Unutilized potential of Erofeev’s equation

Vladimír Kovár*, Martin Palou, Eva Smrčková, Peter Šimon

Institute of Inorganic Chemistry, Technology and Materials, Faculty of Chemical and Food Technology, STU, Radlinského 9, 812 37 Bratislava, Slovakia

*vladimir.kovar@stuba.sk

Abstract

The article analyzes the general equation of chemical kinetics, whose specific case is often cited as Erofeev’s equation. Physical meaning of the function under integral in the general equation is interpreted as a function of reaction conditions. New general concept for the expression of a conversion equation is proposed on a base of analysis, Erofeev’s approach to the individual kinetic particles being maintained. However, in contrary to the Erofeev’s equation the variability of reactivity is not covered by mean value but it is described by a distribution function. The new general equation of chemical kinetics enables to derive a kinetic equation corresponding relating to the known reactivity distribution and time dependence of reaction probability. The derivation of one such equation is illustrated as an example.

Key words: Erofeev’s equation, kinetic equation, kinetic model, reactivity distribution

Introduction

One of the equations often used to describe the nucleation kinetics and subsequent crystal growth is Erofeev’s equation (Erofeev 1946)

\[ \alpha = 1 - \exp\left(-kt^m\right) \]  

where \( \alpha \) is the conversion, \( t \) is time, and \( k > 0, m > 0 \) are parameters independent of time. However the main aim of Erofeev’s article was not to establish equation (1), but the derivation of another equation – the general equation of chemical kinetics

\[ \alpha = 1 - \exp\left(-\int_0^t hdt\right) \]  

where \( h \) is an unspecified time function.
As equation (2) obtains integral, its form cannot be considered as the final one. To obtain the final form, it is necessary to know the form of function $h$. Erofeev presented a few examples of function $h$ in his article. For the reaction controlled by nucleation he stated that function $h$ represents the area of all the crystals surfaces. In the case of a first order reaction he stated (without explanation) that $h$ is a constant. Such „explanations“ do not clarify the physical meaning of function $h$, and therefore cannot be considered adequate. The unclearness referring to the function $h$, is perhaps the reason why the general equation (2) is encountered in literature very scarcely.

The situation with the often used equation (1), which is presented in the Erofeev’s article only as a specific example how to use the general equation (2), is rather different: namely, it is the final form and the user has no need to look behind the form of function $h$ (although he should to do it, at least to check, whether it corresponds to the conditions of his experiment).

The aim of this article is to analyze Erofeev’s general equation of chemical kinetics (2) especially regarding the function $h$ and the possibilities of equation modification.

Derivation of Erofeev’s general equation of chemical kinetics

To understand the physical meaning of function $h$, it is necessary to return to a derivation of equation (2). The derivation consists of two parts:

1. derivation of the general equation for a reaction of one ($i$-th) kinetic particle, where the kinetic particle could be any reacting particle participating in the reaction on atomic level (ion, atom, molecule, ... ),
2. utilisation of the general expression for one ($i$-th) particle to describe the reaction of the whole reactant.

In the first part, Erofeev divided the reaction time from 0 to $t$ into $n$ intervals, where the boundaries $t_0$, $t_1$, ... $t_{k-1}$, $t_k$, ..., $t_n$ satisfy the condition

$$0 = t_0 < t_1 < \ldots < t_{k-1} < t_k < \ldots < t_n = t$$

(3)

Then, for each time interval $[t_{k-1}, t_k]$ he attributed probability $p_{i,k}$ that the $i$-th kinetic particle reacts during this interval. To derive the probability of reaction for this particle during time $t$ he adopted two assumptions.
The first assumption was that the probability that \( i \)-th kinetic particle did not react during time \( t \), was given by the product of probabilities that this kinetic particle did not react in any interval of the time division (3)

\[
1 - P_i = \prod_{k=1}^{n} \left( 1 - P_{i,k} \right).
\]

where \( P_i \) was the probability of the \( i \)-th kinetic particle reaction during time \( t \).

The second Erofeev’s assumption was that for each (\( i \)-th) kinetic particle there existed a positive time function \( h_i \) defined over the interval \([0, t]\) which, for any time interval \([t_{k-1}, t_k]\), determines the reaction probability \( p_{i,k} \) of this kinetic particle by the relationship

\[
p_{i,k} = 1 - \exp \left( - \int_{t_{k-1}}^{t_k} h_i dt \right)
\]

Replacing the probability \( p_{i,k} \) in equation (4) by equation (5), dividing time into \( n \rightarrow \infty \) intervals and rearranging the result, general equation for the reaction of one (\( i \)-th) kinetic particle was obtained in the form

\[
P_i = 1 - \exp \left( - \int_{0}^{t} h_i dt \right)
\]

In accordance with Erofeev’s view, it is necessary to note that equation (6) was derived without using any special assumptions referring to the properties of the reaction system. So, it has absolutely general nature, which means that it holds not only for reaction of the \( i \)-th kinetic particle in solid state, but also in any other reaction and is not limited only to the isothermal conditions. Further, the function \( h_i \) should to take into account all the reaction conditions for the \( i \)-th kinetic particle (temperature, pressure, concentration, …), which leads to its denotation as the time function of local reaction conditions.

