The reaction of cadmium(II) and zinc(II) ions with hydrogen sulfide in molten lithium and potassium chlorides

J. MALÁ and I. SLÁMA

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež near Prague

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Basing on the study of the kinetics of the reaction of hydrogen sulfide with cadmium(II) and zinc(II) ions dissolved in the molten lithium chloride—potassium chloride eutectic mixture at $400-500^{\circ}$ C, the kinetic equation of the above reaction was derived and experimentally verified. The most probable reaction mechanism was proposed and the corresponding relation for the rate of reaction was compared with the kinetic equation. The rate of the investigated reactions was compared with that of the reaction of hydrogen sulfide with pure molten lithium and potassium chloride mixture and with this mixture containing dissolved lead(II) ions. The range of validity of the derived relations is discussed.

For a longer time our attention has concentrated on the study of the reactions of hydrogen sulfide with the molten salt mixtures. Since there are no data on these reactions in the literature, an attempt was done to obtain a primordial conception of their course in the melt from a comparison with analogous reactions in aqueous solutions or, on the other hand, in the solid state. It is known that in aqueous solutions the salts of alkali and alkaline earth metals practically do not react with hydrogen sulfide, whilst the majority of salts of other metals reacts under the formation of sulfides.

According to [1], manganese, cadmium, and silver chlorides react in the solid state at 500°C with hydrogen sulfide to form sulfide.

The behaviour of a group of the salts of alkali metals in the melt was examined by reaction of hydrogen sulfide with the eutectic mixture of lithium and potassium chlorides and bromides, respectively [2, 3]. Hydrogensulfide was the product of this reaction. The behaviour of other cations was tested in the eutectic mixture of lithium and potassium chlorides with addition of lead(II) chloride [4]. It was found that by reaction of hydrogen sulfide with lead(II) ions dissolved in the molten lithium and potassium chloride mixture primarily hydrogensulfide is formed which is then transformed to sulfide by a simultaneous rapid equilibrium reaction. It appeared to be interesting to find out whether this result depends on the influence of the cation or of the reaction medium, and whether the drawn conclusions can be generalized for the melts or if they should be considered as specific for the case of the lead(II) ions. Therefore we decided to study the reaction of hydrogen sulfide with chlorides of other metals in the molten lithium and potassium chloride mixture. For this reason, cadmium(II) and zinc(II) ions were chosen.

Experimental

The reaction vessel consisted of a silica test-tube (diameter 40 mm, length 250 mm) closed by a rubber stopper protected by a teflon foil with openings for the gas inlet and outlet and for sampling the melt. The test-tube was situated in an electrically heated

brass block which acted as a high-temperature thermostat. The temperature was kept constant within $\pm 1^{\circ}$ C by means of a thyristor proportional thermoregulator. The gas flow was controlled by means of a liquid-column manostat and a cipillary flow-meter filled with the silicon oil.

The anal. grade reagents were used. The mixture of lithium and potassium chlorides and of cadmium(II) or zinc(II) chloride was prepared by weighting-in the individual components, pre-dried at 450° C in corresponding amounts, *i.e.* 58 mole % of lithium chloride, 42 mole % of potassium chloride, and 0.2-0.025 mole/kg of cadmium(II) or zinc(II) chloride. This mixture was melted and purified by allowing gaseous hydrogen chloride to bubble through the melt for half an hour. The excess hydrogen chloride was then removed from the melt by a subsequent bubbling of nitrogen for half an hour.

