REACTIONS IN FUSED SALTS. VI.*
REACTION OF DIHYDROGEN SULPHIDE WITH MELTS OF ALKALI CHLORIDES

J.Malá, J.Novák and I.Sláma

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

The equilibrium and kinetics of the reaction of dihydrogen sulphide with chloride ions in an eutectic melt of lithium and potassium chlorides has been studied in the temperature range 400 to 500°C. The SH⁻ ion was found to be the main product of the reaction in melt. A kinetic equation was derived and the equilibrium constant of the reaction was calculated from the experimental data.

Recently, a great deal of attention has been paid to studies[1−5] dealing with the behaviour of sulphur compounds in various melts. The aim of these studies is mainly to explain the green and blue colouration appearing in the solutions, which contain sulphur compounds in some form, at higher temperatures.

Generally, the problem is the stability of alkali metal sulphides in melts. Melting point of potassium sulphide is 840°C, that of sodium sulphide 930°C. Up to the mentioned temperatures both sulphides are stable. However, in the presence of dihydrogen sulphide an equilibrium can be expected between sulphide, hydrogensulphide and dihydrogen sulphide. There is no reference in the literature, how much this equilibrium is manifested at temperatures about 500°C. The only known fact is[6] that in the reaction of cadmium, manganese and silver chlorides only sulphide is formed The presence of heavy metals obviously causes a shift of the equilibrium between sulphide, dihydrogen sulphide and hydrogensulphide to the side of sulphides.

The melting point of potassium and sodium hydrogensulphide is 455−510°C and 350°C, respectively. Potassium hydrogensulphide decomposes to sulphide and dihydrogen sulphide at about 560°C, sodium hydrogensulphide even at a lower temperature. This means that alkali metal hydrogensulphide could exist at the mentioned temperatures.

Therefore, it might be worth while to investigate quantitatively the reaction of dihydrogen sulphide with alkali chlorides at 400−500°C.

EXPERIMENTAL

Apparatus

The experimental arrangement used was described earlier[7]. The reaction test tube was closed by a rubber stopper, wrapped in a teflon foil, with holes left for inlet and outlet of gas and for taking samples from the melt. The flow rate of gases was controlled by a liquid manostat and was measured by a capillary flow-meter filled with silicone oil. Nitrogen was dried over sulphuric acid and magnesium perchlorate and was freed from oxygen by chromium(II) chloride solution. Dihydrogen sulphide was dried with calcium chloride and hydrogen chloride with magnesium perchlorate.

Chemicals, Working Procedure and Analyses

The chemicals used were of reagent grade purity. Eutectic melt of lithium and potassium chlorides was prepared by weighing and fusing appropriate amounts (58 mol% LiCl and 42 mol% KCl) of the compounds. The melt was purified by half an hour's bubbling with hydrogen chloride followed by another half an hour's bubbling with nitrogen.

In kinetic measurements a stream of dihydrogen sulphide was bubbled through the melt. The kinetics was followed by repeated taking samples from the melt which were then analyzed iodometrically for hydrogensulphide. To determine the equilibrium the melt was bubbled with a mixture of dihydrogen sulphide, nitrogen and with a small amount of hydrogen chloride. The latter was admixed by leading the stream of nitrogen through a washing bottle with hydrochloric acid of various concentration. The gas mixture was dried with magnesium perchlorate.

50 g portions of the melt were used for experiments as standard, but the effect of the amount of melt on the reaction rate was examined, too. The content of hydrogen chloride in nitrogen was determined acidimetrically.

RESULTS AND DISCUSSION

The presumed possible products of the reaction of dihydrogen sulphide with chloride ion from the melt are sulphide and hydrogen chloride or hydrogensulphide and hydrogen chloride. The criterion whether hydrogensulphide or sulphide is formed is the ratio of the amount of the evolved hydrogen chloride to the amount of the reducing substances in the melt. The experimentally found value of this ratio is 1, which corresponds to the formation of hydrogensulphide according to reaction

$$H_2S + Cl^- \rightleftharpoons HS^- + HCl. \qquad (A)$$

Reciprocal value of the apparent equilibrium constant of this reaction is given by the relation.

$$K/[Cl^-] = K' = (p_{H_2S}/p_{HCl}) \cdot [HS^-]^{-1}, \qquad (1)$$

where p_{HCl} and p_{H_2S} are partial pressures of hydrogen chloride and dihydrogen sulphide, respectively, in atm, $[HS^-]$ is the concentration of hydrogensulphide in molality (mol/kg).

