

FUNDAMENTAL PRINCIPLES OF KINETIC DATA EVALUATION FROM THERMAL ANALYSIS CURVES

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A method for the evaluation of kinetic data of heterogeneous processes, including the most probable mechanism, from TG traces is described. Results are illustrated for the decarbonization of calcite and magnesite in vacuo, and the dehydration of α -calcium sulphate hemihydrate. The advantages of the approach to the study of the kinetics, resulting in descriptions based on the known process mechanisms are demonstrated.

The study of the kinetics of heterogeneous processes is aimed at the collection of information which makes possible prediction of the rates under given conditions (e.g. in a reactor). The description of the kinetics presents the problem of finding the rate of a process as a function of parameters characterizing the given system.

It is usually assumed that the rate of a process can be described by the relation

$$r = \frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \quad (1)$$

where K is a function only of temperature and $f(\alpha)$ is a function of the fraction decomposed, α , at a given instant. Both these functions may be found by analysis of the experimental data, via two different approaches.

If the conditions of a process are fixed, then a phenomenological description of the kinetics is sufficient and both the above functions ought to fulfil the requirements of fitting the experimental data with sufficient accuracy. $f(\alpha)$ can be chosen to be a suitable algebraic function, usually in the form

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

where the exponent n is a characteristic constant. For more complex processes the functions $f(\alpha)$ should contain additional parameters [1], e.g.

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3)$$

$$f(\alpha) = (1 - \alpha)^n [-\log_e(1 - \alpha)]^p \quad (4)$$

$$f(\alpha) = c_0 + c_1\alpha + c_2\alpha^2 + \dots + c_n\alpha^n \quad (5)$$

to give a better fit to the experimental course of a process. The values of the characteristic constants are usually determined by trial and error.

The function $K(T)$ in Eq. (1) is given by

$$K = Z \cdot e^{-E/RT} \cdot (1 - e^{\Delta G/RT}) \quad (6)$$

where Z is the preexponential factor,

E is the apparent activation energy and

ΔG is the change of free energy corresponding to the given process.

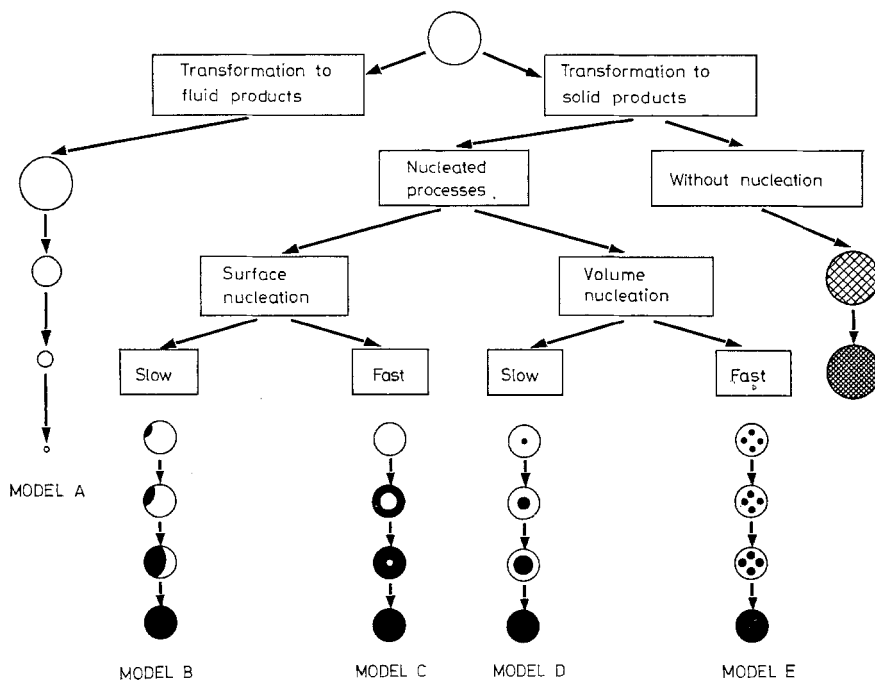


Fig. 1. Models of heterogeneous non-catalytic processes

At the equilibrium temperature, T_e , $\Delta G = 0$ and $r = 0$. If the temperature at which the process proceeds is sufficiently different from the equilibrium temperature, then the term $e^{\Delta G/RT}$ becomes negligible and Eq. (6) gives the normal form of the Arrhenius equation.

