KINETICS OF THE REDUCTION OF THE BARIUM SULPHATE BY HYDROGEN

K.Mocek and E.Erdös

Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2

The reaction rate between the solid barium sulphate and hydrogen has been measured at temperatures of 678°C and 719°C under differential conditions. The dependence of the reaction rate on the degree of conversion exhibits a maximum at approximately 50% of conversion. A kinetic equation has been proposed for the reduction expressing the reaction rate as a function of temperature, composition of the original sample, and of the degree of conversion of the barium sulphate. The rate equation can be readily integrated and reproduces the experimental data with an average deviation $\pm 1.8\%$ in the whole range of variables. The rate of the reduction of barium sulphate by hydrogen is significantly affected by the presence of the barium carbonate in the original sample. The rate constant of the reduction is approximately a linear function of the content of barium carbonate in the original sample.

The rate of the reduction of the barium sulphate has been investigated as a part of a broader programme, *i.e.* of the kinetic study of the system barium sulphite–hydrogen. One of the reactions assumed in this system which could be investigated as an isolated reaction is the reduction of the barium sulphate by hydrogen. This reaction namely takes place at a measurable rate in the range of temperatures at which the system barium sulphite–hydrogen has been investigated. The aim of the kinetic study of the reduction of barium sulphate by hydrogen was to find a rate equation which could be applied for evaluating the experimental data in the system barium sulphite–hydrogen.

The reduction of the barium sulphate by solid reducing agents (coal, coke) is known and technologically applied for a long time[1]. It requires, however, a rather high temperature and the product is contaminated by the reducing agent and ashes. In last years, therefore, the reduction begins to be carried out by means of gaseous reducing agents[2-8] (methane, hydrogen, carbon monoxide). Kinetics of this reduction has been measured at temperatures of 712–815°C in a vacuum circulation apparatus by Šušunov, Sadovnikova, and Andreev[9] who have found that the initial rate of reduction is directly proportional to the partial pressure of hydrogen. Culver, Hamdorf, and Spooner[10] have investigated the kinetics of reduction of the barite by hydrogen under differential conditions at temperatures of 800–1100°C in a flow apparatus and have correlated the data by a rate equation in the form of a power series.

EXPERIMENTAL

Chemicals, Apparatus and Measuring Procedure

The barium sulphate has been prepared by a reaction between the solution of the sodium sulphate and the solid barium carbonate at a temperature of 25°C. Six samples of the barium sulphate have been prepared with different content of barium carbonate which depended on the reaction time (from 15 min up to 24 h). The molar ratio of the sulphate to the carbonate in the reaction mixture was always 1·5 : 1. After the reaction has been finished, the product has been separated from the mother liquor, rinsed on a glass-fritted filter so long as the filtrate gave no reaction with phenolphthaleine and sucked off. The barium sulphate has been dried in air at laboratory temperature, crushed, and the fraction of particle size 0·25—0·33 mm has been used for measurements. The samples contained 62—94% by weight of the barium sulphate, 5·5—36 wt. % of the barium carbonate, and 1—2 wt. % of humidity. The sodium sulphate was an anhydrous A. G. reagent (Spolana, Neratovice) containing approximately 3 wt. % of humidity. The barium carbonate has been prepared by saturation of the barium hydroxide solution (p.a. Lachema, Brno) at 25°C with a purified CO_2. After rinsing and sucking off, the barium carbonate has been dried in air at room temperature. The potassium iodide was an A. G. reagent (Lachema, Brno). The sodium thiosulphate (p.a. Lachema, Brno) contained at min. 99 wt. % of the $Na_2S_2O_3.5 H_2O$ and was used after a twofold crystallization of the commercial sample. The potassium bromate has been used after a twofold crystallization from a pure reagent (Lachema, Brno). The iodine used was resublimed from an analytical grade reagent. The metals used for the calibration of the thermocouple were of the following quality: antimony twice sublimed (Kovohutě, Vestec), aluminium was zone-melted (Kovohutě, Vestec), and the zinc was granulated for laboratory purposes (USSR). The nitrogen used contained oxygen of the order 10^2 (sometimes even 10^3) p.p.m. of O_2. The quality of nitrogen was periodically tested by means of an oxygen analyzer[11] modified for measurements at low oxygen concentrations. In all the measurements the oxygen has been removed from the nitrogen in a copper tower[12] which has been filled up with a copper catalyst containing 42 wt. % of cupric oxide in mixture with silica. At the outlet from the copper tower the purified nitrogen contained maximally 20—30 p.p.m. of oxygen. The copper catalyst has been reactivated for some hours by a nitrogen–hydrogen mixture at a temperature of about 220°C. The hydrogen has been of electrolytic quality and contained approximately 10^1 p.p.m. of oxygen. The quality of hydrogen has been periodically tested by means of an oxygen analyzer[11]. In mea-
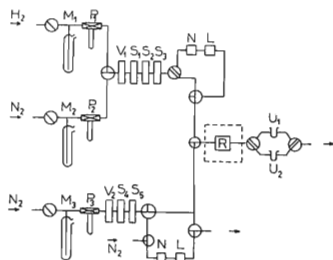

