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METHODOLOGICAL ASPECTS OF STUDYING THE KINETICS OF REVERSIBLE REACTIONS IN SOLID-GAS SYSTEMS

Degree of moving away from equilibrium

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The relationship between the degree of moving away from equilibrium, the kinetic parameters and the experimental conditions is provided by solving a mass balance equation for the gaseous products of reversible decompositions. The ways to reduce the share of the reverse reaction in the total rate of reaction are discussed. The conditions of non-equilibrium $CaCO_3$. decomposition are defined.

The great practical importance of the processes occurring in solid-gas systems has made them a traditional subject of thermoanalytical studies. Recently, such methods have been developed in particular for the study of kinetic relationships in heterogeneous systems [1]. As yet, a unanimous opinion is not to be found in the literature regarding the possibilities of obtaining reliable kinetic information from traditional thermoanalytical methods [2]. In fact, the kinetic parameters determined by different researchers for one and the same reaction often vary considerably. The scattering may be a result of differences in experimental conditions, or in the purities of samples investigated, but it may also stem from the deficiencies of the methods for processing the results.

The majority of the methods widely used to determine kinetic parameters in thermal analysis are based on the one-stage or "overall-one-stage" reaction model. However, not all solid-gas reactions proceed in this manner. In particular, many processes traditionally considered to be model processes in thermal analysis (such as the dehydration of crystal hydrates, transformations of co-ordination compounds, reduction of metal oxides) are reversible, and consequently not one-stage reactions, since the full equation for their rate of reaction should, in the general case, include the rate of the reverse reaction. If the rates of the forward and reverse reactions are comparable, application of the simplest kinetic models becomes impossible; the procedure for finding the kinetic parameters becomes much more intricate if the rate of the reverse reaction is taken into account. Usually, the rate of reverse reaction is not taken into account, and an attempt is made to eliminate its effect on the overall kinetics of the process by using one or another experimental stratagem.

In practice, one of the most frequent recommendations for studying the kinetics of reversible reactions is to carry out the process as far away from equilibrium as possible. For this purpose the application of a dynamic vacuum or an inert gas flow through the sample is a necessary, but not sufficient condition [3]. However, in many cases these measures are not satisfactory means of eliminating the effect of the reverse reaction on the overall kinetics. This is made clear by the fact that the kinetic results change when the experimental conditions, e.g. the flow rate of the inert gas [4] or vacuum [5], are varied. The reason is that for different processes the conditions under which the rate of the reverse reaction becomes negligible differ considerably.

The purpose of this paper is to determine the effect of the reverse reaction on the overall rate of reaction under different conditions, and, depending on the special characteristics, to determine the effects of the different experimental conditions on the approach of the system to equilibrium and on its moving away from it; from these general considerations, recommendations will be concluded for the selection of experimental conditions for the study of reversible reactions.

Let us consider the reversible reaction

$$A_s \rightleftharpoons B_s + C_g \tag{I}$$

The equilibrium constant of this reaction is

$$K = \frac{\overrightarrow{k}}{\overleftarrow{k}} \approx P_p^e$$

where K is the equilibrium constant,

$\overrightarrow{k}$ $\overleftarrow{k}$ are the rate constants of the forward and reverse reactions, respectively, and

P_p^e is the equilibrium pressure of the gaseous product.

The mass balance equation for the gaseous product is

$$\frac{\mathrm{d}C_p}{\mathrm{d}t} + r_{\mathrm{rem}} = \overrightarrow{r} + \overleftarrow{r} \tag{1}$$

where C_p is the concentration of the gaseous product in the sample player,

t is time,

r_{rem} is the rate of removal of the gaseous product from the layer, and

$\overrightarrow{r}$ and $\overleftarrow{r}$ are the rates of the forward and reverse reactions, respectively.