Dependence of the reaction kinetics on the partial pressure of hydrogen sulfide, on the gas flow through the melt, and on the amount of the melt was determined. The lithium chloride—potassium chloride eutectic mixture with an addition of cadmium(II) or zinc(II) chloride was rinsed with a stream of hydrogen sulfide, purity 99.99, from a steel cylinder. The kinetic course was determined by a continuous sampling of the melt. After cooling, the samples were dissolved in water, the precipitate was filtered off, and the content of cadmium(II) and zinc(II) ions was determined by means of chelatometry. For each experiment, 50 g of the melt was used. The reaction of the investigated cations having been finished, the precipitate formed in the melt was analyzed. The melt was cooled under nitrogen, then, in normal atmosphere, lithium and potassium chlorides were dissolved. The precipitate was rinsed with water, filtered, and dried in a dry-box at 80°C. Subsequently, it was dissolved in hot diluted hydrochloric acid and the content of cadmium(II) or zinc(II) ions was determined chelatometrically and the sulfur content iodometrically.

Results and discussion

For the interpretation of the experimental data presented in Figs. 1-4, the empirical kinetic equation was proposed

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

where A and B are constants, a is the initial concentration of cadmium(II) or zinc(II) ions in moles per kg, x is the material amount of cadmium(II) or zinc(II) ions in moles per kg which changes chemically in the time t, (a - x) is the analytical concentration of the cadmium(II) or zinc(II) ions in moles per kg in the time t.

For the proper calculation of the couples t and x, the integral form of eqn (1) was used

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

The calculated values of t and x were compared with those determined experimentally. Comparison of the values calculated using the above equation with the experimental data is presented in Figs. 1-4. From these graphs it is evident that there is very good agreement between the two sets of data both for cadmium(II) and for zine(II) ions and hence it can be assumed that the kinetics of the studied process can be described by the proposed kinetic equation.

The aim of the present work was to propose the most probable mechanism of the reaction under investigation. Its validity and suitability should be verified by the con-



Fig. 1. Dependence of the material amount of the chemically transformed cadmium(II) ions $x \text{ [mol kg}^{-1}\text{]}$ in the time t on the time t [min].

 $p_{\text{H}_{2}\text{S}} = 1$ atm, gas flow $F = 0.2 \,\text{l min}^{-1}$, weight of the melt m = 0.05 kg, temperature [°C]: 1. 500; 2. 450; 3. 420.



Fig. 3. Dependence of the material amount of the chemically transformed zinc(II) ions $x \text{ [mol kg}^{-1}\text{]}$ in the time t on the time t [min].

 $p_{\text{H}2\text{S}} = 1$ atm, gas flow $F = 0.2 \, \text{l min}^{-1}$, weight of the melt $m = 0.05 \, \text{kg}$, temperature [°C]: 1. 500; 2. 450; 3. 415.



Fig. 2. Dependence of the material amount of the chemically transformed cadmium(II) ions $x \text{ [mol kg}^{-1}\text{]}$ in the time t on the time t [min].

Temperature 500°C, gas flow F == 0.2 l min⁻¹, weight of the melt m == 0.05 kg, partial pressure of hydrogen sulfide [atm]: 1. 1; 2. 0.545; 3. 0.42; 4. 0.286.



Fig. 4. Dependence of the material amount of the chemically transformed zinc(II) ions $x \text{ [mol kg}^{-1}\text{]}$ in the time t on the time t [min].

Temperature 500°C, gas flow $F = 0.21 \text{ min}^{-1}$, weight of the melt m = 0.05 kg, partial pressure of hydrogen sulfide [atm]: 1. 1; 2. 0.545; 3. 0.42; 4. 0.286. sistency of the relation for the rate of reaction derived on the basis of this mechanism and the empirical kinetic equation. The reaction mechanism was proposed on the basis of several preliminary experiments and the following consideration.

It was found experimentally that by reaction of hydrogen sulfide with cadmium(II) and zinc(II) ions, respectively, in the former case a white and in the latter case an orange precipitate was formed; these were analytically identified as sulfides of the corresponding metals, while hydrogen chloride was present in the outlet gas.