Fig. 1
Block Scheme of Apparatus
   Description see text.

suring the rate of reduction of the barium sulphate, the traces of oxygen have been removed from hydrogen in a copper tower[12] which resulted in a decrease of oxygen content to some units of p.p.m. Other chemical used were of c.p. reagent grade purity.

The rate of reduction of the barium sulphate by hydrogen has been measured in a flow apparatus under differential conditions with respect to the gas phase. The maximum change of the gas phase concentration on passing through the reactor amounted to 0·5%. The reaction conditions have been chosen in such a way that the resulting rate was not affected by the transfer of the reacting gas to the surface of the solid phase as shown by experiment with variable flow rates. The kinetics of reduction of the barium sulphate by hydrogen has been measured in a quartz reactor in which a platinum bed[13] containing the solid has been situated. The design of the reactor was essentially identical with that of the reactor used previously[14]. The reactor was placed in an electric resistance furnace and the furnace temperature at the level of the bed has been measured by means of a Ni–Ni–Cr thermocouple calibrated to melting points of zinc, aluminium, and antimony. The block scheme of the apparatus is illustrated in the Fig. 1. The hydrogen has been taken from a pressure container and led subsequently through the manosstat M_1, capillary flowmeter P_1, copper tower for removing traces of oxygen V_1, three drying towers S_1, S_2, S_3 filled up with ascarite, calcium chloride, anhydrone (BDH, Poole) and molecular sieve (Calsite 5A) into the reactor R. In measurements of the reduction rates at variable partial pressures, the hydrogen has been mixed before the inlet into the copper tower V_1 with nitrogen flowing through the manostat M_2 and the capillary flowmeter P_2. The partial pressure of hydrogen has been calculated from the flow rates of hydrogen and nitrogen. In measurements in the wet hydrogen, a water saturator N has been inserted behind the drying towers which has been thermostated by water from the constant temperature bath. A drop trap L has been attached to the saturator which has been kept at the same temperature. The partial pressure of water vapour has been calculated from the gas flow rate, from the weight of the water vapour trapped in an U-tube inserted behind the drop trap and filled up with anhydrone, and from the total atmospheric pressure which has been measured by means of the barometer Paulin (Stockholm).

