solutions at about 2° but was stable much below this temperature in the presence of a slight excess of sodium oxide.

The solubility curve of the pentaborate, curve four of the figure, shows no unusual features. There is no evidence of the formation of a lower hydrate, even at the boiling point of the solutions; furthermore, it was found that the solid could be heated in an open weighing bottle to 70° without appreciable loss. Heated to 116° it gradually formed a viscous liquid and began to lose water. At a still higher temperature it, like boric acid, loses boric oxide also.

The Solubility Curve of Sodium Metaborate.— The tetrahydrate of this salt is easily prepared in the form of well-developed crystals of almost any desired size. If separated from congruently saturated solutions below 50° their composition agrees closely with the theoretical value. The dihydrate is more difficult to prepare in the form of well formed crystals but the tetrahydrate readily changes into the dihydrate above 60°. Both solids form solutions which are greatly supersaturated; those saturated above 70° are extremely viscous and assume a glass-like character similar to solutions of sodium silicate. This viscosity greatly delays the attainment of equilibrium in either undersaturated or supersaturated solutions and makes filtration very difficult. On account of these difficulties the solubility values found for temperatures in excess of 80° are less

accurate than those obtained for the rest of the curve. It was not possible to fix the value of the boiling point or the composition of solution saturated at this temperature. The results, plotted as curve five of the figure, fix the value of the transition temperature ($4H_2O \longleftrightarrow 2H_2O$) at 54°. This value was confirmed by heating the tetrahydrate at a constant rate and plotting the temperature–time relation.

Summary of Results

1. The solubilities of boric acid; of the deca-, penta- and tetra-hydrates of sodium tetraborate; of the tetra- and dihydrate of sodium metaborate and of sodium pentaborate have been determined and the values for 5° intervals between 0 and 100° tabulated.

2. The metastable transition temperature ($10H_2O \longleftrightarrow 5H_2O$) of sodium tetraborate has been fixed at 60.8° and the stable transition temperature ($10H_2O \longleftrightarrow 4H_2O$) of the same salt has been fixed at 58.5°. The stable transition temperature ($4H_2O \longleftrightarrow 2H_2O$) of sodium metaborate has been fixed at 54°.

3. Evidence is given that the pentahydrate of sodium pentaborate is stable in contact with its congruently saturated solutions between 10 and 100°, and at still lower temperatures in contact with solutions containing a slight excess of sodium oxide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Solubility of Mercuric Chloride in Aqueous Solutions of Several Chlorides

BY HENRY C. THOMAS

The solubility of mercuric chloride in aqueous chloride solutions has been the subject of many investigations[1–10] since J. Davy[11] first noted in 1822 the extraordinary solubility of this compound in hydrochloric acid. It has been thought

worth while to repeat and extend some of the earlier work in order to obtain solubilities of sufficient accuracy to clear the way for further ideas on the nature of these complex solutions.

Experimental

J. T. Baker "Analyzed" chemicals were used without further purification. Solutions were prepared with chloride-free distilled water.

Concentrated stock solutions of the solute salts were analyzed gravimetrically for their chloride content. At least five analyses were made on each solution, the results of which agreed to within 0.05%. Solutions for the individual solubility determinations were prepared by weight dilution of the stock chloride solutions. The more concentrated solutions containing hydrochloric acid were

(1) HCl: Engel, *Ann. chim. phys.*, **17**, 338 (1889).

(2) CsCl: Foote, *Am. Chem. J.*, **30**, 339 (1903).

(3) BaCl₂: Foote and Bristol, *ibid.*, **32**, 246 (1904).

(4) NaCl, KCl, RbCl: Foote and Levy, *ibid.*, **35**, 239 (1906).

(5) KCl: Tichomirov, *J. Russ. Phys.-Chem. Soc.*, **39**, 731 (1907).

(6) NH₄Cl: Meerburg, *Z. anorg. allgem. Chem.*, **59**, 136 (1908).

