Classic paper

Reactions at surfaces:from atoms to complexity

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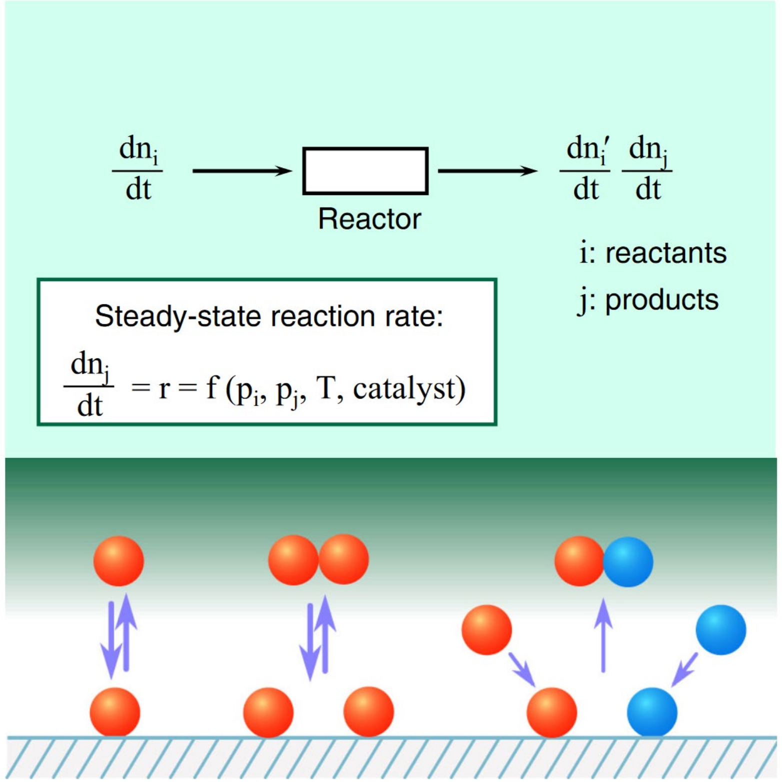
1. INTRODUCTION

