

similar period of time, as mentioned above. There were considerable time intervals in these runs when the temperature did not vary over 0.001 – 0.002° , and when the liquid air is rich in oxygen, the control is quite simple.

The feature of safety should be emphasized, for in the event of collapse of the Pyrex Dewar vessel only a slight amount of liquid oxygen in the tube E could be mixed with the liquid hydrocarbon. The Dewar vessel should be housed on several sides, having windows for observations in the bath, in order to eliminate the possibility of the operator being sprayed with the hydrocarbon bath in event of failure of the Dewar tube. Moreover, the motor driving the stirrer should be removed to as great a distance as is practicable.

It should be added that a new temperature can be reached quickly by adding warm bath material or by cooling with liquid air in a large copper test-tube. The preliminary cooling of the bath to the desired temperature is carried out by this means, care being exercised that no boiling over of liquid air occurs to mix with the bath, especially when using commercial butane. A short portion of the copper tube bent near the top to an angle of about 45° effectively prevents this.

Summary

Various types of cryostats are described, and the precisions, with advantages of each, discussed.

An improved cryostat is described, modeled after the Henning cryostat, which functions at any temperature from 0° to -180° . Its principal features are precision, safety and economy. Test runs showed a steadiness of $\pm 0.01^{\circ}$ at -150° for three hours and $\pm 0.015^{\circ}$ at -180° for a similar period.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 482]

THE SOLUBILITY OF SLIGHTLY SOLUBLE CHLORIDES IN CONCENTRATED CHLORIDE SOLUTIONS

BY JAMES KENDALL AND CHARLES HOWARD SLOAN

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In a previous article from this Laboratory,¹ it was predicted that the solubility of silver chloride in an aqueous solution of a second chloride MCl would increase more and more above the normal value as the radical M was made more electropositive. This prediction was based upon the general rule that the stability of an addition compound is dependent upon the differences in electro-affinity of the radicals of its components.² The validity of this rule for systems of the type $\text{AgCl-MCl-H}_2\text{O}$ was strikingly con-

¹ Kendall, Davidson and Adler, *THIS JOURNAL*, **43**, 1481 (1921).

² Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).

firmed by means of the experimental data of Forbes,³ the order of solubility as M was varied being $H < Ca < Na < Sr < Ba < K$ or NH_4 .

The present article tests the rule further by examining the solubility of silver chloride in other chloride solutions, and by including extensive measurements upon systems of the type $PbCl_2-MCl-H_2O$. The greater solubility of lead chloride was anticipated to influence the solubility curves in two ways: (1) the point of minimum solubility, which is below 0.01 *N* MCl in silver chloride solutions,⁴ should occur at much higher concentrations, and (2) the chances of obtaining direct evidence of compound formation by the isolation of double salts of still lower solubility than the slightly soluble component should be greatly increased. Both of these expectations were realized, as will be seen below.

Silver Chloride Systems

The experimental procedure was substantially identical with that described in detail by Forbes. The thermostat employed was regulated to $25 \pm 0.004^\circ$ by means of a Beaver regulator.⁵ The salts used were c. p. samples, recrystallized twice from distilled water.

1. **Sodium Chloride.**—Investigation of this system, already covered by Forbes, was repeated in order to ensure comparability of results. The data in Table I and all those succeeding are expressed in terms of gram equivalents per liter in the final solution.

