

KINETICS OF THE DISPROPORTIONATION OF BARIUM SULPHITE

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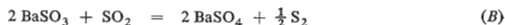
A kinetic equation for the disproportionation of solid barium sulphite has been proposed which expresses the reaction rate as a function of the solid phase composition, temperature, and partial pressure of the water vapour. The rate equation can be readily integrated and it reproduces the experimental data with an average deviation of $\pm 2.1\%$ in the whole range of variables. The disproportionation of the solid barium sulphite in dry nitrogen takes place at a measurable rate at temperatures above 670°C and its effective energy of activation amounts to 61.4 kcal. The rate constant of the disproportionation is a linear function of the partial pressure of water vapour.

The reaction rate of disproportionation has been investigated as a part of a broader research programme, *i.e.* of the kinetic study of the system barium sulphite-hydrogen. One of the reactions assumed in this system which could be studied as an isolated reaction is the disproportionation of the barium sulphite in an inert nitrogen atmosphere. This reaction namely takes place at a measurable rate in the range of temperatures at which the system barium sulphite-hydrogen has been investigated. It was the aim of the kinetic study of the disproportionation of barium sulphite to determine quantitatively the effects of variables on the reaction rate and to find a rate equation which would be applicable in evaluating the experimental data of the system barium sulphite-hydrogen.

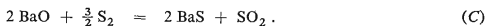
Most of the existing papers on the disproportionation of barium sulphite in dry nitrogen is of mere qualitative nature and deals with the effect of temperature only¹⁻³. The mechanism of disproportionation of sulphites of metals of alkaline earths is given by Nichkovskij and Ketov⁴, who have studied this reaction at temperatures of $600-800^\circ\text{C}$ in a nitrogen atmosphere. The mentioned authors consider the dissociation reaction



as a first step. The sulphur dioxide set free in this reaction oxidizes the sulphite to sulphate according to the equation



and the resulting sulphur reacts with the barium oxide formed in the equation (A) under formation of the sulphide and sulphur dioxide according to the equation



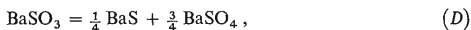
Kinetics of the disproportionation of the barium sulphite prepared by saturating the suspension of the barium carbonate with gaseous sulphur dioxide has been measured by Šušunov, Sadovnikova, and Andrejev⁵. From the values of reaction rates, the activation energy of disproportionation has been computed as 23.6 kcal. No kinetic equation, however, has been suggested in any of the cited papers. The effect of the presence of water vapour in the gas phase and the effect of the particle size of the solid on the rate of disproportionation have not been found in the published papers.

EXPERIMENTAL AND RESULTS

The experimental procedure has been described in paper⁶ and it remains to be added only that the time has been measured in kinetic experiments with a stop watch, the deviation of which did not exceed 0.1 s during 15 min. In measurements in a wet nitrogen the datum on the duration of experiment has been corrected to the free reactor volume which has been found by calibration with water and amounted to 81 ml. The shift of the experiment beginning caused in this way has been calculated for a given flow rate of the gas under assumption of the piston flow. It has been found in preliminary experiments that the dissociation of the barium sulphite according to the equation (A) does not take place. For this reason the analysis of the gas phase has not been carried out.

In studying the rate of disproportionation of the barium sulphite in an inert nitrogen atmosphere, the experimental integral data of the dependence of the conversion degree of the barium sulphite on time have been obtained. After the experiment has been finished, the contents of the sulphite, sulphate, and sulphide have been determined in the solid phase. Since the sulphate and the sulphide were formed in a stoichiometric ratio, these data did not serve as a basis for evaluation of experiments and were used for checking the sulphur balance and for testing the analytical procedure used. The time dependences of the mole fraction of the barium sulphite served as a basis for evaluating the rate data of disproportionation. In the treatment of integral data it is possible to proceed in two ways: *a*) to differentiate the integral data (graphically or numerically), *b*) to integrate the assumed rate relation and to compare the integral data directly with the integral rate equation. The way *a*) has a disadvantage in including the errors due to the differentiation. The way *b*) is sometimes hindered by difficulties in integrating the rate relation. Therefore, a combination of both ways has been selected to treat the rate data of the disproportionation.