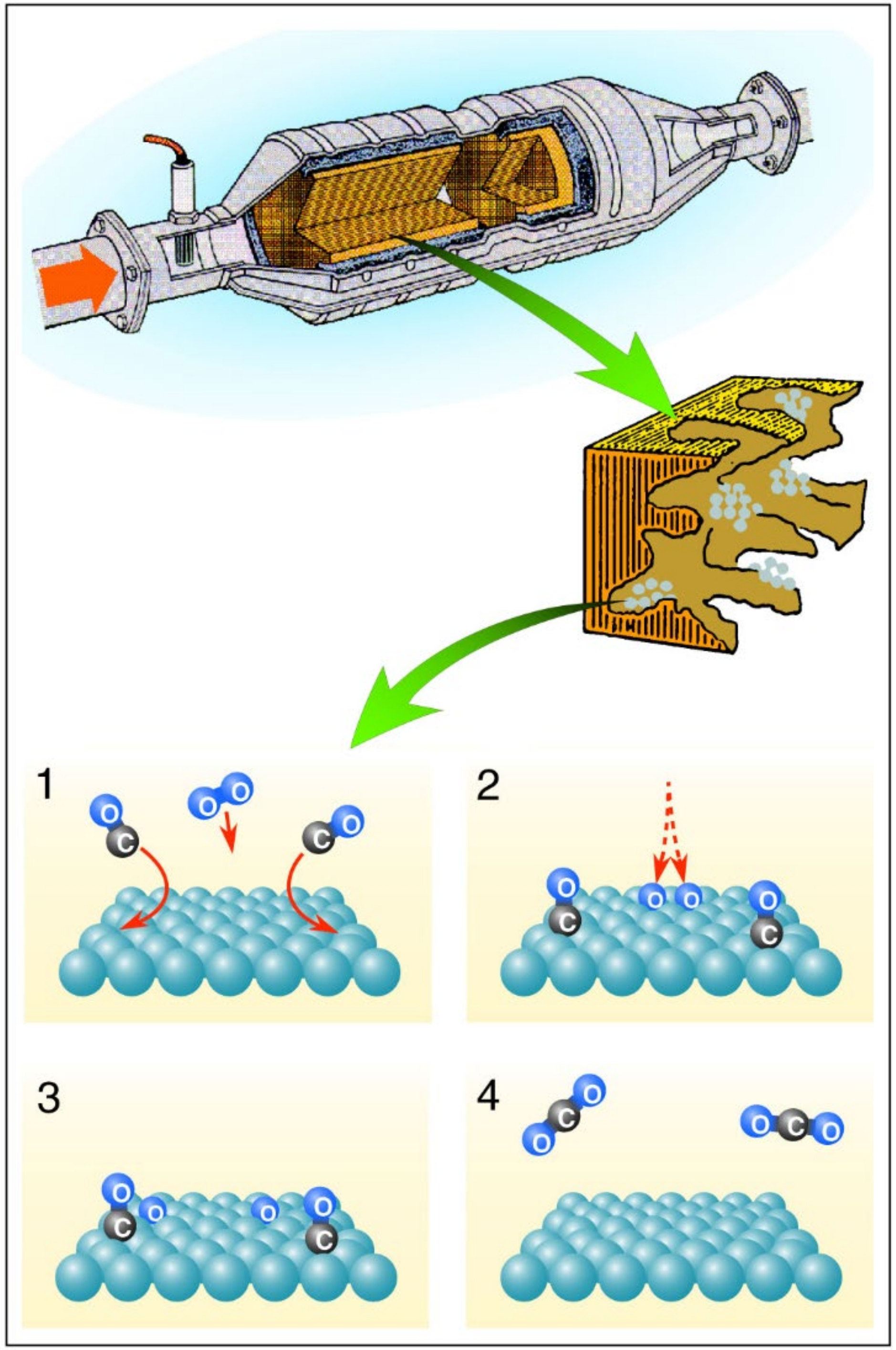
The secretary of the Royal Swedish Academy of Sciences, the famous chemist Jöns Jacob Berzelius, published since 1820 annual review articles on the most significant new developments in his field. Since the early 19th century there were observations from several laboratories whereafter certain substances influenced the progress of a chemical reaction without being consumed and hence apparently not being affected by this reaction. For example, Johann Wolfgang Doebereiner, professor of chemistry at the university of Jena, reported in July 1823 to his minister, J. W. Goethe, *"that finely divided platinum powder causes hydrogen gas to reaction with oxygen gas by mere contact to water whereby the platinum itself is not altered"* [1]. In his report published 1835 Berzelius defined this phenomenon as "catalysis", rather in order to introduce a classification than to offer a possible explanation [2]. Throughout the rest of this century the term catalysis remained heavily debated [3], until around 1900 W. Ostwald proposed its valid definition in terms of the concepts of chemical kinetics: *"A catalyst is a substance which affects the rate of a chemical reaction without being part of its end products"* [4]. In 1909, Ostwald was awarded the Nobel Prize in Chemistry for his contributions to catalysis.

Wilhelm Ostwald
1853 – 1932

Nobel Prize 1909

and T the temperature, and accordingly not all molecular encounters will be successful, but only a fraction $e^{-E^*/kT}$. An increase of the reaction probability (=rate) can be achieved by either increasing the temperature or by lowering the activation energy E*. The latter is provided by the catalyst which through the formation of intermediate compounds with the molecules involved in the reaction provides an alternate reaction path as sketched y the dashed line in fig. 1 which is associated with smaller activation barriers and hence a higher overall reaction rate. In the last step the product molecules are released from the catalyst which now is available for the next reaction cycle. If the reacting molecules and the catalyst are in the same (gaseous or liquid) phase the effect is called homogeneous catalysis. In living systems macromolecules (=enzymes) play the role of catalysts. In technical reactions mostly the interaction of molecules with the surface of a solid is decisive. The principle of this heterogeneous catalysis is depicted schematically in fig. 2.