In the quartz reactor, a quartz case has been placed and sealed which contained the platinum bed with the weighed amount of barium sulphate (approx. 200 mg). Before the start of heating, the reactor was rinsed up with nitrogen at a flow rate of 100 ml/min for an hour at laboratory temperature. The nitrogen has been taken from a pressure tank and led subsequently through the manostat M_3, capillary flowmeter P_3, copper tower for oxygen removal V_2, and through drying towers S_4, S_5 filled up with molecular sieve (Calsite 5 A) into the reactor R. Then the heating of the resistance furnace has been switched on and the reactor has been heated to the reaction temperature at a rate of 12°C/min. The adjusting of the desired reaction temperature and its maintaining has been carried out by means of a compensation regulator KRp (ZPA, Prague). From the moment when the compensation regulator reached the desired reaction temperature, the temperature has been stabilized for 10 minutes at the precise value by means of a variable electric input of the furnace. After this stabilization period the measurement proper began either in the dry or wet hydrogen. The temperature in the furnace has been measured by means of a Ni–NiCr thermocouple connected to the laboratory compensator QLK (Metra, Blansko) and to the galvanometer Multiflex with a precision of 0·2°C; the temperature during the measurement varied in the range of ±1°C. The flow rate of hydrogen or of nitrogen-hydrogen mixture in the measurement of reduction velocity has been kept in the majority experiments at the value of 205—210 ml/min. The content of the water vapour formed by reduction has been determined in the gas phase. The hydrogen or nitrogen-hydrogen mixture have been led into one of two parallely connected absorption tubes U_1, U_2 filled up with anhydrone. The absorber were commutatively connected to the reactor at precise time intervals (5 or 10 min) and weighed on an analytical balance. The hydrogen behind the outlet from the absorber has been burned up in an

especially designed safety device. The duration of individual experiments ranged from 5 to 180 min according to experimental conditions. The time in kinetic measurements has been determined by a stop watch the deviation of which did not exceed 0·1 second during 15 min. The time datum on the beginning of experiment has been corrected to the free volume of reactor which amounted to 81 ml as found by calibration with water. The shift of the time of experiment beginning has been calculated for a given gas flow rate under assumption of a piston flow. The individual experiments have been finished in such a way that the flow of hydrogen through the reactor has been stopped and the reactor has been quickly removed from the furnace. The maximum time of removing the reactor from the furnace amounted to about 15 s. The closed reactor has been cooled to the laboratory temperature and rinsed out with dry nitrogen; the quartz case with the sample in the platinum bed has been removed from the reactor and weighed. The sample after the reduction has been usually slightly sintered and formed an almost compact cylinder. Subsequently an analysis of the solid phase has been carried out in which the content of the barium sulphide has been determined.

Analysis of the original sample. In the samples of barium sulphate the content of barium and of carbon dioxide has been determined. The content of barium sulphate in the sample has been calculated from the difference of both determinations. The total barium content has been determined gravimetrically. The weighed sample was suspended in water and acidified at elevated temperature with hydrochloric acid. Then, an excess of the sulphuric acid has been added[15]. The suspension has been filtered and the precipitate on the filter has been rinsed up, dried, and ignited. After ignition, the barium sulphate has been weighed. The carbon dioxide has been determined by a procedure described in the previous paper[16]. The composition of samples used in kinetic measurements is given in the Table I.

TABLE I

Composition of Samples of Barium Sulphate Used in Kinetic Measurements

| Sample	A	B	C	D	E	F
$BaSO_4$, mol %	81·9	88·2	69·3	84·0	59·5	94·4
$BaCO_3$, mol %	18·1	11·8	30·7	16·0	40·5	5·6

Analysis of the solid phase after reduction. In the first experiment a complete analytical procedure has been carried out determining the sulphide, sulphite, and sulphate in the sample after the reduction[13]. In the reductions of the barium sulphate with hydrogen which have been carried out with different samples to a different degree of reduction, however, no analytically significant amount of barium sulphite has been determined (0·2—0·4 wt. % at max.). Therefore, the complete analysis has been abandoned and the sample after the reduction has been considered as a mixture of the barium sulphide and sulphate which has been analyzed as to the content of the barium sulphide iodometrically[17].

Analysis of the gas phase. In measurements of the rate of reduction of the barium sulphate with hydrogen, the content of water vapour in the gas phase was determined continually. The gas mixture at the reactor outlet has been led into one of two parallely connected absorption U-tubes

filled up with granulated anhydrone. The absorbers were alternatively connected to the reactor at precise time intervals and weighed on an analytical balance with a precision of 0·1 mg. The samples used in the measurements of the reduction rate of the barium sulphate with hydrogen contained from 5 to 40 mol % of barium carbonate. At temperatures of about 700°C the dissociation of the barium carbonate takes place.

