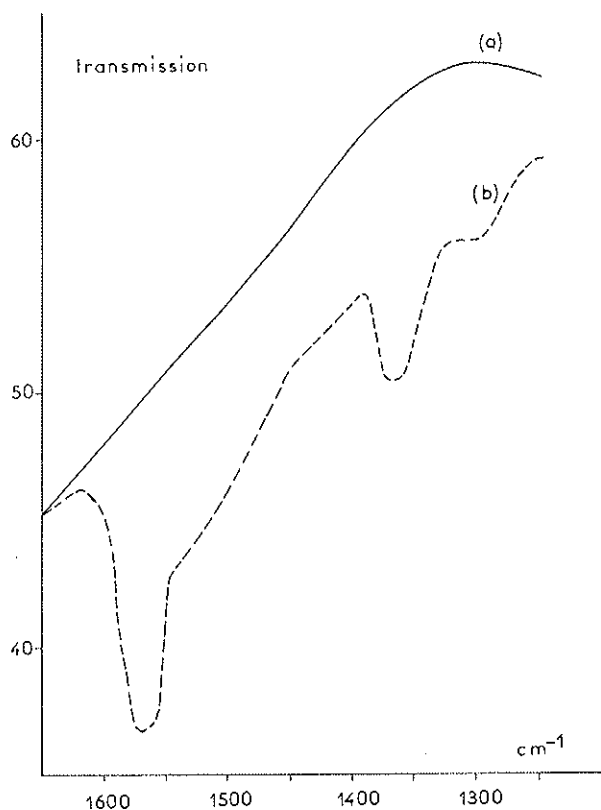


FIG. 15 — Spectre d'absorption infrarouge de l'oxyde de carbone adsorbé sur la thorine,

courbe *a*: spectre de la thorine avant adsorption,

courbe *b*: oxyde de carbone après adsorption 1 h. à 200°C ($p = 148$ mm Hg) et désorption 1 min. à 25°.

éliminer en tant que tel l'oxyde de carbone chimisorbé à cet état.

L'adsorption d'oxygène ne peut être examinée par spectroscopie infrarouge, car elle ne peut influencer que sur les liaisons Th--O dont les bandes de vibration sont responsables de l'opa-

cité de la thorine à partir de 700 cm^{-1} . Mais des travaux antérieurs [12] avaient montré que l'oxygène ne s'adsorbe pas sur la thorine soigneusement désorbée au préalable, quelle que soit la température (de 25 à 500°C).

Si l'on met en contact de l'oxygène gazeux avec un échantillon de thorine ayant chimisorbé préalablement de l'oxyde de carbone, le spectre infrarouge n'est pas modifié tant que la température est inférieure à 300°C . Par contre, dès 350° , les deux bandes de l'ion carboxylate disparaissent et sont remplacées par les quatre bandes du carbonate monodenté, c'est à dire par les bandes d'absorption du gaz carbonique chimisorbé à la même température.

Cette étude spectroscopique confirme donc l'étude cinétique antérieure de l'oxydation catalytique de l'oxyde de carbone au contact de la thorine. Elle est en accord avec le mécanisme avancé plus haut en notamment avec l'étape (b) dont la vitesse est déterminante. Elle précise que cette réaction de l'oxygène gazeux transforme l'oxyde de carbone chimisorbé à l'état d'ion carboxylate en un ion carbonate de structure analogue à celle du carbonate de thorium monodenté donc dissymétrique. Le « carbonate superficiel » ainsi formé ne commence à se désorber qu'à partir de 350°C , ce qui explique que la thorine ne devient un bon catalyseur d'oxydation qu'au dessus de cette température.

Mais l'étude spectroscopique révèle de plus que la thorine peut également donner lieu, à des températures très modérées, à une autre chimisorption du gaz carbonique entraînant la formation d'un ion symétrique analogue par sa structure au carbonate de thorium bidenté. Cette chimisorption ne joue aucun rôle dans l'oxydation catalytique de l'oxyde de carbone. Elle traduit l'affinité bien connue de la thorine pour le gaz carbonique à la température ordinaire et un peu au dessus.

2. *Etude de la décomposition de l'oxyde nitreux catalysée par l'oxyde de nickel* [15]. — L'oxyde de nickel est obtenu

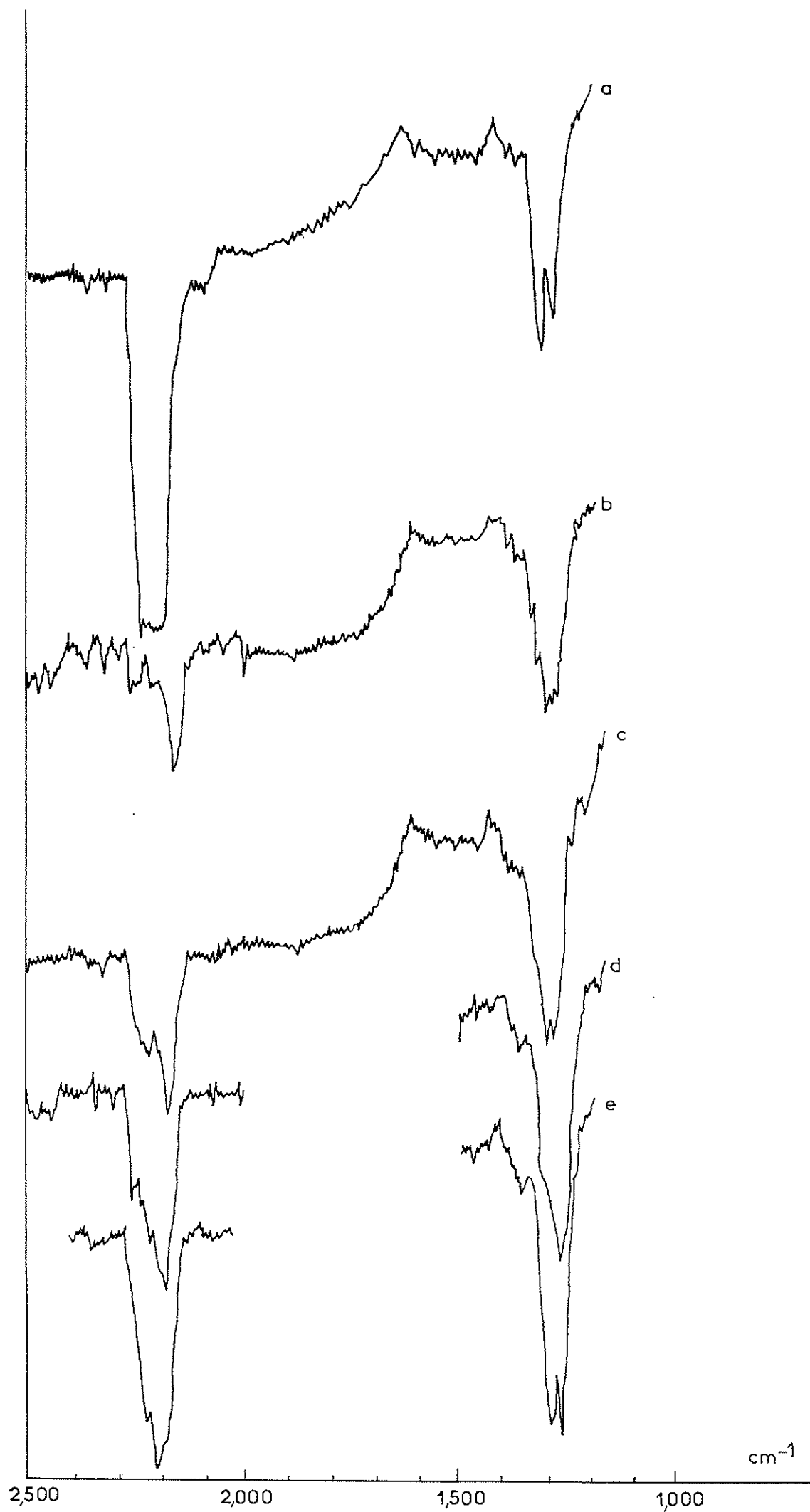


FIG. 16 — Evolution, au cours de la décomposition, du spectre d'absorption infrarouge de l'oxyde nitreux adsorbé sur un oxyde de nickel initialement stoechiométrique ($p = 200$ mm Hg, $T = 150^{\circ}\text{C}$),
 courbe *a*: immédiatement après l'introduction du gaz,
 courbe *b*: après 30 minutes de réaction,
 courbes *c*, *d*, *e*: retour progressif à la température ordinaire en fin de réaction (*c*: 100° , *d*: 35° , *e*: 20°C).

par décomposition à la pression atmosphérique en température lentement croissante jusqu'à 200°C d'un carbonate basique de nickel. Un traitement sous vide à la même température le ramène à la composition stoechiométrique, sa surface spécifique est de 240 m²/g. Il absorbe beaucoup les radiations infrarouges. Aussi faut-il le déposer en couche de quelques 10⁻³ mm sur un disque de fluorine. Une circulation d'air chaud dans une double enceinte maintient ce disque à une température constante. La faible quantité de catalyseur exige d'opérer sous des pressions d'au moins 100 mm Hg de réactif. Pour éliminer l'absorption infrarouge de la phase gazeuse qui masquerait parfois totalement celle de l'adsorbat, une seconde cellule identique mais sans catalyseur est interposée sur le second faisceau du spectromètre et elle est maintenue à la même température.

Le spectre d'absorption infrarouge de l'oxyde nitreux possède, dans l'intervalle 1000-1500 cm⁻¹, deux bandes de vibration-rotation correspondant aux vibrations de valence ν_1 et ν_3 et présentant chacune deux maximums situés respectivement à 1290 et 1310 cm⁻¹ pour ν_1 et à 2190 et 2220 cm⁻¹ pour ν_3 . La bande de la vibration de déformation ν_2 située à 589 cm⁻¹ n'est pas observable avec le dispositif utilisé (disques et fenêtres en fluorine).

Quand l'oxyde nitreux est mis au contact de l'oxyde de nickel stoechiométrique à 150 ou 170°C, le spectre précédent se modifie très rapidement. Ainsi que le montrent les courbes de la fig. 16, l'intensité de la bande d'absorption de ν_3 diminue par rapport à celle de ν_1 et le phénomène s'accroît au fur et à mesure que la décomposition progresse. Puis la bande présentant les deux maximums à 2190 et 2220 cm⁻¹ est remplacée par une bande à un seul maximum à 2160 cm⁻¹ qui s'élargit au cours de la réaction.

Bien que dissymétrique, la molécule N₂O gazeuse se comporte du point de vue spectroscopique comme une molécule presque symétrique et il est difficile d'attribuer les fréquences ν_1 et ν_3 , l'une au groupe N-N, l'autre au groupe N-O. La chi-

misorption de cette molécule sur l'oxyde de nickel, dans les conditions même de la catalyse, paraît donc accroître sa dissymétrie.

Lorsque la réaction catalytique concerne un mélange d'oxyde nitreux et d'oxygène, l'oxyde de nickel se recouvre immédiatement d'ions oxygène chimisorbés et prend une couleur noire. Le spectre de l'oxyde nitreux adsorbé par cet oxyde est différent de celui résultant de l'adsorption sur l'oxyde de nickel stoechiométrique. En début de réaction (fig. 17), c'est l'intensité de la bande ν_1 qui diminue par rapport à celle de la bande ν_3 . Deux nouvelles bandes apparaissent bientôt à 2350 et 1750 cm^{-1} . La première augmente beaucoup d'intensité au cours de la décomposition. Ici encore, la chimisorption dans les conditions de la catalyse accroît la dissymétrie de la molécule N_2O , mais cela de manière différente du cas précédent.

Pour tenter d'expliquer ces résultats, il y a lieu d'envisager les différentes configurations que le complexe adsorbé serait à priori susceptible de prendre. Ces possibilités sont représentées par les quatre modèles de la figure 18. Mais le quatrième modèle paraît pouvoir être rejeté immédiatement parce qu'il est incapable d'expliquer l'effet inhibiteur de l'oxygène chimisorbé sur la décomposition de l'oxyde nitreux.

Au prix d'approximations qui enlèvent incontestablement de la valeur aux conclusions qui vont suivre, un calcul classique permet d'aboutir à des valeurs approchées des fréquences des vibrations des liaisons des trois modèles (I), (II) et (III). Ces valeurs calculées sont données sur la figure 18 ainsi que celles observées au cours de la décomposition.

Quand la chimisorption et la décomposition ont lieu sur un oxyde de nickel initialement stoechiométrique, on observe l'apparition d'une bande à 2160 cm^{-1} donc de fréquence voisine de celle de la vibration ν_3 calculée pour le modèle (I) et très éloignée de la fréquence calculée pour la même vibration du modèle (II). La chimisorption aurait donc lieu par l'atome d'oxygène et la réaction impliquerait la rupture de la liaison

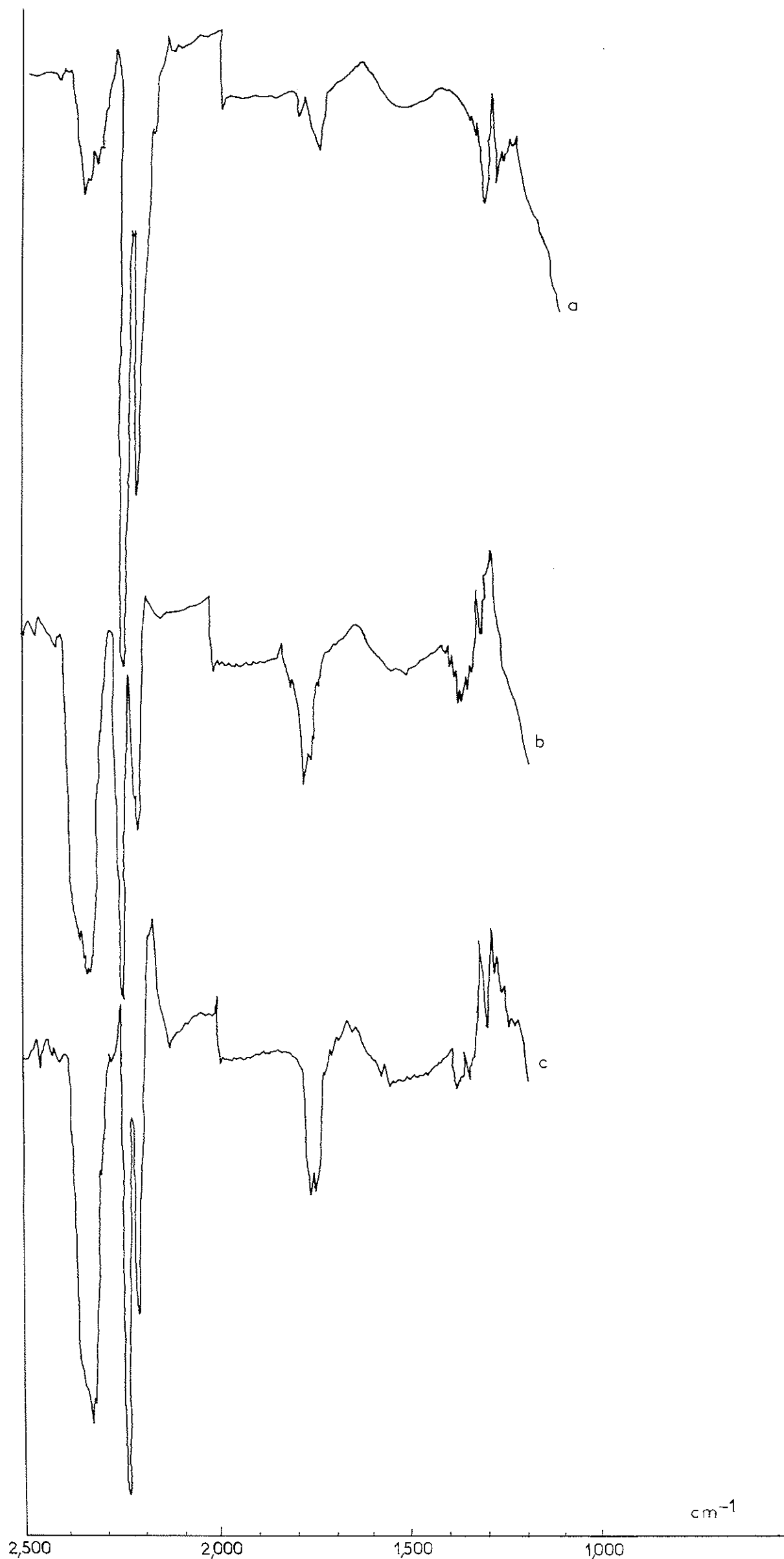


FIG. 17 — Evolution, au cours de la décomposition, du spectre d'absorption infrarouge de l'oxyde nitreux adsorbé sur un oxyde de nickel saturé d'oxygène chimisorbé ($p_{O_2} = 20$ mm, $p_{N_2O} = 80$ mm Hg, $T = 200^\circ C$),
 courbe *a*: quelques minutes après l'introduction du mélange gazeux,
 courbe *b*: au cours de la décomposition,
 courbe *c*: en fin de réaction après retour à la température ordinaire.

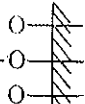
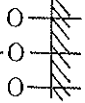
configurations possibles de l'oxyde nitreux adsorbé		fréquences des vibrations (cm ⁻¹)	
		calculées	observées
(a) sur NiO stoechiométrique:			
(I)	$\text{N}-\text{N}-\text{O}-\text{NiO}$ 	$\nu_1 = 803$ $\nu_2 = 548$ $\nu_3 = 2140$	2160
(II)	$\text{O}-\text{N}-\text{N}-\text{NiO}$ 	$\nu_1 = 775$ $\nu_2 = 534$ $\nu_3 = 2070$	
(b) sur NiO saturé d'oxygène chimisorbé:			
(III)	$\text{O}-\text{N}-\text{N}-\text{O}-\text{NiO}$ 	$\nu_1 = 945$ $\nu_2 = 2390$ $\nu_3 = 1770$	2350 1750
(IV)	$\text{N}-\text{N}-\text{O}-\text{O}-\text{NiO}$ 	très improbable	

FIG. 18 — Configurations possibles du complexe résultant de la chimisorption de l'oxyde nitreux sur NiO stoechiométrique et sur NiO ayant chimisorbé de l'oxygène.

N-O, libérant la molécule d'azote et laissant chimisorbé à l'état d'ion O⁻ l'atome d'oxygène qui bloque ainsi un site actif. Cette représentation est donc en accord avec les résultats de nombreuses études cinétiques, elle explique l'effet autoinhibiteur de l'oxygène libéré par la décomposition et vient renforcer les conclusions tirées des variations de la semiconductivité de l'oxyde de nickel qu'entraînent les chimisorptions avec transfert de charge (N₂O⁻ et O⁻).

Quand on opère avec un oxyde de nickel dont la surface est saturé d'oxygène chimisorbé, les spectres infrarouges de l'oxyde nitreux adsorbé révèlent qu'au cours de la décomposition, apparaissent deux bandes à 2350 et 1750 cm^{-1} , valeurs proches des fréquences calculées pour les vibrations ν_2 et ν_3 du modèle (III). Il est évident qu'adsorbée sous cette forme, la molécule d'oxyde nitreux éprouve plus de difficulté que le modèle (I) à se décomposer.

Malgré les analogies tirées d'un calcul rendu incertain par les approximations faites, les conclusions précédentes ne peuvent être tenues que pour provisoires tant que le travail en cours n'aura pas été complété par une étude spectrale dans le domaine 1000-500 cm^{-1} . L'emploi de la fluorine ne l'a pas permis jusqu'ici, mais des matières plus transparentes à l'infrarouge se sont montrées utilisables même aux températures de la réaction catalytique. La présence ou l'absence de bandes d'absorption de fréquences proches de celles calculées pour la vibration ν_2 du modèle (I) et pour la vibration ν_1 du modèle (III) devrait confirmer ou infirmer les hypothèses actuelles.

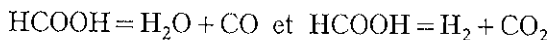
III. TENTATIVES D'ÉTUDE DES ADSORBATS PAR RÉSONANCE MAGNÉTIQUE NUCLÉAIRE

Depuis le début des études de structures moléculaires par résonance magnétique nucléaire, divers auteurs [16] ont tenté d'utiliser cette technique spectrale à l'étude des phases adsorbées dans l'espoir d'en tirer des informations précises sur la nature des interactions adsorbat-adsorbant. Il faut reconnaître que les informations recueillies jusqu'ici sont rares et très incomplètes. Les recherches faites en France dans ce domaine n'ont abouti à une conclusion intéressante que dans un seul cas, celui de la chimisorption de l'acide formique par des silices

amorphes [17]. Mais ces informations demeurent jusqu'ici purement qualitatives.

Il est bien connu qu'en faisant varier les conditions de précipitation des gels de silice, on aboutit, après traitement thermique convenable, à des silices amorphes de texture et degré d'hydratation différents. Pour cette raison, les silices amorphes les plus rigides sont appelées *xérogels* et celles de texture nettement plus lâche, *aérogels*. Le tableau VI résume ces différences.

Dès le début du siècle, SABATIER [19] avait classé les silices amorphes parmi les masses de contact douées simultanément d'activité déshydrogénante et d'activité déshydratante, fait confirmé par divers expérimentateurs, notamment SCHWAB et collaborateurs [20] ainsi que COUTRAY DU PRADEL et IMELIK [21]. Ces derniers ont opéré dans des conditions où les deux réactions de décomposition de l'acide formique:



sont d'ordre nul et ils ont montré que sur xérogel la déshydrogénation est négligeable alors que sur aérogel cette réaction prend une importance croissante avec la température. Les données du tableau VII mettent en lumière ces différences d'activité. L'étude cinétique des deux réactions sur un grand nombre de silices amorphes a montré que, malgré de grandes variations dans l'activité et des écarts notables dans la sélectivité, les énergies apparentes d'activation sont pratiquement les mêmes pour toutes les silices, à condition qu'elles soient très pures: 22 à 24 kcal pour la déshydratation, environ 12 kcal pour la déshydrogénation. Il est clair que la nature des sites actifs vis à vis de l'une ou de l'autre des deux réactions est la même pour toutes les silices. Seul varient d'un solide siliceux à l'autre le nombre de sites déshydrogénants et le nombre de sites déshydratants.

TABLEAU VI --- Principales différences entre xérogels et aérogels de silice.

	<i>xérogels</i>	<i>aérogels</i>
procédé d'élaboration	solutions diluées précipitation lente à température ordinaire	solutions un peu plus concentrées précipitation immédiate éventuellement à chaud
aspect externe	solide vitreux rigide	solide déformable, aspect crayeux
composition chimique	faible teneur en eau chimiquement liée	plus forte teneur en eau chimiquement liée
texture	très grande surface spécifique faible rayon moyen de pores distribution très étroite du rayons des pores	surface spécifique plus faible rayon moyen de pores plus grand large distribution du rayon des pores

TABLEAU VII — *Activités d'un xérogel et d'un aérogel dans la déshydratation et la déshydrogénation de l'acide formique.*

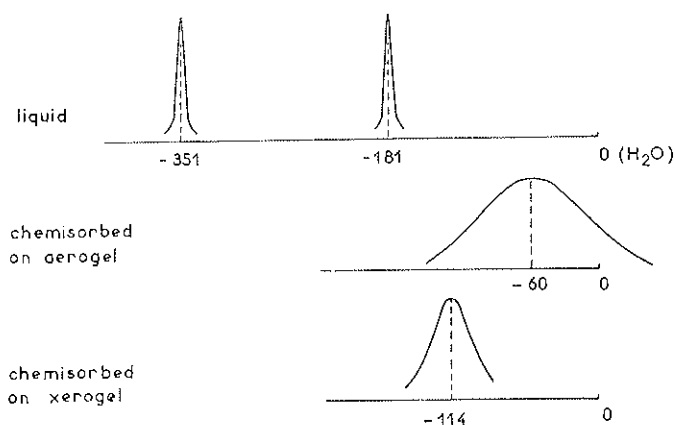
catalyseur	température de catalyse	activités catalytiques	
		déshydratation	déshydrogénation
xérogel	250°C	100%	0
	300°	99%	1%
	350°	95%	5%
aérogel	250°	99%	1%
	300°	85%	15%
	350°	69%	31%

L'étude par spectroscopie infrarouge de l'acide formique chimisorbé sur ces silices a mis en évidence les faits suivants:

- a) l'absence des bandes caractéristiques de l'ion formiate,
- b) une forte interaction de la bande OH de l'acide située vers 3100 cm^{-1} ,

- c) la bande habituelle du groupe C=C vers 1725 cm^{-1} ,
 d) une atténuation des vibrations CH de l'acide.

Il y a donc une forte interaction des groupes OH des molécules d'acide formique avec des sites actifs de toute silice, ainsi qu'une interaction plus faible vis à vis des hydrogène des



N.M.R. spectra of liquid and
chemisorbed formic acid on silica gels

FIG. 19 — Spectre R.M.N. de l'acide formique liquide et adsorbé sur xérogel et aérogel.

groupes CH. Mais la spectroscopie infrarouge est demeurée incapable de différencier les adsorbats sur xérogels de ceux sur aérogels. Par contre, la résonance magnétique nucléaire s'est révélée apte à établir cette distinction [22]. C'est ce que montre les enregistrements reproduits sur la figure 19.

L'acide formique liquide donne deux signaux protoniques, l'un correspondant au groupe OH, l'autre au groupe CH. Chimisorbé sur toute silice amorphe, il n'en donne plus qu'un seul. L'emploi de la molécule HCOOD montre que le signal restant est celui du groupe CH. Ce premier résultat confirme l'importance de l'interaction de la surface avec les groupes OH de l'acide. Mais le signal n'a ni la même position ni le même élargissement pour les adsorbats sur xérogel et sur aérogel. Il est plus large et plus fortement déplacé dans le cas de la chimisorption sur aérogel. Il y a dans ce cas une interaction plus intense entre la surface et les hydrogène de ces groupes et il est logique de voir là la cause de l'activité déshydrogénante des aérogels.

Mais cette interprétation des informations fournies par la R.M.N. est insuffisante, même du point de vue qualitatif. Les travaux résumés dans la première partie du présent mémoire ont clairement établi que les silices amorphes sont dénuées de tout site acide fort et que les seules interactions spécifiques mises en évidence doivent être attribuées aux groupes OH superficiels de ces solides. Ces groupes jouent certainement un rôle important dans la chimisorption et la décomposition de l'acide formique car l'activité catalytique des silices diminue quand un traitement thermique préalable entraîne une déshydratation de plus en plus poussée du catalyseur [23]. Une réhydratation superficielle accroît par contre cette activité.

Pour poursuivre plus avant l'étude par R.M.N. des interactions adsorbat-adsorbant dans le cas de solides tels que la silice amorphe, les alumines actives, les catalyseurs silice-alumine, il paraît indispensable de procéder à une étude quantitative de l'eau chimiquement liée à ces solides. Mais cela se heurte à de grandes difficultés et d'abord à des difficultés expérimentales. Les raies d'absorption des protons du solide sont élargies par des interactions magnétiques. Dans certains cas (xérogels), il est presque indispensable de procéder à un balayage lent et d'utiliser des champs très intenses de radio-fré-

quence pour que les signaux aient une forme à peu près symétrique. Avec la technique habituelle, on obtient des signaux dissymétriques reproduits sur la figure 20 [18]. La dissymétrie augmente avec la température du traitement préalable. Par contre, tous les échantillons d'une silice provenant d'un aéro-

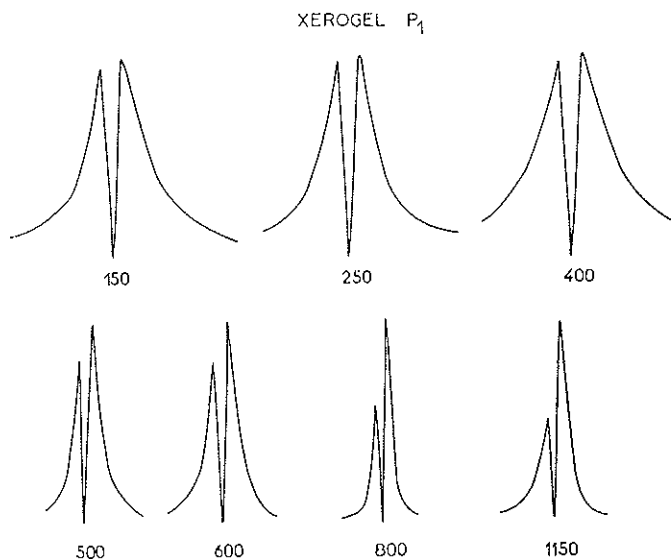


FIG. 20 — Signaux protoniques de silices obtenues par déshydratation d'un xérogel aux températures indiquées.

gel (figure 21) donnent un signal de même largeur et symétrique, quelle que soit la température du traitement. Seule la ligne de base se déplace vers le bas quand cette température augmente de 150 à 600°C pour ne plus varier ensuite.

Le balayage rapide permet de calculer le temps de relaxation spin-réseau pour chacun de ces échantillons. Ce temps augmente avec la température du traitement préalable, mais

surtout les valeurs obtenues sont très différentes pour les silices du xérogel, 0,5 à 3 secondes, et pour les silices de l'aérogel, 10 à 100 millisecondes. Les protons semblent donc bien plus mobiles dans le cas de l'aérogel que dans celui du xérogel. Cela peut paraître un peu surprenant car la densité des groupes OH superficiels est plus grande pour tout échantillon d'aérogel que pour les échantillons de xérogel ayant subi le même traitement thermique.

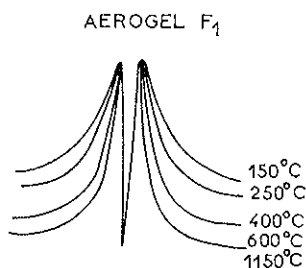


FIG. 21 — Signaux protoniques de silices obtenues par déshydratation d'un aérogel aux température indiquées.

Pour aller plus loin, c'est à dire pour passer de ces informations qualitatives sur l'adsorbat et sur l'adsorbant à une interprétation quantitative, il faudrait disposer d'une théorie capable de rendre compte de l'élargissement et de la déformation des signaux. Des efforts sont actuellement faits dans ce but à l'Institut de Recherches sur la Catalyse [24], ils laissent espérer un progrès notable dans le sens désiré mais il n'est pas encore possible d'en exposer les résultats.

IV. ETUDE PAR RÉSONANCE PARAMAGNÉTIQUE ELECTRONIQUE DES IONS RADICALAIRES FORMES PAR ADSORPTION CHIMIQUE SUR LES ALUMINES ET LES SILICES-ALUMINES

De nombreux travaux [25, 31] ont révélé que l'adsorption par les alumines et les silices-alumines catalytiques d'hydrocarbures et amines aromatiques entraîne la formation d'ions-radicaux positifs. Pour certains catalyseurs, cette formation ne s'observe qu'en présence d'une faible pression d'oxygène. L'existence, à la surface de ces solides, de centres actifs accepteurs d'électrons est donc bien établie. Un premier travail [26] mené en commun au laboratoire du Pr. KEMBALL (Dpt. of Chemistry, The Queen's University, Belfast) et à l'Institut de Recherches sur la Catalyse a apporté la preuve qu'il existe simultanément sur des alumines ayant subi au préalable un traitement thermique convenable, deux types de centres de chimisorption avec transfert de charge, les uns donneurs, les autres accepteurs d'électrons. Depuis lors les travaux ont été étendus aux catalyseurs silice-alumine et l'influence du traitement thermique sur ces propriétés de chimisorption de chaque catalyseur a été précisée [27].

Les catalyseurs étudiés sont d'une part une alumine gamma et une alumine eta obtenues par déshydratation thermique convenable respectivement de la boehmite et de la bayérite, d'autres part les silices-alumines de la firme Ketjen à 13 et 25% d'alumine. Les substances ayant servi aux expériences de chimisorption sont le tétracyanoéthylène (TCNE), le trinitrobenzène et le chloranil comme accepteurs d'électrons, la phénothiazine, le pérylène, le thianthrène, l'anthracène et la ben-zidine comme donneurs d'électrons.

L'appareil utilisé est un spectromètre Varian V-4500, le signal étant détecté après modulation à 10 kc. La concentration en radicaux est mesurée par double intégration du signal et

comparaisons avec une solution benzénique d'un radical stable, le tétraméthyl 2, 2, 6, 6 pipéridone 4 oxyde 1.

1. *Ions radicalaires formés par chimisorption sur alumine.* — Les échantillons des deux aluminas étudiées ont été préalablement traités sous vide durant 12 heures à une température constante entre 200 et 900°C et entraînant une déshydratation plus ou moins poussée.

a) *Formation d'ions radicalaires négatifs.* — Les spectres de R.P.E. enregistrés après adsorption de TCNE par tout échantillon d'alumine ϵ ta ou gamma présente une structure hyperfine reproduite sur la figure 22. On voit nettement 9 composantes séparées de 1,5 gauss. Ce spectre est analogue à celui obtenu par réaction du TCNE avec l'iodure de sodium [28]. Il résulte du couplage de l'électron cédé par le centre d'adsorption avec les spins nucléaires des atomes d'azote. De même un spectre à quatre composantes a été obtenu par chimisorption du trinitrobenzène. Il est donc clair que la surface de tous les échantillons des deux aluminas, quelles que soient les conditions du traitement thermique préalable, possède des centres

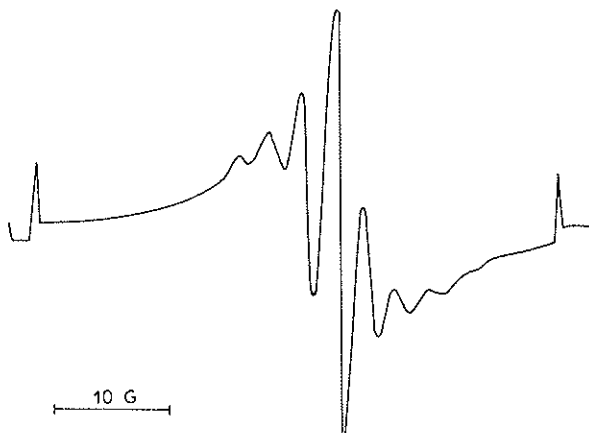


FIG. 22 — Spectre de R.P.E. du tétracyanoéthylène chimisorbé sous vide d'une solution benzénique par l'alumine ϵ ta ou gamma.

donneurs d'électrons capables de céder ces derniers à des molécules ayant une forte affinité électronique.