(7) BaCl₂: Schreinemakers, *Chem. Weekblad*, **7**, 197 (1910).

(8) CuCl₂: Schreinemakers and Thonus, *Proc. Roy. Acad. Sci. Amst.*, **15**, 472 (1912).

(9) LiCl, NaCl, KCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂: Herz and Paul, *Z. anorg. allgem. Chem.*, **82**, 431 (1913).

(10) KCl: Tourneux, *Ann. chim. phys.*, **11**, 225 (1919).

(11) J. Davy, *Phil. Trans.*, **112**, 359 (1822).

analyzed for HCl after saturation with mercuric chloride by weight titration with sodium hydroxide, which had been compared with gravimetrically standardized hydrochloric acid. Using methyl red as the indicator it was found possible to obtain a sharp end-point in solutions containing mercuric chloride if these solutions were treated with an excess of sodium chloride. In the absence of the sodium chloride no definite end-point was obtainable. A check on this procedure showed that the titration results were unaffected to within 0.02% by the presence of the mercuric and sodium chlorides.

The solubilities were measured by the gravimetric determination of mercury as the sulfide. Samples for analysis were drawn through filters of very fine "Pyrex" glass wool. Duplicate determinations, which were always made, agreed to within 0.1%. Three analyses on mercuric chloride dried at 100° gave for the purity of the sample 100.04, 100.05, and 100.13%. Appropriate experiments demonstrated that the treatment of the mercuric sulfide precipitates with acetone and carbon disulfide, in order to remove any possible trace of sulfur, had no effect on the results to within 0.02%. All analyses were made with calibrated weights and significant vacuum corrections were applied. Atomic weights from the table of 1938 were employed. In general the solubilities are considered accurate to within 0.2% of the recorded values except in the cases of the data for calcium chloride solutions. The solutions were saturated by rotating in glass-stoppered bottles end-over-end at 20 r. p. m. for twenty to twenty-four hours in a water thermostat. Analyses made after a forty-eight-hour period of rotation showed that the shorter period was ample for equilibration. The temperature of the thermostat was held at 25.00 ± 0.05°. The thermometer had been compared with a platinum resistance thermometer calibrated by the Bureau of Standards.

The density determinations were made using 30-ml. specific gravity bottles equipped with ground-in plugs and caps. About half of the density determinations were made in duplicate, the duplicates agreeing to within 0.01%. Densities are given relative to water at 4°.

Results

Solubility of Mercuric Chloride in Water.—

Ten determinations on three different solutions of mercuric chloride gave values for the solubility in water at 25.00 ± 0.05° ranging from 0.27003 to 0.27025 m. The average of these determinations is 0.27016 m or 0.25170 mole per kilogram of solution. Duplicate determinations were made of the densities of two saturated solutions. The average of these four determinations, which agreed to within 1 part in 15,000, is $d^{25}_4 = 1.0563$. The corresponding volume concentration of mercuric chloride is 0.26587 mole per liter of solution. This value is somewhat higher than that adopted by the "International Critical Tables,"[12] namely, 0.265 mole per liter. The difference is slightly

(12) "Int. Crit. Tab.," Vol. IV, p. 305.

more than can be accounted for on the basis of temperature fluctuations.

Solubility of Mercuric Chloride in Chloride Solutions.—

In Tables I–VI are recorded the results of the solubility determinations together with the densities of the saturated solutions. All concentrations are given in molality units (moles per kilogram of water). The solubility of mercuric chloride, S_{HgCl_2}, is expressed as moles of mercuric chloride; the concentration of the solute salt, m_{Cl}, is expressed in terms of moles of chloride ion as determined from the analysis of the stock solution. In all cases a continuous solubility curve was taken as sufficient proof that the solid phase was identical with that existing under an aqueous solution, i. e., $HgCl_2$; the data reported refer to this solid phase. In several cases new solid phases were found at high chloride concentrations. No attempt was made to determine the nature of these solids, and only a rough estimate was made of the concentrations at which they first appear.

