



# Fundamental concepts in chemical kinetics

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Received: 24 September 2019 / Accepted: 30 October 2019  
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## Abstract

Students and young researchers will find in this article a clear and accurate presentation of fundamental concepts in chemical kinetics: reaction rates, elementary reactions and mechanisms, kinetic constants and relation to thermodynamics, and energies of activation. The discussions are based on specialized literature without going into detail and avoid misunderstandings and sometimes errors found in the general literature and on the Internet. With this aim, an original approach is sometimes adopted.

**Keywords** Chemical kinetics · Reaction rate · Reaction mechanism · Kinetic constants · Activation energy

## Introduction

“An error does not become truth by reason of multiplied propagation, nor does truth become error because nobody sees it” (Mahatma Gandhi).

Chemical kinetics is a science in itself with its own concepts and methods of reasoning. Its field is the determination, interpretation, and use of the laws which govern the rates of chemical reactions. For truly kinetic investigations, it is not enough to measure the rate of appearance of a product or the disappearance of a reagent. It is also necessary to identify the factors that determine these rates, to quantify their effects, and to try to explain them. This approach is often explained in a very approximate way in chapters devoted to chemical kinetics in general treatises of physical chemistry and on the Internet, sometimes with a few errors. Unfortunately, approximations, misunderstandings, and errors are repeated even if they have been pointed out in specialized articles and books [1–4]. Although the underlying concepts of chemical kinetics did not change fundamentally in the last 50 years, the widespread availability of personal computers means that the evaluation techniques

which were once standard are now outdated. This does not receive enough attention in some recently written textbooks or even in research articles that are not specialized in kinetics but rather use it as a tool. The purpose of this article is to help students and young researchers better understand the concepts and methods of chemical kinetics without going into detail, but avoiding some misinterpretations, allowing one to go beyond an empirical description of the results.

## Definition of the rate of a reaction

A rate of reaction is often defined as the derivative of a concentration with respect to time. This definition is misleading because such a derivative is equal to the rate of a reaction only in very particular cases. According to the IUPAC [5], such a derivative should be called “rate of disappearance” or “rate of appearance”. This confusion is taken up by Wikipedia and is found even in the IUPAC Gold Book. However, *a rate of reaction is a property of a reaction and not of a reactant or a product*. We must therefore begin by saying what the studied reaction is and specify its stoichiometry. Consider the reaction  $a A + b B \rightarrow p P + q Q$ . The extent of this reaction,  $\xi$  (pronounced ksi) is the change in the amount of any reactant divided by its stoichiometric number.

$$\xi = -\Delta n_A/a = -\Delta n_B/b = \Delta n_P/p = \Delta n_Q/q$$

At this point, it should be emphasized that the extent of reaction only makes sense if the studied reaction is a reasonably simple one that does not have any intermediates in significant concentrations. Otherwise, the equality stated above

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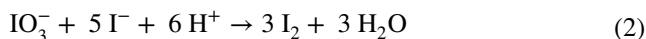
does not even hold because the presence of the intermediate should also be accounted for in a stoichiometric equation. A careful reading of IUPAC recommendations [5] reveals that they actually recognize this possible source of inconsistency and limit the definition of the reaction rate only to cases where the process does not have intermediates in significant concentrations. This does not mean that the reaction must be truly elementary, a point discussed below. It means that the concentrations of possible intermediates must remain much lower than those of the reagents and products.

The correct definition of a reaction rate in a homogeneous closed reactor of volume  $V$  (the case of open reactors will be discussed below) is that given initially by the IUPAC [5].

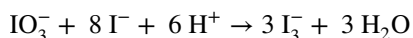
$$r = (d\xi/dt)/V \quad (1)$$

The volume is usually expressed in liters (L) and  $r$  in  $\text{mol L}^{-1} \text{s}^{-1}$ . Reaction rates are intensive quantities, like temperature and concentrations, which can be different in different points of the reactor. Usually, only the ideal case of perfectly mixed reactors is considered. Furthermore, it should be noted that Eq. (1) is based on the change of the amounts of substance in the reactor and not the change in concentrations. This might seem an insignificant difference but is revealed when the overall volume changes during the reaction, an unusual case in solution but frequent in the gas phase. Should the reaction rate be based on concentrations rather than amounts of substance, it would be non-zero as a result of non-constant volume even in the total absence of a chemical reaction.