Pour obtenir des précisions sur la nature des sites superficiels responsables de ces réactions de transfert de charges, les variations de concentration relative des ions-radicaux TCNE^- en fonction de la température du traitement préalable ont été examinées. Les résultats obtenus sont reproduits sur la figure 23. Les variations observées sont particulièrement instructive. La concentration en ions-radicaux négatifs croît d'abord avec la température du traitement préalable. Mais elle passe par un maximum quand cette variable est comprise entre 450

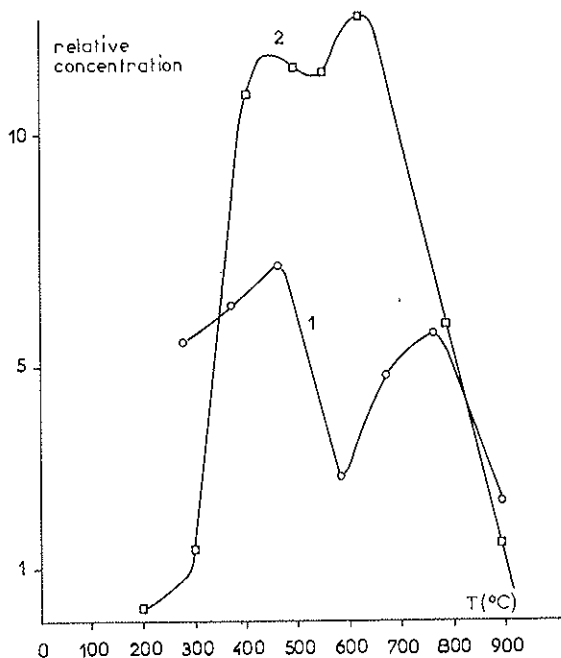


FIG. 23 — Variations, en fonction de la température du traitement thermique préalable de l'alumine, de la concentration relative des ions-radicaux négatifs de tétracyanoéthylène,

courbe 1: chimisorption sur alumine gamma,

courbe 2: chimisorption sur alumine eta.

et 500°C, décroît ensuite jusque vers 550-600° pour atteindre un deuxième maximum obtenu pour une température de traitement de 650° dans le cas de l'alumine ϵ , de 750-800° pour l'alumine γ . C'est pour cette dernière, dont on connaît les propriétés catalytiques, que le minimum est le plus prononcé vers 600°.

L'interprétation de tels résultats ne peut être fondée que sur l'existence de deux types de centres superficiels donneurs d'électrons, les uns n'existant qu'après un traitement thermique modéré, les autres ne prédominant qu'au terme d'un chauffage à 550-600° au moins.

Les alumines traitées en dessous de cette dernière limite possèdent en surface des groupes OH libres ou liés entre eux par ponts hydrogène. Une élévation de la température du traitement de 200 à 500°, bien que déshydratant partiellement le solide, augmente le nombre de groupes OH libres demeurant à la surface. Certains au moins des groupes Al-OH superficiels pourraient donc être des centres donneurs d'électrons. Cette hypothèse est quelque peu étayée par le fait que les trois hydroxydes d'aluminium, l'hydrargillite (gibbsite), la bayérite et la boehmite donnent aussi naissance à des ions-radicaux négatifs par chimisorption de TCNE.

L'augmentation de concentration des ions TCNE⁻ qu'entraîne un traitement des alumines au dessus de 600° ne peut pas être attribué aux mêmes sites superficiels. Réalisé à ces températures, le traitement thermique conduit à un solide pratiquement anhydre (cf. Partie 1-2 du présent mémoire). Dès qu'elle a été traitée à 600° sous vide, une alumine ne titre plus qu'un à deux groupes OH par 100 Å². D'autre part, comme l'ont constaté PRNK et collaborateurs [29], il faut un traitement presque aussi énergique pour qu'apparaissent sur les alumines des centres accepteurs d'électrons. Le mécanisme de déshydratation superficielle proposé par PERI [30] prévoit la formation en surface d'ions:



De tels ions peuvent être tenus pour responsables des deux chimisorptions avec transfert de charge.

b) *Formation d'ions radicalaires positifs.* — Sur un échantillon d'alumine gamma traité sous vide à 500°, l'adsorption de phénothiazine en l'absence d'oxygène colore en brun-orange l'échantillon et l'on obtient un spectre de R.P.E. mal résolu mais présentant quatre épaulements distants de 8,2 gauss. Cela suffit à identifier le radical positif correspondant. L'introduction dans la cellule d'oxygène sous une pression d'environ 1 mm Hg augmente l'intensité du signal qui acquiert une structure hyperfine.

Par contre, l'adsorption de pérylène, de thianthrène et de benzidine sur des échantillons d'alumine déshydratés entre 300 et 900° ne s'accompagne pas de la formation d'un complexe paramagnétique. Ainsi l'adsorption de pérylène sur un échantillon traité à 500°C colore ce dernier en jaune-vert. Mais le signal de R.P.E. (fig. 24a) est large et sans composantes. Il faut introduire dans la cellule des traces d'oxygène pour que le spectre acquiert une structure fine (fig. 24b) à 9 composantes distantes de 3,3 gauss. De même la présence d'oxygène est nécessaire à la formation du complexe adsorbé paramagnétique dans le cas du thianthrène et de la benzidine.

Ce rôle de l'oxygène méritait d'être examiné de plus près. Il a été reconnu que l'introduction d'oxygène s'adsorbant sur la surface du solide a un double effet. Ce gaz diminue le temps de relaxation spin-reseau du complexe paramagnétique et il lève la saturation du signal, ce qui a pour conséquence une augmentation apparente du nombre de spins dosés.

Dans ce but, l'évolution du signal donné par le pérylène adsorbé sur alumine gamma a été examinée en fonction de la pression d'oxygène. Les mesures ont été effectuées en basse (0,05 mw) et haute puissance (0,5 mw). Les résultats obtenus sont résumés dans le tableau VIII. En basse puissance, l'introduction d'oxygène sous très faible pression fait apparaître un

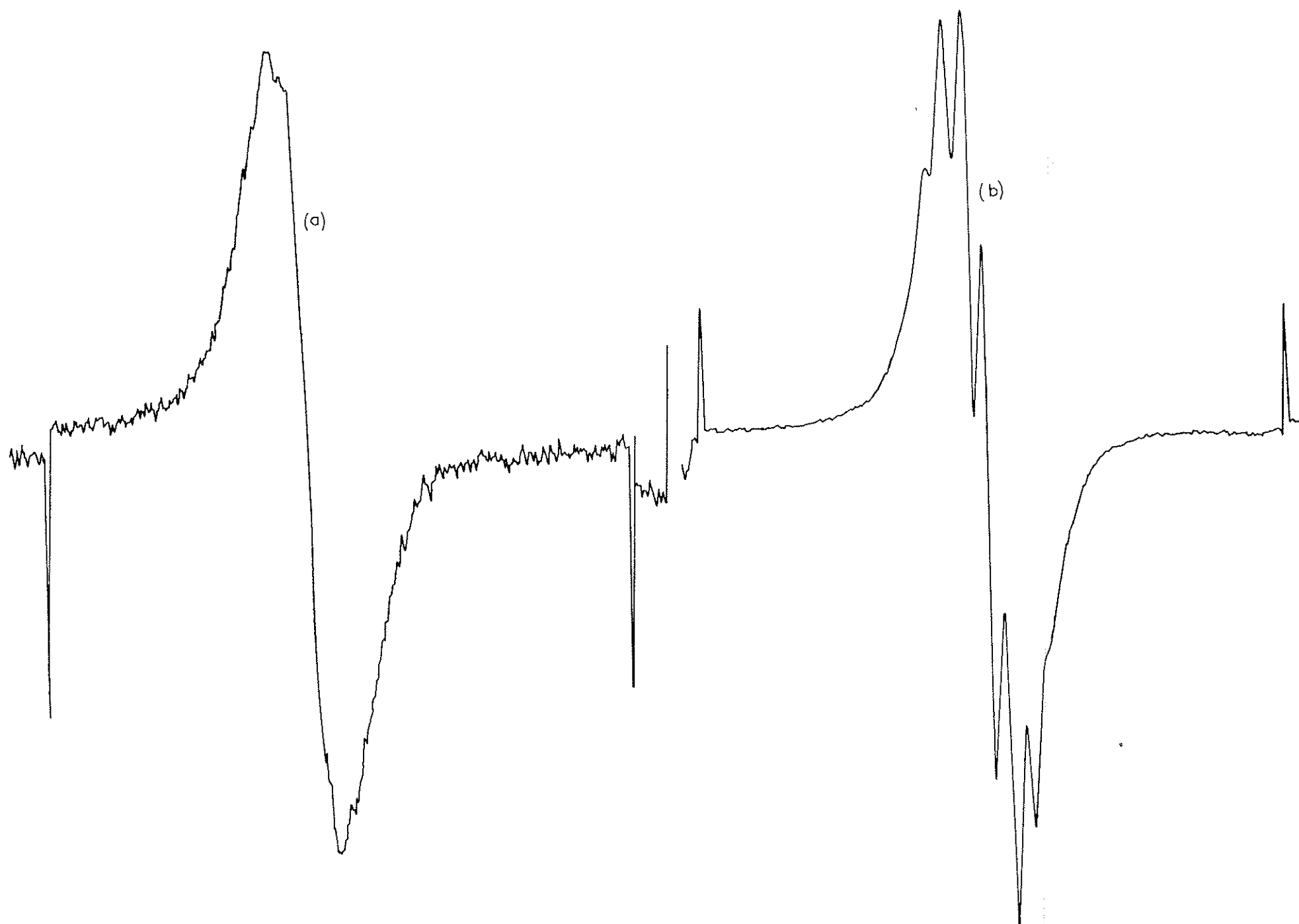


FIG. 24 — Signaux de R.P.E. du pérylène chimisorbé sur alumine gamma,
(a) adsorption sous vide,
(b) adsorption en présence d'oxygène ($p=0,1$ mm).

TABLEAU VIII — *Influence de l'oxygène sur la résolution et l'intensité du signal R.P.E. des ions-radicaux pérylène adsorbés sur alumine gamma.*

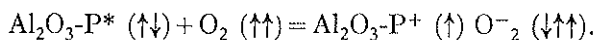
puissance (mw)	pression d'oxygène (mm Hg)	intensité relative	structure du signal
0,05	0	0	pas de signal
	0,026	14	structure hyperfine à 9 raies
	0,042	22	d°
	0,10	15	élargissement du signal, la structure hyperfine a disparu
	0,20	10	d°
	O ₂ évacué	20	structure hyperfine à 9 raies
0,05	0	0	pas de signal
	0,034	15	structure hyperfine à 9 raies
	0,042	20	d°
	0,081	25	d°
	0,16	30	d°
	0,31	40	d°
	1,0	82	élargissement du signal
	1,8	80	d°
	O ₂ évacué	25	structure hyperfine à 9 raies

spectre bien résolu à 9 composantes distantes de 3,6 gauss. Mais quand la pression d'oxygène augmente, le signal s'élargit et son intensité diminue. Le nombre d'ions-radicaux semble donc décroître. La mise sous vide de l'échantillon (ce qui n'implique pas le départ de tout l'oxygène adsorbé) fait réapparaître la structure hyperfine et augmente l'intensité du signal. En haute puissance, par contre, l'intensité du signal croît avec la pression d'oxygène suivant une relation de LANGMUIR et la raie ne s'élargit que pour des pressions d'oxygène d'au moins 1 mm Hg. La mise sous vide de l'échantillon entraîne la réapparition de la structure fine mais, dans ce cas, l'intensité du signal diminue beaucoup.

L'oxygène a donc pour effet de provoquer la réaction de transfert de charge du pérylène au centre accepteur, réaction impossible avec cet hydrocarbure en l'absence de toute molécule O_2 . Mais le paragagnétisme de cette molécule entraîne plus ou moins vite la disparition de la structure fine du fait d'une interaction dipolaire entre l'électron libre de l'ion-radical de pérylène et les électrons « libres » de la molécule O_2 . Le processus d'apparition de l'ion-radical serait donc :

sous vide. $Al_2O_3 + P = Al_2O_3-P^* (\uparrow\downarrow)$

et après introduction d'oxygène :



Il a été vérifié que le même processus se produit avec l'anhydride sulfureux, d'affinité électronique comparable à celle de l'oxygène.

L'influence de la température du traitement thermique préalable sur la concentration relative des ions positifs de phénouthiazine (sous vide) et de pérylène (sous 0,1 mm O_2) a été examinée. Elle se traduit par les courbes des figures 25 et 26. La courbe concernant les ions radicalaires de phénouthiazine est comparable à celle des ions $TCNE^-$ (cf. fig. 23). Elle présente

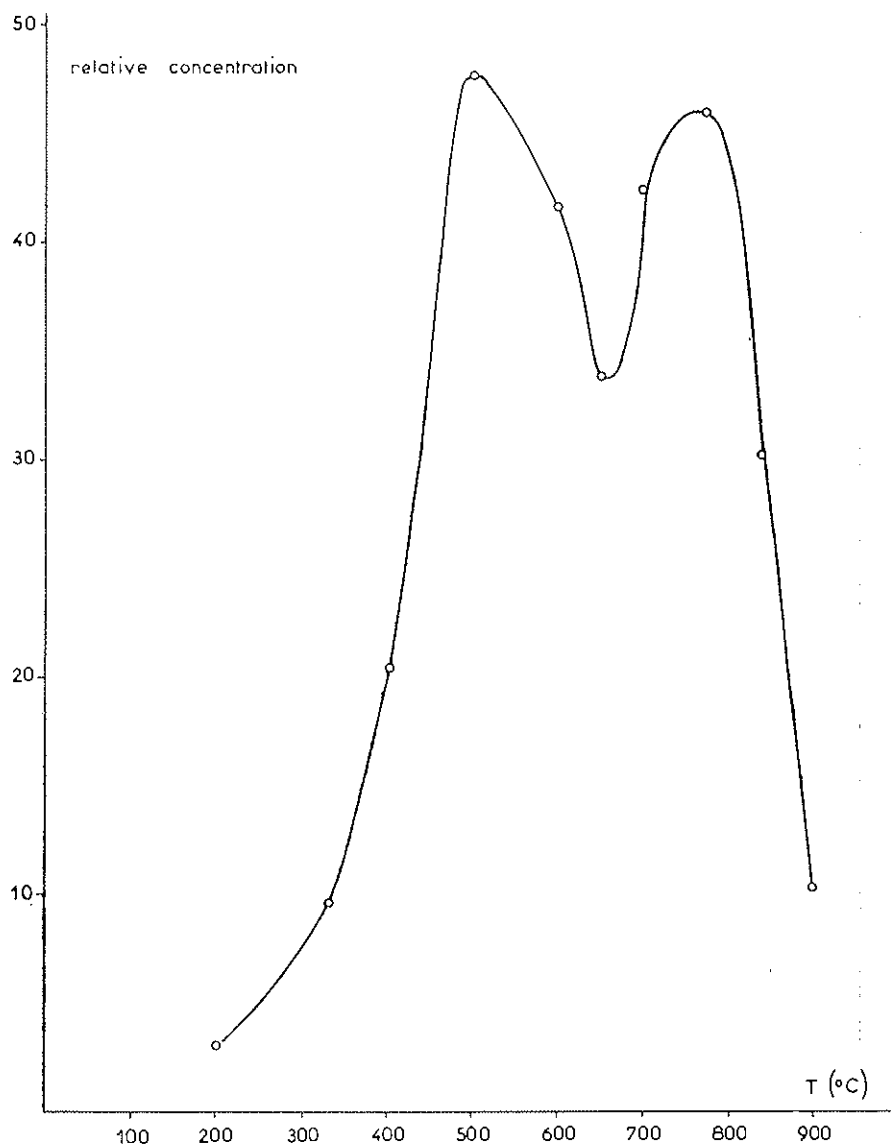


FIG. 25 — Influence de la température d'un traitement préalable sous vide d'une alumine gamma sur la concentration relative des ions-radicaux positifs de phénothiazine adsorbée sous vide.

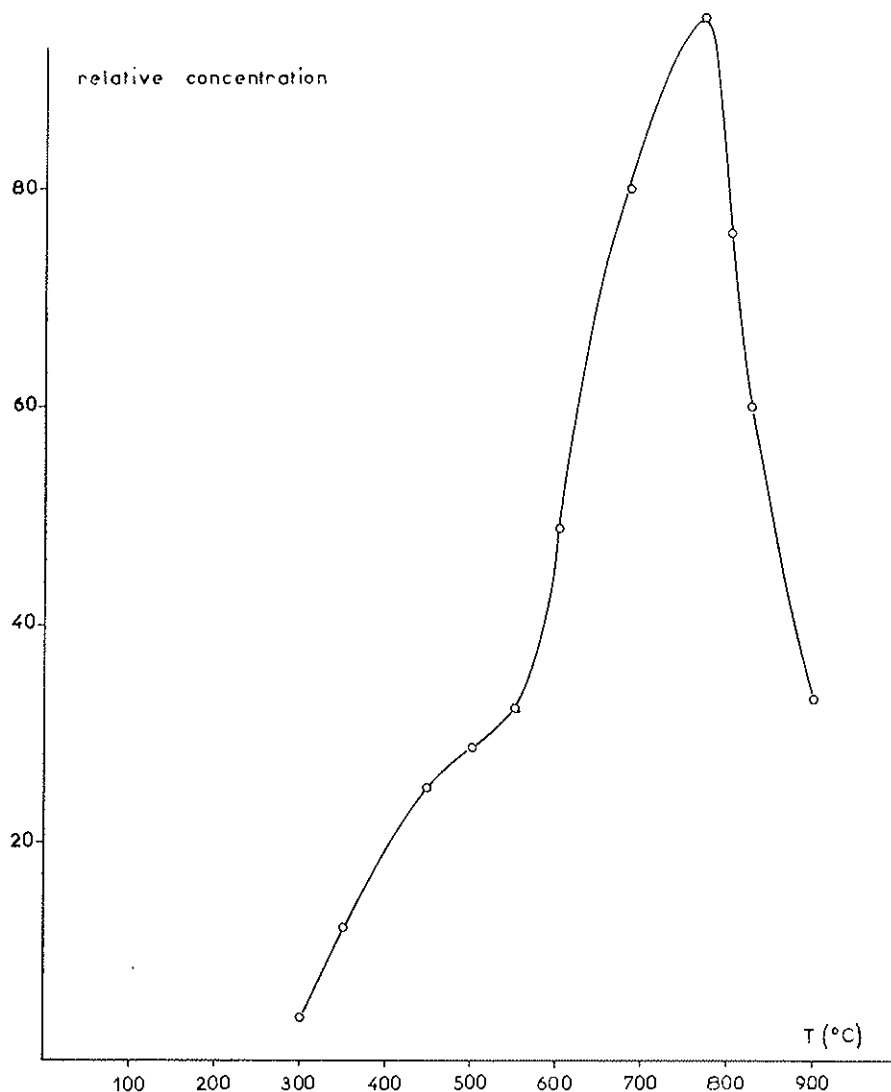


Fig. 26 — Influence de la température d'un traitement préalable sous vide d'une alumine gamma sur la concentration relative des ion-radicaux positifs de pérylène adsorbés sous une pression d'oxygène d'un mm Hg.

deux maximums vers 600 et 750° séparés par un minimum vers 650°C. Par contre celle des ions P^+ ne présente qu'un maximum vers 750°C et, en dessous de 500°, la concentration de ces ions demeure très faible. Il n'est pas inutile de rappeler que les alumines traitées à 750° sont pratiquement exemptes de tout groupe OH superficiel et que vers 450-500° elles n'ont plus en surface que des groupes OH libres.

2. *Ions radicalaires formés par chimisorption sur silice-alumine.* — Les études ont porté sur l'adsorption de molécules à bas potentiel d'ionisation et de molécules à fort affinité électronique. Pour les deux groupes de substances, la présence d'ions radicalaires dans l'adsorbat a été décelée sans ambiguïté.

a) *Formation d'ions radicalaires positifs.* — Divers auteurs ont déjà observé la formation de tels ions par adsorption d'hydrocarbures et d'amines aromatiques sur les catalyseurs silice-alumine [31]. L'étude résumée ici n'a eu pour objectifs que de préciser l'importance de ces adsorptions avec transfert de charges et d'examiner l'influence de la température du traitement préalable du catalyseur sur la concentration relative de chaque espèce d'ions-radicaux positifs.

Le tableau IX donne les concentrations relatives de ces ions positifs formés par adsorption sur le catalyseur à 13% d'alumine préalablement calciné sous vide à 600°. Il permet de comparer ces concentrations au potentiel d'ionisation de trois des substances utilisées. Seules les trois premières de ces substances, c'est à dire celles qui donnent le plus grand nombre d'ions-radicaux par chimisorption, ont un spectre de R.P.E. ayant une structure fine plus ou moins bien résolue:

phénothiazine: spectre dissymétrique, 4 composantes, $\Delta H = 7,9$ gauss,

pérylène: spectre bien résolu à 9 composantes, $\Delta H = 3,3$ gauss,

thianthrène: spectre à peu près symétrique à 4 composantes.

TABLEAU IX — *Nombre d'ions radicalaires positifs adsorbés sur un catalyseur silice-alumine à 13% Al_2O_3 traité à 600°C.*

substance adsorbée	potentiel d'ionisation (ev)	nombre d'ions-radicaux par gramme de catalyseur
phénothiazine	6,7	$3 \cdot 10^{20}$
pérylène	6,9	$1,6 \cdot 10^{19}$
thianthrène	—	$4 \cdot 10^{18}$
anthracène	7,5-8,0	$1,2 \cdot 10^{18}$
benzidine	—	$0,6 \cdot 10^{18}$

Les deux autres réactifs donnent un spectre à raie unique et large.

Les figures 27, 28 et 29 donnent les variations de la concentration relative de chaque espèce d'ions paramagnétiques en fonction de la température du traitement préalable sous vide du catalyseur. Mis à part le minimum observé vers 200-300°C qui doit sans doute être attribué au rôle joué par des molécules d'eau restant chimisorbées à ces températures, tous les adsorbats, à l'exception de celui constitué par des ions de benzidine, ont une concentration qui croît jusque vers 750°. La diminution de concentration aux températures plus élevées de calcination doit être attribuée à un début de frittage du catalyseur, frittage qui entraîne évidemment la disparition rapide des centres

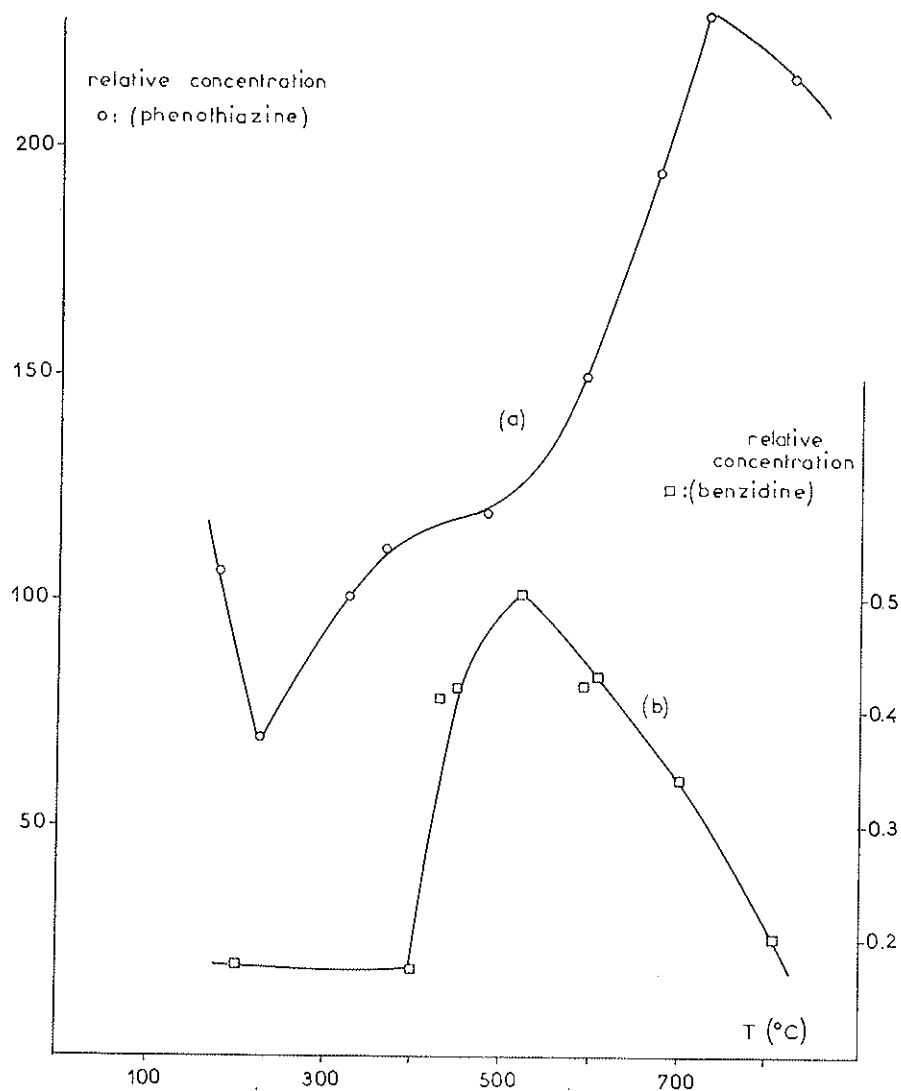


FIG. 27 — Influence de la température d'un traitement préalable d'un catalyseur silice-alumine sur la concentration relative des ions-radicaux positifs,

- (a) adsorption de phénanthroline,
(b) adsorption de benzidine.

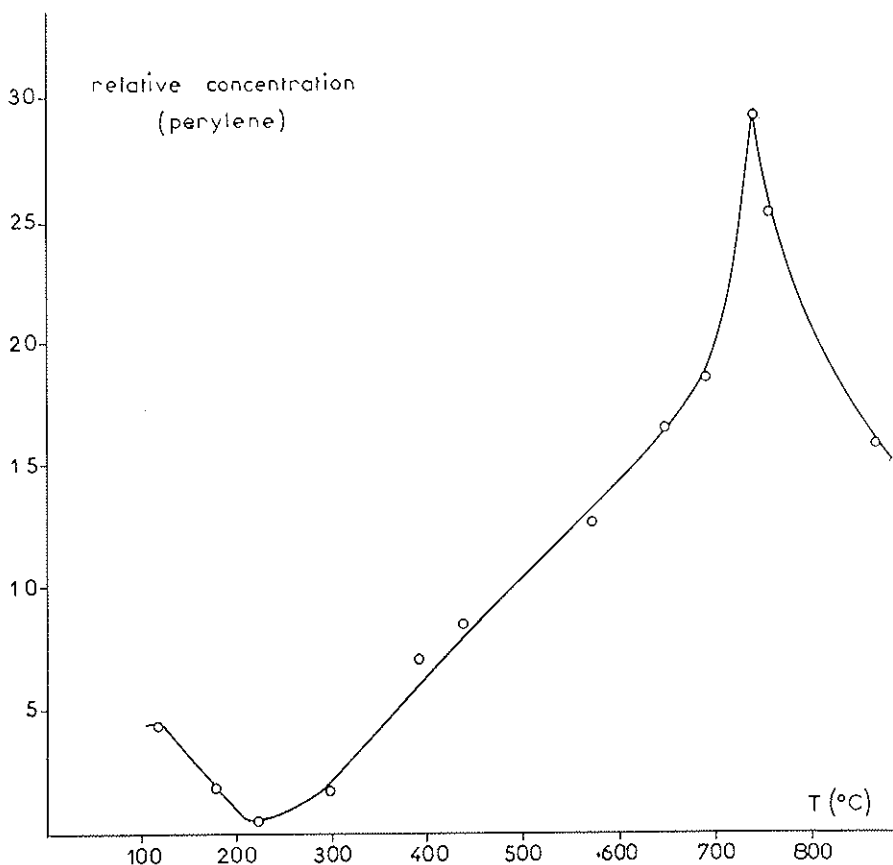


FIG. 28 — Influence de la température d'un traitement préalable d'un catalyseur silice-alumine sur la concentration relative des ions-radicaux positifs de pérylène.

responsables de toute chimisorption en même temps que la perte de toute activité catalytique.

b) *Formation d'ions radicalaires négatifs.* — La présence à la surface des catalyseurs silice-alumine de sites susceptibles

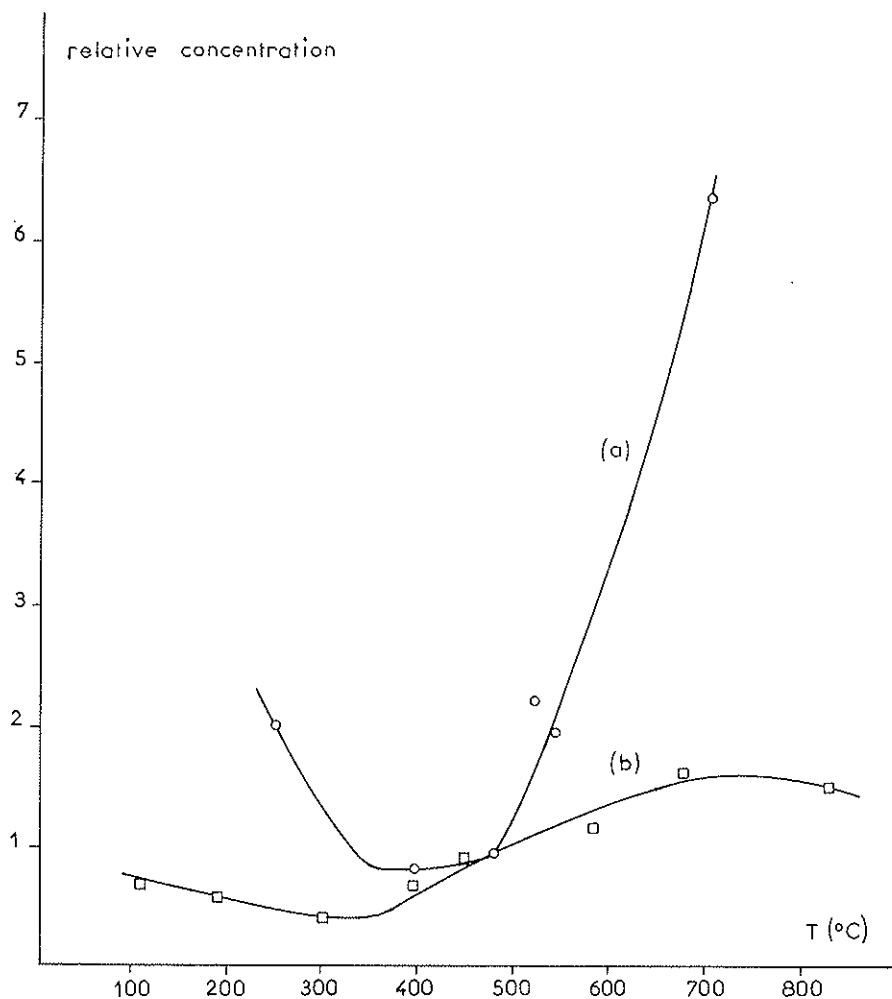


Fig. 29 — Influence de la température d'un traitement préalable d'un catalyseur silice-alumine sur la concentration relative des ions-radicaux positifs,
(a) adsorption de thianthrène,
(b) adsorption d'anthracène.

