

REACTION OF LEAD(II) IONS WITH HYDROGEN SULPHIDE IN A MELT OF LITHIUM AND POTASSIUM CHLORIDE*

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Kinetics of the reaction of hydrogen sulphide with lead(II) ions in an eutectic melt of lithium and potassium chloride was studied in the temperature interval 400–500°C. Kinetic equation of the reaction was derived and experimentally verified. A probable mechanism of the reaction was suggested. The reaction rate of the studied reaction was compared with that of hydrogen sulphide with an eutectic melt of lithium and potassium chloride in the absence of lead(II) ions,

In the preceding communication¹ we have studied the reaction of hydrogen sulphide with molten alkali halides with the result that the eutectic melt of lithium and potassium chloride reacts at 400–500°C with hydrogen sulphide under the formation of hydrosulphides. This rather surprising result led us to the idea to verify the behaviour of the salts of other metal cations at higher temperatures at otherwise the same conditions.

Reactions of some metal halides with hydrogen sulphide proceeding at higher temperatures (about 500°C) are known from the literature². Their products are also sulphides of the respective metals. These reactions, however, were carried out in the solid, highly sintered state. The problem is whether the mentioned compounds react with hydrogen sulphide in the same way even in high-temperature solutions, *i.e.* in melts.

For this reason we decided to follow quantitatively the reaction of some metal cations of some other group of the periodic system than are alkali metals or alkali earth metals with lithium and potassium chloride at 400–500°C. We chose the lead(II) ions with respect to the sufficient solubility of lead(II) chloride in eutectic melt and to the easy and quick analytical determination of lead(II) ions in the melt.

EXPERIMENTAL

Experimental arrangement as well as the procedure of measuring the flow rate of gases were described earlier¹.

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Chemicals, Procedures and Analytical Methods

The chemicals used were of reagent grade purity. Eutectic melt was prepared by weighing the appropriate amounts of previously dried (at 450°C) lithium and potassium chloride (58 mol% and 42 mol%, respectively) and the corresponding amount of lead(II) chloride and by subsequent melting of the mixture. The melt was purified by bubbling with gaseous hydrogen chloride and nitrogen.

The kinetic course of the reaction was followed experimentally: Eutectic melt was bubbled with a stream of hydrogen sulphide (from a steel flask, purity 99.99%) or of a mixture of hydrogen sulphide and nitrogen or of hydrogen sulphide, nitrogen and hydrogen chloride. A black precipitate appeared in the melt during the experiment. Samples for analysis were taken from the melt by a glass pipette in regular time intervals. When taking the samples the melt was not filtered. The change of the time dependence of the decrease of lead(II) ions concentration was determined in dependence on temperature, total flow rate of the gas and on the partial pressure of hydrogen sulphide. Concentration of lead(II) ions was determined after cooling the sample, dissolution in water and removing the precipitate by filtration, by chelatometric titration.

Analysis of the precipitate. After all the lead(II) ions had reacted, the melt was cooled in nitrogen atmosphere. Afterwards, already in normal atmosphere, lithium and potassium chlorides were extracted with water and the remaining precipitate was filtered off and dried at 80°C. It was then decomposed in a closed apparatus by hydrochloric acid under heating and the evolved hydrogen sulphide was titrated, after absorption in ammonia solution of cadmium(II) salt, iodometrically. Lead was determined chelatometrically in the solution after decomposition.

RESULTS AND DISCUSSION

The studied reaction is, from the kinetic point of view, a heterogeneous one. All three phases are present in the system. The gaseous phase is represented by hydrogen sulphide which is admitted into the system and by the mixture of hydrogen sulphide and hydrogen chloride, leaving the system. The liquid phase is the solution of lead(II) ions in the eutectic melt of lithium and potassium chlorides, no matter whether the soluble lead is present in the form of free lead(II) ions or in the form of various complexes. The solid phase is formed in the reaction as a black, water-insoluble precipitate. The ratio of the lead content to the content of sulphur in the precipitate corresponds to the composition of lead(II) sulphide.

