ELSEVIER

Thermochimica Acta 250 (1995) 165–171

thermochimica
acta

A kinetics study of the reaction of dolomite with phosphoric acid using a calorimetric method

Magdalena Olszak-Humienik *, Janina Możejko

Technical University of Szczecin, Department of Chemical Engineering and Physical Chemistry, Szczecin, Poland

Received 2 November 1993; accepted 8 July 1994

Abstract

The kinetics of dissolution of dolomite in phosphoric acid have been investigated by the calorimetric method. From the thermokinetic curves of dolomite with acids, the dependences of the conversion degree upon time and the reaction rate constant were determined. The influence of grain size on the reaction rate of decomposition of dolomite has been studied.

Keywords: Calorimetry; Dolomite; Kinetics; Phosphoric acid

1. Introduction

The kinetics of the reaction of dolomite with phosphoric acid have been investigated as part of a programme to study the decomposition of minerals with acids.

The calorimetric method of following reaction rates was employed. A common calorimetric technique for the determination of rates is to monitor the temperature of the system as a function of time. This technique simultaneously provides thermodynamic and kinetic information and may be helpful in the interpretation of reaction mechanisms. This method is applicable in many cases because most reactions involve enthalpic effects that are sufficiently large to be detected.

This heterogeneous reaction is a typical example of the chemical solution of carbonates with acids associated with carbon dioxide evolution. This process has

---

* Corresponding author.

SSDI 0040-6031(94)01981-9

direct influence on the kinetics of reaction. The investigations were carried out to obtain a mathematical description of the process.

A source of kinetic information is the heat power change $H_r(t)$ generated by the reaction in time t. This quantity of power is connected with the transformation degree $\alpha(t)$

$$\Delta H_r(t) = \Delta H_\infty \alpha(t)$$

where ΔH_∞ is the enthalpy of reaction.

In the calorimetric experiments the temperature changes $\Delta T(t)$ were observed continuously. The quantity $\Delta T(t)$ depends on the transformation degree, the heat effect of the reaction, the heat capacity of the sample under investigation and the characteristics of the recording system.

The main problem of the theory of the calorimetric method as applied to the kinetic study of chemical reactions is the determination of the function relation

$$\alpha(t) = f[\Delta T(t)]$$

In adiabatic calorimetry, the heat capacity of a system is approximately [1]

$$C(T) = \Delta H_\infty / \Delta T_{\mathrm{ad}}$$

and

$$\alpha(t) = \frac{\Delta H_r(t)}{\Delta H_\infty} = \frac{\int_{T(0)}^{T(t)} C(T)\,\mathrm{d}T}{\Delta H_\infty}$$

If temperature increases are small, we can assume that

$$C(T) = \mathrm{const.}$$

and

$$\alpha(t) = \frac{\Delta T}{\Delta T_{\mathrm{ad}}}$$

where ΔT is the actual temperature increase of the system and ΔT_{ad} is the maximum temperature increase.

The transformation degree thus obtained was substituted into the kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha)$$

where k is the rate constant dependent on the temperature, and $f(\alpha)$ the conversion function dependent on the mechanism of the reaction.

Integrating this equation

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{t_0}^t k\,\mathrm{d}t$$

The algebraic expressions of integral $g(\alpha)$ functions for the most common mechanisms operating in decomposition tested in this work are listed in Table 1 [3].

Table 1
Kinetic models investigated

No.	Function $g(\alpha)$	No.	Function $g(\alpha)$
1	α^2	6	$(-\ln(1-\alpha))^{1/2}$
2	$(1-\alpha)\ln(1-\alpha)+\alpha$	7	$(-\ln(1-\alpha))^{1/3}$
3	$3/2(1-(1-\alpha)^{1/2})^2$	8	α
4	$3/2(1-2/3\alpha-(1-\alpha)^{2/3})$	9	$2(1-(1-\alpha)^{1/2})$
5	$(-\ln(1-\alpha))$	10	$3(1-(1-\alpha)^{1/3})$

The correlation coefficient r and Snedecor's variable F were calculated to aid the selection of the $g(\alpha)$ function which best describes the experimental results.

2. Experimental

The calorimetric measurements of the kinetics of the reaction of dolomite with phosphoric acid were carried out in a Dewar-type quasi-adiabatic calorimeter having a vessel with a working capacity of about 700 ml in a special insulating casing [2]. The raw dolomite used in the reaction was from Mine "Zelatowa" (Poland), and contained 16.13% MgO, 33.66% CaO, 2.86% R_2O_3 and 2.54% SiO_2 with the particle size being in the range 0-0.8 mm. Measurements were carried out with 31 g samples of dolomite and 700 g of 20% solution of phosphoric acid. The reactants were thermostated before the reaction at an initial temperature of 20°C. The accuracy of determining the temperature of the system during reaction corresponded to 0.05°C in 0.5-15 min intervals until the temperature of the system was constant. The final products of decomposition were identified by the presence of acid hydrogen and calcium ions. The enthalpy of solution of sodium hydroxide was used to calibrate the calorimeter.