$$BaCO_3 \rightleftharpoons BaO + CO_2 . \qquad (A)$$
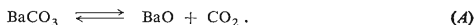
The dissociation tensions of the carbon dioxide for temperatures, at which the rate of reduction of the barium sulphate with hydrogen has been measured, were obtained by extrapolation of the temperature dependence of the dissociation pressure[18] or by calculation from thermodynamic properties of substances[19,20]. The carbon dioxide can react with the hydrogen according to the reaction

$$CO_2 + H_2 \rightleftharpoons H_2O + CO . \qquad (B)$$
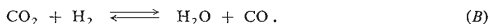
The equilibrium constants of the reaction (B) have been determined from its temperature dependence given by Vvedensky[21]. With the use of published values of dissocation pressures of the carbon dioxide and of the equilibrium constant of reaction (B), the equilibrium pressure of water vapour in the reaction (B) have been calculated for the partial pressure of hydrogen of 1 atm. Simultaneously, the tension of water vapour above the barium carbonate has been determined experimentally in the system barium carbonate–hydrogen under conditions at which the rate of reduction of the barium sulphate with hydrogen has been measured. The calculated and experimentally determined values of the water vapour pressure in the reaction (B) were approximately in agreement so that it was necessary to take into account this reaction in the measurement in the system barium sulphate–hydrogen. From the reasons given above, the weight increments in the absorbers during the measurements of the rate of reduction of the barium sulphate with hydrogen were corrected to the amount of the water vapour formed according to the reaction (B). The corrections have been calculated for weight increments at individual time intervals.

RESULTS

In the rate measurements the following experimental data have been obtained: the total amount of the barium sulphide formed during the experiment and the corrected increments of the water vapour in individual time intervals during the whole experiment. These increments have been assigned to the amounts of the barium sulphide formed according to the reaction stoichiometry. From the reasons mentioned in the analytical part, the solid phase has been considered as a mixture of the barium sulphide and sulphate. The basis for evaluating the rate data on reduction of the barium sulphate with hydrogen consisted in the time dependence of the mole fraction of the barium sulphide. The kinetic equation of the reduction has been obtained by the following procedure. Let us consider one mole of the barium sulphate at the start of the reaction

$$BaSO_4 + 4 H_2 = BaS + 4 H_2O . \qquad (C)$$
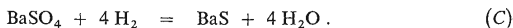
If we denote in the time τ the mole fraction of the barium sulphate as z and the mole

fraction of the barium sulphide as y, then in the absence of the sulphite the following relation is valid: $y + z = 1$. Let us define the reaction rate of reduction by the rate of the barium sulphide formation

$$r_y = dy/d\tau . \tag{1}$$

Assuming, that the reaction rate is a function of temperature and of the solid phase conversion, it is possible to write the kinetic equation in a general form

$$r_y = k_{(T)}g(y, z) . \tag{2}$$

If we assume that the function g is of the form $g = y^e, z^f$, we obtain for the reaction rate

$$r_y = k_{30}y^e(1 - y)^f , \tag{3}$$

where k_{30} denotes the rate constant of the reduction of the barium sulphate with hydrogen. The suitability of the equation (3) has been tested and the optimum values of the exponents e and f have been determined from the experiments with six samples of the barium sulphate with a variable content of the barium carbonate. The rate measurements have been carried out at two reaction temperatures with each sample.
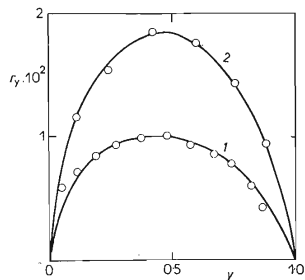

FIG. 2

Dependence of Reaction Rate of Reduction of $BaSO_4$ with Hydrogen r_y on Mole Fraction of BaS y at Carbonate Content in Sample $m = 0.307$

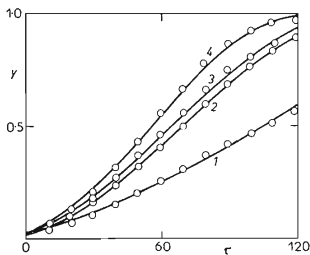Found: 1 679.1°C, 2 719.3°C; curves fitted according to equation (4).

