

REDUCTION OF THE BARIUM SULPHITE BY HYDROGEN

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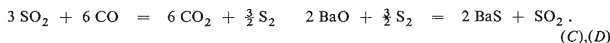
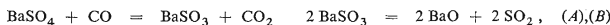
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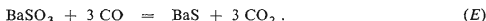
The reaction rate of reduction of the solid barium sulphite with hydrogen has been measured under differential conditions at temperatures of 640–720°C. A complete analysis of the solid after reduction and the analysis of the gas phase during the reduction have shown that at minimum two heterogeneous reactions take place in the action of hydrogen on the barium sulphite. Seven reaction schemes are proposed and discussed consisting of two up to four reactions. It has been shown that it is possible to interpret the experimental data by a mechanism of two consecutive reactions: the disproportionation of the barium sulphite and the consecutive reduction of the barium sulphate with hydrogen to barium sulphide.

The rate of the heterogeneous reaction between the solid barium sulphite and hydrogen has not yet been kinetically investigated. Our first experimental results have shown already that there is no simple reaction but a sequence of at least two reactions. In the range of temperatures at which the reduction rate has been measured, the disproportionation of the original barium sulphite to barium sulphate and barium sulphide takes place to a significant extent. In a consecutive reaction step the barium sulphate is reduced with hydrogen. The final product of the disproportionation and of the reduction reactions is the barium sulphide. The rate of disproportionation of the barium sulphite and the rate of the reduction of barium sulphate with hydrogen have been studied previously^{1,2} as isolated reactions. In the system barium sulphite–hydrogen, four heterogeneous reactions have been considered as probable on the basis of thermodynamic analysis in which only stable compounds have appeared. This paper represents an attempt at an interpretation of experimental results obtained in the measurement of the rate of reaction between the barium sulphite and hydrogen from the point of view of a probable mechanism.

There exist only very few data on the behaviour of the barium sulphite with respect to reducing agents, whereas, the reduction of the barium sulphate (or barite) which is the basis of the industrial production of barium compounds is generally known³. The thermographic investigation of the systems barium sulphite–carbon monoxide, barium sulphate–carbon monoxide, and barium sulphite–argon has been carried out by Pečkovskij and Ketov⁴ at temperatures from 0 up to 1100°C. These authors assume that the reduction of the barium sulphate takes place through an intermediate product of barium sulphite and suggest a mechanism of the thermal decomposition of the barium sulphite in the presence of the carbon monoxide consisting of following reactions



By summing the equations (B), (C) and (D) we obtain:



Finally, Miyamoto⁵ found that the main products of the reduction of the barium sulphite with hydrogen in a silent electric discharge are the barium sulphide in the solid and the hydrogen sulphide in the gas.

EXPERIMENTAL

The barium sulphite has been prepared by a heterogeneous reaction between the solution of the sodium sulphite and the solid barium carbonate at a temperature of 25°C for 24 h. The molar ratio of the sulphite to the carbonate in the reaction mixture has been always 1.5 : 1. After the reaction has been finished, the product has been separated from the mother liquor, thoroughly washed with water on the fritted glass filter (G 3), till the filtrate gave no reaction with the phenolphthaleine, and sucked off. The barium sulphite has been dried in air at laboratory temperature. The dried sample has been crushed, and the fraction of the particle size of 0.25–0.33 mm has been used for measurements. The sample contained 88.5 wt. % of the barium sulphite, 10.0 wt. % of the barium carbonate, and 1.7 wt. % of humidity in average. The sodium sulphite was a pure reagent (Spolana, Neratovice) containing at minimum 97 wt. % of the sodium sulphite. The barium carbonate has been prepared by saturating the solution of barium hydroxide (a.r. Lachema, Brno) at 25°C with a purified gaseous carbon dioxide from a pressure tank. The barium carbonate has been washed, sucked off, and dried in air at a laboratory temperature. The potassium iodide was an analytical grade reagent (Lachema, Brno). The sodium thiosulphate was an analytical grade reagent (Lachema, Brno) containing at minimum 99 wt. % of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$. It has been used after a twofold crystallization from the commercial reagent. The potassium bromate has been used after a twofold crystallization from the pure reagent (Lachema, Brno). The anhydrous used has been an English reagent (The British Drug Houses Ltd., Poole, England). The iodine used has been resublimed from an analytical grade reagent. Metals for calibration of the thermocouple were of the following quality: the antimony twice sublimed (Kovohutě, Vestec), the aluminium was zone-melted (Kovohutě, Vestec), and the zinc was granulated for laboratory purposes (USSR). The nitrogen has been used with an oxygen content of the order of 10^2 p.p.m. (sometimes even 10^3). The quality of nitrogen has been periodically tested by means of an oxygen analyzer according to Hersch⁶ which has been modified for measurement of low concentrations of oxygen. In all the measurements the oxygen has been removed from nitrogen in a copper tower⁷ which has been filled up with a mixture of cupric oxide with silica. The purified nitrogen contained at maximum 20–30 p.p.m. of oxygen. The copper catalyst has been reactivated for some hours with a nitrogen–hydrogen mixture at a temperature of about 220°C. The hydrogen used has been of electrolytic quality with an oxygen content of the order of 10^1 p.p.m. The quality of hydrogen has been periodically determined with an oxygen analyzer⁶ for low oxygen concentrations. In measurement of the reaction rates in the system barium sulphite–hydrogen, the traces of oxygen have been always removed from hydrogen in a copper tower⁷ whereby the oxygen content decreased to units of p.p.m. The remaining substances used have been of an analytical grade purity.

