[Contribution from the Department of Chemistry, Yale University]

EQUILIBRIUM IN THE SYSTEMS, NICKEL CHLORIDE, COBALT CHLORIDE, CUPRIC CHLORIDE—HYDROCHLORIC ACID–WATER

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When any soluble substance is added to a saturated solution of a hydrated salt, the vapor pressure of the solution is lowered and if no other insoluble products are produced, the lowering may be so great that the original hydrate is no longer stable in contact with the solution and a lower hydrate or the anhydrous salt may be deposited. In this way, for instance, lower hydrates of copper sulfate or the anhydrous salt may be deposited from solution when sufficient sulfuric acid is present; and anhydrous sodium sulfate instead of the decahydrate may crystallize below its transition point, by the addition of another salt such as sodium chloride or another liquid such as alcohol.

Hydrogen chloride has the same general effect as any other soluble substance in this respect, and it may therefore happen that lower hydrates of a salt crystallize from solutions containing hydrochloric acid, when a higher hydrate crystallizes from water solution at the same temperature. A number of such cases are known.

If hydrochloric acid could be mixed in all proportions with water and no solid addition products were formed with water or salt, it would be possible, by varying the proportions of acid, to produce all the stable hydrates which a chloride can form, ending finally with the anhydrous salt. Practically any method of preparing lower hydrates by this means is limited by the insufficient concentration of hydrochloric acid in solution and by the fact that chlorides may form solid addition products with the acid.

It is evident from the phase rule that a system composed of water, a metallic chloride and hydrochloric acid and containing a solid salt, solution and vapor, is divariant, since the number of components equals the number of phases. At a given temperature, therefore, the solid may be in equilibrium with a series of saturated solutions containing various amounts of hydrochloric acid. With 2 solids present, the system is univariant, and at a given temperature there is but one solution of fixed concentration and vapor pressure which can be in equilibrium. One such system, containing ferric chloride as the salt, has been investigated throughout a considerable range of temperature by Roozeboom and Schreinemaker.[1]

We have determined the solid phases and the solubility at 0° (and in one case at 25°) of nickel, cobalt and copper chlorides in solutions con-

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[1] Roozeboom and Schreinemaker, *Z. physik. Chem.*, **15**, 588 (1894).

taining increasing amounts of hydrochloric acid up to the point where the solutions were saturated with the acid at atmospheric pressure. Under these conditions, nickel chloride yields successively 3 hydrates, cobalt chloride yields 2 and copper chloride yields but 1. This last is stable throughout the entire range of hydrochloric-acid concentration at 25° but yields an addition product with the acid at 0° when the concentration of acid is sufficiently great.

The solubility of copper chloride and cobalt chloride in hydrochloric acid solutions has been determined by Engel[2] at 0°. The solid phases in equilibrium were not determined by him and the results for each salt when plotted fall on a uniform curve, although in reality there is a well-marked break in the solubility curve at each univariant point.

In the present investigation, a series of mixtures was prepared consisting of suitable proportions of the recrystallized salts and water with continually increasing amounts of acid. Each sample was rotated in a thermostat until equilibrium was reached. Samples for analysis were drawn off through a filter of glass wool. The metal was determined electrolytically and total chlorine as silver chloride, from which the proportions of metallic chloride and hydrochloric acid were calculated. The composition of the solid phases in equilibrium with solutions was determined when necessary by the Schreinemaker graphic method,[3] from the analysis of the wet residues.

TABLE I

NICKEL CHLORIDE

$T = 0°$

Solution		Wet Residue		
$NiCl_2$ %	HCl %	$NiCl_2$ %	HCl %	Solid Phase
35.27	none	...	...	$NiCl_2.6H_2O$
26.71	6.53	...	...	
15.67	14.09	44.27	3.70	
9.68	18.62	...	...	
6.15	21.70	...	...	
5.30	23.03	...	...	
3.65	25.74	43.98	5.38	
4.02	26.16	43.97	5.50	
4.64	25.90	46.84	5.59	$NiCl_2.6H_2O$ and $NiCl_2.4H_2O$
4.47	26.11	45.77	7.06	
4.45	26.23	49.47	6.22	$NiCl_2.4H_2O$
2.92	28.82	45.44	8.87	
1.37	34.57	46.56	9.67	
1.40	35.03	40.73	13.91	$NiCl_2.4H_2O$ and $NiCl_2.2H_2O$

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[2] Engel, *Ann. chim.*, [6] **17,** 338 (1889).

[3] Schreinemaker, *Z. physik. Chem.*, **11,** 76 (1893).

2.29	33.96[a]	57.40	9.17	$NiCl_2.2H_2O$
1.57	34.70[a]	52.46	11.48	
1.06	36.00	56.96	9.69	
0.82	37.22	56.18	10.32	
0.43	40.61	56.20	11.10	

[a] Unstable system. Supersaturated with respect to $NiCl_2.4H_2O$.