FIG. 3

Effect of Content of $BaCO_3$ on Reduction of $BaSO_4$ with Hydrogen at 678°C

Found m: 1 0.118, 2 0.181, 3 0.307, 4 0.405; curves fitted according to equation (3) with $e = {}^1/_2, f = {}^1/_2$.

Two procedures were used to determine the optimum value of exponents in the kinetic equation (3). In the first of them, curves have been drawn through experimental values of the time dependence of the mole fraction of the barium sulphide, and the reaction rate r_y have been determined by graphical differentiation. The dependence of the reaction rate r_y on the content of the barium sulphide is illustrated on the Fig. 2 for one of the six samples of the barium sulphate investigated. The exponents e and f in the equation (3) which has been linearized into the form

$$\log r_y = \log k_{30} + e \log y + f \log (1 - y), \qquad (4)$$

have been evaluated by the method of least squares[22] on a computer for six samples of the barium sulphate at two reaction temperatures. The value of the exponent e ranged within the limits of $0.31 - 0.64$ and the average value of the exponent f amounted to 0.65. These values of exponents, however, were considered as first approximations only, since they might be strongly affected by the subjective drawing of the curves 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 sulphide have been used. The equation (3) in connection with the equation (1) have been modified on integration into the form

$$g_{(y)} = k_{30}\tau + C_3, \qquad (5)$$

where the function $g_{(y)}$ denotes the analytical solution of the binomic integral[22] for the case $(e + f) = 1$ or it represents an integral which was to be solved numerically [the case $(e + f) < 1$]. The analytical solution of the integral has been obtained for the combinations of exponents $e = {}^1/_3, f = {}^2/_3$ and $e = {}^1/_2, f = {}^1/_2$, and the

TABLE II

Average Deviation Δy (%) for Different Forms of Kinetic Equation (3)

m	$y^{1/2}$ $z^{1/2}$		$y^{1/3}$ $z^{2/3}$		$y^{1/2}$ $z^{2/3}$		$y^{2/3}$ $z^{2/3}$	
	t_1	t_2	t_1	t_2	t_1	t_2	t_1	t_2
0·056	1·6	2·3	2·5	0·9	1·7	1·3	1·2	2·4
0·118	1·3	2·2	0·4	0·7	1·0	1·3	1·8	2·2
0·160	0·9	3·7	1·0	1·5	0·5	2·5	1·2	3·6
0·181	0·6	2·0	1·8	1·5	0·7	1·1	0·8	2·0
0·307	1·8	2·5	1·1	2·1	0·8	1·5	1·7	2·3
0·405	1·8	1·2	2·3	2·6	1·4	1·7	1·4	3·6
Average	*1·3*	*2·3*	*1·5*	*1·5*	*1·0*	*1·6*	*1·4*	*2·7*

numerical solution has been carried out for combinations of $e = {}^1/_2, f = {}^2/_3$ and $e = {}^2/_3, f = {}^2/_3$ with the use of the Simpson's rule. The values of exponents of ${}^1/_3$, ${}^1/_2$, and ${}^2/_3$ have been selected on the basis of results obtained in the first procedure. The function $g_{(y)}$ has been calculated for four mentioned combinations of exponents in the rate equation, and the k_{30} and C_3 in the equation (5) have been evaluated by the method of least squares. By means of the value k_{30} and C_3, the kinetic equation (3) has been tested from the point of view of reproduction of the original experimental data. The equation (3) has been solved numerically by the method of Runge–Kutta on a computer HP 9100 B, and a time dependence of the mole fraction of barium sulphide has been computed which has been compared with the experimental values (Table II).