The kinetic equation of disproportionation has been found in the following way. If one mol of the barium sulphite at the beginning of the reaction is considered, which reacts according to the equation



and if the mole fraction of the barium sulphite in the time τ is denoted as x , then the following relations are obtained from stoichiometry for the mole fraction of the sulphide, y , and for the mole fraction of the sulphate, z ,

$$y = \frac{1}{4}(1 - x); \quad z = \frac{3}{4}(1 - x); \quad x + y + z = 1. \quad (1)-(3)$$

The reaction rate of disproportionation is defined by the rate of decreasing of the mole fraction of barium sulphite

$$r_x \equiv - dx/d\tau. \quad (4)$$

Assuming the reaction rate as a function of temperature and of the solid phase composition, the kinetic equation can be written in the form

$$r_x = k_{(T)}f(x, y, z). \quad (5)$$

The effect of the composition of the gas phase (*e.g.* of the partial pressure of water vapour) is included in the rate constant k . If the function f is supposed to be of the form $f = x^a y^b z^c$, then on substitution of equations (1) and (2) the following expression is obtained for the reaction rate

$$r_x = k_{(T)}\left(\frac{1}{4}\right)^b \left(\frac{3}{4}\right)^c x^a (1-x)^b (1-x)^c, \quad (6)$$

which can be rearranged to

$$r_x = k_{20} x^a (1-x)^d, \quad (7)$$

where the exponent $d = b + c$. As a basis for testing the suitability of the suggested form of the rate equation and for determining the optimum values of exponents a and d , the experiments were used in which a high conversion degree of the solid has been obtained as well as the experiments with a higher number of experimental data. Two procedures were used to determine the optimum values of exponents in the kinetic equation suggested.

In the first procedure the curves were drawn through experimental values of the time dependence of mole fraction of the barium sulphite and the reaction rate r_x were determined for individual values of x by graphical differentiation. The dependence of the reaction rate r_x on the mole fraction of sulphite obtained in this way a temperature of 677.5°C, partial pressure of the water vapour of 19.9 Torr, and particle size of 0.25–0.33 mm, is given in the Fig. 1. The values of exponents a and d in the rate equation (7) which has been linearized into a logarithmic form, were determined by the method of least squares⁷. The calculations have been carried out on a computer and the results are given in the Table I. The values of exponents obtained in this way have been considered as a first approximation only, since they might be strongly affected by the subjective drawing of the curve and by the subsequent graphical differentiation.

In the second procedure, the direct experimental data on the time dependence of the mole fraction of the barium sulphite have been used. In the combined equations (4) and (7)

$$-\int dx/x^a(1-x)^d = k_{20} \int d\tau, \quad (8)$$

the integral on the left-hand side of the equation (8) can be expressed in terms of elementary functions, if one of the exponents or its sum is an integer⁷. The general solution has been obtained for the sums of exponents ($a + d$) = 1, 2, 3, 4 and the equation (8) has been transformed into the form

$$f_{(x)} = k_{20}\tau + C_2, \quad (9)$$

where the constants k_{20} and C_2 have been evaluated by the method of averages. For individual sums of exponents at variable values of exponents a and d , the average deviation $\Delta\tau$ and the value of the exponent a has been determined for the minimum average deviation. The minimalization of the time variable has been used for the reason that it was impossible to express x explicitly. For evaluating the dependence of the minimum average deviation $\Delta\tau$ on the value of the exponent a at the sum

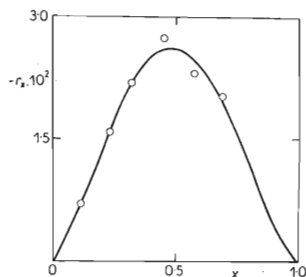


FIG. 1

Dependence of the Reaction Rate of Disproportionation of BaSO_3 r_x on BaSO_3 Content at 677.5°C and $p_{\text{H}_2\text{O}} = 19.9$ Torr with Particle Size of the Sample 0.25 to 0.33 mm

Points: experimental values; curve fitted according to equation (7).

