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A new approach for mathematical modeling of chemical kinetics

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Abstract. A new approach for describing chemical kinetics for reactions in gas phase is proposed, which removes some observed inconsistencies. This new approach is referring mainly to the law of mass actions in both forms, chemical equilibrium and reaction rate. A new interpretation of the activation energy is also given, so that the Arrhenius law becomes consistent with both Boltzmann statistic distribution and the definition of equilibrium constant. It will be shown that the activation energy is not a simple constant, it depends on the temperature at which the reaction begins.

Keywords: law of mass action, Arrhenius law, activation energy, activated complex.

1. Introduction

Since the experimental results are usually difficult to be obtained (or to interpret), it is straightforward to perform theoretical and computational studies which, as such, become very useful for chemical research. However, by analyzing the equations currently used to describe chemical reactions in gas phase from a kinetic point of view, some inconsistencies are found, which will be referred to in the next. There are a lot of examples in all chemistry, but a special attention will be paid to the reactions in gas phase, e.g. combustion reactions [1].

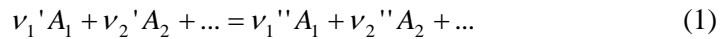
An earlier idea of finding an interpretation to the activation energy was proposed by H. Eyring, which introduced the notion of *activated complex (transition state)* and, along with M. Polanyi, has derived a new equation for chemical kinetics [2], [3]. However, the Eyring model uses a pre-exponential factor in the Arrhenius-like equation, which is far enough from the experimental measurements. Therefore, we will propose a similar equation, but having a pre-exponential factor determined by the collisions theory, which is closer to the experimental data.

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It has to be noted that Arrhenius derived his famous formula in 1889 only by empirical basis, while Eyring used Thermodynamics and Physical Statistics to get a similar formula in 1935. The so-called "activation energy", which is considered as a constant in the formula of Arrhenius and has the meaning of the energy that the molecule in the initial state of the process must acquire before it can take part in the reaction, is actually a quantity depending on the temperature, as it will be shown in the next. A more in-depth analysis of the dependence of reaction rates on temperature can be found in [4].

2. Law of mass action

We will refer to the law related to the rate of a chemical reaction since very often, the equilibrium constant formula is known under the same name. For a chemical reaction of the form



the law of mass action is expressed by the equation [5]:

$$\omega = K C_1^{\nu_1'} C_2^{\nu_2'} \dots = K \prod_i C_i^{\nu_i'} \quad (2)$$

where K = the so-called "reaction rate constant" (which, in fact, is not a constant, but rather a dimensional factor);

ω = the reaction rate, which is defined by the expression [5]:

$$\omega = \frac{1}{\nu_{\gamma}'' - \nu_{\gamma}'} \frac{dC_{\gamma}}{dt} \quad [\text{kmol/m}^3 \cdot \text{s}] \quad (3)$$

C_{γ} = the concentration of the species γ in the mixture wherein the reaction takes place [kmol/m^3].

Inconsistency: There is a dimensional problem regarding the reaction constant K : its dimensions depend on the type of reaction, which causes some mathematical difficulties, especially in numerical processing which needs handling of dimensionless quantities appearing in the considered equations.

This inconsistency could be removed if (at least for gas phase equations) instead of "concentration" C_{γ} the "molar participation" X_{γ} is introduced. The relationship between the 2 quantities is the following:

$$C_{\gamma} = \frac{\rho_{\gamma}}{M_{\gamma}} = \frac{1}{M_{\gamma}} \frac{p_{\gamma}}{R_{\gamma} T} = \frac{p_{\gamma}}{RT} = \frac{p}{RT} X_{\gamma} \quad (4)$$

where M_{γ} = molar mass of species γ [kg/kmol]; p_{γ} = partial pressure of species γ in the gaseous mixture; R_{γ} = gas constant of species γ [kJ/kg.K]; R = universal gas constant [kJ/kmol.K].

In other words, under given conditions of pressure and temperature, the concentration of a species in a mixture subjected to a chemical reaction is directly proportional to the molar participation of that species (which in perfect gases

corresponds to the volume participation). If one defines now the reaction rate by the expression

$$\omega_X = \frac{1}{\nu_\gamma'' - \nu_\gamma'} \frac{dX_\gamma}{dt} \quad [\text{s}^{-1}] \quad (5)$$

then, the law of mass action could be expressed by the equation

$$\omega_X = \bar{K} \prod_i X_i^{\nu_i'} \quad (6)$$

so that, regardless of the type of reaction, the new reaction constant \bar{K} will have the dimension of "1/time", respectively $[\text{s}^{-1}]$, which will obviously simplify the numerical calculations (the molar participation being dimensionless). From the combination of relations (5) and (6), the general equation of time variation of the molar participations of the components in the reaction mixture will be derived:

$$\frac{dX_\gamma}{dt} = (\nu_\gamma'' - \nu_\gamma') \bar{K} \prod_i X_i^{\nu_i'} \quad (7)$$