On the other hand, the following relationship holds for the rate of transformation of the solid reactant:

$$\frac{d\alpha}{dt} = \frac{1}{n_0}\cdot\frac{dn_p}{dt} \tag{2}$$

where α is the degree of conversion of the solid reactant,
n_0 is the number of mols of the solid reactant at the initial moment, and
n_p is the number of mols of the gaseous product.

Equations (1) and (2) form a system whose solution depends on the specific form of the expressions for r_{rem}, $\vec{r}$ and $\overleftarrow{r}$, these again being defined both by the experimental conditions and by the kinetics of the process in question.

Let us first consider reaction (I) under isothermal conditions in a flow reactor with ideal mixing, best suited for studying the kinetics of heterogeneous processes [6]. In this case

$$\frac{d\alpha}{dt} = \frac{1}{n_0}\left(\frac{dC_p}{dt} + \frac{W}{V}C_p\right) = \frac{V}{n_0RT}\left(\frac{dP_p}{dt} + \frac{W}{V}P_p\right) \tag{3}$$

where V is the volume of the gas phase in the sample layer, R is the universal gas constant, T is the absolute temperature and W is the volumetric flow rate of the gas through the reactor.

Assuming that the forward and reverse reactions are both simple:

$$\begin{aligned} \vec{r} &= \vec{k}\cdot\vec{f}(\alpha) \\ \overleftarrow{r} &= \overleftarrow{k}\cdot\overleftarrow{f}(\alpha, P_p) \end{aligned} \tag{4}$$

where $\vec{f}(\alpha)$ and $\overleftarrow{f}(\alpha, P_p)$ are kinetic functions whose forms depend on the mechanism of the process.

To obtain the equations explicitly describing the system, let us consider the boundary cases described in the literature [2, 7].

Case A. The solid product formed in the reaction has a perfect crystalline structure; the forward and reverse processes are localized on the interface between the solid reactant and the product. It can then be assumed that

$$\overleftarrow{f}(\alpha, P_p) = \overleftarrow{f}(\alpha)\cdot\overleftarrow{f}(P_p) \tag{5}$$

and

$$\vec{f}(\alpha) \equiv \overleftarrow{f}(\alpha) = (1-\alpha)^m \tag{6}$$

where $m = 2/3$, $1/2$ or 0 for samples with cubic (spherical), elongated parallelepiped (cylindrical) and flat particles, respectively.

If $f(P_p)$ is expressed by a Langmuir-type relationship, then

$$\overleftarrow{f}(\alpha, P_p) = (1-\alpha)^m \frac{P_p}{1+\sum\limits_j b_jP_j} \tag{7}$$

where b_j is the adsorption coefficient for the j-th component of the gas mixture.

Finally, if $\sum_j b_j P_j \ll 1$, then

$$\frac{d\alpha}{dt} = \vec{r} - \overleftarrow{r} = (1-\alpha)^m(\vec{k} - \overleftarrow{k}P_p) \tag{8}$$

By combining the right-hand sides of Eqs (3) and (8), we obtain

$$\frac{V}{n_0RT}\left(\frac{dP_p}{dt} + \frac{W}{V}P_p\right) = (1-\alpha)^m(\vec{k} - \overleftarrow{k}P_p) \tag{9}$$

In the general case, Eq. (9) is non-linear and its solution can be obtained via (3) by computation. With $m=0$ (the sample particles are flat, or decomposition proceeds preferentially along a single crystallographic axis), an equation having an analytical solution is obtained. Let us choose the function $y = P_p/K$, i.e. the degree of approaching equilibrium, as the desired quantity. Then, with $m=0$ and the initial condition $y=0$ at $t=0$, we obtain

$$y = y_\infty(1 - e^{-t/\tau}) \tag{10}$$

where

$$y_\infty = \frac{1}{1 + \dfrac{W}{kn_0RT}} \tag{11}$$

$$\tau' = \frac{V}{\overleftarrow{k}n_0RT + W}$$

Equations (10) and (11) allow analysis of the effects of different factors on the approach of the system to equilibrium. First, the twofold role of increasing W should be noted. On the one hand, at $W \gg \overleftarrow{k}n_0RT$, the value of $P_p^\infty = Ky_\infty$ is defined only by the value $\vec{k}$ and the reverse reaction can be neglected. However, at W values comparable to $\overleftarrow{k}n_0RT$, the effect of the reverse reaction cannot be neglected, and with increasing W values, τ' will decrease. In the limiting region $W \ll \overleftarrow{k}n_0RT$, $P_p \to P_p^e$, and with increasing W the time required for the establishment of equilibrium will decrease.