Experiments have shown that the reaction rate is indirectly proportional to the partial pressure of hydrogen chloride and that the reaction is not of an integer order towards the concentration of lead(II) ions. According to preliminary experiments the ratio of the substance amount of the formed hydrogen chloride to that of lead(II) ions in the solution equals two.

The conclusion drawn from all these results was that the reaction of lead(II) ions with hydrogen sulphide in melt is a reversible one and cannot be considered a simple reaction of these ions with hydrogen sulphide yielding lead(II) sulphide, as could be expected, since in that case the reaction should necessarily be of the first order with respect to lead(II) ions.

The following form of kinetic equation was proposed for evaluating the kinetic data

$$dx/dt = A/(1 + B(a - x)^{-1/2}), \quad (1)$$

where A and B are constants, a is the initial concentration of lead(II) ions in mol/kg, x is the amount of substance of lead(II) ions in mol/kg which are chemically transformed at the time t , and $(a - x)$ is the analytical concentration of lead(II) ions in mol/kg in time t . Integral form of this equation is

$$t = (x + 2B(\sqrt{a} - \sqrt{a - x}))/A. \quad (2)$$

The meaning of the symbols is the same as in Eq. (1).

This equation was used to simulate the studied chemical process between hydrogen sulphide and lead(II) ions, dissolved in a lithium and potassium chloride melt. The experimental data were compared graphically with those calculated according to Eq. (2), as it is shown in Figs 1 and 2. From both graphs it is evident that the agreement of experimental and calculated values of x is fairly good. Consequently, the ex-

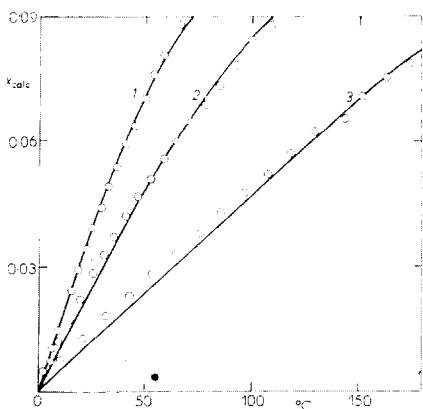


FIG. 1

Dependence of the Amount of Substance of Chemically Transformed Lead(II) Ions x (mol kg⁻¹) on time t (min)

Initial concentration of lead(II) ions $a \approx 0.1$ mol kg⁻¹, mass of the melt $m = 0.05$ kg, flow rate of gas $F = 0.21$ min⁻¹, $p_{\text{H}_2\text{S}} = 1$ atm, temperature: 1 500, 2 450, 3 400°C. ○ Experimental data, full lines are the values calculated according to Eq. (2).

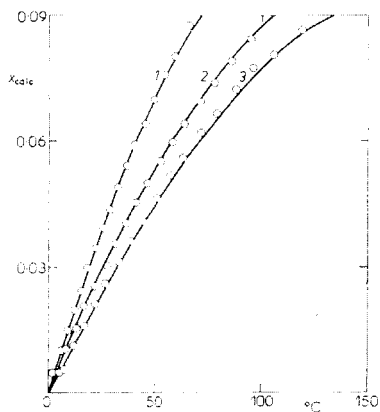
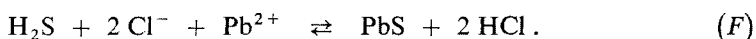
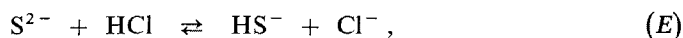
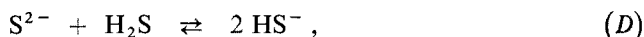
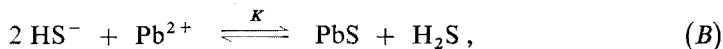
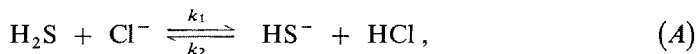


FIG. 2

Dependence of the Amount of Substance of Chemically Transformed Lead(II) Ions, x (mol kg⁻¹) on time t (min)

Initial concentration of lead(II) ions $a \approx 0.1$ mol kg⁻¹, mass of the melt $m = 0.05$ kg, flow rate of gas $F = 0.21$ min⁻¹, temperature 500°C, $p_{\text{H}_2\text{S}}$: 1 1, 2 0.5, 3 0.375 atm. ○ Experimental data, full lines are the values calculated from Eq. (2).