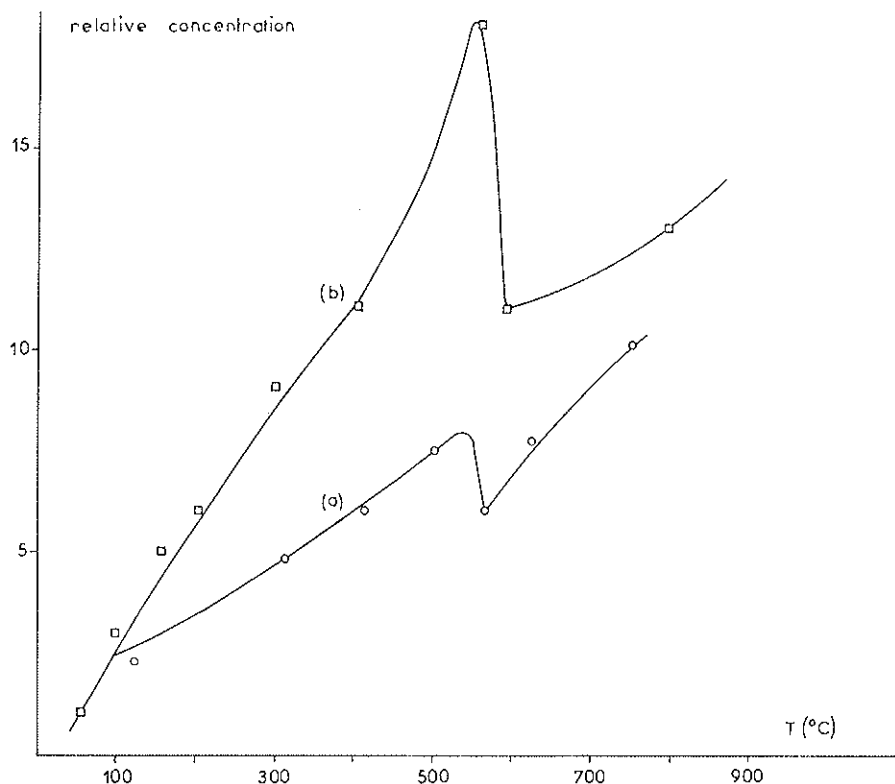


FIG. 30 — Influence de la température d'un traitement préalable de catalyseurs silice-alumine sur la concentration relative des ions radicaux TCNE^- ,

(a) catalyseur à 13% Al_2O_3 ,

(b) catalyseur à 25% Al_2O_3 .

de céder un électron à une molécule dotée d'une affinité électronique suffisante, ne paraît pas avoir été souvent envisagée. Toutefois, GRAGEGOROV, STRELKO et VISSOTSKI [32], ont observé que l'adsorption de parabenzoquinone sur alumine et sur silice-alumine entraîne l'apparition d'une coloration du solide

et d'un signal de R.P.E. qu'ils ont attribué au radical négatif de l'espèce adsorbée.

Deux séries d'échantillons de catalyseurs silice-alumine titrant respectivement 13 et 25% d'alumine ont été calcinés sous vide à diverses températures puis mis sous vide en présence de solutions benzéniques de TCNE, de trinitrobenzène et de chloranil. Dans tous les cas les spectres de R.P.E. obtenus sont caractéristiques des ions négatifs correspondants résultant d'un transfert d'électrons des sites d'adsorption aux molécules de l'adsorbat. Les courbes de la figure 30 représentent les variations, avec la température du traitement préalable, de la concentration relative des ions TCNE^- chimisorbés sur catalyseur à 13 et 25% d'alumine. On retrouve ici les deux maximums déjà observés pour la même chimisorption avec transfert de charge sur aluminos γ et β .

De l'ensemble de cette étude, il apparaît que l'on puisse attribuer la formation d'ions-radicaux négatifs à deux types de sites donneurs d'électrons présents aussi bien à la surface des silices-alumines que des aluminos :

a) des sites OH^- prédominant sur les échantillons traités à température modérée,

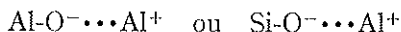
b) des sites Al-O^- ou (et) Si-O^- résultant de la déshydratation superficielle des solides et prédominant après traitement à température élevée.

Le rôle des sites superficiels OH^- trouve une confirmation dans un travail en cours sur les xérogels de silice. Sur ces gels un maximum d'absorption du TCNE à l'état d'ions négatifs est observé pour une température de 300° environ du traitement préalable sous vide, c'est à dire quand la surface de ces gels est débarrassée à peu près complètement de molécules d'eau chimisorbée mais demeure très riche en groupes silanols superficiels.

Par contre, seule l'adsorption de phénothiazine sur alumine milite en faveur de deux types de sites accepteurs d'électrons

(cf. fig. 25) sur les alumines actives. Même en présence d'oxygène, le pérylène, dont le potentiel d'ionisation n'est pourtant supérieur que de 0,2 ev à celui de la phénothiazine, ne présente qu'un maximum d'adsorption en fonction de la température de traitement et cette adsorption n'est importante que sur les échantillons d'alumine traités à haute température. Sur les catalyseurs silice-alumine, des cinq substances utilisées, les quatre qui sont les plus adsorbées, le sont surtout par les échantillons traités préalablement vers 750°C.

À des températures de cet ordre, la déshydratation des alumines comme des silices-alumine doit entraîner la formation en surface de paires d'ions tels que:



et les sites Al^+ pourraient jouer le rôle d'accepteurs d'électrons.

Reste à préciser la nature des centres accepteurs d'électrons qui prédominent sur les alumines traitées à 600° ou en dessous, mais qui n'existent pas, semble-t-il, à la surface des silices-alumines. La seule différence entre échantillons d'alumine et échantillons de silice-alumine est que les premiers se déshydratent plus aisément. L'étude par spectroscopie infrarouge de la chimisorption de bases azotées par les alumines a montré qu'un traitement sous vide vers 500° entraîne la formation de sites de Lewis. C'est à l'existence de ces sites déficitaires en électrons que sont attribuées les principales propriétés catalytiques des alumines. Il est admis par certains auteurs [29] que ceux de ces sites ayant une force suffisante doivent permettre la formation d'ions-radicaux positifs à partir de molécules à bas potentiel d'ionisation comme la phénothiazine ou même, en présence d'oxygène moléculaire, à partir d'hydrocarbures aromatiques. Les résultats précédents semblent en bon accord avec cette interprétation. Tout récemment HIRSCHLER [33] a développé des arguments en faveur du rôle des sites acides protoniques comme accepteurs d'électrons. On ne saurait évidem-

ment tenir ces arguments pour valables dans le cas des aluminés qui ne possèdent pas de tels sites, ni dans celui des silices-aluminés qu'un traitement préalable à 750°C a privées des mêmes sites.

Mais une question demeure encore sans réponse précise. Quels rapprochements peut-on faire entre les propriétés de chimisorption entraînant la formation, sur des sites accepteurs et donneurs d'électrons, de complexes avec transfert de charges et les propriétés de chimisorption sur sites de Lewis et sites de Brönsted? La formation d'ions radicalaires négatifs doit avant tout caractériser des propriétés réductrices et la formation d'ions positifs des propriétés oxydantes, alors que les principales activités catalytiques des aluminés et des silices-aluminés sont interprétées sur la base de leurs propriétés acides. On a cependant reconnu qu'aluminés et silices-aluminés traitées à température élevée (750° par exemple) font preuve d'activité dans des réactions d'oxydation. Il est significatif que tous les solides faisant l'objet de la présente étude chimisorbent la plus grande quantité d'ions positifs après traitement à cette température. Mais on ne peut aller actuellement plus loin pour répondre à la question posée.

CONCLUSION

Les travaux qui viennent d'être résumés mettent avant tout en évidence la diversité des interactions adsorbat-adsorbant dont peut faire preuve un même solide catalytique. Ils montrent également l'influence considérable de la composition chimique superficielle de ces solides sur la nature, le nombre et la force de chaque type de sites d'adsorption.

Seuls les travaux sur la décomposition de l'oxyde nitreux établissent une relation précise entre la nature des interactions

et le mécanisme de l'action catalytique qui s'exerce dans les conditions mêmes où la spectroscopie infrarouge a mis en évidence ces interactions. C'est évidemment dans cette voie qu'il faut persévérer pour établir des liens étroits entre l'activité catalytique et les effets de la chimisorption d'un réactif ou produit de réaction du système catalysé. Mais, comme cela a été précisé dans l'introduction de ce mémoire, cela pose des problèmes d'expérimentation difficilement solubles dans l'état actuel de nos techniques.

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DISCUSSION

Chairman: SCHWAB

SCHWAB

May I ask for comments? I've just one short question. What do you understand with bound OH groups? Are they bound with each other by hydrogen bridges?

PRETTRE

After heating in vacuum at very moderate temperature, there are many OH groups on the surface of silica-alumina. For example on silica there are between 5 and 8 OH groups per 100 Å². At such superficial concentrations it is possible to observe an interaction between two OH groups. That is clearly indicated on the infrared spectra of silica (curves *a* and *b*, fig. 2 of my report) by the band near 3600 cm⁻¹.

SCHWAB

Do you think this is a straight hydrogen bridge, or a bent hydrogen bridge?

PRETTRE

This interaction is interpreted as an hydrogen bond.

SCHWAB

You can't conclude by comparison with other substances, that this is the band of a certain kind of hydrogen bridge?

GRIMLEY

When we are looking at the infrared absorption frequencies of molecules adsorbed on a solid, we must remember that it would be strictly correct to associate such frequencies with normal modes of some surface complex only when the frequency falls outside the acoustic and optical branches of the frequency spectrum of the adsorbent. There are theoretical reasons for the belief that if a surface complex has a normal mode frequency which falls in the frequency spectrum of the adsorbent, then this will be a rather broad absorption peak. Is there any experimental evidence of such rather broad peaks in the absorption spectra of adsorbed molecules?

PRETTRE

In the case of the silica-alumina catalyst, the infrared spectra of chemisorbed ammonia has a band at 1615 cm^{-1} which very close of the 1635 cm^{-1} band of Si-O harmonics (fig. 9 of my report). It is a band of ammonium ion. But this band is not broader as other bands of adsorbed ammonia on silica-alumina (see fig. 10) which are very far from the frequencies of this solid.

GRIMLEY

Do you know any evidence for rather broad peaks in the infrared absorption spectra of chemisorbed molecules? Do you ever see very broad peaks in a spectrum?

PRETTRE

Yes. Generally the peaks are broad.

GRIMLEY

How broad? How broad in cm^{-1} ?

PRETTRE

It is different in each case. The more intense bands of pyridine adsorbed on silica (fig. 4 and 5, curves *c*) are very narrow.

GRIMLEY

Yes, but, can we have a figure? For one case, 100 cm^{-1} ?

PRETTRE

No. In this case, between 20 and 30 cm^{-1} or lower.

GRIMLEY

You don't then see a peak of say 100 cm^{-1} wide?

SCHWAB

I see the figure 14 in the reprint. There are rather broad peaks to be seen. On figure 10 also.

GRIMLEY

Figure 10 would be about 100 cm^{-1} ?

SCHWAB

Yes.

CASIMIR

What was your interpretation of this broadening of the peaks?

GRIMLEY

Well I was looking for information really from someone who had a good deal of experimental information on infrared frequencies of adsorbed molecules generally. I was looking particularly for rather low frequencies, perhaps around 800, perhaps 500 cm^{-1} , which are very broad. This is the sort of thing I'm looking out for. I don't think there are any in this paper, and this is why I raised the matter.

CASIMIR

Were you thinking, Dr. GRIMLEY, about the optical branch of the adsorption spectrum, which might not be different from the frequency of the molecule? Or were you thinking about an acoustical branch of the crystal?

GRIMLEY

I don't think I mind which really. The situation is, I think, that if one wishes to associate a frequency with a localized mode, then this has to be outside the spectrum of frequencies of the solid. If it lies inside, then it must be a rather broad resonance, not a very sharp peak.

CASIMIR

Yes, I would agree there. But the acoustical branch will, in general, be too low because it goes up to the wavelength corresponding to the Debye temperature, which would probably be of the order of a few 100 degrees. So that's also a few 100 cm^{-1} . And these adsorption bands, I think, are rather between 1,000 and a few 1,000 cm^{-1} . So if the thing would have to happen, it would probably be in the optical branch of the crystal spectrum.

GRIMLEY

Yes. This is most likely, but I think the acoustic branch will go up to somewhere around 500 to 800 cm^{-1} , and I think some infrared spectra have been scanned to frequencies as low as this.

BUCKINGHAM

May I make a general point about what one learns about the interaction energy from a study of frequency shifts in the infrared region of the spectrum? It seems to me that what one measures is not the interaction energy itself, but rather how it varies with the vibrations of the nuclei in the molecule. So it's possible to have a very large energy of adsorption which may perhaps depend

insensitively on small changes in the nuclear configuration, thereby giving a small frequency shift. I agree this would be unlikely, but it seems to me that what one actually determines when one measures a frequency shift are the first and second derivatives of the interaction energy with respect to the normal coordinates.

PRETTRE

It is possible. But my conclusions are not founded on the frequency shifts, but on the comparison of the positions of the infrared bands of a molecule in various states (gas, dissolved in various media, combined in complexes) and in adsorbed state. I think that is the best experimental evidence on the nature of an interaction between a solid and an adsorbate.

BUCKINGHAM

My point was not a criticism of your paper — it was merely a general point about what one learns from frequency shifts.

SCHWAB

What we learn from your paper is the clear distinction between four sorts of adsorption on these oxydic non conducting materials: one unspecific van der Waals adsorption which is the London force, one specific van der Waals adsorption through hydrogen bridges and one through coordination, and one through the formation of molecule ions.

And would this also concern, let us say the chemisorption of OH compounds like water and alcohols? Would you also suppose that on a rough surface, we have a carbonium ion?

PRETTRE

Water and alcohols are easily chemisorbed on alumina and silica-alumina. Alumina possesses only Lewis centers for the chemisorption. And alumina and silica-alumina are good catalysts for dehydration of alcohols.

SCHWAB

Yes. Are there any other comments?

GARCÍA DE LA BANDA

I would like to make a comment on the similarity there seems to be between the behaviour of insulators and semiconductors. As Prof. SCHWAB pointed out just now, there are four types of adsorption on silica-alumina, which gives at least three different types of species chemisorbed on the catalyst.

Also, I would like to point out that we can have another information on the symmetry of the molecule from the possible change of selection rules of the vibration frequencies, due to chemisorption itself. It has been used to a small extent, but I think more work of this kind would be very interesting.

Well, finally, for people who are not too familiar with this field, the correlation between the IR and UV spectra, and the activity of catalysts, must be done very carefully. Sometimes we are dealing with a band which belongs to a surface species, which is not the important one for the catalytic phenomena.

SCHWAB

I should say this is a very important point which Prof. GARCÍA has made, that when we see a species in the spectrum it means that

it is a chemisorbed or physisorbed species, but it does not necessarily mean that it is an intermediate in a catalytical reaction. Let us consider the controversy as for the decomposition of formic acid on different catalysts. There is not yet any agreement between the different opinions, because everybody sees another species in the surface, depending on the conditions under which he is working.

PRETTE

Yes, I agree with the view of Prof. GARCÍA DE LA BANDA. I think that many cases of chemisorption which don't concern catalysis. That is the case mentioned in my report of the chemisorption of CO_2 on thoria at room temperature. This chemisorption is inoperative in catalytic oxidation of carbon monoxide but concerns only the superficial carbonatation of the thoria which is easy at room temperature.

SCHWAB

I should like to ask Prof. PRETTE a question on his experimental technique. As far as I know from literature and our own experiments in the infrared absorption measurement on porous solids there are a lot of experimental difficulties from the scattering of the matrix and so on and it would be interesting to know how Prof. PRETTE has achieved this very beautiful narrow bands.

PRETTE

Generally it is necessary to obtain a very thin layer of the adsorbent, 15 mg per square centimeter for thoria which is particularly transparent until 700 cm^{-1} but very much lower for nickel oxide as mentioned in Part II of my report. It is very difficult

in many cases to make such layers in form of disk, particularly for silica. That is the reason of the choice of aerosil which gives more easily a thin disk as many other amorphous silicas.

For thermal pretreatments and chemisorptions, the disk is inserted in a metallic support and put in a glass or silica apparatus which can be heated by an electric furnace, treated in vacuum or in gases of various compositions and pressures.

SCHWAB

Any other question? If this is not the case, then I will try to give a general summary of what, perhaps, in my opinion at least, has come out of this discussion on heterogeneous reactions and on chemisorption. The new features which this part of the discussion brought to the whole picture of inter-molecular forces, are in two directions. One is that here, for the first time, we have dealt with the interaction of the surface and a single molecule which from the point of view of van der Waals forces as well as from the point of view of chemical forces is a new feature as compared with the discussion of the last days. And the other new feature which came in, is that here for the first time we have talked about chemical interaction, and not only van der Waals forces. I mean molecular forces in the sense that between molecules a chemical interaction took place by sharing of electrons and forming of chemical bonds. When one thinks it over afterwards it is a little bit surprising that we did discuss this kind of intermolecular force only for the case of surfaces. It would have been good if we had also a discussion on intermolecular chemical forces in homogeneous phases, for instance the chemical forces which are responsible for solubility of molecules in liquids. This has not come into our discussion and it would be a point which one could touch, perhaps, shortly in this discussion.

SESSION CINQUIEME

SOUS LA PRÉSIDENCE DU

S.E. Prof. Dr. C. CHAGAS

SOME ASPECTS OF MOLECULAR INTERACTION IN BIOLOGICAL ACTIVITY

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It seems plausible to admit that the biological activity of any substance whatsoever, either those pertaining to the organism like a hormone or those exterior to it like a pharmac, when injected in the organism, is the consequence of the interaction between the molecules of this compound and others localized in tissues, either in the external surfaces of the cells or in the interior of the same, a circumstance which makes the study of the interaction much more difficult.

This interaction may be of a very short duration or of a prolonged one, and it can either be the direct cause of the biological consequence of the interaction or be the trigger of a series of events like, for instance, changes of permeability or of molecular configuration, which produce cellular modifications responsible for the biological consequence of the interaction or be the trigger of a series of events like, for instance, changes of permeability or of molecular configuration, which produce cellular modifications responsible for the biological phenomena which occurs as a consequence of the initial interaction. The effect of this interaction may take place at the same place where it occurs, or some place else whereto it is

transferred by up-to-now unknown mechanisms in which probably allosteric effects may play an important role.

It was LANGLEY [1] who first called of the substances belonging to the cells and taking part in the interactions the « receptor substances ». This single denomination was acceptable up to a point when it has been necessary to consider that receptors should be divided in two different classes at least: to the first category belong the specific receptors. This denomination indicates that the interaction of a molecule with this kind of a receptor, in adequate circumstances, will produce a stimulus by which a certain expected biological activity occurs.

The second category encompasses the acceptors. It embodies all other sorts of chemical well defined tissue components able to interact with injected molecules with the occurrence of unexpected effect or without any apparent one.

This division was made clearly necessary when it was seen for instance that together with the expected actions collateral activities appeared, some quite unexpected, and even unwanted. It was made still more compulsory when it was seen that any substance injected into an organism will be largely diffused and may be encountered attached to sites where it will exert no action at all, showing, particularly, in some cases, a greater affinity for the acceptors than for the loci where they should exert their specific action.

ORCHITA [2], for instance, in his very elegant experiments where C-14 marked digitalis' glucosides were first used showed the very large diffusion of digitaline in the body. This is a striking instance where a very specific action is exerted and one looks for a very precise localization of the drug, in the heart fibre.

The experiments of ORCHITA were reproduced with other substances and the results observed the same. It leads to a definite establishment of the division of receptor substances in two large categories already mentioned: specific receptors and acceptors or sites-of-loss.

It is clear, however, that this last denomination must not be considered totally satisfactory as in many instances one may consider that sites-of-loss are really sites where molecules are attached in order that defense barriers of the organism may be established. These sites, for instance, may regulate the blood concentration of the injected drug.

On the other hand, it is very difficult to establish a clear-cut definition of the kind of rôle a receptor substance plays when different effects are exerted by the action of a same molecule.

* * *

The study of the interaction between a molecule possessing biological activity and molecular substances responsible for the resultant action has been pursued broadly in two lines of research. The first one tries to establish how one may apply to the interaction the laws of chemical reaction, as determined by the Henri-Michaelis-Menten equations in the case enzyme-substrate (as first tried out by A.J. CLARK [3]). In the second one, the experimenter essays to determine, by physico-chemical methods, the affinity of the inter-acting molecules and, in particular cases where a high specificity is present, he may try then to reach by models the molecular complementarity responsible for this circumstance.

It is clear that both lines of approach require the knowledge of the molecular structures of the receptor or the acceptor, and its concentration. Thus, when one is trying to determine the association constant, as an evaluation of affinity, both the molecular nature and concentration of the receptor substance must be known; without this knowledge, relative results can be obtained and indefinite data about the kinetic of the process of interaction known.

Many authors have been tempted to investigate the interaction of biological active molecules with receptor substances

in this way and, as the results of the investigations, have obtained some interesting results.

ARIENS and his co-workers [4], for instance, have reached a working hypothesis which, together with its usefulness points to all the intricacies of the problem. It postulates that in studying the biological action of a molecule, one has to distinguish between its chemical affinity to a receptor or acceptor measured in terms of physico-chemical data and a second conceptual characteristic, its « intrinsic activity » which has, at present, to be measured purely in terms of biological results.

This concept originates, for instance, from the study of numerous cases where a drug A active ceases to be of any action even in favourable concentration relationship when the receptor R is treated beforehand by a substance B which has no biological activity by itself whatsoever.

One may assume in this case that molecules of B have a higher affinity for the molecules of R than the molecules of A, in which case A ceases to have any biological activity or loses part of it. One may visualize this supposing that the B molecules cover the receptor molecules.

As it stands, it is apparent that as the chemical affinity measures the chemical reactivity between a molecule and its cellular acceptor, the intrinsic activity is a measure, in empirical terms, of its biological action.

One may question the meaning of many concepts obtained from experiments in which isolated structures were employed, when one tries to apply them to a biological system in which it is clear that the existing structural complexity involves many parameters still unknown. In other words, it is extremely difficult to extrapolate from « in vitro » experiments to the « in vivo » ones.

* * *

It would be impossible to analyse all data published already on this field.

No doubt, one must be very careful when analysing the factual data which have been presented up to now.

First, one has to take in account the fact that even if some light has been brought on the nature of receptors, we must not forget that the rather purified species described from « in vitro » experiments are, in fact, disposed in the cells as very complex structures where, possibly, the distribution of charge is quite different from the one observed when purified substances are analysed.

Another point worth mentioning brings out the fact that biological complexity introduced by the cellular structures engaged may give rise to some difficulties which make the classical physico-chemical analysis problematic.

Studies in which the electroplaques, for instance, have been used, show the existence of a gradient of concentration of an acting drug, distributed at least, in two compartments with two different diffusion constants.

The presence of these two phases indicates that one may assume that the first intermolecular force which is involved in biological interaction we are studying should be of a coulombian character responsible for the long distance attraction followed by the subsequent interaction due to less strong forces (as hydrogenic bonding or VAN DER WAALS interaction). This hypothesis has still to be proved.

It is however doubtful that with our present knowledge of the cellular receptors much progress can be obtained, either in relation to the kinetics of the interaction between molecules and biological receptors, and, in the majority of cases, of the chemical nature of the receptors themselves.

The most sophisticated approach used up to now is the one where variation of biological action is related to the molecular constitution of the interacting pharmacon.

This has been particularly well established in relation to the molecules containing quaternary ammonium radicals.

It may be necessary to say some words of the reasons responsible for this development. It can be attributed to the discovery of a chemical substance responsible for nerve-effector transmission of the nerve influx in some structures. This substance, acetylcholine, was the first small molecule to be determined, possessing a definite specific biological action capable of observation by very simple biological essays. Molecules similar to acetylcholine, and of blocking agents for its action, the curares, first isolated from plants, were synthesized.

The study of the antagonist to acetylcholine is a good example of the way in which our knowledge about an interaction of molecules in biological processes has been pursued and should be sought.

Acetylcholine was identified by HENRI DALE [5] as the « vagustoff » which was described by OTTO LOEWY [6]. Its biological activity on the neuro-muscular junctions was well established by BROWN, VOGT, FELDBERG and DALE [7], and subsequently its importance in the so-called cholinergic structures definitely proved.

Advanced knowledge was gained when KING [8], determined the molecular configuration of D. Tubo-curarine — an alkaloid extracted from *Chondodendrum tomentosum* — usually present in South American Indian's curares, and a most potent neuro-muscular nervous transmission inhibitor. The recognition of its structural formula led DANIEL BOVET and his collaborators [9] to synthesize homologues, the first being the tri-ethylidyde of Gallamine known as flaxedil.

A little later, PATTON and cols., and BOVET and his group, synthesized acetylcholine-like molecules simpler than the alkaloid curares having also an inhibitory effect on neuro-muscular transmission. Accurate analysis, however, has shown that their different molecules act in different mechanisms.

The obtention of synthetic products made it possible to analyse the change of biological activity with molecular configuration. In the particular case of neuro-muscular transmiss-

ion inhibition, some rules could be established in homologue series. Thus, it was seen that the presence of two quaternary ammonium radicals enhances biological activity.

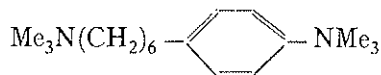
TABLE I

	DHD+
$\text{Mc}_3 \text{N}^+ \text{CH}_2 \text{CH}_2 \text{OCO}(\text{CH}_2)_3 \text{COOCH}_2 \text{CH}_2 \text{N}^+ \text{Mc}_3$	0.15-0.20
$\text{Mc}_3 \text{N}^+ \text{CH}_2 \text{CH}_2 \text{OCO}(\text{CH}_2)_2 \text{COOH}$	5.0
+ Dose Head-drop	

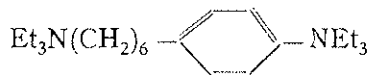
It was also observed that the distance between those two radicals in the natural curare-like molecules, was an important factor in enhancing or establishing biological activity.

It was also shown, as another example, in a rather striking way, that a change of radicals may produce a modification of the biological action of a molecule, and even, in some cases, the opposite one. Thus one may pass from a acetylcholine-like activity, i.e. a depolarizing one, to a true-curare action — in which no permeability change is observed in the membrane — by substituting a methyl group, for ethyl one, as with the derivatives from phenyl-hexane-bis-Trialkyl-ammonium.

TABLE II



(Leptocurare)



(Pachycurare)

Undoubtedly, it is by the recognition of the tri-dimensional configuration of a molecule, encompassing in it all variables involved, that more may be known of its interaction with receptors. The brilliant results obtained by E. WILSON [10] with this molecular approaches, in the study of an antagonist to the very potent anti-cholinesterasic agent, di-iso-propyl-fluoro-phosphate, shows how it may be developed.

It allows also for the identification of some aspects of the nature (and configuration) of receptor substances still one outstanding query-mark.

* * *

The study of curare-like agents, using this classification in a broad sense encircling all molecules able to interrupt neuro-synaptic transmission, has allowed for the first attempts to isolate a receptor substance and thus for a model which may represent an interaction of two molecules having biological importance. Different approaches have been used, one has originated from the group working in Rio de Janeiro [11] where radio-isotopes marked compounds were first used and a second

one from the group under the leadership of D. NACHMANSON [12].

The electroplaque was the biological structure used by the group in Brazil, afterwards employed by the group in New York. It is the electrogenic unit of the electric organ of the « *Electrophorus electricus* », and its cholinergic nature was shown by CHAGAS and his collaborators [13]. (Fig. 1, 2).

The molecular aspects of neuro-effector transmission in a cholinergic system, as a matter of fact, were mostly based on data gathered from the studies with this biological structure. However, when it was employed, part of the mechanism of cholinergic transmission had already reached a state where a molecular support for it could be postulated. It involves the interaction of an enzyme existent in the cholinergic synapses —

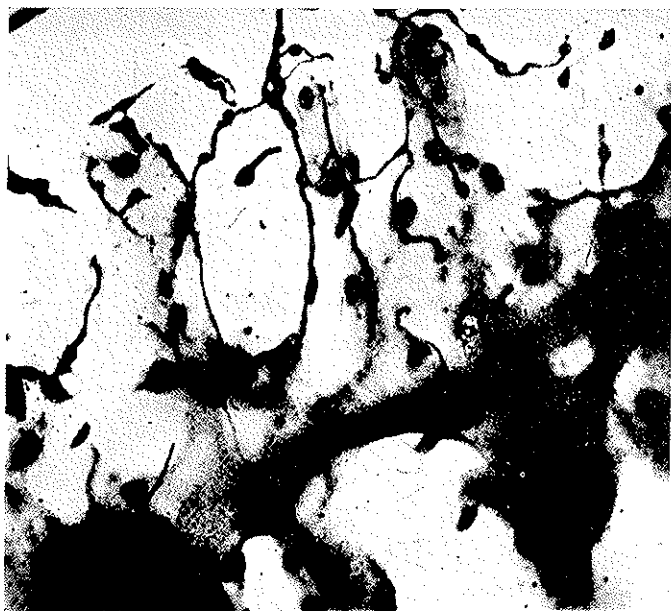


FIG. 1

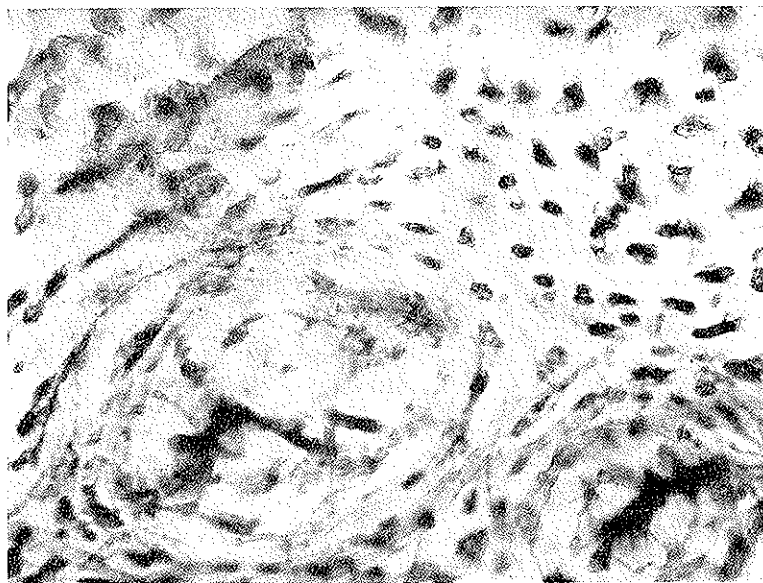


FIG. 2

and very predominant in the electric organ — whereby it hydrolizes formed acetylcholine and the enzyme is reached by inter-ionic attraction between the positive ammonium quaternary ammonium radical and a second site where other types of inter-molecular forces may also play. This working hypothesis resulted in the very brilliant work of E.B. WILSON, already referred to.

The attempts undertaken to isolate the cholinergic receptor by S. EHRENPREISS were done by studying the capacity to precipitate different proteins extracted from the electric organ by curarizing agents. It was later seen however that the complexity of molecular structure of isolated components of the electric organ, when placed « in situ », together with the imp-

possibility of isolating only the proteins placed on the post-synaptic surface of the plaque, allied to a great affinity of almost any proteins extracted from the electric organ towards curarizing agents showed that this attempt was rather fruitless.

The group in Rio de Janeiro, under my direction, has been following another type of approach. Molecules marked with C-14 were employed. It was thus shown that there is a very diffused acceptor in the organism of the true curares. Isolated, it showed to be an acidic muco-polyssacharide [14]. Its rôle in the process of the inhibition of synaptic cholinergic transmission is still difficult to explain. Undoubtedly one working hypothesis would be to admit that, due to its presence in the ground substance it may attach curarising agents, thus intercepting any interaction with the receptor by the mediator-acetylcholine.

All physico-chemical data relating to the interaction of the pure muco-polyssacharide isolated from the electric organ, with different sorts of molecules containing quaternary ammonium radicals point to the predominance of forces from the coulombian type in the reaction.

It is still difficult to relate those « in vitro » data to the « in vivo » experiments. These have shown however that in the organism, true curares tend to be attached probably under a complex form to tissues rich in muco-polyssacharides, and in this sense, the acidic muco-polyssacharide may play the rôle of a site of containment or that of a defence barrier. As a matter of fact, it has been seen that the amount of true curares found after injection, and during curarization, is grossly proportional to the amount of acidic muco-polyssacharides of the organs.

Another attempt of significance is the one tried out by P. WASER using auto-radiographic techniques. It shows interesting and promising results of a quantitative character, but still does not inform on the nature of the cholinergic acceptor.

These results indicate the importance of pursuing studies

on the interaction of molecules extracted from biological structure with interesting active molecules, but one has to point that the extrapolation of « in vitro » to « in vivo » results has to be done very carefully.

The examples presented demonstrate that the study of molecular configuration in relation to biological activity has to play a rôle every day more important in the understanding of biological processes as a whole.

In the particular case of drugs, the study must lead to the establishment of a much more precise knowledge by which the affinity and intrinsic activity of a molecule in relation to its cellular receptor, may be defined in terms of molecular configuration.

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INTERMOLECULAR FORCES IN BIOCHEMISTRY

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There is, perhaps, no field of chemistry or physics which could profit more from a detailed understanding of intermolecular forces than biochemistry. If we consider the interaction and mutual flocculation of antigens and antibodies, or the complicated reproduction processes of RNA- and protein-molecules, or the catalytic activity of certain « sites » of an enzyme molecule, then the predominant feature of these phenomena always appears to be a specific relation between the molecules involved, which can only be explained in terms of specific interactions or intermolecular forces.

However, even semi-quantitative considerations of these intermolecular forces are apparently very difficult, since such considerations are virtually absent in biochemical literature, and are in an initial stage, when they are present. At any rate it may be said, that such considerations have hardly played a part as a « working hypothesis » in an attempt to rationalize the choice between the almost infinitely large number of experiments that can always be set up. In fact such considerations contributed little to the unflagging eagerness of chemists to link up the multitude of facts by « explanations » in some sort of chemical language.

It is interesting to make a comparison with the situation in the chemistry (inorganic or organic) of simpler systems.

In inorganic chemistry, for instance, even before quantum chemistry gave us the weapons to calculate interatomic forces in simple molecules more or less accurately, people like FAJANS, GRIMM, VAN ARKEL and DE BOER and many others, achieved considerable results in classifying the facts according to rather simple models of chemicals forces, including electrical forces between ions or dipoles and polarization forces (KOSSEL, KEE-SOM, DEBIJE), repulsive forces due to interpenetration of electronic shells (BORN-MAYER) and van der Waals-London attractive forces. Of course, these considerations contained a number of empirical data (« size » of ions or atoms, polarizabilities, etc.) or « laws » (repulsive forces) which could only be derived on the basis of quantum mechanical theory.

