Complexity and Analogy in Science
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COMPLEXITY IN CHEMISTRY: FROM DISORDER TO ORDER

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This contribution will address two questions raised in the prologue of this conference:

1. Can science render apparently complex systems in simple underlying theories?
1. Has a complex system necessarily to be complicated?

Our starting point will be disorder as to be expected from a closed system consisting of non-interacting elements, and the role of accident had already been pointed out in 1921 by E. Schrödinger in his Inaugural Lecture at the University of Zürich: "Physical research has unequivocally demonstrated that for the majority of observed phenomena, whose regularity and continuity led to the formulation of the postulate of general causality, the common root for strict laws has to be sought in the accident" [1].

Nevertheless the surrounding nature exhibits objects of considerable order, the most simple of which is found in the inorganic world of minerals and crystals. This order extends frequently down to the atomic scale as can be seen from Fig. 1* showing a section from the (111) surface of an aluminum single crystal surface recorded by scanning tunneling microscopy (STM) with atomic resolution. In order to illustrate the principles of order formation in simple chemical systems I shall focus my presentation in the following on experiments with well-defined single crystal surfaces of this type interacting with molecules from the gas phase.

Fig. 2 shows the image from a Pt(111) surface which had been exposed to a small quantity of O_2 molecules which dissociate upon interaction with the surface and give rise to the bright extra dots (surrounded by dark holes) from the adsorbed O atoms [2]. The energetics of such adsorbed atoms are illustrated by Fig. 3: Motion of the atom perpendicular to the surface is associated with a potential minimum E_{ad} (characteristic for the bonding to the surface) giving rise to the lifetime t_{surf} of the adsorbed species. Motion parallel to the surface is associated with a periodic variation of the potential whereby the barrier $E^\star$ denotes the activation energy for surface diffusion

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* Figures begin on p. 149.

which is much smaller than E_{ad} so that the particle has a residence time t_{site} and makes many jumps between neighboring sites before A eventually desorbs into the gas phase. Fig. 4a shows a snapshot (taken in 0.07 s) from O atoms randomly distributed over a Ru(0001) surface at T=300K. The mean residence of an isolated particle is now reduced to 60 ms, but increases to about 220 ms when two atoms approach each other to a distance of two lattice constants. This is a consequence of weak attractive interactions between neighbors over such a separation. As a consequence the distribution of adsorbed atoms at higher coverages is no longer random, but is characteristic by the formation of two phases as represented by the image of Fig. 4b: A diluted 'gas' phase and a well-ordered quasi-crystalline phase being in equilibrium with each other. The occurrence of phase formation and the formation of a ordered structure has in this case to be attributed to the establishment of thermodynamic equilibrium which is governed by the minimum of the Free Energy F=U–TS=min, with U=(Internal) energy, T=temperature, and S=entropy. In this case the attractive interaction between the adsorbed atoms lowers U and overcompensates disorder by the entropy term. This equilibrium condition holds for *closed* systems which can only exchange heat with the surrounding. We may call the resulting state as 'dead order' since the system is not nurtured by another source of Free Energy.

By contrast, there is another class of observations which we may classify as 'living order', because these are mainly – but not exclusively, as will be shown – found with living systems as exemplified by Fig. 5: The fur of the animal not only exhibits a pattern on macroscopic scale, but periodic motion reflects an addition also temporal order. These effects may certainly not be described on the basis of thermodynamic principles governing equilibrium.

In 1943 E. Schrödinger held a series of lectures which were later published under the title "What is life?" [4]. This book is considered to be a landmark in the development of molecular biology, since it pioneered the concept of molecular (i.e. chemical) basis of the genes. The author, however, admits that his real intention was to find an answer to the question of how living systems may develop into a state of higher order under conditions of an open system far from equilibrium, but he was in fact not able to find a satisfactory answer on the basis of the then known physical laws. However, a theoretical model for this type of structure formation was presented a few years later by the famous mathematician A. Turing in a paper entitled "The chemical basis of morphogenesis" [5], whose abstract reads: "It is suggested that a system of chemical substances, reacting together through a tissue, is adequate to account for the main phenomena of morphogenesis. Such a system, although it may be quite homogeneous, may later develop a pattern or structure due to an instability of the homogeneous state. With such reaction-diffusion systems stationary waves may appear. The theory does not make any new hypothesis; it merely suggests that certain well-known physical laws are sufficient to account for many of the facts".

