two and a half times the concentration of a saturated solution of silver chloride in pure water. The concentrations of the acids given with Fig. 2 are the final values allowing for the dilution and reaction with the silver nitrate. The dotted line indicates the time when the addition of the silver nitrate was complete.

As may be seen the points fall on a smooth curve giving a clear picture of the change with time in the opalescence of a given suspension of silver chloride. The form of this time–opalescence curve was found to be satisfactorily reproducible in duplicate experiments. The absolute value of the opalescence in a given suspension was not as easy to reproduce, especially when the silver nitrate was precipitated in a small concentration of hydrochloric acid without the addition of extra electrolytes. The degree of reproducibility with a larger concentration of chloride both with and without nitric acid is shown in Fig. 2 by the open circles. These are drawn to include all points obtained at even minute intervals in four independent experiments of each kind. In order to give some idea of the reproducibility with smaller concentrations of chloride the two curves A were selected from a series of twelve duplicate experiments so that the difference between them is very nearly the average deviation from the mean of this series.

Tables I and II, which give a summary of the opalescences observed after ten minutes in all experiments which were repeated, contain also columns giving the average deviation from the mean of the opalescences measured at this time, expressed as percentage of the mean opalescence. It is clear that the reproducibility increases as the concentration of chloride increases and also when a comparatively large concentration of nitric acid is present.

Summary

An apparatus has been described for studying the rate of development of opalescence when precipitates are formed in dilute solutions and results have been presented to show the degree of reproducibility attained with it when silver chloride is precipitated in dilute solutions with an excess of hydrochloric acid both with and without the addition of nitric acid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 31]

Thermodynamic Properties of Fused Salt Solutions. VIII. Lead Chloride in Silver Chloride

BY EDWARD J. SALSTROM

The following investigation represents a continuation of a series of thermodynamic studies on fused salts and their solutions.

The lead chloride used in the cells and as a source of electrolytic chlorine was of "Merck C. P." grade containing a maximum impurity of 0.06%. The silver chloride was also obtained from commercial sources, having a maximum impurity limit of 0.014%. A pure silver wire served as the negative electrode while chlorine obtained by the electrolysis of fused lead chloride and bubbled over a treated[1] graphite rod dipping into the cell melt served as the positive electrode. The two salts were carefully weighed out in the desired proportions, fused together in a Pyrex cylinder, mixed by stirring and poured into the cell container.[2] Both the contents of the cell and the chlorine generator were then carefully freed from moisture, oxidation and hydrolysis products by bubbling dry hydrogen chloride through the liquid for at least a half hour. This hydrogen chloride was obtained by dropping concentrated sulfuric acid upon hydrochloric acid and dried by passing over glass beads wet with concentrated sulfuric acid. Apparatus and the method of obtaining measurements have been previously described.[2]

Other investigations, notably those of Lorenz and co-workers,[3] Hildebrand and Ruhle,[4] and Wachter and Hildebrand[5] have been made with the chlorine electrode. With the exception

(1) Salstrom, THIS JOURNAL, **55**, 2426 (1933).

(2) Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).

(3) Lorenz, "Die Electrolyse geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Verlag Wilhelm Knapp, Halle a. S., 1906; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

(4) Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

(5) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).

of the latter work, all previous attempts involved polarization methods and hence introduced uncertainties. The latter investigators succeeded in obtaining a reversible chlorine electrode without polarization by a method essentially the same as that used by the author. These investigators also measured the effect of the change of pressure of the chlorine on the e. m. f. of the cell. The observed results were in very close agreement with values calculated by the aid of the usual formulas; thus a high degree of accuracy may be claimed for the electrode.

As in previous studies these cells involved a thermoelectric effect due to the temperature gradient existing at each electrode. This effect has been measured and the results of the e. m. f. measurements on the cell plus this correction are given in Table I and are plotted in Fig. 1. The values shown under A and G are the results of two separate cells in each case. These are shown in the figure by points of different type. The mean deviation of the points from the straight lines drawn through them in Fig. 1 is less than 0.2 mv. while the maximum deviation is about 0.5 mv. Thus the chlorine electrode has been found to be equally as steady and reproducible in this system as was the bromine electrode in the corresponding bromide solutions.[6]

