Michael Polanyi's pioneering contribution to the most successful theory in chemical kinetics

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ABSTRACT

After a short discussion of early discoveries in chemical kinetics, the history of the attempt to calculate the rate coefficient from first principles is followed. Michael Polanyi's crucial role in the calculation of potential energy surfaces and the development of the transition state theory (TST) in a form that can be used to successfully calculate practically important rate constants is explained. A brief description of TST is outlined, and some recent experimental findings concerning the detection of the transient state are also given.

I. INTRODUCTION

Chemical kinetics deals with the temporal evolution of reactions; with the explanation of the very different rates of particular reactions, and the

effect of temperature, pressure, or the nature of the solvent on the reaction rates. Though the subject has been intensively studied since the middle of the 18th century, there was no theory which would have had practical impact and theoretical consistency at the same time, until Michael Polanyi — working together first with the American chemist Henry Eyring, later both of them independently — developed the transition state theory (TST) which serves as a solid basis for kinetic theories even nowadays, almost 70 years later.

In this paper, after a short summary of the prehistory of the development of the TST, a somewhat more detailed description of the crucial ideas put forward by Polanyi and Eyring is discussed, followed by an outline of the theory and its relevance in chemistry. Finally, recent developments concerning experimental evidence of the transition state are also described.

II. THEORIES OF CHEMICAL KINETICS PRIOR TO 1930

The first quantitative statement concerning the temporal evolution of chemical reactions dates back to 1850, when Ludwig Wilhelmy concluded his research on the hydrolysis of sucrose by writing a differential equation (Wilhelmy, 1850) for the rate of the reaction. Let us generalise this result for reactions between substances A and B:

$$A + B \rightarrow products$$
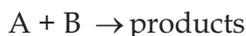
For the derivative of the concentration [A] with respect to time we can write the following equation (using modern notation):

$$-\frac{d[A]}{dt} = k[A][B] \tag{1}$$

This differential equation has been used ever since for the elementary molecular events involving two particles. It is called a bimolecular reaction, and the quantity denoted by k was called the (bimolecular) rate constant, whose name has recently been proposed to change to rate coefficient. Experiments have shown that k is independent of the concentrations [A] and [B] of the two reacting species, but it usually increases very rapidly with increasing temperature. While there was no quantitative explanation of the great difference between the largely different reaction rates

of particular reactions for many decades, there were formal relationships proposed to describe the dependence of the rate coefficient k on the temperature T. The first empirical formula was published by Marcelin Berthelot (1862), which had been used for almost 50 years:

$$k = A \cdot e^{DT} \tag{2}$$

There was an attempt by Leopold Pfaundler (1867) to attach a molecular interpretation to this temperature dependence, based on the results of high-temperature gas dissociation reactions' equilibria. He proposed that only molecules having enough energy are able to react, while molecules with less energy undergo a collision without reaction. Pfaundler did not make any reference to Maxwell's results on the energy distribution of molecules, but based his reasoning on qualitative discussions of this subject by Clausius. His isolated explanation attempt was only cited later by van't Hoff. It was Jacobus Hendricus van't Hoff who derived from the thermodynamic principles of the equilibrium of chemical reactions a new formula for the temperature dependence (van't Hoff, 1884):

