ANALYTICAL EXPRESSIONS FOR TEMPERATURE PROGRAMMED REDUCTION PATTERNS USING SOLID-STATE KINETICS

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(Received 3 May 1985)

ABSTRACT

Using solid-state kinetics, analytical mathematical expressions are derived which describe the pattern generated during a temperature-programmed reduction (TPR) experiment conducted under differential conditions. From these expressions the influence of the heating rate on the TPR peak maximum can be established; it is shown that this influence can, in principle, be approximated by Kissinger's equation, independent of the reduction mechanism selected.

INTRODUCTION

Many methods exist which measure rates of reaction between gases and solids when the temperature increases linearly with time; examples of such methods are DTG, DTA and TPR. The mathematical description of the reaction rates as a function of temperature as measured with this equipment has until now been limited to descriptions using simple fluid–solid reaction mechanisms like the power law [1–4]. In a previous paper [5] a method has been described to calculate TPR patterns using reduction mechanisms obtained from solid-state kinetics. These mechanisms have the advantage of possessing more physical meaning than power-law mechanisms and comparison of thus-calculated patterns and measured patterns can give information about the structure of the solid under study. This has been shown in a previous paper [5] where these reduction mechanisms were successfully used to model the reduction of small Fe_2O_3 particles using TPR experiments.

The method for the calculation of TPR patterns described in ref. 5, however, requires a numerical differentiation step. In the present paper expressions will be derived from which TPR patterns can be calculated without the need of numerical procedures. Using these expressions, Kissinger's equation [1], which is used by many authors to determine the activation energy from the measured peak shift as a function of the heating rate [3], is shown to be approximately valid, independent of the reduction mechanism.

THEORY

In a TPR experiment a solid reacts with hydrogen to form another solid while the temperature increases linearly with time at a heating rate ϕ. The reduction rate can thus be expressed as [2]

$$r = \frac{d\alpha}{dT} = \frac{1}{\phi} k_1(T) f(\alpha) f'(p_{H_2}, p_{H_2O}) \tag{1}$$

where α stands for the degree of conversion of the solid reactant. The temperature dependence of the reaction rate constant, $k_1(T)$, can be expressed using the Arrhenius equation. When differential conditions exist, the gas-phase dependent term $f'(p_{H_2}, p_{H_2O})$ is constant. Equation (1) thus reduces to

$$\frac{d\alpha}{dT} = \frac{A}{\phi} e^{-E/RT} f(\alpha) \tag{2}$$

Equation (2) is a differential equation, the solution of which gives α as a function of T. If this function is differentiated, the resulting $d\alpha/dT$ vs. T function describes the TPR pattern. For the differential equation (2), separation of variables is possible, leading to

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_{T_0}^T e^{-E/RT} dT = S(T) \tag{3}$$

For some gas–solid reaction models which are relevant to reductions, $g(\alpha)$ functions are given in Table 1. The models which were selected are representative for the different rate-determining processes as proposed in solid-state kinetics. Their physical meaning is described elsewhere [6,7].

The temperature-dependent part of eqn. (3), $S(T)$, cannot be solved analytically. However, many good approximations for $S(T)$ exist [2], of which the following was found to be very easy to use for computational purposes [8]

$$S(T) = \frac{AE}{R\phi} \frac{e^{-E/RT}}{(E/RT)[2 + (E/RT)]} = \frac{AT}{\phi} \frac{e^{-E/RT}}{2 + (E/RT)} \tag{4}$$

Equation (4) gives an error in $S(T)$ of less than 1% for $E/RT > 10$ [13]. From eqn. (3), it can be established that

$$\frac{dS(T)}{dT} = \frac{d}{dT} \left\{ \frac{A}{\phi} \int_{T_0}^T e^{-E/RT} dT \right\} = \frac{A}{\phi} e^{-E/RT} \tag{5}$$