In this phenomenological description E , Z and other kinetic parameters (see Eqs (2–5)) are only empirical constants giving the best fit to the experimental data, and do not have any deeper physical meaning. As a consequence, the validity of the kinetic data is limited to the conditions under which the process is studied. Hence, the extrapolation of kinetic data for other conditions may lead to errors.

If the conditions of the process vary, and/or if the character of the product is affected, a different approach to the kinetic study should be chosen.

The first step is directed towards analyzing the part processes and is usually performed by choosing a suitable model for the overall mechanism. Such a hypothesis makes it possible to describe quantitatively the course of the process and to predict how to control the rate of the process. The most important models, based on a single particle, are demonstrated for non-catalytic heterogeneous processes in Fig. 1 [2].

The type of a process is primarily determined by the nature of the products, viz. whether they are liquid or solid. These one-particle models can also be used for a system composed of multiple particles, as well as in the case of two initial reacting species differing in their particle size by at least two orders of magnitude.

A mathematical model best fitting the experimental data is chosen by trial and error, and is assumed to correspond to the most probable mechanism of the process studied. In the second step of the kinetic analysis it is necessary to prove the model by a suitable experimental method, depending on the nature of the process. In this manner a description of the process is finally attained whereby the kinetic equation and all the kinetic constants (Z , E , etc.) can be physically interpreted.

The principal difficulty of kinetic analysis is rooted in the nature of heterogeneous processes, owing to the multiple simultaneous reactions occurring. These must be studied separately using a suitable model system. The most advantageous way is usually direct microscopy on the monocrystals. Nevertheless, much information can be gained from kinetic measurements alone.

For such a study, the isothermal method was long supposed to be the only suitable way. Numerous recent studies have shown that the non-isothermal methods have been underestimated, and that the dynamic technique is a valuable tool in kinetic analyses.

Let us first assume that the course of the process can be described over the whole temperature interval by Eq. (1). If the rate of heating $\Phi = \frac{dT}{dt}$ is constant, then Eq. (1) can be written in the form

$$\frac{d\alpha}{dT} = Z \cdot e^{-E/RT} (1 - e^{AG/RT}) \cdot f(\alpha) \cdot \frac{1}{\Phi} \quad (7)$$

and

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_{T_e}^{T_x} \frac{Z}{\Phi} \cdot e^{-E/RT} \cdot 1 - (e^{AG/RT}) dT \quad (8)$$

where T_e is the temperature of thermodynamic equilibrium. By integrating we obtain

$$g(\alpha) = \frac{ZE}{R\Phi} [p(x) - p(x_e)] - \frac{ZE'}{R\Phi} \cdot e^{-AS/R} [p(x') - p(x'_e)] \quad (9)$$

where $x = \frac{E}{RT}$, $x_e = \frac{E}{RT_e}$, $p(x)$ and/or $\log p(x)$ are tabulated as functions of

temperature [3, 4], E' is the activation energy corresponding to the reverse process and $E' = E - \Delta H$, where ΔH is the enthalpy change for the process, and ΔS is the corresponding entropy change.

When the rate of the reverse reaction can be neglected, the second term in Eq. (9) is zero. If such a process proceeds in a temperature region sufficiently

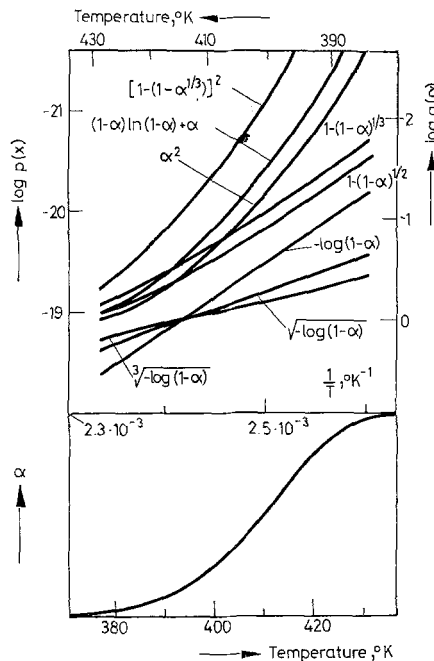


Fig. 2. Method of kinetic data evaluation from TG trace

far from the equilibrium temperature, T_e , then $p(x_e) \ll p(x)$ and Eq. (9) reduces to Doyle's [3] equation

