

KINETIC ANALYSIS OF THE SYSTEM BARIUM SULPHITE-HYDROGEN

K. MOCEK and E. ERDÖS

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Prague 2*

Received February 25th, 1972

The kinetics of heterogeneous reactions in the system barium sulphite-hydrogen have been measured in a fixed-bed reactor under differential conditions with respect to the gas phase. The rate data have been quantitatively treated for the case of the most probable scheme of two consecutive reactions, *i.e.* the disproportionation of the barium sulphite and the subsequent reduction of the barium sulphate with hydrogen to barium sulphide. The rate constant of disproportionation in the hydrogen is fifty times up to one hundred times higher under the same experimental conditions than the rate constant of the reduction of the barium sulphate formed by disproportionation. From the temperature dependence of rate constants the effective energies of activation have been evaluated for the disproportionation of the barium sulphite as 45.7 kcal and for the reduction of the barium sulphate as 30.3 kcal. A significant catalytic effect of the presence of hydrogen in the gas phase on the disproportionation of the barium sulphite has been found. The reaction rate of reduction of the barium sulphate, formed by disproportionation, increases with the partial pressure of hydrogen approximately in a linear manner in the range of 0.1 up to 1.0 atm. The presence of the water vapour reduces the rate of reduction of the barium sulphate with hydrogen in the range of partial pressures from 0 up to 18.7 Torr.

The present paper represents a continuation of the previous work¹, where it has been shown that at least four heterogeneous reactions may be assumed in the system barium sulphite-hydrogen. There is a rather complicated system which cannot be quantitatively described in the case of a higher number of reactions than two, since then it is not possible — without further assumptions — to determine the conversion degrees of individual reaction steps and, consequently, their reaction rates. The most probable scheme of two consecutive reactions, *i.e.* the disproportionation of the barium sulphite and the reduction of the barium sulphate with hydrogen to sulphide, has been selected on the basis of published results¹⁻³. There is an additional advantage of this reaction scheme, namely, that both reactions mentioned above can be studied as isolated reactions^{2,3} with the aim to find out the forms of pertinent kinetic equations. The most suitable expression for the disproportionation of the barium sulphite in nitrogen² has been obtained in the form

$$r_{20} = k_{20}x^{5/3}(1-x)^{4/3} \quad (1)$$

and for the reduction of the barium sulphate with hydrogen³ in the form

$$r_{30} = k_{30}y^{1/2}(1-y)^{1/2} \quad (2)$$

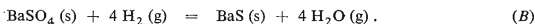
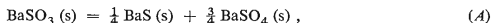
Both reactions, namely, are taking place at a measurable rate in the range of temperatures at which the system barium sulphite-hydrogen has been investigated. The scheme proposed for the quantitative description of the system makes possible to compare the rate data obtained in the

study of isolated reactions^{2,3} with the data of the system barium sulphite-hydrogen, and to evaluate the effects of individual variables on the rates of both reaction steps taking part in the process.

We aimed at obtaining a sufficient experimental material for a system which has not yet been studied kinetically, and at judging the feasibility of the conversion of the barium sulphite to the barium sulphide which represents the end-product of the action of hydrogen onto the barium sulphite. From the physico-chemical point of view, the present paper represents a contribution to the kinetics of heterogeneous reactions between gases and solids.

EXPERIMENTAL AND RESULTS

The chemicals¹, the analytical methods^{1,2}, the apparatus and the measuring procedure³ have been published already. It has been shown in the previous paper¹ that the experimental data of the system barium sulphite-hydrogen can be interpreted by two consecutive reactions, *i.e.* the disproportionation and the reduction of the barium sulphate to sulphide



Let us assume that the rate equations for the reactions (A) and (B) will be of the same general form as in the case of isolated reactions^{2,3}. If we denote the rate of the reaction (A) as r_2 and the rate of the equation (B) as r_3 we can write the general expressions for the reaction rate in the forms

$$r_2 = k_2 x^a y^b z^c, \quad r_3 = k_3 y^e z^f, \quad (3), (4)$$

where k_2 and k_3 are the rate constants of simultaneous partial processes. The optimum values of exponents a , b , c , e , and f were determined by the following procedure. Curves have been drawn through the experimental values of the time dependences of x , y , and z and the rates of the sulphide formation r_y , of the sulphate formation r_z , and of the sulphite decrease r_x have been evaluated by graphical differentiation. The measurable rates of r_y , r_z , and r_x can be expressed from the equations for r_2 and r_3 and from the stoichiometry of reactions (A) and (B) by means of relations

$$r_y = \frac{1}{4} k_2 x^a y^b z^c + k_3 y^e z^f, \quad (5)$$

$$r_z = \frac{3}{4} k_2 x^a y^b z^c - k_3 y^e z^f, \quad r_x = -k_2 x^a y^b z^c. \quad (6), (7)$$