If hydrogen sulfide would react with cadmium(II) or zinc(II) ions to form sulfide, the stoichiometric relation between the amount of the new-formed hydrogen chloride and that of the investigated cation should equal two and the reaction should be of the first order with respect to the concentration of the cation. Experimentally, this relation was virtually found to be equal to two; however, the reaction was not of an integer order with respect to the concentration of cadmium(II) or zinc(II) ions. Hence it can be assumed that, similarly as in the case of the lead(II) ions, the reaction between hydrogen sulfide and cadmium(II) or zinc(II) cations is not a simple direct reaction and it could be described by a more complicated mechanism.

Another set of experimental data has been determined in the study of the dependence of the investigated process on the partial pressure of hydrogen chloride. The rate of the reaction was found to be higher at lower values of the partial pressure of hydrogen chloride.

Since it was found that the reaction is not simple, with regard to the form of the empirical kinetic equation and on the basis of the preceding consideration, the following reaction mechanism which could explain the individual steps of the investigated process was proposed:

$$H_{2}S + Cl^{-} \stackrel{k_{1}}{\rightleftharpoons} HS^{-} + HCl, \qquad (A)$$

$$2HS^{-} + Me^{2+} \stackrel{K}{\approx} MeS + H_2S, \qquad (B)$$

$$MeS \rightleftharpoons Me^{2+} + S^{2-},$$
 (C)

$$S^{2-} + H_2 S \rightleftharpoons 2HS^-,$$
 (D)

$$S^{2-} + HCl \Rightarrow HS^{-} + Cl^{-},$$
 (E)

$$H_2S + 2Cl^- + Me^{2+} \Rightarrow MeS + 2HCl,$$
 (F)

where Me^{2+} denotes the cadmium(II) or zinc(II) cation.

According to the proposed mechanism, hydrogen sulfide reacts with chloride ions in the melt under the formation of hydrogensulfide ions. Subsequently, by a simultaneous rapid equilibrium reaction with cadmium(II) or zinc(II) ions, the hydrogensulfide ions are transformed to sulfides of the corresponding metals. The reaction mechanism is affected also by the solubility product of the new-formed sulfides. The dissolved sulfide ions can either react with hydrogen sulfide to form hydrogensulfide or — with regard to the reversibility of the reaction — with hydrogen chloride to form hydrogensulfide and hydrogen sulfide. The hitherto known values of the order of dissolution of metallic sulfides in the melts are approx. 10^{-15} [5]. Consequently, the concentration of the sulfide ions was considered to be negligible in comparison with the concentration of other components. As decisive for the reaction (F), were considered. According to the Bodenstein's principle, in a steady state the rate of both these reactions should be equal. If the rate of the first reaction is expressed by the increase in the concentration of the hydrogensulfide ions and that of the second reaction by the change of the concentration of the reacting cations, the following relation should hold

$$d[HS^{-}]/dt = -2d[Me^{2+}]/dt, \qquad (3)$$

where $[Me^{2+}]$ is the concentration of the metallic ions.

The rate of the first reaction is given by relation

$$d[HS^{-}]/dt = k_1 \ p_{H_{2}S} - k_2[HS^{-}] \ p_{H_{2}I}$$
(4)

where $p_{\text{H}_2\text{S}}$ is the partial pressure [atm], [HS⁻] is the concentration of the hydrogensulfide ions [mol kg⁻¹], $p_{\text{HC}1}$ is the partial pressure of hydrogen chloride [atm], k_1 [min⁻¹ atm⁻¹] and k_2 [mol kg⁻¹ min⁻¹ atm⁻¹] are the rate constants in both directions of the equilibrium as derived in our previous work [2].