The data allowing to calculate the equilibrium constants at 500°C were determined experimentally for the values of $p_{HCl} = 5\cdot13 \cdot 10^{-4}$, $9\cdot94 \cdot 10^{-4}$, $4\cdot56 \cdot 10^{-3}$ atm for the case when equilibrium is approached from both higher and lower concentration of hydrogensulphide. The corresponding calculated values of equilibrium constant K' are $4\cdot34 \cdot 10^{4}$, $4\cdot28 \cdot 10^{4}$, $4\cdot0 \cdot 10^{4}$ mol kg^{-1}. Constant K is directly proportional to the partial pressure of dihydrogen sulphide and indirectly proportional to the pressure of hydrogen chloride which is another factor supporting the assumption that hydrogensulphide is the product of the reaction of chloride ions with dihydrogen sulphide.

The values of the equilibrium constant can, besides, be calculated by another procedure, *i.e.* assuming that an equilibrium between the liquid and the vapour phase is established at the interphase boundary. The calculation can be carried out using kinetic data and constant K' can be expressed as follows

$$K' = k_2/k_1' = F \cdot p_{H_2S}/24\cdot4 \cdot r \cdot [HS^-] \cdot m,   \tag{2}$$

under the assumption that p_{HCl} is a function of the rate of increase of the concentration of HS$^-$, of the total flow rate and of the weight of the melt. In Eq. (2) k_2 (mol . . kg^{-1} min^{-1} atm^{-1}) and k_1' (min^{-1} atm^{-1}) are rate constants of the studied reaction, F is the total flow of gas (1 min^{-1}) and r is the rate of increase of the concentration of HS$^-$ (mol kg^{-1} min^{-1}), m is the mass of the melt (kg). The value of K' determined in this way for 500°C is $4\cdot31 \cdot 10^{4}$ mol^{-1} kg. Evidently it is comparable with the value of K as determined from equilibrium measurements. From the above it follows that at temperatures up to 500°C only hydrogensulphide is present in the melt in equilibrium with dihydrogen sulphide.

Reaction of dihydrogen sulphide with chloride ions is, from the kinetic point of view, a heterogeneous reversible reaction. Its rate is affected by two factors. It is retarded by the possible simultaneous decomposition of HS$^-$ ions to dihydrogen sulphide and sulphide. Als already mentioned, in a stream of dihydrogen sulphide this factor cannot play a great role, since sulphide could be formed only in a negligible amount. The reaction rate depends on the partial pressure of hydrogen chloride, respectively on the amount of the formed hydrogen chloride which is removed from the system. It follows from the experimental arrangement that the partial pressure of hydrogen chloride is a function of the rate of increase of the concentration of HS$^-$, of the total flow rate of gas and of the weight of the melt. Taking into account these facts and also the finding that the concentration of chloride ions does not change during the reaction, the rate of increase of the concentration of the reaction product can be described by equation

$$r = \frac{k_1' \, p_{H_2S}}{1 + k_2 \, HS^- \, \dfrac{24\cdot4m}{F}},   \tag{B}$$

TABLE I

Comparison of the Calculated Rates of Concentration Increase with Those Found Experimentally

$[HS^-] \cdot 10^3$	$r_{exp} \cdot 10^5$	$r_{calc} \cdot 10^5$	Δr
mol kg^{-1}	mol kg^{-1} min^{-1}	mol kg^{-1} min^{-1}	%

$t = 500°C$, $p_{H_2S} = 1$ atm, $F = 0.2$ l/min, $m = 0.05$ kg

12·00	30·72	30·96	+0·78
17·00	22·97	22·01	−4·18
21·00	17·20	17·87	+3·75
24·4	15·34	15·41	+0·45
27·26	13·87	13·81	−0·43
29·00	12·45	12·99	+4·16
32·80	11·48	11·50	+0·17
34·53	10·87	10·93	+0·55
36·17	10·15	10·44	+2·78
38·71	9·78	9·76	−0·20

$t = 500°C$, $p_{H_2S} = 1$ atm, $F = 0.2$ l/min, $m = 0.145$ kg

8·89	14·93	14·60	−2·26
12·49	9·86	10·42	+5·37
15·24	8·57	8·55	−0·23
18·00	7·41	7·25	−2·21
19·80	6·56	6·59	+0·46
20·70	5·99	6·31	+5·07
23·42	5·52	5·58	+1·08
25·06	4·97	4·92	+1·02
28·04	4·72	4·66	−1·29

$t = 500°C$; $p_{H_2S} = 1$ atm, $F = 0.1$ l/min, $m = 0.05$ kg

8·45	22·33	22·14	−0·86
12·16	15·49	15·46	−0·19
15·00	12·14	12·56	+3·34
17·32	10·74	10·89	+1·38
19·35	9·79	9·76	−0·45
21·26	8·23	8·89	+7·42
22·94	8·18	8·24	+0·73
24·53	7·63	7·71	+1·04
26·05	7·14	7·26	+1·65
27·42	6·52	6·90	+5·80
28·76	6·33	6·58	+3·80
30·00	5·91	6·31	+6·34