To the mathematical properties of the function \( h_i \) let’s add that coming to the end of the reaction (when \( P_i \rightarrow 1 \)), which means in time \( t_{P_i \rightarrow 1} \), it must be

\[
\int_{0}^{t_{P_i \rightarrow 1}} h_i dt \rightarrow \infty
\]

It is necessary to emphasize, that the described Erofeev’s approach enables to assume that the probabilities \( P_i \) vary from one kinetic particle to the other – while the time dependence \( P_i = f_i(t) \) for one particle could be very slow, for another it could differ by several orders (rapid course), that the probability of reaction \( P \) is therefore in any time a random variable having \( P_i \) values.
and that this variable \((P)\) has in any time its own distribution \(f_P(P)\) which depends on time \(t\), analytical forms of functions \(h_i\) and on their parameters (concept of polyreactive reactant, see for example Jesenák 1973).

In the second part of the derivation of general equation of chemical kinetics, Erofeev did not take into account the distribution of reactivity. Applying equation (6) to the whole reactant he assumed that “for finite intervals of time, values \(P_i\) for different molecules of the same component could differ by only infinitely small values”. In fact, in this step of his derivation, he substituted a system of kinetic particles of various reactivity (reactant) by one mean (representative) particle. Negative review of this step (see for example Pančenkov GI, Lebedev VP 1985) should be therefore interpreted on two levels – on physical and on mathematical one. While on the physical level, the negative review is substantiate, on the mathematical level, it is sufficient to simply assign the function \(h\) as a function of mean (representative) reaction conditions for the whole reactant.

Here, it has to be noted again that equation (2) was derived without using any special assumptions referring to the properties of the reaction system (as for example solid state reaction, isothermal conditions, …).

The question of analytical form or closer physical meaning of function \(h\) is not solved, of course, by this analysis but its denomination as the function of the mean (representative) reaction conditions for the whole reactant enables to search after this meaning. For example, if experimental data are satisfactorily fitted by cited equation (1), using equation

\[
h = \frac{1}{1-\alpha} \cdot \frac{\partial \alpha}{\partial t}
\]

which results from equation (2), we can derive the form of function \(h\) as follows

\[
h = km^{m-1}
\]

Then, the obtained course of function \(h\), in relation to the particular reaction conditions, could help us to explain the physical meaning of its parameters (until now attributed to the temperature function and to the dimension of crystal growth). From the mathematical point of view, it can be expected that the obtained course of function \(h\) will have one of the following form:

1. for \(0 < m < 1\), \(h\) is a hyperbolically decreasing time dependence,
2. for \(m = 1\) (first order reaction), \(h\) is a constant,
3. for \(m > 1\), function \(h\) is increasing
   a. if \(1 < m < 2\), concavely,
   b. for \(m = 2\) it is a strait line,
c. if \( m > 2 \), convexly.

Physical meaning of these courses is perhaps logical but not known yet.

Similar analysis can be done for any function \( \alpha = f(t) \), from which the courses of function \( h \) can be obtained using equation (8).

**Taking into account the reactivity distribution**

As we have already stated, the probability \( P_i \) (given by equation (6)) is in any time the value of random variable \( P \), which has in any time its own distribution \( f_P(P) \). Then, the mean value \( E(P) \) of the distribution in any time \( t \) is given by the standard expression

\[
E(P) = \alpha = \int_{P_l}^{P_u} P \cdot f_P(P) \cdot dP
\]  

where \( P_l \) and \( P_u \) are the lower and upper boundaries of the interval, respectively, where the random variable \( P \) is defined at time \( t \).

In such a way equation (10) extends the original Erofeev’s equation (2) because in contrary to it, reactivity distribution is taken into account.

Similarly as in the case of function \( h \), authors have no idea about the analytical form of the distribution function \( f_P(P) \). However, they hope that this article will evoke the interest to find them.