If the rate of the entire studied process is defined by the change in the concentration of the reacting cations, then the rate can be expressed by the relation

$$r = 1/2(k_1 p_{\rm H_2S} - k_2[\rm HS^-] p_{\rm HCl}).$$
⁽⁵⁾

The apparent equilibrium constant of reaction (B) is given by relation

$$K' = p_{\rm H_2S} / [\rm Me^{2+}] [\rm HS^{-}]^2, \tag{6}$$

if we assume that the solubility of hydrogen sulfide is small and the relation between the activity and the partial pressure corresponds to the Henry's law. K' is the aparent equilibrium constant involving the Henry's constants and the activity of the precipitated sulfide, $[Me^{2+}]$ is the concentration of the investigated ions $[mol kg^{-1}]$, p_{H_2S} is the partial pressure of hydrogen sulfide in atm; p_{HC1} in (4) is the partial pressure of hydrogen chloride in atm. The partial pressure of hydrogen chloride for this reaction is proportional to the rate of the reaction, the amount of the melt, and inversely proportional to the gas flow through the melt. The constant of the proportionality, 24.4, corresponds to the volume of one mole of gas at 25°C. By substituting for the partial pressure of hydrogen chloride and for the concentration of the hydrogensulfide ions expressions from eqn (6), and putting them into the eqn (5), the following relation for the rate of the reaction can be obtained

$$r = \frac{p_{\rm H_{2S}} k_{\rm I}/2}{1 + k_2 \frac{24.4 \, m}{F} \cdot \sqrt{\frac{p_{\rm H_{2S}}}{[{\rm Me}^{2+}] \, K'}}},$$
(7)

where k_1 and k_2 are the known rate constants in both directions of the reaction, $p_{\text{H}_{2S}}$ is the partial pressure of hydrogen sulfide in atm, F is the overall gas flow through the melt $[1 \text{ min}^{-1}]$, m is the weight of the melt [kg], K' is the apparent equilibrium constant of the reaction (B). From a comparison with eqn (I) it is evident that if we choose $A = p_{\text{H}_{2S}} k_1/2$ and $B = (24.4 \text{ m} \sqrt{\frac{p_{\text{H}_{2S}}{K'}}} 1/F$, this equation is consistent with eqn (I) and thus the possibility of the explanation of the investigated process on the basis of the proposed reaction mechanism is verified.

The results of the study of the reaction of cadmium(II) and zine(II) ions with hydrogen sulfide in the molten lithium chloride and potassium chloride mixture are analogous



Fig. 5. Comparison of the rate of the reaction of hydrogen sulfide with the molten alkali chloride mixture with the rates of reaction of hydrogen sulfide with this melt in the presence of lead(II), cadmium(II), and zinc(II) ions, respectively, $r = [\text{mol } \text{kg}^{-1} \text{ min}^{-1}]$ in dependence on the time t [min].

Temperature 500°C, gas flow through the melt $F = 0.21 \text{ min}^{-1}$, weight of the melt m = 0.05 kg. 1. molten alkali chloride mixture; 2. lead(II) ions; 3. cadmium(II) ions; 4. zinc(II) ions.

to those of the study of hydrogen sulfide with lead(II) ions in the same melt. The cadmium(II) and zinc(II) ions do not react with hydrogen sulfide to form sulfide; they only speed up the reaction of hydrogen sulfide with the chloride ions by removing the hydrosulfide ions from the system forming sulfides. Thus the reaction mechanism is the same as in the reaction of the lead(II) ions with hydrogen sulfide; however, the rates of these processes are different as it is evident from Fig. 5. With respect to the rate of the reaction (A), the cadmium(II) and zinc(II) ions appear to be more effective than the lead(II) ions. The acceleration of the reaction (A) brought about by the cations dissolved in the melt depends on the equilibrium constant of the reaction (B) for the corresponding cation. The values of these equilibrium constants are plotted in Table 1. For comparison, also

Table 1

t [°C]	$K'_{\mathrm{Cd}^{2+}}$	$K'_{\mathrm{Zn}^{2+}}$	$K'_{\mathrm{Pb}^{2+}}$
410	······································		1.56×10^{10}
415		$3.147 imes 10^9$	
420	$4.83 imes 10^9$		
450	$5.44 imes 10^8$	4.689×10^8	$1.48 imes 10^{\circ}$
500	4.67×10^{7}	3.86×10^7	$1.44 imes 10^7$

Dependence of the equilibrium constants of the reaction (B) on the temperature

* The values according to [4].

