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Mechanism and kinetics of the dehydration of magnesium oxalate dihydrate

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Abstract

This paper describes the process of random nucleation and subsequent growth of the crystal nucleus, starting by setting up a physical model. A formula for the specific rate of the reaction has been worked out both in the induction period and in the period of increasing reaction rate. Thus the calculation of activation energy has been done for both periods. Then, taking the dehydration of magnesium oxalate dihydrate as an example, the model and formula were both tested. Experiments prove that the nucleation processes comply with the power function rules. In the period of crystal nucleus formation and growth, the activation energy is 82.49 kJ mol^{-1}. In the diffusion period the activation energy becomes larger when α increases. The result is in satisfactory agreement with literature data.

INTRODUCTION

For many solid thermal decomposition reactions, in particular dehydration of salt hydrates random nucleation is the controlling mechanism. There are many reports [1–5] on the identification of the mechanism function in this process and on the study of its kinetics. Yet, the treatment of kinetics is done within the limitation of $\alpha = 0.1$–0.9, so the kinetic parameter is a macroscopic average value. Few studies have tried to examine the random nucleation process microscopically. In this paper, we develop a relative physical model of this process and, taking the dehydration of magnesium oxalate dihydrate as an example, have identified the process mechanism and calculated the kinetic parameter. Results agree well with the literature data.

THEORETICAL ANALYSIS

The thermal dehydration of a salt hydrate is a gas–solid reaction. This kind of topochemical reaction mainly takes place at the interface between

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the reaction and product solid phases, the area of the phase interface changing all the time as the reaction proceeds. Thus, the reaction rate changes with time too. The kinetic behaviour of this kind of reaction is more complex than that of a homogeneous reaction or a heterogeneous catalysis reaction. In order to study kinetics of topochemical reactions, first, the specific rate of the reaction needs to be determined, i.e. the reaction rate on one unit of phase interface. To derive the value of the specific rate of reaction, the kinetic parameters in the process (activation energy, frequency factor and reaction order, etc.) can be determined by normal kinetic methods.

Physical model

When a topochemical reaction occurs on the surface of a solid, first, individual crystal nuclei of solid product are formed. Because of the energy difference on the surface caused by the edge, corner and crystal lattice defects, further reaction is mainly limited to the interface between the reaction solid phase and product solid phase. Gradually, the reaction moves towards the inside of the particles. According to this model, the kinetic pattern of the process should be: stage one, crystal nuclei of the new phase are slowly formed (the induction period); stage two, crystal nucleus growth basically replaces crystal nucleus formation, the interface of solid phases enlarges, and the reaction rate increases (reaction rate increasing period). Along with the further growth of crystal nuclei, the solid phase interface reaches a maximum, as does the apparent reaction rate. Afterwards, comes the third stage in which some individual crystal nuclei coalesce, leading to the decrease of phase interface and slowing down of the reaction rate, until eventually a continuous layer of solid product forms. Then, with the moving of phase interface towards the interior of the particles, the reaction will change from its surface kinetic period to its diffusion period. The diffusion resistance caused when molecules are penetrating through the product layer will exert more and more influence on the reaction kinetic conditions.

Reaction kinetics equation

On the basis of the above physical model, the reaction rate is in direct proportion to the area of the phase interface. The general formula of the kinetics equation is

$$\frac{dn}{dt} = W = kf(C_g, C_s)S_i \qquad (1)$$

where n is the number of moles of product present at time t, k is the reaction rate constant, W the reaction rate, S_i the area of solid phase interface (usually a function of time), $f(C_g, C_s)$ is a particular function of the concentration of solid and gaseous reactants in the interface range between starting material and product.

Identifying the correct form for $f(C_g, C_s)$ is a general problem in kinetics but, by neglecting diffusion resistance (in stages one and two), it is not a particular problem with solid phases involved in the reaction. So, in those stages, we shall take C_g, C_s and $f(C_g, C_s)$ as constants. Therefore, at constant temperature the reaction rate depends only on the S_i value

$$\frac{\mathrm{d}n}{\mathrm{d}t} = KS_i \tag{2}$$

where $K = \mathrm{d}n/S_i\mathrm{d}t$ is the specific rate of the reaction, which is just the value which we require.