The success of such considerations has in recent years been reinforced by permitting quantum mechanical « corrections » upon the classical model. I should like to mention two examples. The first is taken from a large group of oxydic compounds containing transition metal elements, for instance the spinels, whose atomic arrangement and magnetic properties could be more or less completely described (VERWEY, E.W. GORTER, BLASSE [1]) by the classical Born-Madelung picture. In some cases, however, it is necessary to take into account the energy change caused by the fact that the magnetic ions are subjected to a splitting of their *d*-levels in the electrostatic crystal field. This is essentially a correction for the fact that the charge distribution in the ions with an incompletely filled *d*-shell is a non-spherical one. The second example is to be found in the work of L. JANSSEN [2] which shows that the validity or applicability of the classical model can be considerably extended by introducing multiparticle interactions in the calculation of the repulsive forces and the van der Waals-London forces. By introducing three-particle interaction, which takes into ac-

count that the forces are not simply given by a $f(R)$, but also by a function of the angle formed by 3 atoms, it was shown that there is a quantitative explanation for the crystal structures of the noble gases, and for the transition NaCl structure $\rightarrow$ CsCl structure under the influence of pressure for all the alkali halides, and even for the crystal structures of II-VI compounds and III-V compounds, on the basis of an ionic picture.

I am stressing these examples, because they show that in many cases a quasi-classical picture is able to supply a reasonable basis for the estimation of chemical forces although, of course, a complete theory should start from a detailed consideration of the wave functions and their mutual interactions based on quantum chemistry. As a matter of fact, the quantum chemical approach, even in rough approximations, has been of considerable value in discussing properties of organic molecules, in seeking to understand the nature of complexes, in surface chemistry, in the theory of catalysis and in many other cases.

In biochemistry the intermolecular forces are comparatively weak and it is therefore all the more reasonable to expect useful results from calculations based on the classical model, provided, of course, that such calculations are practicable.

There are a number of difficulties to be discussed.

1. Perhaps the most serious difficulty is that biochemical systems are systems of molecules and ions in water. Hence, apart from the interaction between different molecules, there is always the interaction between these molecules and water and the mutual interaction of the water molecules themselves. The total free energy change in a re-arrangement of molecules (for instance, in the transition of a double helix into single coils, or even in a partial transition of this type) is a free energy difference due to the three interactions mentioned above.

If we denote the interacting molecules by M_1 and M_2 there is always the difference between the interactions

$$M_1 - M_2 \text{ and } H_2O - H_2O \quad (A)$$

on the one hand and the interactions

$$M_1 - H_2O \text{ and } M_2 - H_2O \quad (B)$$

on the other. The free energies associated with (A) and (B) may be almost equally large, and the difference

$$(A) - (B) = \Delta F$$

may therefore be much smaller than either (A) or (B). This may imply that relatively small variations in either (A) or (B) are responsible for the specificity shown by biochemical interactions.

2. The free energy difference consists of an enthalpy and an entropy difference. In certain cases, for instance in the case of a transition of a double helix into two more or less random coils, the entropy difference may be a rather important part of the free energy difference, and its calculation depends on knowledge of the conformation of the random coil, and therefore also on the interactions within the single coil.

The enthalpy difference $(A) - (B)$, even in simple cases, consists in the classical model of several terms:

- a) van der Waals-London attraction;
- b) electrostatic attractions and repulsions due to polar groups;

- c) electrostatic attractions and repulsions due to dissociated groups (if such groups are present; in this case, too, the ions in solution have to be taken into account);
- d) Born-Mayer repulsion, due to interpenetration of electronic shells.

Considering the important part played by water molecules in the whole pattern of interaction, it seems worth while to start with a few remarks on the chemical forces where water molecules are involved. First of all we have to discuss the chemical forces in pure water, because the forces between water molecules are of the same nature as those which, for instance, play an important part in the interaction between protein molecules and water.

According to the basic paper of BERNAL and FOWLER [3] these forces are predominantly of a Coulombic nature, and can be described as the electrostatic attraction due to the characteristic charge distribution within the water molecule. The latter is largely determined by the rather peripheral position of the protons at an angle of about 109° . Therefore, in the crystal structure of ice, each water molecule is surrounded by four other molecules: two molecules which are bound to the two positive poles of the central molecule, and two which are pointing one positive pole towards the latter. According to their theory liquid water has a fluctuating somewhat broken-down ice structure, in which the « hydrogen bonds » between the molecules are weakened by a slightly increased average distance of the water molecules from each other and by some bending of the bonds away from the most favourable tetrahedral angle (as a consequence of which the average coordination number has been increased to a value between 4 and 5 and accordingly, the density of the liquid is higher than that of the solid). Point-charge models for the charge distribution, based on the Bernal and Fowler picture, have been used to cal-

culate the heat of evaporation of ice, or the hydration energies of ions, with reasonable results [4].

Such calculations show that in ice (and water) the electrostatic attraction (including polarization: the dipole moment of the water molecule is here considerably larger than that of the free molecule) is by far the largest contribution to the total interaction energy; moreover, the less important contributions, the London-van der Waals attraction and the Born-Mayer repulsion, more or less cancel each other.

Point charge models of this type, though chosen such that they lead to the right dipole moment, have the disadvantage that they do not correspond to values of the main quadrupole moments as can be estimated on the basis of our present knowledge of the wave functions [5]. These models account insufficiently for the negative charge in the outer regions of the molecule. It is difficult to estimate the effect of this insufficiency upon the calculations mentioned above. An alternative way to account for the electrical field of the charge distribution is given by its development in dipole moment, quadrupole moment, etc. It has been shown [6] that, in principle, this method enables one to explain « experimental » hydration energies, especially the fact that anions are more strongly hydrated than cations of the same size. Quite recently COULSON and EISENBERG [7] have based calculations of the interaction of water molecules in ice on the charge distribution as given by this method. They give a very careful analysis of the electrical field of the neighbouring molecules increasing the dipole moment of an isolated molecule, 1.84 D, to about 2.60 D. In the calculation of the total Coulombic interaction energy they include second and further neighbours.

At any rate these calculations show that the forces between water molecules are predominantly of an electrostatic nature and, accordingly, there is no reason to assume that the « hydrogen bond » is more than a bond which can be understood

as a result of the characteristic charge distribution in the molecules involved.

Hence there is not sufficient theoretical basis for a theory of water which has been developed by NÉMETHY and SCHERAGA [8] as an extension of the ideas of FRANK and EVANS and is based on the assumption that water contains regions with ice-structure (containing between 30° and 0°C roughly 50-100 water molecules in thermal equilibrium with a medium of completely broken-down water with high coordination number or a more or less close-packed structure; in the former regions the H₂O molecules are held together by hydrogen bonds, in the latter by dipole forces only. It is not possible, however, to make such a sharp distinction between hydrogen bond force and dipole force, because the field of the water molecule as discussed above, will also be effective if the angles are less favourable, though to a smaller extent. Moreover, the further consequence, a description in terms of entirely different types of water molecules (N. and S. even distinguish 5 different types with different energy levels, according to the number of hydrogen bonds, 0, 1, ... 4 respectively, and their location in the « clusters »), though in kinetic equilibrium with each other, is not very consistent with the general concept of a liquid structure in which all molecules are in principle equivalent in a continually changing arrangement and all intermediate states between strongly bound and weakly bound molecules should be possible (¹).

In this connection it is interesting to mention the concept « hydrophobic bond », introduced by KLOTZ [9] and KAUZ-

(¹) Recently, SPARNAIJ has tried to give an improved Statistical theory of water (M.J. SPARNAIJ, « J. Coll. Int. Science », 22, 23 (1966)). This theory is essentially based on a modification of the picture of BERNAL and FOWLER given by LEENARD-JONES and POPLÉ (« Proc. Roy. Soc. », A 205, 155, 163 (1951)), in which liquid water is described as a continuously changing distorted ice-structure; this distortion and the corresponding loss of long distance order is mainly effected by a bending of the hydrogen bonds.

MANN [10], indicating the fact that in an aqueous medium hydrocarbon chains, or the hydrophobic side-chains of protein molecules, attract each other. The free energy difference responsible for this attraction is predominantly an entropy effect, as can be demonstrated with the aid of thermodynamic data for diluted solutions of hydrocarbons in water. These data show that the low solubility of these hydrocarbons is due to a decrease of the entropy, and not to an increase of the enthalpy. It seems therefore that the amount of order in the water structure is increased by the presence of the dissolved molecules. (NÉMETHY and SCHERAGA try to explain this by assuming that the hydrocarbon molecules increase the size of the ice-like clusters). It is interesting to make a comparison with the formation of hydrates by noble gases, lower hydrocarbons and many other molecules, showing that a crystalized « cage » is formed around such molecules. A detailed analysis of the electrostatic, van der Waals-London and repulsive forces in such a hydrate seems worth while.

The van der Waals-London interaction of the central molecule with its immediate environment seems to be important, as the entropy behaviour of the free surface of water is opposite to that of water adjacent to a hydro-carbon molecule (surface entropy positive with respect to bulk, indicating a larger amount of freedom for the orientation of the water molecules in the surface). It therefore seems justified to designate the hydrophobic bond as the result of van der Waals-London interaction, though not simply as the effect of such an attraction between the hydrophobic molecules alone.

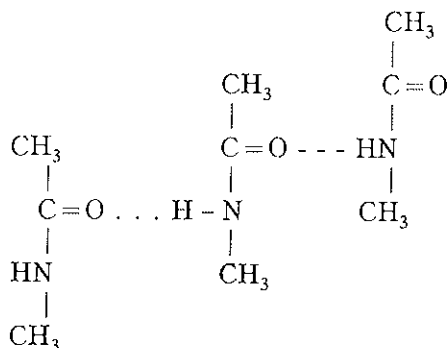
Returning now to biochemical systems, we may say that we know very little about the various types of interactions mentioned earlier in specific cases.

One point suggested above, namely that the hydrogen bond interaction between the NH group and the CO group in peptides may be of the same order of magnitude as the interaction of

these groups with water molecules, is clearly shown by the behaviour of the simple peptide molecule



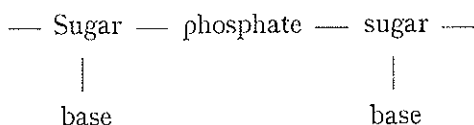
in water. This molecule should easily be able to form aggregates of the form



but from measurements and thermodynamic data given by KLOTZ and FRANTZEN [11] it has been found that ΔH is practically zero, and accordingly, in consequence of the larger entropy of the free molecules, the ΔF is 3.1 kcal/mol. The hydrogen bond between CO and NH in polypeptides will play a part, for instance, in the free energy determining the conformation of a protein molecule (interaction of NH and CO from the same protein molecule in competition with their interaction with water molecules), but cannot be the only basis for the stability of such a conformation (helix, etc.), i.e. other forces have to be considered too. In the case of proteins some success has been obtained with the detailed consideration of steric hindrance (repulsive forces in a simplified presentation)

and the effect of interaction between hydrophobic side-chains (SCHERAGA).

Several authors have tried to calculate the energies involved in the interaction between two polynucleic acid chains. A point of special interest is the behaviour of DNA which, according to WATSON and CRICK, forms a double helix in which two molecules form a double strand and turn around one another like threads of a screw. In salt solutions these double helices show a sort of « melting point » and dissociate into simple strands. In the single molecule, with the general structure



(sugar in DNA is deoxyribose) the properties are specifically determined by the type of base. In DNA there are four types of base, and it has been assumed that adenine always pairs with thymine in the other chain, and guanine with cytosine. Hydrogen bond formation may play a role here, but it is still a point of discussion whether these hydrogen bonds constitute an important fraction of the total energy of interaction. The first calculations, based on the atomic positions as determined by X-rays (LANGRIDGE), were done by DE VOE and TINOCO [12]. In these calculations the electrostatic contributions were approximated by using the dipole moments of the base groups (from 2.8 D in adenine to 8.0 D in cytosine). SINANOGLU, ABDULNUR and KESTNER [13] have tried to improve the calculation of the dispersion forces by taking into account the effect of the solvent. This implies the introduction of multi-particle interaction, with the result that the van der Waals-London contribution (an important fraction of the total interaction energy) is somewhat (10-30%) reduced. A further improvement of the theory has been attempted by BRADLEY, LIFSON and HONIG [14], who substituted the dipole-dipole ap-

proximation by a more detailed model of the charge distribution.

In a way this step can be compared with the introduction of the Bernal and Fowler model for the water molecule instead of the simple dipole model. It is clear that only thus is the specific interaction due to hydrogen bonding taken into account. The whole pattern of interaction is too complicated to be considered here in detail. The calculations, however, show that both the electrostatic part of the interaction (of which the hydrogen bonding energy of G...C and A...T, or in RNA A...U (Uracil) is itself only a part, though a rather significant one) and the van der Waals-London contribution are important in the total picture. A more detailed consideration of the influence of the solvent, especially of the competing hydrogen bond type interaction between the base groups and the water molecules, has yet to be put forward.

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DISCUSSION

Chairman: CHAGAS

WIDOM

I would like to say a word or two in defense of my colleague, SCHERAGA. I think that one of the ideas that leads to the notion that a black and white distinction should be made between hydrogen bonds made and broken, which is the basis of the criticism, is that when you go to the liquid from the solid, as you say, the average co-ordination number actually increases. So the question is, how can one understand that there is a positive latent heat of fusion? How can one understand that the system must absorb energy in order to go to a state that actually has a higher co-ordination number? The only way one can understand it is to say that in the liquid the number of made hydrogen bonds is smaller — that is you have to some extent broken down the hydrogen bonding structure. Though you have produced a geometry in which any one molecule has more neighbours, these neighbours do not appear in a regularly hydrogen bonded structure to the same extent that they do in solids. So, just to understand the existence of a positive latent heat of fusion, one is almost forced to the conclusion that there is a black and white distinction to be made between a hydrogen bond made and a hydrogen bond broken. Then, to turn this into a question, I would say, can you, from your picture of the structure of liquid and solid water, understand more or less quantitatively the observed energy of fusion of the solid?

VERWEY

A more or less quantitative understanding of the energy of fusion of ice would be very welcome. As far as I know nobody has ever tried to attack this problem. The somewhat larger coordination number of the liquid structure will, indeed, increase the van der Waals-London attraction, the slightly larger average distance of the molecules will decrease the total interaction. The most important term will nevertheless be the change in the energy of the hydrogen bonds, whatever that is. If one believes, as I do, that the hydrogen bond is predominantly of an electrostatic nature, one will have to find the increase of the energy in a detailed consideration of this interaction as a consequence of deviations from the ideal arrangement as present in ice. In such a consideration the effect of second and further neighbours cannot be neglected, and it may be that the relative stability of the ice structure can be partly explained by the fact this cooperative interaction with neighbours outside the first coordination shell is much more favourable in the crystal.

BUCKINGHAM

I'd like to take up the question of the transition from the solid to the liquid states of these hydrogen bonded substances. In 1951 POPLÉ (Proc. Roy. Soc. 205 A, 163) produced a model of solid and liquid water in which he assumed that the co-ordination number of 4 remained fixed, and the change from the solid to the liquid simply involved the ability to bend the hydrogen bonds. In the solid there are straight bonds — essentially a tetrahedral arrangement about the molecule being considered; in the liquid Pople assumed that these 4 hydrogen bonds remained attached, but were given flexibility. This increased flexibility permitted the increase in density that's observed on melting — increase in co-ordination number, if you like, but POPLÉ preferred to look upon it as a

constant co-ordination number, coupled with an increase in flexibility. So in his model the entropy change was entirely due to bending of hydrogen bonds, and he did, as I remember it, obtain qualitative agreement with observed entropies.

One can link the question to the infra-red spectrum, to some extent, here.

LÖWDIN

I think this charge distribution picture is a very useful one, and I feel that in order to get a first understanding of these things, this is the right way of approach. At the same time we should remember that it violates the virial theorem. There is no discussion of the kinetic energy here. And to take a parallel, when we discuss cohesive properties — let us say of ionic crystals — we divide it up into Madelung energy and Born-Mayer repulsion. And we forget the kinetic energy.

Still, the cohesive energy of sodium chloride is -183 Kcal/mole. And this term consists of $+183$ Kcal/mole increased kinetic energy, and -366 Kcal/mole decrease in potential energy. So we should remember that the simple potential pictures are good, but that they are over-simplified.

GRIMLEY

I think what we should learn from Prof. LÖWDIN's remark really is that we don't know when we can get away with a classical picture. His statement about the cohesive energy of ionic crystals is a very important one. Many chemists would think that they can get away with a picture of the main cohesion being due to electrostatic forces, and this is totally wrong. We are in a situation where we don't realize that we must modify our picture. We get so used to thinking of these terms, and I think that this is what Prof. LÖWDIN is trying to warn us against.

RICCI

I would like to point out that this type of water structure as ice-like clusters is not satisfactorily, because we know that this structure has a certain time of life. Therefore if we are considering some properties to measure them we must average over a time longer than the life time of the structure, we certainly are wrong in thinking that this structure has any meaning. BROCKHOUSE did a very beautiful experiment using neutron inelastic scattering on water, and he showed that the life time of such a type of ice-like clusters, is something about 10^{-12} seconds which I think is a very short one. As far as thermodynamical considerations are concerned, I think that it is right that one can separate the potential energy, and the kinetic one, but in this case in the potential part one must consider not the idealized structure but the radial distribution function.

I would like also to consider a third point: when one is saying that it is possible to determine the water structure by means, for instance, X — ray diffraction we are not at all looking the hydrogen atoms. And one just can say that the oxygen atoms have such and such distribution. However the hydrogen position can be inferred by other kinds of measurements, like infra-red or nuclear magnetic resonance.

VERWEY

I fully agree with Prof. RICCI that it has very little sense to describe the liquid structure of water in terms of relatively large ice-like « clusters » containing some 100 molecules dispersed in « normal » water if the lifetime of such clusters is so small.

With respect to the second remark of Prof. RICCI I may add that some work on the radial distribution of water molecules around a central molecule in liquid water has been carried out by HEEMSKERK and VAN PANTHALEON VAN ECK at the Koninklijke/Shell labo-

ratory in Amsterdam (see, for instance, Rec. trav. chim 81, 904 (1962)). They advocate a liquid structure with a coordination number 6, provided by a somewhat distorted simple cubic lattice. Dr. BRAUN, from our laboratory, believes, however, that the X — ray evidence is so scanty that it hardly permits to decide between this picture and the classical Bernal and Fowler theory.

BERNSTEIN

I just wanted to mention the experiments of LEVY and co-workers at Oak-Ridge National Laboratory on the neutron diffraction of water. Are these results not considered to be of interest?

RICCI

This kind of scattering is an elastic one. If you want to derive the life-time of any structure you must go into the details of energy exchange between your probe particle and your system.

WIDOM

I would like to take up again the question of the short life-time of any structure that is postulated in the liquid, and, with the chairman's permission, I'd like to go to the blackboard.

The point that I'm going to make is that the life-time of any particular structure in a liquid is really entirely irrelevant as far as determining the thermodynamic properties of that liquid is concerned. And I want to explain what I mean by that, firstly thinking of a liquid of simple molecules — spherical molecules — and then we'll see immediately how those ideas can be generalized to talk about water.

Suppose you imagine, as you look at the structure that a liquid has at some particular instant, that you freeze all the molecules fixed into position. You have a liquid of infinite extent. Wherever all the molecules find themselves at some particular instant — pin them right there. Don't allow them to move any more. But now take another molecule that's identical to the molecules of which that liquid is composed, and let it wander through this entire frozen fluid — I don't mean frozen in the real sense; I mean frozen just in having had its motion stopped — let it wander all through the fluid, and supposing at some point in space — some general point in the fluid as this molecule wanders — it finds an interaction potential with all the other molecules of the fluid. And this varies from point to point as this molecule goes around testing the structure, this is a function of position in space. Likewise, $\exp - \frac{\psi}{kT}$ is such a function of the position of the wandering test molecule at any instant.

Now we can ask what is the mean value of this, where this mean value is calculated by having this test molecule wander through the frozen fluid, and giving equal weight to equal elements of volume, simply evaluating the average of this quantity.

This quantity determines the thermodynamics of the fluid, and it is in fact exactly equal to the ratio of the number density to the activity, so that the activity as a function of density and temperature is given by this formula. Whatever has been the configuration at an arbitrary instant, is the one that determines the thermodynamic properties. If you find somewhere in the fluid, as of course you will, any particular structure, (you might for example find some very regular structure at some instant — you might just through fluctuations find some very regular structure at one point in the fluid) then indeed 10^{-12} seconds later or 10^{-14} seconds later, it will no longer look like this, but somewhere else at the other side of the beaker, it will.

And that's just exactly what you're doing in taking this average. So that how long any particular structure lasts has nothing to do

with the thermodynamic properties of the fluid, because indeed it may disappear in almost an instant, but that same structure will reappear somewhere else, and it is only an instantaneous configuration of the fluid that is significant in determining the thermodynamic properties.

And now if we can go on from simple molecules to something like water in this average our test molecule should not only wander around and give equal weight to equal elements of volume in this average, but in addition that test molecule should rotate and give equal weight to equal elements of volume in its rotational space. But it's essentially the same story. Thank you.

GRIMLEY

Is don't understand that at all, because what is the significance of this parameter T in your formula? You have got all molecules frozen, so what is the significance of talking about temperature?

WIDOM

That's entirely correct. I didn't mean to imply that this formula was transparent, but I said nevertheless it is correct, and it is a fundamental formula in statistical mechanics.

Now, let me state over again the prescription. I'm not saying that our fluid is frozen. I'm saying that if you want to calculate the thermodynamic activity of the fluid, imagine doing the following. Take the structure that the liquid has at a given temperature — that's important because the temperature will surely determine all elements of its structure, will determine how frequently any particular configuration will arise and so on, and fix the molecules in that position. Having done that, but not until you have done that, take another molecule, identical to those of which the fluid is composed, let it wander, and measure the average value of this quantity in the way that I said. That is the thermodynamic quantity. The value of this average depends on the temperature, not only

because of the explicit appearance of T , but because the kinds of interaction potentials that the wandering test molecule feels depends on the kinds of structures it sees present in the liquid, and they in turn have of course been determined by the temperature. That's what you had in mind. Indeed the structure of the fluid is determined by the temperature, and the structure of the fluid appears here explicitly, because this ϕ is a potential energy of interaction that the test molecules sees. The point of having a fluid that's frozen and not frozen at the same time is a little subtle, but if you follow the rules of the game, as I stated them, follow them precisely, out comes the activity of the fluid.

RICCI

I have only one remark. The life-time of the structure enters in another way. You must average your expression on the overall fluid. Therefore the probability of having such an arrangement plays an important role because you said that if we have such a structure in one place and at a certain time we will have it in another place in a following time. But, how many of these structures exist in the fluid at a fixed time? This is the problem. And now the life-time is involved in such a way that you can also select a very small region of the fluid, and follow it during time obtaining the same answer.

WIDOM

Yes. I'm in entire agreement with you, Dr. RICCI. You can see, in precisely the way you mentioned last, how one could have restated all this in terms of the time. Instead of allowing this test molecule to wander, we'll hold the test molecule fixed and we'll allow the fluid molecules to take up configurations that they would even in the absence of the test molecule. Don't let it disturb the

fluid. Let it be only a measurer. Hold the test molecule fixed at a point and then make this a time average instead of an average over space. And they will be entirely equivalent, this being essentially the ergodic property of statistical mechanics. So I'm agreeing entirely with your remark.

CHAGAS

Are there any other questions? I thank Dr. VERWEY for his presentation, and also for the interest that the members of our group have shown to his paper.

SOME PROPERTIES OF THE HYDROGEN BONDS IN BIOCHEMISTRY WITH PARTICULAR REFERENCE TO THE STABILITY OF THE GENETIC CODE

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I. INTRODUCTION

During the last three decades, there has been a very strong tendency towards the unification of all the natural sciences: physics, chemistry, and biology. After the discovery of modern quantum theory in 1925, physics and chemistry were unified in 1928 through the quantum-mechanical explanation of the nature of the covalent chemical bond by HEITLER and LONDON [1] leading to the development of quantum chemistry. In cellular biology, most of the important achievements have been obtained by considering the cells as huge chemical and physical systems subject to the ordinary laws of chemistry and physics, which has lead to the development of biochemistry and biophysics. In the recent development, more and more emphasis has been put on the fundamental molecular structure of the living systems and on the detailed electronic and protonic structure of the molecules involved leading to the development

of molecular and submolecular biology [2]. The electrons and protons are fundamental particles which do not obey the laws of classical physics but the laws of modern quantum mechanics, and the detailed structure of the biologically interesting molecules has hence to be treated by quantum chemistry which has lead to the opening of a new field which should perhaps be called « quantum biology ». In describing nature in terms of a few elementary particles, physics, chemistry, and biology have hence established a common basis, and we note that this unification has become conceivable only through the development of modern quantum theory in addition to and as a consequence of the fundamental experimental discoveries.

It is clear that, also in the biological systems, the question of intermolecular forces must be of essential importance and, in this paper, we will concentrate our interest on a particular link between molecules which is known as the « hydrogen bond ». The fundamental importance of this bond in biology seems to have been first clearly pointed out by PAULING [3] and his associates, who used it to explain the stability of the secondary structure of the proteins in the helical polypeptides. Today it is believed that the hydrogen bond plays a fundamental role in many of the most important aspects of biochemistry, and in this paper we will particularly discuss the properties of the hydrogen bond in connection with questions concerning the structure and stability of the genetic code.

2. STRUCTURE AND STABILITY OF DNA; INTRODUCTION

The development in biology during the last three decades has shown that the genetic message in the chromosomes is contained in a giant molecule called deoxyribonucleic acid (DNA). Of the landmarks of the history of this fascinating discovery we will here mention only GRIFFITH and his genetic

transformation principle in 1928, AVERY, MAC LEOD, and McCARTY and their identification of the compound carrying the transformation and the genetic message with the well-known deoxyribonucleic acid in 1944, CHARGAFF and his pioneering studies of the base contents of DNA in 1950, WILKINS and his X-ray investigations of the stereo structure of DNA in 1953, and finally the Watson-Crick stereo model of DNA in the same year. For a more complete account, we would like to refer the reader to another paper [4]. According to the Watson-Crick [5] model, the DNA molecule is a double helix consisting of two intertwined helical sugar-phosphate chains held together by a sequence of pairs of nitrogen bases joined by hydrogen bonds. There are only four such nitrogen bases involved, namely adenine A, guanine G, thymine T, and cytosine C. Depending on the special structure of these hydrogen bonds, the pairing of the nitrogen bases in DNA is specific according to the scheme A-T, G-C, and each base pair consists of two « complementary » bases. There is strong evidence for believing that the genetic information is contained in the sequence of base pairs along the DNA-molecule or, which is apparently the same, in the sequence of bases along a single strand, i.e. in the form of a « chemical script » of four symbols, e.g. ATTAGCATG... . Even for such a simple organism as *E. COLI*, the script contains about two million « signs ».

Before the cell duplication, the DNA-molecule has to replicate itself and, in this process, the hydrogen bonds are released, the two DNA strands become at least partly free, and each one serves as a template for the formation of a new complementary strand formed from mutation material in the environment, so that two complete DNA molecules with the same base-pair sequence as the original one are produced. The schematic structure of DNA, the rough template character of the base pairs, and the selection of complementary bases at DNA-replication are illustrated in Figs. 1-3, respectively.

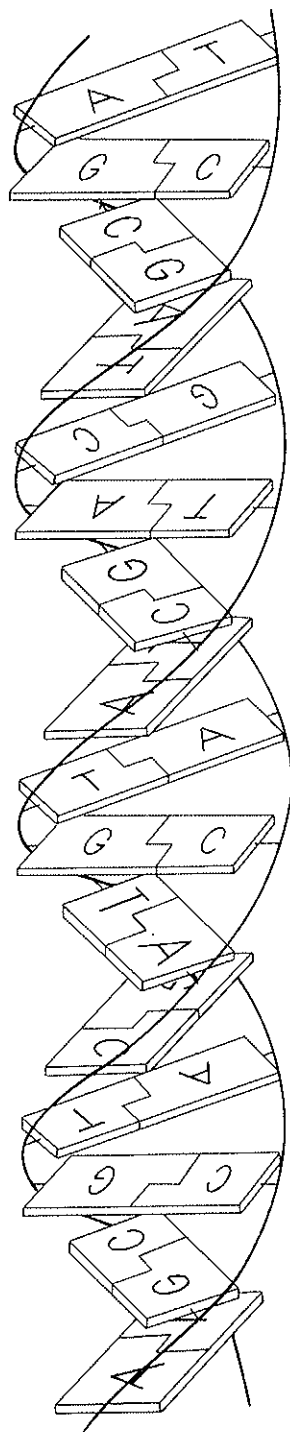


FIG. 1a — Schematic structure of the DNA molecule carrying the genetic code.

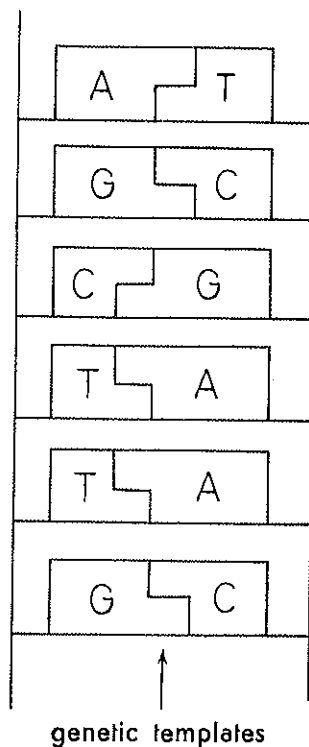


FIG. 1b — The structure of the genetic code unwound. The genetic templates are the surfaces in the middle indicated by the broken lines; they are held together by hydrogen bonds.

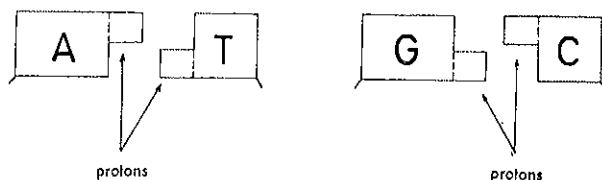


FIG. 2 — Schematic form of the templates formed by the normal bases occurring in DNA.

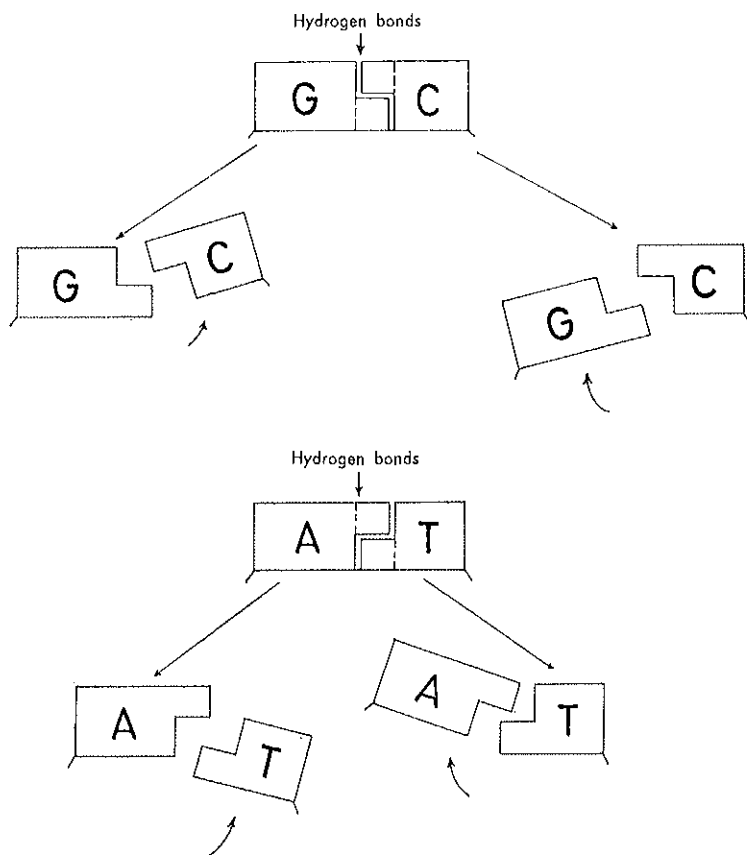


FIG. 3 — Selection of complementary bases at the replication of DNA; curved arrows indicate that the bases come from the environment.

WATSON and CRICK also pointed out that the nitrogen bases may occur in certain rare tautomeric forms A^* , T^* , G^* , and C^* , which have another pairing scheme A^*-C , G^*-T , etc. depending on the change of the template; see Fig. 4. Incorporation of these tautomeric forms may then cause errors in the genetic code leading to mutations; see Fig. 5.

The template idea of the genetic code may to a certain extent be tested by treating DNA with certain chemicals which change the template in a specific way, as e.g. nitrous acid. This compound causes an « oxidative deamination » of the bases which influences the template, so that, for instance, adenine goes over into hypoxanthine with a guanine-like template. It turns out that nitrous acid, as well as other compounds with a similar template effect, are strong mutagens [6].

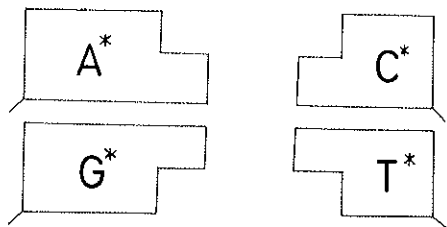


FIG. 4 — Schematic form of the templates of the rare tautomeric forms of the bases occurring in DNA.