TABLE I
SILVER CHLORIDE IN SODIUM CHLORIDE SOLUTIONS

[NaCl]	0.90	1.10	1.22	1.39	1.61	1.93	2.22	2.37
[AgCl] $\times 10^3$	0.099	0.131	0.139	0.183	0.253	0.391	0.542	0.623
	2.87	3.16	3.40	3.82	4.11	4.39	4.81	5.00
	1.000	1.366	2.074	2.491	3.126	3.825	5.105	5.882

These results are most readily checked against those of Forbes by plotting $\log [AgCl]$ against $\log [NaCl]$ (see Fig. 1). The two curves agree perfectly except at concentrations below 2 *N* sodium chloride, where the method begins to become inaccurate. Owing to this unreliability of the data at the lower concentrations, we feel that Forbes' conclusion that the solubility curves in this and similar systems consist of straight parallel lines connected by shorter curved portions, is scarcely justified. Forbes deduces that definite complex anions (for example, $AgCl_3^{=}$, $AgCl_4^{=}$ and $AgCl_5^{=}$) predominate through considerable concentration ranges. Such a rapid transition from one complex to another as required by Forbes does not seem probable, and our own curves, which show a continuous change of slope at the lower concentrations, indicate gradual and progressive dissociation of the various complexes existent in the solution.

³ Forbes, *THIS JOURNAL*, **33**, 1937 (1911).

⁴ Glowczynski, *Kolloidchem. Beihefte*, **6**, 147 (1914).

⁵ Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

2. **Lithium Chloride.**—The high position of lithium in the electrode potential series suggests that the presence of this salt should increase the solubility of silver chloride much more effectively than sodium chloride,

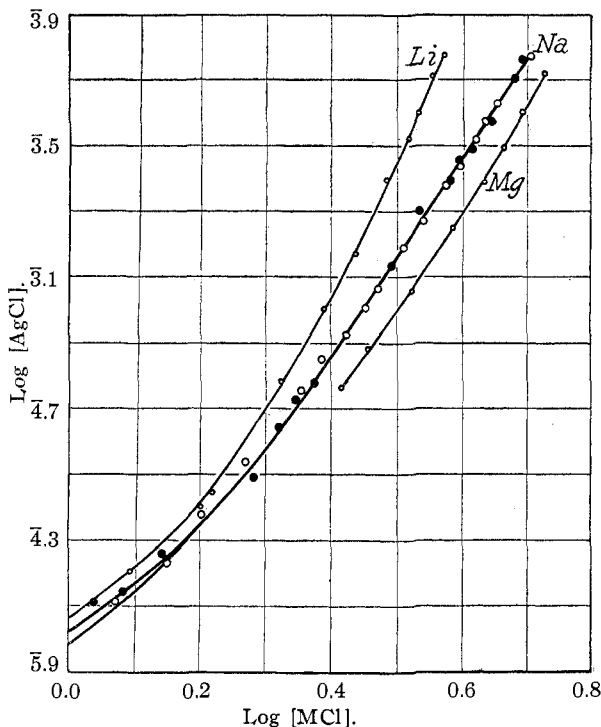


Fig. 1.—Solubility of silver chloride in solutions of sodium, lithium and magnesium chlorides. [The concentrations are in g. equiv. per liter. For NaCl, white circles represent data of Forbes and black dots the data of Kendall and Sloan.]

and slightly more than potassium chloride. The experimental data fall into exact agreement with this suggestion.

TABLE II
SILVER CHLORIDE IN LITHIUM CHLORIDE SOLUTIONS

[LiCl]	0.44	1.24	1.65	2.10	2.44	2.74
[AgCl] × 10 ³	0.100	0.180	0.281	0.605	1.010	1.480
	3.01	3.30	3.40	3.60	3.75	3.78
	2.458	3.278	3.925	5.084	5.922	6.000

3. **Magnesium Chloride.**—The solubility curve for silver chloride, in this case, may be expected to fall between the corresponding curves for the calcium chloride and the hydrochloric acid systems. Again the observed position accords with the predicted.