In order to simplify the analysis, consider the situation at $t = 0$ when the growing speed of crystal nuclei is independent of direction. That is to say, the growing crystal nuclei are spherical (more exactly, they are hemispherical with the outside surface of the reaction solid phase as the hemisphere base). Now, consider the growing situation of an individual crystal nucleus with radius r. The area of the interface between this crystal nucleus and reaction solid phase is s_i'

$$s_i' = 2\pi r^2 \tag{3}$$

The volume V_i' is

$$V_i' = \tfrac{2}{3}\pi r^3 \tag{3a}$$

The bottom of the crystal nucleus covers an area of the outside surface S_π'

$$S_\pi' = \pi r^2 \tag{3b}$$

From eqn. (2), the reaction rate of this crystal nucleus surface can be shown to be

$$\frac{\mathrm{d}n'}{\mathrm{d}t} = KS_i' = 2\pi K r^2 \tag{4}$$

in other words, the mole number n' of product in the crystal nucleus is

$$n' = \frac{V_i'd}{M} = \frac{2\pi r^3 d}{3M}$$

$$\frac{\mathrm{d}n'}{\mathrm{d}t} = \frac{2\pi d}{M} r^2 \frac{\mathrm{d}r}{\mathrm{d}t} \tag{5}$$

where d is the density of product and M its molecular weight. From eqns. (4) and (5) we get

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{KM}{d} \qquad \text{or} \qquad r = Bt \tag{6}$$

because when $t = 0$, $r = 0$, in the formula

$$B = \frac{KM}{d} \tag{7}$$

In other words, in the situation hypothesised the radius of an individual crystal nucleus increases at a constant speed. From eqns (3) and (6), the surface area of the growing crystal nucleus is

$$S_i' = 2\pi B^2 t^2 \tag{8}$$

The volume is

$$V_i' = \tfrac{2}{3}\pi B^3 t^3 \tag{8a}$$

For the part of the crystal nucleus δN formed at τ time $(0 \leqslant \tau \leqslant t)$, the reaction rate at t is

$$\delta_w = 2\pi B^2 K (t-\tau)^2 \delta N$$

or

$$d_w = 2\pi B^2 K (t-\tau)^2 \frac{\mathrm{d}N}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{9}$$

For all crystal nuclei

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 2\pi B^2 K \int_{\tau=0}^{\tau=t} (t-\tau)^2 \frac{\mathrm{d}N}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{10}$$

Formula (10) fits the initial stage of the process. At this time, the coalescence of individual crystal nuclei can be neglected. At the end of the rate increasing stage this equation will no longer apply.

The size of the crystal nucleus growing rate is dominated by the crystal nucleus forming rule, different forms of the rules can be summed up as [6,7]

$$\frac{\mathrm{d}N}{\mathrm{d}\tau} = N_0 m \exp-(m\tau) \qquad \text{Exponential function} \tag{11}$$

$$\frac{\mathrm{d}N}{\mathrm{d}\tau} = ab\tau^{b-1} \qquad \text{Power function} \tag{12}$$

Quite possibly, more complex relations will appear to fit specific situations. The theoretical explanation of these functions is of little importance to the determination of the K value, because K depends only on the crystal nucleus growing rate and can be calculated by using other well known methods.

For the exponential rule (11), formula (10) can be integrated by transformation to give

$$n = 2\pi N_0 B^2 K \left[\frac{t^3}{3} - \frac{t^2}{m} + \frac{2t}{m^2} - \frac{2}{m^3} + \frac{2}{m^3}\exp-(mt) \right] \tag{13}$$

or

$$w = 2\pi N_0 B^2 K \left[t^2 - \frac{2t}{m} + \frac{2}{m^2} - \frac{2}{m^2} \exp - (mt) \right] \tag{14}$$

A kinetic equation convenient for treatment of experimental data is easily produced by combining eqns. (13) and (14), without much transformation

$$\frac{n}{t^3} = B - \frac{1}{m}\frac{w}{t^3} \tag{15}$$

where

$$B = \tfrac{2}{3}\pi N_0 K^3 \frac{M^2}{d^2} \tag{16}$$

So, if crystal nucleus formation depends on the exponential rule, the experimental data should fall on a straight line in n/t^3–w/t^3 coordinates.