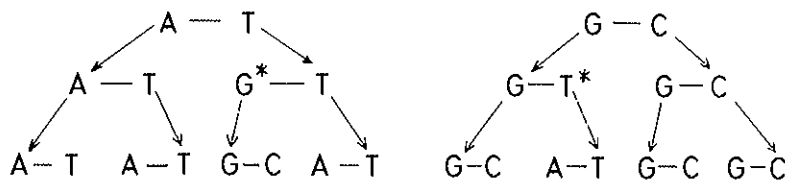


FIG. 5 — Effect of incorporation errors; note that diagrams are only very schematic, and that the processes in reality are considerably more complicated (see also Fig. 30).

The Watson-Crick model of DNA, the complementarity concept, and the template idea have been of fundamental importance in the recent development of biochemistry and medicine. Even if these ideas have been almost universally accepted, they have also been criticized by some prominent scientists who have questioned whether the template really has such physical and chemical properties that it explains the enormous stability of the genetic code over thousands and thousands of years. COMMONER [7] has expressed the opinion that, at the normal temperature of the human body ($T=310^{\circ}$ K), the thermal disturbances of the order $kT=0,03$ eV are enough to destroy in the long run any perfect order of electrical charges in the template, and that any theory of the stability of the genetic code has to take this fact into account. HEITLER [8] — one of the fathers of quantum chemistry — chose in 1964 the DNA-replication as an example of a biological process which has such an enormous accuracy that it can hardly be understood on the basis of the present laws of physics and chemistry.

The problem of the occurrence of incorporation errors in the DNA replication (see Fig. 5) was further emphasized by some recent measurements of the tautomeric equilibrium constants of some of the nitrogen bases by KATRIZKY and WARING [9] which indicated that somewhat less than 1% of the « short » bases may occur in the rare tautomeric forms.

This implies that, since a DNA molecule usually consists of more than a million base pairs, there may be several hundred tautomeric errors per replication. Experience tells us, however, that the replication mechanism is remarkably exact, and that such a large number of incorporation errors in some way is avoided.

It is hard to give reliable figures for the internal stability of DNA or for the over-all accuracy at a DNA-replication. After careful studies of experimental mutation rates, FREESE [10] has found that the probability for a spontaneous error per

base pair and generation should be in the range 10^{-8} to 10^{-10} , which means that spontaneous mutations are exceedingly rare events and that the genetic code has a most unusual internal and replication stability.

Since the Watson-Crick model is of such a fundamental importance, the author felt that it may be worthwhile to investigate the problem of the stability of the genetic code as expressed in the template idea in greater theoretical detail. A preliminary study [11] of the problem showed that there is an additional element of instability in the hydrogen bonds themselves. In classical chemistry, a hydrogen bond is a hydrogen atom simultaneously attracted to two electronegative atoms, but, in modern terminology, a hydrogen bond is a proton shared between two electron lone pairs. Each electron pair gives rise to a potential well for the proton, and the proton is hence usually situated in a « double-well » potential with two classical equilibrium points. The proton may jump from one of these equilibrium positions to the other by going over the potential barrier between them [12], or it may move through the barrier by means of the quantum-mechanical tunnel effect as emphasized by the author [11]. If a proton changes place, it may cause another proton to move to keep the gross electric neutrality, and the total effect will be a change of the genetic templates which is equivalent to an internal tautomeric shift; see Figs. 6 and 7. This effect is temperature dependent and, at $T = 310^{\circ}\text{K}$, this proton transfer above or through the barrier may be a very important source of error which may greatly disturb the stability of the genetic code. In our study, it seemed hence necessary to take the possibility of such proton jumps into full account.

Theoretical investigations of the stability of the genetic code have been carried out at the Quantum Chemistry Group of Uppsala University during the last three years. Even if the results I can report here are only of a preliminary nature, they are still highly favourable in the sense that they indicate



FIG. 6 — Internal tautomeric shift in a base pair in DNA through proton exchange by means of the quantum-mechanical tunnel effect or above the barrier.

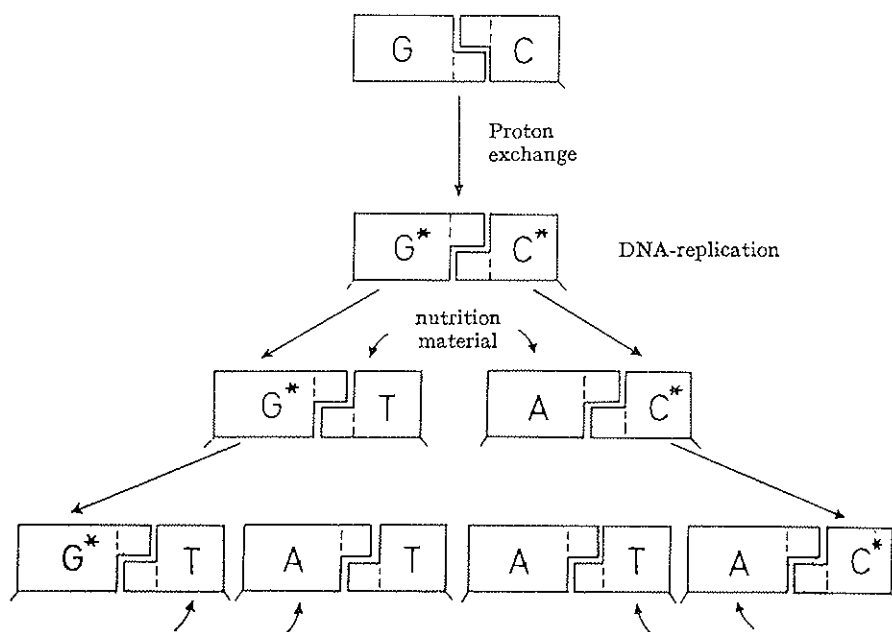


FIG. 7 — Formation of rare base pairs through proton exchange and the associated replication scheme.

that the genetic code in the Watson-Crick model seems to have enough long-time stability to correspond to the experimental experience.

It should perhaps be pointed out that our main problem has not been to find new mutation mechanisms but to explain *why spontaneous mutations as a whole are as rare as they are*, in spite of all possible disturbances of the genetic code. In this connection, we believe that we have clarified at least some of the possible mechanisms for spontaneous mutations as well as some specific models for induced mutations caused by radiation or the influence of specific chemicals. All theoretical results obtained so far confirm the template idea and the importance of the hydrogen bonds in storing and transferring the genetic information.

3. THEORETICAL ANALYSIS OF THE CHARACTER OF THE GENETIC CODE

In the previous section, we have only indicated the genetic template in a very crude way, and it is now desirable to analyze it in greater detail. The nucleic acids were discovered by MIESCHER in 1868, and their chemical structure had been revealed by skilful chemical methods by HAMMARSTEN, TODD, CASPERSSON, and many others [13] long before one had realized their fundamental importance in genetics. It had been found that they consisted of sugar-phosphate chains to which there were four nitrogen bases (A, G, T, C) attached. In the « tetranucleotide hypothesis », it was assumed that these bases occurred repeatedly in a regular order, but CHARGAFF could show that this is not the case and that, for DNA, one has only the rule $[A]=[T]$, $[G]=[C]$ for the molar contents. In the Watson-Crick model of DNA, the nitrogen bases may occur in an arbitrary order corresponding to the « genetic

script », and the Chargaff rule forms the essential experimental basis for the specific base pairing A-T, G-C in linking two chains together in the double helix.

The stereostructure of DNA is illustrated in Figs. 8 and 9. We will here particularly emphasize the nature of the hydrogen bonds, and we note that the A-T pair has two and the G-C pair three such bonds consisting of hydrogen atoms shared between the electronegative atoms nitrogen and oxygen in the combinations $\text{NH} \dots \text{N}$ or $\text{NH} \dots \text{O}$.

In order to proceed, it is necessary to study these hydrogen bonds in greater detail, and we will then also consider their electronic structure. According to LEWIS, it is convenient to let a chemical symbol denote the atomic nucleus plus the electronic rare-gas shell and indicate the valence electrons with additional dots. In this notation, the symbol H means hence

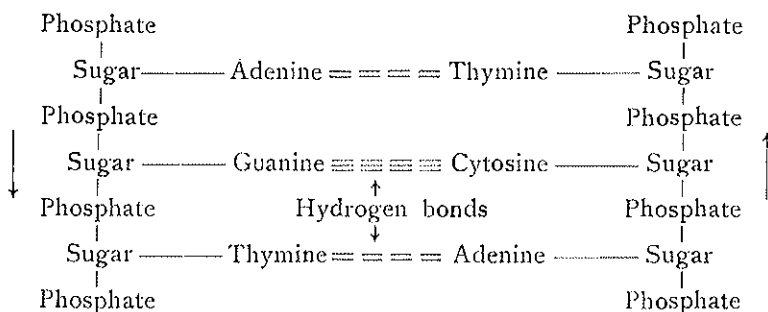
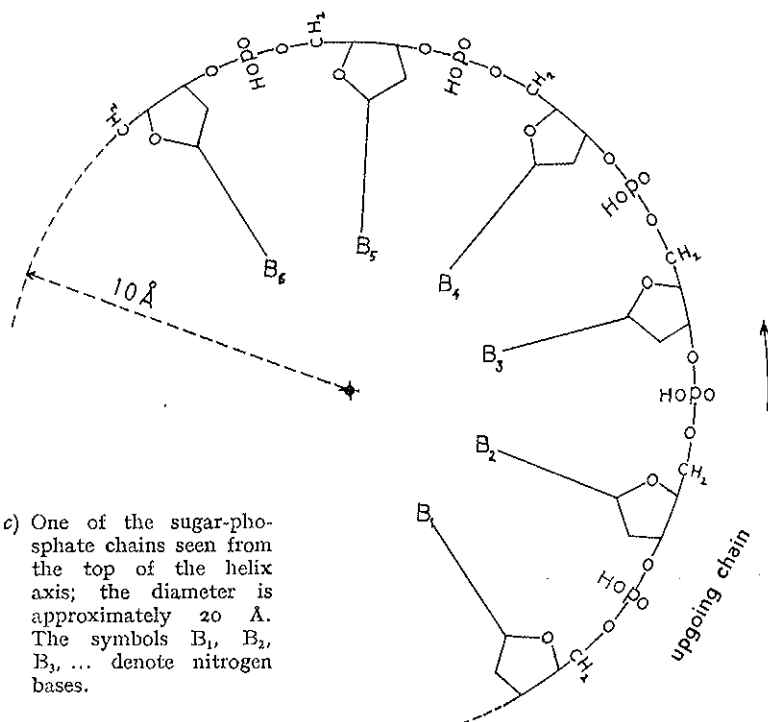
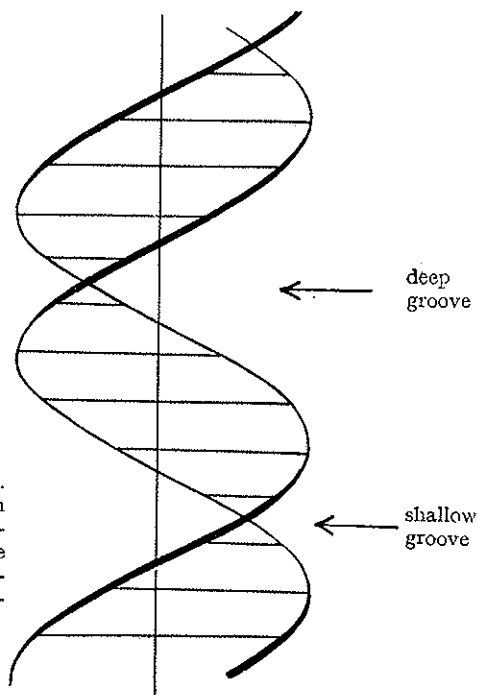


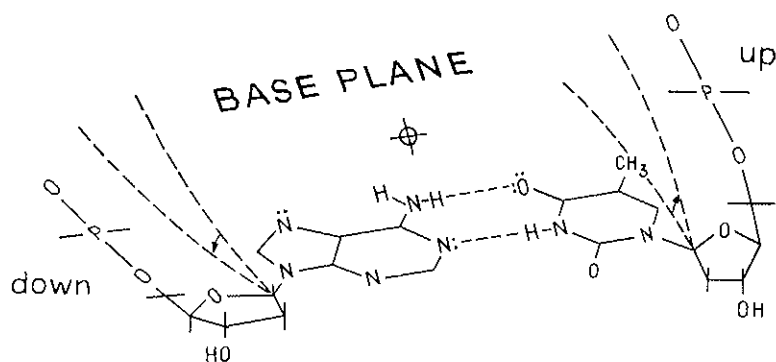
FIG. 8 — Schematic structure of DNA:

a) Linear representation of the DNA molecule.

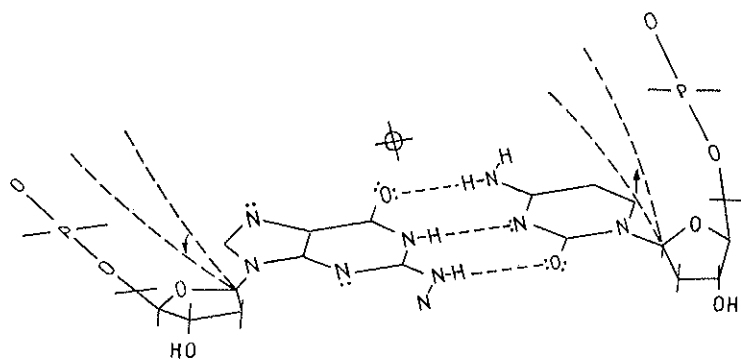
- b) Double helix of DNA.
Note that there are ten base pairs per full revolution, and that the distance between neighbouring base pair planes is 3.4 Å.



- c) One of the sugar-phosphate chains seen from the top of the helix axis; the diameter is approximately 20 Å. The symbols B₁, B₂, B₃, ... denote nitrogen bases.



(a)

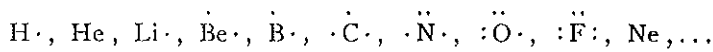


(b)

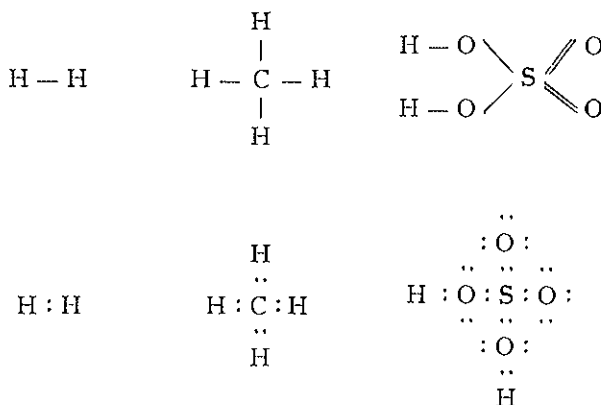
FIG. 9 — The normal base pairs in DNA:

- a) A-T base pair with two hydrogen bonds.
 b) G-C base pair with three hydrogen bonds.

a *proton*, whereas the hydrogen atom is denoted by H. For the lightest elements, one obtains the notations:



LEWIS also observed in 1916 that, in a chemical compound, each covalent bond was in some way associated with an *electron pair*: shared between the two atoms linked by the bond, for instance:



The deeper explanation of this bond was later given by quantum-mechanical methods by HEITLER and LONDON [1]. Each bond has further a particular direction, and this directional property was treated quantum-mechanically by the idea of orbital hybridization introduced independently by SLATER [14] and PAULING [15] in 1932. An atomic *s*-orbital is spherically symmetric around the nucleus, whereas a *p*-orbital

has an angular distribution in the form of dumb-bell consisting of two spheres with different signs; see Fig. 10. By a superposition of an s -orbital and a p_k -orbital, one obtains a hybrid

$$(1) \quad h = \alpha s + \beta p_k, \quad (\alpha > 0, \beta > 0)$$

which has its maximum electron density in the k direction. The normalization gives $\alpha^2 + \beta^2 = 1$, and the ratio $n = \beta^2 / \alpha^2$ is often used to characterize the hybrid which is given the symbol sp^n . We note further that the geometrical angle θ_{12} between two hybrid sp^{n_1} and sp^{n_2} is given by the formula [16]

$$(2) \quad \cos \theta_{12} = - (n_1 n_2)^{-1/2},$$

giving the connection between the geometrical structure of the molecule and the amount of hybridization of various bonds. We note finally that, if one has four hybrids characterized by the numbers n_1, n_2, n_3 , and n_4 , one has the additional relation $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 + \alpha_4^2 = 1$, since the total amount of s character has to be used up by the hybrids. This gives the auxiliary condition:

$$(3) \quad (n_1 + 1)^{-1} + (n_2 + 1)^{-1} + (n_3 + 1)^{-1} + (n_4 + 1)^{-1} = 1.$$

The carbon atom in the methane molecule CH_4 is characterized by four equivalent valence arms having $n=3$ and the hybridization sp^3 . On the other hand, the carbon atom in the benzene molecule C_6H_6 has three equivalent valence arms in

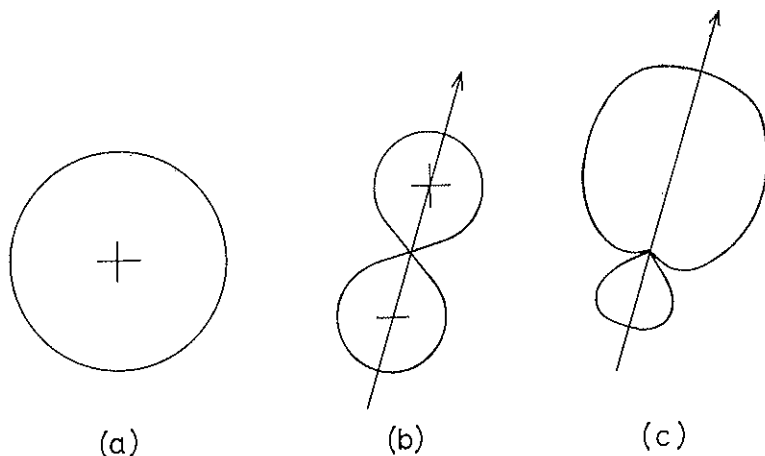


FIG. 10 — Schematic diagrams of angular distributions of various orbitals:
(a) s -orbital, (b) p -orbital and (c) hybrid.

a plane forming an angle of 120° with each other, and application of (2) gives then $n=2$ and the hybridization sp^2 . For the fourth hybrid, one obtains according to (3) that $n_4=\infty$, which means that this hybrid is a pure p -orbital perpendicular to the molecular plane; see Fig. 11. The benzene molecule contains a total of $6 \times 4 + 6 = 30$ valence electrons, of which 24 are contained in the 12 single bonds in the σ -skeleton formed by the sp^2 hybridized orbitals, whereas 6 are assigned to the so-called π -electron cloud associated with the six pure $2p_z$ -orbitals. According to the new ideas developed by HÜCKEL [17] in 1931-1932, one may construct six molecular orbitals associated with the benzene ring by linear combination of the six atomic $2p_z$ -orbitals, perpendicular to the ring, and the six π -electrons are then assigned to the three molecular orbitals having the lowest energy with two electrons in each. There are hence three empty molecular π -orbitals, and there is a considerable

energy gap between the highest occupied orbital and the lowest empty orbital.

This quantum-mechanical picture gives an excellent explanation of the saturated character of the benzene molecule and its aromatic properties. The Hückel scheme with mobile π -electrons around the ring replaces thus the classical chemical picture with alternating single and double bonds. This model

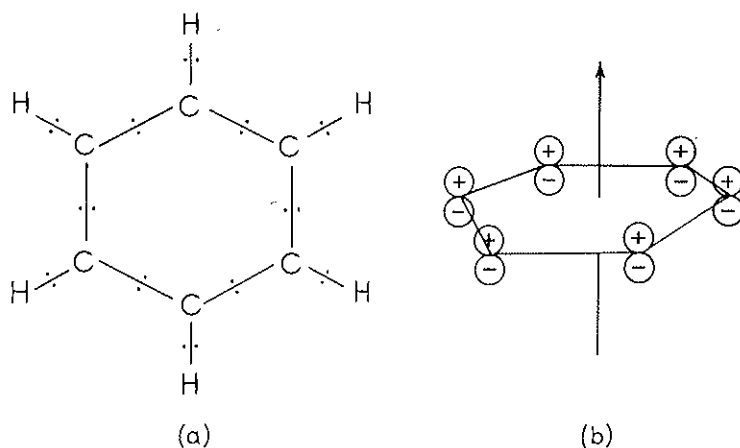


FIG. 11 — Electronic distribution in the benzene molecule C_6H_6 :
(a) σ -skeleton, (b) π -electron cloud.

holds not only for the benzene molecule but for the conjugated systems in general, and we will in the following deal with such a system by considering the σ -skeleton formed by the single bonds in the plane of the molecule and with the π -electron cloud replacing the classical double bonds.

This separation of the electrons into two groups is very important also for the analysis of the character of the genetic code. In order to approach this problem, we will now carry

out a thought experiment consisting of dropping one of the protons in the benzene ring in Fig. 11 into the neighbouring carbon nucleus giving rise to a nitrogen nucleus; see Fig. 12. This leads to the formation of a pyridine molecule characterized by having an *electron lone pair* sitting in a sp^2 hybrid on the nitrogen atom, and this lone pair will attract every proton or positive group in the neighbourhood. This tendency of pyr-

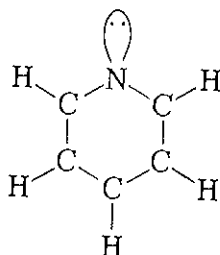


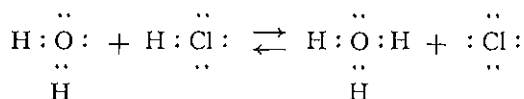
FIG. 12 — Pyridine molecule with an electron lone pair on the nitrogen atom pointing out from the ring.

idine to try to catch a proton and become a pyridinium ion $C_5NH_6^+$ gives it a characteristic « base » character.

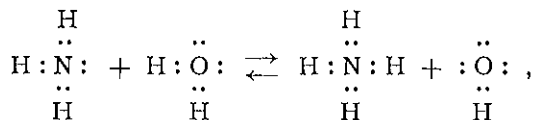
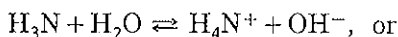
In general, protons are usually attached to molecules by means of electron pairs and, in many cases, the bonding is so strong that it is very hard to remove the protons. According to LEWIS, however, there is a very important class of chemical compounds in which the easy removal or attachment of protons is one of the fundamental chemical properties, namely the acids and the bases. They are characterized by the reaction:



The main feature of the base is hence that it has at least one *electron lone pair* available, and the hybridization theory gives a much better understanding of the properties of localized electron pairs than was possible before modern quantum theory. An acid is characterized by having « loose » protons which are more or less easily removed. There are also molecules which like water are both proton donors and acceptors, and one and the same molecule may hence have both properties. An electrolytic dissociation of the type $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ is much better understood if one considers the fact that it occurs when hydrogen chloride is dissolved in water, and that a molecule of the latter steals a proton from a molecule of the former, so that $\text{H}_2\text{O} + \text{HCl} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$, or



The hydrogen chloride HCl is hence a proton donor or a Lewis acid, and we note that the hydronium ion H_3O^+ is here a very natural consequence of the hybridization theory. For the dissociation associated with the solution of ammonia H_3N in water, one has similarly



which means that H_3N is a proton acceptor or a Lewis base.

A very interesting phenomenon occurs in a liquid or solid system of molecules having free electron lone pairs, since there will then be a competition between the molecules to catch any available free or loose protons in the environment. If two molecules through their electron lone pairs are attracted to one and the same proton, the molecules are said to be joined by a *hydrogen bond*. In modern terminology, a hydrogen bond is hence a link between two molecules which consists of a *proton shared between two electron lone pairs*. A hydrogen bond between two pyridine molecules is illustrated in Fig. 13.

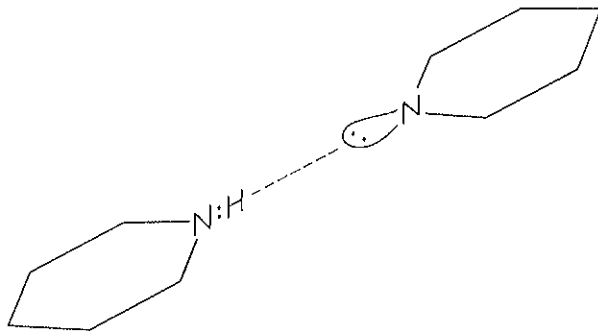


FIG. 13 — Hydrogen bond between two pyridine molecules consisting of a proton H shared between two electron pairs.

A hydrogen bond is a comparatively weak chemical bond having a binding energy of the order 6-12 kcal/mole. It is of fundamental importance in ordinary chemistry as well as in biochemistry, and here we will study its properties in connection with DNA and the genetic code.

The genetic code as a proton-electronpair pattern. — Let us now consider the hydrogen bonds between the base pairs in DNA and resolve the two hydrogen bonds in the adenine-thym-

ine pair and the three hydrogen bonds in the guanine-cytosine pair into their proton and electronpair components. From the chemical structures in Fig. 9, we obtain the results indicated in Fig. 14, which imply that the genetic code consists of a pattern of elementary particles, and that each base has a char-

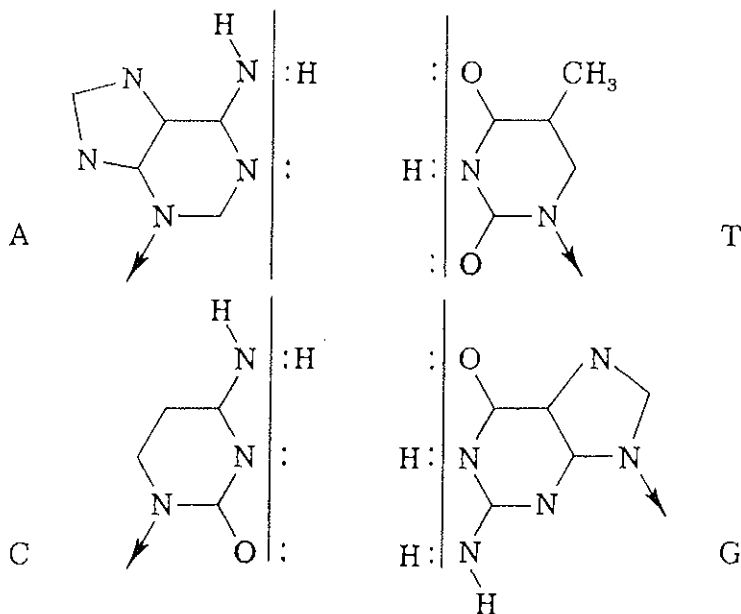


FIG. 14 — The hydrogen bonds between the normal base pairs in DNA resolved into their proton-electronpair components; note that here H denotes a proton and the symbol : an electron pair according to Lewis.

acteristic template consisting of protons and electronpairs as outlined in Fig. 15. These detailed patterns may now be compared with the schematic templates used in the introductory part in Fig. 2.

If a proton is moved from its normal electronpair to a free

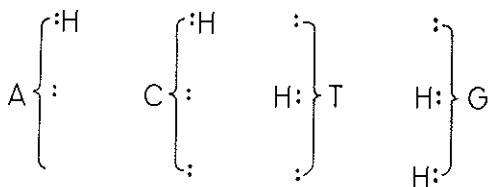


FIG. 15 — The proton-electronpair code of the normal nitrogen bases; compare the schematic templates in Fig. 2.

electronpair within the same template, one obtains a tautomeric form which may be important as a possible cause of errors in the DNA replication mechanism. The proton-electronpair codes of these tautomeric forms are outlined in Fig. 16, and they should be compared with the schematic templates illustrated

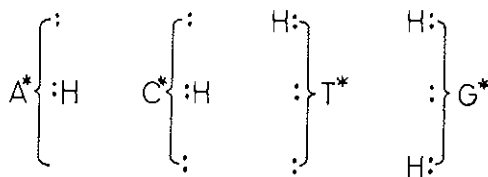


FIG. 16 — The proton-electronpair code of some rare tautomeric forms of the nitrogen bases; compare the schematic templates in Fig. 4.

in Fig. 4. There are, of course, many other tautomers which may be of importance in other connections, but we will here limit our discussion to the main forms listed in Fig. 16.

It is perhaps somewhat surprising that the genetic code ultimately consists of a rather simple combination of elementary particles, and we will now show that this may have important consequences.

Hydrogen bond as a double-well potential; tunnel effect

Each electron pair in a hydrogen bond attracts the proton, and this attraction may physically be described as a potential well with a specific minimum representing the classical equilibrium position of the proton. Since there are two electron pairs involved, the proton in a hydrogen bond feels a potential which is the superposition of two single-well potentials with different minima and which is hence usually a *double-well potential*; see Fig. 17. The two minima in this potential are



FIG. 17 — Typical double-well potentials felt by a proton in a hydrogen bond; the left-hand potential is symmetric, and the right-hand potential is asymmetric.

usually not of the same height, but we will discuss both the symmetric and asymmetric case. In classical physics, a particle would stay in one of the wells, unless it has sufficient energy to pass the « potential barrier » in the form of the maximum separating the two minima.

In modern physics, the circumstances are rather different since the proton is an elementary particle which obeys the laws of quantum theory and may be described as a « wave packet » having the ability to penetrate also into classically forbidden regions. This phenomenon is an immediate consequence of

SCHRÖDINGER's wave equation, and it implies that, if two classically permitted regions are separated by a potential barrier leading to a classically forbidden region, an elementary particle may penetrate the classically forbidden region from one permitted region to another; see Fig. 18. This so-called *tunnel effect* was discovered independently by GAMOW [18] and by GURNEY and CONDON [19] in 1928-29 in explaining the general phenomenon of radioactivity which involves the escape of certain particles through nuclear potential barriers. The tunnel effect is now a well-known phenomenon in physics, as e.g. in the predissociation of molecules in molecular spectroscopy, in the ammonia clock, in the tunneling diodes, in corrosion, etc.

The tunnel effect is treated in most textbooks in quantum theory. The probability that the wave packet will pass the potential barrier upon hitting it is called the transmission coefficient g , and this quantity is given approximately by the formula:

$$(4) \quad \begin{aligned} g &\approx e^{-2K}, \\ K &= \frac{2\pi}{h} \int_{x_1}^{x_2} \{ 2m [E - V(x)] \}^{1/2} dx, \end{aligned}$$

with the notations used in Fig. 18; m is the mass of the particle, and h is Planck's constant.

It is instructive to start with the problem of *tunneling out of a single well*; see Fig. 18. The particle is from the very beginning in the left-hand well, where it oscillates with the frequency ν_1 and hits the barrier ν_1 times per second. It is convenient to introduce the notations

$$(5) \quad c_1 = \nu_1 g, \quad \tau_1 = 1/c_1 = 1/\nu_1 g,$$

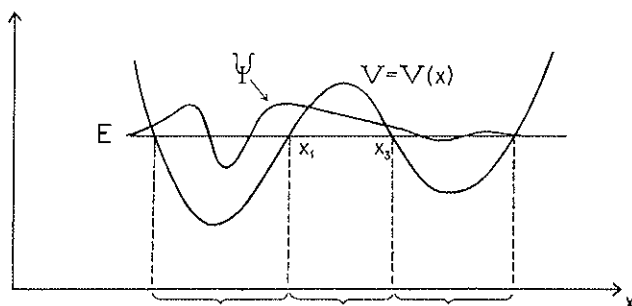


FIG. 18 — Tunneling of a wave packet through a classically forbidden region; transmission coefficient $g \approx \exp(-2K)$ according to formula (4).

and c_1 will be called the « tunneling rate » and τ_1 the « tunneling time » with a physical meaning which will be described below. In our applications, the transmission coefficient g will be very small, so that $g \ll 1$.

At every hit of the wave packet, the population in a particular energy level of the left-hand well will be decreased by a factor $(1-g)$, and, after p hits, the decrease will hence be described by the factor $(1-g)^p$. If the energy level population is originally a_1 , the population after t secs will thus be

$$(6) \quad n_1(t) = a_1 (1-g)^{[c_1 t]},$$

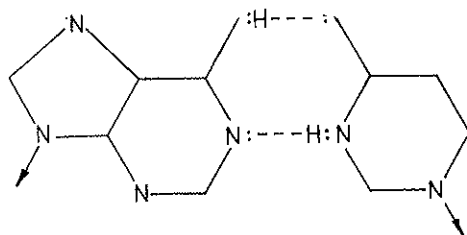


FIG. 19 — Typical base pairing through hydrogen bonds in DNA.

which is a step function. However, if the transmission coefficient g is sufficiently small, the quantity $(1 - 1/g^{-1})^{1/g}$ may be approximated by the number e^{-1} , which leads to the « smeared out » formula:

$$(7) \quad n_1(t) = a_1 \left\{ (1 - 1/g^{-1})^{1/g} \right\} g^{(v_1 t)} \approx a_1 e^{-c_1 t}$$

This means that the step function may be replaced by a function with a continuous derivative satisfying the simple differential equation:

$$(8) \quad \frac{dn_1}{dt} = -c_1 n_1,$$

The part of the population which has passed the barrier during the time t is hence:

$$(9) \quad n_3(t) = a_1 (1 - e^{-t/\tau_1}).$$

The « tunneling time » τ_1 is the time requested for the original population to decrease by a factor e^{-1} and, for very small times $t \ll \tau_1$, one may use the linear relation $n_3(t) \approx a_1 t / \tau_1$.

