REACTION OF HYDROGEN SULPHIDE WITH BROMIDE IONS IN A MELT OF LITHIUM AND POTASSIUM BROMIDES*

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On the basis of equilibrium and kinetic studies of the reaction of hydrogen sulphide with bromide ions in an eutectic melt of lithium and potassium bromides at 400—500°C a stoichiometric scheme of the reaction was established, the equilibrium constant was calculated and the kinetic equation of the reaction was derived. The resulting values were compared with the values describing the course of the reaction of hydrogen sulphide with chloride melts. A model was proposed for the studied process, involving the effect of transport phenomena and its applicability was discussed.

In our previous communication[1] we have followed the reaction of chloride ions with hydrogen sulphide in a melt of lithium and potassium chlorides. We have determined the apparent equilibrium constant of this reaction and derived a relation for the reaction rate. In view of the fact that this reaction could in general serve to studying the sulphur compounds in melts, it seemed of interest to know how the found values are affected by the change of the melt or of the anion in the three-component system Li, K, X where X is a halogenide anion. The hitherto commonly used melts in our experiments with halogenides are chloride and bromide eutectica. These melts would also most possibly come into consideration in further studies of sulphur reactions in melts. Therefore the subject of this paper is the study of the reaction of hydrogen sulphide with an eutectic melt of lithium and potassium bromide and comparison of the course of this reaction with that of the reaction of hydrogen sulphide with chloride melts.

EXPERIMENTAL

Experimental arrangement and working procedure were described in paper[1]. Eutectic melt was prepared by weighing appropriate amounts of previously dried (at 450°C) lithium and potassium bromide (60 mol% LiBr and 40 mol% KBr) and by melting the mixture. The melt was purified by a stream of hydrogen bromide whose excess was removed by subsequent bubbling with nitrogen. The chemicals used were of reagent grade purity, hydrogen sulphide, taken from steel flask, was of 99·99% purity.

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RESULTS AND DISCUSSION

With respect to the similarity of the system Li–K–Cl and Li–K–Br it could be expected that the products of the reaction of hydrogen sulphide with bromide ions would be similar as in the reaction with chloride ions, *i.e.* hydrosulphide and hydrogen bromide. The experimentally found ratio of the amount of substance of the formed hydrogen bromide to the amount of reducing substances (mol HBr/mol red. subst. = = 1) has verified this expectation. Hydrogen sulphide reacts with bromide ions of the melt according to the following stoichiometric scheme

$$H_2S_{(g)} + Br^-_{(f)} = HS^-_{(f)} + HBr_{(g)}. \qquad (A)$$
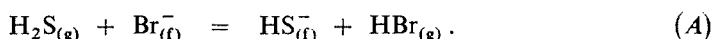
Reciprocal value of the equilibrium constant of the studied reaction is defined as follows

$$K = \frac{p_{H_2S} \cdot a_{Br^-}}{p_{HBr} \cdot a_{HS^-}} = \frac{p_{H_2S} \cdot X_{Br^-} \cdot \gamma_{Br^-}}{p_{HBr} \cdot X_{HS^-} \cdot \gamma_{HS^-}}, \qquad (1)$$

where p_{H_2S} (atm) and p_{HBr} (atm) are partial pressures of hydrogen sulphide and of hydrogen bromide, respectively, a_{Br^-}, a_{HS^-} are the activities of bromide and hydrosulphide ions, X_{Br^-}, X_{HS^-} are the respective mole fractions and γ_{Br^-} and γ_{HS^-} are the activity coefficients of bromide and hydrosulphide ions, respectively.

In our experimental arrangement the highest attainable concentrations of hydrosulphide ions were, expressed in mole fractions, of the order of magnitude 10^{-3}. Concentration of bromide ions corresponds practically to a pure substance, *i.e.* to the case when its activity approaches unity. From these data it is evident that the concentration of hydrosulphide ions is negligible against the concentration of bromide ions. The activity of hydrosulphide ions can be assumed to obey the Henry law and the activity coefficient of hydrosulphide ions should be constant. This assumption is confirmed by the linear dependence of the ratio of partial pressures of hydrogen sulphide to hydrogen bromide on the concentration of hydrosulphide ions (Table I) The slope of this straight line is given by the relation $K \cdot \gamma_{HS^-}/X_{Br^-} \cdot \gamma_{Br^-}$. On the basis of these deductions the apparent equilibrium constant of the reaction of hydrogen sulphide with bromides can be expressed by the relation

$$K' = p_{H_2S}/p_{HBr} \cdot X_{HS^-}, \qquad (2)$$

in which γ_{HS^-}, γ_{Br^-} and X_{Br^-} are included in constant K'. Data for calculating the equilibrium constant K' were obtained by approximation to the equilibrium from the sides of lower and higher than equilibrium concentrations cf hydrosulphide ions. These values are presented in Table I. The value of apparent equilibrium constant

calculated from the mentioned data is $1.525 . 10^5$. The comparable value of equilibrium constant of the reaction of chloride ions with hydrogen sulphide ranges between $4.0 - 4.34 . 10^4$.