Equation (5) holds when T_0 is much smaller than T. From eqn. (5) it follows that

$$\frac{d^2 S(T)}{dT^2} = \frac{d}{dT} \left\{ \frac{A}{\phi} e^{-E/RT} \right\} = \frac{A}{\phi} e^{-E/RT} E/RT^2 = E/RT^2 \frac{dS(T)}{dT} \tag{6}$$

TABLE 1

g(α) functions for different reduction models together with the resulting TPR equations and the constants in eqn. (15). In these equations, $S(T)$ has been abbreviated to S. S can be calculated from eqn. (4)

Reduction model	g(α)	TPR equation	$C(S(T_{max}))$ in eqn. (15)
Three-dimensional nucleation according to Avrami	$[-3\ln(1-\alpha)]^{1/3}$	$\dfrac{d\alpha}{dT} = e^{-1/3 S^3} S^2 \dfrac{A}{\phi} e^{-E/RT}$	$\left[\ln\left(\dfrac{S^3-2}{S}\right)\right]_{T=T_{max}}$
Two-dimensional nucleation according to Avrami	$[-2\ln(1-\alpha)]^{1/2}$	$\dfrac{d\alpha}{dT} = e^{-1/2 S^2} S \dfrac{A}{\phi} e^{-E/RT}$	$\left[\ln\left(\dfrac{S^2-1}{S}\right)\right]_{T=T_{max}}$
Two-dimensional phase-boundary [a,b]	$1-(1-\alpha)^{1/2}$	$\dfrac{d\alpha}{dT} = 2(1-S)\dfrac{A}{\phi} e^{-E/RT}$	$[-\ln(1-S)]_{T=T_{max}}$
Three-dimensional phase-boundary [a,b]	$1-(1-\alpha)^{1/3}$	$\dfrac{d\alpha}{dT} = 3(1-S)^2 \dfrac{A}{\phi} e^{-E/RT}$	$\left[\ln\left(\dfrac{2}{1-S}\right)\right]_{T=T_{max}}$
Unimolecular decay model	$-\ln(1-\alpha)$	$\dfrac{d\alpha}{dT} = e^{-S}\dfrac{A}{\phi} e^{-E/RT}$	0
Three-dimensional diffusion according to Jander [a,c]	$[1-(1-\alpha)^{1/3}]^2$	$\dfrac{d\alpha}{dT} = \dfrac{3}{2}\dfrac{(1-\sqrt{S})^2}{\sqrt{S}}\dfrac{A}{\phi} e^{-E/RT}$	$\left\{\ln\left[\dfrac{(1-\sqrt{S})^2}{2S\sqrt{S}} - \dfrac{1-\sqrt{S}}{S}\right] - \ln\left[\dfrac{(1-\sqrt{S})^2}{\sqrt{S}}\right]\right\}_{T=T_{max}}$

[a] These models are geometrically defined as shrinking-core or contracting-sphere models with reaction proceeding topochemically.

[b] Chemical reaction as rate-determining step.

[c] Gas diffusion through the product layer as rate-determining step.

Using eqns. (3)–(5) and Table 1, an analytical expression for a TPR pattern can be obtained. As an example of such an expression, a TPR pattern for the three-dimensional nucleation model according to Avrami will be calculated. Inserting in eqn. (3) the g(α) function for this model as given in Table 1, one obtains

$$[-3\ln(1-\alpha)]^{1/3} = S(T) \tag{7}$$

Equation (7) can be rewritten as

$$\alpha = 1 - e^{-1/3S(T)^3} \tag{8}$$

From eqn. (8), in combination with eqn. (5), it follows that

$$\frac{d\alpha}{dT} = e^{-1/3S(T)^3}S(T)^2\frac{dS(T)}{dT} = \frac{A}{\phi}e^{-E/RT}S(T)^2\,e^{-1/3S(T)^3} \tag{9}$$

Equation (9) describes the reduction rate as a function of temperature under temperature-programmed conditions, i.e., a TPR pattern.

In Table 1 expressions similar to eqn. (9) are given which describe the TPR patterns for the different reduction mechanisms selected. These TPR patterns can be calculated using eqn. (4) as approximation for $S(T)$.