In order to get an idea of the tunneling times for various potential barriers, we have in Table I tabulated τ_1 as a function of the barrier width a_0 (in Å) and barrier height V_0 (in eV) for a parabolic barrier for a proton and a deuteron under the assumption that the proton frequency in the well is approximately $\nu_1 = 10^{13} \text{ sec}^{-1}$. The quantity τ_1 turns out to be a function of the parameter $\chi_0 = a_0 \sqrt{V_0}$, which varies from $\tau_1 = 10^{-13} \text{ sec}$ for $\chi_0 = 0$ to $\tau_1 = 3 \times 10^9 \text{ years}$ for $\chi_0 = 2$; the latter time cor-

TABLE I. — *Tunneling times τ_1 for the proton and the deuteron as functions of the barrier width a_0 (in Å) and barrier height V_0 (in eV).*

$a_0/\sqrt{V_0}$	Proton τ_1	Deuteron τ_1
0	10^{-13} sec	10^{-13} sec
0.1	$10^{-11.5}$ sec	10^{-11} sec
0.2	10^{-10} sec	10^{-9} sec
0.3	$10^{-8.5}$ sec	10^{-6} sec
0.4	10^{-7} sec	10^{-4} sec
0.5	$10^{-5.5}$ sec	10^{-2} sec
0.6	10^{-4} sec	1.3 sec
0.7	10^{-2}	2 min
0.8	10^{-1}	3.7 hrs
0.9	3 sec	20 days
1.0	2 min	8 years
1.1	53 min	10^3 years
1.2	1.16 days	1.3×10^5 years
1.3	1.22 months	1.7×10^7 years
1.4	3 years	2.2×10^9 years
1.5	100 years	
1.6	3000 years	
1.7	10^5 years	
1.8	3×10^6 years	
1.9	10^8 years	
2.0	3×10^9 years	

responds to the age of the universe according to the modern estimates just presented here in Dr. SANDAGE's lecture.

If the thermal equilibrium is quickly reached in the left-hand well, the population will assume a Boltzmann distribution over the various energy levels proportional to the Boltzmann factor $B = \exp \{ -\Delta V/kT \}$. The Boltzmann factor is tabulated in Table II for three typical temperatures: $T = 273^\circ\text{K}$, 310°K , and 373°K .

After these preparations, we will now study the tunneling in a double-well potential, in which case particular attention has to be devoted to the question of « back-tunneling » from the more shallow to the deeper well. Let us assume that initially at the time $t=0$, the particle is entirely in the left-hand well having the part $a_1(E)$ of its population in a specific energy level E with the transmission coefficient $g=g(E)$. If $n_1=n_1(t)$ and $n_3=n_3(t)$ denote the parts of the population in this level at time t in the two wells, respectively, one obtains by generalizing (8) a system of differential equations:

$$(10) \quad \begin{cases} \frac{dn_1}{dt} = -c_1 n_1 + c_3 n_3, \\ \frac{dn_3}{dt} = c_1 n_1 - c_3 n_3, \end{cases}$$

where $c_1 = \nu_1 g$ and $c_3 = \nu_3 g$ are the rates for tunneling in the two opposite directions. The initial condition $n_1(0) = a_1$, $n_3(0) = 0$ corresponds to the solution

$$(11) \quad \begin{aligned} n_1(t) &= \frac{c_3 a_1}{c_1 + c_3} + \frac{c_1 a_1}{c_1 + c_3} e^{-(c_1 + c_3)t}, \\ n_3(t) &= \frac{c_1 a_1}{c_1 + c_3} - \frac{c_1 a_1}{c_1 + c_3} e^{-(c_1 + c_3)t}. \end{aligned}$$

TABLE II. — Boltzmann factors $B = \exp \{ -\Delta V/kT \}$ for three temperatures T as functions of ΔV (in eV).

V	T = 273°K $^{10}\log B$	T = 310°K $^{10}\log B$	T = 373°K $^{10}\log B$
0	0	0	0
0.1	— 1.846	— 1.626	— 1.351
0.2	— 3.692	— 3.252	— 2.702
0.3	— 5.538	— 4.878	— 4.053
0.4	— 7.384	— 6.504	— 5.404
0.5	— 9.230	— 8.130	— 6.755
0.6	— 11.076	— 9.756	— 8.106
0.7	— 12.922	— 11.382	— 9.457
0.8	— 14.768	— 13.008	— 10.808
0.9	— 16.614	— 14.634	— 12.159
1.0	— 18.460	— 16.260	— 13.510
1.5	— 27.690	— 24.390	— 20.265
2.0	— 36.920	— 32.520	— 27.020
2.5	— 46.150	— 40.650	— 33.775
3.0	— 55.380	— 48.780	— 40.530
3.5	— 64.610	— 56.910	— 47.285
4.0	— 73.840	— 65.040	— 54.040
4.5	— 83.070	— 73.170	— 60.795
5.0	— 92.300	— 81.300	— 67.550

The time $\tau_{1,3} = (c_1 + c_3)^{-1}$ may be denoted as the relaxation time characteristic for the double-well potential. For small times, $t \ll \tau_{1,3}$, the tunneling part of the population is given by the formula:

$$(12) \quad n_3 \approx a_1 c_1 t - a_1 c_1 (c_1 + c_3) \frac{t^2}{2!} + \dots,$$

where the linear term is associated with only left-right tunneling, and the quadratic term shows also the first effect of the « back-tunneling ».

For $t \gg \tau_{1,3}$, the solutions have an entirely different character, since $n_1(t)$ and $n_3(t)$ quickly approach the constant values:

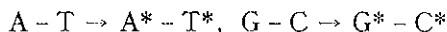
$$(13) \quad n_1 = \frac{v_3 a_1}{v_1 + v_3}, \quad n_3 = \frac{v_1 a_1}{v_1 + v_3},$$

which are essentially independent of the value of the transmission coefficient g . The quantities (13) correspond to an equilibrium situation, in which one has $v_1 n_1 = v_3 n_3$. In this case, the system is approaching a thermal equilibrium over the energy levels of the double well with the population of each level divided into the fractions $v_3 : v_1$ over the two separate wells. These results imply that, in a first approximation, the final distribution of the particle population is independent of the particle mass m . This similarity between the proton and the deuteron for $t \gg \tau_{1,3}$ has to be remembered in interpreting such mutation experiments as are aimed at studying the tunneling phenomena in general by using deuterated organisms [20].

Spontaneous proton tunneling in DNA. — Let us now consider a DNA molecule in its stable form during a period when

it is biologically inactive, so that the genetic message is not undergoing replication or transcription. According to Fig. 14, one can express the essential properties of the base pairing through hydrogen bonds as shown in Fig. 19.

Even if the double-well potentials in the hydrogen bonds are rather asymmetric, one can expect that there will always be a small probability for proton transfer in each bond through (and above) the potential barrier in accordance with the results discussed previously. If the two bases are originally equally charged, the tunneling of one proton in one direction will very likely induce a tunneling of the other proton in the reverse direction to keep balance between the gross electric charges. This « simultaneous » proton exchange hence implies the base transitions:



which lead to the production of pairs of tautomeric bases. If the hydrogen bonds are released in this position, the tautomeric forms will lead to errors in the next replication, i.e. to mutations, as indicated in Fig. 6. This means that it is necessary to consider also the possibility of an internal proton exchange in studying the stability of the genetic code in DNA.

The problem is complicated by the fact that, in each base pair, there are at least two hydrogen bonds involved, which means that one has to study the motion and stability of two protons in a four-well potential. Since the movements of the protons will further influence and polarize both the σ and π electron clouds, a complete solution involves a solution of a quantum-mechanical many-body problem. Before treating this problem, we will now first discuss the influence of the incorporation errors on the stability of DNA.

4. STABILITY OF GENETIC CODE AT REPLICATION

In connection with the DNA replication process, WATSON and CRICK [5] suggested that the hydrogen bonds between the base pairs in some way were released, that the two DNA strands become at least partly free, and that each one of them serves as a template for the formation of a new complementary strand formed from nutrition material in the environment, so that two complete DNA molecules with the same base-pair sequence as the original one are produced. However, WATSON and CRICK did not discuss the obviously rather complicated unwinding - winding mechanism involved in this replication, and this problem has later been discussed by many authors [21].

Through the experiments by MESELSON and STAHL [22], TAYLOR [23], YOSHIKAWA and SUEOKA [24], NAGATA [25], and CAIRNS [26], it has been shown rather conclusively that each one of the daughter molecules actually contains one strand from the parent molecule of DNA. As to the unwinding-winding mechanism, one has now essentially adopted the Y-model or « speedometer-cable » model first suggested by DELBRÜCK and STENR [21], and experimental support for this model has also been obtained through Cairn's pictures of the replication process produced by autoradiography [26]. It should be observed, however, that there are still some difficulties in this model associated with the enzymes necessary to build the two new sugar-phosphate chains of different polarity simultaneously, and particularly the work by KORNBERG [27] is of importance in this connection.

Here we will adopt the Y-model as the starting point for our study, and we will particularly focus the interest on the replication zone itself. The results have previously been reported by the author [28] at the Ravello Conference in 1963.

Following a suggestion by CRICK [29], we will assume that the genetic code is opened up to the environment by rotating one of the strands 180° with respect to the axis of the helix; see Figs. 20 and 21. Two new nucleotides may now be added from nutrition material in the environment, so that there are a total

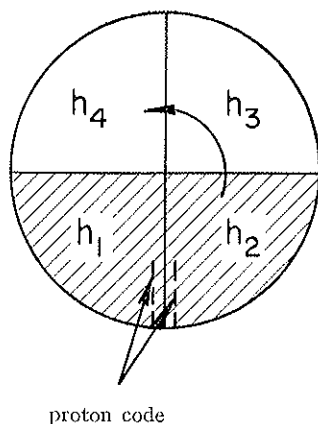


Fig. 20 — Geometry of the base plane in DNA and opening of the genetic code by rotating one strand 180° around the helical axis.

of four nucleotide bases in the replication region which may be characterized as a « replication plane », even if the exact steric conditions may be rather varying. Depending on the attachments to the sugar-phosphate chains, the four bases will in the next stage of the process be separated into two base pairs in such a way that each daughter molecule will get one old base and one new base in complete agreement with the original Watson-Crick model; see Fig. 22.

It is now instructive to study the detailed structure of the « replication plane » consisting of four nucleotide bases, and

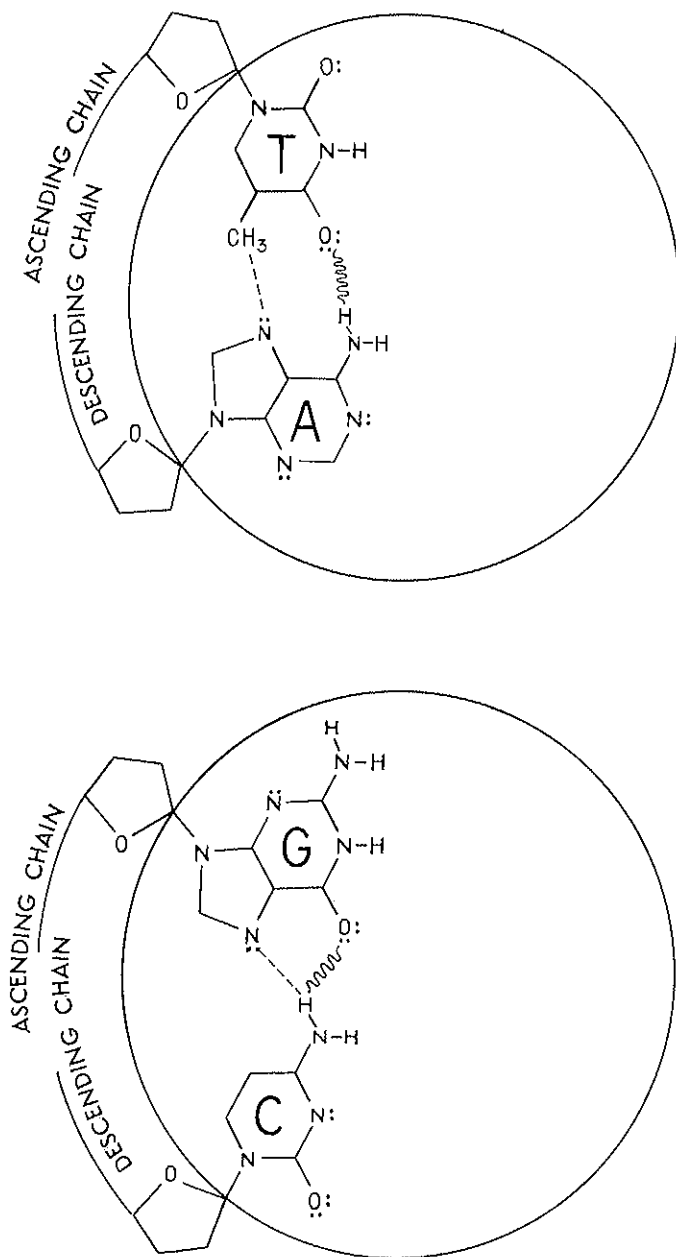


FIG. 21 — Following a suggestion by CRICK, the genetic code may be opened to the environment by rotating one strand 180° around the helical axis; the figure illustrates the two nucleotide base pairs in the « open » position ready for the addition of a pair of complementary bases. The symbol $\sim$ indicates a temporary hydrogen bond.

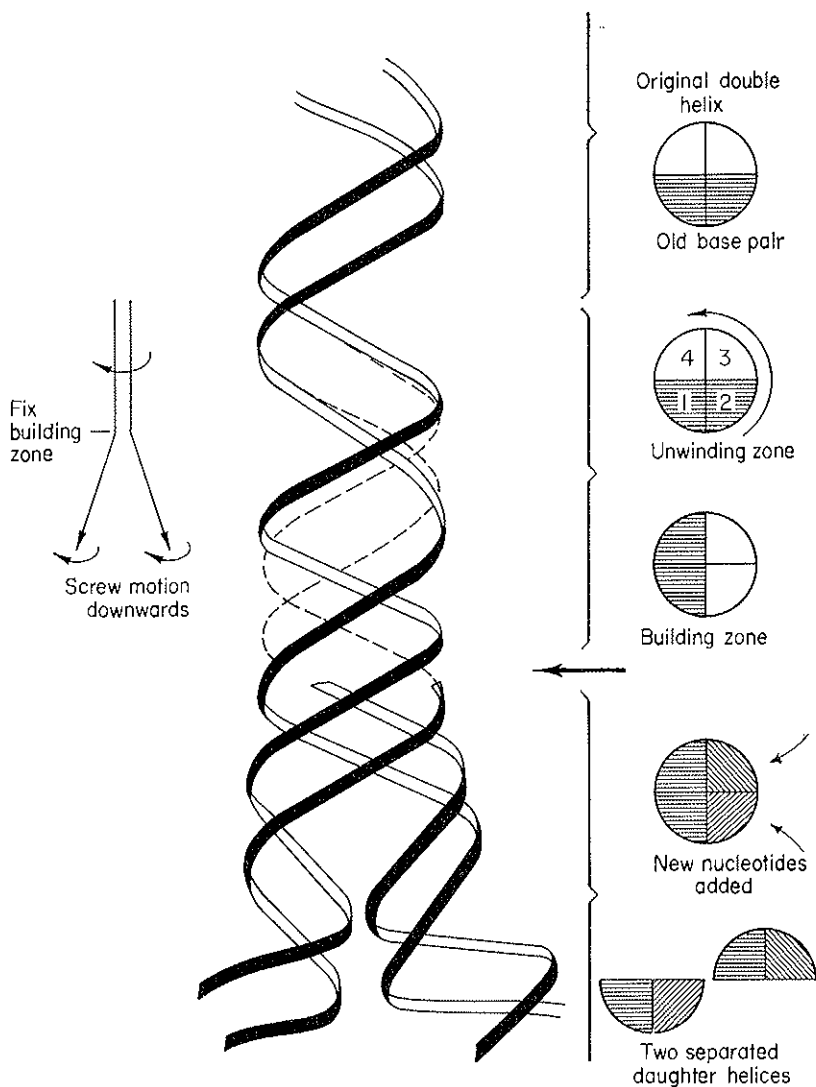


FIG. 22 — Study of the Y-model combined with the idea that the genetic code is opened by rotating one of the strands 180° around the helical axis in the replication zone. Note particularly the occurrence of four nucleotides together in the « replication plane ».

the result is illustrated in Fig. 23. The figures indicate that, in normal replication, the replication plane may be stabilized by at least two temporary hydrogen bonds and that, around the helical axis, one has a *parallelogram* consisting of two amino groups and two keto groups situated in opposite corners.

It is interesting to analyze also the « replication plane » which occurs if one tries to incorporate a rare tautomeric base from the environment; see Fig. 24. The normal hydrogen bonds will fit as before, but we note that, instead of the two temporary hydrogen bonds, one will obtain only one such bond and an antibonding combination in which either two protons or two electron lone pairs will meet. The appearance of the various parallelograms around the helical axis is indicated in Fig. 25. Since a replication plane with a single tautomeric error has an energy which is several electron volts higher than the normal replication plane, the probability for the incorporation of a single rare tautomer is correspondingly small, as may be seen from the Boltzmann factors in Table II.

Actually such a « purification » procedure in the DNA synthesis seems to be strongly needed in order to prevent an excess of incorporation errors, since the tautomeric forms of the nucleotide bases — as we have pointed out before — do not seem to be as « rare » as was originally anticipated. Particularly for some of the pyrimidine bases, the measured equilibrium constants K are comparatively high. For methylcytosine, KENNER [30] et al. has found the value $K=10^{-4.7}$, and, for uracil and bromuracil, KATRIZKY and WARING [30] have found the values $K=10^{-3.3}$ and $K=10^{-1.7}$, respectively. One cannot expect that the nutrition material should necessarily be in tautomeric equilibrium, but the figures give some indications of the orders of magnitude. The occurrence of a « replication plane » in the Y-model of the DNA synthesis may hence be of essential importance for the accuracy of the DNA replication.

In concluding this section, it should be observed that the mechanism of the replication plane does not prevent the incor-

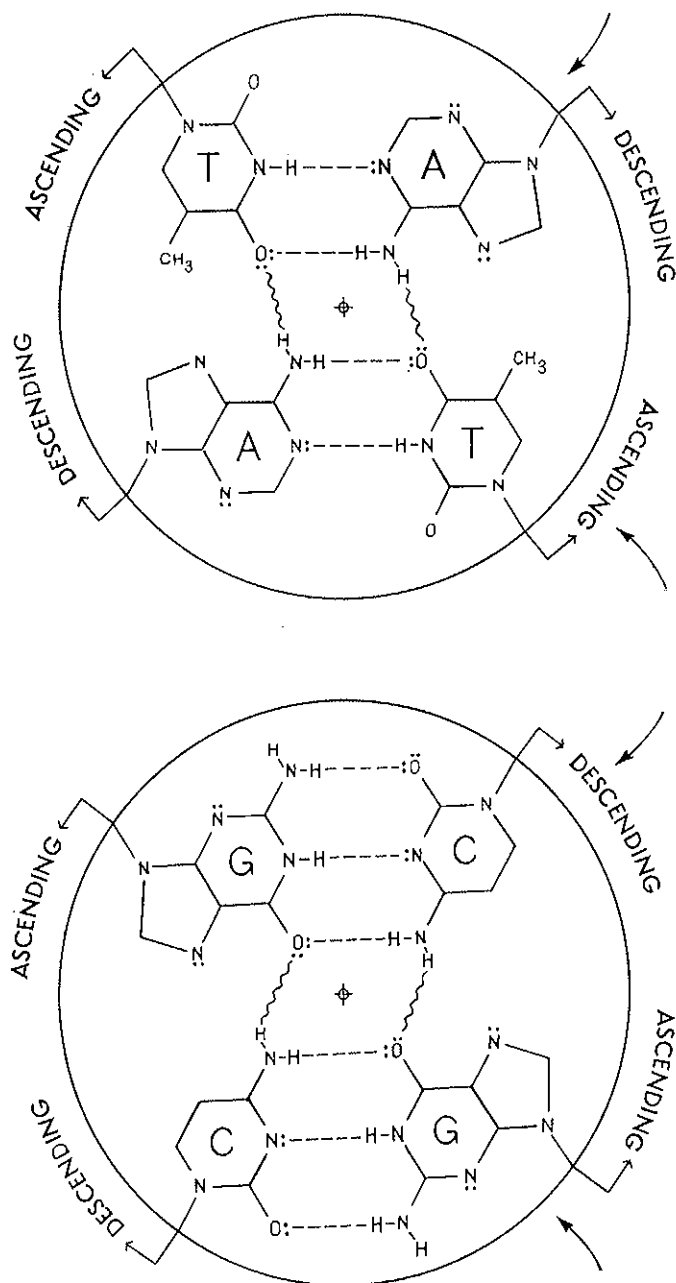


FIG. 23 — The four bases in the « replication plane » after the addition of two new nucleotides from the environment. Note the occurrence of a parallelogram consisting of two aminogroups and two ketogroups around the helical axis and the temporary hydrogen bonds denoted by ~.

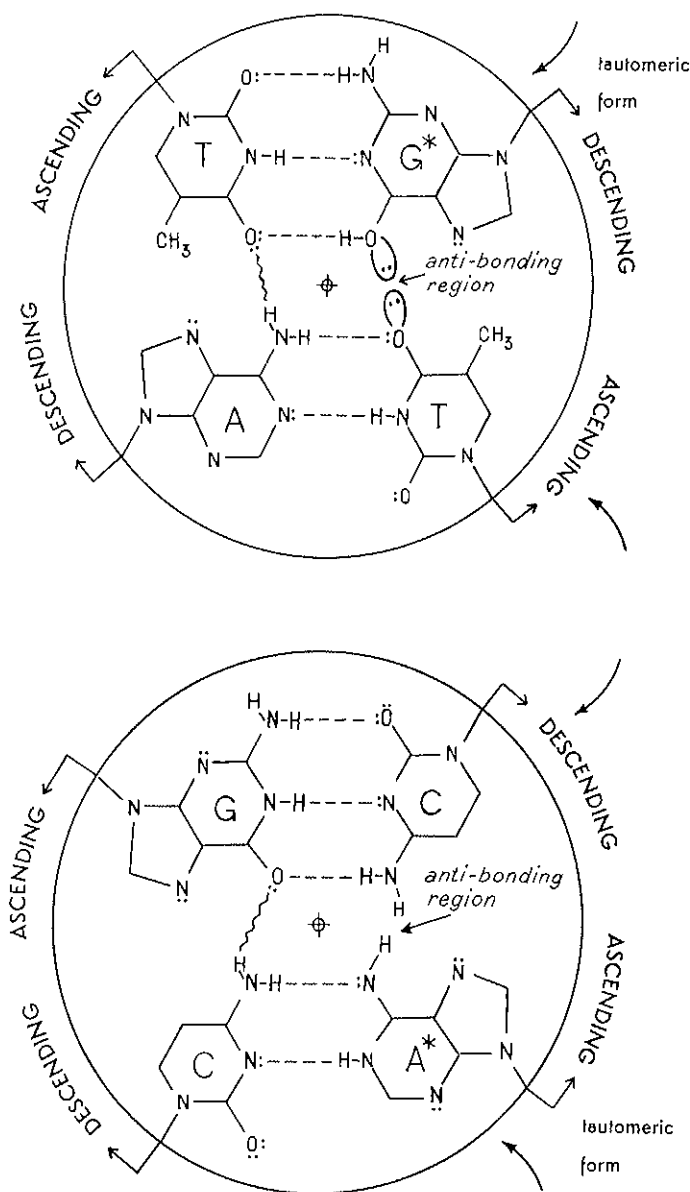


FIG. 24 — The four nitrogen bases in the replication plane in the case of the incorporation of a single tautomeric base from the environment.

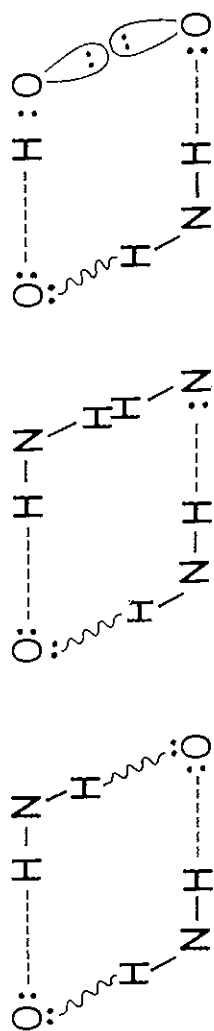


FIG. 25 — The four key groups around the center of the replication plane in the normal case and in the case of the incorporation of a single tautomeric error: (a) TA-AT plane, (b) TA-AC* plane, (c) TC*-AT plane.

poration of « tautomeric pairs of complementary bases ». The probability of such an event is to some extent regulated by the product $K \times K'$, where K and K' are the tautomeric equilibrium constants for a complementary pair of nitrogen bases. The purine bases have many tautomeric forms, and the equilibrium constants for the forms characterized by the codes outlined in Fig. 16 have not yet been accurately measured. It does not seem unreasonable, however, to expect that the value of the product $K \times K'$ will be of the same order of magnitude as the spontaneous mutation probabilities per base pair and generation, i.e. in the range 10^{-8} to 10^{-11} as previously mentioned. The replication scheme associated with the incorporation of a tautomeric pair of complementary bases is not as straightforward as one may first expect, however, and this problem will be further discussed at the end of next section; see particularly Fig. 30.

5. INTERNAL STABILITY OF THE GENETIC CODE IN DNA

In order to investigate the internal stability of the genetic code in the base pairs in DNA, it is necessary to study the problem of the proton exchange as outlined in Sec. 3. This problem can only be solved by evaluating the potential energy surfaces for the protons by calculating the complete charge distributions in the G-C and A-T base pairs for various positions of the protons in the hydrogen bonds. Since the protons in their motion are going to strongly polarize the clouds of the mobile π -electrons as well as the σ -electrons in the lone pairs, this is a rather formidable problem even with the help of modern electronic computers.

One may get a first rough idea of the shape and depth of the potential wells by considering the binding of the proton in

some simple inorganic compounds, as water and ammonia. According to PAULING, for example, the average energy of the OH bond in water is 110.6 kcal/mole or 4.794 eV, the bond distance is 0.96 Å, and the stretching frequency is 3657.05 cm^{-1} or $\nu = 1.0963 \times 10^{14} \text{ sec}^{-1}$. The average energy of the NH bond in ammonia is 93.4 kcal/mole or 4.049 eV, the bond distance is 1.01 Å, and the stretching frequency is 3336.7 cm^{-1} or $\nu = 1.0094 \times 10^{14} \text{ sec}^{-1}$. However, it should be observed that, in the DNA base pairs, these bonds are essentially modified by the fact that the oxygen and nitrogen atoms belong to conjugated systems with mobile π -electrons, which are easily polarized by the protons. The figures mentioned above give anyway an idea of the orders of magnitude one can expect to meet for the fundamental quantities involved.

The charge and bond orders of the G-C and A-T base pairs in the Hückel scheme were first evaluated by the PULLMANS [31]. Using these data, the author [28] made a first rough estimate which indicated that it may be of interest to start the entire investigation by evaluating the double-well potential for the proton in the middle bond in the G-C base pair.

At this time, it was also felt that, in order to get reliable results, it would be necessary to refine the π -electron calculations beyond the Hückel scheme, and a semiempirical MO-LCAO-SCF method for studying the base pairs was developed by REIN and LADIK [32]. Using the charge orders for the G-C pair obtained in this way, LADIK [33] calculated the potential felt by the proton in the middle hydrogen bond under the assumption that both the π - and the σ -electrons stayed unpolarized, and he found a double-well potential with an energy difference of 2.72 eV between the two minima and a potential barrier of 3.40 eV with respect to the lowest minimum. It was clear that, even if this result was qualitatively correct, the figures were greatly exaggerated depending on the neglect of polarization.

In order to take the polarizing effect of the proton into full

account, REIN and HARRIS [34] developed a refined MO-LCAO-SCF method in which one considered explicitly the twentyfour π -electrons of the G-C base pair as well as the four σ -electrons of the hydrogen bond under consideration; the calculations contain still one adjustable parameter K of the type introduced by WOLFSBERG and HELMHOLTZ [35]. The polarizing effect of the proton was studied by solving the SCF equations repeatedly for twelve subsequent protonic positions along the hydrogen bond. The resulting potential was again a double-well potential with the energy difference 1.4 eV between the two minima and the barrier 1.8 eV with respect to the deepest minimum. Even the excited and ionic states of the G-C pair have been treated in a similar way [36], and the results indicate that proton transfer in the hydrogen bonds may be an important factor in the theory of induced mutations caused by radiation or by charge-transfer compounds.

It has been pointed out in Sec. 3. that, if a proton moves from one equilibrium position to the other in a hydrogen bond, it is likely to induce the reverse motion of a proton in another hydrogen bond in order to maintain the gross electric neutrality of the system. The first investigation of the potential energy surface associated with the motion of two protons was carried out by REIN and HARRIS [37] in a study of the two « upper » hydrogen bonds in the G-C base pair. The MO-LCAO-SCF equations for this system of twentyfour π -electrons and twelve σ -electrons were solved for 74 configurations of the two protons in the $N:H \dots : N$ bond and the upper $O: \dots H:N$ bond. The calculations were carried out for several values of the Wolfsberg-Helmholtz parameter K , and finally comparatively high values ($K \approx 1.5$) were chosen. The potential energy surface has four minima corresponding to different metastable tautomeric forms, and the equilibration among the tautomers through proton tunneling is estimated to be comparatively fast with a time constant of 3.8×10^{-5} sec; see Fig. 26. The energy difference between the normal form G-C and the tautomeric

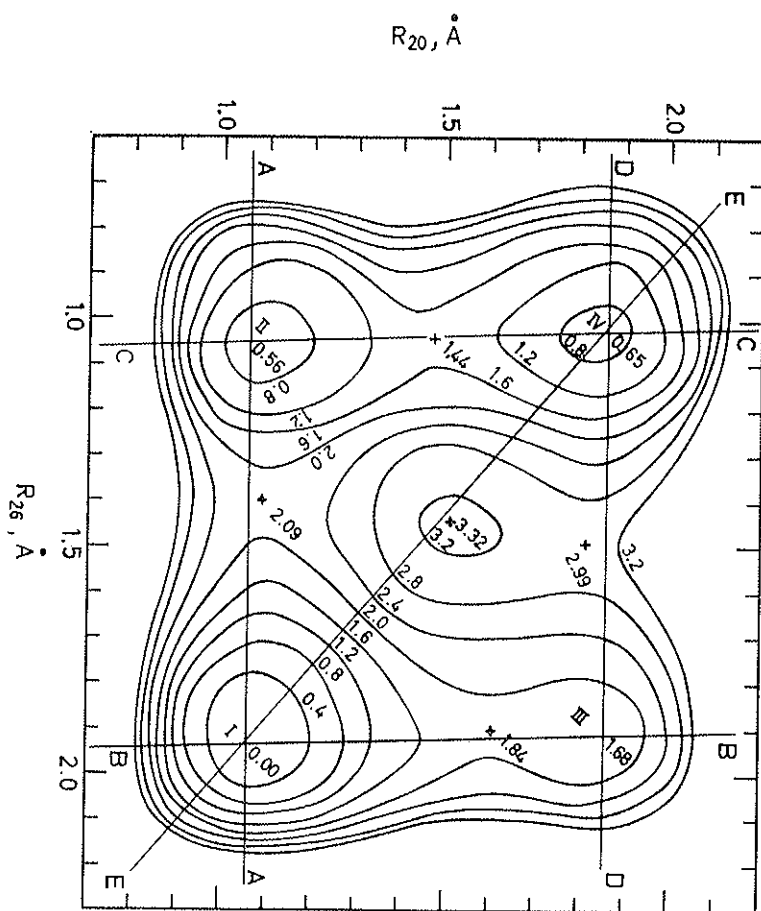


FIG. 26 — Potential energy surface for the motion of the two protons in the two upper hydrogen bonds of the guanine-cytosine base pair according to REIN and HARRIS (reference 37). All energies are expressed in electron volts with respect to the deepest minimum. The coordinates R_{26} and R_{20} indicate the distances from the guanine molecule for the upper proton and the middle proton, respectively.

form G^*-C^* obtained by double proton exchange along the two hydrogen bonds is 0.65 eV , and the characteristic potential for simultaneous proton exchange is illustrated in Fig. 27. We note that the equilibrium is quickly achieved, and that the energy difference 0.65 eV at 310°K according to Table II corresponds to a Boltzmann factor of $B=10^{-10.5}$. For a more detailed discussion, the reader is referred to reference 37.

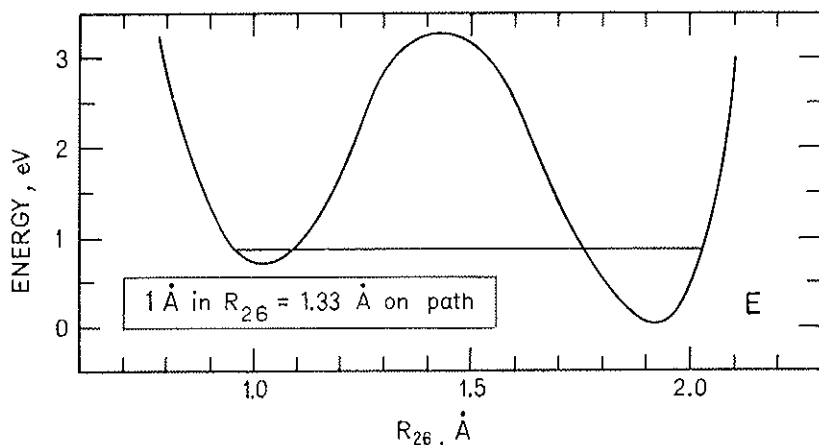


FIG. 27 — Potential energy curve for the simultaneous motion of two protons in the upper hydrogen bonds of the guanine-cytosine base pair according to REIN and HARRIS (reference 37). Note that an energy difference of 0.65 eV at 310°K corresponds to a Boltzmann factor of $B=10^{-10.5}$.