The values of equilibrium constant were also calculated from kinetic data[1] using Eq. (3)

$$K'' = k_2/k_1 = F . p_{H_2S}/24.4 . . r . m \left[HS^- \right] , \qquad (3)$$

where k_2 and k_1 are rate constants in both directions of the reaction $(mol\ kg^{-1} . min^{-1}\ atm^{-1})$ and $(min^{-1}\ atm^{-1})$, respectively (see Table II), F is the total flow of gas $(1\ min^{-1})$, r is the reaction rate $(mol\ kg^{-1}\ min^{-1})$, m is the weight of the melt

TABLE I

Data for the Calculation of Equilibrium Constant

p_{HBr} atm	$X_{HS^-} . 10^3$	$X_{HS^-(av.)} . 10^{-5}$	$\dfrac{p_{H_2S}}{p_{HBr}} . 10^{-3}$
$3.12 . 10^{-2}$	0.00997	1.07	0.016
$3.12 . 10^{-2}$	0.01145		
$2.225 . 10^{-4}$	1.598	150.1	2.26
$2.225 . 10^{-4}$	1.404		
$1.925 . 10^{-4}$	1.749	170.0	2.59
$1.925 . 10^{-4}$	1.648		
$1.03 . 10^{-4}$	3.946	320.25	4.85
$1.03 . 10^{-4}$	2.459		

TABLE II

Values of Rate Constants and of the Equilibrium Constant Calculated from Kinetic Data

Temperature °C	k_1 $min^{-1}\ atm^{-1}$	k_2 $mol\ kg^{-1}\ min^{-1}\ atm^{-1}$	K''
400	$6.00 . 10^{-4}$	932.98	$1.56 . 10^6$
450	$2.00 . 10^{-3}$	1 042.8	$5.21 . 10^5$
500	$7.41 . 10^{-3}$	1 143.0	$1.54 . 10^5$
800[a]	—	—	$1.76 . 10^3$

[a] Obtained by extrapolation according to Arrhenius equation.

(kg), $[HS^-]$ is the concentration of hydrosulphide ion $(mol\ kg^{-1})$. The value of equilibrium constant, calculated as just described can be compared with the value obtained from equilibrium measurements after converting molalities to mole fractions. Its value $1.54 . 10^5$ is in good accordance with the value obtained from equilibrium data $(1.525 . 10^5)$. This is a proof that an equilibrium is really established on the interphase boundary between the liquid and gaseous phase, *i.e.* between hydrosulphide and hydrogen sulphide.

When studying the kinetic course of the reaction it was found that the rate of the reaction of hydrogen sulphide with bromide ions depends, in the given experimental arrangement used, on the partial pressure of hydrogen bromide or on the amount of substance of hydrogen bromide leaving the system, wherein the partial pressure of hydrogen bromide is a function of the reaction rate, of the total flow rate of gas through the melt and on the weight of the melt. On the basis of these findings and also with respect to the fact that the concentration of bromide ions is practically constant in the course of the reaction, a kinetic equation was derived for the rate of the studied reaction in the form

$$r = k'_1 . p_{H_2S}/(1 + k_2 . [HS^-] 24.4m/F),\qquad(4)$$

where the meaning of the symbols is the same as in Eq. (3). A comparison of experimental data with those obtained according to the above equation is presented in Figs 1 and 2. As can be seen from the graphs the agreement of both values is fairly good. Consequently, it can be assumed that the experimental data comply with the proposed kinetic equation.

Comparison of the reaction of hydrogen sulphide with chloride or bromide ions revealed that both ions react with hydrogen sulphide according to the same stoichiometric reaction scheme, that the kinetic data obey the same kinetic equation and that the value of equilibrium constants and of reaction rates are lower in the case of bromide ions. This finding is in agreement with the preliminary assumption made on comparing the known values of bond dissociation energies. According to Durant[2] the value of the dissociation energy of the Br–H bond equals 87.3 kcal, that of the Cl–H bond is 102.7 kcal. From this we can assume that the equilibrium in the reaction of chloride ions with hydrogen sulphide is shifted more in the direction of hydrosulphide ions and of hydrogen chloride than it is in the case of the reaction of bromide ions with hydrogen sulphide. Also the size of bromide and chloride ions could have some effect.