$$g(\alpha) = \frac{ZE}{R\Phi} \cdot p(x). \quad (10)$$

In the logarithmic form, Eq. (10) becomes

$$\log g(\alpha) - \log p(x) = \log \frac{ZE}{R\Phi}. \quad (11)$$

The function $p(x)$ is an approximately linear function of the reciprocal temperature [5]. Because the term $\frac{ZE}{R\Phi}$ (as shown by Zsakó [4]) is temperature-independent, $\log g(\alpha)$ must also be a linear function of the reciprocal temperature. This condition leads to the possibility of determining the function $g(\alpha)$ which

corresponds to the correct mechanism of the process in question. The principle of this analysis is shown in Figs 2 and 3.

Fig. 2 demonstrates the procedure for evaluating the TG curve. The lower curve corresponds to the kinetic equation $g(\alpha) = -\log(1 - \alpha)$, $E = 30 \text{ kcal mole}^{-1}$,

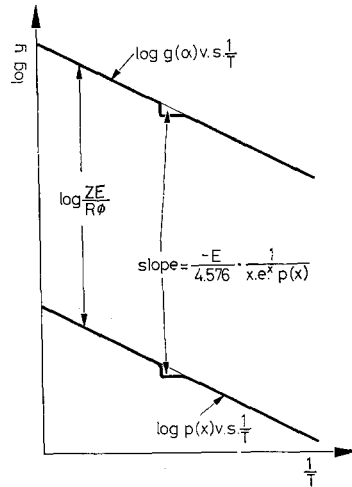


Fig. 3. Plot of Doyle's equation

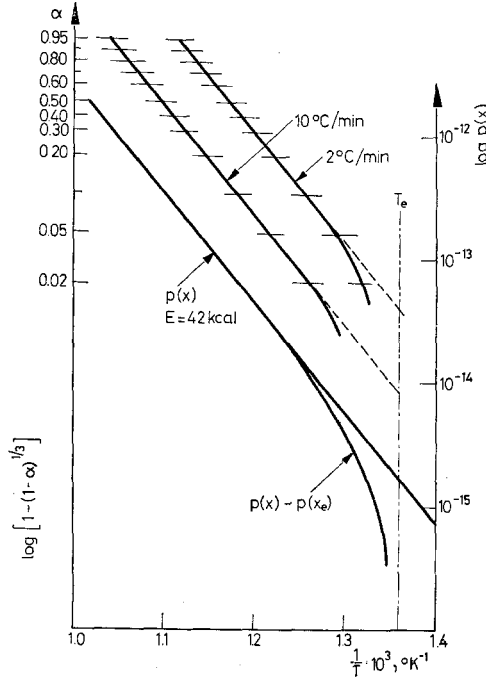


Fig. 4. Decarbonization of calcite

$Z = 10^{13} \text{ s}^{-1} \text{ mole}^{-1}$ and $\Phi = 1^\circ \text{C min}^{-1}$. The upper curves are plots of $\log g(\alpha)$ vs. $\frac{1}{T}$ calculated from the TG curve for various types of $g(\alpha)$. A straight line is clearly given only by the plots of $\log [-\log (1 - \alpha)]^n$ vs. $\frac{1}{T}$, where $n = 1, 1/2$, and $1/3$.

Figure 3 shows a plot of Eq. (11) and demonstrates the principle of the evaluation of the activation energy, E , from the slope of the straight line, and the determination of the frequency factor, Z , from the difference between the straight lines, $\log p(x)$ and $\log g(\alpha)$.

The first practical example introduced is the decarbonization kinetics of calcite, which has been dealt with by numerous authors [6–8]. It may be treated by the equation

$$\frac{d\alpha}{dt} = Z \cdot e^{-E/RT} (1 - \alpha)^{2/3} \quad (12)$$

obtained on the assumption that a phase-boundary reaction is the rate-controlling process. For this case

$$g(\alpha) = 1 - (1 - \alpha)^{1/3}. \quad (13)$$

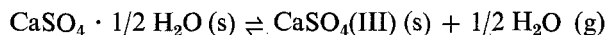
If this mechanism is correct, the plot of $\log [1 - (1 - \alpha)^{1/3}]$ vs. $\frac{1}{T}$ calculated from the TG trace ought to be a straight line. The plot for two rates of heating ($\Phi = 10^\circ \text{ min}^{-1}$, and $\Phi = 1^\circ \text{ min}^{-1}$) are shown in Fig. 4. It can be seen that for the higher heating rate ($\Phi = 10^\circ \text{ min}^{-1}$) the necessary conditions of Eq. (11) are well fulfilled, and the activation energy determined, $E = 42 \text{ kcal mole}^{-1}$, is in good agreement with the values reported in the literature [5–7].