To show the difference between a rate of reaction and a rate of appearance or disappearance, let us take the example discussed in more detail previously [6]. The reduction of iodate to iodine, reaction (2), known as the Dushman reaction, can be followed by the formation of the triiodide ion, reaction (3).



Let us consider the overall process at high iodide ion concentration written as follows:



The extent and the rate of this reaction cannot be defined when  $\text{I}_2$  is a significant intermediate. On the other hand, reaction (2) also involves intermediates but their concentrations remain negligible so that 3 moles of iodine are effectively formed for 1 mole of iodate consumed. Therefore, it is possible to study the reaction rate of processes (2) and (3). When a reaction with significant intermediates is encountered, its decomposition to simpler reactions is a general

strategy that must be followed in all cases. This reality is not emphasized enough despite its logical importance.

Returning to reactions (2) and (3), the rate of disappearance of iodate ions is equal to the reaction rate  $r_2$  but the rate of iodine appearance it is not a rate of reaction. The correct relations are

$$d[\text{I}_2]/dt = 3r_2 - r_3 \quad d[\text{I}_3^-]/dt = r_3$$

We could replace  $(dn_i/dt)/V$  with  $d[C_i]/dt$  because the volume remains constant during this reaction. The sum  $d[\text{I}_2]/dt + d[\text{I}_3^-]/dt$  can be measured by absorptometry at the isobestic point and is proportional to  $r_2$  but must be divided by the stoichiometric coefficient 3. Unfortunately, the stoichiometric coefficients are often forgotten in the calculations of reaction rates, which may give the impression that different authors have measured different rates.

Consider now a gas burner with a stationary flame. There is no concentration derivative with respect to time, but there are obviously rates of combustion reactions. Open reactors require a special treatment. It is necessary to write a mass balance equation expressing that the difference between what enters and what goes out is equal to what remains in the reactor plus or minus what is consumed or produced by the reactions. For a compound  $i$  and several reactions  $j$ , Eq. (4) is obtained.

$$F_{\text{in},i} - F_{\text{out},i} = dn_i/dt - V \sum \nu_{i,j} r_j \quad (4)$$

$F_{\text{in},i}$  and  $F_{\text{out},i}$  are the input and output flows of the compound  $i$  in  $\text{mol s}^{-1}$ ,  $n_i$  is the number of moles of this compound in the reactor of volume  $V$ ,  $r_j$  is the rate of reaction  $j$ ,  $\nu_{i,j}$  is the stoichiometric number of compound  $i$  in reaction  $j$ .<sup>1</sup> Equation (4) applied to a closed reactor ( $F_{\text{in},i} = F_{\text{out},i} = 0$ ) with only one reaction is equivalent to Eq. (1). For open reactors in a stationary state, it gives  $\sum \nu_{i,j} r_j = (F_{\text{out},i} - F_{\text{in},i})/V$ . It is important to emphasize that, in this case, the rates of reactions are not related to changes over time but to changes in flows. Kinetic studies in open reactors, especially in a continuous stirred tank reactor (CSTR), require more equipment than in closed reactors but have several benefits. The collection of the data is much easier in a stationary state, the analysis of these data requires only the resolution of analytical equations, and much more accurate rate values are obtained. In summary, reaction rates can appear in different equations but the concept is always the same. A rate of reaction is the extent of a well-defined reaction per unit time and unit volume. For reactions at an interface it is per unit surface.

<sup>1</sup> Two conventions are used for the sign of the stoichiometric coefficients, depending on the authors and the context. The coefficients are usually represented by positive numbers. It can also be agreed that they are positive for the products and negative for the reagents, as in Eq. 4.

## Rate laws and mechanisms

The rates of chemical reactions may be complicated functions of many factors depending on the type of reactions, homogeneous or heterogeneous, photochemical, catalyzed by different types of catalysts, etc. It is only in the simplest cases, obeying *power law kinetics*, that the rates can be represented by an equation of the form (5):

$$r = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma} \quad (5)$$

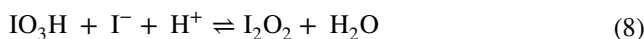
[A], [B], and [C] are the reagent concentrations and  $\alpha$ ,  $\beta$ , and  $\gamma$  (alpha, beta, and gamma) are the reaction orders with respect to A, B, and C. Their values cannot be known a priori and must be determined experimentally but they are typically constant.  $k$  is a constant supposed to depend only on the temperature. In practice,  $k$  is constant only in a concentration range depending on the mechanism of the reaction. Moreover, we will see that the kinetic constants depend on the ionic strength of the solutions.

