CC.—*The Precipitation of Cadmium Sulphide from Aqueous Solutions of Cadmium Chloride in the Presence of Hydrochloric Acid and Other Chlorides.*

By SUBRAMONIA KRISHNAMURTI.

THE object of this investigation was to determine the relation between the concentration of cadmium chloride and the minimum concentration of hydrochloric acid required to prevent the precipitation of cadmium sulphide by hydrogen sulphide at constant temperature and pressure, and to ascertain the effect of various chlorides on this relation. It will be seen that the introduction of the activity concept renders this familiar problem of analytical practice capable of much more exact theoretical treatment. The present paper forms an introduction to the study of this and allied reactions from this point of view. Amongst previous workers on the precipitation of sulphides, mention may be made of Bruner and Zawadski (*Bull. Acad. Sci. Cracow*, 1909, 267; *Z. anorg. Chem.*, 1910, **67**, 454), who studied more especially the precipitation of thallous sulphide, and of Baubigny (*Compt. rend.*, 1888, **107**, 1148), who investigated the concentration of free acid required to prevent the precipitation of zinc sulphide from solutions of zinc sulphate. Reference may also be made to the work of Bruni and Padoa (*Atti R. Accad. Lincei*, 1905, **14**, ii, 525) and of Glixelli (*Z. anorg. Chem.*, 1907, **55**, 297).

EXPERIMENTAL.

The apparatus used was very simple. A stream of washed and pre-heated hydrogen sulphide was bubbled through the solution contained in a suitable vessel, placed in a thermostat at 25°. The gas escaped through an oil-trap. In order to prevent the oxidation of hydrogen sulphide, air-free water was used in making up all solutions, whilst a stream of carbon dioxide was passed through the apparatus and solution for a considerable time before the hydrogen sulphide was admitted. A pre-saturator (also in the thermostat) contained hydrochloric acid of the same concentration as that contained in the precipitation vessel. In order to obtain reproducible results, in addition to the above precautions the precipitation vessel must be cleaned very thoroughly before use. The experiments were carried out by making up a series of solutions having the same concentration of cadmium chloride and gradually increasing concentrations of hydrochloric acid. In this way, two neighbouring solutions were obtained, in one of which a precipitate just appeared whilst in the other it did not. These two solutions were then made the limiting members of a new series in which the acid concentrations were graded more closely than before, and the interval between precipitation and non-precipitation was thus more accurately determined. Proceeding in this way, it was found possible to distinguish between two solutions differing by not more than 0·1*N*. The mean of these two hydrochloric acid concentrations was taken as giving the " critical " concentration for the given solution of cadmium chloride (expressed as mols. per litre), and the results are in the first two columns of Table I.

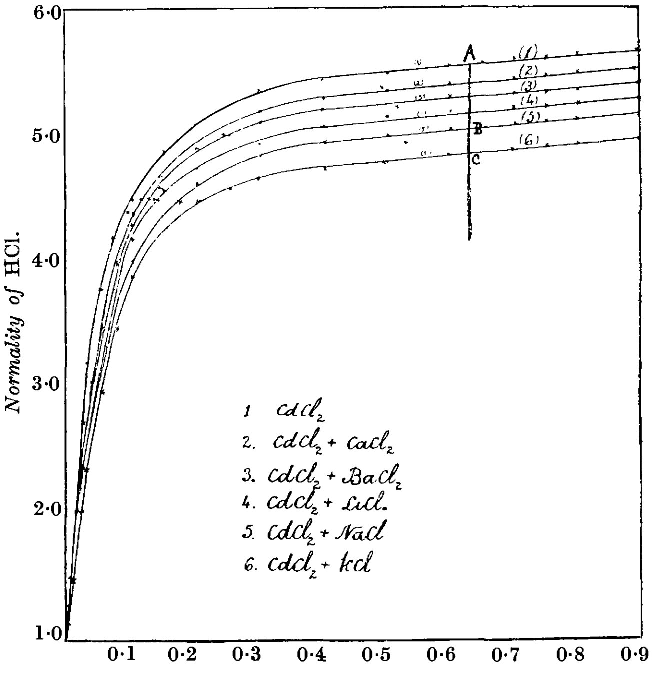
A second series of experiments was made with solutions in which the chloride of potassium, sodium, lithium, barium, or calcium was added so as to be present in *N*-concentration. The results are in the last five columns of Table I, which show in each case the critical concentrations of hydrochloric acid corresponding to each concentration of cadmium chloride.