perimental data can be assumed to comply with the proposed kinetic equation. The following reaction mechanism was finally proposed



Hydrogen sulphide reacts first with chloride ions in the melt to form hydrosulphide ions which only then react in a simultaneous fast equilibrium reaction with lead(II) ions to afford lead(II) sulphide. Reaction (C) gives the solubility product of lead(I) sulphide. Equilibrium (D) is in our experimental arrangement, *i.e.* in a stream of hydrogen sulphide, entirely shifted towards the right-hand side of the equation. Equation (E) represents in the presence of hydrogen chloride the first step to the re-evolution of hydrogen sulphide *via* hydrosulphide. The comparability of the very small values of solubility products of metal sulphides, that have been up to now measured in melts³ (of the order approximately 10^{-15}) allows the assumption that the concentration of sulphide ions in the melt is negligibly small, as compared with the concentrations of other components. The reaction mechanism is thus reduced to two steps, corresponding to the over-all stoichiometric equation (F).

The first step of this mechanism is the reaction which was studied in paper¹. Its reaction rate was defined as the rate of increase of hydrosulphide ions according to the relation

$$d[\text{HS}^-]/dt = k_1 p_{\text{H}_2\text{S}} - k_2 [\text{HS}^-] p_{\text{HCl}}, \quad (3)$$

where k_1 ($\text{min}^{-1}\text{atm}^{-1}$) and k_2 ($\text{mol kg}^{-1}\text{min}^{-1}\text{atm}^{-1}$) are the known values of rate constants in the direction of the reaction and in the opposite direction, respectively, $p_{\text{H}_2\text{S}}$ and p_{HCl} are the partial pressures of the respective gases, in atm and $[\text{HS}^-]$ is the concentration of hydrosulphide in molalities (mol kg^{-1}).

The rate of reaction (B) is defined as the decrease of lead(II) ions concentration. In the stationary state, in accordance with the Bodenstein principle, the rate of increase of hydrosulphide ions must equal the rate of decrease of lead(II) ions

$$-2d[\text{Pb}^{2+}]/dt = d[\text{HS}^-]/dt. \quad (4)$$

TABLE I

Comparison of the Rate of Reaction of Chloride Ions with H_2S in the Presence and in the Absence of Lead(II) Ions

Time min	$r_{\text{calc}} \cdot 10^{5a}$ $\text{mol kg}^{-1} \text{min}^{-1}$	$r_{\text{exp}} \cdot 10^{5b}$ $\text{mol kg}^{-1} \text{min}^{-1}$	$r_{\text{Cl}^-} \cdot 10^{5c}$ $\text{mol kg}^{-1} \text{min}^{-1}$
$t = 500^\circ\text{C}, p_{\text{H}_2\text{S}} = 1 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$			
3:15	166.67	178.00	79.41
6:60	163.33	162.00	52.19
9:12	160.09	159.06	44.81
12:25	156.62	155.16	38.86
15:52	152.94	150.00	34.31
18:82	148.74	146.18	31.60
22:17	144.77	140.04	28.84
25:69	140.39	136.70	27.00
29:23	135.98	133.37	25.38
33:06	131.05	130.07	24.10
36:91	125.75	127.89	23.07
40:95	120.15	125.40	21.39
45:34	113.84	122.85	20.36
49:88	107.08	117.90	19.52
54:68	99.54	115.80	18.66
59:67	91.04	100.00	17.87
65:72	81.25	95.00	16.99
72:38	69.15	78.41	16.28
80:52	46.67	63.37	15.29
$t = 500^\circ\text{C}, p_{\text{H}_2\text{S}} = 0.5 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$			
4:15	118.00	117.30	47.65
8:45	115.31	114.65	34.03
12:82	113.00	112.89	27.60
17:29	110.60	110.69	23.81
21:86	107.90	107.50	21.62
26:55	105.00	104.60	19.00
31:36	102.30	101.70	17.31
36:36	99.20	99.40	16.14
41:50	95.70	95.30	15.11
46:84	92.00	91.80	14.10
52:37	88.10	86.02	13.41
58:19	83.70	82.30	12.61
64:35	78.80	76.35	12.12
70:90	73.40	71.60	11.61
78:02	67.30	63.98	11.07
85:86	59.70	58.90	10.51
94:94	50.30	51.30	10.02
106:36	37.20	40.66	9.47