Similarly, if the crystal nucleus growth rate depends on eqn. (12), which is the power function rule, we get from eqn. (10), after a series of transformation

$$\lg n = q \lg t + \lg \beta_1 \tag{17}$$

$$\beta_1 = \frac{4\pi K^3 M^2 a}{d^2(q-1)(q-2)} \qquad q = b + 3 \tag{17a}$$

or

$$\frac{n}{t} = \frac{w}{q} \tag{18}$$

At this reaction rate, the growing product weight is determined by

$$W = \frac{4\pi B^2 K a t^q}{(q-1)(q-2)}$$

$$n = \frac{4\pi K B^2 a t^q}{q(q-1)(q-2)} \tag{19}$$

Therefore, when crystal nuclei grow according to the power function rule, the experimental data, before reaching the maximum of reaction rate, should fall on a straight line in coordinates $\lg n$–$\lg t$; and should be a straight line through the origin in coordinates $n/t - w$. When approaching the rate maximum, large departures from the above relation can be predicted.

Determination of specific rate of the reaction K

It is not difficult to see that the specific rate of reaction can not be directly determined by eqns. (13)–(16) or (17)–(19) because the constants in the formula, except the K value, also include the parameters a, b, m and N_0 from eqns. (11) and (12). So, eqns. (13)–(16) and (17)–(19) can only be used to explain the applicability of eqns. (11) or (12), and to determine the exponent b in eqn. (12) or m in formula (11). In order to decide the size of the specific rate of the reaction, the condition at maximum reaction rate can be used. At this time, the bottom of the crystal nucleus totally covers the surface of the reacting matter. We get the following approximate equation:

$$S_\pi = S \tag{20}$$

where S is the surface area of the solid reaction matter at $t = 0$, S_π is the total area of the bottom of the growing crystal nucleus which covers the surface of the solid reaction matter.

Taking condition (20) into consideration and using eqns. (17)–(19), the specific rate of the reaction, K, can be determined. (Note that this only applies to the power function nucleation rule (12).)

For a hemispherical crystal nucleus

$$S_\pi = \tfrac{1}{2} S_1 \tag{21}$$

from which we derive

$$\frac{2\pi\beta^2 a\, t_{\max}^{q-1}}{(q-1)(q-2)} = S \tag{22}$$

By transformation we get

$$KS = \frac{n_{\max} q}{2t_{\max}} \tag{23}$$

or

$$KS_g = \frac{n_{\max}}{g} \frac{q}{2t_{\max}} \tag{24}$$

where S_g is the specific surface area of the original sample; $n_{\max}/g$, when $t = t_{\max}$, is the mole number of 1g original sample conversion. Thus, the K value can be determined from the experimental data at the start of the kinetic curve and the maximum rate.

As to the point of the maximum rate, whatever the nucleation rule is, we directly get the following equation from formulae (2), (20) and (21)

$$KS = \frac{1}{2} \left| \frac{\mathrm{d}n}{\mathrm{d}t} \right|_{\max} \tag{25}$$

or

$$KS_g = \frac{1}{2g} \left| \frac{\mathrm{d}n}{\mathrm{d}t} \right|_{\max} \tag{26}$$

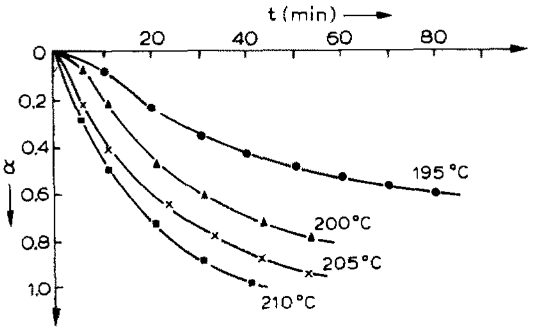

Fig. 1. TG curves of $MgC_2O_4 \cdot 2H_2O$ dehydration at constant temperature.