**New kinetic equations**

Similarly as equation (2), equation (10) also enables to derive conversion dependence \( \alpha = f(t) \) for actual reaction conditions. To derive this equation, except of function \( h \) also the form of the distribution function \( f_P(P) \) is needed. The derivation procedure is illustrated on the following simple example:

Let’s consider experimental data \( \alpha = f(t) \) (in this illustrative example the same data are used, on which Erofeev demonstrated the suitability of equation (1) for the description of conversion dependencies – decomposition of AgMnO₄, Sieverts and Theberath 1922). Let’s consider two statements related to the chemical reaction and conditions in which it runs

Functions \( h_i \) have the same analytical form for all kinetic particles, and this unified form is given as follows

\[
h_i = mk_i t^{m-1}
\]  

where parameter \( k_i \) is from interval \( <k_l, k_u> \) and it is the only one, which causes the variability of \( h_i \) values at time \( t \) (the same values of parameter \( m \) are used in this calculation as those used
by Erofeev). Then, according to equation (6), for the reaction probability $P_i$ of any kinetic particle it goes

$$P_i = 1 - \exp(-k_i t^m)$$

(12)

And further, let the distribution function $f_i(P)$ have the form of an increasing function

$$f_i(P) = \frac{1}{\ln \frac{1-P_i}{1-P}} \cdot \frac{1}{1-P}$$

(13)

Then, according to equation (10), we get

$$\alpha = 1 - \frac{P_u - P_i}{\ln \frac{1-P_i}{1-P_u}}$$

(14)

As the variable $P_i$ is given by equation (12), and function $h_i$ is given by equation (11), the resulting equation (14) can be rewritten into the form of time dependence

$$\alpha = 1 - \frac{\exp(-k_i t^m) - \exp(-k_i f^m)}{t^m(k_u - k_i)}$$

(15)

It should be noted that the dependence according to equation (15) has a classical course (for $t = 0$ the conversion $\alpha$ is 0, and for $t \to \infty \alpha = 1$), with an inflex point for $m > 1$ at time $t_{in}$ given by relationship

$$\frac{m(k_u f_{in}^m)^2 + (m+1)(k_u f_{in}^m + 1)}{m(k_i f_{in}^m)^2 + (m+1)(k_i f_{in}^m + 1)} = \exp\left[k_u f_{in}^m \right]$$

(16)

Further, the illustrative equation (15), in which only parameter $k_i$ causes the variability of $h_i$ values at time $t$, can be considered as extended form of equation (1), because for $k_i = k_u = k$ equation (15) degenerates to equation (1). And because of its higher number of parameters (three), equation (15) is more flexible than equation (1) with only two parameters.

The correspondence of equation (15) to experimental data can be checked by fitting this data. In this way, we will get the numerical values of parameters (the results are presented in Table 1).
Table 1: Parameters of equation (15) for experimental data (Sieverts and Theberath 1922); the values of parameter $m$ were those used by Erofeev in evaluating the same data.

<table>
<thead>
<tr>
<th>experiment</th>
<th>$m$</th>
<th>$k_l$</th>
<th>$k_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>51 (8 points)</td>
<td>6</td>
<td>$6.96 \times 10^{-19}$</td>
<td>$6.96 \times 10^{-19}$</td>
</tr>
<tr>
<td>39 (9 points)</td>
<td>4</td>
<td>0.0</td>
<td>$4.77 \times 10^{-12}$</td>
</tr>
<tr>
<td>42 (8 points)</td>
<td>3</td>
<td>$2.83 \times 10^{-9}$</td>
<td>$2.83 \times 10^{-9}$</td>
</tr>
<tr>
<td>41 (11 points)</td>
<td>4</td>
<td>$9.63 \times 10^{-13}$</td>
<td>$2.79 \times 10^{-12}$</td>
</tr>
<tr>
<td>52 (8 points)</td>
<td>3</td>
<td>$3.35 \times 10^{-9}$</td>
<td>$3.35 \times 10^{-9}$</td>
</tr>
<tr>
<td>69 (7 points)</td>
<td>2</td>
<td>$9.07 \times 10^{-6}$</td>
<td>$9.07 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Discussion

As can be seen in Table 1, in four cases (experiments 51, 42, 52 and 69) degeneration of equation (15) to equation (1) occurred, because $k_l = k_u = k$. In these cases, the considered model, defined by equations (11) and (13), describes the decomposition of all AgMnO$_4$ molecules identically. However, these results contradict to the assumption on reactant polyreactivity, and therefore, the supposed model was refused for these four cases.

In the other two cases (experiments 39 and 41), equation (15) gives unequal values of $k_l$ and $k_u$. As it can be supposed that there also exists another combination of functions $h$ and $f_p(P)$ acceptably describing these experimental data, this inequality does not mean automatically that the model has to be accepted. Criterion for the proper combination choice is the aim of further study.

To compare the calculation results to those of equation (1), let’s add that equation (1) gives for experiment 39 value $k = 2.01 \times 10^{-12}$ and for experiment 41 value $k = 1.78 \times 10^{-12}$. The corresponding least square sums are, of course, a little bit higher (experiment 39: $7.971 \times 10^{-3}$ compared with $5.945 \times 10^{-3}$ in case of equation (15), experiment 41: $1.932 \times 10^{-3}$ compared with $1.463 \times 10^{-3}$).