$$k = A \cdot e^{-\frac{E}{RT}} \tag{3}$$

for the case when the critical energy E necessary for the reaction was independent of temperature. (van't Hoff received the first Nobel prize in chemistry in 1901 for his results in chemical kinetics.) The molecular level explanation of Eq. (3) was given by Svante Arrhenius (1889). He interpreted the exponential factor in the equation using the Boltzmann distribution of energy, and called E the activation energy. Molecules having less energy then E are not "active" in the sense that they do not undergo reactions. As equation (3) was popularised by Arrhenius, it is still called the Arrhenius equation. It is also an empirical equation, as the constant A (called the pre-exponential factor) is not explained at all, though it is also responsible for the great variety of the rate of particular reactions. The first theoretical treatment of the rate of chemical reactions beyond empirical description was made by René Marcelin (1915), a French scientist who died in action in World War I at a young age. He used concepts of both thermodynamic and kinetic origin, and described a chemical reaction between N atomic species in a $2N$-dimensional phase space, evoking statistical methods proposed by Gibbs. The foundations of his theoretical treatment were correct and elegant, but the solution of the relevant equations to get results of practical importance was not feasible at that time. His ideas were further explored a decade later by several researchers (K.F. Herzfeld, 1925; R.C. Tolman, 1927; R.H. Fowler, 1929), who practically

outlined the basis of TST, but faced the same problem of not being able to give numerical solutions that could have been used in practical applications.

While the above-mentioned theoretical efforts had been based on mechanical equations of motion and statistical physics, there was a different approach in the meantime, based on the kinetic theory of gases, called the collision theory (Lewis, 1918). Its model system was two elastic spheres colliding, and having reaction if their energy exceeds the activation energy E, or simply flying apart after an elastic collision if they have less energy. The resulting formula for the bimolecular rate coefficient is

$$k = Z_{AB} \cdot e^{-\frac{E}{RT}} \tag{4}$$

The exponential factor also originates in the Boltzmann distribution, while Z_{AB} is the collision factor, the rate of collision between molecules A and B, which can be calculated from the kinetic theory of gases. This result gives quite good values for the rate coefficient of reactions between monatomic species — as expected from its basic assumptions -, but it often fails by several orders of magnitude for practically interesting reactions between molecules having more complicated structures. Thus, it cannot be considered as a general theory of chemical reaction rates.

III. MICHAEL POLANYI'S INVOLVEMENT IN THE THEORY OF CHEMICAL REACTION RATES

Michael Polanyi's Ph.D. thesis (1917) had great impact on his scientific career, which is also true for his probably greatest achievement in the field of chemistry; his contribution to the development of the transition state theory. To further trace his interest in molecular interactions, we can recall his 1921 talk given in Berlin on the topic of his thesis, the bold idea of the long-distance (adsorption) interaction between molecules. In the discussions after his talk it turned out that neither Nernst nor Einstein believed that there exist such long-distance interactions. Those interactions were not possible on the basis of the current atomic theory developed by Bohr. (This aspect is discussed in more details in the article by Füstöss of the present volume.)

Despite of this discouraging event, Polanyi did not abandon his idea, as it is well indicated by his common paper with London on the explanation

of these forces based on quantum mechanical ideas further developed by London (London and Polanyi, 1930). Meanwhile, he was involved in the revival of the theoretical attempts to describe chemical reactions at the elementary molecular level, indicated by his paper written with Wigner (Polanyi and Wigner, 1925).

The crucial step towards a successful kinetic theory was made when Polanyi applied the new tools offered by the London theory to calculate molecular interactions in reactive systems. It was at this time that the National Research Fellow from the U.S., Henry Eyring entered his laboratory. They began to work together on the project of the quantum-mechanical calculation of the activation energy, and in connection with it, the calculation of the potential energy surfaces (PES) for simple chemical reactions in the gas phase. Their common results had been published first as preliminary reports ("vorläufige Mitteilungen") in the periodical *Naturwissenschaften* (Polanyi and Eyring, 1930), and fully explained later in the *Zeitschrift für physikalischen Chemie* (Polanyi and Eyring, 1932). At the same time, Wigner and Pelczer also worked on this subject in the Polanyi laboratory in Berlin, and published a study of the equilibrium reaction between ortho- and para-hydrogen, based on the new method of PES (Pelczer and Wigner, 1932). Michael Polanyi, who moved from Berlin to Manchester at this time, continued to work on the practical exploration of the TST, just like Henry Eyring did after he returned to the United States. Their seminal papers were published in 1935, explaining the details of what has become the transition state theory later. It is surprising, how close the two explanations are, even if they have been written by different people, at different places (Evans and Polanyi, 1935; Eyring, 1935).