the corresponding values for the reaction of hydrogen sulfide with lead(II) ions are presented. The most instructive demonstration of the influence of different cations on the rate of the reaction is the dependence of the concentration of hydrogensulfide ions calculated from the values of the equilibrium constants of the reaction (B) on the concentration of the investigated cations. This dependence is presented in Figs. 6-9. The concentrations of hydrogensulfide are plotted in a logarithmic scale. On these graphs, the y axis represents the level of the reaction in the absence of cadmium(II) and zinc(II) ions, *i.e.* the concentration of hydrogensulfide ions attained by reaction of hydrogen sulfide with the molten alkali chloride mixture alone. From these figures it can be seen that the concentration of cadmium(II) ions in the order of 10^{-2} molal decreases the concentration of hydrogensulfide ions at 500°C by more than half an order. A further increase in the concentration Fig. 6. Dependence of the logarithm of the concentration of hydrogensulfide ions on the concentration of cadmium(II) ions [mol kg⁻¹]. Partial pressure of hydrogen sulfide = 1 atm, temperature [°C]; 1. 500; 2. 450; 3. 420.

of cadmium(II) ions does not exhibit such a pronounced influence on the decrease of the concentration of hydrogensulfide ions. At two other experimental temperatures this decrease in the concentration of hydrogensulfide ions is equally pronounced at the 0.01 molal concentration of the cadmium(II) ions. The zinc(II) ions effect an analogous, though somewhat smaller decrease in the concentration of hydrogensulfide ions.





The relations derived in this work are based on the presumption of a steady state. However, this assumption need not be satisfied in the entire concentration range of the investigated cations. By reaction of cadmium(II) and zinc(II) ions with the hydrogensulfide ions in the melt, the concentration of these cations decreases to such a degree that

Fig. 8. Dependence of the logarithm of the concentration of hydrogensulfide ions on the concentration of zinc(II) ions [mol kg⁻¹]. $p_{\rm H_{2S}} = 1$ atm, temperature [°C]: 1. 500; 2. 450; 3. 415.





Fig. 9. Dependence of the logarithm of the concentration of hydrogensulfide ions on the concentration of the zinc(II) ions [mol kg⁻¹].

Temperature = 500°C, $p_{H_{2}S}$ [atm]: 1. 1; 2. 0.545; 3. 0.42; 4. 0.286.

the remaining cations are not able to bind the hydrogensulfide ions formed by the reaction (A) which leads to an increase of the sulfur content in the melt in the form of both sulfide and hydrogensulfide. Then the rate of the overall process is given by the rate of the first step of the reaction mechanism, this suppressing the validity of the relation (3). The relation between the change in the concentration of the reacting cations and the increase in the material amount of sulfur in the same volume of the melt can be then expressed by the equation

$$-2\mathrm{d}[\mathrm{Me}^{2+}]/\mathrm{d}t = X \,\mathrm{d}[S]/\mathrm{d}t = X \,\mathrm{d}[\mathrm{HS}^{-}]/\mathrm{d}t,\tag{8}$$

where d[HS⁻]/dt is the rate of the increase of hydrogensulfide ions by reaction of the chloride ions with hydrogen sulfide, X is a dimensionless parameter = d Me²⁺/dS, d Me²⁺ and dS are the changes in the material amounts of the investigated cations and of sulfur for an imperceptible change in the range of the reaction. In the steady state at an excess of the bivalent cations, the value X = 1, whilst with a decreasing concentration of the reacting cations the value of X decreases. From the balance relations concerning the total amount of sulfur in the melt it follows that

$$\Delta S = -\Delta \mathrm{Me}^{2+} + \Delta \mathrm{HS}^{-}.$$
(9)

For an imperceptible change in the range of the reaction, the change of the material quantity of the investigated cations and of the hydrogensulfide ions is expressed by equations

$$[\mathrm{Me}^{2+}]_1 = [\mathrm{Me}^{2+}]_0 - \varDelta [\mathrm{Me}^{2+}], \tag{10}$$

$$[HS^{-}]_{1} = [HS^{-}]_{0} + \Delta [HS^{-}].$$
(11)

If we choose $\frac{\Delta Me^{2+}}{\Delta S} = X$, then $\frac{\Delta HS^{-}}{\Delta S} = 1 - X$.