At present, reaction-diffusion systems of the Turing type are indeed generally accepted as mechanism underlying (macroscopic) structure formation in biological systems [6,7]. The essential aspect is that we are no longer dealing with closed systems attempting to reach thermodynamic equilibrium, but with open systems far from equilibrium in which e.g. an ongoing chemical reaction serves as a continuous source of Free Energy. In Turing's concept chemical reaction is coupled to diffusion, and mathematical description is achieved in terms of coupled nonlinear differential equations. The theoretical framework for the chemical systems of the present context was essentially developed by Prigogine [8] who denoted the resulting effects of order as 'dissipative structures' because the supply of Free Energy is dissipated in the form of heat. An even more general concept was developed by Haken [9] and denoted as "synergetics". The consequences of complexity resulting along these principles for chemical systems will be presented with the catalytic oxidation of carbon monoxide on a Pt(110) surface whose mechanism is illustrated in Fig. 6. This reaction which is of importance for car exhaust removal comprises bonding (chemisorption) to the surface of CO through the carbon atom and dissociative adsorption of O_2, followed by recombination of both surface species (CO_{ad} and O_{ad}) to CO_2 which is then immediately released into the gas phase. Under steady-state flow conditions the rate of CO_2 formation will usually be constant and determined by temperature T and the partial pressures for the reactants, p_{CO} and p_{O_2}, respectively. In special cases, however, this is not the case, but the rate will start to oscillate periodically with time. This is shown in Fig. 7 where for constant T and p_{CO} at the point marked by an arrow the O_2 partial pressure is stepwise increased where after the rate slowly grows and then oscillates [10].

Another example of this kind is presented in Fig. 8 which shows the variation with time of the number of furs from hares and lynxes delivered to the Hudson's Bay Company [11]. The oscillating populations of both species are coupled to each other with some phase shift. The reason seems to be quite obvious: If the lynxes find enough food (=hares) their population will grow, while that of the hares will decay as soon as their birth rate cannot compensate the loss any more. When the supply of food ceases, the lynxes begin to starve and their population decays so that of the hares can recover. Although the actual situation is somewhat different, the essential features of the concentrations x and y of the two species can be approximately modelled by two coupled, nonlinear ordinary differential equations (Lotka-Volterra model) as shown in Fig. 9 together with their solution for properly chosen parameters a and b which reproduces qualitatively the observed behavior.

An essential aspect of mathematical modelling consists in the description in terms of nonlinear coupled differential equations, hence also the denotion 'nonlinear dynamics' for this actual field of research.

In a similar manner the temporal oscillations in the CO oxidation on a Pt(110) surface as reproduced in Fig. 7 can be modeled with a set of three coupled nonlinear differential equations, with the coverages of CO and O and the fraction of the surface structure being present in the 1x1 phase. Solution for properly chosen kinetic parameters (derived from experiment) is reproduced in Fig. 10 and reproduces indeed the observed behavior [12].

However, the theoretical description is so far not yet complete: If an extended system exhibits temporal oscillations as a whole, lateral coupling between different parts is required in order to reach synchronization. Hence the state variables c_i (i.e. the surface concentrations in our case) depend not only on temporal, but also on spatial coordinates. Coupling takes place through diffusion so that description is achieved through a set of coupled nonlinear partial differential equations of the type $\frac{\partial c_i}{\partial t}=f_i\left(c_j,p_k\right)+D_i\nabla^2 c_i$ whereby f_i denotes the kinetics (depending on the concentrations and on the external parameters) and the last term (generalized) diffusion. The length scale of the resulting spatio-temporal concentration patterns is no longer determined by atomic dimensions but by the diffusion length which in our case is of the order of micrometers [13]. These patterns can be imaged by the technique of photoemission electron microscopy (PEEM) [14]: Adsorbed O and CO species are accompanied by different dipole moments and hence different intensities of electrons emitted by UV light. Dark areas in the images are mainly O-covered while brighter patches are CO-covered. As an example, Fig. 11 shows so-called target patterns, concentric elliptic waves propagating somewhat faster in direction of the Pt(110) surface along which direction CO diffusion is also faster, on a background changing periodically between bright (=CO-covered) and dark (=O-covered), reflecting the periodic variation of the integral reaction rate while the external parameters of temperature and partial pressures of the reactants are kept constant [15].