Using formula (26) it is possible to derive K from the data obtained when the reaction rate reaches its maximum. The nucleation mechanism does not need to be studied in detail.

EXPERIMENTAL

In this paper, magnesium oxalate dihydrate is produced through double decomposition of magnesium chloride solution and potassium oxalate. Its composition is identified by TG and elemental analysis. The thermogravimetry analysis was done on a micro-thermobalance made by the Shanghai Balancing Instrument Factory.

Four thermogravimetric runs at constant temperature were done in the dehydration temperature range of magnesium oxalate dihydrate. Sample weight was about 15 mg and the nitrogen gas flux was 30 ml min^{-1}. The TG curve is shown in Fig. 1.

RESULT AND DISCUSSION

Nucleation rule

In order to obtain the specific rate of the reaction, the character of the nucleation rule of the reacting matter (anhydrous magnesium oxalate) should be first determined. As described above, if the crystal nucleus grows according to a power function rule, at the start of the kinetic curve (before the maximum reaction rate) the experimental data should be on one straight line in lg n–lg t coordinates. The relavant data are shown in Figs. 2 and 3.

It is clearly seen from the figures that in the coordinates of the exponential rule, the experimental points depart from the linear relation (Fig. 2); in the coordinate of the power function rule, the experimental points all lie on the same straight line (Fig. 3). This proves that nucleation of the

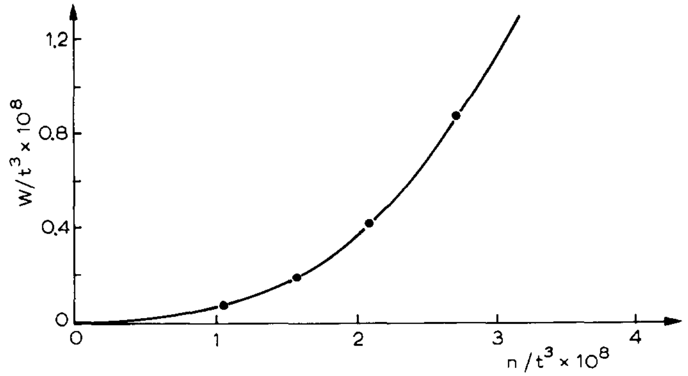

Fig. 2. Relation of W/t^3 with n/t^3.

dehydration of magnesium oxalate dihydrate is described by the power function rule.

Determination of the K *value*

From the above statement, when the crystal nuclei of the solid product grow according to the power function rule, the specific rate of the reaction can be calculated by using eqns. (23) or (24). If the specific surface area of the reacting matter is unknown, its reaction capacity can also be described directly by using $K_g = KS_g$; K_g is the specific rate of the reaction of 1 g of reacting matter. The K_g value can also be determined according to the maximum rate from eqn. (26). The result is shown in Table 1.

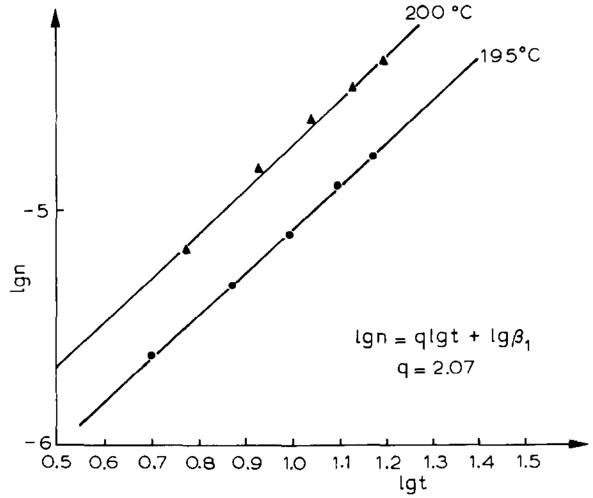

Fig. 3. Relation of lg n with lg t.

