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Empiricism or self-consistent theory in chemical kinetics?

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Abstract

To give theoretical background for mechanochemical kinetics, we need first of all to find a possibility to predict the kinetic parameters for real chemical processes by determining rate constants and reaction orders without developing strictly specialized and, to a great extent, artificial models, i.e. to derive the kinetic law of mass action from "first principles". However, the kinetic law of mass action has had only an empirical basis from the first experiments of Gulberg and Waage until now, in contrast to the classical law of mass action for chemical equilibrium rigorously derived in chemical thermodynamics from equilibrium condition. Nevertheless, in this paper, an attempt to derive the kinetic law of mass action from "first principles" is made in macroscopic formulation. It has turned out to be possible owing to the methods of thermodynamics of irreversible processes that were unknown in Gulberg and Waage's time.

Keywords: Mechanochemical processing; Kinetics; Thermodynamic modeling

1. Introduction

Mechanochemical reactions in solids are heterogeneous non-equilibrium reactions. Kinetics of mechanochemical reactions usually is described by means of ordinary chemical kinetics using chemical affinity as the driving force of reaction:

$$J_i = f\left(\frac{\tilde{A}_i}{RT}\right) \tag{1}$$

where the function f is, in general, a *law of chemical kinetics*; J_i the rate of each ith partial reaction and the affinity $\tilde{A}_i$ is a linear combination of chemical potentials and stoichiometric coefficients. If for simplicity and clarity we analyze a simple chemical reaction where the substance 1 turns into 2 in the conditions of stationary regime $1 \leftrightarrow 2$ the common kinetic equation is:

$$J = k\left(\exp\frac{\tilde{A}}{RT} - 1\right) = k\left(\exp\frac{\mu_1 - \mu_2}{RT} - 1\right) \tag{2}$$

where $k = k_r c_r$ and k_r is the rate constant of the reverse reaction, c_r is the concentration of the product. However, this kinetic equation up today has not a theoretical base because it is derived from the empiric kinetic law of mass action.

In general, mechanical action may be applied to change k_r, or/and c_r, or/and μ_1, or/and μ_2. To change k_r the mechanical action needs to influence free energy of activated complex (it is still open problem). How does mechanical action change c_r is not clear for non-equilibrium state. What indeed remains it is mechanical change of chemical potentials μ_1 and μ_2, which can be very influential due to exponents: a small change of μ will results in a great change of J. However, the function f up today has only empirical derivation. In fact, until now all handbooks on chemical kinetics and chemical thermodynamics start the description of kinetics with so called *kinetic law of mass action* given below by Eq. (3), which is a basic *postulate* of chemical kinetics. Long time ago, Guldberg and Waage [1] proposed this generic law to describe their observations on the rate of chemical reactions as a linear function of concentrations c_i of substances:

$$J = k_f c_j - k_r c_r, \tag{3}$$

where k_f and k_r are rate constants of the forward and reverse reactions, respectively, c_j and c_r are concentrations of reactants and products, respectively.

Eq. (1) represents the kinetic law of mass action, which has had only an empirical basis until now, in contrast to the classical law of mass action for chemical equilibrium rigorously derived in chemical thermodynamics from equilibrium condition [2]. Although, apparently, the first published experimental observation of the linear dependence of the chemical reaction rate (inversion of sucrose) on the concentrations of reagents was

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made in 1850 by Wilhelmy [3], at about the same time Guldberg and Waage carried out their work on the "law of mass action" and derived an equilibrium equation on the basis of assumed empirical kinetic equations [1]. They studied chemical affinity ("forces") and tentatively suggested that the rates of reactions might be proportional to the forces which are proportional to concentrations [4]. Thus, for the reaction

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} + d\mathrm{D} \tag{4}$$

the force in the left-to-right direction should be proportional to $[\mathrm{A}]^a[\mathrm{B}]^b$, and the force acting from the right to the left is proportional to $[\mathrm{C}]^c[\mathrm{D}]^d$. It was assumed that if the forces in a system were equal and oppositely directed, chemical equilibrium was reached with the equilibrium constant:

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^b}. \tag{5}$$

However, Eq. (3) was *only postulated* on the basis of experimental observations, because it could not be obtained by any method of chemical thermodynamics concerned with equilibrium processes while chemical reactions are essentially irreversible processes.