TABLE I.

	Limiting concentrations of HCl in the presence of					
$CdCl_2$.	—	*N*-KCl.	*N*-NaCl.	*N*-LiCl.	*N*-$BaCl_2$.	*N*-$CaCl_2$.
0·005	1·50	1·20	1·30	1·35	1·40	1·40
0·01	2·05	1·50	1·60	1·65	1·75	1·80
0·03	3·20	2·40	2·50	2·55	2·60	2·65
0·05	3·80	3·00	3·15	3·25	3·35	3·50
0·08	—	3·50	3·60	3·75	4·10	4·15
0·10	4·50	3·90	4·00	4·20	4·30	4·40
0·20	5·20	4·50	4·60	4·70	4·90	5·00
0·30	5·40	4·60	4·85	4·95	5·10	5·20
0·40	5·45	4·75	4·95	5·05	5·20	5·30
0·50	5·55	4·80	5·00	5·15	5·25	5·35
0·60	5·60	4·85	5·05	5·20	5·30	5·40
0·70	5·65	4·90	5·10	5·25	5·35	5·45
0·80	5·70	4·95	5·10	5·25	5·35	5·50
0·90	5·70	4·95	5·15	5·30	5·40	5·55
1·00	5·75	5·00	5·20	5·30	5·40	5·60

The results contained in Table I are shown in Fig. 1. It will be seen that the critical concentration of hydrochloric acid increases very rapidly with increase of cadmium chloride concentration for the lower concentrations, whilst for the higher concentrations the variation of the hydrochloric acid concentration is comparatively small. It will also be seen that the effect of the neutral chlorides is to lower the critical concentration of hydrochloric acid corresponding to any given concentration of cadmium chloride, which means that in the presence of these chlorides a lower concentration of hydrochloric acid suffices to prevent precipitation of cadmium sulphide, thus pointing to an activation of the acid by the neutral chloride.

FIG. 1.



The Time Factor.—A surprising feature of these results is the relatively high concentrations of hydrochloric acid required just to prevent precipitation. This critical concentration increases rapidly with time. Passing in hydrogen sulphide for 5 minutes and for 1 hour, respectively, gave the results shown in the two lower curves of Fig. 2. On increasing the duration of passage of the gas, the critical concentration of hydrochloric acid steadily rose, reaching a limit after about 6 hours (see highest curve), *i.e.*, further passage of the gas produced no measurable variation in the required concentration of acid. Glixelli (*loc. cit.*) noticed a similar " period of induction " in his experiments on the precipitation of zinc sulphide. The experimental results given in Table I correspond in all cases to a duration of 6 hours for the passage of hydrogen sulphide. The influence of this apparent supersaturation effect is shown in Table II, which gives, for a 0·1*M*-solution of cadmium chloride at 25°, the critical concentrations of hydrochloric acid corresponding to different lengths of time.

FIG. 2.

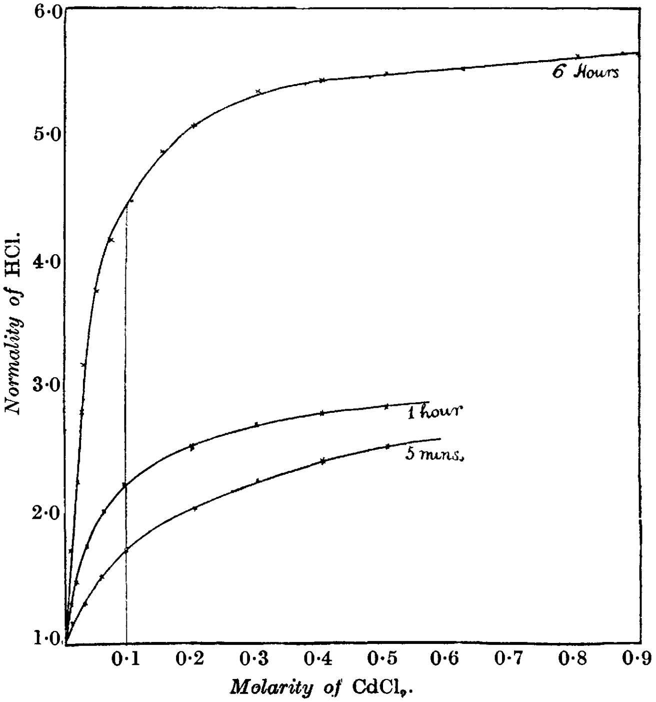


TABLE II.