On the basis of paper[3] we were able to estimate our results also from the thermodynamic point of view. In the cited paper the authors studied the reaction of gaseous hydrogen chloride with bromide ions in the systems hydrogen chloride, hydrogen bromide and melt(M, N), (Cl^-, Br^-), where M and N are alkali metals, in our case

lithium and potassium and they determined the equilibrium constants of these reactions at 800°C using the relation

$$K = p_{HBr}/p_{HCl} \cdot a_{(Li,K)Cl^-}/a_{(Li,K)Br^-} =$$

$$= \underbrace{p_{HBr}/p_{HCl} \cdot X_{Cl^-}/X_{Br^-}}_{K'} \gamma_{(Li,K)Cl^-}/\gamma_{(Li,K)Br^-}, \qquad (5)$$

where K is the equilibrium constant of the studied reaction, a are the activities of the respective components, K' is the apparent equilibrium constant of the reaction and X_{Br^-} and X_{Cl^-} are ionic fractions.

The values of equilibrium constants as determined by the cited authors indicate that chloride always prevails in equilibrium mixtures of bromide and chloride. This also agrees with the assumption that in the reaction of hydrogen sulphide with chlo-
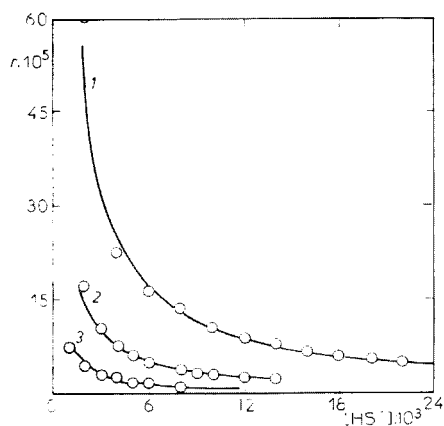

FIG. 1

Comparison of the Values of Reaction Rates r_{calc} (mol kg^{-1} min^{-1}) Calculated from Kinetic Equation (4) with the Experimentally Found Values, r_{exp}, in Dependence on the Concentration of Hydrosulphide Ions (mol kg^{-1})

Mass of the melt $m = 0.05$ kg, flow rate of gas $F = 0.2$ l min^{-1}, $p_{H_2S} = 1$ atm, temperature, °C: 1 500, 2 450, 3 400; ○ experimental data, full line values calculated from Eq. (4).
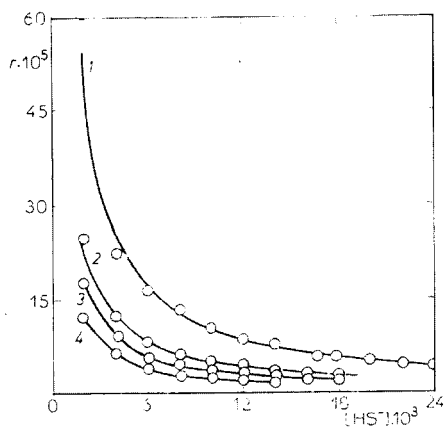

Fig. 2

Comparison of the Values of Reaction Rates r_{calc} (mol kg^{-1} min^{-1}) Calculated from Kinetic Equation (4) with the Experimentally Found Values, r_{exp}, in Dependence on the Concentration of Hydrosulphide Ions (mol kg^{-1})

Mass of the melt $m = 0.05$ kg, flow rate of gas $F = 0.2$ l min^{-1}, temperature 500°C, p_{H_2S} (atm): 1 1, 2 0.5, 3 0.375, 4 0.25; ○ experimental data, full line values calculated from Eq. (4).
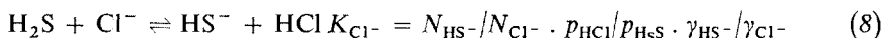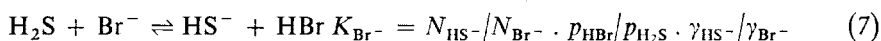
ride ions the value of equilibrium constant is higher than in the reaction of hydrogen sulphide with bromide ions.

The considerations presented in paper[3] are based on the assumption that mixtures of bromide and chloride form regular solutions. By applying the theory of regular solutions to the mentioned system we obtained a final relation for equilibrium constants K and K', valid for a constant ratio of lithium to potassium concentrations

$$\log K' = \left(b_{Li}N_{Li} + b_k N_k\right)/2{\cdot}303RT(N_{Cl^-}-N_{Br^-}) + \log K \,, \qquad (6)$$

where b_{Li} and b_K are constants, K and K' are the ideal and apparent equilibrium constants of the reaction, respectively, and N are ionic fractions. From Eq. (6) it can be seen that with equimolar concentration of chloride and bromide ions the first term of the equation is zero and $\log K' = \log K$.

