EXTENSION OF THE DIFFUSIONAL KINETICS MODELS INVOLVING CHANGES IN ACTIVATION ENERGY

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On the basis of previous modifications of the Zhuravlev and Ginstling-Brounshtein models, a generalization of kinetic diffusional models is proposed. With the assumption that the rate of the activation energy change during the reaction is inversely proportional to the reaction time, it has been shown that all diffusional kinetic equations in heterogeneous systems take the form $F(\alpha) = KT^n$, where $F(\alpha)$ is a function of the degree of conversion α and K and n are constants related to the rate constant.

In heterogeneous kinetics the total rate of reaction can be limited either by a chemical process or by diffusion. Most of the models devoted to the latter case lead to kinetic equations obtained under the assumption that the activation energy does not change during the process. However, to explain certain experimental results it has been necessary to assume that the activation energy does vary during the reaction process, as for instance in the reduction of V_2O_5 by gaseous ammonia, or the oxidation of VO_2 and V_6O_{13}, as shown by Małecki et al. [2–5]. Another typical example is supplied by studies of the thermal decomposition of Co_3O_4: Berthod [6] could not find an adequate kinetic equation, while Deshmukh et al. [7] proposed two different equations corresponding to different stages of decomposition. Finally, Małecki, Doumerc et al. were able to describe the kinetics of this reaction in the whole range of decomposition, using a unique equation derived from Ginstling-Brounshtein's model, in which the activation energy was assumed to change with the degree of decomposition [8, 9].

It is also worthwhile to note that Kröger and Ziegler previously modified Jander's equation, assuming that the coefficient of diffusion is inversely pro-

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portional to the time, which can also result from a time-dependence of the activation energy.

In fact, from the theoretical point of view, changes in activation energy during a reaction in which the rate-limiting step is diffusion are expected when one considers changes in chemical composition, in concentration of defects, as well as in the compactness and texture of the medium in which diffusion occurs. Up to now, however, no attempts have been made to work out a general method to account for these activation energy variations.

In the present paper it will be shown that it is possible to modify and extend all existing models concerning reactions in which diffusion is the rate-limiting step, using a very simple phenomenological hypothesis taking into account the change in activation energy during the process.

Time-dependence of activation energy

The kinetics of reduction of V_2O_5 by gaseous ammonia has been described by the following equation [2]:

$$[(1-\alpha)^{-1/3} - 1]^2 = Kt^n \tag{1}$$

where α is the degree of conversion, K and n being constants. The same equation has also been used for kinetic analysis of the oxidation of VO_2 and V_6O_{13} [3–5].

Analysis of experimental variations of the degree of decomposition vs. time for the thermal decomposition of Co_3O_4 led to the equation [8]:

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = Kt^n \tag{2}$$

Both Eqs (1) and (2) have been derived using the same simple phenomenological assumption concerning the time-dependence of the activation energy [1, 9]:

$$\frac{dE(t)}{dt} = \frac{k_E}{t} \tag{3}$$

where $E(t)$ is the activation energy, t is the reaction time and k_E is a constant.

Equation (3) involves the assumption that the changing rate of $E(t)$ tends to zero as t tends to infinity. Such a situation ought to be observed if, when the reaction approaches completion, the medium in which diffusion occurs tends to a steady state.

It has been shown that, with the assumption of Eq. (3), Eq. (1) can be deduced from Zhuravlev's model [1], and Eq. (2) from Ginstling–Brounshtein's model [9].

We therefore propose here to extend this phenomenological approach to all existing diffusional kinetic models.

Extension of diffusional kinetic models

Generally, for reactions the rate of which is limited by diffusion, we may write:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{4}$$

where k is the rate constant and $f(\alpha)$ is a function whose form depends on the kinetic model used.

Assuming that k follows an Arrhenius law, we have:

$$k = k_0 \exp\left(-E/RT\right) \tag{5}$$

where the symbols have their usual meaning.

Integration of Eq. (3) gives:

$$E(t) = k_E \ln t + \text{const.} \tag{6}$$

To determine the integration constant in Eq. (6), we take $E_{0.5} = E(t_{0.5})$, where $t_{0.5}$ corresponds to the time at which $\alpha = 0.5$.