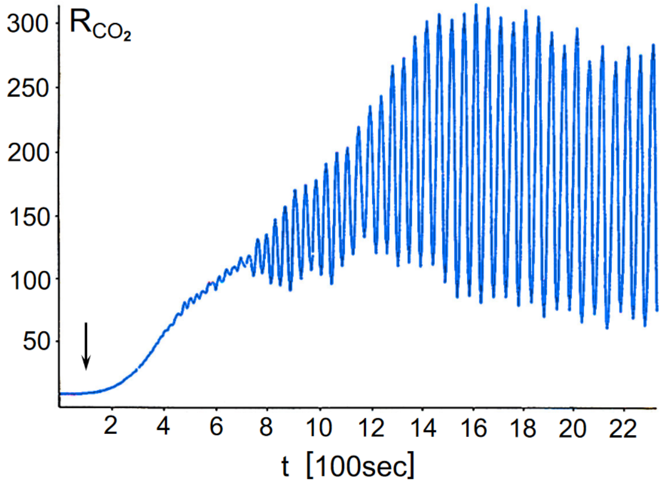
3. SELF-ORGANISATION AND COMPLEXITY: OXIDATION OF CARBON MONOXIDE

One of the major applications of heterogeneous catalysis in our days concerns protection of the environment through removal of toxic substances from car exhausts. Oxidation of carbon monoxide to carbon dioxide, $2CO + O_2 \rightarrow 2CO_2$, is the simplest of these reactions and is depicted schematically in fig. 12. The exhaust gas flows through the catalytic converter where the molecules interact with the surfaces of finely divided metal particles from the platinum group. Thereby the O_2 molecules are dissociatively chemisorbed, and the formed O_{ad} species interact with chemisorbed CO molecules to CO_2 which is immediately released into the gas phase.

sorption of CO, leading to a mixed phase as reproduced in fig. 13c where the two reactants are in close contact and can readily recombine to CO_2. Under steady-state flow conditions in a mixture of O_2+CO the surface of the catalyst will soon be fully covered by adsorbed CO which prevents oxygen adsorption and hence suppresses the reaction. This problem can only be overcome if the temperature is high enough (≥450 K) to enable continuous desorption of part of the adsorbed CO so that gaseous O_2 may compete for these free adsorption sites. (This is the reason why the catalyst of your car does not work in the cold but needs a certain minimum temperature.) The sequence of

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

Under steady-state flow conditions the rate of product formation will usually be constant and a function of the external parameters temperature and partial pressure of O_2 and CO, – however, with exceptions under rare conditions: Already around 1970, it was found in Wicke's laboratory [33] that with supported Pt catalysts sometimes the rate exhibits temporal oscillations. Such a situation can also be found with a well-defined Pt(110) surface as shown in fig. 15 [34]: At the time marked by an arrow the O_2-pressure was steplike raised from 2.0 to 2.7×10^{-4} mbar. As a consequence the rate slowly increases and then develops periodic variations with finally constant high amplitudes.