With the reaction constant thus defined, an equivalent form of the above equation can now be derived, in which the concentrations appear. Thus, from (4) it follows:

$$X_\gamma = \frac{RT}{p} C_\gamma \Rightarrow \frac{dX_\gamma}{dt} = \frac{RT}{p} \frac{dC_\gamma}{dt} \quad (8)$$

(we have assumed that the reaction takes place at constant pressure and temperature, otherwise appropriate corrections need to be applied).

Consequently, equation (7) becomes:

$$\frac{dC_\gamma}{dt} = (\nu_\gamma'' - \nu_\gamma') \bar{K} \left(\frac{RT}{p} \right)^{\sum_i \nu_i' - 1} \prod_i C_i^{\nu_i'} \quad (9)$$

By comparing now (9) with (2) and (3), the relationship between the constants K and \bar{K} will be found:

$$K = \bar{K} \left(\frac{RT}{p} \right)^{\sum_i \nu_i' - 1} \quad (10)$$

from where one can see very clearly the dependence of the dimensions of the classical constant K on the type of reaction, the other constant having always the same dimension $[\text{s}^{-1}]$.

Another problem arises with complex reactions, whose mechanisms involve successive elementary reactions, branching, etc. In such cases, the law of mass action in the form (2) can no longer be applied to the global reaction (ignoring the intermediate phases), and the exponents would no longer be equal to the number of moles, eventually having fractional values. Example: for the reaction



an expression of the reaction rate of the following form was determined:

$$\frac{dC_{\text{HBr}}}{dt} = 2 \frac{K_1 C_{\text{H}_2} C_{\text{Br}_2}^{3/2}}{C_{\text{Br}_2} + K_2 C_{\text{HBr}}} \quad (12)$$

Inconsistency: In such cases, it is no longer possible to define the equilibrium constant in the standard form by considering the reaction in both directions, that is:

$$K_C = \frac{\prod_i C_i^{v_i''}}{\prod_i C_i^{v_i'}}. \quad (13)$$

The reaction rate considering both directions of progress is:

$$\frac{dC_\gamma}{dt} = (v_\gamma'' - v_\gamma') \left[K_1 \prod_i C_i^{v_i'} - K_2 \prod_i C_i^{v_i''} \right]. \quad (14)$$

At equilibrium, the expression in the bracket must be zero, which gives the expression for the equilibrium constant:

$$K_1 \prod_i C_i^{v_i'} - K_2 \prod_i C_i^{v_i''} = 0 \Rightarrow K_C = \frac{K_1}{K_2}. \quad (15)$$

It is obvious that, in the case of complex reactions that apparently do not obey the law (2), the equilibrium constant can no longer be defined according to (13), which would imply a different approach. On the other hand, formula (13) is consistent with Chemical Thermodynamics because, from the definition of Gibbs free energy and from the application of 1'st law, the following relation is found [5]:

$$K_X = \frac{\prod_i X_i^{v_i''}}{\prod_i X_i^{v_i'}} = \exp\left(-\frac{\Delta G_r^{(T)}}{RT}\right), \quad (16)$$

where $G^{(T)}$ is the molar Gibbs free energy [kJ/kmol] at temperature T and $\Delta G_r^{(T)}$ represents the variation of molar Gibbs free energy during the reaction:

$$G^{(T)} = H - T \cdot S, \quad G^{(T)} = \sum_i G_i^{(T)} \quad (17)$$

$$\Delta G_r^{(T)} = \sum_i G_{Pi}^{(T)} - \sum_i G_{Ri}^{(T)} \quad (18)$$

where H = enthalpy, S = entropy, $[]_R$ stands for "reactants" and $[]_P$ means "reaction products" (round notations stand for molar quantities). Considering relation (4), the equilibrium constant in (16) can also be written as:

$$K_X = \frac{\prod_i \left(\frac{RT}{p}\right)^{v_i''} C_i^{v_i''}}{\prod_i \left(\frac{RT}{p}\right)^{v_i'} C_i^{v_i'}} = \left(\frac{RT}{p}\right)^{\sum_i (v_i'' - v_i')} \frac{\prod_i C_i^{v_i''}}{\prod_i C_i^{v_i'}} = \left(\frac{RT}{p}\right)^{\sum_i (v_i'' - v_i')} K_C \quad (19)$$

whence

$$K_C = \left(\frac{p}{RT}\right)^{\sum_i (v_i'' - v_i')} \cdot K_X = \left(\frac{p}{RT}\right)^{\sum_i (v_i'' - v_i')} \cdot \exp\left(-\frac{\Delta G_r^{(T)}}{RT}\right) \quad (20)$$

Thus, the expression of the equilibrium constant "in concentrations" is derived only on thermodynamic bases.