TABLE I

THE SOLUBILITY OF MERCURIC CHLORIDE IN SOLUTIONS OF HYDROCHLORIC ACID

m_{Cl}	S_{HgCl_2}	d^{25}_4
0.09862	0.3747	....
.13354	.4144	....
.2001	...	1.1048
.2227	.5076	....
.4599	.7549	....
.5008	...	1.1728
.6979	1.0065	....
.7016	0.9973	....
.9344	1.2508	....
.9939	...	1.2797
1.1504	1.4872	....
1.1669	1.5024	....
1.4039	1.7628	....
1.6557	2.104	....
1.7339	2.125	1.4203
1.8861	2.292	....
2.102	2.535	1.5007
2.288	...	1.5360
3.166	3.750	1.6647
3.698	...	1.7670
4.428	5.232	1.8903
4.948	...	1.9714
5.889	6.929	2.0509
6.189	7.246	2.1343
6.577	7.704	2.1741
7.866	9.122	2.3161
9.319	10.64	2.4459
10.14	11.07	....

A different solid phase appeared at a concentration of HCl between 10.14 and 12.26 m.

TABLE II

THE SOLUBILITY OF MERCURIC CHLORIDE IN SOLUTIONS OF LITHIUM CHLORIDE

m_{Cl}	S_{HgCl_2}	d^{25}_4
0.10177	0.3757	1.0809
.3022	.5741	1.1264
.5058	.7667	1.1696
1.0015	1.2307	1.2690
1.6170	1.8121	1.3839
2.194	2.363	1.4851
2.800	2.950	1.5847
3.401	3.536	1.6788
4.006	4.141	1.7663
4.625	4.755	1.8517
5.435	5.568	1.9541
6.166	6.296	2.0392
6.990	7.109	2.1277
7.991	8.089	2.2246

No different solid phase was found.

TABLE III

THE SOLUBILITY OF MERCURIC CHLORIDE IN CALCIUM CHLORIDE SOLUTIONS

m_{Cl}	S_{HgCl_2}	d^{25}_4
0.10680	0.3811	1.0845
.19928	.4720	1.1075
.4028	.6690	1.1563
.6043	.8617	1.2027
1.0064	1.2456	1.2923
1.4624	1.687	1.3942
1.6114	1.823	1.4181
2.475	2.668	1.5864
2.518	2.717	1.5924
2.957	3.144	1.6735
3.223	3.413	1.7209
3.481	3.666	1.7689
4.098	4.246	1.8548
5.261	5.401	2.0249
6.233	6.350	2.1357

A different solid phase appeared at approximately 3.25 mCaCl$_2$.

TABLE IV

THE SOLUBILITY OF MERCURIC CHLORIDE IN ALUMINUM CHLORIDE SOLUTIONS

m_{Cl}	S_{HgCl_2}	d^{25}_4
0.09052	0.3634	1.0794
.14989	.4227	1.0939
.3026	.5686	1.1299
.6016	.8537	1.1984
.9010	1.1412	1.2650
1.1932	1.4216	1.3276
1.5076	1.7181	1.3913
2.405	2.592	1.5674
3.317	3.484	1.7314
4.243	4.359	1.8786
5.108[a]	5.139	1.9992
5.835[a]	5.742	....

[a] These solutions may refer to a different solid phase.

TABLE V

THE SOLUBILITY OF MERCURIC CHLORIDE IN LITHIUM CHLORIDE–CALCIUM CHLORIDE SOLUTIONS

m_{Cl}	S_{HgCl_2}	d^{25}_4
1.0394	1.2704	1.2873
1.6502	1.854	1.4128
2.087	2.271	1.4900
2.650	2.824	1.5939
2.748	2.888	1.6012
2.996	3.164	1.6512
4.008	4.158	1.8110
4.132	4.276	1.8231
4.969	5.120	1.9482
5.066	5.210	1.9609
5.160	5.275	1.9609
6.182	6.303	2.0909
7.237	7.340	2.2070

No different solid phase was found. The concentration ratio of the solute salts is constant throughout the table and is equal to (LiCl)/(CaCl$_2$) = 2.0013.