For the lower heating rate, however, the function $\log g(\alpha)$ is not linear, particularly in the low-temperature region (i.e. low values of α). This results from the fact that the decomposition up to $\alpha = 0.2$ takes place in the temperature interval where the value of $p(x_e)$ cannot be neglected with respect to $p(x)$ and the following equation must be used instead

$$\log g(\alpha) - \log [p(x) - p(x_e)] = \log \frac{ZE}{R\Phi}. \quad (14)$$

The function $\log [p(x) - p(x_e)]$ is not linearly dependent on $\frac{1}{T}$ (see Fig. 4) but the difference between $\log g(\alpha)$ and $\log [p(x) - p(x_e)]$ remains temperature-independent. Hence, the function $\log g(\alpha)$ vs. $\frac{1}{T}$ is, of course, a curve. It is evident that the use of a high heating rate seems to be advantageous. The possibility of employing rapid heating, however, is limited by the self-cooling of the sample and the associated accuracy of the temperature measurement.

A very important group of simultaneous processes are the reversible ones. An excellent example is the dehydration of calcium sulphate hemihydrate



which may be compared to the non-displacive modification transformation, because anhydrite (III) has the same structure as the hemihydrate.

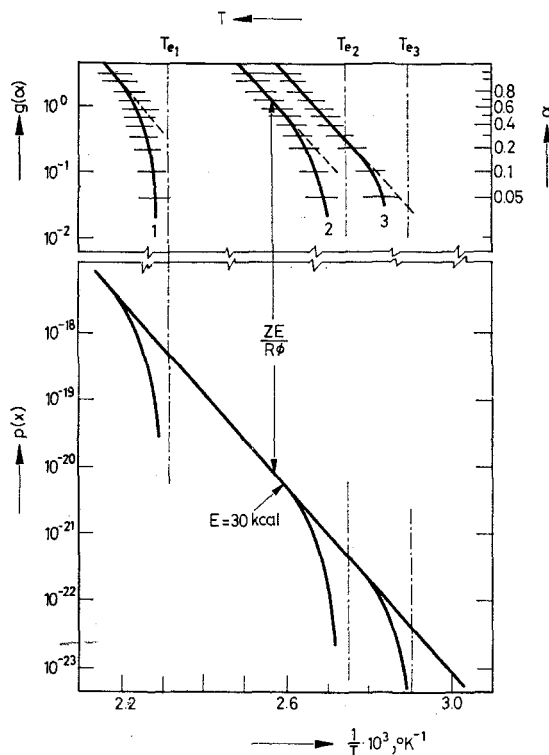


Fig. 5. Dehydration of $\alpha\text{-CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$. Curve 1: $p_{\text{H}_2\text{O}} = 0.006$ atm; Curve 2: $p_{\text{H}_2\text{O}} = 0.031$ atm; Curve 3: $p_{\text{H}_2\text{O}} = 1$ atm

From isothermal measurements [9] it has been shown that the kinetics may be expressed by the following equation:

$$-\log(1 - \alpha) = kt.$$

The same result is indicated by the non-isothermal TG measurement. The kinetic analysis is complicated by the fact that the dehydration proceeds close to the equilibrium temperature so that it is necessary to use Eq. (14). Fig. 5 shows that with increasing water vapour pressure both the equilibrium temperature and the whole curve are shifted to higher values. Nevertheless, it appears that the mecha-

nism of the process does not alter. From the plot in Fig. 5 it is evident that if Eq. (11) is used (i.e. the correction for equilibrium is neglected) incorrect values of the activation energy result.

In most cases heterogeneous processes are series of consecutive processes, the slowest one being rate-determining. The rates of individual processes often depend on the conditions (temperature, pressure, etc.) which determine the rate-controlling process.