2. Arrhenius and Eyring equations in chemical kinetics

In 1889, Arrhenius analyzed temperature dependence of measured reaction rates according to the equation which is now called the Arrhenius equation. However, it would be fair to emphasize that this equation was certainly first suggested by van't Hoff in 1884 [5]. Indeed, van't Hoff analyzed the temperature dependence of the equilibrium constant (now called the van't Hoff equation) and of the forward and reverse reaction rates. The effect of temperature on the reactions rates k was found by Arrhenius empirically as a linear relationship between $\log k$ and $1/T$. In fact, the relationship is of the same form as the one in van't Hoff analysis:

$$\frac{\partial \ln k}{\partial (1/T)} = -\frac{E_{\mathrm{a}}}{R}, \tag{6}$$

where E_{a} is an empirical calorimetric parameter called the *activation energy* and k is the observed reaction rate. More specifically, Arrhenius did not consider a temperature dependence of the energy E_{a} and therefore adopted van't Hoff's simpler equation:

$$k = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right), \tag{7}$$

where A is a pre-exponential term expressed in the same units as k. An assumption inherent in most applications of the Arrhenius equation to kinetic analysis is that this energetic term has some inherent meaning and correlates with the enthalpic activation barrier for the process under study. It turns out that this is a reasonable assumption, at least for reactions that are characterized by large (>10 kcal/mol) E_{a} values. Similarly, the pre-exponential factor A is often qualitatively correlated with the entropic component of the activation barrier.

The introduction of a value E_{a} having the dimension of energy and called activation energy (strictly speaking, a better name would be *experimental activation energy*) gives rise to many speculations. Note, by the way, that the term activation energy implies overcoming certain energetic barrier, which is obvious in models of the collision theory and of the transition state theory [6], but is never obvious in the Arrhenius law. One of such speculations can be demonstrated as the "derivation" of the Tafel equation from the Arrhenius equation assuming E_{a} to be a linear function of overpotential. Obviously, E_{a} becomes clearly defined only in case of its application to a specific physical model of a barrier process, which, however, is usually far from the actual pattern of the reaction. Therefore, experimentally measured E_{a} values often contain little information about the process mechanism, except cases of characteristically differing E_{a} values (for instance, for diffusion or chemical activation).

At the same time, Arrhenius gave an original interpretation of energy barrier: he suggested that the equilibrium is established between normal and active molecules of the reactant, which are able to form products without further addition of energy. Later, this suggestion formed the basis of the modern transition state theory and Eyring equation, which is a theoretical construct based on *transition state* model. In 1917, Trautz and Lewis independently proposed that the rate of reaction is determined by the frequency of molecular collisions. This is now known as the collision theory of chemical reaction kinetics [6].

Finally, in 1935, Eyring developed a statistical treatment called the theory of absolute reaction rates or transition state theory, according to which the reaction occurs in two steps: (a) equilibrated conversion of the reactant(s) into an activated complex; (b) decomposition of the complex (which occurs at a definite rate) [6]. However, he was forced to use Eq. (3), i.e. postulate. Both the Arrhenius and Eyring equations described the temperature dependence of the reaction rate. Strictly speaking, the Arrhenius equation can be applied only to gas reactions. The Arrhenius equation is founded on the empirical observation that conducting a reaction at a higher temperature increases the reaction rate. The Eyring equation is used in the study of gas, condensed and mixed phase reactions—all cases where a simple collision model is not very helpful [6]. The collision model of the reaction rate assumes that the rate constant is written as Eq. (7) with $A = pZ$, where Z is the collision rate and p is the steric factor. If we consider this equation in terms of changing temperature, the steric factor clearly does not depend on temperature. Z turns out to be only magnitude weakly dependent on temperature: varying T from 500 to 600 K changes Z by less than 10%. It is, therefore, a reasonable approximation to assume that the pZ part of the above equation is constant, and we come to the Arrhenius equation again.

The Eyring equation is derived in the theory of absolute reaction rates using linear rate-concentration dependences of Eq. (3) type as a postulate ([6], pp. 12–13) and introducing a specific rate (rate constant) in the form:

$$k_{\mathrm{c}} = \frac{k_{\mathrm{B}}T}{h}\exp\left(-\frac{\Delta F^{+}}{RT}\right), \tag{8}$$

where k_B and h are Boltzmann and Planck constants, respectively, and ΔF^{+} is the free energy of activation. Further replacement of the exponent with its equivalent in terms of the partition functions of the species using the methods of statistical mechanics expands and complicates the analysis, but does not change the fact that the mentioned postulate underlies it.

3. It is possible to proceed without postulates and activation energy

Meanwhile, classic thermodynamics using the Gibbs formulation of the condition for chemical equilibrium can give the *classic law of mass action* strictly enough only for the equilibrium constant, but *not for the reaction rate*.