By appropriate combination of equilibrium constants of the systems of hydrogen sulphide with chloride or bromide ions a comparable value can be obtained of the equilibrium constant of the reaction of bromide ions with gaseous hydrogen chloride,

$$H_2S + Br^- \rightleftharpoons HS^- + HBr \; K_{Br^-} = N_{HS^-}/N_{Br^-} \cdot p_{HBr}/p_{H_2S} \cdot \gamma_{HS^-}/\gamma_{Br^-} \qquad (7)$$

$$H_2S + Cl^- \rightleftharpoons HS^- + HCl \; K_{Cl^-} = N_{HS^-}/N_{Cl^-} \cdot p_{HCl}/p_{H_2S} \cdot \gamma_{HS^-}/\gamma_{Cl^-} \qquad (8)$$

$$Br^- + HCl \rightleftharpoons Cl^- + HBr \; K = K_{Br^-}/K_{Cl^-} =$$

$$= N_{Cl^-}/N_{Br^-} \cdot p_{HBr}/p_{HCl} \cdot \gamma_{Cl^-}/\gamma_{Br^-} \cdot \qquad (9)$$

The values to be compared must be obtained at the same temperature and in otherwise comparable systems. In the first approximation the first condition was fulfilled by extrapolating our values to 800°C. As for the second condition, the value of the equilibrium constant should be calculated for a system with constant lithium to potassium ions concentrations and for an equimolar mixture of bromide and chloride in the melt. However, it must be borne in mind that the term γ_{HS^-} appears in Eq. (7), representing the activity coefficient of hydrosulphide ion in the melt of lithium and potassium bromide, whereas in Eq. (8) γ_{HS^-} is the activity coefficient of hydrosulphide ion in the melt of lithium and potassium chloride. The equilibrium constants can be compared only provided that the ratio of γ_{HS^-}(chloride melt)$/\gamma_{HS^-}$(bromide melt) approaches unity. Also the condition of constant ratio of cation concentrations of the melt was not fulfilled exactly. Two systems, *i.e.* bromide and chloride eutectica, were compared. The Li : K ratio in the first one is 60 : 40, in chlorides 58 : 42. This difference was thought to be negligible, because according to[3] only a difference of 10% in the ionic fractions of lithium and potassium may cause an error of about 9% in the calculation of equilibrium constant.

The value of equilibrium constant according to paper[3] is 0·356. After rearrangement and calculation from our experimental data we obtained the value 0·386. The agreement of these results is fairly good, considering that the comparison could be performed only under simplifying assumptions.

The studied reaction is a heterogeneous one; gaseous and liquid components react with each other. This is a case when the effect of transport phenomena, *i.e.* of diffusion, cannot be excluded. A rough indication of the effect of diffusion is usually a low value of the activation energy[4] and the change of the rate of the studied process with changing contact interphase boundary, or with changing contact time of both phases. Preliminary experiments have shown that the rate of the studied reaction increases with increasing surface area of the interphase boundary which was achieved by using a narrower reaction vessel at the same flow rate of gas through the melt and at the same volume of the melt. To be able to find out whether diffusion is the rate governing process, it would be necessary to construct a model, describing the rate of the studied reaction, which would include the effects of both adsorption and diffusion of gas into the melt. We tried to do so, using the knowledge and assumptions from monograph[5].
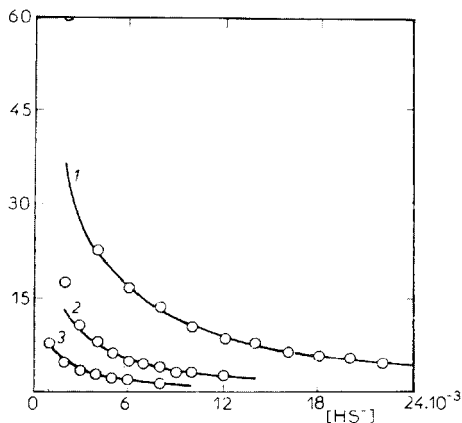

FIG. 3

Comparison of the Values of Rates of the Studied Process, r_{dif}, Calculated according to the Diffusion Model with the Experimentally Found Values