TABLE I
(Continued)

[HS⁻] . 10³ mol kg⁻¹	r_{exp} . 10⁵ mol kg⁻¹ min⁻¹	r_{calc} . 10⁵ mol kg⁻¹ min⁻¹	Δr %
	$t = 500°C$, $p_{H_2S} = 0.5$ atm, $F = 0.2$ l/min, $m = 0.05$ kg		
8·46	22·57	21·74	−3·82
12·13	15·84	15·32	−3·28
14·9	12·23	12·52	+2·32
17·15	10·66	10·91	+2·29
19·21	9·97	9·76	−2·15
21·2	8·54	8·85	+3·50
22·78	8·1	8·25	+1·82
24·39	7·71	7·71	0·00
25·87	7·24	7·27	+0·41
27·28	6·73	6·90	+2·46
28·59	6·46	6·59	+1·97
	$t = 500°C$, $p_{H_2S} = 0.177$ atm, $F = 0.2$ l/min, $m = 0.05$ kg		
6·00	10·41	10·70	+2·71
8·63	7·56	7·55	−0·13
10·67	6·21	6·14	−1·14
12·42	5·41	5·30	−2·08
13·95	4·77	4·73	−0·85
15·3	4·29	4·32	+0·69
16·54	4·01	4·00	−0·25
17·70	3·80	3·74	−1·60
18·81	3·55	3·53	−0·57
	$t = 450°C$, $p_{H_2S} = 1$ atm, $F = 0.2$ l/min, $m = 0.05$ kg		
8·28	14·20	14·18	−0·14
11·77	9·91	10·09	+1·78
14·5	8·14	8·23	+1·09
16·81	7·13	7·12	−0·14
18·33	6·32	6·54	+3·36
20·65	5·75	5·82	+1·20
22·82	5·33	5·27	−1·14
23·82	4·97	5·05	+1·58
25·34	4·81	4·75	−1·26
27·2	4·43	4·43	0·00

TABLE I
(Continued)

[HS⁻] . 10³ mol kg⁻¹	r_{exp} . 10⁵ mol kg⁻¹ min⁻¹	r_{calc} . 10⁵ mol kg⁻¹ min⁻¹	Δr %

$t = 400°C, p_{H_2S} = 1 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$

[HS⁻] . 10³ mol kg⁻¹	r_{exp} . 10⁵ mol kg⁻¹ min⁻¹	r_{calc} . 10⁵ mol kg⁻¹ min⁻¹	Δr %
4·48	7·92	8·19	+3·30
6·47	5·71	5·82	+1·89
8·02	4·73	4·75	+0·42
9·34	4·26	4·11	−3·65
10·52	3·60	3·80	+5·26
11·56	3·31	3·34	+0·90
12·52	3·15	3·10	−1·61
13·43	2·82	2·89	+2·42
14·29	2·77	2·72	−1·84
15·11	2·62	2·58	−1·55
15·88	2·46	2·46	0·00

where k_1' is the reaction rate constant in the sense of reaction (A), k_2 is the reaction rate constant in the opposite sense.

The values of the rate of concentration increase both calculated and found experimentally are presented in Table I. Comparison of both these values shows that the mean relative standard deviation of the measured values is c. $\pm 2\%$. Thus it can be stated that the experimental data are in fairly good agreement with the proposed kinetic equation.

Activation energy was calculated from the determined kinetic Constants: $k_1'(400°C) = 1 . 10^{-3}, k_2 (400°C) = 4·1 . 10^2, k_1'(450°C) = 4·97 . 10^2, k_1 (500°C) = 13·0 .10^{-3}, k_2 (500°C) = 5·6 . 10^2$. Its value is 25·6 kcal for k_1' and 3·1 kcal for k_2.

The results of the investigation of the reaction of dihydrogen sulphide with chloride ions point to new possibilities of the study of sulphur compounds in melts. The studied reaction is actually a route of preparation of hydrogensulphide in a melt of potassium and lithium chlorides. According to preliminary experiments hydrogensulphide is far more soluble in the melt than sulphide, thus allowing to use a wider concentration range in studying sulphur compounds in melts. However, the knowledge of the decomposition reaction of hydrogensulphide to sulphide is indispensable.

Reaction of dihydrogen sulphide with chloride ions is not the only reaction to prepare hydrogensulphide in melt. It can also be prepared by reaction of dihydrogen sulphide with sulphide, hydroxide or carbonate ions.

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