TABLE I

E. M. F. VALUES OF THE CELL, Ag(s), $PbCl_2$ IN AgCl(LIQ.), Cl_2(g)

Temp., °C.	E. m. f. obs., volt
Cell A (N_1 = 1.000)	
470.7	0.9085
471.4	.9083
479.1	.9064
482.3	.9054
495.7	.9014
498.1	.9009
509.8	.8968
512.1	.8964
536.3	.8890
538.3	.8883
551.8	.8844
562.0	.8822
566.5	.8804
567.8	.8802
568.0	.8801
573.2	.8786
597.8	.8718
600.3	.8715
Cell B (N_1 = 0.800)	
484.0	0.9192
490.7	.9175
513.9	.9108
514.9	.9104
524.0	.9080
548.7	.9012
575.7	.8941
577.0	.8939
598.6	.8882
620.1	.8828
Cell C (N_1 = 0.600)	
484.8	0.9395
502.1	.9347
531.7	.9272
534.8	.9265
566.5	.9187
587.0	.9137
613.2	.9078
Cell D (N_1 = 0.450)	
462.0	0.9636
475.9	.9602
476.9	.9598
503.8	.9537
525.2	.9489
526.4	.9486
558.0	.9417
559.6	.9415
580.9	.9371
581.5	.9370
600.5	.9329
600.9	.9328
614.2	.9301
Cell E (N_1 = 0.300)	
478.0	0.9862
506.6	.9804
536.3	.9748
568.9	.9688
597.5	.9637
Cell F (N_1 = 0.200)	
498.6	1.0091
509.3	1.0072
527.4	1.0042
555.8	0.9997
566.9	.9979
593.6	.9940
617.1	.9905
Cell G (N_1 = 0.100)	
522.5	1.0498
523.3	1.0499
539.0	1.0482
548.3	1.0469
549.5	1.0466
564.6	1.0454
566.0	1.0458
580.4	1.0445
596.1	1.0425
604.2	1.0424

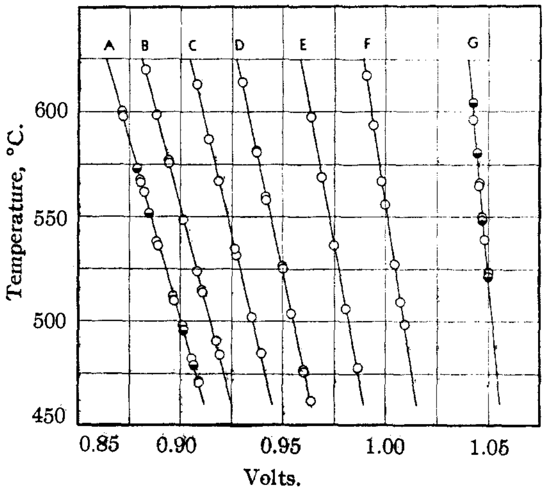

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, $PbCl_2$ in AgCl, Cl_2. The mole fractions of cells A to G are 1.000, 0.800, 0.600, 0.450, 0.300, 0.200 and 0.100, respectively.

As in former studies it was considered desirable to measure the density of a 50 mole per cent. solution. The method used was the same as that previously described.[6] The densities observed are given in Table II.

TABLE II

DENSITIES OF A 50 MOLE PER CENT. SOLUTION OF SILVER CHLORIDE AND LEAD CHLORIDE

Temp., °C.	Density	Temp., °C.	Density
428.1	5.013	502.5	4.903
436.3	4.989	521.9	4.878
452.8	4.969	536.3	4.860
462.7	4.956	546.3	4.848
476.5	4.937	559.1	4.831
487.9	4.922	576.4	4.810

The above values may be expressed by the equation, $d^t = 5.547 - 0.00128t$. Using the

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(6) Salstrom, THIS JOURNAL, 54, 2653 (1932).

value of Lorenz and Höchberg for the density of silver chloride[7] and Wachter and Hildebrand's[5] value for the density of lead chloride, the molal volume of the solution calculated on the basis of additivity is found to be 43.02 cc. at 500°. The observed molal volume at this temperature is 42.94 cc., which is equivalent to a contraction in volume of less than 0.2% upon mixing.