TABLE III
SILVER CHLORIDE IN MAGNESIUM CHLORIDE SOLUTIONS

$\frac{1}{2}$ [MgCl ₂]	[AgCl] × 10 ³	$\frac{1}{2}$ [MgCl ₂]	[AgCl] × 10 ³
2.60	0.580	4.30	2.530
2.86	0.768	4.58	3.138
3.34	1.165	4.66	3.338
3.85	1.773	4.91	4.042
4.20	2.345	5.36	5.264

Lead Chloride Systems

The method of Forbes for the production of a saturated solution was also followed in our study of these systems, with the exception that, in view of the fact that a double salt was frequently the least soluble solid phase, crystallization was induced by cooling below 25° instead of by seeding. To determine the composition of a double salt, the cooling was continued until sufficient crystals for an analysis had separated. These crystals were then freed from adhering mother liquor as completely as possible and analyzed for lead by the sulfate method, for chloride by the Mohr titration, and for water by heating to constant weight. The barium, strontium, calcium and magnesium complexes were also checked by determining the respective second metal content, the sulfate method being used for barium and strontium, the oxalate for calcium, and the pyrophosphate for magnesium.

The concentrations employed in each series varied from about 0.2 g. equivalent of metal chloride to the vicinity of saturation. Below 0.2 *N* the solubility curve, in most systems, is dropping too sharply to permit accurate determinations by the method followed.

1. **Hydrogen Chloride.**—The system lead chloride-hydrochloric acid-water has been investigated previously at 25.2° by von Ende,⁶ but the results here obtained are not in good agreement with his recorded values.

TABLE IV
LEAD CHLORIDE IN HYDROCHLORIC ACID

[HCl]	[PbCl ₂] × 10 ²	[HCl]	[PbCl ₂] × 10 ²
0.20	1.320	2.90	1.180
.30	1.180	3.25	1.247
.50	1.020	3.52	1.330
.80	0.984	3.58	1.340
1.00	.981	4.02	1.495
1.30	.985	4.30	1.604
1.72	1.014	4.70	1.812
1.86	1.023	5.16	2.161
2.04	1.042	5.50	2.500
2.09	1.060	5.60	2.611
2.57	1.126	5.78	2.802

⁶ (a) Von Ende, *Z. anorg. Chem.*, **26**, 148 (1901). For values at other temperatures see (b) Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, pp. 353-4.

The hydrochloric acid employed by us was a constant-boiling mixture prepared by distillation from a mixture of equal volumes of concd. acid and water. Von Ende does not mention any purification of his acid from the commercial product.

It will be evident from Table IV and from the diagram (Fig. 2) that the addition of hydrogen chloride causes at first a very sharp drop in the solubility of lead chloride from its initial value (7.756×10^{-2} g. equiv. per liter),⁷ and that the very flat minimum which ensues on further addition

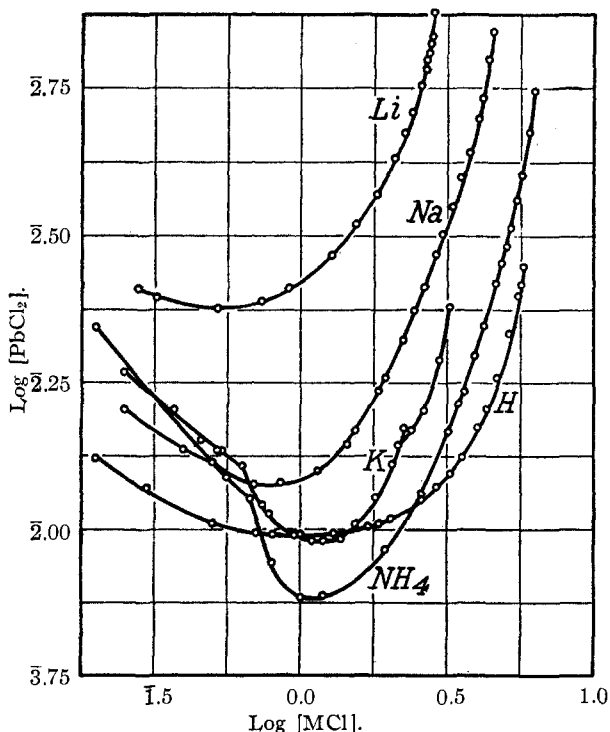


Fig. 2.—Solubility of lead chloride in chloride solutions of type MCl. The concentrations are in g. equiv. per liter.

of acid is followed by a slow but steady increase. Analysis showed that the solid phase was the neutral salt throughout, although at the higher concentrations considerable difficulty was experienced in freeing the crystals from adhering acid sufficiently to obtain concordant analyses.