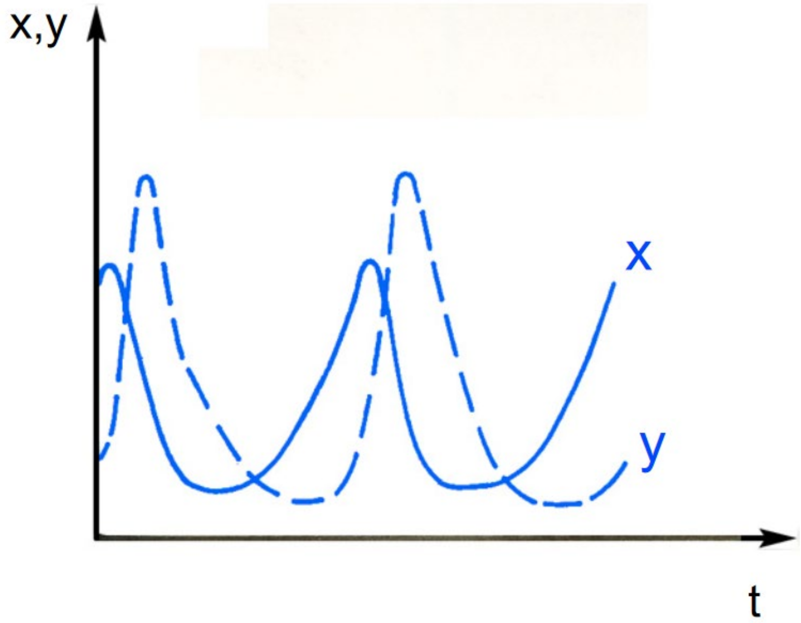
470 K; $p_{CO} = 3 \times 10^{-5}$ mbar; $p_{O_2} = 2.0 \rightarrow 2.7 \times 10^{-4}$ mbar

Characteristic for the present system is that it is far away from equilibrium and may develop so-called dissipative structures as explored in detail by Prigogine (Nobel Prize 1977) [35] and by Haken [36] in the framework of synergetics. A particularly spectacular example for such behavior from population dynamics is reproduced in fig. 16 [37] which shows the variation with time of the number of furs from hares and lynxes delivered to Hudson's Bay