TABLE VI

THE SOLUBILITY OF MERCURIC CHLORIDE IN LITHIUM CHLORIDE–ALUMINUM CHLORIDE SOLUTIONS

m_{Cl}	S_{HgCl_2}	d^{25}_4
0.8639	1.1032	1.2506
1.1962	1.4164	1.3169
1.9913	2.180	1.4700
3.008	3.166	1.6471
3.991	4.124	1.8001
4.965	5.071	1.9376
5.491	5.573	2.0044

No different solid phase was found. The concentration ratio of the solute salts is constant throughout the table and is equal to (LiCl)/(AlCl$_3$) = 2.9990.

Solubilities at round values of the concentration of the added chloride ion were read from large scale plots of the quantity S_{HgCl_2}–m_{Cl} vs. m_{Cl}. Using a simple deviation plot the densities were likewise interpolated to these round concentrations. These smoothed values of the solubilities and densities are given in Table VII.

In the cases of the solutions containing calcium chloride the results are quite erratic. Although special care was taken in the preparation and analysis of these solutions, the inconsistencies are several times the expected experimental error. No difficulty was experienced in obtaining duplicate analyses on a single solution, but the results do not give as smooth a deviation plot as do the data on solutions containing no calcium chloride. No adequate explanation of these results has been found. However, a sufficient number of determinations were made so that it is believed that the smoothed values at round concentrations are quite reliable.

TABLE VII

THE SOLUBILITY OF MERCURIC CHLORIDE IN CHLORIDE SOLUTIONS AT ROUND CONCENTRATIONS

m_{Cl}	HCl		LiCl		CaCl₂		AlCl₃		LiCl-CaCl₂[a]		LiCl-AlCl₃[b]	
	S_{HgCl_2}	d^{25}_4	S_{HgCl_2}	d^{25}_4	S_{HgCl_2}	d^{25}_4	S_{HgCl_2}	d^{25}_4	S_{HgCl_2}	d^{25}_4	S_{HgCl_2}	d^{25}_4
0.1	0.376	1.0801	0.375	1.0801	0.375	1.0821	0.373	1.0816	0.376	1.0795	0.375	1.0798
.2	.481	1.1035	.475	1.1031	.478	1.1074	.471	1.1057	.478	1.1026	.475	1.1030
.3	.586	1.1266	.572	1.1257	.573	1.1318	.568	1.1293	.576	1.1256	.572	1.1263
.5	.795	1.1728	.761	1.1684	.762	1.1788	.758	1.1753	.763	1.1708	.762	1.1714
1.0	1.325	1.2823	1.230	1.2693	1.239	1.2908	1.235	1.2864	1.233	1.2790	1.231	1.2781
2.0	2.420	1.4814	2.177	1.4516	2.207	1.4960	2.196	1.4899	2.188	1.4767	2.189	1.4715
3.0	3.557	1.6598	3.145	1.6169	3.185	1.6805	3.175	1.6762	3.162	1.6515	3.158	1.6457
4.0	4.726	1.8253	4.134	1.7661	4.164	1.8429	4.132	1.8419	4.145	1.8071	4.133	1.8013
5.0	5.901	1.9774	5.132	1.9003	5.144	1.9878	5.044	1.9848	5.132	1.9449	5.104	1.9418
6.0	7.054	2.1101	6.131	2.0206	6.123	2.1111			6.121	2.0695		
7.0	8.176	2.2261	7.120	2.1287					7.111	2.1816		
8.0	9.264	2.3283	8.097	2.2251								
9.0	10.309	2.4193										

[a] Concentration ratio of solute salts: (LiCl)/(CaCl₂) = 2.0013.   [b] Concentration ratio of solute salts: (LiCl)/(AlCl₃) = 2.9990.