Under other external parameters, typical spiral waves may develop as reproduced in Fig. 12, propagating with front velocities of several micrometers per second [16]. Spiral waves are ubiquitous in nature, ranging from galaxies to hurricanes to animals. In our case the underlying mechanism is well established and can be formulated in terms of the set of reaction-diffusion equations shown in Fig. 13 which contain for simplicity only diffusion of the fastest species, adsorbed CO (=u) [17]. Numerical solution of these partial differential equations yields for properly chosen parameters, indeed the evolution of spiral patterns from a random initial distribution as reproduced in Fig. 14. Slight changes of the parameters, however, yield breakup of the spirals and development of a turbulent (chaotic) state as shown in Fig. 15, and Fig. 16 presents experimental verification of this situation.

If we now return to the questions posed at the beginning, clear answers can be given: The example of catalytic oxidation of CO at a Pt(110) single crystal surface is certainly a simple system for which the details of the mechanism are known down to the atomic scale. Nevertheless it exhibits all features of complexity from pattern formation to chaos. This complex system can be successfully modeled theoretically on the basis of three differential equations derived from the experimentally established mechanism. Thus a complex system has by no means to be complicated.

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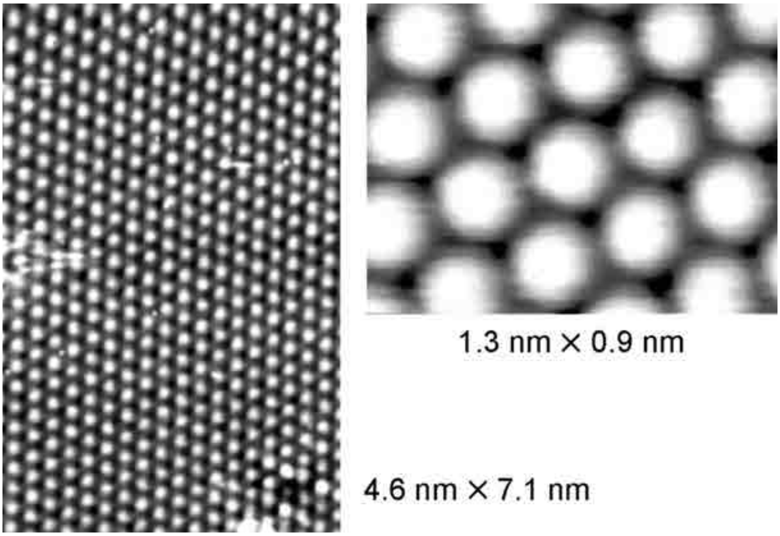

Figure 1. Al(111) single crystal surface as imaged by scanning tunneling microscopy (STM).

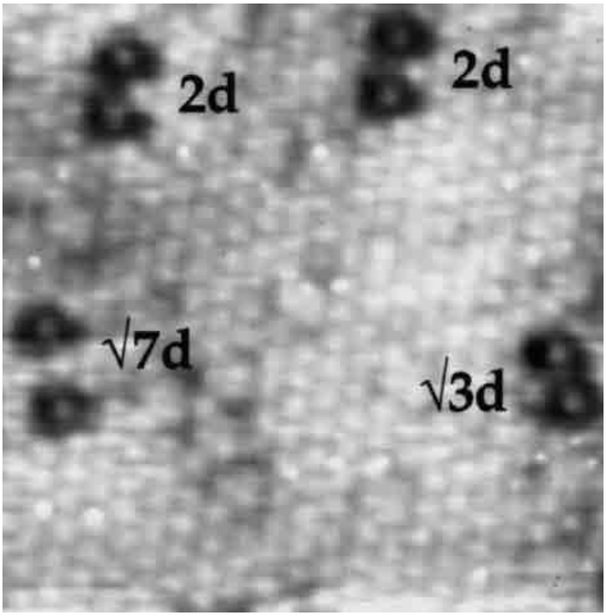

Figure 2. STM image from a Pt(111) surface (5.3x5.5 nm^2) after exposure to a small quantity of O_2 molecules at 165 K showing the formation of adsorbed O atoms.