IV.   THE TRANSITION STATE THEORY

Transition state theory, as we know it nowadays, was developed by many scientists. Both papers, referred to at the end of the previous section, give credits to Tolman (1927), Herzfeld (1925), Pelzer and Wigner (1932), and Polanyi and Wigner (1928). In addition, Polanyi also mentions his pioneering work (Polanyi, 1920), while Eyring mentions the book of Fowler (1929). Those who contributed to the formulation that could be successfully used in practice were all working for a while in the Berlin laboratory of Michael Polanyi.

The theory is based on quantum mechanical calculations of the potential energy surfaces of a reacting system. The basic characteristics of such a

surface can be seen on Figure 1, for the case of a collinear reaction between an atom A and a molecule BC, the so-called B-atom exchange reaction:

$$A + BC \rightarrow AB + C \qquad (5)$$

At the point denoted by 1, the distance between the atoms B and C is that of the usual (equilibrium) distance in a BC molecule, while the distance between A and B is large, with practically no interaction between the atom A and B — the latter bound in the molecule BC. Obviously, this is the reactant state of reaction (5). Similarly, the point denoted by 3 is the product state of the reaction. The potential energy shape of the surface at the point denoted by 1 shows the (Morse type) potential energy profile of a diatomic molecule AB; while at 3, a similar potential energy profile of the diatomic molecule BC can be seen. This potential energy, as a function of the internuclear distances r_{AB} and r_{BC} , forms a continuous surface which is called the potential energy surface of the reacting system consisting of the atoms A, B and C. In the case of a collinear reaction, this is a three-dimensional surface. (If the three atoms are not arranged collinearly (along a line), there is an additional angular variable to fully characterise the configuration of the three atoms, which is not so simple to show and more complicated to calculate.) This surface can be projected onto a plane, which results in a plot similar to a topographic contour map showing elevation data. Isolines on this contour map indicate values of the potential energy. Apart from the easy-to-draw two-dimensional structure of these maps, details in the valley between points 1 and 3 are also readily seen (Figure 1b).

During the reaction, the reactant molecules' nuclei always assume a position, so the "reaction path" is a continuous curve on the potential energy surface. In the case of the collinear reaction (5), an oscillating BC molecule is approaching the A atom. The relevant reaction path is shown as a dashed curve with an arrow indicating the direction of the movement in Fig. 1b. If we arrange this reaction path along a linear coordinate and plot the potential energy above the path according to the vertical axis, we get the energy profile of the reaction, as shown in Fig. 1c. The "topography" of the reaction is easily seen in this diagram; there is a potential barrier for the reacting system to climb in order to proceed to the product state.
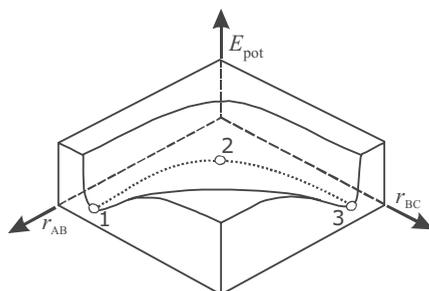
Figure 1. *a) The potential energy E_{pot} for the collinear reaction $A+BC \rightarrow AB+C$ (where all three atoms are arranged in a linear configuration) as a function of the distances r_{AB} between atoms A and B, and r_{BC} between B and C.*
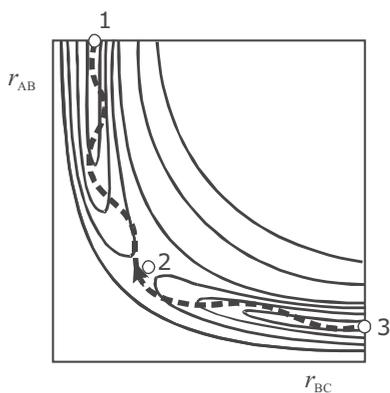
Figure 1. *b) The same potential energy surface (PES) projected onto the $r_{AB} - r_{BC}$ plane as a contour map. The reaction coordinate is shown as a thick dashed line. The arrow indicates the passage of the system from the reactants to the products.*
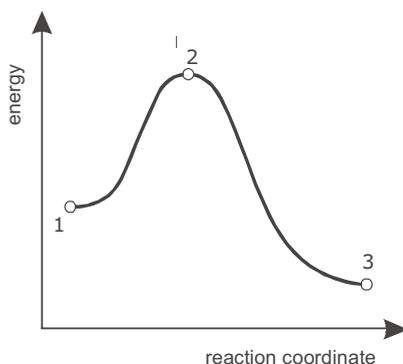
Figure 1. *c) Potential energy above the reaction coordinate. Numbers indicate 1: the reactant state, 2: the saddle point of the surface, 3: the product state.*