Mols. HCl per litre	1·7	2·3	4·5
Time (min.)	5	60	300

E.M.F. Measurements.—If we apply the simple laws of chemical equilibrium to the ionic reactions occurring in such a precipitation of sulphide, then, for the points on the " precipitation curve " (*i.e.*, the curve separating the region of precipitation from that of non-precipitation), we have the two equations

$$[\mathrm{Cd}^{\bullet\bullet}] \,.\, [\mathrm{S}''] = \mathit{const.}$$
$$[\mathrm{H}^{\bullet}]^2 \,.\, [\mathrm{S}''] = K[\mathrm{H_2S}].$$

The first equation involves, of course, the doubtful assumption that the points on the precipitation curve correspond to equilibrium with a definite crystalline cadmium sulphide present in not too fine a state of division. If we assume further that the solubility of the hydrogen sulphide and also its dissociation constant do not appreciably change with the total electrolyte content of the solution, then the right-hand member of the second equation remains constant, and division of the equations gives $[\mathrm{Cd}^{\bullet\bullet}]/[\mathrm{H}^{\bullet}]^2 = \mathit{const.}$, an equation which is often used in elementary treatises on the theory of inorganic analysis. For very dilute solutions, we may use the approximate form $[\mathrm{CdCl_2}]/[\mathrm{HCl}]^2 = \mathit{const.}$ If we apply this equation to the results given in columns 1 and 2 of Table I for the dilute solutions of cadmium chloride (although the corresponding concentrations of hydrochloric acid are by no means dilute), we obtain the results shown in Table III : the quotient rises slowly.

TABLE III.

$[\mathrm{CdCl_2}]$	0·005	0·01	0·02	0·03	0·05	0·10
$[\mathrm{HCl}]$	1·50	2·05	2·75	3·20	3·80	4·50
$10^4 \times [\mathrm{CdCl_2}]/[\mathrm{HCl}]^2$ ...	22	25	26	29	34	49

Rewriting the former equations in terms of activities, we have

$$a_{\mathrm{Cd}} \,.\, a_{\mathrm{S}} = L$$
$$a_{\mathrm{H}}{}^2 \,.\, a_{\mathrm{S}} = K_1 a_{\mathrm{H_2S}}$$

where L is the activity of the solid sulphide and K_1 the " thermodynamic " dissociation constant of hydrogen sulphide. Since the temperature and the pressure of hydrogen sulphide in the gas phase are constant, $a_{\mathrm{H_2S}}$ is now strictly constant. We may also regard K_1 as a constant, hence for points on the precipitation curve

$$a_{\mathrm{H}}{}^2/a_{\mathrm{Cd}} = K_1 a_{\mathrm{H_2S}}/L = \mathit{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation will be much more exact than the former one, although it still involves the assumption that we are dealing, along the precipitation curve, with a definite " solid " cadmium sulphide of not too small a grain size, or, at all events, of constant grain size in the different experiments. It is possible to test equation (1) by measuring the *E.M.F.* of cells of the type Cd amalgam | $\mathrm{CdCl_2}+\mathrm{HCl}$ | $\mathrm{H_2}$ gas at constant pressure. A dilute cadmium amalgam of definite concentration is used instead of solid metallic cadmium, in order to avoid irreversible evolution of hydrogen at the cadmium electrode. The *E.M.F.* of the cell is given by the equation

$$E = E_0 + RT/2F \, . \log a_{\mathrm{H}}{}^2/a_{\mathrm{Cd}} \quad . \quad . \quad . \quad . \quad (2)$$

Hence, if we employ in the cell solutions corresponding in composition and concentration to points on the precipitation curve, E will be constant if equation (1) holds good for such points, since we may neglect the effect of the dissolved hydrogen sulphide. Cells of this sort were set up, with hydrogen electrodes of the usual type, and yielded constant and reproducible results after an hour. The results are in Table IV (to the nearest millivolt).