By assigning some tolerated value $y \ll \varepsilon$, we obtain for reaction (I)

$$y = \frac{1 - e^{-t/\tau'}}{1 + \dfrac{W}{\overleftarrow{k}n_0RT}} \leqslant \varepsilon \tag{12}$$

This expression will define the interval t in which the effect of the reverse reaction may be neglected at given values of W and ε:

$$t \leqslant -\frac{V\ln\left[1 - \varepsilon\left(1 + \dfrac{W}{\overleftarrow{k}n_0RT}\right)\right]}{\overleftarrow{k}n_0RT + W} \tag{13}$$

or the necessary values of W at given ε; in particular, for $t \gg \tau'$:

$$W \geqslant \frac{\vec{k} n_0 RT(1-\varepsilon)}{\varepsilon} \tag{14}$$

Equation (18) may also be used for the correct choice of n_0 and V. Thus, at increasing n_0 values, the time for a process taking place far from equilibrium will increase, that is, Eq. (18) will quantitatively express the requirement for reduction of the sample mass [3]. It is obvious that an increase of V will lead to the same effect at unchanged n_0. Since V is the free volume in the layer of the solid reactant, it can be increased either by using samples with a particle size distribution as narrow as possible, or by diluting the sample with an inert solid. These techniques are desirable from the points of view both of establishing the true form of $f(\alpha)$ (monodisperseness [3]) and of eliminating temperature gradients in the sample ("mechanical dilution" [8]).

In the most adverse cases, these techniques serving to ensure remoteness from equilibrium will not be very effective. As an example, let us consider the decomposition of $CaCO_3$.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \tag{II}$$

From thermodynamic data [9], for this reaction $K = 2.8 \cdot 10^8 \exp\left(-\frac{21{,}400}{T}\right)$ (atm). Let us evaluate $\vec{k}$. For this purpose, let us assure that the first and limiting step of the forward reaction is the decomposition of the CO_3^{2-} ion proceeding over an activated complex differing only slightly in its structure from the initial state, and that the coordinate of the reaction is related to one of the C—O bonds. Then, for the frequency factor $\vec{z}$ we have

$$\vec{z} = \varkappa \frac{kT}{h} \cdot \frac{1}{Q_v^{\text{dis}}}$$

where $\varkappa$ is the transmission coefficient, k is the Boltzmann constant, h is the Planck constant, and Q_v^{dis} is the oscillation sum for the states of the bond being split.

Assuming that the wave number of the bond being split is 1482 cm^{-1} [10], the value of Q_v^{dis} at 1000 K will be equal to 1.14. Then, at $\varkappa = 1$, $\vec{z} = 1.82 \cdot 10^{10}$ T s^{-1}.

For a $CaCO_3$ sample with a specific surface area of 0.1 m^2/g (particle size ~10 μm), with the surface area of one CO_3^{2-} assumed to be 50 Å, we have

$$\vec{k} = 3.3 \cdot 10^{-5} \vec{z} e^{-E/RT} = 6.0 \cdot 10^5 \; Te^{-E/RT}$$

The coefficient $3.3 \cdot 10^{-5}$ represents the share of the surface of the CO_3^{2-} ions in the initial sample.

Taking the value $E = 205$ kJ/mol [2], at 1000 K we obtain $\vec{k} = 0.030\ \mathrm{s}^{-1}$. On the other hand, under these conditions $K = 0.118$ atm, and hence $\overleftarrow{k} = 0.25\ \mathrm{s}^{-1}\ \mathrm{atm}^{-1}$.