From the courses of r_y , r_z , and r_x , the extreme values of the following rates were determined: the first and the second maximum of the sulphide formation, $(r_y)_I$ and $(r_y)_{II}$, the maximum of the sulphate decrease, $(-r_z)$, as well as the content of individual components in the extremes. The values of exponents in rate equations were selected in the vicinity of optimized values which have been obtained in the kinetic study of both isolated reactions^{2,3}. From the condition $r_z = 0$ and from the composition of the solid at this point, the ratio of the rate constants k_2/k_3 have been calculated by means of the equation (6) for a series of kinetic equations with variable exponents. By means of the ratio of k_2/k_3 and of the five extremes, an average value of the constants k_3 and its average deviation in percents were calculated. Some types of the rate equations and the average deviation of the constant k_3 are given in the Table I which is, however, of informatory

value only, and the results of this treatment were considered as a first approximation. Nevertheless, two important facts are evident from the Table I. Better results were obtained with a symmetrical form for the rate equation of the reduction of the barium sulphate ($e = f$) and with the sum of exponents ($e + f$) close to unity. For the disproportionation it is more advantageous if the concentration terms x and z are stressed in the rate equation. The determination of the ratio k_2/k_3 , however, is very sensitive to the precise composition of the solid at the point of $r_z = 0$. Therefore, from all the five extremes of the reaction rates (Table II) the minimum of the average deviation of the constant k_3 has been determined for selected values of the ratio k_2/k_3 . From the Table II it is evident, that the best results have been obtained for the sum of exponents ($a + b + c = 3$) at the minimum value of the exponent b . The minimalization resulted in optimum values of exponents in the rate equations of the partial processes (3) and (4). The rate equation (4) is of the same forms as the rate equation which has been proposed in the study of the isolated reduction of the barium sulphate by hydrogen³. The results of the first approximate procedure in the treatment of rates in extremes (Table I), and in the majority of cases the minimalization of deviations (Table II) have shown that it is advantageous to stress the concentration terms x and z in the rate equation (3) and to neglect practically the exponent b . Hereafter, the rate equation (3) was used in the form

$$r_2 = k_2 x^{5/3} z^{4/3} . \quad (8)$$

The rate equations (5)–(7) may be, therefore, transformed into the concrete forms

$$-dx/d\tau = k_2 x^{5/3} z^{4/3} , \quad (9)$$

$$dy/d\tau = \frac{1}{4} k_2 x^{5/3} z^{4/3} + k_3 y^{1/2} z^{1/2} , \quad (10)$$

$$dz/d\tau = \frac{3}{4} k_2 x^{5/3} z^{4/3} - k_3 y^{1/2} z^{1/2} . \quad (11)$$

TABLE I

Types of Rate Equations r_2 , r_3 and Average Deviation of Constant k_3

$r_2/k_2 =$	$r_3/k_3 =$	Average deviation	
		$\pm \delta k_3$ %	k_2/k_3
$xy^{2/3}$	$y^{1/2} z^{1/2}$	32.7	19.2
$xy^{1/3} z^{1/3}$	$y^{1/2} z^{1/2}$	19.6	15.7
$xz^{2/3}$	$y^{1/2} z^{1/2}$	13.1	12.8
$x^{3/2} y^{3/2}$	$y^{1/2} z^{1/2}$	55.3	189.3
$x^{3/2} y z^{1/2}$	$y^{1/2} z^{1/2}$	29.0	139.8
$x^{3/2} y^{1/2} z$	$y^{1/2} z^{1/2}$	18.5	103.3
$x^{3/2} z^{3/2}$	$y^{1/2} z^{1/2}$	18.1	76.3
$xz^{2/3}$	$y^{2/3} z$	14.5	8.3
$xz^{2/3}$	$y^{1/3} z^{2/3}$	16.6	14.2
$xz^{2/3}$	$y^{2/3} z^{2/3}$	12.7	9.8
$xz^{2/3}$	$y^{1/2} z^{2/3}$	14.0	11.8

The suitability of the proposed equations has been tested by the reproduction of the primary time dependences of x , y , and z . For this purpose, the set of differential equation (9), (10), and (11) has been solved numerically by the Runge-Kutta's method of the fourth order on the computer Hewlett-Packard (HP 2116 B) under the condition

$$x + y + z = 1. \quad (12)$$

The precise values of the constants k_2 and k_3 have been computed by the minimalization of the function

$$f(k_2, k_3) = \sum_{i=1}^N p_i [(\bar{x}_i - x_i)^2 + (\bar{y}_i - y_i)^2 + (\bar{z}_i - z_i)^2] \quad (13)$$