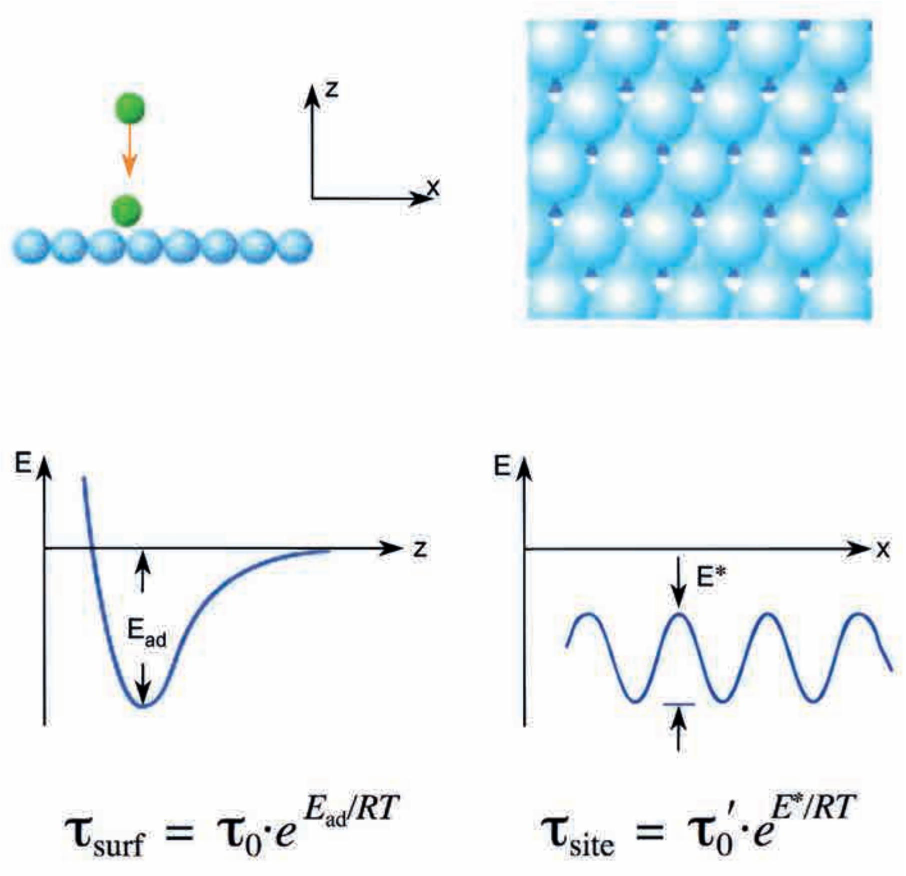

Figure 3. Potential of an atom interacting with a surface along the z- and x-directions.

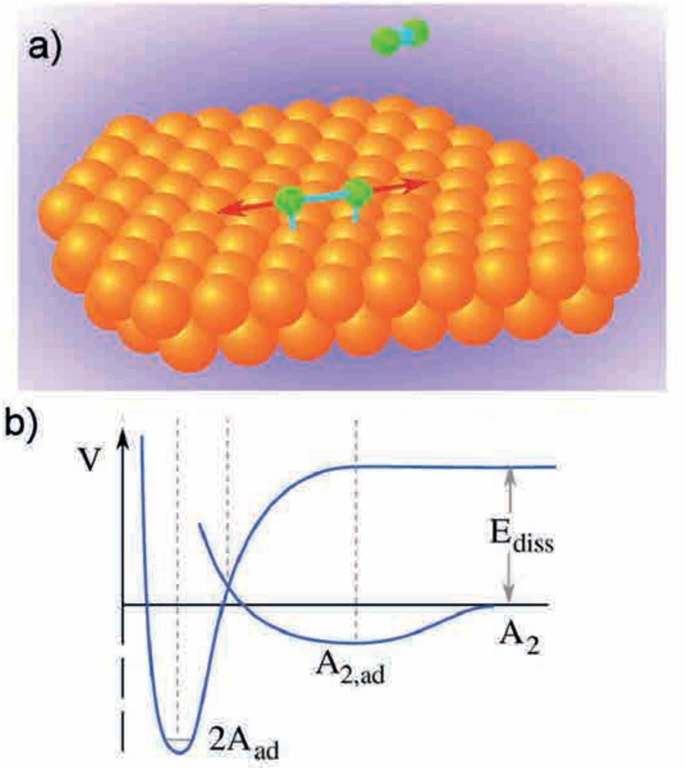

Figure 4. STM snapshots from O atoms adsorbed on a Ru(001) surface at 300 K. a) at very small coverage, b) at higher coverage.

Figure 5. The fur of a cheetah exhibits patches reflecting 'living order'.