If the sample mass is 10^{-2} g (10^{-4} mol), $V \simeq 3.5 \cdot 10^{-3}\ \mathrm{cm}^3$, and $W = 1\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, for $\varepsilon = 0.01$, from Eq. (13) we obtain $t \leqslant 1.8 \cdot 10^{-2}$ s. Even for a hundredfold dilution of $CaCO_3$ with an inert solid (quartz, corundum), $t \leqslant 1.8$ s, i.e. the rate of the reverse reaction very rapidly becomes comparable with the rate of the forward reaction, and (in addition) from $t > 2.7$ min on, $y > 0.5$, i.e. the process proceeds close to equilibrium.

The necessary value of W is determined from Eq. (14); at $\varepsilon = 0.01$, $W = 210\ \mathrm{cm}^3/\mathrm{s}$, and at $\varepsilon = 0.5$, $W = 2.05\ \mathrm{cm}^3/\mathrm{s}$. Thus, the calculation demonstrates that, for the reaction in question, the rate of the reverse reaction is comparable to that of the forward reaction even at relatively small sample masses and high flow rates of the inert gas.

Case B. The solid product is X-ray-amorphous or forms a phase pseudomorphous with the initial solid reactant. This case is observed at very low pressures of the product gas and indicates that the process consists of a number of consecutive steps, including readsorption of the product gas by the total volume of the solid product. In this case we may assume that

$$\begin{aligned} \vec{f}(\alpha) &= (1-\alpha)^m \\ \overleftarrow{f}(\alpha, P_p) &= \alpha \overleftarrow{f}(P_p) \end{aligned} \tag{15}$$

Then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \vec{k}(1-\alpha)^m - \overleftarrow{k}\alpha \overleftarrow{f}(P_p) \tag{16}$$

On combining the right-hand sides of Eqs (3) and (16), we obtain

$$\frac{V}{n_0 RT}\left(\frac{\mathrm{d}P_p}{\mathrm{d}t} + \frac{W}{V} P_p\right) = \overleftarrow{k}(1-\alpha)^m - \overleftarrow{k}\alpha \overleftarrow{f}(P_p) \tag{17}$$

Equations (17) and (3) give a system whose solution can be obtained by computation. However, this case differs from the former one by the more arbitrary character of the assumptions utilized and by the greater indefiniteness not only of the kinetics, but also of the thermodynamics of the process, since the final stage is, to a certain extent, difficult to define. Therefore, one should attempt as far as possible to avoid experiments under conditions leading to the formation of pseudomorphous or X-ray-amorphous products.*

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* It should be noted that experiments highly informative from the aspect of kinetic information, e.g. direct observation of the speed of shift of the interface between phases in high vacuum, frequently lead to the formation of an irregular solid product.

It is of interest to discuss how reversible reactions proceed in non-flow sample holders of solid samples, since this is the case in a large number of commercial thermoanalytical apparatuses manufactured by various companies. For reaction (I), the differential equation system is

$$-\frac{DV}{RT}\cdot\frac{\partial^2 P_p}{\partial x^2} = \frac{\partial \alpha}{\partial t} n_0 - \frac{V}{RT}\frac{\partial P_p}{\partial t} \tag{18}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \vec{k}\vec{f}(\alpha) - \overleftarrow{k}\overleftarrow{f}(\alpha, P_p)$$

where D is the diffusion coefficient, and x is a co-ordinate related to the direction from the bottom of the vessel holding the sample towards its surface.