A largely used concept in chemical kinetics is that of the elementary reaction. According to IUPAC, it is a chemical reaction in which chemical species react directly to form products in a single step without need to postulate intermediates to describe the reaction on a molecular scale. The kinetic law of these reactions is always simple. There are three kinds of elementary reactions: (1) unimolecular  $A \rightarrow$  products with the rate law  $r = k[A]$ ; (2) bimolecular  $A + B \rightarrow$  products with the rate law  $r = k[A][B]$ ; (3) termolecular  $A + B + C \rightarrow$  products with the rate law  $r = k[A][B][C]$ . It is generally accepted that termolecular reactions are very improbable because three-body collisions are rare and most often result in fact from two bimolecular reactions. One of us, however, has shown [7, 8] that termolecular elementary reactions might be more common than generally assumed as the rate of three-body collisions is only tiny compared to the rate of two-body collisions but not to the rates of some reactions in both gas and solution phases.

Complex reactions are combinations of elementary reactions and one of the aims of chemical kinetics is to determine these combinations. A reaction mechanism is an attempt to explain the experimental results in terms of phenomena at the molecular level. A mechanism can never be proved. It only becomes more likely when the number of experimental facts supporting it increases but it remains always possible that new observations require one to modify it. Let us take as example the Dushman reaction (2), one of those whose kinetics has been studied the most [9]. Its rate in non-buffered acidic solutions is given by

$$r_2 = (k'_2 + k''_2[I^-]) [IO_3^-][I^-][H^+]^2. \quad (6)$$

This rate equation does not match the possibilities for elementary reactions so the process cannot be simple. The observed rate Eq. (6) can be explained by assuming that the first steps of the mechanism are (7–10).



The iodine content of the intermediate species HOI, HOIO, and OIO<sup>-</sup> is then transformed into I<sub>2</sub> in reactions that occur after the so-called rate-determining step, the dominant “bottleneck” in the entire process. Separate studies using isolated HOI, HOIO, and OIO<sup>-</sup> as reactants may provide information on the later steps, but this information remains irrelevant as far as the rate of the Dushman reaction is concerned. A general feature of kinetic studies is that they only provide information on the rate of the rate-determining steps and processes that occur before that. It should also be noted that we used the concept of reaction rate for the Dushman reaction although it has a number of intermediates. This means that none of them attain concentrations that are comparable to that of the reactants or products at any time during the reaction. Therefore, the very low amounts of these species do not change the stoichiometric relationships at the usual accuracy of experiments.

Two types of approximations are commonly used to derive the kinetic law corresponding to a mechanism, the quasi-equilibrium and quasi-steady-state approximations. We do not discuss them here because the reader will find excellent discussions of these approximations elsewhere [1–3, 10]. If reactions (7) and (8) are almost at equilibrium, we deduce  $[I_2O_2] = K_7K_8 [IO_3^-][I^-][H^+]^2$  and the experimental rate law (6) with  $k'_2 = k_{10}K_7K_8$  and  $k''_2 = k_9K_7K_8$ .

The assumed Dushman mechanism also offers an example of the postulate of reducibility of chemical systems [4, p. 5]. The concept of elementary reactions is generally used intuitively in the writing of reactions mechanisms adopting the loose definition “A reaction for which no reaction intermediates have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale”. In practice, elementary reactions are recognized by their properties. They have a well-defined stoichiometry and reaction orders equal to the stoichiometric coefficients. However, this does not prove that the reaction is indeed elementary and we suggest to use the term *quasi-elementary reactions* for those that have these characteristics. The existence of the intermediate I<sub>2</sub>O<sub>2</sub> was proposed in 1930 by Bray [11] to explain

the kinetic law (6) and is supported by later experiments [12]. However,  $I_2O_2$  has never been isolated, its structure is unknown, and it could be replaced by  $H_2I_2O_3$ . Moreover, reaction (8) could involve the intermediate  $IO_3H_2^+$ . Bray had also proposed the existence of the intermediate  $I_3O_2^-$  so that reaction (10) could also be only quasi-elementary. This illustrates the precautions to take when trying to explain a kinetic law and the uncertainties related to the concept of elementary reactions.