Mass of the melt $m = 0·05$ kg, flow rate of gas $F = 0·2$ l min^{-1}, $p_{H_2S} = 1$ atm, temperature (°C): *1* 500, *2* 450, *3* 400; $(k_L a)$ (s^{-1}): *1* 0·375, *2* 0·286, *3* 0·161.
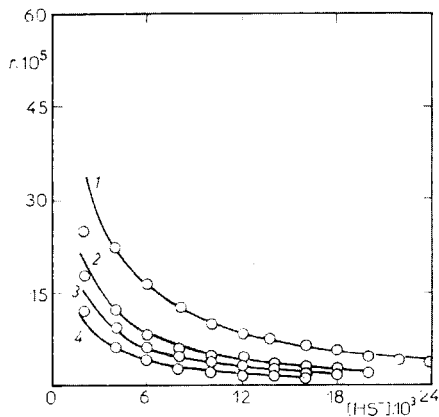
FIG. 4

Comparison of the Values of Rates of the Studied Process, r_{dif}, Calculated according to the Diffusion Model with Experimentally Found Values

Mass of the melt $m = 0·05$ kg, flow rate of gas $F = 0·2$ l min^{-1}, temperature 500°C, p_{H_2S} (atm): *1* 1, *2* 0·5, *3* 0·75, *4* 0·25; $k_L a$ (s^{-1}): *1* 0·375, *2* 0·37, *3* 0·26, *4* 0·238.

From our experiments it followed that the reaction is reversible and that it is fast enough to allow the equilibrium to be established in any moment, not only in the bulk phase but also in the interphase boundary, as can be seen from Eq. (3). Thus it can be assumed that, expressed in terms of diffusion, the studied reaction is an "instantaneous reversible reaction".

Consequently, the rate of the studied process can be imagined as the rate of adsorption of sulphur compounds into the melt wherein the meaning of the term sulphur compounds is the total amount of sulphur consisting of the amount of hydrogen sulphide dissolved in the melt and the amount of hydrogen sulphide transformed to hydrosulphide in the diffusion layer.

According to[5] it must hold for reaction (A) that concentrations of individual components of the reaction in the interphase boundary and in the bulky phase are given by the relations

$$K = [HS^-]^* \cdot [HBr]^*/[Br^-]^* \cdot [H_2S]^* = [HS^-]^0 \cdot [HBr]^0/[Br^-]^0 \cdot [H_2S]^0, \tag{10}$$

in which the superscript $*$ denotes concentration in the interphase boundary and ^{0} the concentration in the bulky phase. The rate of hydrogen sulphide absorption is defined as follows

$$r_D = k_L a\{([H_2S]^* + (D_{HS^-}[HS^-]^*/D_{H_2S}) - ([H_2S]^0 + (D_{HS^-}[HS^-]^0/D_{H_2S}))\}, \tag{11}$$

where k_L is the coefficient of physical mass transfer $(cm\ s^{-1})$, a is the surface area of the gas–liquid boundary, related to a volume unit of the system (cm^{-1}) and D_{HS^-} and D_{H_2S}, are diffusion coefficients of hydrosulphide and of the dissolved hydrogen sulphide, respectively $(cm^2\ s^{-1})$.

Taking into account that the experimentally followed concentration of hydrosulphide is considerably higher in the course of the reaction than the concentration of dissolved hydrogen sulphide and that the diffusion coefficients of hydrosulphide and of hydrogen sulphide do not differ too much, we obtain

$$r_D = k_L a([HS^-]^* - [HS^-]^0). \tag{12}$$

Expressing $[HS^-]^*$ from Eq. (10) and expressing the partial pressures of hydrogen bromide as a function of the reaction rate, of the total flow rate of gas and of the amount of melt, we can on rearrangement obtain the final quadratic equation of the reaction rate

$$24 \cdot 4m/F \cdot r_D + 24 \cdot 4m/F \cdot [HS^-]^0 \cdot k_L a r_D - K' \cdot p_{H_2S} \cdot k_L a = 0. \tag{13}$$

$k_L a$ was chosen as the adjustable parameter of this equation and the values of r_D were calculated by regression.

Figs 3 and 4 show the comparison of the calculated reaction rates according to this model with the experimentally determined values. As can be seen the values calculated on the basis of diffusion model are in fairly good accordance with the experimental values so that it is rather difficult to decide which of the models is more probable. To prove the plausibility of the diffusion model it would be necessary to carry out the experiment at least in the range of two orders of magnitude of the $k_L a$ values. This cannot be accomplished in our experimental arrangement. Moreover, many simplifying assumptions had to be made so that the values obtained from the diffusion model are of a rather preliminary character.

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