With the simplifying assumptions analogous to those for obtaining Eq. (10), the following equation is obtained, which can be solved analytically:

$$\frac{\partial y}{\partial t} - D\frac{\partial^2 y}{\partial x^2} = -\frac{\overleftarrow{k} n_0 RT}{V}(1-y) \tag{19}$$

With initial and limiting conditions assuming the absence of product gas in the layer at the beginning of the process, and the rapid removal of the product gas from the surface of the sample:

$$\begin{cases} t=0 \\ y=0 \end{cases} \quad \begin{cases} x=0 \\ \dfrac{\partial y}{\partial x} = 0 \end{cases} \quad \begin{cases} x=x_0 \\ y=0 \end{cases}$$

where x_0 is the layer thickness, the general solution has the form

$$y(x, t) = \frac{16ax_0^2}{\pi^3 D} \sum_{l=0}^{\infty} \frac{\sin\dfrac{\pi(2l+1)}{2}\left(1+\dfrac{x}{x_0}\right)}{(2l+1)\left[\dfrac{4ax_0^2}{\pi^2 D} + (2l+1)^2\right]} \left\{1 - \exp\left\{-\left[\frac{\pi^2(2l+1)^2}{4x_0^2}D + a\right]t\right\}\right\} \tag{20}$$

where $l = 0, 1, 2, \ldots$, and

$$a = \frac{\overleftarrow{k} n_0 RT}{V}.$$

The series in Eq. (20) is convergent, and as concerns the exponential expression it is sufficient to consider only the first member ($l=0$). Then, the characteristic time for establishment of the steady-state distribution of product gas pressure in the layer τ'' is

$$\tau'' = \left[\left(\frac{\pi}{2x_0}\right)^2 D + \frac{\bar{k}n_0RT}{V}\right]^{-1} \tag{21}$$

A comparison of Eqs (11) and (21) permits determination of the value at which the efficiencies of product gas removal by diffusion and by inert gas flow are commensurable:

$$x_0 \leqslant \frac{\pi}{2}\sqrt{D\cdot\frac{V}{W}} \tag{22}$$

At $D = 0.1$ cm^2/s and $V/W = 0.1$ s, $x_0 \leqslant 1.6$ mm, corresponding, for example, to the holder plate in the derivatograph manufactured by MOM. However, the presence of a pressure gradient of the product gas in the layer makes the kinetic situation rather undefined, not allowing reliable values for the kinetic parameters.

In the above example for $CaCO_3$ decomposition at 1000 K, $D \approx 0.3$ cm^2/s; at $x_0 = 1$ mm, Eq. (21) yields $\tau'' = 1.5\cdot 10^{-3}$ s, i.e. steady-state pressure distribution of the product gas will be established practically momentaneously, as described by the equation

$$y(x,\infty) = \frac{16ax_0^2}{\pi^3 D}\sum_{l=0}^{\infty}\frac{\sin\frac{\pi(2l+1)}{2}\left(1+\frac{x}{x_0}\right)}{(2l+1)\left[\frac{4ax_0^2}{\pi^2 D}+(2l+1)^2\right]} \tag{23}$$

In Fig. 1, the relationships $y(x, \infty)$ *vs.* x are represented for the above case. The

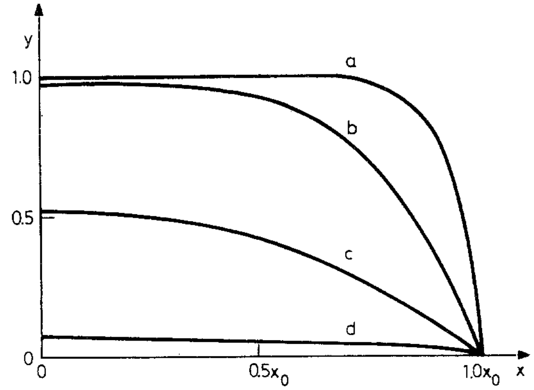

Fig. 1 Steady-state distribution of CO_2 pressure in the layer for $CaCO_3$ decomposition (1000 K) in a non-flow cell: *(a)* $x_0 = 6$ mm, *(b)* $x_0 = 1$ mm, *(c)* $x_0 = 1$ mm, tenfold dilution, *(d)* $x_0 = 1$ mm, hundredfold dilution

mean values for the total layer $\bar{y}$ are 0.98, 0.78, 0.36 and 0.06, corresponding to the curves *a*, *b*, *c* and *d* in Fig. 1. That is, only at a hundredfold dilution of the sample with an inert substance and with a plate-shaped holder ($x_0 = 1$ mm) is efficient removal of the product gas ensured. In work with an undiluted sample and a crucible sample holder ($x_0 = 6$ mm), the steady state will be established very close to equilibrium.