TABLE I
(Continued)

Time min	$r_{\text{calc}} \cdot 10^{5a}$ mol kg ⁻¹ min ⁻¹	$r_{\text{exp}} \cdot 10^{5b}$ mol kg ⁻¹ min ⁻¹	$r_{\text{Cl}^-} \cdot 10^{5c}$ mol kg ⁻¹ min ⁻¹
$t = 500^\circ\text{C}, p_{\text{H}_2\text{S}} = 0.286 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$			
6:72	73.52	81.89	33.77
13:60	72.37	78.90	19.96
20:59	70.99	77.53	16.24
27:63	69.66	73.99	14.02
35:00	68.13	72.99	12.46
42:37	66.43	71.10	11.32
50:00	64.81	69.36	10.46
57:85	62.84	68.87	9.69
65:97	60.98	66.84	9.07
74:25	58.86	65.68	8.56
82:90	56.54	63.04	8.10
91:94	53.91	61.07	7.69
101:50	50.96	58.04	7.32
111:67	47.69	54.38	6.98
112:58	43.87	49.33	6.66
134:57	39.24	40.76	6.36
147:26	33.27	31.82	6.18
165:50	24.83	26.40	5.74
$t = 500^\circ\text{C}, p_{\text{H}_2\text{S}} = 1 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.1 \text{ kg}$			
5:31	93.79	100.00	37.49
10:68	91.55	95.54	24.30
16:26	89.16	92.47	19.58
20:91	87.37	90.00	17.26
27:77	84.31	86.60	15.26
32:75	82.28	84.77	13.96
40:00	78.98	80.17	12.50
45:31	76.65	75.42	11.94
53:17	73.10	74.04	11.02
58:92	70.50	69.72	10.50
67:51	66.46	65.97	9.72
73:53	63.53	62.50	9.44
83:45	58.77	59.63	8.93
90:58	55.32	56.52	8.52
101:98	49.43	54.34	8.00
110:62	45.05	49.27	7.63
125:23	37.27	44.29	7.21
136:80	30.79	38.67	6.87
162:38	15.75	20.63	6.33

TABLE I
(Continued)

Time min	$r_{\text{calc}} \cdot 10^{5a}$ mol kg ⁻¹ min ⁻¹	$r_{\text{exp}} \cdot 10^{5b}$ mol kg ⁻¹ min ⁻¹	$r_{\text{Cl}^-} \cdot 10^{5c}$ mol kg ⁻¹ min ⁻¹
$t = 500^\circ\text{C}, p_{\text{H}_2\text{S}} = 1 \text{ atm}, F = 0.1 \text{ l/min}, m = 0.05 \text{ kg}$			
5:37	92:20	86:92	42:79
10:86	89:90	85:00	29:52
16:54	87:47	84:05	24:25
22:25	85:08	83:13	19:52
28:28	82:48	82:20	18:39
34:42	79:85	80:17	16:77
40:77	77:01	79:65	15:29
47:42	74:03	77:00	14:15
54:28	67:01	74:90	13:26
61:52	67:50	73:14	12:49
69:17	63:91	71:96	11:89
77:25	59:96	65:38	11:10
85:82	55:75	61:63	10:54
95:29	50:98	59:90	9:99
105:58	45:65	59:00	9:56
117:32	39:42	50:92	9:00
131:38	31:68	41:57	8:52
150:47	20:52	29:66	7:95
$t = 450^\circ\text{C}, p_{\text{H}_2\text{S}} = 1 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$			
5:14	101:09	104:90	33:63
9:73	100:54	104:40	24:74
14:84	98:93	100:32	20:24
20:00	97:37	97:92	17:36
25:14	95:86	95:90	15:39
30:54	93:91	93:43	13:98
35:65	92:50	90:10	13:08
41:08	90:69	88:14	12:58
46:81	88:52	87:80	11:37
52:49	86:05	84:26	10:77
58:38	83:71	80:00	10:23
64:59	80:44	77:45	9:74
70:86	77:41	70:00	9:29
77:57	73:41	68:64	8:89
84:54	69:29	65:00	8:49
92:05	63:79	56:80	8:12
100:27	56:92	51:56	7:81
109:89	47:07	40:00	7:58
122:76	29:74	—	6:55