TABLE II

Optimization of Exponents in Rate Equation (3)

Values of exponents			$k_3 \cdot 10^2$ min^{-1}	k_2/k_3	Average deviation
a	b	c			$\pm \delta k_3$ % rel.
1	0	1/2	1.78	9.5	10.2
1	0	2/3	1.77	11.5	11.1
4/3	0	2/3	1.46	19.0	5.9
5/4	0	3/4	1.55	18.0	6.1
6/5	0	4/5	1.57	18.0	7.2
2	0	1	1.32	52.0	8.0
3/2	0	3/2	1.43	54.0	6.5
9/5	0	6/5	1.31	56.0	4.7
3/2	0	1	1.39	33.0	3.3
3/2	1/4	3/4	1.45	37.0	4.1
3/2	1/2	1/2	1.50	42.0	5.3
3/2	3/4	1/4	1.55	48.0	6.3
3/2	0	3/2	1.43	54.0	6.5
3/2	1/4	5/4	1.45	64.0	7.1
3/2	1/2	1	1.51	72.0	8.0
3/2	3/4	3/4	1.54	85.0	9.2
3/2	1	1/2	1.66	90.0	10.2
3/2	5/4	1/4	1.77	98.0	11.5
5/3	0	4/3	1.35	56.0	3.8
5/3	1/3	1	1.39	68.0	3.1
5/3	2/3	2/3	1.38	88.0	3.7
5/3	1	1/3	1.46	102.0	5.2

TABLE III
Values of Rate Constants in System Barium Sulphite-Hydrogen

Temperature °C	$p(\text{H}_2)$ atm	$p(\text{H}_2\text{O})$ Torr	$k_2 \cdot 10^2$ min^{-1}	$k_3 \cdot 10^2$ min^{-1}
638.3	1.0	0	23.70	0.585
677.5	1.0	0	66.11	1.130
717.6	1.0	0	188.33	2.207
677.5	0.5	0	52.96	0.770
677.8	0.1	0	31.67	0.515
677.6	1.0	18.7	65.56	0.485
677.6	1.0	3.9	55.00	0.915

by means of the screening method. The time dependences of x , y , and z were then reproduced from the optimum values of k_2 and k_3 for all the experimental conditions (Table III) and compared with the experimental values (Figs 1–4). The rate equations of the disproportionation of the barium sulphite in the hydrogen and of the reduction of the barium sulphate, formed by disproportionation, with hydrogen in the forms

$$r_2 = k_2 x^{5/3} z^{4/3}, \quad r_3 = k_3 y^{1/2} z^{1/2} \quad (8), (14)$$

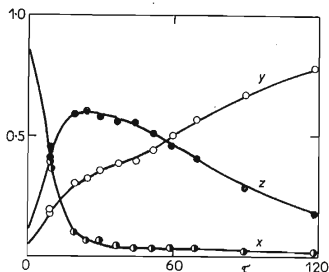


FIG. 1

Time Course of Content of Solid Phases
in System Barium Sulphite-Hydrogen

t 677.5°C, $p(\text{H}_2)$ 1 atm, \circ BaS, \bullet BaSO₄,
 \ominus BaSO₃, curves fitted according to Eqs
(9)–(11).

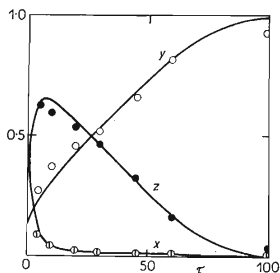


FIG. 2

Time Course of Content of Solid Phases
in System Barium Sulphite-Hydrogen

t 717.6°C, $p(\text{H}_2)$ 1 atm, \circ BaS, \bullet BaSO₄,
 \ominus BaSO₃, curves fitted according to Eqs
(9)–(11).