Since the basic equation of chemical kinetics given by Eq. (3) is until today only postulated, but not derived theoretically, a basic question arises: what is it—empiricism or self-consistent theory in chemical kinetics? The answer is evident: unless the *kinetic law of mass action* is derived strictly on the basis of fundamental laws, the chemical kinetics will not be based on self-consistent theory. Hence, the problem is to find a way for deriving the kinetic law of mass action without any postulates. To solve this problem, we must apply *thermodynamics of irreversible processes* because we are dealing with irreversible chemical reactions.

However, the conviction that the use of basic Eq. (3) as a postulate confirmed only empirically is inevitable is so deep-rooted with the researchers that even in non-equilibrium thermodynamics, when describing chemical reactions, authors usually refer to Eq. (3) as a postulate [2]. Thus, even in non-equilibrium thermodynamics they proceed from the idea that it is accepted from the experiment in chemical kinetics that the kinetic law of acting masses, i.e. Eq. (3), is valid for reactions in ideal gases or in dilute solutions. Then this equation is used as a postulate for deriving the kinetic equation in the form of the reaction rate dependence on chemical affinity [2]. Thus, the problem of substantiation of the kinetic equation calls for a solution.

Therefore, we are forced to revise this approach and suggest a different way. Making attempts to derive the kinetic law of mass action from the first principles, we have to resort to a different approach and use a fundamental transport law which is well proven in non-equilibrium thermodynamics by statistical methods. In non-equilibrium thermodynamics, generalized forces (in chemistry they imply the reaction affinity $\tilde{A}$ as its driving thermodynamic force) are connected with generalized fluxes (in chemistry they imply the reaction rate J) and their action produces entropy with the rate $\partial S/\partial t = J\tilde{A}/T$. The function $J = f(\tilde{A}/RT)$ is, in general, an *unknown law of chemical kinetics*.

For the sake of simplicity and clarity, let us analyze a simple chemical reaction, where the substance 1 turns into 2 under the conditions of a stationary regime. These conditions are satisfied if the height of the barrier to be overcome greatly exceeds the difference of chemical potentials corresponding to these states and almost all the molecules are distributed between the initial and the final state of the present reaction. Intermediate products on the top of the barrier are unstable and decompose into the initial and final product. Thus, there is no product accumulation along the reaction path x, and therefore the flux is constant everywhere.

To find the reaction rate J, we subdivide the reaction path along its x-coordinate into a finite number of segments Δx_i with chemical potential differences $\Delta\mu_i$ corresponding to these segments ($\sum_i \Delta\mu_i = \Delta\mu$) [7]. Then the total reaction may be represented as a chain of consecutive substance transformations proceeding in consecutive i partial reactions with respective chemical affinity $\tilde{A}_i = -\Delta\mu_i$, the value $\sum_i \tilde{A}_i = \tilde{A}$ representing the affinity of the total reaction, i.e. $\tilde{A} = -\Delta\mu$. On sufficiently small segments ($\tilde{A}_i \ll RT$ is achievable, since the number of segments is arbitrary) the unknown function $J_i = f(\tilde{A}_i/RT)$ can be linearized for small arguments (according to the physical sense, $J_i = 0$ if $\tilde{A}_i = 0$):

$$J_i = \tilde{A}_i \left(\frac{\partial J_i}{\partial \tilde{A}_i}\right)_{\Delta x_i \to 0} = -\left(\frac{k_i \Delta x_i}{RT}\right)_{\Delta x_i \to 0} \frac{\partial \mu_i(x)}{\partial x} = -L_i\, \mathrm{grad}\mu_i, \tag{9}$$

where we have used $[\Delta\mu_i/\Delta x_i]_{\Delta x_i \to 0} = \partial\mu_i(x)/\partial x$, and k_i and L_i are certain constants. The linear form of this equation is invariant for all transport phenomena (diffusion, electric current, heat conduction, filtration, migration, etc.). Summing–integrating the entropy production along the total reaction path and using the conditions of stationary regime $J = J_i$, we obtain for the reaction on the whole:

$$T\frac{\partial S}{\partial t} = T\sum_i \frac{\partial S_i}{\partial t} = -\sum_i J_i \frac{\partial \mu_i(x)}{\partial x} |\Delta x_i|_{\Delta x_i \to 0} = -J\int_1^2 \frac{\partial \mu(x)}{\partial x}\,\mathrm{d}x = -J\Delta\mu = J\tilde{A}, \tag{10}$$

where integration is carried out over the entire reaction path from the initial (1) to the final (2) state.