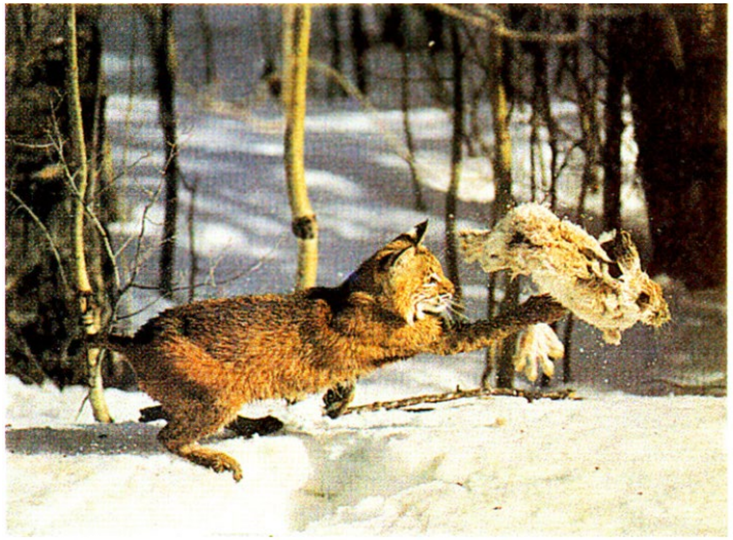
Lotka-Volterra Model

$$\frac{dx}{dt} = \alpha_1 x - \alpha_2 xy$$

$$\frac{dy}{dt} = \beta_1 xy - \beta_2 y$$

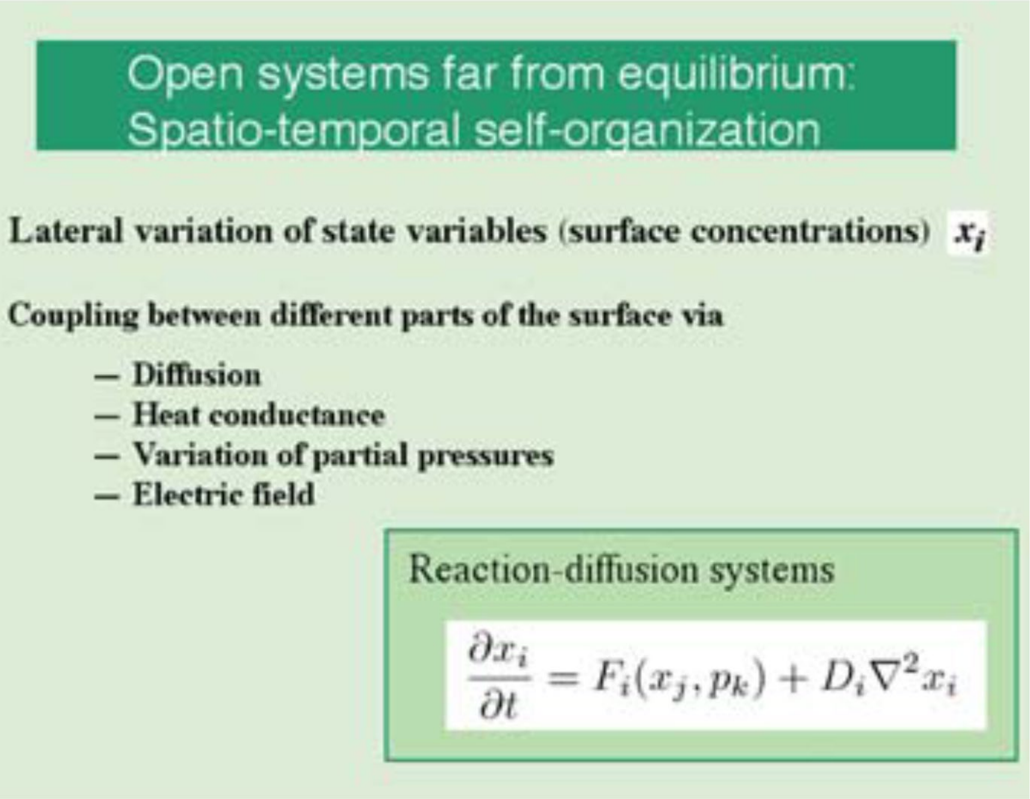


Company. The oscillating populations of both species are coupled to each other with a certain phase shift. The reason seems to be quite obvious: If the lynxes find enough food (=hares) their population grows, while that of the hares decays as soon as their birth rate cannot compensate their loss any more. When the supply of hares drops, the lynxes begin to starve and their population also decays so that that of the hares can recover. The variations of the populations of the two species x and y can be modeled in the language of chemical kinetics in terms of two coupled nonlinear (ordinary) differential equations (Lotka-Volterra model) as shown in fig. 17 together with their solution for properly chosen parameters α and β. This solution exhibits just the



However, so far the story is still incomplete: If the elements of an extended system exhibit temporal oscillations as a whole, some kind of lateral coupling between these elements is required in order to achieve synchronization. As a consequence of these considerations the state variables (i.e. the surface concentrations of the adsorbates x_i) are in general not only depending on time t but also on the spatial coordinates r_i. As summarized in fig. 20 coupling between different regions on the surface is achieved by transport processes. If

Under isothermal conditions at low pressures local differences of the surface concentrations cause surface diffusion of the adsorbates, and mathematical description can now be obtained in terms of reaction-diffusion equations, i.e. a set of coupled nonlinear partial differential equations combining the kinetics with the diffusion of the adsorbed species (fig. 20). The length scale of the resulting spatio-temporal concentration patterns is no longer governed by atomic dimensions but by the so-called diffusion length, which in our case is of the order of tens of microns [45]. These patterns were