Table II

Cobalt Chloride

$T = 0°$

Solution		Wet Residue		Solid Phase
$CoCl_2$ %	HCl %	$CoCl_2$ %	HCl %	
31.66	none	...	...	$CoCl_2.6H_2O$
25.58	3.26	...	...	
17.78	8.74	...	...	
12.79	12.44	...	...	
5.97	19.01	...	...	
4.74	20.51	...	...	
2.69	25.66	...	...	
3.07	27.27	...	...	
6.34	29.38	...	...	
9.91	29.15	49.73	3.36	
11.58	28.97	45.73	6.53	
12.42	29.14	63.02	4.41	$CoCl_2.6H_2O$ and $CoCl_2.2H_2O$
12.88	28.84	54.27	6.28	
12.66	30.27	64.84	5.81	$CoCl_2.2H_2O$
15.11	33.03	63.84	7.11	
15.12	33.86	60.30	9.07	

Table III

Copper Chloride

$T = 0°$

Solution		Wet Residue		Solid Phase
$CuCl_2$ %	HCl %	$CuCl_2$ %	HCl %	
40.92	...	...	...	$CuCl_2.2H_2O$
34.82	3.72	...	...	
23.82	10.35	...	...	
15.64	16.71	...	...	
12.12	21.82	...	...	
11.92	25.64	...	...	
13.86	29.02	63.08	7.04	
17.70	31.01	54.47	14.08	$CuCl_2.2H_2O$ and $HCl.CuCl_2.3H_2O$
17.14	31.31	58.42	11.93	
15.66	32.66	41.41	22.79	$HCl.CuCl_2.3H_2O$
14.13	34.55	44.02	22.26	
12.29	36.82	40.84	23.94	
11.85	37.19	41.31	23.67	

TABLE IV
COPPER CHLORIDE
$T = 25°$

Solution		Wet Residue		
$CuCl_2$ %	HCl %	$CuCl_2$ %	HCl %	Solid Phase
43.32	none	...	...	$CuCl_2.2H_2O$
32.85	6.52	...	...	
23.74	12.95	68.37	2.48	
18.34	18.08	...	...	
17.71	19.92	...	...	
17.01	22.26	...	...	
18.20	25.07	66.02	5.27	
22.65	27.76	39.81	18.87	
23.29	27.94	39.31	19.63	
24.07	28.05	...	...	
25.65	28.49	62.81	8.08	

The composition of the solutions has been plotted in Figs. 1, 2 and 3. The univariant ternary systems are represented by black dots (using the average of the solubility determinations) and the other results by circles or crosses.

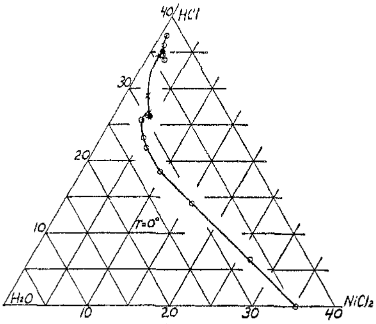

Fig. 1.

To avoid confusion in the diagrams, the composition of the residues has been omitted but, excluding for the moment the case of the compound, $HCl.CuCl_2.3H_2O$, all the residues of divariant systems lie very close to the lines connecting the composition of the solution with the composition of the corresponding hydrate and there can be no doubt of the existence of these and the absence of other intermediate hydrates. The composition of the above-mentioned addition product with hydrochloric acid is more difficult to determine as only a short length of the solubility curve could be obtained and the lines connecting solution and residue lie too nearly parallel to give the point of intersection with certainty. The formula given above corresponds to the results obtained more closely than any other formula of simple ratios. The

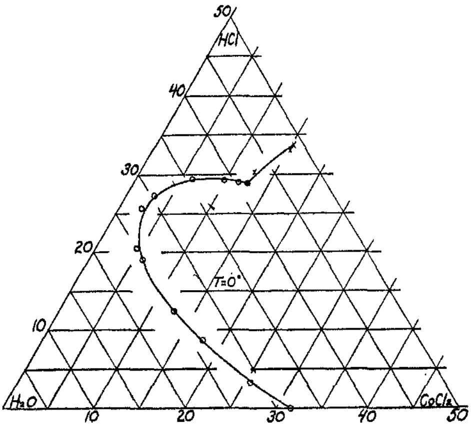

Fig. 2.

same formula was obtained by Engel[2] for this compound, but no evidence of the compound, $CuCl_2.2HCl.5H_2O$, described by Sabatier,[4] has been obtained. The formation of the tetrahydrate of nickel chloride and the absence of the corresponding cobalt compound are quite definitely shown. The existence of this hydrate of nickel chloride had been inferred from the vapor-pressure relations[5] and the solubility results now confirm this conclusion.

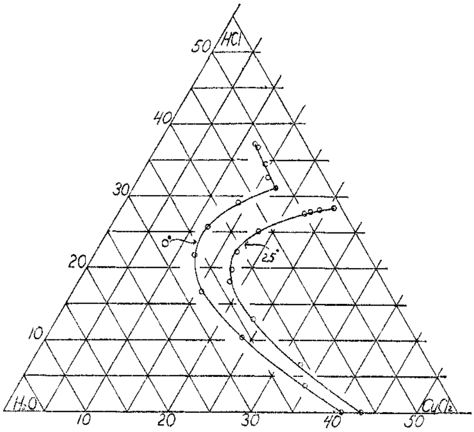

Fig. 3.

In regard to solubility, all the salts show a rapid decrease at first, as the acid content increases, due to the common-ion effect. The subsequent increase due to complex formation is most marked in the case of cupric chloride, which deposits an addition product at 0°, and hardly noticeable in the case of nickel chloride. The difference in solubility between 2 such similar salts as nickel and cobalt chlorides in conc. hydrochloric acid is somewhat striking. It is probable that a method of freeing nickel chloride from small amounts of cobalt chloride might well be based on this difference in solubility.

Summary

The solubility at 0° (and in one case at 25°) of the chlorides of nickel, cobalt and copper has been determined in the presence of increasing amounts of hydrochloric acid.

The solid phases in equilibrium with the solutions have also been determined.

Cupric chloride forms one addition product with hydrochloric acid. Nickel chloride yields the tetrahydrate and dihydrate, besides the ordinary hexahydrate, while cobalt chloride yields, besides the hexahydrate, only the dihydrate.

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[4] Sabatier, *Compt. rend.*, **106**, 1724 (1888).

[5] Derby and Yngve, This Journal, **38**, 1439 (1916).