Chapter 8

Conclusion

> Only after completing the composition planned have we learned what the beginning should have been.
>
> Blais Pascal

Kinetic studies are naturally divided into "applied" and "detailed". In the first case, the aim of our investigation is to construct a model (ideally a simple one) to describe the observed kinetic relationships and to use this model for the calculation of a chemical reactor. In the second case, the study is aimed at the interpretation of a detailed mechanism. Despite the ever-growing possibilities provided by physical investigation methods, kinetics has been and still remains a unique instrument of reaction mechanism studies *under reaction conditions*. One cannot see a yawning gap between applied and detailed kinetics. But we must not be too hopeful. For real chemical systems (e.g. petrochemical and coal-chemical), including a great number of components and reactions with concentrations of intermediates that are not usually measured during the experiment, one cannot hope in the near future to obtain reliable detailed models. It is due to this fact that most industrial catalytic reactors are (and apparently will be) constructed on the basis of simple Langmuir-type models.

Both branches of kinetics, i.e. applied and detailed, are connected with mathematical kinetics dealing with the construction and examination of mathematical models of chemical kinetics. Thus applied mathematical kinetics is useful for both applied and detailed kinetics.

But what must we aim at? Is it a semiempirical applied model relating the observed variables and containing parameters that have no direct physicochemical sense? Or is it a complex detailed model corresponding to a hypothetical system of chemical conversions, assuming that a given kinetic law for some individual reaction, e.g. the law of mass-action, is valid? This dilemma arose long ago. Practically speaking, it is the difference between the two approaches of chemical kinetics. On the one hand it is the Guldberg and Waage kinetics and on the other it is that of van't Hoff. Guldberg and Waage should, apparently, be considered as founders of "applied kinetics". Their formulation (1879) of the principal law for the chemical reaction rate

$$V = kp^{\alpha}q^{\beta}r^{\gamma}$$

where p, q, and r are the "acting masses" of the reactants, contains no limitations for the exponents α, β, and γ. Van't Hoff, who gave a classification for reactions (according to the number of reacting molecules), is apparently a pioneer of the "detailed" kinetics. Though van't Hoff studied only one-step reactions, he is sure to have understood that the reaction is a sufficiently complex process. His followers Ostwald and Kistjakowski, Bach and Engler, Luther and Shilov have proved the interpretation of a chemical reaction as a complex multi-step system of chemical conversions. "A reaction is not a one-act drama" wrote the German physico-chemist Schönbein. Christiansen compared the problem of establishing a reaction mechanism to the solution of a crossword puzzle. Despite the considerable successes, the main of which is the formulation of chain-reaction theory (Semenov, Hinshelwood), the situation in chemical kinetics some years later was described by Daniels as total confusion. The problem had arisen to "relate" kinetic laws for individual steps. Only one thing was not clear: what base should be chosen for this "relation"?

We believe, nowadays that "a light at the end of the tunnel" has appeared and there is a hope for a general approach to the solution of this most urgent kinetic problem, since we have proper "fixed" points. Most important is thermodynamics applied to study chemical reactions characterized by complex detailed mechanisms. One should relate thermodynamic and kinetic laws at various levels, supporting kinetics on both micro and macro levels.

Modern thermodynamics provides possibilities to represent kinetic equations for all elementary reactions in various chemical (both homogeneous and heterogeneous) systems in uniform form. The same is suggested for chemical diffusion (in this connection, see ref. 1).

A new interesting fact is that the application of thermodynamic functions of states together with material balances suggests a non-trivial consideration concerning the system behaviour not only under equilibrium but also in the course of approaching this equilibrium.

In particular, we can now determine such a field of composition that has never been realized during the approach to equilibrium from given initial conditions. This is the so-called "unattainability region" [2,3].

Finally, it appears that the kinetic models of complex reactions contain two types of components independent of and dependent on the complex mechanism structure [4–7]. Hence the thermodynamic correctness of these models is ensured. The analysis of simple classes indicates that an unusual analog arises for the equation of state relating the observed characteristics of the open chemical system, i.e. *a kinetic polynomial* [7]. This polynomial distinctly shows how a complex kinetic relationship is assembled from simple reaction equations.

So far a complete theory has not been formulated, but now the direction in which to move is clear.

We believe, the main trends in the present investigations of kinetic models for catalytic reactions are as follows.

(1) General analysis. The aim of investigations here is to establish a relation between the type of reaction behaviour (dynamic and steady-state)

and its mechanism. The results obtained make it possible, for example, to select types of mechanisms having some dynamic behaviour, and to interpret experimental data qualitatively.

(2) Analysis of the simplest non-linear kinetic models (in particular, of kinetic models for heterogeneous catalysis). The aim is to select the simplest non-linear kinetic models to carry out the most complete investigation of their steady-state and relaxation characteristics. The obtained systems of typical relationships facilitates the interpretation of complex reactions, including simpler "typical" units.

(3) Kinetic analysis of concrete catalytic reactions. In the kinetics of heterogeneous catalysis, such reactions are usually model oxidation reactions (e.g. CO and H_2 oxidation) over metals.

If the behaviour of complex chemical (in our case catalytic) reactions is known, it will be clear in what way these reactions can be carried out under optimal conditions. The results of studying kinetic models must be used as a basis for the mathematical modelling of chemical reactors to perform processes with probable non-trivial kinetic behaviour. It is real systems that can appear to show such behaviour: first far from equilibrium, second non-linear, and third multi-dimensional. One can hardly believe that their associated difficulties will be overcome completely, but it is necessary to approach an effective theory accounting for several important problems and first of all provide fundamentals to interpret the dependence between the type of observed kinetic relationships and the mechanism structure.