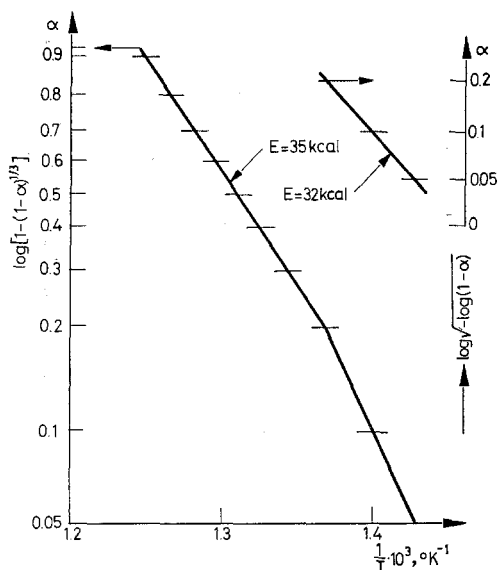


Fig. 6. Decarbonization of magnesite

An example is the decarbonization of magnesite in vacuum. It seems logical to assume that the rate-determining step is a phase-boundary reaction and that for the case of spherical symmetry gives

$$g(\alpha) = 1 - \sqrt[3]{1 - \alpha}.$$

The plot $\log g(\alpha)$ vs. $\frac{1}{T}$ calculated from the TG trace is shown in Fig. 6. The assumption is evidently fulfilled for $\alpha < 0.2$, while the activation energy $E = 35$ kcal mole⁻¹ agrees with the results of other authors. For $\alpha < 0.2$ the plot is not linear. As the equilibrium temperature falls well below the temperature interval in which the decarbonization proceeds, the non-linearity of the plot $\log g(\alpha)$ vs. $\frac{1}{T}$ must be attributed to some other reason than that in the case of the decarbonization of calcite.

At the beginning of the process it is probable that nucleation of MgO on the magnesite crystal surface becomes the rate-determining step. The corresponding $g(\alpha)$ may be expressed as $\sqrt{-\log(1-\alpha)}$. A plot of this function versus reciprocal temperature calculated for $\alpha < 0.2$ is linear (see Fig. 6), and corresponds to an activation energy of $E = 32 \text{ kcal mole}^{-1}$. At $\alpha = 0.2$ the rate of nucleation reaches its maximum value as the surface of the magnesite crystals becomes covered by product MgO and the further process is governed by a phase-boundary reaction.

As has been shown in the above examples, the non-isothermal method may provide valuable information on the mechanisms and kinetics of non-catalytic heterogeneous processes. The advantages can be formulated in the following conclusions:

1. The determination of the activation energy is easier, and in most cases more accurate, using the non-isothermal method, because the temperature of the system is well defined in the whole course of the process. This is in contrast with isothermal methods where an unwanted advance in the process, until the precise working temperature is attained, is difficult to avoid.
2. A single non-isothermal run is sufficient to provide all the information necessary to determine the temperature at which the change of mechanism takes place. This is the main advantage of non-isothermal methods over isothermal ones.
3. The probable mechanism of the process can be simply determined from non-isothermal measurement only when the process proceeds in a temperature interval sufficiently far above the thermodynamic equilibrium temperature.

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RÉSUMÉ — On décrit une méthode pour évaluer à partir des courbes TG les données cinétiques des processus hétérogènes et déterminer le mécanisme le plus probable. On présente les résultats à l'aide de l'exemple de la décarbonatation sous vide de la calcite et de magnesite et de la déshydratation du sulfate hémihydraté de calcium (forme α). On montre les avantages de l'approximation utilisée pour l'étude de la cinétique qui permet de décrire sur des bases sûres le mécanisme du processus.

ZUSAMMENFASSUNG — Die Methode der Auswertung kinetischer Daten heterogener Vorgänge, den wahrscheinlichsten Mechanismus aus TG-Spuren mit inbegriffen, wird beschrieben. Die Ergebnisse wurden an Hand der Beispiele der Decarbonierung von Calcit und Magnesit im Vakuum und der Dehydratisierung von α -Calciumsulfat-hämihydrat veranschaulicht. Die Vorteile der Näherung zum Studium der Kinetik, welche eine Beschreibung des Vorganges auf Grund eines bekannten Mechanismus ergibt, werden gezeigt.

Резюме — На основании кривых ТГ описан метод расчета кинетических данных гетерогенных процессов, включая наиболее вероятный механизм. Полученные результаты показаны на примерах декарбонизации кальцита и магнезита в вакууме и дегидратации полугидрата α -сульфата кальция. Продемонстрированы преимущества над подходом к изучению кинетики, выражающимся в описании, основанном на известном механизме процесса.