If the reaction is carried out under programmed heating conditions, a further factor will appear enabling the system to move away from equilibrium. Let us use the symbol $\Delta T_e = T_2 - T_1$ for the temperature difference at which the values of the equilibrium constants differ by a factor e:

$$\frac{K_{T_2}}{K_{T_1}} = e^{-\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} \approx e^{\frac{\Delta H \Delta T_e}{RT^2}} = e$$

Then:

$$\Delta T_e = \frac{RT^2}{\Delta H} \tag{24}$$

For linear heating at a heating rate q, the time τ^* during which the value of K will increase by a factor e is

$$\tau^* = \frac{\Delta T_e}{q} = \frac{RT_2}{q\Delta H} \tag{25}$$

Thus, if equilibrium exists in the system at a certain moment, then, for heating at a heating rate q over a period τ^* in the absence of removal of the product gas and of the forward and reverse reactions, P_p would become less than K by a factor e. In a realistic case, the relationship between P_p and K is defined by τ^* and τ' (or τ''): at $\tau^* \ll \tau'$ (or τ''), the system moves away from equilibrium; at $\tau^* > \tau'$ (or τ''), the process will proceed continuously under conditions close to equilibrium.

References

1 W. Wendlandt, Thermal methods of analysis (Russian translation). Mir, Moscow 1978.

2 M. Brown, D. Dollimore and A. Halvey, Reactions of solids (Russian translation). Mir, Moscow 1983.

3 V. A. Logvinenko, Thermal analysis of coordination compounds and clathrates (in Russian). Nauka, Novosibirsk, 1982.

4 A. V. Nikolaev, V. A. Logvinenko and V. M. Gorbachev, J. Thermal Anal., 6 (1971) 473.

5 J. Roquerol and M. Ganteaume, J. Thermal Anal., 11 (1977) 201.

6 B. Delmon, Introduction à la cinétique hétérogène, Paris, 1969.

7 S. Z. Roginsky, Heterogeneous catalysis: some theoretical questions (in Russian). Nauka, Moscow, 1979.

8 A. G. Merzhanov, V. V. Barzykin, A. S. Shteinberg and V. T. Gontkovskaya, Thermochim. Acta, 21 (1977) 301.

9 M. Kh. Karapetyants and M. K. Karapetyants, Fundamental thermodynamic constants of inorganic and organic substances (in Russian). Khimiya, Moscow 1968.

10 Infrared spectra of inorganic compounds. Ed. R. A. Nyquist and R. O. Kagel, Academic Press, New York–London 1971.

Zusammenfassung — Durch Lösen einer Massebilanzgleichung für gasförmige Produkte reversibler Zersetzungsvorgänge konnte der Zusammenhang zwischen der Entfernung zum Gleichgewicht und der kinetischen Parameter sowie der experimentellen Bedingungen festgestellt werden. Es werden Wege besprochen, um den Anteil der Rückreaktion an der totalen Reaktionsgeschwindigkeit zu mindern. Die Bedingungen für eine Nicht-Gleichgewichtszersetzung von $CaCO_3$ werden gekennzeichnet.

Резюме — Выведена взаимосвязь между степенью отклонения от равновесия, кинетическими параметрами и экспериментальными условиями путем решения уравнения весового баланса для газообразных продуктов обратимых реакций разложения. Обсуждены пути понижения доли обратно протекаемых реакций в общей скорости реакции. Определены условия неравновесного разложения карбоната кальция.