2. Lithium Chloride.—A pure sample of the salt was prepared as described by Kendall, Crittenden and Miller.⁸ This system has not been studied previously.

⁷ Compare Ref. 6 b, pp. 353–6.

⁸ Kendall, Crittenden and Miller, *THIS JOURNAL*, **45**, 976 (1923).

TABLE V
LEAD CHLORIDE IN LITHIUM CHLORIDE SOLUTIONS

[LiCl]	[PbCl ₂] × 10 ²	[LiCl]	[PbCl ₂] × 10 ²
0.28	2.565	2.10	4.300
.32	2.500	2.26	4.729
.52	2.384	2.40	5.144
.74	2.449	2.58	5.723
.91	2.582	2.68	6.086
1.28	2.945	2.72	6.317
1.55	3.306	2.75	6.507
1.81	3.720	2.82	6.930

The increase in solubility, after the minimum is once passed, is here exceedingly rapid. Analysis of the crystals separating showed that the saturating solid phase, throughout the whole concentration region examined above, was the double salt $\text{LiCl} \cdot 2\text{PbCl}_2$. The mean of the results obtained in four determinations is given below.

Calcd.: Pb, 69.2; Cl, 29.6. Found: Pb, 69.0; Cl, 29.6.

3. Ammonium Chloride.—The solubility of lead chloride in solutions of ammonium chloride at 22° has been the subject of a careful investigation by Brönsted.⁹ Allowing for the temperature difference, the results given in Table VI are in excellent agreement with those recorded by him.

TABLE VI
LEAD CHLORIDE IN AMMONIUM CHLORIDE SOLUTIONS

[NH ₄ Cl]	[PbCl ₂] × 10 ²	[NH ₄ Cl]	[PbCl ₂] × 10 ²
0.20	2.207	4.22	2.220
.50	1.305	4.64	2.620
.56	1.224	4.83	2.836
.80	0.878	5.00	3.030
1.00	.765	5.09	3.142
1.20	.769	5.20	3.264
1.96	.923	5.46	3.645
2.57	1.142	5.66	4.000
3.18	1.462	6.00	4.723
3.47	1.643	6.28	5.507
3.60	1.721	6.30	5.601
3.93	1.982		

Analytical determinations indicated that the saturating solid phase, at all concentrations above 0.6 *N* (compare Fig. 2), corresponded to the double salt $\text{NH}_4\text{Cl} \cdot 2\text{PbCl}_2$. The results of four analyses are averaged below.

Calcd. for $\text{NH}_4\text{Cl} \cdot 2\text{PbCl}_2$: Pb, 68.0; Cl, 29.1. Found: Pb, 68.0; Cl, 29.1.

The solubility curve of the compound presents a minimum at about 1.1 *N* ammonium chloride and rises steadily thereafter.

4. Sodium Chloride.—This system has been examined recently by

⁹ Brönsted, *Z. physik. Chem.*, **77**, 132 (1911).

Herz and Hellebrandt¹⁰ at 25°; a few measurements by Demassieux¹¹ at 14° are also available for comparison. The agreement is fairly good for the more dilute solutions, but wide deviations appear above 2 *N*.