TABLE I

(Continued)

Time min	$r_{\text{calc}} \cdot 10^{5a}$ mol kg ⁻¹ min ⁻¹	$r_{\text{exp}} \cdot 10^{5b}$ mol kg ⁻¹ min ⁻¹	$r_{\text{Cl}^-} \cdot 10^{5c}$ mol kg ⁻¹ min ⁻¹
$t = 400^\circ\text{C}, p_{\text{H}_2\text{S}} = 1 \text{ atm}, F = 0.2 \text{ l/min}, m = 0.05 \text{ kg}$			
10:60	46.95	57.14	13.75
21:40	46.86	54.49	9.76
32:00	46.77	50.79	8.00
42:60	46.69	47.75	6.90
53:40	46.60	46.57	6.15
64:20	46.47	46.18	5.48
75:80	46.34	46.07	5.19
85:80	46.21	45.85	4.60
96:60	46.04	45.48	4.35
107:40	45.87	44.86	4.12
118:40	45.66	43.87	3.96
129:40	45.41	43.43	3.77
140:40	45.13	41.49	3.64
151:60	44.76	40.00	3.51
162:80	44.33	37.61	3.42
174:00	43.70	36.03	3.28

^a Reaction rates calculated from Eq. (8). ^b Reaction rates calculated using the experimental data.

^c Corresponding rates of reaction of chloride ions with H₂S in the absence of lead(II) ions.

The rate of the studied reaction, defined by the decrease of lead(II) ions concentration is given by the expression

$$r = 1/2(k_1 p_{\text{H}_2\text{S}} - k[\text{HS}^-] p_{\text{HCl}}). \quad (5)$$

Concentration of hydrosulphide ions can be expressed from the relation for the equilibrium constant of the second step of mechanism (B)

$$K = (a_{\text{PbS}} \cdot a_{\text{H}_2\text{S}})/(a_{\text{Pb}^{2+}} \cdot a_{\text{HS}^-}), \quad (6)$$

where a denote the activities of the individual components. Their values, however, are not known and therefore only the value of the concentration equilibrium constant of the reaction can be calculated, where the activities are substituted by concentrations. Assuming that, owing to the small solubility of hydrogen sulphide in the melt, the relation between partial pressure of the gas and the concentration of the dissolved hydrogen sulphide will obey the Henry law, the value of the concentration equilibrium

constant of reaction (B) in which both the Henry constant and the activity of lead(II) sulphide is included, is given by the expression

$$K' = p_{\text{H}_2\text{S}} / ([\text{Pb}^{2+}] \cdot [\text{HS}^-]), \quad (7)$$

where $p_{\text{H}_2\text{S}}$ is the partial pressure of hydrogen sulphide in atm, $[\text{Pb}^{2+}]$ is the concentration of lead(II) ions in the melt in mol/kg, $[\text{HS}^-]$ is the concentration of hydrosulphide in mol/kg.

On substituting for the concentration of hydrosulphide ions from (7) into (5), the following final expression is obtained for the rate of the studied reaction

$$r = \frac{(k_1/2) p_{\text{H}_2\text{S}}}{(1 + k_2 24.4 m/F) (p_{\text{H}_2\text{S}}/(\text{Pb}^{2+} \cdot K'))^{1/2}}, \quad (8)$$

where k_1 and k_2 are the known rate constants in the direction of the reaction and in opposite direction, $p_{\text{H}_2\text{S}}$ is the partial pressure of hydrogen sulphide in atm, F is the total flow of gas through the melt (l min^{-1}), m is the weight of the melt (kg) and K' is the concentration equilibrium constant of reaction (B).