## Kinetics and thermodynamics

Thermodynamics gives no indication about the kinetic laws, but it imposes constraints that must be taken into account and that are often forgotten or misunderstood. We will discuss two such constraints, additional ones are found in electrochemistry [13]. First, any reaction at constant temperature and pressure must involve a decrease of Gibbs energy. Second, the equilibrium constant of a reversible reaction can impose a relation between the kinetic constants in the forward and backward directions.

There are currently theoretical models for estimating, with relatively good accuracy, the energy of molecules in the gas phase. The results of these calculations are sometimes used to say that a reaction is possible or not but this conclusion is often precipitate. The variation of Gibbs energy for a reaction  $aA + bB \rightleftharpoons pP + qQ$  is given by

$$\Delta_r G = \Delta_r G^\circ + RT \ln([P]^p [Q]^q) / ([A]^a [B]^b).$$

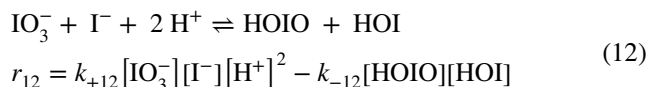
The reaction can only occur in the direction corresponding to  $\Delta_r G < 0$ . Let us first note that this condition concerns the effective variation  $\Delta_r G$  and not the variation under the standard conditions  $\Delta_r G^\circ$ . During a complex reaction, one step of the mechanism may occur in the direction corresponding to  $\Delta_r G^\circ > 0$  simply because another reaction rapidly consumes a product and maintains its concentration very low. Similarly, in electrochemistry, a reaction can occur in the direction corresponding to  $\Delta E^\circ < 0$  if one of its products is consumed quickly enough. Second, the theoretical calculations give the internal energies and, in the best cases, the enthalpies of formation. We can deduce  $\Delta_r H^\circ$  in standard conditions but not  $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ . There are entropy-driven reactions for which  $\Delta_r G^\circ < 0$  although  $\Delta_r H^\circ > 0$  because  $T\Delta_r S^\circ$  is positive and large enough [14]. It is necessary to know the standard entropies  $S^\circ$  to be able to calculate the equilibrium constants  $K_{eq} = \exp(-\Delta_r G^\circ/RT)$  and it must be regretted that the theoretical calculations in the gas phase usually do not continue to the most useful quantity, the Gibbs energy.

Consider now a quasi-elementary reaction  $A + B \rightleftharpoons P + Q$  with the rate law  $r = k_+[A][B] - k_-[P][Q]$ . The kinetic constants in both directions are linked by relation (11) often presented as a consequence of the principle of microscopic reversibility for elementary reactions.

$$k_+/k_- = K_{eq} \quad (11)$$

However, we have seen that it is difficult to decide if a reaction is indeed elementary and we propose a different approach. At equilibrium, the rates in the forward and backward directions are equal giving  $k_+[A]_{eq}[B]_{eq} = k_-[P]_{eq}[Q]_{eq}$  and  $[P]_{eq}[Q]_{eq}/[A]_{eq}[B]_{eq} = k_+/k_-$ . This relation must be strictly equivalent to the thermodynamic expression of equilibrium, which enforces relation (11). It is not necessary that the reaction be effectively elementary; it is enough that it is quasi-elementary. When  $K_{eq}$  is known, the value of a kinetic constant imposes the value of the other. In addition, some complicated mechanisms may involve reactions that are linear combinations of others. Equation (11) then imposes a relation between their kinetic constants. Ignoring it leads to predicting impossible behaviors [15].

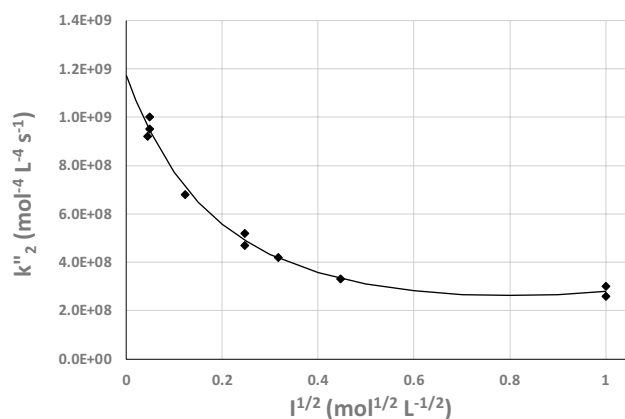
During the oscillating Bray–Liebhafsky reaction, reactions (7–9) can occur alternately in one direction then in the other [16–19]. Their sum is the reversible quasi-elementary reaction (12).