The above-derived equations can also be used to calculate the displacement of the TPR peak maximum as a function of the heating rate. This can be done as follows.

At the TPR peak maximum, $T = T_{max}$, the following equation holds

$$\frac{d}{dT}\left(\frac{d\alpha}{dT}\right)_{T=T_{max}} = 0 \tag{10}$$

Again taking as an example the three-dimensional nucleation model of Avrami, eqn. (10) can be solved. Combination of eqn. (9) with eqn. (10) gives

$$\frac{d^2\alpha}{dT^2} = e^{-(1/3)S(T)^3}\frac{dS(T)}{dT}\left\{\frac{dS(T)}{dT}\left[2S(T) - 2S(T)^2\right] + S(T)^2\frac{E}{RT^2}\right\} = 0 \tag{11}$$

From eqn. (11) in combination with eqn. (5) it follows that

$$\frac{A}{\phi}e^{-E/RT_{max}}\left[2S(T_{max}) - S(T_{max})^4\right] + S(T_{max})^2\frac{E}{RT_{max}^2} = 0 \tag{12}$$

Rearranging eqn. (12) leads to

$$\frac{E}{RT_{max}^2} = \frac{A}{\phi}e^{-E/RT_{max}}\left\{\frac{S(T_{max})^3 - 2}{S(T_{max})}\right\} \tag{13}$$

Taking logarithms gives

$$\ln(\phi/T_{max}^2) = \ln(AR/E) - E/RT_{max} + \ln\left[\frac{S(T_{max})^3 - 2}{S(T_{max})}\right] \tag{14}$$

Equation (14) gives the relationship between ϕ and T_{max} for a reduction according to the three-dimensional nucleation model of Avrami–Erofeev. For the other reduction models in Table 1, similar expressions can be derived, which can all be described according to

$$\ln\left(\phi/T_{max}^2\right) = \ln(AR/E) - E/RT_{max} + C(S(T_{max}))$$ (15)

in which $C(S(T_{max}))$ is a function of $S(T_{max})$ alone. The expressions for $C(S(T_{max}))$ for the different reduction models used in this study are given in Table 1.

The equation which is generally used to describe the change in T_{max} with the heating rate, ϕ [1–4], is the following, which was first derived by Kissinger [1]

$$\ln\left(\phi/T_{max}^2\right) = -E/RT_{max} + C'$$ (16)

in which C' is a constant. This equation has been used with success in many studies using temperature-programmed techniques such as TPR [3–5,9–12]. It can be seen from eqn. (15) that when the change in the value of $C(S(T_{max}))$ upon increasing or decreasing the heating rate, ϕ, is much smaller than the change in the values of both $\ln(\phi/T_{max}^2)$ and E/RT_{max}; $C(S(T_{max}))$ can be approximated by a constant, allowing eqn. (16) to be valid. This does not always have to be the case, however: if the A and E values and the reduction model for the reduction of small Fe_2O_3 particles, described in a previous paper [5] ($A = 1.5 \times 10^6$ s^{-1}, $E = 111$ kJ mol^{-1} and the three-dimensional nucleation model according to Avrami–Erofeev as reduction model), are used, application of eqn. (16) leads to a systematic error of about 5% in the activation energy if measurements are conducted at heating rates between 0.2 and 20 K min^{-1}. This error has the same order of magnitude as the error caused by the measuring method.

Summarizing, it can thus be concluded that eqn. (16) can, in principle, be used to determine the value of the activation energy, E, from the change of T_{max} with the heating rate, ϕ. Deviations from eqn. (16), however, can occur, but this can be checked using eqn. (15) in combination with Table 1.

CONCLUSIONS

TPR patterns can be described by analytical expressions using solid-state kinetics; such equations are tabulated in Table 1 for reduction models representative for the different rate-determining processes as proposed in solid-state kinetics.

Kissinger's equation (eqn. 16) can, in principle, be used to determine the activation energy from the change in the TPR peak maximum with the heating rate; when the value of the pre-exponential factor and the reduction

model are also known, its use can be checked with eqn. (15) in combination with Table 1.

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