Open systems far from equilibrium:
Spatio-temporal self-organization

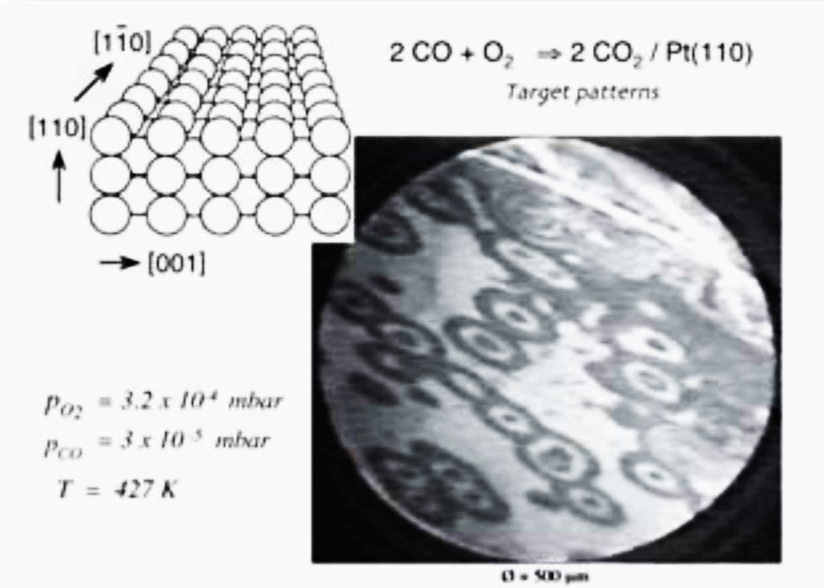
Lateral variation of state variables (surface concentrations) x_i

Coupling between different parts of the surface via

- **Diffusion**
- **Heat conductance**
- **Variation of partial pressures**
- **Electric field**

Reaction-diffusion systems

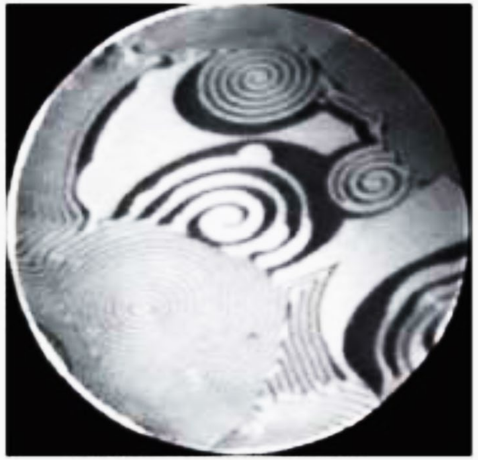
$$\frac{\partial x_i}{\partial t} = F_i(x_j, p_k) + D_i \nabla^2 x_i$$



imaged by the technique of photoemission electron microscopy (PEEM) [46]: Adsorbed O and CO species are accompanied by different electric dipole moments and hence different work function changes which in turn give rise to varying intensities of photoemitted electrons. In the images to be shown dark areas are essentially O-covered while brighter patches are CO-covered. As an example fig. 21 shows so-called target patterns, concentric elliptic features propagating preferentially along the [1$\bar{1}$0]-direction of the Pt(110) surface (where CO diffusion is faster than along the [001]-direction) on a background changing periodically between bright (=CO covered) and dark (=O covered), while the external parameters of temperature and partial pressures are kept constant as indicated [47].

Under other external parameters typical spiral waves as shown in fig. 22 develop and propagate with front speeds of a few μm/s. The core of a spiral is often formed by a region on the surface with enhanced defect density, and this effect is also responsible for the fact that the wavelengths of the spiral vary to some extent [48].

Spiral waves during CO-oxidation on Pt(110)



PEEM images with 500 μm diameter,
steady-state conditions: p_{O_2} = 4 x 10^{-4} mbar, p_{CO} = 4.3 x 10^{-5} mbar, T = 448 K

We reached now a state where a system which in principle is very simple (a chemical reaction occurring between two diatomic molecules on a well-defined single crystal surface with fixed external parameters and for which all individual reaction steps are known) and which nevertheless exhibit rather complex behavior. Such effects are generally expected for open systems far from equilibrium and are hence believed to govern also the whole nature. Our system can be considered to be a rather simple model for studying these types of phenomena. One might for example be interested to modify pattern from a turbulent initial state by different strength and delay of the feedback is reproduced in fig. 26. These patterns are reminiscent of similar phenomena found in nature (fig. 27), but also on Vincent van Gogh's vision of our world in his painting "star night" (fig. 28).