Thus, the general form of the entropy production in the course of a chemical reaction is valid for chemical reactions described by any non-linear kinetic law. A linear phenomenological equation in the invariant form of the transport equation (resulting from the entropy production calculation) approximates the reaction rate near the equilibrium state or at sufficiently small Δx_i segment of the reaction path. Of course, this does not necessarily mean the existence without fail of a linear dependence of the reaction rate on the total affinity of the entire reaction consisting of several slow sequential partial reactions for which the linearization is possible.

To find the unknown kinetic law $J = f(\tilde{A}/RT)$, let us write a standard expression of chemical potential through the activity $a(x)$:

$$\mu(x) = RT \ln a(x) + \mu^0(x), \tag{11}$$

where $\mu^0(x)$ is a standard value for every point x (i.e. a profile of the standard chemical potential along x-coordinate). Substituting into the general transport equation, one obtains:

$$J(x) = -L(x)\frac{\partial \mu(x)}{\partial x} = -\frac{RTL(x)}{a(x)} \exp\left[-\frac{\mu^0(x)}{RT}\right] \frac{\partial}{\partial x} \exp\frac{\mu(x)}{RT}. \tag{12}$$

Subdividing this equation as follows:

$$J(x)\frac{a(x)\exp(\mu^0(x)/RT)}{L(x)} = -RT\frac{\partial}{\partial x}\exp\frac{\mu(x)}{RT} \tag{13}$$

and integrating along x from the initial state (1) to the final (2) state with the account for the conditions of a stationary regime $J(x) = J$ over the entire path from 1 to 2, one obtains:

$$J = \frac{RT\exp(\mu_2/RT)}{\int_1^2 (a(x)/L(x))\exp(\mu^0(x)/RT)\mathrm{d}x}\left(\exp\frac{\mu_1-\mu_2}{RT}-1\right), \tag{14}$$

where subscripts 1 and 2 are related to chemical potentials and activity in the states 1 and 2, respectively. Denoting the constant quantity by

$$L = \frac{\exp(\mu_2/RT)}{\int_1^2 (a(x)/L(x))\exp(\mu^0(x)/RT)\mathrm{d}x}, \tag{15}$$

we obtain the general kinetic law:

$$J = RTL\left(\exp\frac{\mu_1-\mu_2}{RT}-1\right) = RTL\left(\exp\frac{\tilde{A}}{RT}-1\right) = k\left(\exp\frac{\tilde{A}}{RT}-1\right), \tag{16}$$

that in linear approximation for $\widetilde{A}_i \ll RT$ (near equilibrium state) transforms into the linear form of transport equations:

$$J = L\tilde{A}. \tag{17}$$

Now, we can rigorously derive the kinetic law of mass action in the form which was earlier only postulated from experimental observations. Let us denote:

$$k_\mathrm{r} = \frac{RT\exp(\mu_2^0/RT)}{\int_1^2 (a(x)/L(x))\exp(\mu^0(x)/RT)\mathrm{d}x} \quad \text{and}$$

$$k_\mathrm{f} = k_\mathrm{r}\exp\left(-\frac{\mu_2^0-\mu_1^0}{RT}\right). \tag{18}$$

Substituting Eq. (18) into the general kinetic law (16) with account of Eq. (11) written for μ_2, we rigorously obtain the kinetic law of mass action in the form of Eq. (3):

$$J = k_\mathrm{f}a_1 - k_\mathrm{r}a_2 = k'_\mathrm{f}c_1 - k'_\mathrm{r}c_2 \tag{19}$$

and the classic law of mass action:

$$K \equiv \frac{k_\mathrm{f}}{k_\mathrm{r}} = \exp\left(-\frac{\mu_2^0-\mu_1^0}{RT}\right) = \frac{a_2^\mathrm{eq}}{a_1^\mathrm{eq}} \tag{20}$$

where k_f and k_r are the rate constants of the forward and reverse reactions, respectively; superscript eq denotes the activity in the equilibrium state with the equilibrium constant K.

Unfortunately, usually an opposite situation takes place, namely, a kinetic equation in the form of Eq. (16) is obtained from the empirically and then postulated Eq. (3) (see, e.g. [2], etc.). We, however, derive the kinetic Eq. (16) without resorting to empirical Eq. (3) and, in the long run, obtain Eq. (3) rigorously from the first principles.

4. Conclusion

The kinetic law of mass actions is derived rigorously from non-equilibrium thermodynamics using invariant properties of the transport law applied to the elementary steps along the reaction path. Therefore, all non-linear equations of chemical kinetics became scientifically rigorous, and theoretical derivation of the kinetic law of mass action in chemistry and mechanochemistry becomes possible without an empirical background, use of postulates and resort to the activation energy.

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