TABLE I
Values of Exponents and Rate Constants in Equation (7)

Temperature $^\circ\text{C}$	$p_{\text{H}_2\text{O}}$ Torr	Particle size, mm	$k_{20} \cdot 10^2$ min^{-1}	a	d
677.7	9.9	0.25—0.33	15.13	1.46	1.51
677.5	19.9	0.25—0.33	23.06	1.51	1.63
677.6	19.7	0.10—0.12	51.58	1.95	2.10

$(a + d) = 1, 2, 3, 4$ and the dependence of the minimum deviation $\Delta\tau$ on the sum $(a + d) = 1, 2, 3, 4$, the quadratic correlation equation has been used. In this way the optimum value of the exponent $a = 1.65$ and the optimum sum of exponent $(a + d) = 3.15$ have been found. For these values, however, no analytical solution of the integral of the left-hand side of the equation (8) exists. Therefore, a form of the kinetic equation has been sought with such values of exponents that would approach the optimized values as closely as possible, while the integral would be accessible to an analytical solution, and the equation would fulfil simultaneously the experimental finding that the reaction rate exhibits a maximum in the vicinity of a conversion of 50%. From this point of view the following equation appeared as the most convenient

$$- dx/d\tau = k_{20}x^{5/3}(1-x)^{4/3}, \quad (10)$$

which, on integrating, assumes the form

$$\frac{3}{2} \left(\frac{1-x}{x} \right)^{2/3} - 3 \left(\frac{x}{1-x} \right)^{1/3} = k_{20}\tau + C_2. \quad (11)$$

The rate constant k_{20} and the integration constant C_2 have been determined by the method of least squares for all experimental conditions by using the computer HP 9100 B. From the value C_2 for $\tau = 0$, it is possible to calculate the content of the barium sulphite at the beginning of the proper measurement, *i.e.* after finishing the stabilization period. By means of the values k_{20} and C_2 calculated in this way, the kinetic equation (10) has been tested with regard to the reproduction of original experimental data. The differential equation (10) has been solved numerically by the method of Runge-Kutta on the computer HP 9100 B and the time dependence of the mole fraction of barium sulphite has been computed and compared with the experimentally found course.

The effect of temperature on the reaction rate of disproportionation is visualized in Fig. 2. Neither the experimental points nor the curves start from the origin of coordinates, since the barium sulphite has been partially decomposed by the preliminary heating to the desired temperature and by the ten minutes' stabilization. The mole fraction of the barium sulphite at the beginning of measurement determined from five experiments at a temperature of 677.6°C amounted to 0.853 ± 0.011 and at a temperature of 694.0°C determined from three experiments amounted to 0.792 ± 0.020 . The measurements have been carried out even at a temperature of 639°C, the results, however, were rather irreproducible owing to the small reaction rates and therefore they have not been taken as a basis for further evaluations. The study of the disproportionation rate at a temperature of about 718°C proved to be inconvenient because at the beginning of the measurement more than 50% of the original barium sulphite have been decomposed by the preliminary heating to the desired temperature and by the subsequent stabilization.

The effect of the particle size of the solid on the reaction rate of disproportionation of barium sulphite has been investigated with two fractions of the barium sulphite of 0.10–0.12 mm and 0.25–0.33 mm (Fig. 3).

The effect of the partial pressure of water vapour on the disproportionation rate has been studied at the temperature of 677.6°C in dry nitrogen and on three levels of the partial pressure of water vapour (3.9, 9.9, and 19.9 Torr) with a particle size of the barium sulphite of 0.25–0.33 mm (Fig. 4). The rate of disproportionation has been measured with the particle size 0.10–0.12 mm at a temperature of 677.4°C in dry nitrogen and at two partial pressures of the water vapour (3.8 and 19.7 Torr). The dependence of the rate constant of disproportionation, k_{20} , on the partial pressure of the water vapour is visualized in the Fig. 5. The rate constants calculated from the experimental rate data of disproportionation by the method of least squares exhibit an average accuracy of 7.1%. As it is evident from the summary Table II, the best agreement with the suggested form of the kinetic equation (10) has been obtained in experiments in which the degree of conversion exceeded 90%. A poorer result has been obtained in measurements with a partial pressure of water vapour of 3.9 Torr and with both particle sizes of the barium sulphite. The degree of con-

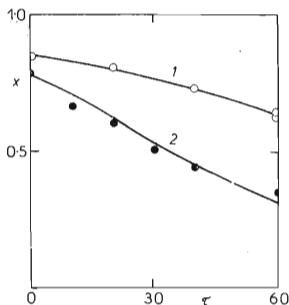


FIG. 2

Effect of Temperature on Disproportionation of BaSO_3 in Dry Nitrogen with Particle Size of 0.25–0.33 mm

Experimental values: 1 677.6°C, 2 694.0°C; curves fitted according to equation (10).