Apparatus and procedure of measurement. The kinetic measurements in the system barium sulphite-hydrogen have been carried out in a flow apparatus under differential conditions with respect to the gas phase. The maximum change of the gas phase concentration on passing the reactor amounted to 0.5%. The reaction conditions have been selected in such a way that the resulting rate has not been affected by the transport of the reacting gas to the surface of the solid, as it has been shown in experiments with a variable flow rate. Since, in addition to the reduction, the disproportionation of the barium sulphite, in which heat is set free, is taking place, the temperature drop between the surface of the solid and the main stream of the gas has been estimated. The calculation has been carried out according to Hougen and Watson⁸ and it has been found that the temperature drop is not significant (1.5°C). Apparatus and the procedure of measurement have been identical with those used previously².

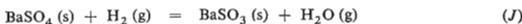
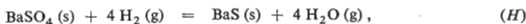
Analysis of the original sample. In the sample of the barium sulphite the content of the barium sulphite, and the total content of the sulphur dioxide and of carbon dioxide have been determined. The content of barium carbonate has been calculated from the difference of both determinations. The content of barium sulphite has been determined in the way described in the book by Čůta⁹. The solid sample has been dissolved in an acidified solution of iodine the excess of which has been titrated with the sodium thiosulphate. The total content of the sulphur dioxide and carbon dioxide has been determined in such a way that both gaseous components have been set free from the solid sample with perchloric acid and displaced with nitrogen into an absorber. The gases have been absorbed in a solution of barium hydroxide, the excess of which has been determined by titration¹⁰ with HCl.

Analysis of the solid after reduction. In the sample after reduction, the content of the barium sulphide, sulphite, and sulphate has been determined by an analytical procedure described previously¹¹.

Analysis of the gas phase. In the gas phase, the content of the water vapour has been determined continually. The gas mixture at the reactor outlet has been led into one of two parallelly connected U-tubes filled up with granulated anhydron. 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 weight of the filled up absorber amounted to about 45 g and the weight of the anhydron amounted to 8–10 g. The samples of the barium sulphite used in the rate measurement contained 88.9 mol % of the barium sulphite and 11.1 mol % of the barium carbonate. For the reasons given in the paper², it has been necessary to correct the weight increments in absorbers to the amount of water vapour formed in the reaction between the dissociation carbon dioxide and hydrogen. The corrections have been calculated for weight increments in individual time intervals.

RESULTS AND DISCUSSION

In the system barium sulphite-hydrogen, the following four reactions have been considered as possible in which only the known stable compounds do appear. The literature research on thermodynamics properties of reacting and final substances¹²⁻²¹



has shown that the weakest point consists in the data on the barium sulphide and sulphite which either exhibit a great dispersion or have been estimated approximately by means of empirical rules²⁰. It has been found from the calculated values of equilibrium constants of the reactions (F), (G), and (H) that these reactions are practically irreversible in the temperature range of 400–800°C, and that the barium sulphite is a thermodynamically unstable substance. These conclusions are in an agreement with our previous results which were obtained in the measurement of the rate of reduction of the barium sulphate with hydrogen². The probability of the barium sulphite formation according to the reaction (J) increases with increasing temperature. It has not been possible, therefore, to eliminate any of the reactions considered (F), (G), (H) and (J). It is probable that in the system barium sulphite–hydrogen at temperatures above 600°C, the reaction (G), *i.e.* the disproportionation of the barium sulphite and at least one of the reduction reaction, will always take place.