TABLE 1

Calculation of specific rate of reaction

Quantity	Experiment no.			
	1	2	3	4
Sample mass (g)	0.01609	0.01615	0.01411	0.01479
Temp. (°C)	195	200	205	210
q from Fig. 3	2.07	2.07	2.07	2.07
t_{max} (min)	13.75	9.75	5.75	4.75
n_{max} (mol)	1.44×10^{-5}	1.95×10^{-5}	1.53×10^{-5}	1.53×10^{-5}
w_{max} (mol min^{-1})	1.72×10^{-6}	3.61×10^{-6}	4.89×10^{-6}	6.67×10^{-6}
KS_g from formula (24)	6.73×10^{-5}	1.28×10^{-4}	1.95×10^{-4}	2.25×10^{-4}
KS_g from formula (26)	5.35×10^{-5}	1.12×10^{-4}	1.73×10^{-4}	2.25×10^{-4}
Average value of KS_g (mol min^{-1})	6.04×10^{-5}	1.20×10^{-4}	1.84×10^{-4}	2.25×10^{-4}

From the data in Table 1, we can see that (1) KS_g values from different experiments are close to each other, so the applicability of the formula has been tested to a certain extent; (2) q values determined at different temperatures are rather similar, which shows that the crystal shapes in all experiments are the same. Under these circumstances, the activation energy of reaction can be derived precisely from the specific rate of the reaction.

Determination of activation energy

The activation energy in the stage before the maximum reaction rate in the dehydration of magnesium oxalate dihydrate can be calculated by using the KS_g value. The stage is the real process of random nucleation and subsequent growth. From Fig. 4 we can see that the data lie on the same straight line in an Arrhenius equation plot. Through linear regression, the

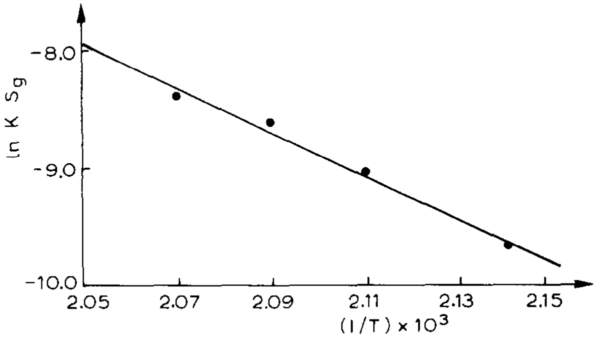

Fig. 4. Calculation of the activation energy in the stage of random nucleation and crystal nucleus growth.

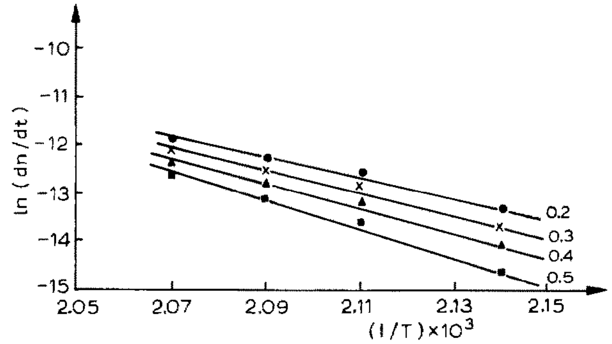

Fig. 5. Calculation of the activation energy in the diffusion stage.

activation energy of the reaction is calculated as 82.49 kJ mol^{-1}, with correlation coefficient $r = 0.9728$.

After the reaction rate reaches the maximum value, the continuous layer of solid product develops. Because the crystal nucleus shape in all experiments is the same, we can say that the area of interface between product and reaction matter and the effective thickness of the product layer at the same degree of conversion should also be the same. They are independent of the reaction temperature. Therefore, we can calculate the activation energy in the diffusion stage by using the relation between reaction rate at different temperatures with the same degree of conversion.