Using essentially the technique and computational programs developed in this way, LUNELL and SPERBER [38] have evaluated the potential energy surface for the motion of the two protons in the hydrogen bonds of the A-T base pair, and the results are illustrated in Fig. 28. There are apparently three equilibrium positions, and the curve along the diagonal is given in more detail in Fig. 29. Since the potential barriers are comparatively high ($\approx 2.7 \text{ eV}$), it is easily shown that only a

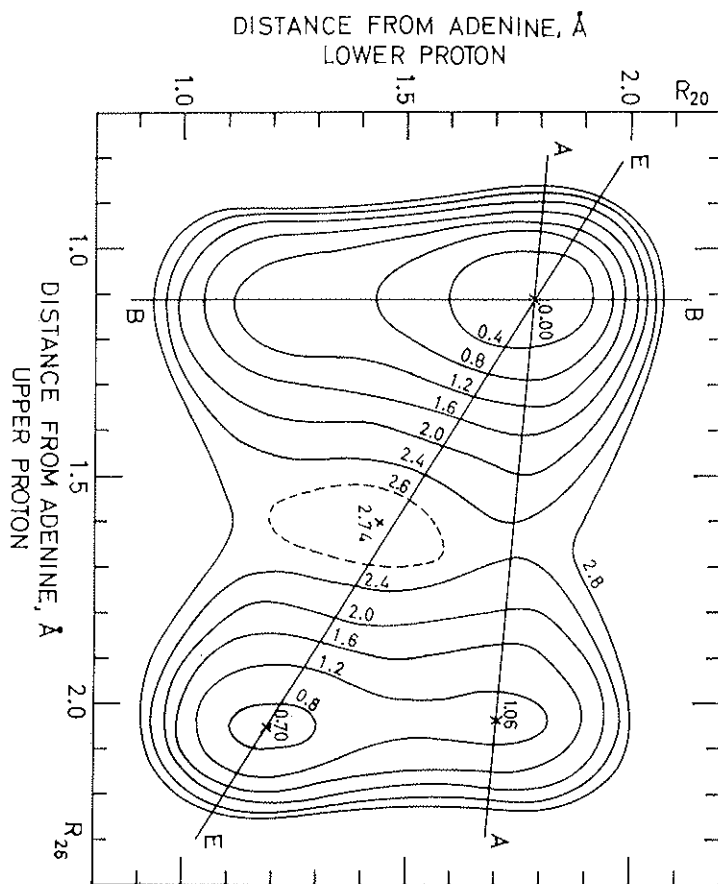


FIG. 28 — Potential energy surface for the motion of the two protons in the hydrogen bonds of the adenine-thymine base pair according to LUNELL and SPERBER (reference 38). All energies are expressed in electron volts with respect to the deepest minimum.

negligible amount of the proton population may pass over the barrier, whereas the tautomeric equilibrium is instead quickly achieved through the tunnel effect. The energy difference between the normal form A-T and the main tautomeric form A*-T* obtained through double proton exchange is 0.7 eV,

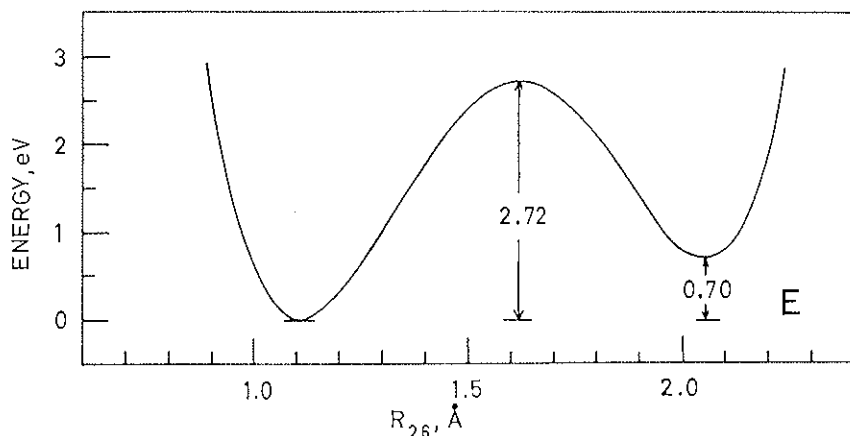


FIG. 29 — Potential energy curve for the simultaneous motion of two protons in the hydrogen bonds of the adenine-thymine base pair according to LUNELL and SPERBER (reference 38). Note that an energy difference of 0.7 eV at 310°K corresponds to a Boltzmann factor of $B=10^{-11.4}$.

which at $T=310^{\circ}\text{K}$ corresponds to a Boltzmann factor of $B=10^{-11.4}$. This result implies that the A-T base pair has a somewhat higher internal stability against mutations than the G-C base pair, in full agreement with data obtained by the PULLMANS [39] in an entirely different way.

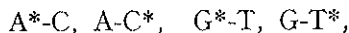
These calculations have been carried out by means of the IBM 7090 computer at FOA in Stockholm and the CD 3600 computer at the University of Uppsala. Even if these calcula-

tions are some of the most elaborate studies of simple conjugated systems performed so far, they are far from being sufficiently accurate for our purpose, and it is particularly desirable to refine the treatment of the lone pairs and the σ -skeleton in general and eliminate the use of the Wolfsberg-Helmholtz parameter K . Work along these lines is in progress.

Even in their present form, the figures obtained are probably accurate enough to permit at least a qualitative discussion of the problem of the internal stability of the genetic code in DNA. First of all, we observe that the potential barriers seem to be high enough to prevent any significant part of the proton population to pass above the barriers, and that essentially all proton transfer occurs through the tunnel effect with comparatively short tunneling times ($\approx 10^{-5}$ sec), so that the tautomeric equilibria are quickly achieved. The energy difference between the normal base pairs and the tautomeric base pairs obtained through proton exchange is 0.65 eV and 0.7 eV for the G-C and A-T pairs, respectively, and these figures correspond to the Boltzmann factors $10^{-10.5}$ and $10^{-11.4}$. These factors should be compared with the spontaneous mutation probabilities per base pair and generation, which experimentally lie in the range between 10^{-8} and 10^{-11} according to FREESE [10]. Such an agreement is certainly « too good to be true », and we have all reasons to be critical against so good results. However, it seems anyway rather satisfying that the genetic code in DNA even within rather wide margins seems to be sufficiently stable even with respect to proton tunneling. So far, all data obtained confirm the Watson-Crick model.

Proton-tunneling in the « rare » base pairs. — At normal temperature, say $T=310^{\circ}\text{K}$, proton exchange in the normal base pairs G-C and A-T is a quick but exceedingly rare event leading to the formation of the tautomeric pairs $\text{G}^*\text{-C}^*$ and

A*-T*. It is now of interest to study the phenomenon of proton tunneling in the four anomalous base pairs:



which are related two and two by double proton exchange. A study [40] of the π -electron energies favors the forms A-C* and G*-T, in which the bases A and T are normal. In time for the Study Week, LUNELL and SPERBER [38] have concluded a calculation of the double-well potential for the A*-C base pair and found that the form A-C* has a total energy which is 0.5 eV lower than the form A*-C and that the potential barrier in the middle is 1.05 eV with respect to the higher minimum. This result implies that the form A*-C is *unstable* with respect to double proton exchange and quickly goes over practically completely to the form A-C*. Preliminary calculations indicate that a similar result holds also for the G-T* pair which through double proton exchange goes over into the form G*-T.

This double proton exchange in the « rare » base pairs seems to be of essential importance in discussing the effect of incorporation errors at DNA replication. One can expect that the nutrition material at the replication contains all the nucleosidetriphosphates of the bases A, T, G, C and their « rare » tautomeric formes A*, T*, G*, C* of the type described in Fig. 16, as well as other tautomeric forms. One may get an idea of the probability distribution over the various forms by calculating their total energies. However, since only the difference in energy between the normal and the tautomeric form is of importance, one may, in a first approximation, calculate the difference between the energies of the mobile electrons, since the change in polarization of these electrons is one of the main effects of the replacement of the proton in the tautomeric shift.

The π -electron energies of the nitrogen bases and their

tautomeric forms were first evaluated in the Hückel scheme by the PULLMANS [31].

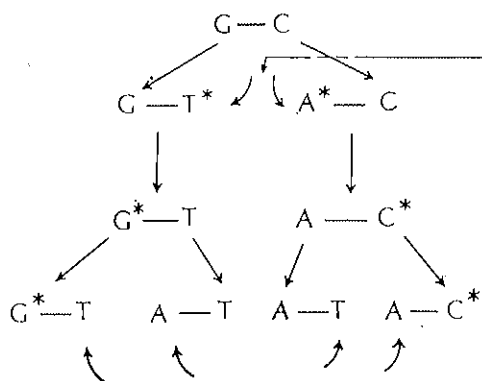
Using slightly modified data from reference 4, p. 296, one gets the following result:

	A	T	G	C
Normal form:	$12\alpha + 17.214 \beta$	$12\alpha + 22.512 \beta$	$14\alpha + 22.094 \beta$	$10\alpha + 16.096 \beta$
Tautomeric form:	$12\alpha + 16.940 \beta$	$12\alpha + 21.798 \beta$	$14\alpha + 21.482 \beta$	$10\alpha + 15.962 \beta$
Difference:	0.274β	0.714β	0.612β	0.032β

where β is the Hückel bond integral with the approximate value $\beta \approx -18 \text{ kcal/mole} = -0.78 \text{ eV}$. The results imply that, of all four nitrogen bases, cytosine C is most likely to occur in its tautomeric form C* — a result already obtained by the PULLMANS [39] — and the other bases come then in the order adenine A, guanine G, and thymine T.

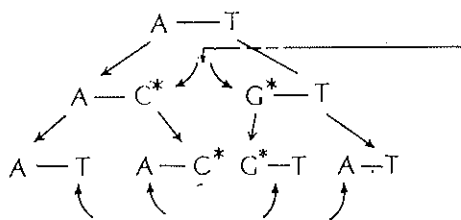
In sec. 4, it was shown that the incorporation of a single tautomeric base in the « replication plane » was highly improbable, but that one could not exclude the incorporation of a tautomeric pair of complementary bases (A*, T*) or (G*, C*). The π -electron data given above indicate that the probability for the occurrence of a complementary tautomeric pair is much smaller for (A*, T*) than for (G*, C*), and the essential incorporation error involves the latter pair.

It should be observed, however, that the replication schemes will be modified by the previously mentioned unstability of A*-C and G-T* with respect to double proton exchange. In Fig. 30a, we have outlined the replication scheme of a G-C base pair after the incorporation of the tautomeric pair (T*, A*) in the replication plane, and we note that the process leads to



Incorporation of a tautomeric pair (T*, A*) from the environment in the replication plane.

(a)



Incorporation of a tautomeric pair (C*, G*) from the environment in the replication plane.

(b)

FIG. 30 — Replication scheme for the normal base pairs under incorporation of tautomeric pairs of complementary bases; note that the pair (T*, A*) occurring in (a) is apparently rare in comparison to the pair (C*, G*) occurring in (b).

a mutation $G-C \rightarrow A-T$ which undergoes « biological amplification » by the factors 2, 4, 8, 16, 32, . . . etc. In Fig. 30b, we have sketched the replication scheme of an A-T base pair after incorporation of the tautomeric pair (C*, G*), and we note that the process does not lead to a mutation until the forms C* and G* in some way have undergone a tautomeric shift and gone over into the normal forms. Available data indicate that, if the pair (C*, G*) is very rare at tautomeric equilibrium, the pair (T*, A*) should be exceedingly rare,

and the processes discussed above may then also be of importance in the purification of DNA replication with respect to errors leading to mutations and in explaining « why spontaneous mutations are so rare ». The figures in this section are, of course, highly preliminary, and it seems essential to study these problems with considerably more accuracy in greater detail.

6. BIOLOGICAL SIGNIFICANCE OF THE STABILITY OF DNA

The DNA molecule carrying the genetic message is situated in the chromosomes in the cell nucleus, and from this position it regulates the entire metabolism of the cell, particularly the protein synthesis occurring in the ribosomes in the cytoplasm. The genetic instruction is carried from the DNA molecule to the various parts of the cell by a certain compound called messenger-RNA. This is also a ribonucleic acid which seems to be essentially one-stranded and contains the ordinary four nitrogen bases but with thymine T replaced by uracil U, which is analogous to thymine having the methyl group replaced by hydrogen. It seems clear that, in the *transcription* of the genetic message, messenger-RNA is synthesized in the deep groove of DNA by means of the template principle, but it is not yet experimentally known whether this involves a temporary opening of the genetic code by releasing the hydrogen bonds or whether the genetic message is « read » in a proton-electronpair « copy » associated with the 6-amino and 6-keto groups in the deep groove of DNA; see Fig. 14. For a survey of the literature in this field, we would like to refer to reference 4.

The messenger-RNA regulates again the protein synthesis in the ribosomes by the template principle. Each one of the

twenty amino acids is attached to an « adapter » in the form of a comparatively small molecule of soluble RNA (s-RNA) which carries the amino acid to its correct place on the messenger RNA by means of complementarity between a small nucleotide part of the adapter and the template. There are further good reasons for believing that a triplet of consecutive bases in the genetic message of DNA corresponds to one amino acid, and a great deal of research is currently devoted to this so-called coding problem. The metabolism of the cell seems hence to be essentially regulated by the simple rule:



which is now almost universally accepted as the basis for the entire molecular biology.

Mutations and Evolution of Life. — As mentioned in the introduction, one has strong experimental evidence that the change of the genetic template of a single base pair may lead to a change of one amino acid in a specific protein, which means that the change of a single sign in the genetic code may lead to a mutation [6]. Since the introduction of the Watson-Crick model of DNA, it has seemed clear that the occurrence of spontaneous mutations in some way should be associated with the natural occurrence of tautomeric forms of the base pair, and the main problem has not been to find possible mutation mechanisms but instead to explain « why spontaneous mutations are as rare events as they are ». The purpose of the study reported here has also been to show that the genetic code has sufficient stability against incorporation errors as well as against proton exchange through tunnel effects.

At the same time, it is rather fascinating to realize that the tautomeric forms differ from the normal forms only by having a single proton replaced a distance which is approximately

2, 3 Å, or that tautomeric forms may be produced by having a proton changing its place by jumping about 1 Å. One of the strongest driving forces in the evolution of living organisms on the earth through mutations may hence be proton jumps over a distance of $1 \text{ Å} = 10^{-8} \text{ cm}$ facilitated by the quantum-mechanical tunnel effect.

The spontaneous mutations involve changes of base pairs of the type $A-T \rightleftharpoons G-C$ which are reversible. Our study indicates that the A-T pair should have higher stability than the G-C pair, which implies that the spontaneous mutations should in the long run favor the direction $G-C \rightarrow A-T$. It is perhaps not a mere coincidence that CHARGAFF's investigations of the base contents of DNA show that the higher organism have a considerably larger content of A-T pairs than G-C pairs in their DNA-molecules.

Our result that the genetic template in DNA consists essentially of a pattern of protons and electron pairs is of importance also in discussing mechanisms for *induced mutations*. If one of the strands of DNA becomes electrically charged — through weak UV-radiation, through ionizing radiation, or through charge-transfer reactions — it seems very likely that all protons of the hydrogen bonds in the base pairs may end up on one and the same side leading to ionic tautomeric forms which will then cause deletions at the DNA-replication. For a more detailed account, we will refer to references 4, 33, 36, and 37.

In connection with mutagens having a certain steric structure, as e.g. acridine, it is interesting to study to what an extent such compounds may be incorporated in the replication planes instead of new nucleotides (see Figs. 21 and 23), since this would lead to a simple interchelation mechanism. Errors of this type lead to mutations which are irreversible, since they depend on deletions in the genetic message.

Aging. — Even the aging of biological organisms is today a phenomenon which is often considered on the basis of mo-

lecular and submolecular biology. Several authors have emphasized the importance of possible damage to the genetic code and the occurrence of somatic mutations as causes of aging [41].

In this connection, there is a distinct difference between unicellular and multicellular organisms. A unicellular organism propagates by cell division and, since one cell suddenly becomes two, two become four, etc., a cell lacks individual identity and cannot age in the ordinary sense, particularly if the time span between two cell divisions is comparatively short. If such a cell becomes damaged, it will either die directly or lose out in the struggle for existence in competition with normal cells. This implies that a system of such cells will usually not show any loss of vigor with time.

In multicellular organisms, the circumstances are rather different. The metabolism of each cell is regulated by its genetic code which is read over and over again in the formation of messenger-RNA necessary for the protein synthesis. The transcription is carried out by means of such templates that hydrogen bonds are formed and broken again. Our study in Sec. 5 as to the double-well potentials indicates that each hydrogen bond between complementary base pairs contains inevitably a « proton error » of the order of magnitude 10^{-10} to 10^{-11} , which becomes manifested when the bond is broken, since the protons are then forced to « choose side ». This means that every transcription introduces necessarily a small error in the proton-electronpair code of DNA which has been utilized for this purpose, i.e. there is a specific loss of genetic information of the cell concerned which is essentially proportional to the number of transcriptions, i.e. to the rate of metabolism of the cell. Since the proton error mentioned above is certainly only a lower bound, it seems worthwhile to investigate whether this loss of genetic information through repeated transcriptions in any way may be related to the primary cause of the phenomenon of aging.

It is rather remarkable that, in multicellular organisms, the gametes are set aside in an early stage of life and are not brought to full metabolism and maturity until the time they are really needed.

In this connection, one should observe that the multicellular organisms have two types of tissues, which will here be denoted by I and II, and which differ by their modes of replication. Tissues of type I renew themselves periodically by cell replication, whereas, in tissues of type II, the cells have stopped their replication at a certain stage of life, so that such a tissue belongs to the mature organism once and for all. Nerve cells and brain cells are typical examples of the second type.

In tissues of type I, where the cells divide frequently, a large damage to the genetic code will usually cause only little harm, since the corresponding cell will immediately lose out in competition with the normal cells. On the other hand, there is a certain « average » loss of the genetic code in all the cells through the metabolism which may cause tissues of this type to age, even if half of the DNA-molecule are sorted out at every replication.

In tissues of type II, where the cells belong to the mature organism once and for all, the loss of the genetic information through the repeated transcriptions necessary for the protein synthesis and the general metabolism is a still more serious phenomenon, since the cell may finally lose the information necessary to produce vital structural proteins or enzymes and will finally die. It does not seem unreasonable to think that the primary cause of aging of multicellular organisms would be concentrated to such cells, and it seems at least worthwhile to study these problems in greater detail, and particularly a closer investigation of the transcription process would be of essential importance.

Occurrence of Tumors and Cancer. — A tumor may be described as an « individual within the individual », and it

seems rather natural that many authors have discussed the possibility that tumors and cancer may be caused by *somatic* mutations, i.e. changes in the genetic code in the cells of the body. Cancer may be described as the growth of abnormal cells in the organism which have a higher rate of metabolism and replication power than the normal cells and which hence take over the organic material in large areas and form malignant tumors. It is characteristic for the cancer cells that they often seem to lose the specificity of the tissue from which they originate, that they easily form daughter tumors (metastasis), and that they do not seem to activate the ordinary immunological reactions of the organism.

The theory of the cause of cancer is complicated by the fact that many chemical compounds which are strong mutagens are not carcinogenic, and vice versa, and today it seems hardly justified to assume that somatic mutations associated with certain changes in the genetic code would be the only cause of tumors. In the *deletion hypothesis*, cancer is assumed to be essentially caused by the fact that some growth-controlling factors in the cell or in the organism — enzymes, hormones, etc. — for some reasons have been deleted. This may depend on an error in the DNA molecule itself, e.g. through a somatic mutation, or it may depend on other errors along the basic assembly line DNA→RNA→proteins in the hormone producing cells or in the cells of the tissue directly concerned.

In discussing these problems, it is important to understand how the cell differentiation in a multicellular organism is achieved. One knows from experience that each cell of the organism has the same complete genetic message contained in a system of DNA molecules but also that, in the differentiated cells, only a very small part of this information is utilized for the synthesis of the structural proteins and enzymes which are needed. PLATT [42] has compared the system of DNA molecules with a book with many chapters, in which only a specific chapter is « read » and utilized for controlling the metabolism

in a special type of cell, whereas all the other chapters are « closed ». The reading of the open chapter of the book is regulated by processes of the type successfully investigated by JACOB and MONOD [43], but one still does not know whether similar processes regulate also the closed chapters, or whether they are simply « closed » by certain molecules blocking the reading of the deep groove in DNA.

One may wonder how a cell obtains such a specific message as « read chapter one », « read chapter two », etc. The simplest mechanism is based on the idea that a certain information I , which originally may have been obtained e.g. by reading a single strand of DNA, is not duplicated before a cell division but is instead divided into two parts, $I = I_1 + I_2$, going into different daughter cells. This leads to a replication scheme which is schematically illustrated in Fig. 31.

When the material in a tissue is renewed, it is essential that both the DNA molecule as well as the molecules regulating the reading of DNA are properly duplicated before cell division. The DNA molecule has a stabilizing protein (histone) in its shallow groove, and it seems very likely that it has a similar protein cover also in the deep groove, which may be removed for replication and transcription of the genetic message. If, at a cell replication, some of the molecules which eventually block certain parts of the deep groove of DNA would be *deleted*, the cell would lose part of its differentiation and probably get a foreign appearance in the tissue. However, since the cell does not contain any molecules which are foreign to the organism, the usual immunological reactions are not immediately activated. For the moment, one does not know what happens when a skin cell starts reading the chapter about brain cells, but it seems certainly worthwhile to investigate the existence and properties of partly « dedifferentiated » cells in connection with the problem of tumors and cancer. It is also important to consider the DNA molecule with its protein cover, i.e. as a *nucleoprotein*, and we note that a DNA molecule

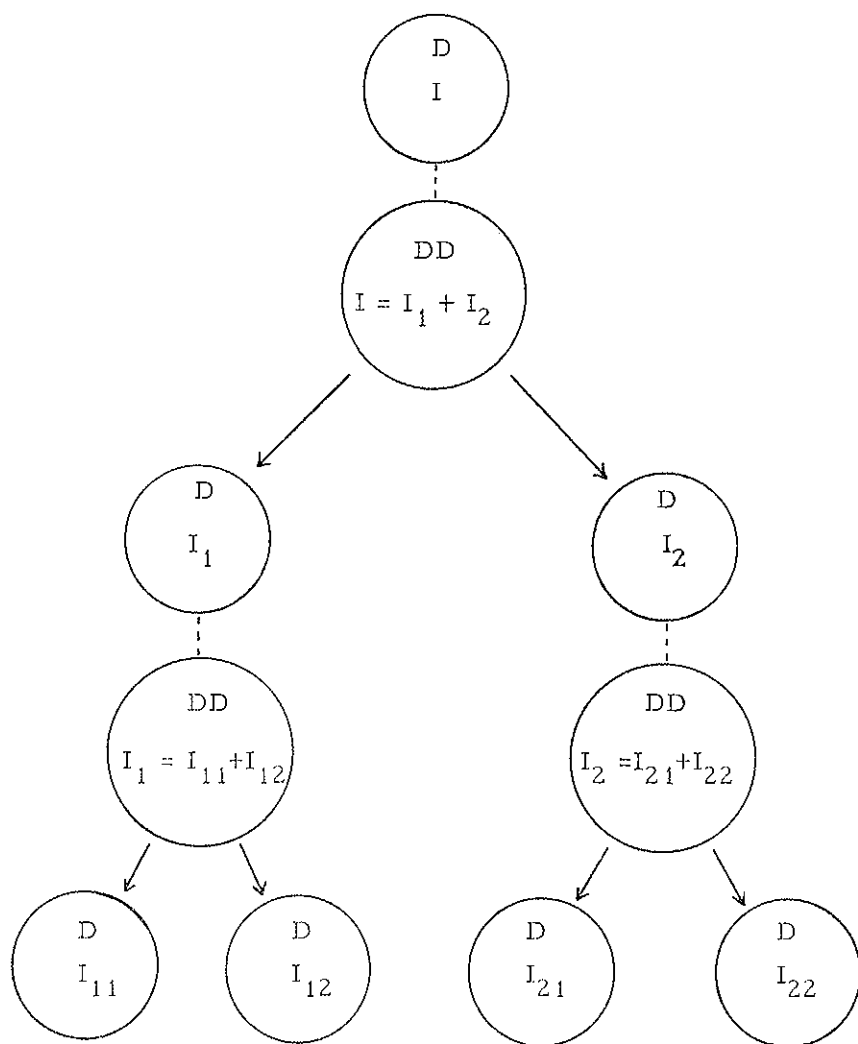


FIG. 31 — Cell replication leading to a differentiation of the cells. D = DNA content, I = Information for reading DNA.

without its proper framework may be very dangerous to the organism — not because of lack of genetic information, but because of *too much* information simultaneously.

This variant of the deletion hypothesis is appealing from the point of view that it explains the tendency of cancer to form daughter tumors through defect nucleoproteins as well as the lack of strong immunological reactions. There may be many reasons for the deletion of the transcription-controlling molecules: there may be a basic enzyme missing through aging or through damage to the genetic code caused by radiation or chemicals, or the controlling molecules themselves may have been damaged by radiation or by chemicals (including external viruses). This is certainly an immense area of research, and we have here only tried to emphasize the fact that, in connection with tumors and cancer, one should not only investigate the genetic message but also the instructions for reading this message, including the « blocking » of a large part of the genetic code in any differentiated cell.

The interest is again focused on the genetic code and the reading and blocking of the message in the *deep groove* of DNA, and it seems rather obvious that the templates formed by proton-electronpair patterns and the molding of new templates through hydrogen bonds are going to play a fundamental role also in this connection.

Memory. — Our analysis of the genetic code in Sec. 3 shows that, in the DNA and RNA molecules, nature has found an excellent mechanism for the long-time storage of information in the form of a proton-electronpair code of the type



Counting the proton, one gets the symbols 0 or 1, and such a storage is hence completely analogous to the storage mechanism in a modern electronic computer, with the difference that the « microcomponents » used by nature can hardly be beaten by any technical development. The question is now whether nature is using a similar type of device also for storing short-time information of the type usually referred to as « memory » — the ordinary conscious memory, the reflex memory, the « chemical memory » rendering immunity against diseases, etc. There are strong indications that nature is utilizing DNA and RNA molecules also for this purpose, but very little is known about the detailed mechanism. It seems very likely, however, that the hydrogen bonds are of basic importance also in this important field of biology.

Conclusions. — In this section, we have discussed certain fundamental biological problems from the point of view of the Watson-Crick model and the study of the stability of the genetic code carried out in Secs. 3-5. There is hardly any question that all these problems have been greatly over-simplified, and that a complete discussion has to include not only the properties of the DNA molecule and the metabolic assembly line DNA→RNA→proteins, but the cell and the organism as a whole. It is clear that a great deal of additional experimental information is needed to give the theory a firmer ground to work on. It is evident, however, that hydrogen bonds are going to play a fundamental role even in the refined theories to come.

7. ACKNOWLEDGEMENTS

The program for the research as to the nature of the genetic code in DNA and its stability was outlined by the author in the Technical Note No. 85 which was dedicated to His Majesty,

the Swedish King Gustaf VI Adolf, on his 80-year birthday on November 11, 1962. The generous support from King Gustaf VI Adolf's 70-Years Fund for Swedish Culture and Knut and Alice Wallenberg's Foundation for this research is gratefully acknowledged. The research program was later modified, and the modernized version has appeared as Technical Note QB 7 (1963); a revised version was finally published in 1965 in reference 4.

The study of the proton exchange in the base pairs of DNA involves the evolution of rather complicated potential energy surfaces. Even with the help of modern electronic computers, this is a rather formidable problem which was undertaken as a group effort by the Uppsala Quantum Chemistry Group. The author would like to express his sincere gratitude to the U.S. Cancer Institute for a research grant which made this investigation possible. Computer time was generously granted by FOA, Stockholm, and by Uppsala University, which is also gratefully acknowledged.

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DISCUSSION

Chairman: CHAGAS

OVERBEEK

I enjoyed your lecture very much, Dr. LÖWDIN. I have three questions to ask. The first one is related to the equilibrium constants for the tautomeric forms of the bases that you mentioned quite in the beginning. These equilibrium constants were of the order 10^{-3} , but this is in aqueous surroundings, and in the DNA the surroundings may be quite different, and so these figures may not be very relevant. That is my first question.

The second question is, when you make the quantum mechanical calculations, you treat pairs of molecules in a vacuum, and should you not treat the environment as well, perhaps by introducing something like a dielectric constant which would change the electric energies?

The last question, is your remark about ageing? I have not understood why the frequent reading of DNA should make the danger of misreading greater for a later RNA which is copied from the DNA, than from an RNA which is copied in the beginning. I have not seen that the DNA itself is changed by the process of serving as a template for RNA.

LÖWDIN

I thank Dr. OVERBEEK for his questions. I have to agree wholeheartedly with the first one; there is a great deal of difficulty in knowing what is the actual environment of DNA during replication but one thinks that the tautomeric equilibrium constants are about the same as they would in aqueous solution. However, one should observe that, even if water is not present, there are a great deal of protons and electron lone-pairs present anyway in the immediate environment. It is perhaps rather interesting that the equilibrium constants found for the complementary base-pairs in coupled position may very well turn out to be something which is close to what they would be for separated bases at normal pH in the solution. But I agree with the difficulty, and the problem should be further investigated.

The second question is a very interesting one, which we do not try to treat simply by introducing a dielectric constant. We are here not dealing with systems «in a bulk», but with molecules which are unique or occur only twice in the cell, so we have instead chosen a different approach. In studying a specific base-pair, we are considering also the two neighbouring base-pairs, the two next-nearest neighbours, the two next-next nearest neighbours etc. Since there are four different base-pairs (A-T, T-A, G-C, and C-G), there are 16 different combinations of nearest neighbours, and 256 combinations involving also next-nearest neighbours, etc. The problem is being studied, but it will take some time before we have the solution.

As to the problem of ageing and its connection with the transcription of DNA, the main point in the template idea is that a hydrogen bond has to be formed and broken which introduces the possibility for a proton jump and a proton «error» of at least the order of magnitude 10^{-11} , probably considerably higher. The error depends also on where the genetic message in DNA is actually «read» in transcription. Most of the molecular biologists today seem to believe that the genetic code is opened up momentarily,

whereas STENT and ZUBAY, using the beautiful experimental results as to the formation of polyhelices obtained by RICH, have suggested that the genetic code is read on the protein-electron pairs situated on the base-pairs in their normal positions in the deep groove of DNA. The first thing one would have to do is to clear up the question where the genetic code in DNA is actually « read », but for this one needs experiments and experiments.

VERWEY

I have the following difficulty. If, by the mechanism of double tunnelling two isomer-bases have been formed, and immediately after that the double helix is untwisted so that the bases are separated, the free strands will be immediately surrounded by the aqueous medium. This medium contains large amounts of protons and can easily transport protons. It takes a short time before the replication starts. Should one not expect that in the meantime the displaced protons leak back via the medium so that the original bases are formed back and the mutation is annihilated?

LÖWDIN

When it comes to water, I would like to tell that we are right in the middle of an investigation, so unfortunately I have nothing to report today. I am just as interested in water as you are, and it may turn out that water is a very dangerous poison for DNA.

VERWEY

How large is the time before the replication starts? How does it compare with 10^{-5} seconds?

[22] Löwdin - pag. 69

LÖWDIN

The actual synthesis time for a base pair is 10^{-3} sec, which is a comparatively slow process, so there is plenty of time for water molecules to come in and interfere — if they are present. Of course, one knows that water is a big proton donor and proton acceptor, but no one knows the exchange mechanism with the nucleoside bases — just as no one knows the proton exchange mechanism for the classical Lewis acids and bases.

GRIMLEY

Your difficulty really is that the important quantity, the tunnelling time, is very sensitive to the parameters of the barrier. In this situations do you have any confidence that you can actually make a calculation which we should believe?

LÖWDIN

No, absolutely not, because quantum mechanics by itself is a baby; I would say that, unless we learn very good and strict quantum mechanical methods and have patience in developing our mathematical and numerical methods, the theory is not going to produce numbers which are reliable independent of the experiments. I believe very much in simple and quick theories for the help of the chemists, but I think that perhaps we have got a little bit too much of them and too little of reliable quantum-mechanical calculations. On the other hand I would like to say in all modesty, in favour of REIN, HARRIS, LUNELL and SPERBER, that the quantum-mechanical calculations reported here, are probably better than anything comparable which has so far appeared on similar systems in the literature. But the computational costs have been considerable, and we still have a very long way to go.

GARCÍA DE LA BANDA

I would like to have a little more information about these substances which « teach » the different kinds of cells how to read the genetic code.

LÖWDIN

Yes, as you know, we don't know too much about the differentiation of the cells, but I think one should investigate the possibility that some molecules are simply blocking the reading of DNA by sitting in the deep groove of DNA, and that these molecules are replicating at the same time as DNA. The purpose of this blocking is to see that in a differentiated cell the wrong chapters of DNA are not being read. It is not easy to study such molecules, simply because they are « closing up » the whole thing, and that is probably the reason why we so far know so little. For the moment, most of the research is going into studying the regularity processes for the reading of the open part of DNA of the Jacob-Monod type. I wish I knew more.