TABLE VII

LEAD CHLORIDE IN SODIUM CHLORIDE SOLUTION			
[NaCl]	[PbCl ₂] × 10 ²	[NaCl]	[PbCl ₂] × 10 ²
0.25	1.603	2.46	2.370
.40	1.370	2.66	2.606
.50	1.300	2.90	2.944
.70	1.192	3.06	3.188
.86	1.205	3.29	3.545
1.14	1.261	3.54	3.966
1.46	1.403	3.78	4.407
1.56	1.468	4.04	5.008
1.85	1.725	4.18	5.431
1.96	1.807	4.39	6.302
2.25	2.100	4.50	7.009

Analysis of the solid phase showed that the compound NaCl.2PbCl₂ was present at all concentrations above 0.5 *N*. The mean of the results of four analyses is given below.

Calcd.: Pb, 67.4; Cl, 28.8. Found: Pb, 67.5; Cl, 28.8.

5. **Potassium Chloride.**—Data for the system are already available from the work of Brönsted,¹² von Ende,⁶ and Demassieux,¹¹ carried out at 20°, 25.2° and 14°, respectively. The results here obtained parallel closely those of Brönsted; the agreement with the figures recorded by the other investigators is only fair.

TABLE VIII

LEAD CHLORIDE IN POTASSIUM CHLORIDE SOLUTION			
[KCl]	[PbCl ₂] × 10 ²	[KCl]	[PbCl ₂] × 10 ²
0.25	1.850	1.30	0.965
.37	1.600	1.55	1.025
.46	1.422	1.80	1.134
.52	1.362	2.07	1.287
.54	1.354	2.17	1.388
.63	1.277	2.26	1.489
.74	1.102	2.41	1.480
.78	1.063	2.65	1.601
.97	0.981	2.98	1.943
1.10	.960	3.00	1.966
1.20	.960	3.20	2.402

The curve (see Fig. 2) shows two very sharp breaks. Up to a salt concentration of 0.6 *N*, lead chloride is the stable solid phase and the solubility,

¹⁰ Herz and Hellebrandt, *Z. anorg. Chem.*, **130**, 188 (1923).

¹¹ Demassieux, *Compt. rend.*, **158**, 183, 702 (1914).

¹² Brönsted, *Z. physik. Chem.*, **80**, 206 (1912).

after the rapid initial drop, is decreasing rather slowly. Between 0.6 *N* and 2.2 *N*, the solid in equilibrium with the saturated solution is the compound $\text{KCl} \cdot 2\text{PbCl}_2$, the solubility curve for which passes through a minimum at about 1.2 *N*. Analysis within this range gave the following results.

Calcd.: Pb, 65.6; Cl, 28.1. Found: Pb, 65.6; Cl, 28.1.

Above 2.2 *N* the stable phase is the compound $\text{KCl} \cdot \text{PbCl}_2$, with a solubility rapidly increasing with concentration. Analyses of the solid in equilibrium with the saturated solution in this region gave the following results.

Calcd.: Pb, 58.8; Cl, 30.2. Found: Pb, 58.8; Cl, 30.2.

It is to be noted that Brönsted reports this latter compound as a hydrate with the composition $\text{KCl} \cdot \text{PbCl}_2 \cdot \frac{1}{3}\text{H}_2\text{O}$; the samples analyzed in this work, however, were uniformly anhydrous.

6. **Magnesium Chloride.**—This system has not been previously studied. Some difficulty was encountered in preparing standard samples of magnesium chloride, the anhydrous salt being always faintly basic and the percentage of water in the hydrated crystals being slightly variable. The procedure finally adopted was to recrystallize the material several times in order to obtain the hexahydrate, to prepare a solution from this, and to analyze the solution for magnesium and chloride content.