The effect of temperature, of the partial pressure of hydrogen and of the partial pressure of the water vapour on the rate of heterogeneous reaction has been investigated experimentally in the system barium sulphite–hydrogen. The results of measurements have been obtained as time dependences of the content of sulphite, sulphide, and sulphate in the reacted barium sulphite (Fig. 1 and 2). It is evident from these dependences that, in addition to the thermal decomposition (disproportionation) of the barium sulphite, one or more reduction reactions are taking place. The time course of the mole fraction of the sulphate (curve *z* in the Fig. 1) proves that the dis-

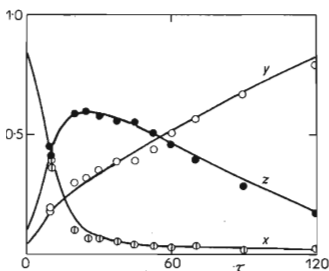


FIG. 1

Time Course of Content of Solid Phase (in mole fractions) in System Barium Sulphite-Hydrogen at 677.5°C and Partial Pressure of Hydrogen of 1 atm

x BaSO₃, *y* BaS, *z* BaSO₄.

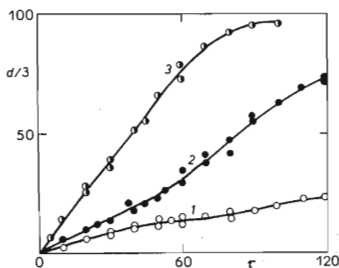


FIG. 2

Effect of Temperature on Reaction between Solid Barium Sulphite and Hydrogen
1 638.3°C, 2 677.5°C, 3 717.6°C.

proportionation of the barium sulphite takes place to a significant extent. The content of the barium sulphate in the solid increases very rapidly at the start of the reaction till it reaches a maximum value of $z \approx 0.60$, and then decreases owing to the reduction with hydrogen. The steep increase of the barium sulphate content at the start of the reaction can be explained in terms of the reaction scheme considered [(F) to (J)] by disproportionation only in which the sulphate is formed. The minimum degree of conversion of the reaction (G) can be estimated according to stoichiometry as having the value of 0.8, since the sulphate can be simultaneously reduced by hydrogen.

It was the aim to find such a reaction scheme which would not be complicated and, at the same time, it would well reproduce the experimental data. In the selection of a suitable reaction scheme, the experimental findings have been considered which will be mentioned later in this chapter. Under the assumption that in the system barium sulphite-hydrogen the disproportionation and at least one reduction reaction is always taking place, there exist in total seven reaction schemes which are formed by combinations from the set equations of (F) to (J) (Table I).

TABLE I
Summary of Reaction Schemes Formed by Combinations from Set of Equations (F) to (J)

Number of reactions	I	II	III
4	(F), (G) (H), (J)	—	—
3	(G), (F), (J)	(F), (G), (H)	(G), (H), (J)
2	(G), (F)	(G), (H)	(G), (J)

For the combination 4-I, the expressions for the degree of conversion of individual reactions will be derived. As a basis, let us select one mol of the barium sulphite at the start of the reaction. If the amount of the reacting substance reacted according to the reaction (F) is denoted as α , according to the reaction (G) as β , according to the reaction (H) as γ , and according to the reaction (J) as δ , then the number of moles of individual components in the system in the time τ will be determined by relations

$$n(\text{BaS}) \equiv y = \frac{1}{4}\beta + \alpha + \gamma \quad (1)$$

$$n(\text{BaSO}_3) \equiv x = 1 - \beta + \delta - \alpha \quad (2)$$

$$n(\text{BaSO}_4) \equiv z = \frac{3}{4}\beta - \gamma - \delta \quad (3)$$

$$n(\text{H}_2\text{O}) \equiv d = 3\alpha + 4\gamma + \delta \quad (4)$$

By summing the equations (1), (2), and (3) we obtain the following expression

$$x + y + z = 1, \quad (5)$$

which represents the balance of sulphur. By summing the equations (2) and (3) we obtain

$$x + z = 1 - \frac{1}{4}\beta - \gamma - \alpha \quad (6)$$

and by summing the equations (3) and (4)

$$z + d = \frac{3}{4}\beta + 3\alpha + 3\gamma \quad (7)$$

On rearranging the equation (7) and on comparing it with the equation (1) the following relation is obtained

$$z + d = 3\gamma, \quad (8)$$

from which an expression is obtained on combining with the sulphur balance and on eliminating γ

$$4z + 3x + d = 3. \quad (9)$$

This equation represents the balance of oxygen.