1. Forecast for tomorrow

At the risk (a great risk!) of being taken for prophets, we will make an attempt to predict "hot points" in mathematical kinetics, i.e. the problems to be investigated in the near future.

(1) Elaboration of a new mathematical software for the kinetic steady- and non-steady-state experiments: in particular, the reliable provision for the primary interpretation of kinetic data, new methods (program-adaptive and completely adaptive) of performing informative steady-state kinetic experiments and radically new methods of carrying non-steady-state experiments oriented for the establishment of reaction mechanisms. Finally, it is the development of complex methods involving a combination of kinetic and physical (adsorptive, isotopic, spectroscopic) studies.

(2) Analysis of critical phenomena. Here, a working method will rapidly become the evolving qualitative theory of differential equations. It will be the basis for the elaboration of methods for the experimental search for critical phenomena. To carry out a detailed qualitative analysis of complex dynamics, special programs will be used.

(3) Estimation of limit parameters for technological processes. These estimates will be obtained in terms of the recently formulated theory that

permits us to determine thermodynamically admittable trajectories along which a chemical system passes from its initial (non-equilibrium) state into the final (equilibrium) state (see refs. 2,3,6, and 8). This theory has already been realized in the software used for the analysis of several industrial reactions [9].

(4) Analysis of structure formation processes by using Monte Carlo methods. Monte Carlo methods will be used extensively for the calculation of processes during which new phases are formed. In particular, these are adsorption–desorption, diffusion, and reactions on the surfaces of solids. The results of this modelling will be used to decode structures formed on catalyst surfaces.

To analyze processes in which molecular interactions are considerable, use will be made of theoretical methods that have been applied extensively in phase transition physics, in particular the method of the transfer matrix.

(5) Application of computer analytical methods. Extensive use of computer analytic methods are thought to intensify theoretical analysis drastically. They will be applied, in particular, to study kinetic models of complex reactions that can be represented by systems of non-linear algebraic equations, for the detailed bifurcation analysis, etc.

2. Afterthoughts to the conclusion

At present the kinetics of complex catalytic reactions is a field involving the application of, on the one hand, physicochemical methods that provide possibilities for the direct determination of intermediate concentrations, and, on the other, new ideas in mathematics and theoretical physics promoting the interpretation of complex steady- and non-steady-state behaviour.

Actively working groups are sure to include physical chemists (experimental and theoretical) and mathematicians (pure and applied). "Graphs theory", "dynamics", "non-linear oscillations", "chaos", "attractor", "synergetics", "catastrophes" and finally "fractals"; these are the key words of modern kinetics.

To interpret new experimental chemical kinetic data characterized by complex dynamic behaviour (hysteresis, self-oscillations) proved to be vitally important for the adoption of new general scientific ideas. The methods of the qualitative theory of differential equations and of graph theory permitted us to perform the analysis for the effect of mechanism structures on the kinetic peculiarities of catalytic reactions [6,10,11]. This tendency will be deepened. To our mind, fast progress is to be expected in studying distributed systems. Despite the complexity of the processes observed (wave and autowave), their interpretation is ensured by a new apparatus that is both effective and simple.

Let us hope that chemical kinetics will soon obtain a new theoretical building. Thermodynamics will ensure strength and "correctness" of this building, and new methods of mathematical physics provide the possibility of living in it with a comfort that is worthy of civilized men.

But one other fact is also of interest: a reverse movement has started, away from chemical kinetics. Formulation of the problems that have arisen here attract the attention of mathematicians and physicists working in various fields and having a variety of tastes. In our country it is common practice to hold conferences devoted to mathematical problems in chemistry. Several symposia on "Mathematical Methods in Chemical Kinetics" have been held. In 1987 an international journal (*Journal of Mathematical Chemistry*) was founded.

In the opinion of Profs. Shabat and Spivak, the theory of differential equations, usually presented in terms of mechanics and radiophysics, can now be constructed on the basis of chemical kinetics. This viewpoint seems to be valid. But we believe the interpenetration of physicochemical and mathematical ideas can appear much more effective than simply successive illustrations and mutual support. This greater possibility was felt as long ago as in the 19th century by the great American mathematician J.J. Sylvester. After becoming acquainted with the records of Prof. Frankland's lectures for student chemists, Sylvester wrote: "I am greatly impressed by the harmony or homology (rather than analogy) that exists between chemical and algebraic theories. When I look through the pages of the "Records" I feel like Alladin walking in the garden where each tree is decorated by emeralds, or like Kaspar Hauser first liberated from a dark camera and looking into the glittering star sky. What unspeakable riches of so far undiscovered algebraic content is included in the results achieved by the patient and long-term work of our colleagues - chemists even ignorant of these riches".

We have already mentioned the view of Daniels on the confusion in chemical kinetics. Horiuti emphasized this view by using the word "chaos". The experiment discovered a complex kinetic behaviour which is likely to have supported this point of view. But the situation has changed drastically in the last 10 years. New concepts of mathematical physics connected with the study of non-linear systems make us understand: complex dynamics ("chaos") is the result of a certain law. In kinetic Chaos, we can notice Harmony and Hope to see it more clearly.

We hope that the reader will understand: modern chemical kinetics is once again experiencing romantic times, the period of *Sturm und Drang*, when new experiments and new theories persistently prompt each other to further progress.

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