The height of the top of the barrier (denoted by 2) measured from the level of the reactants (denoted by 1) is called the activation energy. The top of the barrier is a saddle point on the three-dimensional surface, as it is indicated by the point marked 2 in both figures 1a and 1b. The reaction path always crosses the barrier in the saddle region. In a broader sense, a surface in the saddle region, perpendicular to the reaction coordinate is called the transition state, which has the property that once the system of reacting particles has crossed this surface, it proceeds to the product valley. In a narrower sense, the saddle point of Fig. 1a and 1b, or the top of the barrier of Fig. 1c is called the transition state.

The invention of Polanyi and Eyring was that they calculated the PES using the approximation that the reacting system's electronic structure would rearrange to an equilibrium state in every nuclear configuration (this is the Born-Oppenheimer approximation), and that they performed PES calculations using the simplified quantum-mechanical method of London. Following the PES calculations, they developed independently a formalism to express the rate of passage of the reacting system across the saddle point as a motion along a single harmonic coordinate. Finally, they supposed that there exists a (quasi) equilibrium between the reactants and the transition state (or activated complex, as Eyring called it), which is the state corresponding to the saddle point of the PES. These conditions allowed the first time in history to calculate practically relevant rate constants on a theoretically sound basis.

The "reaction mechanism" associated to TST can be written as
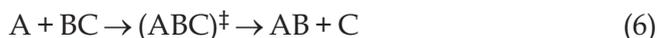
$$A + BC \rightarrow (ABC)^{\ddagger} \rightarrow AB + C \tag{6}$$

The species $(ABC)^{\ddagger}$ is the transition state. Its concentration can be expressed from the equilibrium constant $K^{\ddagger}$ of the first reaction in scheme (6):

$$K^{\ddagger} = \frac{\left[(ABC)^{\ddagger}\right]}{[A][BC]} \tag{7}$$

$$[(ABC)^{\ddagger}] = K^{\ddagger}[A][B] \ , \tag{8}$$

where square brackets denote concentrations. The equilibrium constant $K^{\ddagger}$ can be expressed from standard statistical thermodynamics as

$$K^{\ddagger} = \frac{Q_{(ABC)^{\ddagger}}}{Q_A Q_B} e^{-\frac{E_0}{RT}} \tag{9}$$

Here, Q_x means the standard molar canonical partition function, R is the gas constant, T is temperature, and E_0 is the reaction energy at $T = 0$, i.e., $E_0 = E_0 (ABC^{\ddagger}) — E_0 (A) — E_0 (B)$. Once the stationary concentration of the transition state is known, the only thing needed is the rate of decomposition of this state. This rate can be calculated by factoring out the harmonic vibration along the reaction coordinate from the partition function $Q_{(ABC)^{\ddagger}}$ (let us denote the rest by $Q_{\ddagger}$), transforming it into a translation along a distance , and finding the decomposition rate from this translational motion. It turns out that the arbitrary translation length cancels, and the resulting expression for the rate constant is

$$k = \frac{k_B T}{h} \frac{Q_{\ddagger}}{Q_A Q_B} e^{-\frac{E_0}{RT}} \; , \tag{10}$$

where k_B is the Boltzmann constant and h is the Planck constant. The beauty of Eq. (10) is in its simplicity and the well founded theoretical aspects it is based on. It is the factor containing the partition functions that is sensitive for the structural details of molecules of complicated structures, which yields in very good results for the rate constant, never seen before.