TABLE IV.

$CdCl_2$ (mol./litre)	0·005	0·01	0·02	0·05	0·08	0·10	0·20	0·30	0·50
HCl (mols./litre)	1·50	2·05	2·75	3·80	4·20	4·50	5·20	5·40	5·55
E.M.F. (millivolts)	481	481	481	481	482	481	482	482	480

The constancy in the *E.M.F.* indicates that the points on the observed precipitation curve do correspond to definite equilibria, and supports the view that this curve is a true border curve separating the region of precipitation from that of solution (non-precipitation).

Neutral Salt Effect.—The curves numbered (2) to (6) in Fig. 1 show the changes in the precipitation curve caused by the presence (in N-concentration) of a series of neutral chlorides. The interpretation of these neutral salt effects from the point of view of ionic activities can be seen from a consideration of the figure. At the point A on the precipitation curve of cadmium chloride (*i.e.*, without addition of any neutral chloride) we have the relation

$$a_{\mathrm{H}}{}^2/a_{\mathrm{Cd}} = K_1 a_{\mathrm{H_2S}}/L.$$

Suppose now that the solution corresponding to point A is made N with respect to, *e.g.*, potassium chloride, everything else remaining the same. Since A lies above C, it is clear that A now falls in the non-precipitation region, and hence $a_{\mathrm{Cd}} \cdot a_{\mathrm{S}} < L$. In the mixed solution corresponding to point A, therefore, $a_{\mathrm{H}}{}^2/a_{\mathrm{Cd}} > K_1 a_{\mathrm{H_2S}}/L$. The effect of the addition of potassium chloride has thus been to increase the value of the quotient $a_{\mathrm{H}}{}^2/a_{\mathrm{Cd}}$ and this value can be brought back to the original value, $K_1 a_{\mathrm{H_2S}}/L$, only by reducing the concentration of hydrochloric acid to the value corresponding to point C. Now it is well known that the addition of chlorides can increase the value of a_{H} in a solution of hydrochloric acid (Poma, *Z. physikal. Chem.*, 1914, **88**, 671; Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2460; Fales and Nelson, *ibid.*, 1915, **37**, 2769; Thomas and Baldwin, *ibid.*, 1919, **41**, 1981). In the present case, this action will produce a very marked result, owing to the occurrence of a_H^2 in the numerator of the quotient. It is probable that owing to complex anion formation and other causes the addition of chlorine ions (from the neutral chlorides) will *decrease* the value of a_{Cd} occurring in the denominator. We have therefore good reasons for concluding that the addition of a neutral chloride will increase the value of a_H^2/a_{Cd}.

If we ascribe the chief effect to the increase in the value of a_H, we should expect from the results of the investigations previously quoted that the effect would decrease in the order $LiCl > NaCl > KCl$, whereas the results in Table I would appear to give the order $KCl > NaCl > LiCl$.

Further discussion of this matter would not be profitable without more detailed and extensive data.

Summary.

1. The concentrations of hydrochloric acid which are just sufficient to prevent precipitation of solutions of cadmium chloride by hydrogen sulphide at 25° and atmospheric pressure have been determined.

2. The effects produced on these critical concentrations of hydrochloric acid by a number of neutral chlorides in *N*-concentration have been determined.

3. The cadmium chloride–hydrochloric acid " precipitation " curve has been considered from the point of view of ionic activity, and predictions based thereon have been confirmed by *E.M.F.* measurements.

4. The effects produced by the addition of neutral chlorides have been considered in the light of previous work on the influence of such salts on the hydrogen-ion activity.

5. The precipitation experiments reveal a " supersaturation " or " induction " delay in the appearance of the precipitate, an effect previously noted by Glixelli in the precipitation of zinc sulphide.

It is intended to extend this investigation and to include allied cases.

The work described was carried out at the suggestion and under the direction of Professor F. G. Donnan, to whom the author desires to express his thanks for advice and assistance.

THE WILLIAM RAMSAY INORGANIC AND PHYSICAL
CHEMISTRY LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, April* 15*th*, 1926.]