From the expression derived it follows that it is sufficient to determine analytically only two arbitrarily selected quantities, *e.g.* the amount of barium sulphide and sulphate, and the remaining two, *i.e.* the barium sulphite and the water of reduction, can be calculated from the relations (5) and (9). It can be easily shown that it is not possible to calculate the degree of conversion of any of the mentioned reactions on the basis of the equations derived above, even if a complete analysis of the system is available. The same expressions and the same conclusion is reached, even in the case of the combination of three reactions. In the case of combination of two

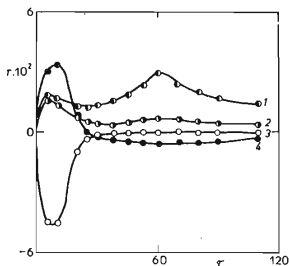


Fig. 3

Dependence of Reaction Rates in System Barium Sulphite-Hydrogen on Time at 677.5°C and Partial Pressure of Hydrogen of 1 atm

$$1 r_d, 2 r_y, 3 r_x, 4 r_z.$$

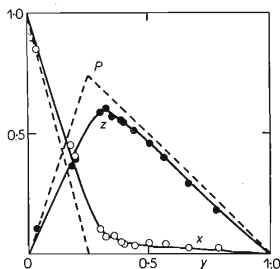


FIG. 4

Reaction Course in System Barium Sulphite-Hydrogen with Elimination of Time Variable at 677.5°C and Partial Pressure of Hydrogen of 1 atm

x BaS, y BaS, z BaSO₄, --- the theoretical limiting courses.

reactions only, it is possible to determine the degrees of conversion of both reactions, even though the expressions for calculating the system composition are identical with the equations (5) and (9). The experimental data obtained have been interpreted by a system of two consecutive reactions: the disproportionation and the consecutive reduction of the barium sulphate with hydrogen to barium sulphide (combination 2-II). The curves have been drawn through the experimental values of time dependences of x , y , z , d , and the reaction rates of formation of the sulphide r_y , of the sulphate r_z , of the water of reduction r_d , and the rate of the sulphite decrease r_x have been determined graphically for experimental values of τ (Fig. 3). It is evident from the Fig. 3 that the course of r_y exhibits two rather distinct maxima, the rate of r_z increases from the start to a maximum, then decreases to zero and in the following it assumes negative values with an appearance of a flat minimum. The rate of the sulphite decrease, r_x , increases initially to a maximum, then decreases and approaches asymptotically the zero value. The combination of reactions 2-III, *i.e.* the disproportionation and reduction of the sulphate to sulphite, is improbable for two reasons. In the first place, the barium sulphide would be formed in one reaction only, *i.e.* in the disproportionation, for which one maximum only has been found¹ in studying this reaction in a nitrogen atmosphere as an isolated reaction; this finding is in contradiction with the experimentally found existence of two maxima of the rate of sulphide formation. In the second place, a very small amount of the sulphite (0.2 to 0.4 wt. %) has been found in a wide range of conversions of the barium sulphate in the reduction of the barium sulphate with hydrogen which has been investigated as an isolated reaction². It has been shown² that this finding is not consistent with the considered combination of reactions.

The combinations of reactions 2-I, *i.e.* the disproportionation and the reduction of the sulphite to sulphide, is excluded because the barium sulphate would be formed in the disproportionation only and would be gradually accumulated in the system. This is in contradiction with reality, since the content of barium sulphate in the solid initially increases till it reaches a maximum value of $z \approx 0.60$, and then decreases in consequence of the reduction with hydrogen. The reaction course at a temperature of 677.5°C and at a partial pressure of hydrogen of 1 atm is illustrated in the Fig. 4 by a dependence of the content of the sulphate (curve z) and sulphite (curve x) on the content of barium sulphide which is the only monotonously increasing quantity in the system. The dotted straight lines in this figure represent the limiting cases for the course of the content of sulphate and sulphite under assumption that initially a complete disproportionation of the sulphite takes place in the system and then the reduction of the formed sulphate with hydrogen occurs. The theoretical course of the sulphate content in this limiting case is given by two abscissas \overline{OP} and \overline{PI} . The experimentally found course of the sulphate content approaches the theoretical course and in the limits (*i.e.* for $y = 0$ and $y = 1$), the values of tangents of the experimental curves are practically identical with the theoretical ones. From the Fig. 4,

therefore, it is possible to deduce even a qualitative conclusion that the rate constant of disproportionation will be substantially higher than the rate constant of the reduction of barium sulphate with hydrogen. It is evident that in the system barium sulphite–hydrogen the disproportionation of the barium sulphite takes place predominantly at the start of the reaction; the product of this disproportionation is the barium sulphate which is reduced by hydrogen in the next reaction step. The reduction of the barium sulphate is frequently interpreted²² by a mechanism of consecutive reactions (*J*) and (*G*), *i.e.* the combination 2-III, which, however, does not seem as probable for the reasons given above. The same conclusion has been reached in the previous paper² too. For the reduction of the barium sulphate, a mechanism is sometimes suggested^{4,23}, expressed by the consecutive reactions (*J*) and (*F*), which, however, proved to be as little probable² as well.