Discussion

In Fig. 1 curves are shown for the relation between S_{HgCl_2}/m_{Cl} and the stoichiometric molality of the solute chloride ion. The course of these curves is quite striking in that they show that in all cases the solubility of the mercuric chloride approaches at high concentration the molality of the solute chloride ion. While there is insufficient evidence to draw any exact conclusions as to the nature of the solute species present in these solutions, nevertheless the common form of the curves suggests that in all cases the HgCl₂–Cl⁻ complex is of the same nature. The data are adequate to demonstrate the specific effects of the cation present. In the case of hydrochloric acid the solubility is markedly higher than that in
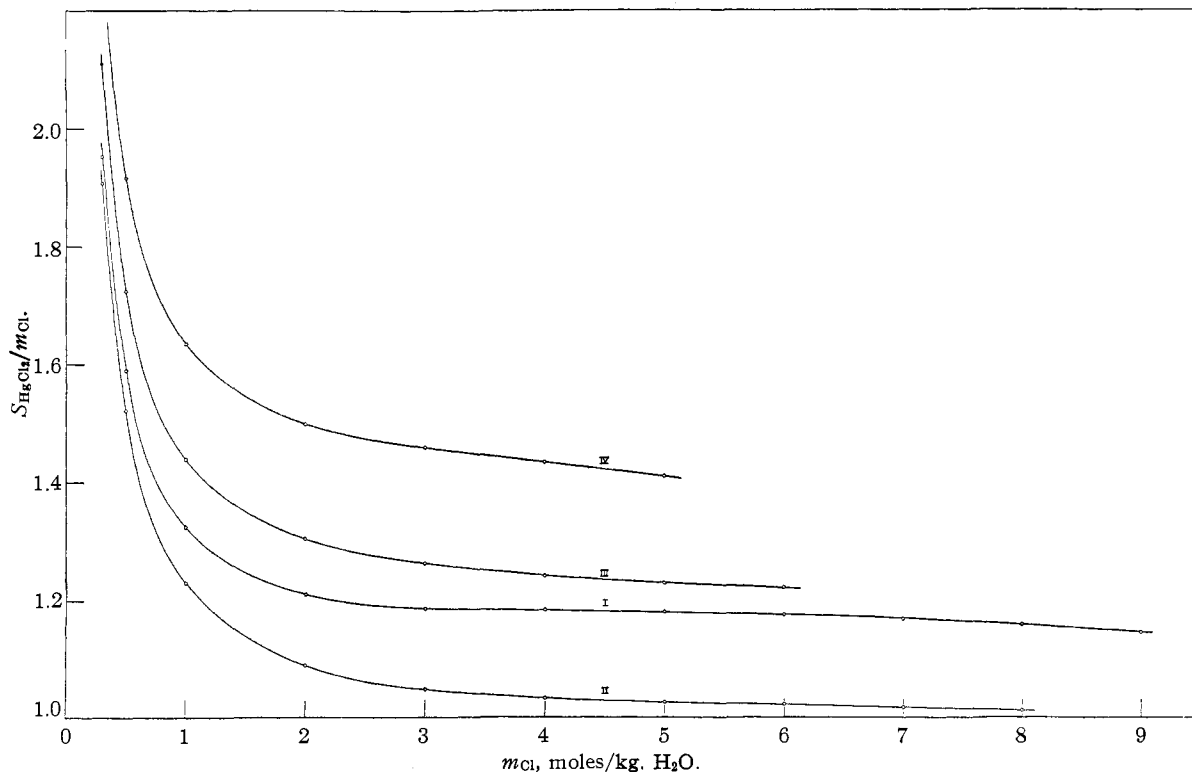

Fig. 1.—The solubility of mercuric chloride in chloride solutions: I, HCl; II, LiCl; III, CaCl₂; IV, AlCl₃. Curves III and IV have been displaced upward 0.2 and 0.4 unit, respectively.

the lithium chloride solutions, showing a specific effect due to the hydrogen ion. Much further information on the properties of these solutions will be necessary before any quantitative analysis of these effects can be attempted.