The constants  $k_{+12}$  and  $k_{-12}$  were measured independently, which makes it possible to calculate  $K_{eq}(12) = k_{+12}/k_{-12}$  and  $\Delta_r G^\circ(12)$ . The Gibbs energies of formation of  $IO_3^-$ ,  $I^-$ , and  $HOI$  being known, one can deduce the Gibbs energies of formation of  $HOIO$ . As this compound is unstable, its Gibbs energy could not be measured by other methods but using the relation between thermodynamics and chemical kinetics. In conclusion, although thermodynamics gives no prior indication about the rates, there are nevertheless important links between kinetics and thermodynamics.

## Kinetic constants and activities

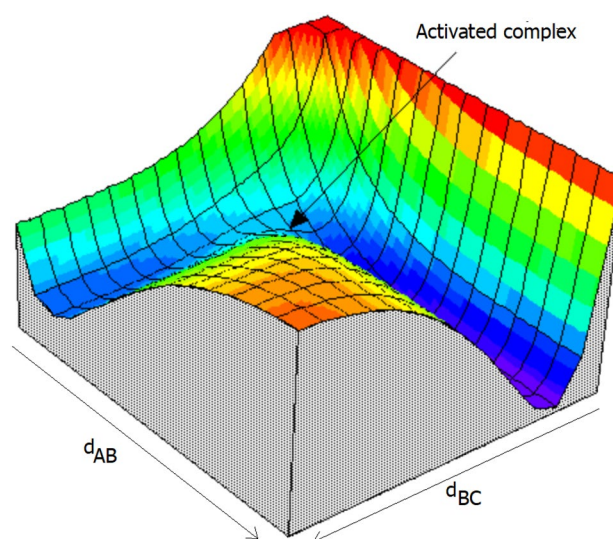
In the previous section, equilibrium constants were expressed as functions of concentrations. This is an approximation and the relation  $K_{eq} = \exp(-\Delta_r G^\circ/RT)$  is only correct if  $K_{eq}$  is expressed as a function of the activities. What happens to relation (11) in this case? The question “Are activities needed in chemical kinetics?” has been analyzed in detail recently [7] with the conclusion that reaction rates must continue to be expressed as functions of concentrations, but that kinetic constants are functions



**Fig. 1** Effect of the ionic strength on the rate constant of the Dushman reaction

of activity coefficients. This dependence can be important in the case of ionic reactions. Let us continue with our example of the Dushman reaction. The values of  $k''_2$  in Eq. (6) have been measured by different authors [1, 20–22] as a function of the ionic strength in mixtures of  $\text{KIO}_3$ ,  $\text{NaI}$ ,  $\text{HClO}_4$ , and  $\text{NaClO}_4$ . The results are shown in Fig. 1. It can be seen that when ionic strength increases from  $I = 2 \times 10^{-3}$  M to  $I = 0.2$  M, the value of  $k''_2$  decreases by more than a factor 3. This is far from negligible.  $k''_2$  varies little between  $I = 0.2$  M and  $I = 1$  M because the activity coefficients of most monovalent ions go through a minimum of 0.7–0.8 in this range of ionic strength. It is not the case for bivalent or trivalent ions and the effect of ionic strength can be much larger. Neglecting the effect of ionic strength on kinetic constants, and therefore on reaction rates, has led to serious errors in the interpretation of experimental results.

It must also be noted that an equilibrium constant as a function of the concentrations  $K_{\text{eq}} = [\text{P}]^p[\text{Q}]^q/([\text{A}]^a[\text{B}]^b)$  has dimensions unless  $p + q = a + b$ , while a thermodynamic equilibrium constant  $K^\circ_{\text{eq}} = \exp(-\Delta_r G^\circ/RT)$  is dimensionless. This apparent contradiction is discussed in the IUPAC Green Book [23], which emphasized that the standard state must be specified. Let us go back to the definition of chemical potentials,  $\mu = \mu_0 + RT \ln(c/c_0)$ . Activities should be used in this definition but we replace them with concentrations to avoid mixing difficulties.  $\mu_0$  is the chemical potential if the concentration  $c = c_0$ . As for any potential, we must choose a reference.  $c_0 = 1 \text{ mol L}^{-1}$  was chosen and is no longer written in the equations because its numerical value is 1. However, we must remember that it is implied in all the derived equations. Thus,  $K^\circ_{\text{eq}}$  is equal to  $[\text{P}]^p[\text{Q}]^q/([\text{A}]^a[\text{B}]^b) \times c_0^{(a+b-p-q)}$  without dimensions. This is an approximation and the exact relation involves activity coefficients [23]. We can choose the practical units we use, but the numerical value of  $K_{\text{eq}}$  can be different if we use  $\text{mol L}^{-1}$  or  $\text{mol m}^{-3}$ . The