Thus:

$$E(t) = E_{0.5} + k_E \ln\left(t/t_{0.5}\right) \tag{7}$$

Introducing Eq. (7) into Eq. (5), we have:

$$k = k_0 t_{0.5}^{k_E/R} \cdot t^{-k_E/RT} \exp\left(-E_{0.5}/RT\right) \tag{8}$$

Taking into account Eq. (8), Eq. (4) becomes after integration:

$$F(\alpha) = Kt^n \tag{9}$$

where:

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{10}$$

$$n = 1 - (k_E/RT)$$

$$K = \frac{1}{n} k_0 t_{0.5}^{1-n} \exp\left(-E_{0.5}/RT\right) \tag{11}$$

To eliminate $t_{0.5}$ from Eq. (11), using Eq. (9) we may write:

$$F(0.5) = Kt_{0.5}^n$$
$$\text{and}$$

$$t_{0.5} = \frac{n}{k_0} F(0.5) \exp\left(E_{0.5}/RT\right) \tag{12}$$

Substituting Eq. (12) into Eq. (11):

$$K = f(0.5) \left[\frac{k_0 \exp\left(-E_{0.5}/RT\right)}{nF(0.5)} \right]^n \tag{13}$$

Integration of Eq. (4), assuming as in most existing models a time-independent activation energy (i.e. $k_E = 0$), would give:

$$F(\alpha) = kt \tag{14}$$

Finally, introduction of the time-dependence of the activation energy leads to equations similar to Eq. (9) and differing from Eq. (14) only by the presence of an exponent n in the right-hand term.

Determination of time-dependence of activation energy

Fitting experimental data into Eq. (9) leads to determination of the parameters K and n. Using Eq. (13) in the form:

$$\ln\left[n\left(\frac{K}{F(0.5)}\right)^{1/n} \right] = \ln\left(\frac{k_0}{F(0.5)}\right) - \frac{E_{0.5}}{RT} \tag{15}$$

if the temperature-dependence of both parameters is known $E_{0.5}$ can be determined from a plot of the left-hand side of Eq. (15) *vs.* $1/T$.

The α-dependence of the activation energy can be determined on the basis of Eq. (7). From Eq. (9) we have:

$$t_{0.5} = [F(0.5)/K]^{1/n}$$

$$t = [F(\alpha)/K]^{1/n}$$

and from Eq. (10):

$$k_E = (1-n)RT$$

Introduction of the above equations into Eq. (7) gives:

$$E(\alpha) = E_{0.5} + \frac{(1-n)RT}{n} \ln \frac{F(\alpha)}{F(0.5)} \tag{16}$$

The validity of Eq. (16) is obviously limited to the range of values of α within which the assumption corresponding to Eq. (3) can be applied.

Previous determinations of the activation energy proposed in Refs 2, 3 and 8 did not assume for the activation energy any a priori given form of either time-dependence or α-dependence. They were based on the simple hypothesis that the

equation giving the reaction rate can be separated into two factors, only one of them depending on temperature and being taken as the rate constant obeying an Arrhenius law. It should be emphasized that, using the method described in the present paper, such an assumption is no longer required in the determination of $E(\alpha)$.

Conclusions

The following remarks may be made:

On the basis of the above considerations it was possible to extend two diffusional models, which have been used to describe the kinetics of a solid-gas reaction [2–5] and of a thermal decomposition [8, 9].

Therefore, an approach extending the existing kinetic diffusional models to reactions in which the activation energy changes as the reaction proceeds seems to have a quite general meaning.

The fitting of the experimental data into diffusional kinetic models (corresponding to Eq. (14)) should be carried out using logarithmic coordinates: $\log F(\alpha)$ vs. $\log t$ (due to the form of Eq. (9)). If significant slope shifts with respect to 1 are observed, the possibility of a variation of the activation energy with the degree of conversion must be considered.

We have already emphasized that the assumption of Eq. (3) has only phenomenological significance. However, the constant k_E should be related as the reaction proceeds to some microscopic modifications of the medium in which diffusion occurs.

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Zusammenfassung — Auf Grund vorangegangener Modifikationen der Modelle von Zhuravlev und Ginstling–Brounshtein wird eine Verallgemeinerung der kinetischen Diffusionsmodelle vorgeschlagen. Mit der Annahme, daß die Geschwindigkeit der Änderung der Aktivierungsenergie während der Reaktion umgekehrt proportional der Reaktionszeit ist, wird gezeigt, daß alle kinetischen Diffusionsgleichungen für heterogene Systeme die Form $F(\alpha) = KT^n$ haben, wo $F(\alpha)$ eine Funktion des Konversionsgrades α und K und n mit der Geschwindigkeitskonstante in Beziehung stehende Konstanten sind.

Резюме — На основании ранее модифицированных моделей Журавлева и Гинстленга–Браунсфина предложены обобщенные кинетические диффузионные модели. Предполагая, что изменение скорости энергии активации во время реакции обратно пропорционально времени реакции, было показано, что для гетерогенных систем все диффузионные кинетические уравнения принимают вид $F(\alpha) = KT^n$, где $F(\alpha)$ — функция степени превращения α, а K и n — являются постоянными относительно константы скорости.