If we still decide to accept the proposed model (15) for the two mentioned experiments, then we reach a clear quantitative picture on reactivity distribution and its change during the reaction course. For experiment 41, the reaction conditions are given by equation (11), where values $k_i$ are from the interval $<9.63 \times 10^{-13}$; $2.79 \times 10^{-12}>$ (value $m = 4$.
was determined by Erofeev). From this it follows for the lower and upper limits of reaction conditions

\[ h_l = 3.85 \times 10^{-12} t^3 \quad \quad h_u = 1.12 \times 10^{-11} t^3 \]  

(17)

and for the lower and upper limits of reaction probability

\[ P_l = 1 - \exp(-9.63 \times 10^{-13} t^4) \quad \quad P_u = 1 - \exp(-2.79 \times 10^{-12} t^4) \]  

(18)

The mean value of the distribution (conversion \( \alpha \)) is then given by the relationship

\[ \alpha = 1 - \frac{\exp(-9.63 \times 10^{-13} t^4) - \exp(-2.79 \times 10^{-12} t^4)}{1.83 \times 10^{-12} t^4} \]  

(19)

Graphically, equations (17) – (19) are plotted in Figs. 1 and 2 (in Fig. 2 together with experimental data).

Fig. 1 Range of reaction conditions limited by curves \( h_l \) and \( h_u \).

As the actual conditions of the evaluated experiments are inaccessible, authors cannot provide a closer interpretation of the dependencies in Fig. 1.
The reactivity distribution in any time $t$ is given by the increasing function

$$f_P(P) = \frac{1}{1.83 \times 10^{-12} t^4} \frac{1}{1 - P}$$

(20)

and it is graphically plotted in Fig. 3 for the chosen experimental times (602 h, 767 h and 1006 h).

Fig. 3. Reactivity distribution in the experimental times 602 h, 767 h and 1006 h.

Another view on the $f_P(P)$ function course can be obtained using equation

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\[ f_{p_i}(P_i) = \frac{\exp(k_i t^m)}{(k_u - k_i)^m} \] (21)

which is the combination of equations (12) and (13). This equation enables to see the change of the distribution function for one \((i\text{-th})\) particle in dependence on time (Fig. 4). It is a convex function with a minimum at time

\[ t_{\text{min}}(P_i) = \frac{1}{\sqrt[2]{k_i}} \] (22)

from which it follows that for all particles it goes

\[ P_{i,\text{min}} = 1 - \frac{1}{e} \approx 0.632 \] (23)

The individual kinetic particles reach this value of probability in time interval from \(t_{\text{min}}(P_u) = 773.5\) h till \(t_{\text{min}}(P_l) = 1009.4\) h, conversion reaches it at time \(t = 863.15\) h.

![Graph showing time dependence of the distribution function for three kinetic particles](image)

**Fig. 4** Examples of time dependence of the distribution function for three chosen kinetic particles \((k_1 = 9.63 \times 10^{-13}, k_2 = 1.80 \times 10^{-12}, k_3 = 2.79 \times 10^{-12})\)

It can be assumed that interpretation of equation (23), according to which the time dependencies of the distribution functions for each kinetic particle have the minimum values just at \(P_i \approx 0.632\), has also a physical meaning.

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The tree dimensional view on the relationships of time $t$, of the reaction probability $P$ and the distribution $f_P(P)$ of this probability is graphically plotted, according to equation (20), in Fig. 5.

![Three dimensional view on the area limited by changing the distribution $f_P(P)$ of the reactivity $P$ in time $t$.](image)

Fig. 5 Three dimensional view on the area limited by changing the distribution $f_P(P)$ of the reactivity $P$ in time $t$.

For experiment 39, similar figures should be obtained. It is interesting that $k_l \approx 0$ in this experiment. Then, the conversion relationship turns as follows

$$\alpha = 1 - \frac{1 - \exp(-k_u t^m)}{t^m k_u}$$

so now, equation (24) has the same number of parameters as equation (1).
Conclusion

Modified general equation of chemical kinetics in contrary to its original form takes into account also the reactivity distribution. New form of the general equation does not include an actual form of function \( h \), neither that of reactivity distribution \( f_\rho(P) \). This will be the aim of further study.

On the base of the reaction conditions \( h \) and the distribution of the reaction probability \( f_\rho(P) \), the new general equation of chemical kinetics enables to derive actual conversion dependencies \( \alpha = f(t) \). A backward procedure leading from conversion dependencies \( \alpha = f(t) \) to functions \( h \) and \( f_\rho(P) \) is mathematically impossible. Experimental data fitting by function \( \alpha = f(t) \), derived from particular functions \( h \) and \( f_\rho(P) \), therefore serves only for refusing the incorrect forms of these two model defining functions. In a case of model acceptance, functions \( h \) and \( f_\rho(P) \) enable deeper study of chemical reaction.

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