CHAGAS

I have a small question. One statement you made which I could not understand at the beginning, was that this sort of mutation is different from the classic mutation. I think that the point mutation was a name given to something which had no molecular basis at all, and this corresponds exactly to the change in the base pairs.

LÖWDIN

I think that most molecular biologists would agree that they consider the change of a single base pair being the cause of a

point mutation, but there are also the classical biologists who don't believe too much in molecular biology who claim that their entire terminology is being destroyed.

SCHWAB

I have a short question concerning cancer produced by chemical means. A number of substances produces cancer, and the opinion has been put forward that this comes through the incorporation of a foreign molecule instead of a base into the RNA. What do you think in terms of your ideas?

LÖWDIN

Essentially it has been believed that carcinogenesis is caused by somatic mutations, by either foreign molecules being sandwiched between the base pairs or by changing the genetic code in some other way so that the protein synthesis has been partly destroyed or brought out of balance. It seemed very natural when we started this work to assume that cancer could be blamed on somatic mutations, but later we have also become interested in the reading process and the blocking of large parts of DNA, and now we like to see some more experiments carried out on the reading of DNA.

CONCLUSIONS

FINAL STATEMENT

The study week had been carefully organised by His Excellency Prof. P. DEBYE, but unfortunately, he was unable to preside at the meeting owing to illness. In these circumstances, I opening the meeting and proceeded to nominate chairmen for each daily session. This was agreed as follows: Prof. HIRSCHFELDER (Monday), Prof. CASIMIR (Tuesday), myself (Wednesday), Prof. SCHWAB (Thursday), and Prof. CHAGAS (Friday).

These daily meetings were highly successful and followed the previously prepared plans laid out by Prof. DEBYE.

At the last session, held on the Friday, the Chairmen agreed with Prof. WIDOM on the main points raised in the various papers read, and also with the following debates which took place. Prof. RICCI was of great assistance in this connection, and summaries were sent to Prof. DEBYE so that he could prepare and draft the final statement.

Unfortunately, although Prof. DEBYE recovered sufficiently to read these summaries, he was prevented from concluding this task, owing to sudden death, causing the loss of the world's leading physical chemist.

However, as the summaries prepared by Chairmen of daily sessions together with Prof. WIDOM had received the approval of Prof. DEBYE, and this I am able to confirm, they will be printed here in their original form.

SAN-ICHIRO MIZUSHIMA
Pontifical Academician and
President of the Study Week

SESSION ON MONDAY (Prof. HIRSCHFELDER *Presiding*)

Intermolecular forces are responsible for most of the physical and chemical properties of matter. Although the exact nature of these forces is very complicated, there are no conceptional difficulties. At small separation, the largest forces are due to electron exchange or chemical valance. At larger separation, they arise from the interaction of permanent or induced electric moments. In order to determine intermolecular forces quantitatively, both precise experimentation and theoretical calculations are required. The determination of properties of the isolated molecules will be useful in predicting the long range interaction. Molecular beam scattering experiments (involving interference effects) will be particularly useful in determining the interaction energy on a function of separation. With the use of new types of quantum mechanical techniques and high speed computing machines, it should be possible to calculate the intermolecular force accurately on the basis of accepted laws of physics. Much experimental and theoretical research is required to make our knowledge of intermolecular forces quantitative.

Short range repulsive forces have been obtained from « classical cross section » of high energy molecular beams. Long range interactions have been obtained from the « quantum cross section » of low energy (thermal) molecular beams. The energy dependence of the « rainbow maxima » determine the maximum energy of attraction and the corresponding intermolecular separation. Quantum mechanical interference effects are useful in making additional interpretations. At the present time the accuracy of the experiments is not sufficient to uniquely determine the intermolecular potential. With improved velocity and angular resolution molecular beams will serve as a sensitive probe for determining intermolecular forces.

The long-range electrostatic and induction forces are dependent on the charge distribution and various polarizabilities

of the isolated molecules. Simple experiments have been devised for measuring these permanent and induced moments. These moments should be determined for a variety of important molecular species, especially for excited electronic states — where information is particularly lacking.

(Summarized by HIRSCHFELDER; Speaker: HIRSCHFELDER, BUCKINGHAM, and BERNSTEIN).

SESSION ON TUESDAY (Prof. CASIMIR *Presiding*)

From a theoretical point of view there exists agreement, that for neutral, non-polar molecules at a distance large compared with the molecular dimensions the predominant term in the interaction is the London-van der Waals force. Also the retardation effect is based on incontroversial theory.

The interaction between macroscopic bodies can be derived by simple integration but also by more rigorous methods. Fortunately the discrepancy between the two methods are only slight. The theoretical situation is reasonably clear, although a further elaboration of the theory for intermediate distances and special geometries would be desirable.

OVERBEEK reported on measurements of the attractive force between solids at distances of $1000\text{\AA}$ and more. On the whole these experiments confirm the theoretical predictions and although a further increase of precision would be gratifying, the situation would appear to be well in hand.

The study of soap films on the other hand, reported on by LYKLEMA, revealed some problems. Although these experiments provide evidence for the existence of long range attractive forces, there were certain discrepancies: these forces did not show retardation effects even at great distance and their absolute magnitude was larger than to be expected for London-van der Waals forces. It was one of the results of our discus-

sions that here dipole-dipole interactions of the KEESOM type may play a predominant role.

LYKLEMA reported also on the stability of colloids. The general ideas of the Derjaguin-Landau-Verwey-Overbeek theory are well confirmed, but quantitatively the situation is somewhat less satisfactory. In view of the rather complicated nature of the situation this is not surprising. Here again attention should be paid to forces of the Keesom type.

BOWDEN reported on measurements which are in a way intermediate between the truly macroscopic experiments and those on colloids and liquid films. They comprise a careful study of atomically flat surfaces, especially of mica. The techniques for examining such surfaces were discussed. Experiments are still in progress. It is to be hoped that they will yield reliable data on macroscopic van der Waals forces in a region where they are getting very large.

Useful work should be possible along all of the lines indicated above, but special attention should be paid to dipole-dipole forces. It was also suggested that an investigation on interaction of macroscopic bodies immersed in liquids would be of interest. Here the use of He II might offer interesting future possibilities.

(Summarized by CASIMIR; Speaker: CASIMIR, OVERBEEK, LYKLEMA, and BOWDEN).

SESSION ON WEDNESDAY (Prof. MIZUSHIMA *Presiding*)

A truly fundamental theory of liquids, relating their properties to intermolecular forces by applying rigorously the laws of statistical mechanics, is still lacking. Nevertheless, a number of useful approximations are known, and these theoretical results, combined with experimental measurements, have led us to a picture of fluid systems in which we may have some

confidence. The radial distribution function, and correlation functions in general, were found to be the most direct and fruitful way of describing the connection between intermolecular forces and the nature of fluid systems.

There was general agreement on the connection between light scattering and thermodynamic properties of a scattering fluid, in particular on the basic theory of critical opalescence. It is still highly uncertain, however, whether the theoretically predicted features of the small-angle scattering near the critical point have been observed experimentally. A major difficulty is the uncertainty in the correction for multiple scattering. It is of pressing importance that reliable experimental answers to these questions be obtained.

Our studies have made clear that, on the important question of liquid structure, the older interpretation of liquids as being quasi-crystalline are rather misleading, and, indeed, the radial distribution functions of liquids lack some of the essential features of crystalline order.

The very new field of inelastic scattering of light, and the study of its connection with transport properties and space-time correlation functions, shows very great promise of leading to important measurements. The data from such experiments are not yet very extensive, and progress in this field should be given every encouragement.

As to the potential functions so far used for free molecules and molecular crystals, an improvement was made so that the values of force constants obtained from spectroscopic data are now in good agreement with those found by experiments other than infrared and Raman measurements.

New electron diffraction pattern and electron micrograph of the oxide formed at the initial stage of oxidation on the surface of pure iron single crystal was observed. The coherence of the very thin oxide with iron surface was discussed. (Also the possible coherent force between the oxide and the metal surface).

(Summarized by WIDOM and MIZUSHIMA; Speaker: CHU, FIXMAN, WIDOM, RICCI and MIZUSHIMA).

SESSION ON THURSDAY (Prof. SCHWAB *Presiding*)

The application of the theory of van der Waals forces to the physical interaction of molecules with solid surfaces has not yet been worked out, although the basic notions are now well known. As for the exchange forces of chemisorption, a statistical treatment, based on semiconductor theory, gives a general frame, and the quantum mechanical treatment, at least of intermolecular interaction along the surface, is in a hopeful beginning. Experiments in catalysis leave no doubt that in many cases charge transitions depending on the electronic nature of the solid and the molecules result in the formation of covalent bonds. Here, the consideration of localized surface orbitals and the introduction of ligand field theory appear to gain increasing importance. Modern physical methods of experimentation, especially spectroscopic ones, give already increasing information on different types of bonding. It is desirable to apply such methods broadly and to well defined systems and at the same time to develop further the quantum mechanical treatment of both kinds of surface forces.

(Summarized by SCHWAB; Speaker: SCHWAB, GRIMLEY, GARCÍA DE LA BANDA, and PRETTRE).

SESSION ON FRIDAY (Prof. CHAGAS *Presiding*)

The possibilities of recognition of the molecular forces involved in biological phenomena were discussed. It became clear that two approaches to the question are equally important.

The first one tries to focus the forces responsible for the interaction between molecules considered of biological significance by extrapolating to them the physical or physico-chemical data obtained from the theoretical analysis, or those from « *in vitro* » experiments wherein purified or pure systems are employed. The second experimental data are taken, and it is tried to see how they may indicate in its interpretation the involvement of known physical concepts. It was understood that both approaches are complementary, and needed in order to attain a common objective. In the first one it was stressed that a work as molecular configuration is involved, being the main feature in the specificity claim of all biological reactions, it seems that a cautious quantum mechanics analysis should be tried, mostly whenever quantitative expressions can be reached, and be put to experimental testing afterwards. In this sense it was pointed out that knowledge on the interaction of water molecules with other biologically active molecules should be actively studied in a theoretical approach as much as in an experimental basis. As an example of the first approach, the study of the stability of hydrogen bonding in the preservation of genetic code was also subject to scrutiny. It was generally agreed, however, that much speculative work has still to be undertaken, and probably new tools of theoretical investigation developed in order to obtain a general theoretical view of the intermolecular force acting in a biological system. The second approach was discussed, taking as a specific example, the inhibition of cholinergic nerve-impulse transmission by curare-like agents. It was agreed that the instrumental approach — as for instance the use of the modern physical techniques so fruitfully utilized in the nonliving system — has to be thoroughly improved if more knowledge has to be gained in the analysis of this type of biological interactions. It was particularly stressed that more recognition of the cellular molecular species must be upgraded before any firm analysis of

the intermolecular forces involves in such reactions should be imposed. This knowledge would allow also for the obtention of essential thermodynamocular data still unknown.

(Summarized by CHAGAS; Speaker: CHAGAS, LÖWDIN and VERWEY).

NOTE COLLECTIVE FINALE

La Semaine d'Etude fut remarquablement organisée par Son Excellence le Professeur P. DEBYE que son état de santé empêcha malheureusement de présider la réunion. J'ouvris la réunion et demandai à cinq des participants de présider l'une des sessions journalières: le Prof. HIRSCHFELDER le lundi, le Prof. CASIMIR le mardi, moi le mercredi, le Prof. SCHWAB le jeudi et le Prof. CHAGAS le vendredi.

La réunion se déroula selon le plan établi par le Prof. DEBYE et fut un plein succès. Durant le dernier après-midi (le vendredi), les présidents et le Prof. WIDOM résumèrent les points principaux des communications et des discussions des sessions journalières. Pour la préparation du rapport final, les résumés furent envoyés au Prof. DEBYE. Celui-ci s'était rétabli en un mois et put lire ces documents. Mais, à notre grand regret, ce physicochimiste de réputation mondiale mourait avant d'avoir pu préparer son rapport. En conséquence, les résumés préparés par les présidents de session et par le Prof. WIDOM ont été publiés ici dans leur forme originale, car je savais que le Prof. DEBYE était d'accord sur l'essentiel de ces documents.

SAN-ICHIRO MIZUSHIMA
Académicien Pontifical et Pré-
sident de la Semaine d'Etude

SESSION DU LUNDI (Prof. HIRSCHFELDER, *Président*)

Les forces intermoléculaires sont responsables de la plupart des propriétés physiques et chimiques de la matière. Bien que la nature exacte de ces forces soit très complexe, il n'y a pas de difficultés de conception. A faible distance, les forces les plus grandes sont dues à un échange d'électron ou une valence chimique. A plus grande distance, ces forces résultent de moments électriques permanents ou induits. Une expérimentation précise et des calculs théoriques sont simultanément nécessaires pour définir quantitativement les forces intermoléculaires. La détermination des propriétés des molécules isolées sera utile à la prévision des interactions à grande distance. Les expériences de diffraction des jets moléculaires (comprenant les effets d'interférence) doivent être particulièrement utiles pour définir l'énergie d'interaction en fonction de la distance. L'emploi des nouvelles techniques de la mécanique quantique et des ordinateurs à grande vitesse rend possible le calcul précis d'une force intermoléculaire sur la base des lois classiques de la physique. De nombreuses recherches expérimentales et théoriques sont nécessaires pour rendre quantitatives nos connaissances des forces intermoléculaires.

Les forces répulsives à courte distance ont été obtenues à l'aide des jets moléculaires de grande énergie dans la « conception classique de la section efficace ». Les jets moléculaires de faible énergie (thermique) fournissent, à l'aide de la « conception quantique de la section efficace », les interactions à longue distance. La relation entre l'énergie et le « maximum du spectre » détermine l'énergie maximale d'attraction et la distance intermoléculaire correspondante. Les effets d'interférence de la mécanique quantique sont utiles pour l'obtention de compléments d'interprétation. Actuellement la précision des expériences n'est pas suffisante pour déterminer sans équivoque le potentiel intermoléculaire. Une plus grande vitesse et une meilleure résolution angulaire des jets moléculaires rendront la mé-

thode d'investigation plus sensible pour la détermination des forces intermoléculaires.

Les forces électrostatiques et d'induction à grande distance dépendent de la distribution des charges et des polarisibilités différentes des molécules isolées. Des expériences simples ont été conçues pour mesurer les moments permanents et induits. Ces moments devront être mesurés pour nombre d'espèces moléculaires importantes, spécialement pour les états excités pour lesquels le manque d'information est particulièrement flagrant.

(Résumé par HIRSCHFELDER; communications de: HIRSCHFELDER, BUCKINGHAM et BERNSTEIN).

SESSION DU MARDI (Prof. CASIMIR, *Président*)

D'un point de vue théorique, il y a accord sur le fait que, pour les molécules neutres et non polaires, à une distance importante par rapport aux dimensions moléculaires, le terme principal de l'interaction soit les forces de London-van der Waals. L'effet de retardation est donc basé sur une théorie incontestée.

L'interaction entre corps macroscopiques peut être obtenue par une simple intégration, mais aussi à l'aide de méthodes plus rigoureuses. Heureusement, il n'y qu'une faible différence entre les deux méthodes. La situation théorique est raisonnablement claire bien que, pour les distances intermédiaires et les arrangements géométriques spéciaux, un nouveau perfectionnement de la théorie soit désirable.

OVERBEEK a présenté un rapport sur les mesures de la force d'attraction entre solides à des distances de 1000 Å ou plus. Somme toute, ces expériences confirment les prévisions théoriques et, bien qu'une plus grande amélioration de leur précision soit désirable, la situation semble bien en main.

D'autre part, l'étude des films de savon rapportée par LYKLEMA, a révélé quelques problèmes. Bien que ces expériences aient prouvé l'existence de forces attractives à longue distance, il y a certains désaccords: ces forces ne peuvent expliquer les effets de retardation même à grande distance et leur valeur absolue est supérieure à celle à attendre des forces de London-van der Waals. Un des résultats de nos discussions est que, dans ce cas, les interactions dipôle-dipôle du type Keesom peuvent jouer un rôle prédominant.

LYKLEMA a également présenté un rapport sur la stabilité des colloïdes. Les idées générales de la théorie de Derjaguin-Landau-Verwey-Overbeek sont bien confirmées, mais la situation est moins satisfaisante du point de vue quantitatif. Cela n'est pas surprenant en raison de la nature plutôt compliquée de la situation. Ici aussi, il faut faire attention aux forces du type forces de Keesom.

BOWDEN a présenté un rapport sur des mesures qui sont à mi-chemin entre les expériences vraiment macroscopiques et celles sur les colloïdes et les films liquides. Dans ces expériences, est incluse une étude soignée de surfaces planes à l'échelle atomique, spécialement la surface du mica. Les techniques d'examen de telles surfaces ont été discutées. Les expériences sont encore en cours. Il est souhaitable qu'elles puissent fournir des données dignes de confiance sur les forces macroscopiques de van der Waals à des distances pour lesquelles elles deviennent importantes.

Un travail utile doit être possible dans les directions qui viennent d'être indiquées, mais une attention spéciale doit être accordée aux forces dipôle-dipôle. Il a été également suggéré qu'une recherche sur l'interaction de corps macroscopiques immergés dans des liquides serait intéressante. Ici, l'emploi de He II pourra offrir d'intéressantes possibilités.

(Résumé par CASIMIR; communications de: CASIMIR, OVERBEEK, LYKLEMA et BOWDEN).

SESSION DU MERCREDI (Prof. MIZUSHIMA, *Président*)

Il n'y a pas encore une théorie vraiment fondamentale des liquides qui relie leurs propriétés aux forces intermoléculaires par une application rigoureuse des lois de la mécanique statistique. Néanmoins, un certain nombre d'approximations utiles sont connues et ces résultats théoriques, combinés aux mesures expérimentales, ont conduit à une représentation des systèmes fluides dans laquelle nous pouvons avoir une certaine confiance. Il a été trouvé que la fonction de distribution radiale et, en général, les fonctions de corrélation sont la voie la plus directe et la plus féconde pour décrire les relations entre les forces intermoléculaires et la nature des systèmes fluides.

L'accord est général sur la relation entre la diffusion de la lumière et les propriétés thermodynamiques du fluide diffusant, en particulier sur la théorie fondamentale de l'opalescence critique. Il est toutefois encore très incertain que l'on ait observé expérimentalement ce que la théorie prédit des caractères de la diffusion aux petits angles au voisinage du point critique. Une difficulté majeure est l'incertitude concernant la correction à apporter pour la diffusion multiple. Il est urgent et important que l'expérience fournisse à ces questions une réponse digne de confiance.

Nos études ont montré clairement que, sur l'importante question de la structure des liquides, la vieille interprétation selon laquelle les liquides sont quasi-cristallins, tend à induire en erreur et, par conséquent, que les fonctions de distribution radiale des liquides sont privées de certaines des caractéristiques essentielles de l'ordre cristallin.

Le champ très nouveau de la diffusion inélastique de la lumière et l'étude de ses relations avec les propriétés de transport et avec les fonctions de corrélation espace-temps, paraissent offrir de très grands espoirs d'aboutir à des résultats expérimentaux importants. Ces résultats ne sont pas encore très nombreux et le progrès dans ce domaine mérite tous les encouragements.

En ce qui concerne les fonctions potentielles utilisées jusqu'ici pour les molécules indépendantes et les cristaux moléculaires, un perfectionnement y a été apporté de telle sorte que les valeurs des constantes de forces obtenues à partir des données spectroscopiques sont maintenant en bon accord avec celles fournies par des expériences autres que les mesures infrarouges et Raman.

Il a été observé un nouveau diagramme de diffraction des électrons et une nouvelle micrographie électronique de l'oxyde formé durant l'étape initiale de l'oxydation superficielle d'un monocristal de fer pur. La cohésion de la très mince couche d'oxyde avec la surface de fer a été discutée. (Egalement la possibilité d'une force de cohésion entre l'oxyde et la surface métallique).

(Résumé par WIDOM et MIZUSHIMA; communication de CHU, FIXMAN, WIDOM, RICCI et MIZUSHIMA).

SESSION DU JEUDI (Prof. SCHWAB, *Président*)

L'application de la théorie des forces de van der Waals à l'interaction physique des molécules avec des surfaces solides n'a pas encore été élaborée, bien que les notions de base soient actuellement bien connues. En ce qui concerne les forces d'échange de la chimisorption, un traitement statistique basé sur la théorie des semiconducteurs fournit un cadre général et le traitement quantique débute de manière très prometteuse, au moins en ce qui concerne l'interaction intermoléculaire le long de la surface. Les expériences en catalyse établissent sans contestation que, dans de nombreux cas, des transferts de charges dépendant de la nature électronique du solide et de celle des molécules ont pour résultat la formation de liaisons de covalence. Dans ce domaine, la prise en considération d'orbitales

localisées à la surface et l'introduction de la théorie du champ de coordinat (ligand field theory) apparaissent comme prenant une importance croissante. Les méthodes expérimentales de la physique moderne, tout particulièrement les méthodes spectroscopiques, fournissent déjà un nombre croissant d'informations sur les différentes sortes de liaisons. Il est désirable que de telles méthodes soient largement appliquées à des systèmes bien définis et qu'en même temps se développe davantage le traitement par la mécanique quantique des deux espèces de forces superficielles.

(Résumé par SCHWAB; communications de: SCHWAB, GRIMLEY, GARCÍA DE LA BANDA et PRETTE).

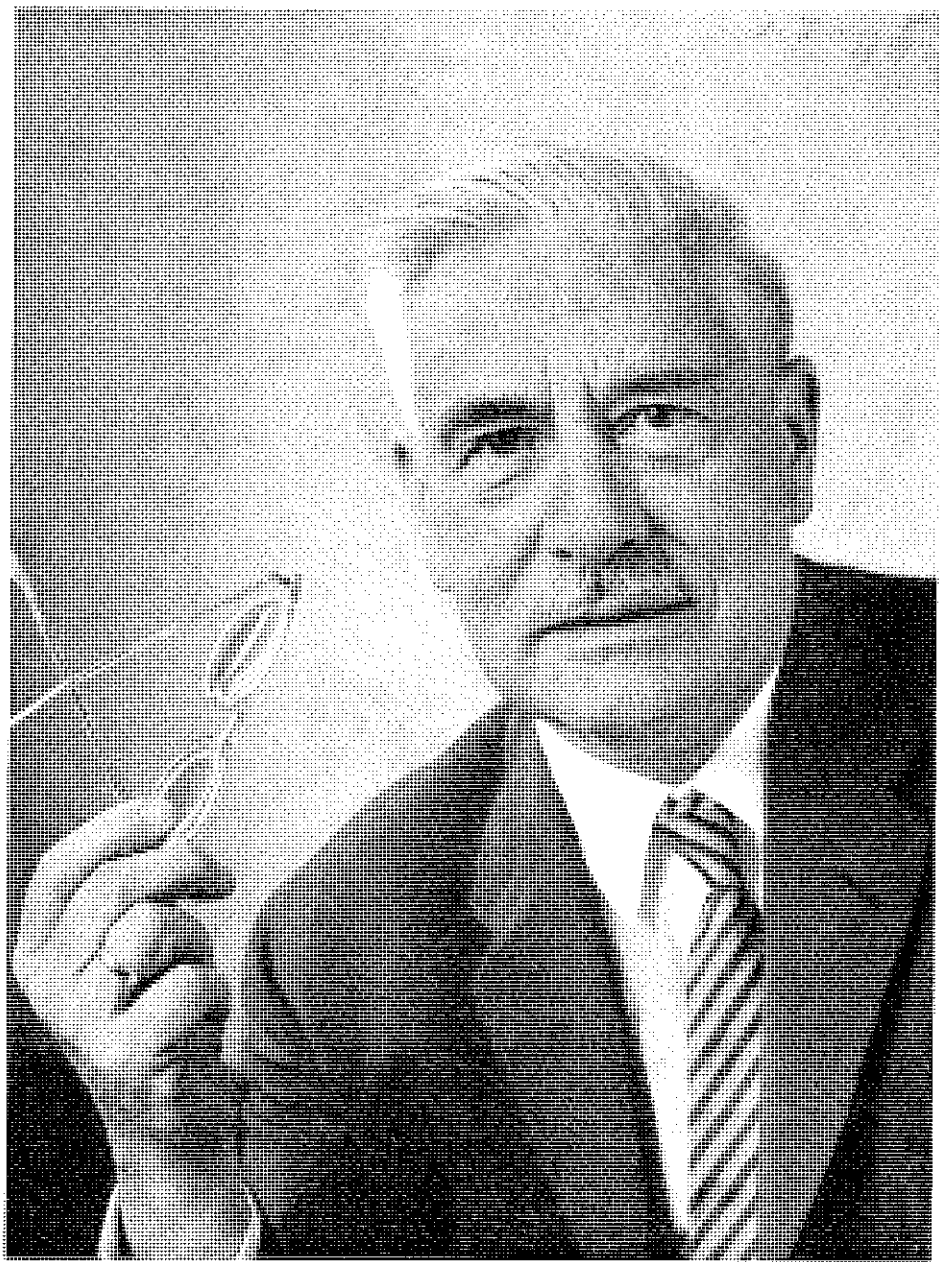
SESSION DU VENDREDI (Prof. CHAGAS, *Président*)

Il a été discuté des possibilités d'identification des forces moléculaires impliquées dans les phénomènes biologiques. Il est apparu clairement que deux approches de cette question sont d'égale importance. La première tente d'identifier les forces responsables des interactions entre molécules d'intérêt biologique, par extrapolation de données physiques et physicochimiques qui sont obtenues, soit à partir d'analyse théorique, soit à partir de mesures « in vitro » sur des systèmes purifiés ou purs. La seconde regroupe des données expérimentales et tente de relier leur interprétation aux concepts physiques connus. Il a été reconnu que les deux approches sont complémentaires et nécessaires pour atteindre un objectif qui leur est commun. Dans le premier cas, il a été souligné qu'un changement de conformation moléculaire est la caractéristique principale de la spécificité exigée de toutes les réactions biologiques. Il semble qu'une soigneuse analyse quantique devrait être tentée, surtout quand il est possible de parvenir à des expressions quantitatives,

et que cette analyse soit ensuite testée expérimentalement. Dans ce sens, il a été signalé que la connaissance de l'interaction des molécules d'eau avec d'autres molécules biologiquement actives, doit être développée tant en ce qui concerne l'approche théorique que sur une base expérimentale. En exemple de la première approche, l'étude de la stabilité de la liaison hydrogène dans la préservation du code génétique a été l'objet d'un examen minutieux. Il a été cependant généralement convenu que plus de travail spéculatif demeure encore à entreprendre et qu'il faudra probablement développer de nouveaux concepts pour l'investigation théorique dans le but d'obtenir une vue générale théorique des forces intermoléculaires intervenant dans un système biologique. La seconde approche a été discutée en prenant comme exemple spécifique l'inhibition par les agents de type curare de la transmission de l'influx nerveux cholinergique. Il a été convenu que l'approche instrumentale — comme par exemple l'emploi des techniques physiques modernes si efficacement utilisées dans la matière inerte — doit être notablement perfectionnée si l'on veut obtenir une meilleure connaissance de la compréhension de ce type d'interactions biologiques. Il a été particulièrement souligné que l'on doit accéder à une meilleure identification des espèces moléculaires de la cellule avant que puisse s'imposer toute analyse solide des forces intermoléculaires impliquées dans de telles réactions. Ces connaissances devraient aussi permettre d'obtenir les données thermodynamique essentielles encore inconnues.

(Résumé par CHAGAS; communications de: CHAGAS, LÖWDIN et VERWEY).

APPENDIX



P. J. J. J.

PIETER JOSEF WILLIAM DEBYE

The sudden and untimely death on Nov. 22, 1966 of His Excellency Prof. Dr. PIETER J.W. DEBYE, Pontifical Academician, Todd Professor of Chemistry, Emeritus at Cornell University came as a great shock to the learned world and as a still greater one to his friends.

He was born on March 24, 1884, at MAASTRICHT in the Netherlands, and attended elementary and secondary schools in that city. He entered the University of Aachen and received his diploma in electric engineering in 1905. In the meantime he began to be interested in chemistry and physics under the influence of Prof. MAX WIEN and Prof. SOMMERFELD, both of whom were there at that time.

In 1906 Dr. DEBYE was invited to accompany Dr. SOMMERFELD to München when the latter was called to the chair of theoretical physics and in two years he presented his doctoral thesis which showed he was a genius for mathematics also.

When Dr. DEBYE was twenty-seven years old, the University of Zürich offered him a full professorship in theoretical physics to succeed Prof. EINSTEIN. Here he developed two fundamental theories which have opened new research frontiers: i.e. the theory of polar molecules, and the theory of specific heats of solids. Dr. DEBYE then returned to his homeland, as Professor of Theoretical Physics at Utrecht, but in 1913 was invited to Göttingen where he settled down for seven

years. Notwithstanding the difficulties arising from World War I, he worked out the powder method of X-ray diffraction for solids in collaboration with Dr. SCHERRER. In 1920, he moved once again to Zürich as Professor of Experimental Physics and Director of the Physical Laboratory at Eidgenössische Technische Hochschule. In this period Dr. DEBYE published two important papers, one on the theory of strong electrolyte and the other on magnetic cooling.

For the next seven years, starting in 1927 Dr. DEBYE was the Director of the Physical Institute in Leipzig. Here work on X-ray scattering in gases, on dipole moments, and on properties of electrolytes was actively continued. In 1934 Dr. DEBYE left Leipzig for Berlin, to accept the joint posts of Professor at the University of Berlin and Director at the Kaiser Wilhelm Institute — now the Max Planck Institute. This was built with funds of the Rockefeller Foundation. In 1936 Dr. DEBYE's outstanding work received formal international recognition through the award of the Nobel Prize in Chemistry.

Soon after the Berlin Laboratory started, the World War II broke out, when he was informed from the Kaiser-Wilhelm Gesellschaft that he could no longer enter the laboratory except by becoming a German citizen. When he refused, he was advised by the Ministry of Education to stay at home. This is the ridiculous thing which the Nazi did, but this resulted in the inestimable benefit for the U.S.A.

It was an invitation to give the Baker Lecture at Cornell University that brought Dr. DEBYE to the States in 1940. Right after that, he was appointed Professor of Chemistry and Head of the Department of Chemistry, and was named Todd Professor of Chemistry in 1948. At Cornell, he was interested in macromolecules and colloid chemistry to which he brought new ideas as usual. He proposed a new method based on light scattering for the determination of molecular weights of polymers with his son PIETER P. DEBYE. His micelle theory was also worked out during this time, as well as the technique of

thermal diffusion. In 1950, he became Professor Emeritus. However, this did not mean the retirement from his researches; on the contrary he could devote all his time to research. The study of critical phenomena of liquid mixtures, that of the range of molecular forces, etc. have been carried out actively. In addition to researches, Dr. DEBYE was very active in making scientists even after his retirement. He gave lectures in one place or another almost weekly in the States and averaged two lecture trips to Europe annually.

Dr. DEBYE was asked by the Pontifical Academy of Sciences to organize a meeting (the Study Week) on molecular forces to be held in April, 1966. He organized this Study Week very nicely. However, he could not preside at the meeting because just at the time of his departure from Kennedy Airport in New York for Vatican City he suffered a heart attack and had to go to a hospital. Nevertheless the meeting took place according to Dr. DEBYE's plan and were very successful. The participants were anxious that as soon as he had completely recovered he would be able to read the papers presented and the stenographic records of the discussions. Within a month Dr. DEBYE had recovered and started to resume his travelling to give lectures and consultations. However it was only a few months later, when countries all over the world to our regret reported the passing away of one of the world's leading physical chemists.

In addition to the Nobel Prize, Dr. DEBYE was awarded the Rumford Medal of the Royal Society of London (1930), the Lorentz Medal of the Royal Dutch Academy at Amsterdam (1935), the Franklin Medal of the Franklin Institute (1937), the Willard Gibbs Medal (1949) and the Priestley Medal (1963) of the American Chemical Society, the Max Planck Medal of the West German Physical Society (1950), and National Medal of Science (1965). He received the doctor's degree, « honoris causa », from the Universities of Liège, Brussels, Oxford, Sofia, Harvard, Notre Dame, Maintz, etc. and Po-

lytechnic Institute of Brooklyn, Eidgenoessische Technische Hochschule, and Technische Hochschule, Aachen. In addition to Pontifical Academy the following academies elected him to membership: American Academy (Boston), Franklin Institute (Philadelphia), National Academy (Washington, D.C.), New York Academy (New York), Royal Dutch Academy (Amsterdam), Royal Society (London), Royal Institution of Great Britain (London), Royal Danish Academy (Copenhagen), Academies of Berlin, Göttingen, and München (Germany), Academies of Brussels and Liège (Belgium), Royal Irish Academy (Dublin), Indian Academy (Bangalore), National Institute of Science (India), and the Real Sociedad Española de Física y Química (Madrid), Academy of Science (USSR), (Hungary) and (Argentina).

In 1939 Maastricht, the town of his birth, unveiled his statue in the City Hall. This seemed to have given him the greatest pleasure among the many honors he received.

Dr. DEBYE was undoubtedly one of the world's leading scientist of this century, and lived to be a center of universal affection and esteem. Whereever Dr. DEBYE worked, he exerted a great influence on those who were fortunate enough to be in touch with him. Physical chemists all over the world bear a tremendous debt of gratitude for his genius in science and also in making scientists.

SAN-ICHIRO MIZUSHIMA

Pontifical Academician and
President of the Study Week

PIETER JOSEF WILLIAM DEBYE

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