In conclusion, in order to eliminate the inconsistency, it is proposed to apply the law of mass action in the form (6) on any chemical reaction, so that agreement with experience will be obtained by acting only on the reaction constant. At the same time, using the equilibrium constant "in molar participations", which is dimensionless, is consistent with the law of mass action written in the proposed form (6).

3. Law of s. Arrhenius

Arrhenius' empirical determination of the law that bears his name was a significant step forward in the understanding of the kinetic mechanism governing chemical reactions, especially in terms of the influence of temperature on the rate of reaction, as well as the conditions under which a chemical reaction may or may not occur spontaneously. The expression of Arrhenius' law, as it is found in most papers of Physical Chemistry, has the form:

$$K = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (21)$$

where K = reaction constant, as it appears in the law of mass action (2)

A = pre-exponential factor (or "frequency factor")

E_a = activation energy (molar, in [kJ/kmol])

According to the currently accepted theory, "activation energy" means the energy barrier that must be overcome by the molecules participating in a chemical reaction in order for it to take place. In this sense, it is most often exemplified by a diagram in the form of fig. 1:

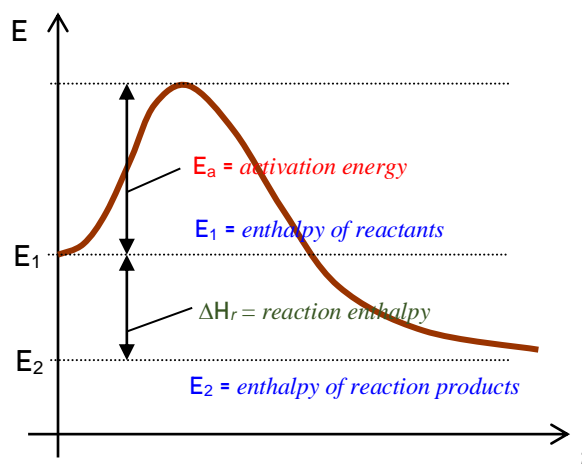


Fig. 1. Evolution of an exothermic chemical reaction.

Usually, in Chemistry applications, the quantities A and E_a are determined experimentally; thus, for the activation energy, the values lie in general in the domain

$$E_a = 10000 \dots 200000 \text{ kJ/kmol}$$

depending on the nature of the reaction, but being considered constant for a given chemical reaction.

Inconsistency: If the activation energy is viewed as the difference between an energy threshold and the energy (enthalpy) of the reactants (as shown in the diagram), then it cannot be constant, it will depend on the temperature at which the diagram was considered. The energy threshold that must be exceeded in order for the reaction to take place is also called the "energy of the activated complex" (or "transition state energy"), referring to a virtual intermediate compound that is formed during the chemical reaction, after which it disappears.

Example: Methane (CH_4) has an autoignition temperature in air of 580°C at a pressure of 1 bar [6]. It means that at this temperature, the activation energy of the combustion reaction is null, which does not follow from the Arrhenius formula.

As the energy diagram shows, only the energy of the activated complex can be regarded as a specific constant of the considered reaction. Also, in the same interpretation, the activation energy differs according to the direction that chemical reaction follows, the difference being the reaction enthalpy which, as it is known, depends on the temperature. In conclusion, in the above interpretation, the indicated values of the activation energy for a given chemical reaction should necessarily be accompanied by the temperature at which they are reported.

On the other hand, it is known from Statistical Physics that the fraction of the total number of molecules of a gas with an energy higher than a certain threshold E^* is given, according to Boltzmann distribution law, by the expression:

$$N_{E^*} \sim \exp\left(-\frac{E^*}{RT}\right). \quad (22)$$

Since the reaction rate is proportional to the number of molecules that overcome a certain energy barrier, it follows that the quantity E_a from the Arrhenius formula would actually be the energy of the activated complex, which is a constant (does not depend on temperature):

$$K = A \cdot \exp\left(-\frac{E^*}{RT}\right). \quad (23)$$

However, in the form above, Arrhenius' law is no longer consistent with the definition of the equilibrium constant:

$$K_C = \frac{K_1}{K_2} = \frac{A_1}{A_2} \rightarrow \text{FALSE!}$$

This inconsistency was removed for the first time by H. Eyring [1] by introducing a new formula for the reaction constant:

$$\bar{K}_1 = \frac{RT}{N_A h_P} \exp\left(-\frac{G^* - G_R^{(T)}}{RT}\right) \text{ [s}^{-1}\text{]} \quad (24)$$

where N_A = Avogadro's number, $N_A = 6.023 \cdot 10^{26}$ [kmol⁻¹], h_P = Planck constant, $h_P = 6.626 \cdot 10^{-34}$ [J.s], G^* = Gibbs free energy of activated complex [kJ/kmol]. Since the pre-exponential factor in Eyring's formula doesn't contain any information about the reacting components, we propose a similar formula, but with a different pre-exponential factor whose meaning will be detailed further:

$$\begin{aligned} \bar{K}_1 &= \bar{A} \cdot \exp\left(-\frac{G^* - G_R^{(T)}}{RT}\right) \\ \bar{K}_2 &= \bar{A} \cdot \exp\left(-\frac{G^* - G_P^{(T)}}{RT}\right) \end{aligned} \quad (25)$$

where the subscripts have the meaning [_R] = reactants, [_P] = reaction products. Returning to the energy diagram, the equations (25) can also be written in the following form wherein the Gibbs free energies are detailed:

$$\bar{K}_1 = \bar{A} \cdot \exp\left[-\frac{G^* - (\sum H_{Ri} - T \sum S_{Ri})}{RT}\right] = \bar{A} \cdot \exp\left(\frac{S^* - \sum S_{Ri}}{R}\right) \exp\left(-\frac{H^* - \sum H_{Ri}}{RT}\right) \quad (26)$$

so that, if one interprets the activation energy as having the expression

$$E_a^{(1)} = H^* - \sum H_{Ri} \quad (27)$$

for the forward direction and

$$E_a^{(2)} = H^* - \sum H_{Pi} \quad (28)$$

for the backward reaction, then this will be a function of temperature, and Arrhenius' law becomes consistent with both Boltzmann's law and the definition of the equilibrium constant. It follows that the reaction constants for forward and backward reactions will be given by:

$$\bar{K}_1 = \bar{A}_1 \exp\left(-\frac{E_a^{(1)}}{RT}\right), \quad \bar{K}_2 = \bar{A}_2 \exp\left(-\frac{E_a^{(2)}}{RT}\right) \quad (29)$$

where

$$\bar{A}_1 = \bar{A} \cdot \exp\left(\frac{S^* - \sum S_{Ri}}{R}\right), \quad \bar{A}_2 = \bar{A} \cdot \exp\left(\frac{S^* - \sum S_{Pi}}{R}\right) \quad (30)$$

If we refer further to the law of mass action in the form (6) wherein the constant \bar{K} has the inverse dimension of "time", that is [s⁻¹], then the "frequency factor" \bar{A} from modified Arrhenius' law (25) will represent indeed the frequency of molecular collisions in the gaseous mixture subjected to the chemical reaction. A simple reasoning leads to the idea that the frequency of collisions is nothing but the

ratio between the average speed of molecular agitation \bar{w}_m and the average free path between two successive collisions \bar{l}_c , both quantities being calculable with formulas given by Statistical Physics [6]:

$$\bar{w}_m = \sqrt{\frac{8}{\pi} RT} = \sqrt{\frac{8}{\pi} \frac{RT}{M}} \quad (30)$$

$$\bar{l}_c = \frac{V}{\pi\sqrt{2} \cdot N \cdot \sigma_0^2} = \frac{1}{\pi\sqrt{2} \cdot N_A \cdot \sigma_0^2} \cdot \frac{RT}{P} \quad (31)$$

where $V =$ volume [m³]

$N =$ total number of molecules in volume V

$\sigma_0 =$ diameter of molecules (average value for the mixture) [m]

The expression for the factor \bar{A} is thus obtained:

$$\bar{A} = \frac{\bar{w}_m}{\bar{l}_c} = 4\sqrt{\pi} \cdot N_A \sigma_0^2 \frac{P}{\sqrt{MR T}} \quad [s^{-1}] \quad (32)$$

In conclusion, a law of the mass action that is consistent both dimensionally and with the other laws of Thermochemistry, will be described by the expression:

$$\frac{dX_\gamma}{dt} = (v_\gamma'' - v_\gamma') \bar{K} \prod_i X_i^{v_i'} \quad (33)$$

where

$$\bar{K} = 4\sqrt{\pi} N_A \sigma_0^2 \frac{P}{\sqrt{MR T}} \exp\left(-\frac{G^* - G_R^{(T)}}{RT}\right) \quad [s^{-1}] \quad (34)$$

(average values for molecular masses M and molecule diameters σ_0 in the reacting mixture needs to be considered). One can see that the only constant which has to be determined experimentally is G^* .