3. Results and discussion

The calorimetric measurements provided the actual temperature of the system with time for specific particle sizes of dolomite. The results obtained for the acid solution of dolomite are shown in Fig. 1.

The results indicate that this process runs quickly in the first 30 min of reaction. The maximum temperature increase becomes less with increasing particle size of dolomite. From the ratio of the actual temperature increase to the maximum value of the temperature increase, the actual transformation degree α was determined for all the measurements. Changes in the transformation degree with time for different particle sizes of raw dolomite are shown in Fig. 2.

Based on the $\alpha(t)$ dependence, the $g(\alpha)$ functions from the well-known models (Table 1) which best described the experimental results of decomposition were

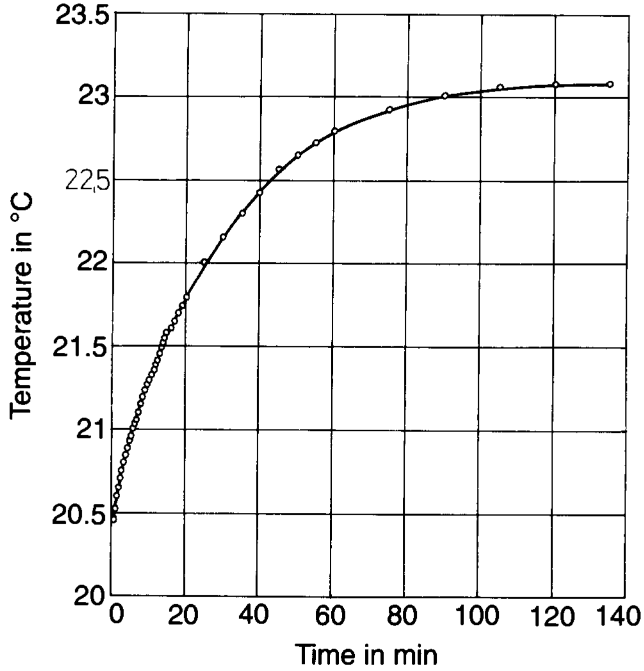

Fig. 1. The temperature increase with time ($d_z = 0.25$ mm).

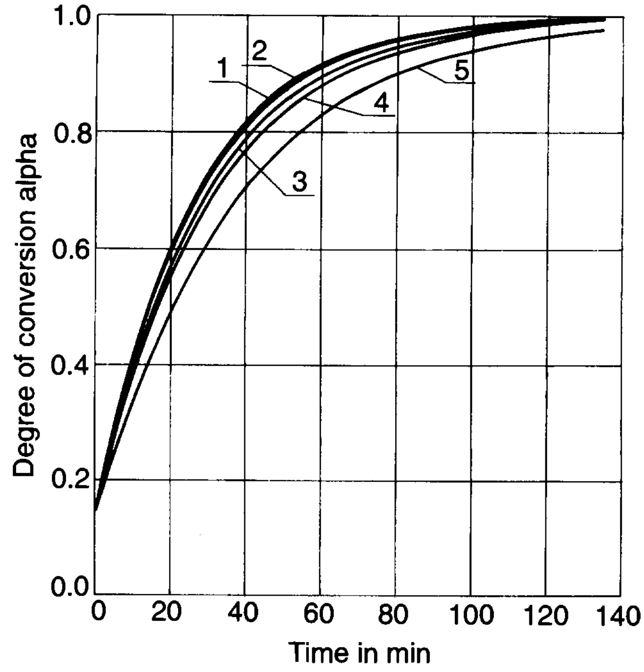

Fig. 2. Changes in conversion degree with time for different particle sizes: curve 1, $d_z = 0.25$ mm; curve 2, $d_z = 0.32$ mm; curve 3, $d_z = 0.44$ mm; curve 4, $d_z = 0.55$ mm; and curve 5, $d_z = 0.7$ mm.

chosen. Two variants for the description of the experimental data were considered by means of the least-squares method

Variant 1: $g(\alpha) = kt$
Variant 2: $g(\alpha) = kt + b$

where b is a constant.

The kinetic analysis was made using a microcomputer. The results obtained for the different models (using Variant 2, which was preferred) are listed in Table 2.

From Table 2 it can be seen that the best fitting expression for this reaction is the first-order reaction

$$g(\alpha) = -\ln(1-\alpha)$$

Values of the reaction constant obtained for different particle sizes of dolomite for this model have been changed from 0.0386 min^{-1} (for an equivalent diameter d_z of 0.25 mm) to 0.0270 min^{-1} (for $d_z = 0.7$ mm). The reaction rate constant is plotted as a function of particle size in Fig. 3. This dependence can be described by the equation

$$k = 0.0402 - 0.0253 d_z^2$$

These results may be useful in the processing of minerals with acids and in the physicochemical study of decomposition reaction.