TABLE IV

Average Deviations between Experimental and Calculated Values of x , y , and z

Temperature °C	$p(\text{H}_2)$ atm	$p(\text{H}_2\text{O})$ Torr	Deviations			Average deviation %
			$\pm\Delta x$ %	$\pm\Delta y$ %	$\pm\Delta z$ %	
638.3	1.0	0	4.4	3.6	2.0	3.4
677.5	1.0	0	1.4	1.9	1.4	1.6
717.6	1.0	0	0.6	3.4	2.6	2.2
677.5	0.5	0	1.9	2.0	2.7	2.2
677.8	0.1	0	4.7	2.0	3.2	3.3
677.6	1.0	18.7	1.7	1.6	1.5	1.6
677.6	1.0	3.9	2.0	1.4	1.9	1.8

with the optimized values of k_2 and k_3 reproduce the primary experimental data with an average deviation of $\pm 2.3\%$ (Table IV). The dependence of the rate constant of disproportionation of the barium sulphite, k_2 , on the partial pressure of hydrogen is evident from the Table III. From the temperature dependences of the rate constants of the partial processes k_2 and k_3 the effective activation energies were evaluated of the disproportionation of the barium sulphite in hydrogen E_2 and of the reduction of the barium sulphate, formed by disproportionation, with hydrogen E_3 . The

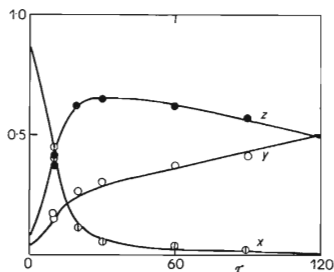
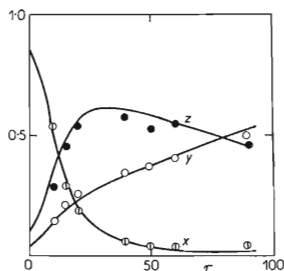


FIG. 3

Time Course of Content of Solid Phases in System Barium Sulphite-Hydrogen

t 677.5°C, $p(\text{H}_2)$ 0.5 atm, \circ BaS, \bullet BaSO₄, \ominus BaSO₃, curves fitted according to Eqs (9)–(11).

FIG. 4

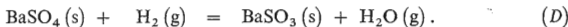
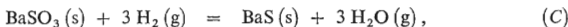
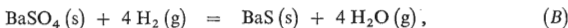
Time Course of Content of Solid Phases in System Barium Sulphite-Hydrogen

t 677.5°C, $p(\text{H}_2)$ 1.0 atm, $p(\text{H}_2\text{O})$ 18.7 Torr, \circ BaS, \bullet BaSO₄, \ominus BaSO₃, curves fitted according to Eqs (9)–(11).

constants of the linearized Arrhenius equation have been determined by the method of the least squares, and from the slopes the value of the effective activation energies have been determined as E_2 45.7 kcal and E_3 30.3 kcal.

DISCUSSION

In the system barium sulphite-hydrogen, the following four reactions have been considered in which only the known stable compounds do appear:



The same set of reactions, however, may be admitted even for the reduction of the barium sulphate with hydrogen which has been studied as an isolated reaction³. The facultative reaction schemes for the system barium sulphite-hydrogen have been discussed in previous papers^{1,3}, and for the quantitative description of the system, the mechanism of two consecutive reactions has been selected on the basis of experimental results: the disproportionation of the barium sulphite and the reduction of the barium sulphate, formed by disproportionation, with hydrogen to barium sulphide¹. The published mechanism of the reduction of the barium sulphate with hydrogen⁴ which would be applicable even for the system barium sulphite-hydrogen has not been considered here for the reasons given previously^{1,3}. In the kinetic measurements of the system barium sulphite-hydrogen, a significant effect has been detected of the presence of hydrogen in the gas phase on the disproportionation of the barium sulphite. The dependence of the rate constant of disproportionation k_2 on the partial pressure of hydrogen exhibit an evident saturation character (Table III). From the dependence of the rate constant of disproportionation in nitrogen on the partial pressure of the water vapour found previously², the catalytic constant of the water vapour has been computed as $k(\text{H}_2\text{O}) = 1.014 \cdot 10^{-2} (\text{min}^{-1} \text{Torr}^{-1})$, and by means of this value and of the value of k_2 at 677.5°C and $p(\text{H}_2) = 1 \text{ atm}$, the catalytic constant of hydrogen has been computed as $k(\text{H}_2) = 0.0825 \cdot 10^{-2} (\text{min}^{-1} \text{Torr}^{-1})$. It is evident from the comparison of both constants that the catalytic effect of the water vapour on the disproportionation of the barium sulphite is approximately by one order higher than the catalytic effect of hydrogen. The reaction rate of the reduction of the barium sulphate formed by disproportionation with hydrogen at a temperature of 677.6°C is approximately a linear function of the partial pressure of hydrogen in the range of pressures from 0.1 to 1.0 atm (Table III). The presence