TABLE 2

Calculation of activation energy in the diffusion stage

T(K)	$1/T$	α	t(min)	dn/dt	ln(dn/dt)
468	2.14×10^{-3}	0.2	18.03	1.62×10^{-6}	−13.33
		0.3	25.58	1.22×10^{-6}	−13.62
		0.4	37.12	0.76×10^{-6}	−14.09
		0.5	56.00	0.45×10^{-6}	−14.61
473	2.11×10^{-3}	0.2	10.38	3.61×10^{-6}	−12.53
		0.3	13.55	3.24×10^{-6}	−12.64
		0.4	16.85	2.36×10^{-6}	−12.96
		0.5	22.83	1.48×10^{-6}	−13.42
478	2.09×10^{-3}	0.2	5.80	4.63×10^{-6}	−12.28
		0.3	7.82	3.77×10^{-6}	−12.49
		0.4	10.63	2.86×10^{-6}	−12.76
		0.5	14.68	2.04×10^{-6}	−13.10
483	2.07×10^{-3}	0.2	4.90	6.37×10^{-6}	−11.96
		0.3	6.50	5.51×10^{-6}	−12.11
		0.4	8.75	4.45×10^{-6}	−12.32
		0.5	11.50	3.31×10^{-6}	−12.62

TABLE 3

Activation energy in the diffusion stage

α	E (kJ mol^{-1})	r
0.2	82.10	0.9637
0.3	88.14	0.9422
0.4	103.58	0.9418
0.5	118.88	0.9602

Figure 5 shows the relation between the logarithm of reaction rate and the reciprocal of absolute temperature at several degrees of conversion. It can be seen that the experimental points lie on the same straight lines, proving that this method can be used to calculate activation energies in the diffusion stage. When the degree of conversion is high, the slope of the line is large, which shows that in this stage the activation energy is related to the degree of conversion. Activation energy becomes high as the reaction interface moves into the interior of the particles. This can be explained by an increase in diffusion resistance.

The data in Table 2 are used to perform linear regression of $\ln(\mathrm{d}n/\mathrm{d}t)$–$1/T$ at different degrees of conversion, producing the activation energy in values of diffusion stage as shown in Table 3.

Tanaka and Tokumitsu [8] studied the dehydration of magnesium oxalate dihydrate by thermogravimetry at constant temperature and at linearly increasing temperature. The process is identified as having the $A_{2.36}$ mechanism of nucleation and subsequent growth of crystal nuclei. The activation energy is 103.9 kJ mol^{-1}. In this paper, we show that random nucleation complies with the power function rule and in the stages of crystal nucleus formation and growth the activation energy is 82.49 kJ mol^{-1}. The activation energy becomes large when α is large, in the diffusion stage. In comparison, published [8] data are close to the statistical average value in each stage.

CONCLUSION

In this paper, the process of random nucleation and subsequent crystal nucleus growth have been examined by establishing a physical model, then calculating the formula for the specific rate of the reaction in the induction period and the rate-increasing period. Therefore, the determination of activation energy in this stage has been realized. Furthermore, taking the dehydration of magnesium oxalate dihydrate as an example, we tested the physical model and formula. The result is satisfactory.

REFERENCES

1 S.G. Sinha, N.D. Deshpande and D.A. Deshpande, Thermochim. Acta, 156 (1989) 1–10.
2 A. Szafranek, J. Therm. Anal., 34 (1988) 917–926.
3 W.W. Wendlandt, J. Chem. Educ., 38 (1961) 571.
4 T. Kiyohiro and R. Otsuka, Thermochim. Acta, 147 (1989) 127–138.
5 S.G. Sinha, N.D. Deshpande and D.A. Deshpande, Thermochim. Acta, 113 (1987) 95–104.
6 A.Y. Lozofski, Kinet. Catal., 1 (1963) 97–108.
7 A.Y. Lozofski, Kinet. Catal., 3 (1963) 373–381.
8 H. Tanaka and M. Tokumitsu, J. Therm. Anal., 29 (1984) 87–93.