TABLE IX
LEAD CHLORIDE IN MAGNESIUM CHLORIDE SOLUTIONS

$[\text{MgCl}_2]$	$[\text{PbCl}_2] \times 10^2$	$[\text{MgCl}_2]$	$[\text{PbCl}_2] \times 10^2$
0.12	1.084	4.86	1.832
0.27	0.802	5.42	2.303
0.60	0.625	5.94	2.902
0.85	0.618	6.36	3.488
1.58	0.689	6.78	4.251
1.83	0.723	7.08	4.844
2.62	0.915	7.58	5.944
3.54	1.205	7.98	7.000
3.87	1.329	8.12	7.360
4.36	1.564		

The results are expressed graphically in Fig. 3. A minimum in the solubility at about 0.8 g. equiv. of magnesium chloride is followed by a very rapid increase, the saturating solid phase throughout the whole concentration range examined being $\text{MgCl}_2 \cdot \text{PbCl}_2 \cdot 6\text{H}_2\text{O}$. The analytical data obtained from four analyses were averaged.

Calcd.: Pb, 43.0; Cl, 29.5; Mg, 5.05; H_2O , 22.4. Found: Pb, 43.1; Cl, 29.5; Mg, 5.03; H_2O , 22.5.

7. **Calcium Chloride.**—This system, as well as those comprising the strontium and barium salts, has been investigated by Herz and Hellebrandt.¹⁰ The agreement of our results with those which they have recorded is very poor in all three cases.

The method used for making up standard calcium chloride solutions was exactly similar to that described in the case of magnesium chloride above.

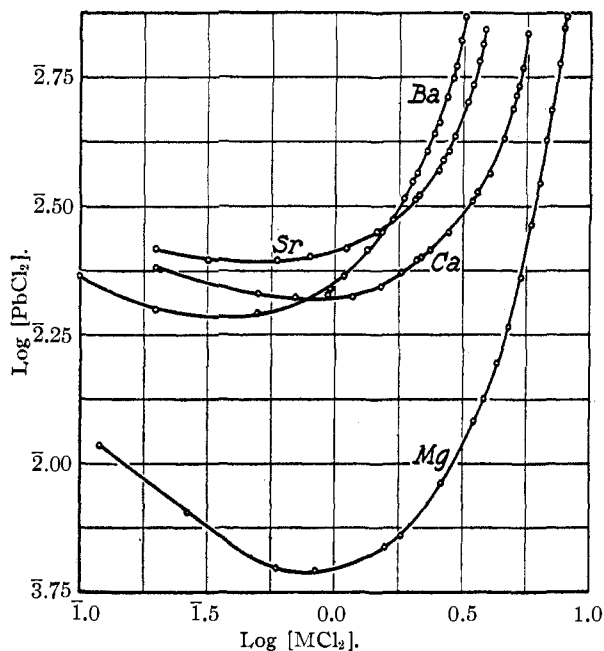


Fig. 3.—Solubility of lead chloride in chloride solutions of type MCl_2 . The concentrations are in g. equiv. per liter.

TABLE X

LEAD CHLORIDE IN CALCIUM CHLORIDE SOLUTIONS			
[CaCl ₂]	[PbCl ₂] × 10 ²	[CaCl ₂]	[PbCl ₂] × 10 ²
0.20	2.402	3.44	3.227
0.50	2.144	3.63	3.360
0.70	2.100	4.06	3.655
0.94	2.122	4.60	4.260
1.18	2.106	5.02	4.903
1.52	2.208	5.18	5.202
1.84	2.350	5.27	5.400
2.10	2.480	5.43	5.831
2.19	2.522	5.62	6.500
2.38	2.601	5.68	6.821
2.80	2.807		

The minimum in the solubility curve (Fig. 3) is by no means so pronounced as in the magnesium system. The solid phase throughout is the compound $CaCl_2 \cdot PbCl_2 \cdot 6H_2O$. The analytical results obtained were as follows.

Calcd.: Pb, 41.7; Cl, 28.5; Ca, 8.06; H₂O, 21.7. Found: Pb, 41.7; Cl, 28.5; Ca, 8.02; H₂O, 21.8.