of the water vapour in the gas phase diminishes the rate of reduction of the barium sulphate with hydrogen, as it is evident from the Table III. From the temperature dependences of the rate constants of both partial processes, the effective activation energy of the disproportionation of the barium sulphite in hydrogen E_2 has been computed as 45.7 kcal, and the effective activation energy of the reduction of the barium sulphate, formed by disproportionation, with hydrogen E_3 has been computed as 30.3 kcal. The catalytic effect of the hydrogen on the disproportionation is evident even from the comparison of the effective activation energies of disproportionation in the nitrogen E_{20} 61.4 kcal² and in the hydrogen E_2 45.7 kcal. The difference between the values of effective activation energies of the reduction of the barium sulphate with hydrogen $E_{30} = 19.4$ kcal³ and of the reduction of the barium sulphate, formed by disproportionation, E_3 30.3 kcal, may be explained by the different way of preparation of the solid phase used in kinetic measurements.

The results of the kinetic measurements in the system barium sulphite-hydrogen may be summarized into the following conclusions: 1. The rate data may be interpreted with a sufficient accuracy by a mechanism of two consecutive reactions; the disproportionation of the barium sulphite and the reduction of the barium sulphate, formed by disproportionation, with hydrogen to the barium sulphide. 2. The rate constant of the disproportionation k_2 , is fifty times up to one hundred times higher than the rate constant of the reduction, k_3 , under the same experimental conditions. 3. With the same content of the carbonate in the original sample, the values of the rate constants k_3 , evaluated for the partial process in the system barium sulphite-hydrogen, are in a good agreement with the values of the rate constants k_{30} obtained in the study of the isolated reduction of the barium sulphate with hydrogen³.

We thank Dr J. Strublová for her technical assistance and Dr P. Voňka, Department of Physical Chemistry, Institute of Chemical Technology for programming and computing work.

LIST OF SYMBOLS

a, b, c, e, f	exponents in general forms of rate equations
E_2	effective activation energy of disproportionation in hydrogen (kcal)
E_{20}	effective activation energy of disproportionation in nitrogen (kcal)
E_3	effective activation energy of reduction of barium sulphate formed by disproportionation, in system barium sulphite-hydrogen (kcal)
E_{30}	effective activation energy of reduction of barium sulphate in system barium sulphate-hydrogen (kcal)
k_2	rate constant of disproportionation in hydrogen (min^{-1})
k_{20}	rate constant of disproportionation in nitrogen (min^{-1})
k_3	rate constant of reduction of barium sulphate, formed by disproportionation, in system barium sulphite-hydrogen (min^{-1})
k_{30}	rate constant of reduction of barium sulphate in system barium sulphate-hydrogen (min^{-1})
δk_3	average deviation of rate constant k_3 (% rel.)

$k(\text{H}_2)$	catalytic constant of hydrogen ($\text{min}^{-1} \text{Torr}^{-1}$)
$k(\text{H}_2\text{O})$	catalytic constant of water vapour ($\text{min}^{-1} \text{Torr}^{-1}$)
N	number of experimental determinations in equation (13)
p_i	weight of experimental determination in equation (13)
$p(\text{H}_2)$	partial pressure of hydrogen (atm)
$p(\text{H}_2\text{O})$	partial pressure of water vapour (Torr)
r_2	rate of disproportionation in system barium sulphite-hydrogen (min^{-1})
r_{20}	rate of disproportionation in nitrogen (min^{-1})
r_3	rate of reduction of barium sulphate formed by disproportionation in system barium sulphite-hydrogen (min^{-1})
r_{30}	rate of reduction of barium sulphate in system barium sulphate-hydrogen (min^{-1})
r_x	rate of decrease of barium sulphite (min^{-1})
r_y	rate of formation of barium sulphide (min^{-1})
r_z	rate of formation of barium sulphate (min^{-1})
t	temperature ($^{\circ}\text{C}$)
τ	time (min)
x, y, z	mole fraction of barium sulphite, sulphide and sulphate
x_i, y_i, z_i	experimental values of $x, y,$ and z in equation (13)
$\bar{x}_i, \bar{y}_i, \bar{z}_i$	calculated values of $x, y,$ and z from the equation (13)
$\Delta x, \Delta y, \Delta z$	average deviations from experimental values of x, y and z in absolute percents

REFERENCES

1. Mocek K., Erdös E.: This Journal 38, 7 (1973).
2. Mocek K., Erdös E.: This Journal 37, 3376 (1972).
3. Mocek K., Erdös E.: This Journal 37, 3386 (1972).
4. Šušunov V. A., Sadovnikova G. I., Andrejev B. Y.: Ž. Fiz. Chim. 28, 1472 (1954).

Translated by the author (E. E.).