Comparison with Eq. (1) clearly shows that if we choose $A = (k_1/2) p_{\text{H}_2\text{S}}$ and $B = k_2(24.4 m/F) (p_{\text{H}_2\text{S}}/K')^{1/2}$, the proposed mechanism is in accordance with the original kinetic equation which agrees with the experimental data.

Estimation of the obtained results can lead to the conclusion that lead(II) ions, dissolved in the melt of lithium and potassium chloride do not react with hydrogen sulphide themselves, but their presence only enhances the reaction of chloride ions with hydrogen sulphide, by removing hydrosulphide ions from the system in the reaction yielding lead(II) sulphide. The measure of how much lead(II) ions contribute to the rate increase of the reaction of hydrogen sulphide with halide ions is the value of the equilibrium constant of the second step of the mechanism. Its values are $1.56 \cdot 10^{10}$ at 400°C , $1.48 \cdot 10^8$ at 450°C and $1.55 \cdot 10^7$ at 500°C .

The increase in the rate of reaction of hydrogen sulphide with chloride ions as compared with the reaction in the absence of lead(II) ions can be seen from Table I where the rate constants of both the reactions with and without lead(II) ions are presented for given times.

The scope of validity of the above conclusions can be illustrated as follows. Concentration of lead(II) ions decreases in the course of the reaction and finally the lead(II) ions are no more able to consume the hydrosulphide ions formed in the first reaction. Consequently, sulphur accumulates in the melt not only as lead(II) sulphate but also in the form of hydrosulphide ions. Equation (4) is no more valid. The dependence of the change in the concentration of lead(II) ions on the increase in the substance amount of total sulphur in a constant volume of the melt can be expressed by the relation

$$-2d[\text{Pb}^{2+}] dt = X d[\text{S}]/dt = X d[\text{HS}^-]/dt, \quad (9)$$

where X is a dimensionless parameter $= d\text{Pb}/d\text{S}$, $d\text{Pb}$ and $d\text{S}$ are the changes in the amounts of substance of lead and sulphur, respectively in the melt, per an infinitesimal change of the reaction extent.

In a steady state, in excess of lead(II) ions $X = 1$ and decreases with their decreasing concentration. On the basis of balance relations for sulphur in the melt an equation was derived enabling to calculate X in dependence on the concentration of lead(II) ions in the following form

$$(1/K'[\text{Pb}_0])^{1/2} + (1 - X) \Delta = (1/K'([\text{Pb}_0] - X\Delta))^{1/2}, \quad (10)$$

where K' is the concentration equilibrium constant of reaction (B), $[\text{Pb}_0]$ is the initial concentration of lead(II) ions for a negligible change of the reaction extent.

It was found by calculation for a chosen difference in concentration $\Delta = 0.001$ that for 500°C at $1.2 \cdot 10^{-2} \text{ m-Pb}^{2+}$ the value of X equals 0.9; it differs by 10% from the value in a steady state. The value of X at 450°C and at $6 \cdot 10^{-4} \text{ m-Pb}^{2+}$ and at 400°C and at $1.5 \cdot 10^{-3} \text{ m-Pb}^{2+}$ is 0.9. These low values of Pb^{2+} concentration are either beyond the limits of our experimental conditions, or they lie in the limiting regions where the error in the analytic determination is already comparable with the deviation of X from the steady state. Thus, the validity of Eq. (4) can be expected for all values found in our experimental arrangement.

From the above deduction it is clear that the kinetic course of the studied reaction can be interpreted in terms of three regions, gradually changing from one to another over the whole concentration range of lead(II) ions. In the region of high concentrations the reaction of lead(II) ions with hydrosulphide ions takes place, causing an increase of the rate of reaction of hydrogen sulphide with chloride ions in the melt. In the region of low lead(II) ions concentration the second reaction of the proposed mechanism can be neglected and the reaction rate is given by the rate of reaction of hydrogen sulphide with the chloride ions in the melt.

The third, transition region, lying between the mentioned two regions, cannot be experimentally verified owing to the present state of our experimental technique, however, some information on it can be drawn from Eqs (9) and (10).

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