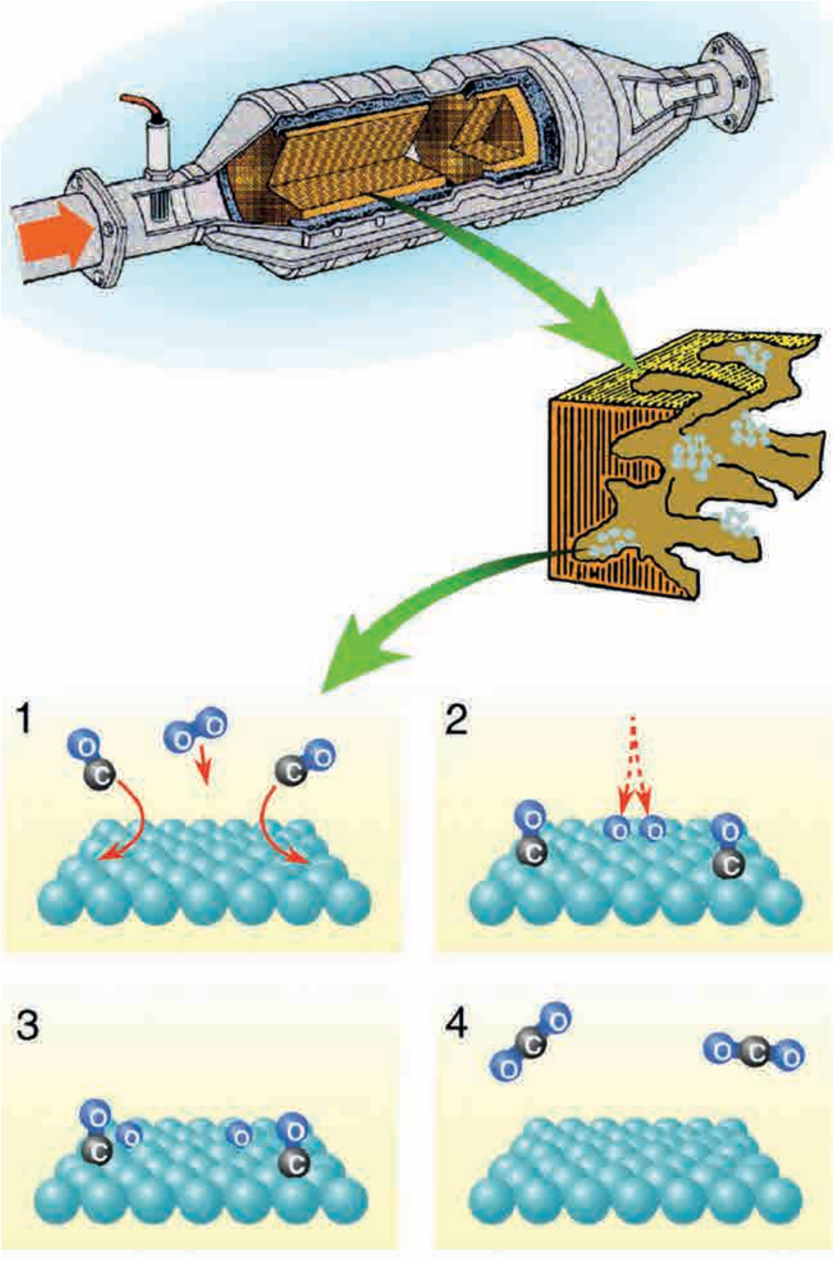

Figure 6. Schematic illustration of the mechanism of catalytic CO oxidation.

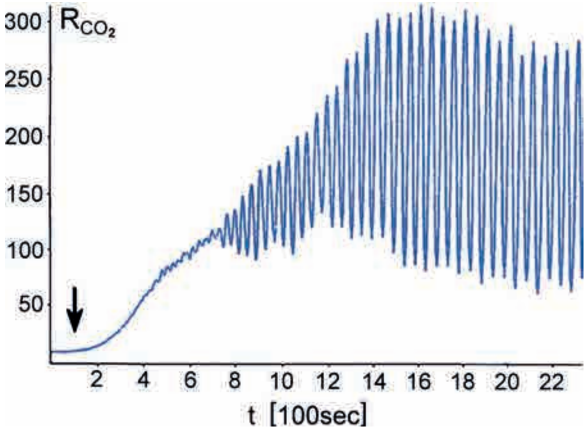

Figure 7. The rate of the catalytic CO oxidation on a Pt(110) surface as function of time when at the point marked by an arrow the steady-state partial pressure of O_2 is stepwise increased.