**Fig. 2** Potential energy surface for a reaction  $\text{AB} + \text{C} \rightleftharpoons \text{A} + \text{BC}$

numerical values given by the tabulated thermodynamic values are those obtained if we use  $\text{mol L}^{-1}$ . In the gas phase,  $p_0 = 1 \text{ atm}$  was chosen as reference and the tabulated thermodynamic values are given for pressures in atm, not in pascals.

## Activation energy

The effect of temperature on the rate constants is usually described using the Arrhenius equation.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (13)$$

$E_a$  is the Arrhenius activation energy and  $A$  is the pre-exponential factor.  $E_a$  and  $A$  are assumed to be independent of the temperature, at least in a restricted range. Actually, they depend on the temperature and the Arrhenius equation is only one of the numerous empirical equations that were proposed to describe the effect of temperature on kinetic constants [1]. Note that, according to the Arrhenius equation, a plot of  $k$  as a function of  $T$  gives an S curve and that  $k$  tends to the maximum value  $A$  when  $T$  tends to infinity. It is not an exponential as sometimes written. A more interesting approach to the concept of activation energy is given by the transition state theory. The potential energy of the system is represented as a function of bond lengths and angles and the reaction is seen as the motion of a point on the obtained hypersurface. In order to obtain a visual representation of this approach, consider the simplest case of a reaction  $\text{AB} + \text{C} \rightleftharpoons \text{A} + \text{BC}$  with a potential energy depending only on the distances  $d_{\text{AB}}$  between A and B and  $d_{\text{BC}}$  between B and C. This is represented in Fig. 2.

The reactants are located in the valley on the left of the figure and the products in the valley on the right. The reaction is seen as a climb up the left valley to the highest point, the saddle point, followed by a way down in the valley on the right. The configuration of the system at the saddle point is called the activated complex. Starting with this representation, different approaches were used with the aim to obtain expressions for the kinetic constant assuming that the activated complex is in equilibrium with the reactants. However, a real equilibrium would imply that when the system arrives at the saddle point, it has a much larger probability to return to the reactants than to continue to the products, which is very unlikely. This problem was discussed in particular by Laidler [1] and by Kondratiev [2] who showed that it is not a real equilibrium. We propose the following original approach to understand why the activated complex is said to be in equilibrium with the reagents, even though it is not. Consider the system globally at equilibrium, so that the activated complex is indeed in equilibrium with the reagents, and calculate the rate. Then, remove the products. The main assumption is that the reagents on the other side of the hill do not “see” that the products have been removed and continue to react at the same rate. Expressions of the rate constants obtained at equilibrium remain valid out of equilibrium. This is not necessarily true but is a more likely assumption than the usual one.

Two methods are commonly used to obtain expressions for the kinetic constant. The thermodynamic approach assumes that the rate is given by the product of the concentration of the activated complex  $[X^\ddagger]$  and the frequency of vibration of the link that is breaking. This gives  $r = (k_B T/h) [X^\ddagger]$  where  $k_B$  is Boltzmann’s constant and  $h$  is Planck’s constant. Then, the equilibrium assumption is introduced. Taking two previous comments into account, we write the rate as a function of concentrations including the difference between activities and concentrations into the rate constant and we explicitly keep the reference concentration  $c_0 = 1 \text{ mol L}^{-1}$ . This gives  $([X^\ddagger]/c_0) = K^\ddagger ([AB]/c_0) ([C]/c_0)$ ,  $r = (k_B T/h) K^\ddagger [AB][C]/c_0$ , and  $k = (k_B T/h) K^\ddagger/c_0$ . Using  $K^\ddagger = \exp(-\Delta^\ddagger G^\circ/RT)$  we obtain the popular Eq. (14).