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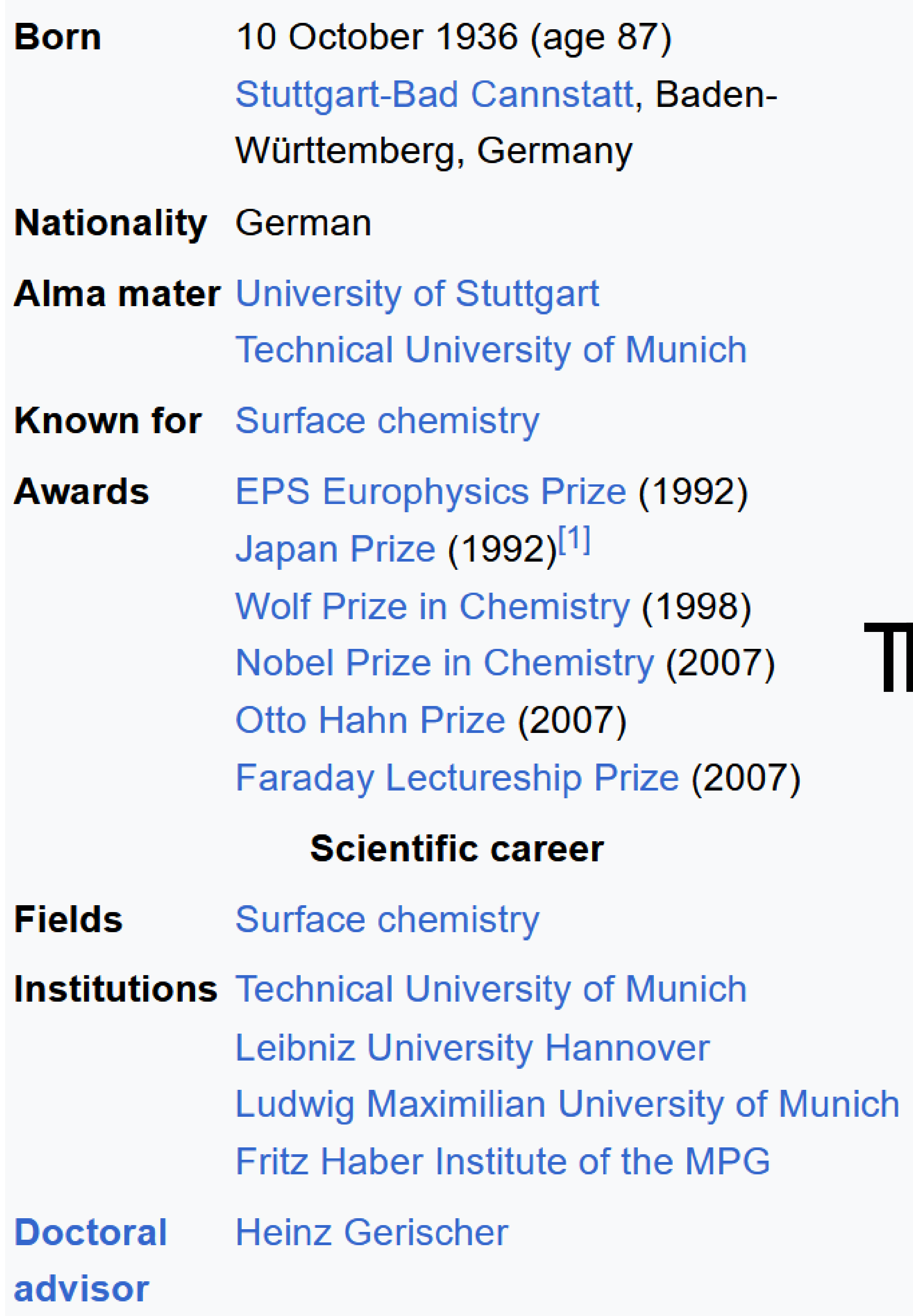

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Scientific career	
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Thank you