It is evident from the Fig. 2 that the reaction rate of the reduction reaches a maximum at a conversion of approximately 50%. This finding has been verified in the treatment of other rate measurements with samples containing various amounts of barium carbonate. For this reason, the alternative with exponents ${}^1/_3$ and ${}^2/_3$ has not been used in the description of the reduction. The alternatives with a sum of exponents $(e + f) > 1$ have not been considered because of difficulties in the treatment of experimental data by numerical integration although the alternative denoted by the number 3 yielded the best result in the average deviation. The gain of 0·5% in the average deviation does not appear as significant on comparing the alternatives 1 and 3 with respect to the error which was inherent in the determination of the quantity y (approx. 0·5%). On the basis of the preceding analysis, the alterna-
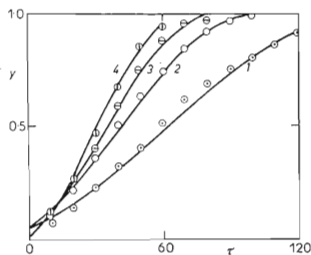

FIG. 4

Effect of $BaCO_3$ Content on Reduction of $BaSO_4$ with Hydrogen at 719°C

Found m; 1 0·118, 2 0·181, 3 0·307, 4 0·405; curves fitted according to equation (3) with $e = {}^1/_2, f = {}^1/_2$.
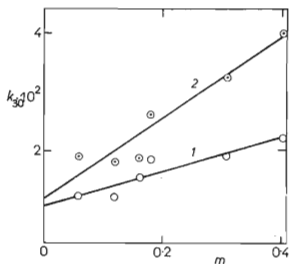
FIG. 5

Dependence of Rate Constant of Reduction of $BaSO_4$ with Hydrogen, k_{30}, on Content of $BaCO_3$ (m) in Sample

Found: 1 678°C, 2 719°C; course fitted by the method of least squares.

tive 1 has been selected for the description of the rate of reduction of barium sulphate with hydrogen, *i.e.* the kinetic equation (3) with $e = f = {}^1/_2$. The comparison of the experimental values with the calculated ones is illustrated in the Fig. 3 and 4. The summary of the computed rate constants k_{30} and of the deviations $\Delta y(\%)$ for both reaction temperatures with six samples of the barium sulphate containing variable amounts of barium carbonate is given in the Table III, which includes also the standard deviation $s_{30}(\%)$ in the determination of the rate constant. The rate constants k_{30} calculated from the experimental data by the method of least squares exhibit an average accuracy of 3·0% with six samples of the barium sulphate containing 5—40 mol % of the barium carbonate. From the Table III, the effect of temperature and of the content of barium carbonate in the sample on the values of the effective rate constant k_{30} is evident. From the temperature dependence of the rate constant k_{30}, the effective activation energies of the reduction of the barium sulphate with hydrogen have been calculated for six samples of the barium sulphate, and the average value of the effective activation energy of reduction has been determined as $E_{30} = 19\cdot4 \pm \pm 5\cdot1$ kcal. The dependence of the rate constant k_{30} on the content of the barium carbonate (m) in the sample of the barium sulphate at two temperatures $t_1 \approx 678°C$ and $t_2 \approx 719°C$ is illustrated in the Fig. 5.

DISCUSSION

The reduction of the barium sulphate with hydrogen is one of the four reactions considered in the system barium sulphite–hydrogen which will be published next. In this system, the barium sulphate is formed by the disproportionation of the original sulphite, and in the following reaction step, the sulphate is reduced by hydrogen. The rate of reduction of the barium sulphate, therefore, has been studied as the rate of an isolated reaction under conditions at which the system barium sulphite–hydrogen has been kinetically investigated. The reduction of the barium sulphate is usually[9] interpreted by the mechanism of the following consecutive reactions

$$BaSO_4 + H_2 = BaSO_3 + H_2O, \qquad (D)$$

$$BaSO_3 = {}^1/_4 BaS + {}^3/_4 BaSO_4. \qquad (E)$$
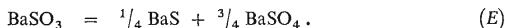
If the rate of the reaction (D) is denoted as r_D and the rate of reaction (E) as r_E, then the resulting rate of the barium sulphite formation, r_x is given by the difference of both rates. Since in the reduction of the barium sulphate with hydrogen in a wide range of conversions (5—80%) only very small and practically constant amount of the barium sulphite has been found (0·2—0·4 wt. %), it is possible to apply the method of the quasistationary state to the system

$$r_x = r_D - r_E = 0. \qquad (6)$$

If it is possible to describe the rates of reactions (D) and (E) by means of rate equations in the general form