$$k = \frac{k_B T}{h} \frac{1}{c_0} \exp\left(\frac{\Delta^\ddagger S^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H^\circ}{RT}\right) \quad (14)$$

The factor  $1/c_0$  is never written except in [4, p. 99] and [24, p. 38]. The unit of  $k_B T/h$  being  $\text{s}^{-1}$ , the usual expression seems to imply that the unit of  $k$  is  $\text{s}^{-1}$  instead of  $\text{mol}^{-1} \text{ L s}^{-1}$ . A more serious problem with this equation is that, as noted by Laidler [1], the activated complex is just a transition state, not a “normal” molecule, so that its concentration is not well defined. Consequently,  $K^\ddagger$ ,  $\Delta^\ddagger S^\circ$ , and  $\Delta^\ddagger H^\circ$  do not have a clear meaning. Moreover, the energy in Fig. 2 appears as

an enthalpy of activation and not as an internal energy of activation, sum of the potential and kinetic energies.

The second method is based on statistical mechanics. The equilibrium constant is expressed by the following equation where  $q_{AB}$  and  $q_C$  represent the partition functions of the reactants.  $q_\ddagger$  is the partition function of the activated complex not including the motion over the saddle point.<sup>2</sup>

$$k = \frac{k_B T}{h} \frac{1}{c_0} \frac{q_\ddagger}{q_{AB} q_C} \exp\left(-\frac{E^0}{RT}\right) \quad (15)$$

In this equation, the activation energy  $E^0$  appears more clearly as the difference between the average internal energy of reacting complexes and the average internal energy of reactants [1, Sect. 3.1.2]. Another advantage of Eq. (15) is to allow an estimation of the pre-exponential factor based on the structure of the molecules in the gas phase. An estimate in solution is not currently possible because complicated interactions with the solvent must be taken into account. An interesting, more detailed discussion of Eq. (15) can be found in Ref. [25].

## Conclusions

We can measure concentration derivatives over time and look for correlations with reagent concentrations. We can write differential equations and study their properties. This may be interesting, but if we want to make a connection between the macroscopic observations and the microscopic properties of atoms, molecules, and ions, we must carefully specify some fundamental concepts. A reaction rate is a property of a reaction, not of reagents or products. A reaction cannot be understood without first clarifying its stoichiometry and its rate must be expressed as a function of its extent  $\xi$ . Then, we must be aware that a mechanism explaining our observations is only a model of reality that unavoidably involves approximations and that is always subject to revision. The reactions constituting this model are not necessarily elementary, in the sense that they do not involve intermediate compounds, and we have introduced the concept of a quasi-elementary reaction, a reaction which has a well-defined stoichiometry and orders equal to the stoichiometric coefficients. It is also important to note that, although a reaction with a very large equilibrium constant can have a very low rate, there are links between kinetics and chemical thermodynamics. One of these links is the relation between kinetic constants and equilibrium constant  $k_+/k_- = K_{\text{eq}}$ . On the one hand, numerical simulations can predict behaviors

<sup>2</sup> The derivation of this expression is given by Laidler [1], Sect. 4.5.3. We have inserted the term  $1/c_0$  for the same reason as in Eq. 14.

that have no chemical meaning if it is not strictly verified for quasi-elementary reactions. On the other hand, erroneous values of kinetic constants can be obtained if it is used for reactions that are not quasi-elementary. This relation shows also that since the equilibrium constants are functions of the activity coefficients, so are the kinetic constants. The concept of activation energy must also be specified. What is sometimes called Arrhenius's "law" is only a useful but empirical correlation and its pre-exponential factor depends on temperature. The transition state theory provides a more accurate approach to the concept of activation energy.

The chapters devoted to chemical kinetics in general chemistry textbooks and the information found on the Internet often contain misunderstandings and sometimes errors. The concepts are not always clearly explained and approximations are often implied. Corrections and precisions can be found in books and articles specialized in chemical kinetics. However, it is not easy to review this abundant specialized literature to find clear and exact explanations of the main concepts of chemical kinetics. We have summarized the main ideas, sometimes with an original approach, in a way we hope will help young researchers.

**Acknowledgements** Work at the University of Pécs was financed by the Higher Education Institutional Excellence Program of the Ministry of Human Capacities in Hungary, within the framework of the 1st thematic program of the University of Pécs.

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