Taking $[HS^-]_1$ and $[HS^-]_0$ from eqn (6), the following relation for the calculation of the X values in dependence on the concentration of the investigated cations for the partial pressure of hydrogen sulfide equal to 1 atm is obtained

$$\sqrt{\frac{1}{K'[\mathrm{Me}^{2+}]_0}} + (1-X)\,\Delta S = \sqrt{\frac{1}{K'([\mathrm{Me}^{2+}]_0 - X\Delta S)}}\,,\tag{12}$$

where K' is the value of the apparent equilibrium constant of the reaction (B), [Me]₀ is an arbitrary concentration of the reacting ions before the imperceptible change in the range of the reaction. The X values were calculated for the selected concentration differences $\Delta S = 0.001$. The dependence of X on the concentration of the cadmium(II)



Fig. 10. Dependence of the dimensionless parameter X from eqn (12) on the concentration of cadmium(II) ions for the range 0.75-1. $p_{\rm H_{2S}} = 1$ atm, temperature [°C]: 1.500; 2.450; 3.420.

and zinc(II) ions is presented in Figs. 10 and 11. The straight line p represents a 10 percent deviation from X = 1, *i.e.* from the steady state. The ten percent deviation is comparable with the error of the analytical determination of the concentration of the investigated cations. The corresponding concentration of the investigated cations was therefore chosen as a limiting concentration of these cations, where the reaction still can be considered as occurring in the steady state. Figs. 10 and 11 representing this area indicate that in the reaction of cadmium(II) ions with hydrogen sulfide this limiting value of the concentration of cadmium(II) ions is 8×10^{-3} at 500°C, 4×10^{-3} at 450°C, and 2.3×10^{-3} at 420°C. In the reaction of the zinc(II) ions with hydrogen sulfide, there is a ten percent deviation from the steady state at the concentration of the zinc(II)ions 8.5×10^{-3} at 500°C, 2.9×10^{-3} at 450°C, and 2.0×10^{-3} at 415°C. These low concentrations of the investigated cations are already beyond the experimentally investigated range of concentrations. As regards the concentrations of the investigated cations below the above limiting values, they can be estimated only on the basis of eqn (12). At very low concentrations of the investigated cations, the reaction of cations with hydrogensulfide ions will be negligible in comparison with the reaction of the formation of the hydrogensulfide ions and the kinetics of the reaction will be determined by the rate



Fig. 11. Dependence of the dimensionless parameter X from eqn (12) on the concentration of the zinc(II) ions for the range 0.75-1.

 $p_{\text{H}_{2S}} = 1$ atm, temperature [°C]: 1. 500; 2. 450 3. 415. of the reaction of hydrogen sulfide with the molten lithium and potassium chloride mixture to form hydrogensulfide.

From the study of the reaction of cadmium(II) and zinc(II) ions dissolved in the molten lithium and potassium chloride mixture it follows that these ions react with hydrogen sulfide by the same mechanism as do the lead(II) ions, however, the rate of the reaction of hydrogen sulfide with cadmium(II) and zinc(II) ions is greater than that of the reaction with lead(II) ions. The obtained results indicate also the influence of the reaction medium (the melt) on the investigated reaction. It can be assumed that the molten alkali chlorides mixture is not an inert medium with respect to the investigated reaction.

This work was not intended to be a systematic investigation of the behaviour of individual cations and on their methodical classification into groups. It was demonstrated that the reaction of hydrogen sulfide with different metals in molten alkali chlorides does not lead automatically to the formation of sulfides but a more complicated mechanism should be considered.

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