8. Strontium Chloride.—The data are given in Table XI.

TABLE XI
LEAD CHLORIDE IN STRONTIUM CHLORIDE SOLUTIONS

[SrCl ₂]	[PbCl ₂] × 10 ²	[SrCl ₂]	[PbCl ₂] × 10 ²
0.20	2.633	2.66	3.869
0.32	2.502	2.80	4.027
0.60	2.480	2.96	4.304
0.80	2.522	3.32	5.032
1.12	2.620	3.36	5.118
1.46	2.821	3.47	5.440
1.70	2.985	3.64	6.009
2.06	3.260	3.78	6.502
2.12	3.303	3.88	6.940
2.55	3.705		

The compound which exists as stable phase over these concentrations is the anhydrous double salt SrCl₂.PbCl₂. Analysis gave results as follows.

Calcd.: Pb, 47.4; Cl, 32.5; Sr, 20.1. Found: Pb, 47.5; Cl, 32.5; Sr, 20.0.

9. Barium Chloride.—The hydrate BaCl₂.2H₂O, obtained pure by recrystallization, was used in making up the solutions in this system.

TABLE XII
LEAD CHLORIDE IN BARIUM CHLORIDE SOLUTIONS

[BaCl ₂]	[PbCl ₂] × 10 ²	[BaCl ₂]	[PbCl ₂] × 10 ²
0.10	2.322	2.30	4.030
0.20	2.000	2.45	4.361
0.50	1.966	2.56	4.600
0.96	2.180	2.76	5.135
1.09	2.322	2.90	5.598
1.35	2.600	2.98	5.922
1.54	2.820	3.12	6.600
1.86	3.275	3.21	7.148
2.02	3.524	3.26	7.362
2.10	3.662		

Here again the saturating phase throughout is the anhydrous equimolecular compound. The analytical data are as follows.

Calcd.: Pb, 42.6; Cl, 29.2; Ba, 28.2. Found: Pb, 42.6; Cl, 29.5; Ba, 28.3.

10. Mercuric Chloride.—This system has been examined previously by Noyes¹³ and by Formánek.¹⁴

TABLE XIII
LEAD CHLORIDE IN MERCURIC CHLORIDE SOLUTION

[HgCl ₂]	[PbCl ₂] × 10 ²	[HgCl ₂]	[PbCl ₂] × 10 ²
0.06	8.85	0.15	10.74
0.10	9.83	0.50	13.84

¹³ Noyes, *Z. physik. Chem.*, 9, 623 (1892).

¹⁴ Formánek, *Chem. Zentr.*, 18, 270 (1887).

The results in Table XIII agree with those recorded in the literature in showing a solubility curve continuously rising with concentration of mercuric chloride. This abnormality is obviously connected with the low ionization of mercuric chloride in aqueous solution. The solid phase over the above range proved to be the compound $\text{HgCl}_2 \cdot \text{PbCl}_2$, analysis giving results as follows.

Calcd.: Pb, 37.7; Cl, 25.8; Hg, 36.5. Found: Pb, 37.8; Cl, 25.8; Hg, 36.5.

General Discussion

The significance of the results obtained may be most readily grasped by reference to the accompanying diagrams, Fig. 2 giving the data for salts of the type MCl , and Fig. 3 the data for salts of the type MCl_2 . Concentrations in these diagrams are logarithmic, as in Fig. 1.

In every case except that of the hydrochloric acid system the saturating solid phase over the whole (or almost the whole) concentration range is a double salt. Potassium chloride, indeed, gives two such compounds with lead chloride. While the appearance of these compounds might be expected to disarrange the order of solubilities in the various systems, since the relative solubilities of the various compounds cannot be predicted to be in the same order as those of the simple salt, yet examination of the curves shows that this disarrangement is not extreme. At the lowest concentrations for salts of the type MCl , the order is $\text{H} < \text{Na} < \text{K}$ or $\text{NH}_4 < \text{Li}$, which is exactly the order of electrode potential diversity. At the highest concentrations, on the other hand, the order is $\text{H} < \text{NH}_4 < \text{K} < \text{Na} < \text{Li}$. The only change is in the position of sodium.