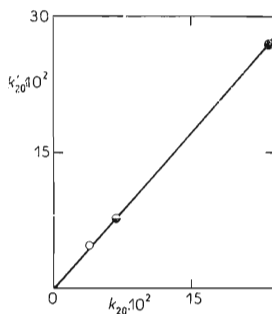


FIG. 3

Effect of Particle Size of BaSO_3 on Reaction Rate of Disproportionation at 677.5°C in Dry and Wet N_2

Experimental values: \circ dry nitrogen, \bullet $p_{\text{H}_2\text{O}}$ 3.9 Torr, \bullet $p_{\text{H}_2\text{O}}$ 19.8 Torr, k'_{20} rate constant with particle size 0.10–0.12 mm, k_{20} rate constant with particle size 0.25 to 0.33 mm; curve fitted according to the method of least squares.

TABLE II
Results of Disproportionation

Temperature °C	P_{H_2O} Torr	Particle size mm	Average deviation $\pm \Delta x$, % abs.	$k_{20} \cdot 10^2$ min^{-1}	s_{20} %
677.6	0	0.25–0.33	1.0	3.93 ± 0.267	6.8
677.5	3.9	0.25–0.33	2.4	6.69 ± 0.589	8.8
677.7	9.9	0.25–0.33	2.2	14.66 ± 0.704	4.8
677.5	19.9	0.25–0.33	2.2	23.56 ± 0.565	2.4
677.5	0	0.10–0.12	1.0	4.72 ± 0.376	8.0
677.0	3.8	0.10–0.12	3.0	7.54 ± 0.946	12.5
677.6	19.7	0.10–0.12	2.5	26.82 ± 1.277	4.8
694.0	0	0.25–0.33	2.8	6.82 ± 0.604	8.9

version of 55% only has been obtained in these experiments and a relatively small number of experimental data have been obtained. The effective activation energy of disproportionation has been calculated according to the Arrhenius relation from the values of the rate constants k_{20} at temperature of 694.0°C and 677.6°C and a value of E_{20} 61.4 kcal have been obtained.

DISCUSSION

The reaction rate of the disproportionation depends mainly on three factors: temperature, presence of the water vapour in the gas phase, and the way of preparation of the solid. The effect of the way of preparation of the solid has been determined qualitatively in preliminary experiments, however, in all the measurements carried out in this work samples of the barium sulphite were used which were prepared in a uniform way, *i.e.* by a heterogeneous reaction between the solid barium carbonate and an aqueous solution of the sodium sulphite. The rate data on disproportionation of the barium sulphite have been obtained as a time dependence of the mole fraction of barium sulphite having a typical sigmoid shape which is characteristic for the time course of heat decompositions of solids⁸.

The course of these reactions uses to be interpreted by a localized formation of the nuclei in a crystal (*e.g.* crystal planes, edges, tops, defects), by a growth of nuclei in two or three dimensions and, after reaching the point of inflection, by a decrease of the reaction rate owing to overlapping nuclei and in this way by a decrease of the phase interface between the original and the newly formed phase. Rather great number of kinetic equations derived under these assumptions may be found in the published papers. From the point of view of the treatment of results the topokinetic equation of Erofeev⁹ for $n = 3$ in the form

$$[-\ln(1 - \alpha)]^{1/n} = k\tau \quad (12)$$

and the Prout-Tompkins⁸ equation

$$\ln [\alpha/(1 - \alpha)] = k\tau, \quad (13)$$

are interesting.

The rate equations derived from the topokinetic equations (12) and (13) exhibit a maximum of the reaction rate for $\alpha = 0.4865$ (for $n = 3$) and $\alpha = 0.500$ resp. which approach the observed maximum of the disproportionation rate very closely.