TST can be used to any rate processes, where there is a potential barrier to pass for the reacting system, as for example to viscous flow or diffusion in condensed phases. A detailed exploration of the fields of its applicability is given in the book written by Eyring and co-workers (Gladstone et al., 1942). In spite of its virtual simplicity and practical applicability, it took a long time for TST to gain wider popularity among chemists. As it was based on quite new quantum mechanical techniques, and statistical ideas not widely known by chemists, there was an "activation barrier" for them to understand this theory. It was not before the late fifties of the 20th century that it became slowly part of university curricula.

Another problem of its acceptance was the inaccessibility of experimental support for the existence of the supposed species called transition state or activated complex. Already at the moment of the development of TST it was clear that the lifetime of the transition state is in the range of the period of molecular vibrations, which is of the order of 1 picosecond (ps), or even less. No measurements could be imagined in the thirties, or even in the fifties with such time resolution. The first indirect proof of the existence of the transition state has been done by John C. Polanyi, the son of Michael Polanyi, in the seventies, which was worth of a

Nobel prize in 1986. John Polanyi and his co-workers studied highly dilute flames, *e. g.* the reaction

$$F + Na_2 \rightarrow NaF + Na^* \qquad (11)$$

According to TST, this reaction proceeds via the transition state $(F\ldots Na\ldots Na)^{\ddagger}$. They detected the fluorescence of the excited state Na*, and found that there are wide "wings" at both sides of the expected and measured NaD spectral line. Though the intensity of these wings was only less then one millionth of the NaD peak, it was detected with an excellent signal-to-noise ratio, and it could be associated with the fluorescence of an excited Na atom bound in the transition state $(F\ldots Na\ldots Na)^{\ddagger}$. A detailed description of the results can be found in Foth et. al. (1982).

With the advent of ultrafast pulse lasers in the eighties, the time resolution finally attained the sub-picosecond region. For his pioneering work in the application of this new technique to the transient spectroscopy of the transition state, Ahmed H. Zewail also received a Nobel prize in 1999. He has managed to measure the temporal evolution on a femtosecond $(10^{-15}$ s) time scale of the spectra of different activated complexes of monomolecular dissociation processes, and also that of some bimolecular reactions similar to reaction (5). His results are summarized, for example, in Zewail (1988) and (1994). A Hungarian monograph on this topic can be found in Keszei (1999).

The last three decades marked the "triumph" of TST theory in chemical kinetics. It still serves as a most general basis for theoretical explanations as well as practical calculations. Though the technical details of actual calculations are much more sophisticated than at the time when Polanyi and Eyring have developed the basic theory, it is still essentially the same. There are only few results obtained with an approach without the Born-Oppenheimer approximation. This approach is based on the numerical solution of the full time-dependent Schrödinger equation for the reacting system, which solution provides both the potential energy and the actual trajectory of the system. This solution contains less approximations and provide more precise results for the rate constant. However, this technique can be applied — for the time being — only for not more than four atoms, as numerical calculations involved are very much time consuming. Further development in numerical methods and computing speed may help to extend this method for more complicated molecules. An overview of this method with the discussion of cases where it outperforms traditional TST can be read in Fang and Hammes-Schiffer (1998).

Further reading on the topics of the transition state and its development can be found in the special issue of the *Journal of Physical Chemistry* (Laidler *et al.,* 1983; Noyes and Epstein, 1983).

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