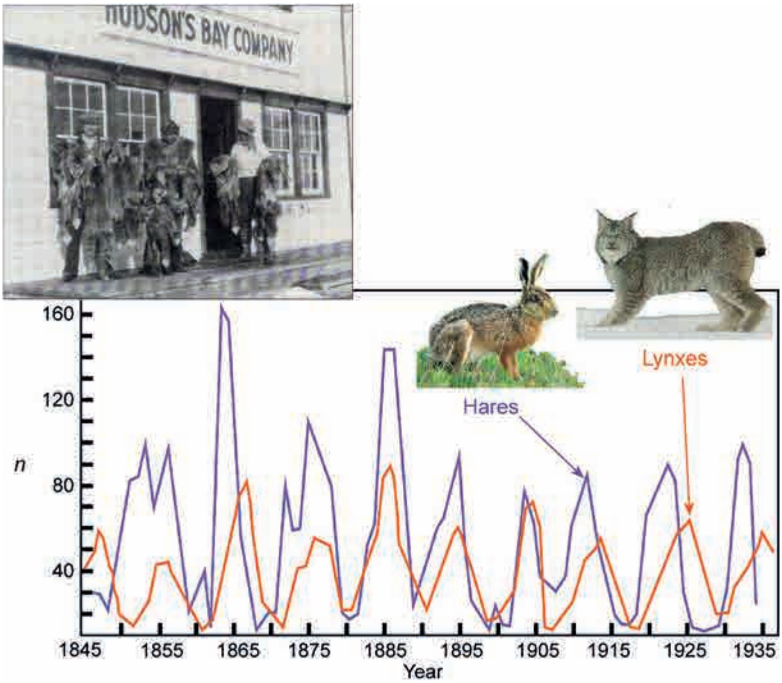

Figure 8. Variation of the number of furs n (in thousands) from hares and lynxes delivered to the Hudson's Bay Company over the years.

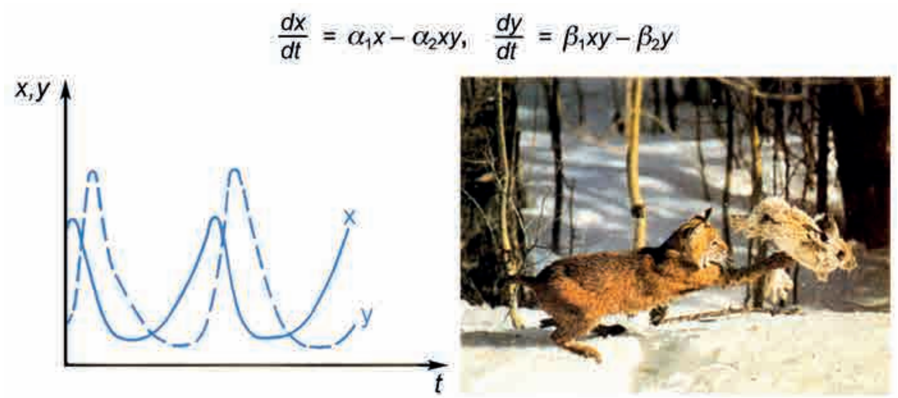

Figure 9. The Lotka-Volterra model for the concentrations of hares x and lynxes y and the solution of the two coupled ordinary differential equations.