Our treatment of the rate measurements has been based on the Langmuir's idea¹⁰ that the reaction takes place on the phase boundary and the rate equation (7) has been proposed under assumption that the reaction rate is proportional to the extent of the phase boundary which depends on the degree of the reaction conversion. Special forms of the kinetic equation of the general form (7) are frequently used in the published papers. For the exponents $a = 1$ and $d = 1$ it is known as the Prout-Tompkins equation⁸ and for the exponents $a = \frac{2}{3}$ and $d = \frac{2}{3}$ as the Erofeev equation⁹. None of these equations, however, has been applicable to our data. The best agreement with the experimental values have been achieved with $(a + d) = 3.15$ and $a = 1.65$. Since there exists no analytical solution of the rate equations with these values of exponents, the sum of exponents has been adjusted with a good approximation to the value of 3 and the optimum combination of both exponents has been sought. The least deviation from experimental values has been found for the kinetic

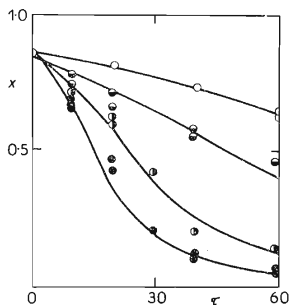


FIG. 4

Effect of the Partial Pressure of Water Vapour on Disproportionation of BaSO_3 at 677.6°C with Particle Size $0.25\text{--}0.33\ \mu\text{m}$

Experimental values: \circ dry N_2 , \odot $p_{\text{H}_2\text{O}}$ 3.9 Torr \bullet $p_{\text{H}_2\text{O}}$ 9.9 Torr, \bullet $p_{\text{H}_2\text{O}}$ 19.9 Torr; curves fitted according to the equation (10).

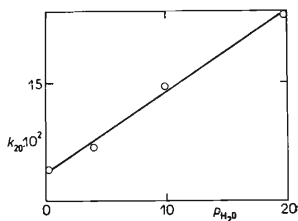


FIG. 5

Dependence of the Rate Constant of Disproportionation k_{20} on Partial Pressure of Water Vapour at 677.6°C and Particle Size $0.25\text{--}0.33\ \mu\text{m}$

Experimental values: \circ ; curve fitted according to the method of least squares.

equation in the form (10) which reproduces the time dependence of the mole fraction of the barium sulphite with an average deviation of $\pm 2.1\%$ in the whole range of variables. This precision appears satisfactory in view of the reproducibility of individual experiments which amounted to $\pm 1.5\%$. The effective activation energy of the disproportionation of the barium sulphite in dry nitrogen determined here as $E_{20} = 61.4$ kcal is in agreement with the value $E_{20} = 65.1$ kcal (ref.⁶) found previously. This has been evaluated approximatively from the reaction rates determined at one degree of conversion of the solid (30%). The value of 61.4 kcal, however, differs almost by a threefold from the value 23.6 kcal which is given by Šušunov, Sadovnikova, and Andreev⁵. The difference may be explained by a different way of preparation of the barium sulphite which has been used for kinetic measurements by the authors mentioned above⁵. In addition, the effect of the presence of the water vapour in the gas phase on the disproportionation has been investigated, which is not mentioned in the literature. At the temperature of 677.6°C it has been found that the reaction rate of the disproportionation is directly proportional to the partial pressure of the water vapour in the range from 0 to 20 Torr (Fig. 5). It is possible to explain the catalytic effects of the water vapour by that the water vapour acts as an oxygen carrier and thus supports the disproportionation. The effect of the particle size of the barium sulphite on the disproportionation has not been by far so important as the effect of the temperature and water vapour (Table II, Fig. 3).

We thank Dr J. Strublová for her technical assistance.

LIST OF SYMBOLS

a, b, c, d	exponents in rate equations (6) and (7)
α	reacted fraction of original solid
E	activation energy (kcal)
E_{20}	effective activation energy of disproportionation of barium sulphite in nitrogen (kcal)
k_{20}	rate constant of disproportionation of barium sulphite with particle size of 0.25–0.33 mm in nitrogen (min^{-1})
k'_{20}	rate constant of disproportionation of barium sulphite with particle size 0.10–0.12 mm in nitrogen (min^{-1})
$p_{\text{H}_2\text{O}}$	partial pressure of water vapour in gas phase (Torr)
r_x	reaction rate of disproportionation of barium sulphite in nitrogen defined by equation (4) (min^{-1})
s_{20}	standard deviation of rate constant k_{20} (%)
τ	time (min)
x, y, z	mole fraction of barium sulphite, sulphide, sulphate in the solid phase

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