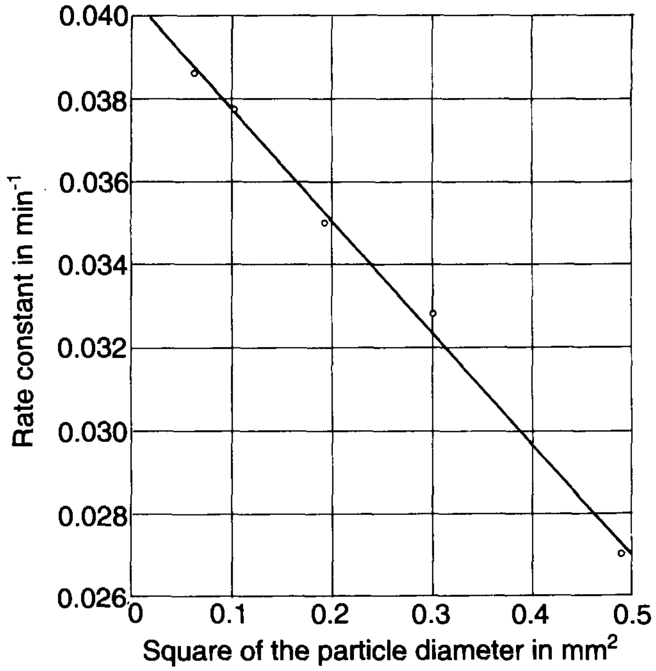

Fig. 3. The influence of particle size on the reaction rate.

4. Conclusions

The calorimetric method of studying kinetics is useful for measuring the solution reaction rate of minerals with acid. The solution reaction of dolomite with

Table 2
Results of the investigations

d_2/mm	No. of function	k/min^{-1}	b	r	F
0.25	1	0.0111	0.0739	0.9654	603.60
	2	0.0102	0.0111	0.9879	1779.35
	3	0.0083	−0.0389	0.9931	3138.23
	4	0.0045	−0.0050	0.9948	4162.44
	5	0.0386	0.1430	0.9988	17722.21
	6	0.0162	0.5529	0.9850	1437.11
	7	0.0104	0.6907	0.9700	700.88
	8	0.0090	0.3137	0.9182	236.58
	9	0.0170	0.2956	0.9750	846.60
	10	0.0218	0.2698	0.9889	1955.52
0.32	1	0.0110	0.0729	0.9683	661.43
	2	0.0101	0.0104	0.9888	1936.87
	3	0.0081	−0.0381	0.9923	2825.60
	4	0.0045	−0.0052	0.9948	4174.36
	5	0.0377	0.1504	0.9988	18942.92
	6	0.0159	0.5571	0.9877	1750.50
	7	0.0102	0.6942	0.9749	842.87
	8	0.0089	0.3153	0.9264	266.37
	9	0.0168	0.2973	0.9781	969.92
	10	0.0215	0.2720	0.9904	2266.92
0.44	1	0.0099	0.0812	0.9522	463.86
	2	0.0092	0.0184	0.9777	973.49
	3	0.0076	−0.0328	0.9933	3316.59
	4	0.0041	−0.0017	0.9870	1696.50
	5	0.0350	0.1680	0.9967	6774.72
	6	0.0146	0.5597	0.9752	874.34
	7	0.0094	0.6939	0.9586	509.89
	8	0.0080	0.3161	0.9040	201.08
	9	0.0153	0.3038	0.9632	578.00
	10	0.0197	0.2815	0.9790	1035.38
0.55	1	0.0106	0.0527	0.9774	940.57
	2	0.0094	0.0006	0.9934	3318.96
	3	0.0070	−0.0341	0.9915	2563.97
	4	0.0041	−0.0073	0.9969	7041.08
	5	0.0328	0.1494	0.9994	39013.01
	6	0.0147	0.5330	0.9852	1452.08
	7	0.0098	0.6727	0.9705	712.27
	8	0.0089	0.2861	0.9349	305.41
	9	0.0159	0.2666	0.9812	1134.70
	10	0.0199	0.2447	0.9919	2669.23

Table 2 (continued)

d_2/mm	No. of function	k/min^{-1}	b	r	F
0.70	1	0.0096	0.0202	0.9956	4898.74
	2	0.0075	−0.0079	0.9977	9461.05
	3	0.0043	−0.0180	0.9866	1566.56
	4	0.0030	−0.0066	0.9958	5122.51
	5	0.0270	0.1374	0.9985	14362.21
	6	0.0126	0.4933	0.9795	1018.04
	7	0.0088	0.6347	0.9633	553.27
	8	0.0092	0.2307	0.9631	550.33
	9	0.0141	0.2170	0.9887	1876.94
	10	0.0165	0.2062	0.9944	3620.62

phosphoric acid at an initial temperature 20°C can be described by a first-order equation. Under the experimental conditions, the reaction rate constant depends linearly on the grain size of the dolomite.

References

[1] N.M. Emanuel and G.B. Siergiejew, Wybrane metody badania kinetyki reakcji chemicznych, PWN, Warszawa, 1988.

[2] M. Olszak-Humienik and J. Możejko, J. Therm. Anal., 38 (1992) 1683.

[3] B. Pacewska, J. Therm. Anal., 36 (1990) 2021.