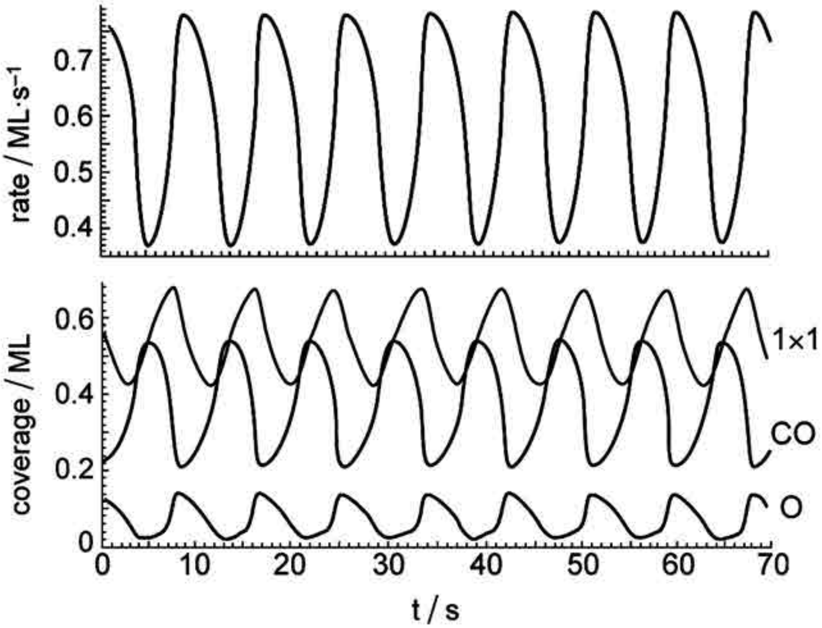

Figure 10. Solutions for the differential equations describing the reaction rate, as well of the concentrations of adsorbed O and CO and 1x1 surface phase during the catalytic CO oxidation on a Pt(110) surface at $T = 540$ K, $=6.7\text{x}10^{-5}$ mbar, $p_{CO} = 3\text{x}10^{-5}$ mbar.

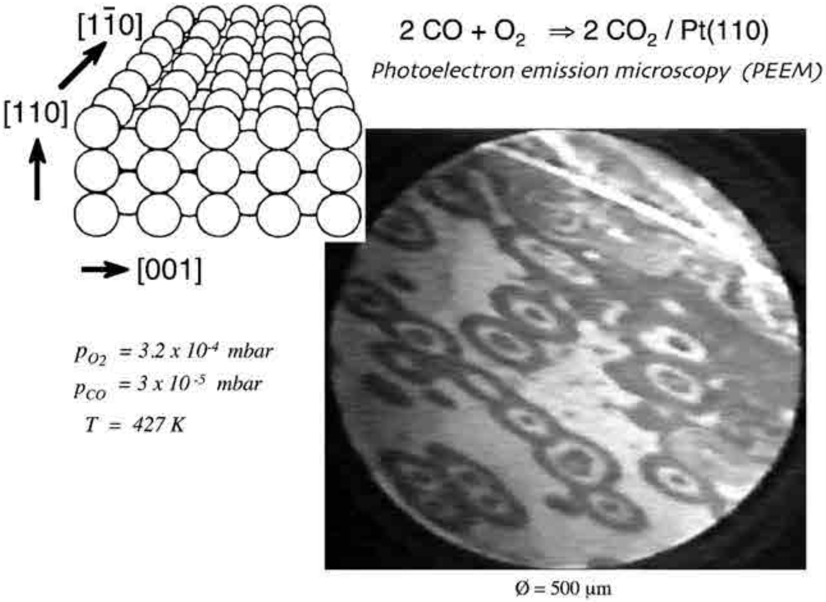

Figure 11. Target patterns during the catalytic CO oxidation on a Pt(110) surface as imaged by photoemission electron microscopy (PEEM).

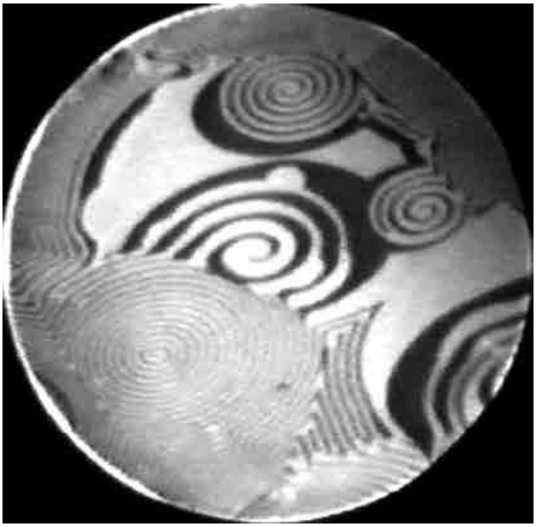

Figure 12. PEEM image from a typical spiral wave formed on a Pt(110) surface during catalytic CO oxidation.