$$r_D = k_D x^g y^e z^f ; \qquad r_E = k_E x^a y^b z^c , \qquad (7), (8)$$

then combining with the equation (6) and rearranging we obtain

$$k_D' y^e z^f = k_E' y^b z^c . \qquad (9)$$

A linear relation between log y and log z follows from the relation (9) on a simple rearrangement. The experimentally found course of this dependence, however, is practically an equal-axis hyperbola. For that reason, the two-step mechanism of the reaction (D) and (E) has not been considered for the reduction of the barium sulphate with hydrogen. The same conclusion is achieved assuming a reaction mechanism expressed by the equations
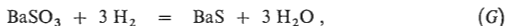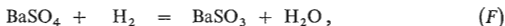
$$BaSO_4 + H_2 = BaSO_3 + H_2O , \qquad (F)$$

$$BaSO_3 + 3 H_2 = BaS + 3 H_2O , \qquad (G)$$

TABLE III

Summary of Results of Reduction of Barium Sulphate with Hydrogen

m	Temperature °C	$\pm\Delta y$ % abs.	$k_{30} \cdot 10^2$ min^{-1}	s_{30} %
0·056	678·2	1·6	1·21 ± 0·052	4·3
	718·1	2·3	1·88 ± 0·059	3·1
0·118	677·7	1·3	1·19 ± 0·029	2·5
	719·1	2·2	1·80 ± 0·053	2·9
0·160	678·2	0·9	1·55 ± 0·021	1·4
	718·9	3·7	1·83 ± 0·092	5·0
0·181	678·7	0·6	1·84 ± 0·014	0·7
	718·6	2·0	2·62 ± 0·070	2·7
0·307	679·1	1·8	1·90 ± 0·048	2·5
	719·3	2·5	3·24 ± 0·166	5·1
0·405	678·4	1·8	2·20 ± 0·068	3·1
	718·6	1·2	4·01 ± 0·109	2·7

which is sometimes cited[23,24]. The presence of sulphur dioxide has not been detected in the analysis of the gas phase and the total sulphur balance referred to the original barium sulphate has been determined with a precision of $\pm 1-2\%$. On the basis of experimental findings and of the analysis given above, it has been therefore assumed that the reduction of the barium sulphate takes place probably according to the reaction (C).

The time dependence of the mole fraction of the barium sulphide obtained in measurements of the rate of reduction of the barium sulphate with hydrogen, has a sigmoid shape with a maximum of the reaction rate at a conversion of the solid phase of approximately 50% (Fig. 2). For this reason, the shrinking core model[25] has not been found suitable for the quantitative description of the reduction. The relation (3) has been found as a suitable form of the kinetic equation; it is in agreement with the Langmuir's idea[26] that the reaction takes place on the phase boundary. The exponents of the rate equation have been determined by minimalization of the deviations from experimental data. The minimum average deviation have been obtained for nonintegrable values of exponents $e = {}^1/_2$ and $f = {}^2/_3$. The kinetic equation with exponents of $e = {}^1/_2$ and $f = {}^1/_2$ has been used for further treatment of kinetic measurements, since it reproduced the experimental data with a satisfactory precision and on integration it yielded a simple relation. This equation reproduced the experimental data with an average deviation of $\Delta y = \pm 1\cdot 8\%$ with six samples of the barium sulphate at two temperatures. The calculated effective activation energy of reduction $E_{30} = 19\cdot 4 \pm 5\cdot 1$ kcal differs greatly from the value 47 kcal which is given by Šušunov, Sadovnikova and Andreev[9]. The difference can be explained by a different way of preparation of the barium sulphate which has been used by the mentioned authors[9] in kinetic measurements. Further on, a significant effect of the content of barium carbonate in the original sample on the reaction rate of reduction has been found (Fig. 3–5). The effect of the carbonate content could be explained by a higher degree of dispersity of the active solid phase (barium sulphate), by a greater defectness of the crystal lattice of the barium sulphate, or by a greater porosity of the solid phase in consequence of the dissociation of the barium carbonate.