On the basis of experimental findings mentioned in this paper, it is possible to interpret the rate data in the system barium sulphite–hydrogen by a mechanism of two consecutive reactions, *i.e.* the disproportionation of the barium sulphite and the consecutive reduction of the barium sulphate with hydrogen to barium sulphide. In the system barium sulphite–hydrogen it is possible to admit even more complicated reaction schemes, which, however, give no possibility to determine the rates of individual reaction steps without introduction of further assumptions. The scheme of two consecutive reactions proposed here is simple and reproduces qualitatively all the phenomena found experimentally.

We thank Dr J. Strublová for her technical assistance.

LIST OF SYMBOLS

<i>d</i>	number of moles of water vapour in gas phase formed from 1 mole of BaSO ₃
<i>d/3</i>	degree of reduction (%)
<i>r_x</i>	rate of decrease of BaSO ₃ (min ⁻¹)
<i>r_y</i>	rate of BaS formation (min ⁻¹)
<i>r_z</i>	rate of BaSO ₄ formation (min ⁻¹)
<i>r_d</i>	rate of water vapour formation (min ⁻¹)
<i>x, y, z</i>	mole fraction of BaSO ₃ , BaS and BaSO ₄
<i>α, β, γ, δ</i>	degrees of conversion of reactions (<i>F</i>), (<i>G</i>), (<i>H</i>), (<i>J</i>)
<i>τ</i>	time (min)

REFERENCES

1. Mocek K., Erdős E.: *This Journal* 37, 3376 (1972).
2. Mocek K., Erdős E.: *This Journal* 37, 3386 (1972).
3. Pozin E. M.: *Technologija Mineralnych Solej*. Gochimizdat, Moscow 1961.
4. Pečkovskij V. V., Ketov A. N.: *Ž. Prikl. Chim.* 33, 1719 (1960).
5. Miyamoto S.: *Bull. Chem. Soc. Japan* 12, 313 (1937).
6. Hersch P.: *Brit. Pat.* 707 323, 750 254 (1954).

7. Lux H.: *Anorganisch-Chemische Experimentierkunst*, 2, Auf., p. 66. Barth, Leipzig 1959.
8. Hougen O. A., Watson K. M.: *Chemical Process Principles*, Part 3, *Kinetics and Catalysis*, p. 986. Wiley, New York 1948.
9. Čůta F.: *Analytická chemie odměrná*, p. 194, 335. Published by Nakladatelství ČSAV, Prague 1956.
10. Mareček J., Erdős E.: This Journal 35, 1803 (1970).
11. Mocek K., Erdős E.: This Journal 36, 494 (1971).
12. Rossini F. D.: *Selected Values of Chemical Thermodynamics Properties*. Natl. Bur. Std. Circular 500, Washington 1952.
13. Erdős E.: This Journal 27, 1428 (1962).
14. Mareček J., Erdős E.: This Journal 35, 1017 (1970).
15. Ravdel A. A., Novikova N. A.: *Ž. Prikl. Chim.* 36, 1433 (1963).
16. Kelley K. K.: *Bull. U.S. Bur. Mines* 477 (1950).
17. Bricke E. V., Kapustinskij A. F.: *Termičeskije Konstanty Neorganičeskich Veščestv*. Izd. Akad. Nauk SSSR, Moscow—Leningrad 1949.
18. Latimer W. M.: *J. Am. Chem. Soc.* 73, 1480 (1951).
19. Kireev V. A.: *Ž. Obšč. Chim.* 16, 1569 (1946).
20. Karapetjanc M. Ch.: *Chimičeskaja Thermodynamika*, Goschimizdat, Moscow 1949.
21. Erdős E.: This Journal 27, 2273 (1962).
22. Šušunov V. A., Sadovnikova G. I., Andrejev B. Y.: *Ž. Fiz. Chim.* 28, 1472 (1954).
23. Pečkovskij V. V., Ketov A. N.: *Zb. Nauč. Tr. Permsk. Polytech. Inst.* 10, 3—32 (1961); *Chem. Abstr.* 57, 16120 (1962).

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