4. Application for a second order equation

The following reaction is analyzed:



In table 1, the thermodynamic properties of reactants at $T_0 = 300$ K are given.

Table 1. Thermodynamic properties of reactants at $T_0 = 300$ K [7]

Reactant	$(C_p)_m$ [kJ/kmol.K]	M [kg/kmol]	H [kJ/kmol]	S [kJ/kmol.K]	σ_0 [m]
N	20,8	14	472790	153,4	$1,85 \cdot 10^{-10}$
O ₂	32	32	50	205,3	$3,5 \cdot 10^{-10}$
Average values	-	19,5	-	-	$2,8 \cdot 10^{-10}$
Total values	52,8	-	472840	358,7	-

The activation energy can be used to compute the enthalpy of activated complex, according to (27):

$$H^* = E_a^{(1)} + \sum H_{Ri} \quad (36)$$

where $E_a^{(1)} = 29900 \text{ kJ/kmol}$ (NIST database [7]). One obtains:

$$H^* = 29900 + 472840 = 502740 \text{ kJ/kmol .}$$

Assuming average constant specific heats on given temperature intervals [8], the corresponding temperature of activated complex can be computed:

$$T^* = T_0 + \frac{H^* - H(T_0)}{\sum_i (C_p)_i} = 300 + \frac{29900}{52,8} = 866.3 \text{ K}$$

The entropy of activated complex will be:

$$S(T^*) = S(T_0) + \sum_i (C_p)_i \cdot \ln \frac{T^*}{T_0} = 358.7 + 52.8 \times \ln \frac{866.3}{300} = 414.7 \text{ kJ/kmol.K}$$

The normalized pre-exponential factor for the forward reaction will be:

$$\bar{A}_1 = 4\sqrt{\pi} N_A (\sigma_0^2)_m \frac{P}{\sqrt{MR T_0}} \exp\left(\frac{S^* - \sum S_{Ri}}{R}\right)$$

where, for M, the reduced mass [9] was considered:

$$M = \frac{2M_N M_{O2}}{M_N + M_{O2}} = 19,5 \text{ kg/kmol}$$

One obtains:

$$\bar{A}_1 = 4 \cdot 10^{12} \text{ s}^{-1}, \quad \bar{A} = 4.8 \cdot 10^9 \text{ s}^{-1}$$

According to Eyring formula one gets:

$$\bar{A}_1 = \frac{RT}{N_A h_p} \exp\left(\frac{S^* - \sum S_{Ri}}{R}\right) = 5.2 \cdot 10^{15} \text{ s}^{-1}, \quad \bar{A} = 6.2 \cdot 10^{12} \text{ s}^{-1}$$

that is three orders of magnitude larger.

For sake of comparison with the data presented in the literature, the non-normalized pre-exponential factor will be computed according to (10):

$$A_1 = \bar{A}_1 \left(\frac{RT}{p}\right)^{\sum_i \nu_i - 1} = \bar{A}_1 \cdot \frac{RT_0}{p} = 4 \cdot 10^{12} \times \frac{8314 \times 300}{10^5} = 10^{14} \text{ m}^3 / \text{kmol.s}$$

Eyring formula gives:

$$A_1 = 5.2 \cdot 10^{15} \times \frac{8314 \times 300}{10^5} = 1,3 \cdot 10^{17} \text{ m}^3 / \text{kmol.s}$$

In NIST database [7] one finds

$$A_1 = 9 \cdot 10^9 \text{ m}^3 / \text{kmol.s}$$

so that we can conclude that our proposed formulas give results closer to those found in published documents, yet far enough from experimental determinations.

As such, an additional correction has to be applied to the pre-exponential factor derived from collision theory, which is known as “steric factor”, ρ .

5. Conclusions

In order to obtain a new equation dimensionally consistent describing the law of mass action referring to the reaction rate, a new definition for the reaction constant was given such that it will have the same unit of measurement [s^{-1}] no matter what kind of reaction is considered. On the other hand, instead of concentrations of gaseous reacting components in the equation of mass action, their molar participations were considered, which are dimensionless quantities.

It was proved also that the activation energy in Arrhenius' formula cannot be constant, so that the Eyring model of transition state was considered and adapted by changing the expression of pre-exponential factor according to the results of Molecular and Statistical Physics. Thus, an alternative Arrhenius-like formula was proposed, which is consistent with both Boltzmann's distribution and the definition of the equilibrium constant.

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