For the alkaline earth metals, similarly, the solubility order of the compounds at the highest concentrations examined is $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$, which again corresponds to the order of electrode potential diversity. In other words, although it could not be predicted on theoretical grounds that the solubility order should be independent of the nature of the saturating phase, and although at intermediate concentrations marked individual deviations are apparent, yet the general solubility rules are evidently modified only to a secondary extent by the appearance of addition complexes.¹⁵

Summary

The solubility curves of silver chloride in aqueous solutions of sodium, lithium and magnesium chlorides, and of lead chloride in aqueous solutions of hydrogen, lithium, ammonium, sodium, potassium, magnesium, calcium, strontium, barium and mercuric chlorides at 25° have been determined.

In the silver chloride systems, the relative positions of the various curves with respect to the previous results of Forbes for other metal chlorides are in accordance with the principle of electrode potential diversity developed in earlier articles of this series.

¹⁵ Compare Kendall and Davidson, *THIS JOURNAL*, **43**, 989 (1921).

In the lead chloride systems, the problem is complicated somewhat by the fact that the saturating phase at higher concentrations is, in general, a double salt. The following compounds have been isolated, of which those marked with an asterisk are new: $\text{LiCl} \cdot 2\text{PbCl}_2^*$; $\text{NH}_4\text{Cl} \cdot 2\text{PbCl}_2$; $\text{NaCl} \cdot 2\text{PbCl}_2^*$; $\text{KCl} \cdot 2\text{PbCl}_2$; $\text{KCl} \cdot \text{PbCl}_2^*$; $\text{MgCl}_2 \cdot \text{PbCl}_2 \cdot 6\text{H}_2\text{O}^*$; $\text{CaCl}_2 \cdot \text{PbCl}_2$; $6\text{H}_2\text{O}^*$; $\text{SrCl}_2 \cdot \text{PbCl}_2^*$; $\text{BaCl}_2 \cdot \text{PbCl}_2^*$; $\text{HgCl}_2 \cdot \text{PbCl}_2^*$.

It has been found that the relative positions of the curves at high concentrations are only slightly varied by the appearance of such complexes, the general order of solubilities being still as predicted by the rule of electrode potentials.

In a later article, the data obtained will be analyzed by Professor V. K. La Mer in greater detail from the standpoint of the Debye and Hückel theory.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE ACTION OF AMMONIA AND OF A SOLUTION OF POTASSIUM AMIDE IN LIQUID AMMONIA ON CERTAIN HALIDES OF MOLYBDENUM AND TUNGSTEN

BY F. W. BERGSTROM

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Introduction

In the investigation described below, which is a continuation of previous work upon the formation of amides, imides, nitrides and ammono salts,¹ an account is given of the preparation and properties of potassium ammono-molybdite and ammonotungstite, together with a few observations concerning the behavior of the halides of molybdenum and tungsten toward gaseous and liquid ammonia.

Preparation of Materials

Anhydrous halides of molybdenum and tungsten were prepared as described in a previous article.² Tungsten dibromide and dichloride were prepared by reduction of heated tungsten hexachloride and pentabromide, respectively, in a stream of hydrogen. Molybdenum dibromide was prepared by passing diluted bromine vapor over strongly heated molybdenum powder. Molybdenum pentachloride and tungsten pentabromide and hexachloride, which were readily attacked by moist air, were preserved in small sealed containers containing enough material for an individual experiment.²

Action of Gaseous and Liquid Ammonia on the Halides of Molybdenum and Tungsten

Molybdenum dibromide, tungsten dibromide and tungsten dichloride were converted by the action of liquid ammonia into very slightly soluble

¹ (a) Bergstrom, *THIS JOURNAL*, **46**, 1545; (b) 2631 (1924).

² Ref. 1 a, p. 1547.