LIST OF SYMBOLS

$a, b, c,$	
e, f, g	exponents in rate equations (3), (7), and (8)
C_3	integration constant in equation (5)
E_{30}	average value of effective activation energy of reduction of the barium sulphate with hydrogen (kcal)
k_{30}	rate constant of reduction of barium sulphate with hydrogen (min^{-1})
k_D, k_E	rate constants of reactions (D) and (E) in equations (7) and (8)

k'_D, k'_E constants in relation (9)

m mole fraction of barium carbonate in sample

r_D, r_E rates of reactions (D) and (E) defined by equations (7) and (8)

r_x rate of barium sulphite formation

r_y reaction rate of reduction of barium sulphate with hydrogen defined by relation (1) (min^{-1})

s standard deviation (%)

Δy average deviation of experimental and calculated value of y (%)

x, y, z mole fractions of barium sulphite, sulphide, sulphate in the solid

τ time (min)

REFERENCES

1. Pozin E. M.: *Technologija Mineralnych Solej.* Goschimizdat, Moscow 1961.
2. Osamu Kamiike: J. Soc. Chem. Ind. Japan *46*, 879 (1943); Chem. Abstr. *42*, 6996 (1948).
3. Salvi G., Fiumara A.: Riv. Comb. *12*, 525 (1958); Chem. Abstr. *53*, 3622 (1959).
4. Gavrilova Z. F., Safilin N. S.: Chim. promyšlennost, Inform. Nauč. Tech. Zb. *3*, 32 (1965); Chem. Abstr. *64*, 1692 (1966).
5. Mostowitsch W.: Metalurgie *6*, 463 (1909).
6. Wells A. E.: J. Ind. Eng. Chem. *8*, 771 (1916).
7. Marino L., Danesi D.: Gazz. Chim. Ital. *43 I*, 429 (1913).
8. Někrič M. I.: Ž. Prikl. Chim. *11*, 885 (1938).
9. Šušunov V. A., Sadovnikova G. I., Andrejev B. Y.: Ž. Fiz. Chim. *28*, 1472 (1954).
10. Culver R., Hamdorf C. J., Spooner E. C. R.: J. Appl. Chem. (London) *8*, 810 (1958).
11. Hersch P.: Brit. Pat. 707323, 750254 (1954).
12. Lux H.: *Anorganisch-chemische Experimentierkunst,* 2. Aufl., p. 66. Barth Verlag, Leipzig 1959.
13. Mocek K., Erdös E.: This Journal *36*, 494 (1971).
14. Bareš J.: *Thesis.* Czechoslovak Academy of Sciences, Prague 1962.
15. Hillebrand W. F., Lundell G. E., Bright H. A., Hoffman J. I.: *Vybrané metody anorganické analysy.* Published by SNTL, Prague 1958.
16. Mareček J., Erdös E.: This Journal *35*, 1803 (1970).
17. Čůta F.: *Analytická chemie odměrná,* p. 194, 335. Published by Nakladatelství ČSAV, Prague 1956.
18. D'Ans J., Lax E.: *Taschenbuch für Chemiker und Physiker,* p. 883. Springer, Berlin 1943.
19. Kubashewski O., Evans E. L.: *Metallurgical Thermochemistry,* 2nd Ed. Pergamon Press, London 1955.
20. Adami L. H., Conway K. C.: Natl. Bur. Mines, R. I. *1966*, 6822.
21. Vvedenskij A. A.: *Termodynamické výpočty petrochemických pochodů,* p. 243. Published by SNTL, Prague 1963.
22. Rektorys K.: *Přehled užité matematiky,* p. 1067, 410. Published by SNTL, Prague 1968.
23. Pečkovskij V. V., Ketov A. N.: Ž. Prikl. Chim. *33*, 1719 (1960).
24. Pečkovskij V. V., Ketov A. N.: Zb. Nauč. Tr. Permsk. Polytechn. Inst. *10*, 3−32 (1961); Chem. Abstr. *57*, 16120 (1962).
25. Levenspiel O.: *Theorie a výpočty chemických reaktorů,* p. 344. Published by SNTL, Prague 1967.
26. Langmuir I.: J. Am. Chem. Soc. *38*, 2263 (1916).

Translated by the author (E. E.).