In connection with the present data an attempt was made to test the applicability in the case of a weak electrolyte of Åkerlöf's equation[13] for the solubility of strong electrolytes. Åkerlöf[14] has derived equations to fit the data of Herz and Paul[9] on the solubility of mercuric chloride in solutions of lithium and calcium chlorides. Since the data of these latter authors exhibit internal inconsistencies of several per cent., the agreement of the equations with the data in these two cases cannot be considered as very significant. It has been found impossible to fit similar equations to the data of this paper. The Åkerlöf equation is of the form

$$\log P = f(m)$$

where P is the thermodynamic solubility product and $f(m)$ contains terms in $\log m$ and hence cannot be solved explicitly for m. Writing

$$\delta_i = \log P - f(m_i)$$

it is possible to calculate and minimize $\Sigma \delta_i^2$ and thus develop a least square procedure for treating

(13) Åkerlöf and Thomas, THIS JOURNAL, **56**, 593 (1934).
(14) Åkerlöf, *J. Phys. Chem.*, **41**, 1053 (1937).

the data. The necessary equations have been derived and applied to the present data in the cases of hydrochloric acid and lithium chloride solutions. The equations so obtained do not reproduce the experimental data, and the constants of the equations are so widely discrepant that they lose all physical significance. That the least square procedure is adequate has been tested by applying it to the case of potassium ferricyanide in potassium chloride solutions.[14] An entirely satisfactory equation was thus obtained. The least square calculations were done using the smoothed data, hence the ill effects of one or two somewhat erroneous determinations have been largely avoided. It appears, then, that while the Åkerlöf equation gives excellent results with strong electrolytes it cannot be applied to the case of a weak electrolyte which forms complex ions in solution.

Summary

1. The solubility at 25° of mercuric chloride in water and in solutions of various chlorides has been determined.

2. In the concentration range corresponding to the solid phase $HgCl_2$ the results suggest that the $HgCl_2$–Cl^- complex is similar in all cases studied.

The Critical Constants of Ethane

BY JAMES A. BEATTIE, GOUQ-JEN SU AND GERALD L. SIMARD

The critical constants of propane,[1] *n*-butane,[2] and *n*-heptane[3] have all been determined in the same apparatus by the compressibility method.[4] The compressibility of ethane from 25 to 250° and from 0.5 to 5.0 moles per liter has been studied[5]; and in the course of the extension of these measurements to a density of 10 moles per liter, we determined the compressibility of ethane for several isotherms in the critical region and located the critical point. Several determinations

(1) J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).
(2) J. A. Beattie, G. L. Simard and G.-J. Su, THIS JOURNAL, **61**, 24 (1939).
(3) J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1937).
(4) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).
(5) J. A. Beattie, C. Hadlock and H. Poffenberger, *J. Chem. Phys.*, **3**, 93 (1935).

of the critical data for ethane are reported in the literature and they will be considered later.

The method of operation has been described elsewhere[4]; for ethane the all-steel bomb was used. The ethane was from the same stock used in the earlier measurements[5] and was supplied by the Buffalo Laboratory of The Linde Air Products Company through the courtesy of Dr. L. I. Dana. It was distilled several times to re-

TABLE I

THE EFFECT OF VARYING THE VAPOR VOLUME ON THE VAPOR PRESSURE OF ETHANE AT 25.00° (INT.)

Vapor volume, cc.	40	25	14	6
V. p., normal atm.	41.377	41.378	41.378	41.379
Vapor volume, cc.	3	0.7	0.4	0.2
V. p., normal atm.	41.379	41.378	41.378	41.378