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \;/\; Pt(110)$$

Reaction-diffusion model:

$\theta_{CO} \equiv u;\ \theta_0 \equiv v;\ \theta_{1\times 1} \equiv w\ (\theta_{1\times 2} = 1 - w)$

$$CO + * \rightleftarrows CO_{ad}$$

$$O_2 + 2* \rightarrow 2\,O_{ad}$$

$$O_{ad} + CO_{ad} \rightarrow CO_2 + 2*$$

$$(1\times 2) \xrightarrow{CO_{ad}} (1\times 1)$$

$$\frac{\partial u}{\partial t} = s(CO)p_{CO} - k_2 u - k_3 uv + D\nabla^2 u \quad (1)$$

$$\frac{\partial v}{\partial t} = s(O_2)p_{O_2} - k_3 uv \quad (2)$$

$$\frac{\partial w}{\partial t} = k_5[f(u) - w] \quad (3)$$

$$s(CO) = k_1(1 - u^3)$$

$$s(CO_2) = k_4[s_1 w + s_2(1 - w)](1 - u\text{-}v)^2$$

Figure 13. The set of 3 partial differential equations (reaction-diffusion equations) modeling the formation of spatio-temporal concentration patterns for adsorbed CO(=u) and O(=w) on a Pt(110) surface during the catalytic CO oxidation.

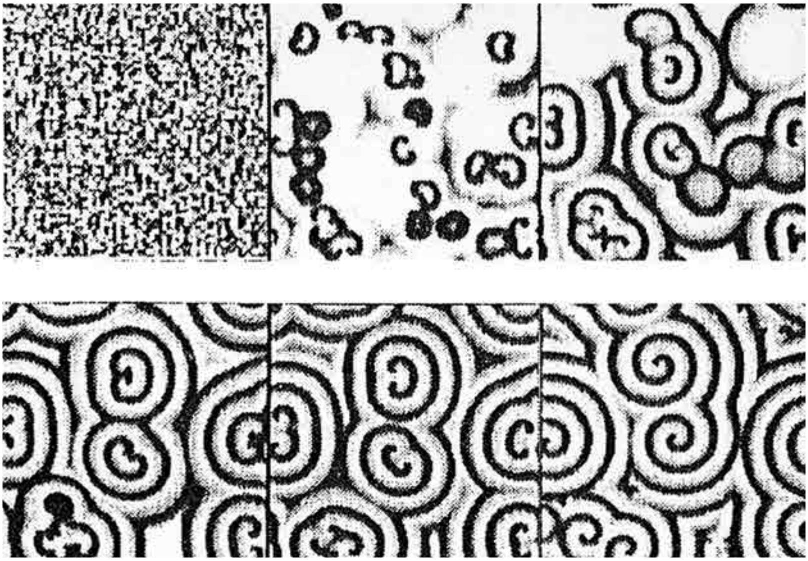

Figure 14. Numerical solutions of the preceding differential equations for a certain set of parameters with progressing time.

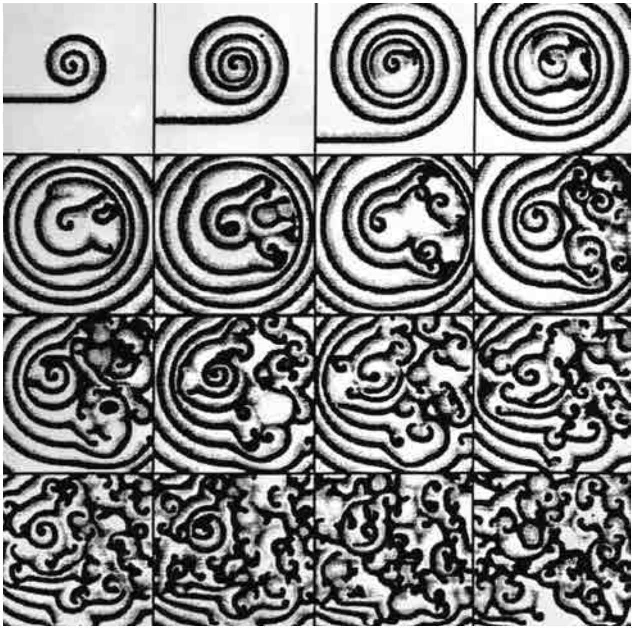

Figure 15. Upon slight variation of the parameters the computer simulations exhibit the break-up of the spiral waves and the transition to chemical turbulence (chaos).

Figure 16. PEEM image (0.36x0.36 mm^2) from a Pt(110) surface in the state of chemical turbulence during catalytic CO oxidation at T=548 K, =4x10^{-4} mbar, p_{CO}=1.2x10^{-4} mbar.