Since our chief interest lies in the relation of free energy to composition at constant temperature, the author obtained from Fig. 1 plotted on a large scale the intersections at the round temperatures 500 and 600°, getting the values of the e. m. f., **E**, given in Table III, together with the values of $d\mathbf{E}/dT$ at the different compositions. By means of the well-known thermodynamic equations, values for the entropy of formation, ΔS_1, entropy of dilution, $\bar{S}_1$, free energy of formation, ΔF_1, and free energy of dilution, $\bar{F}_1$, activity of the solvent, a_1, activity coefficient, a_1/N_1, where N_1 is the mole fraction of the solvent, and the heat of formation, ΔH_1, have been calculated. These values are included in Table III.

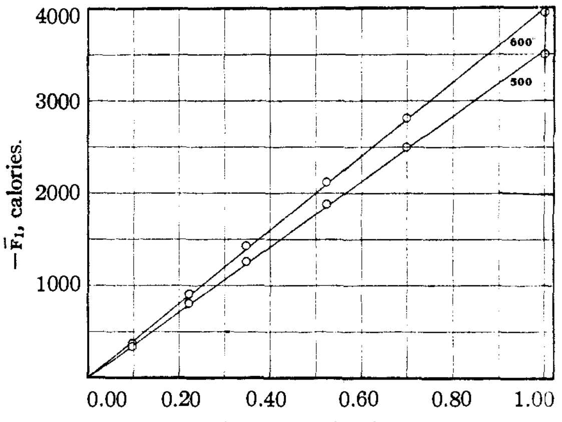

Fig. 2.—Change in free energy of silver chloride at 500 and 600° upon dilution with lead chloride. The calculated values are shown by the curves, while the observed values are represented by circles.

TABLE III

THERMODYNAMIC PROPERTIES OF SILVER CHLORIDE DILUTED WITH LEAD CHLORIDE AT 500°

N_1	1.000	0.800	0.600	0.450	0.300	0.200	0.100
$\log 1/N_1$	0.0000	0.0969	0.2218	0.3468	0.5229	0.6990	1.000
$d\mathbf{E}/dt$, mv./deg.	−0.292	−0.270	−0.245	−0.220	−0.186	−0.156	−0.094
ΔS_1, cal./deg.	−6.74	−6.23	−5.65	−5.08	−4.29	−3.60	−2.17
$\bar{S}_1$, cal./deg.	0	0.51	1.09	1.66	2.45	3.14	4.57
E (volt)	0.9001	0.9148	0.9352	0.9549	0.9817	1.0086	1.0518
ΔF_1 (cal.)	−20770	−21110	−21580	−22030	−22650	−23270	−24270
$\bar{F}_1$ (cal.)	0	−340	−810	−1260	−1880	−2500	−3500
a_1	1.000	0.801	0.590	0.439	0.294	0.196	0.102
a_1/N_1	1.00	1.00	0.98	0.98	0.98	0.98	1.02
at 600°							
E (volt)	0.8709	0.8878	0.9107	0.9329	0.9631	0.9930	1.0424
ΔF_1 (cal.)	−20100	−20470	−21010	−21530	−22220	−22910	−24050
$\bar{F}_1$ (cal.)	0	−370	−910	−1430	−2120	−2810	−3950
a_1	1.000	0.799	0.589	0.439	0.294	0.197	0.103
a_1/N_1	1.00	1.00	0.98	0.98	0.98	0.99	1.03
ΔH_1 (cal.)	−25980	−25940	−25950	−25950	−25970	−26050	−25950

If it is assumed, first, that these solutions obey Raoult's law and that both salts are un-ionized, the free energy of dilution of silver chloride by lead chloride may be calculated by the equation $\bar{F}_1 = RT \ln N_1$ since then $N_1 = a_1$. By plotting these calculated values of $\bar{F}_1$ at 500° and 600° against their respective log $(1/N_1)$ the two curves shown in Fig. 2 are obtained. The observed free energies of solution are shown in the figure by circles. It is thus evident that these observed and calculated values are in very close agreement, the maximum deviation being less than sixty calories.

If it is assumed, second, that Raoult's law is obeyed and that both salts are completely ionized, but that the partial substitution of silver by lead ion can be made without changing any of the interionic forces, then if n_1 moles of silver chloride and n_2 moles of lead chloride are taken there will be n_1 moles of Ag^+, n_2 moles of Pb^{++} and $n_1 + 2n_2$ moles of Cl^-. The activity of Ag^+ would then be $2n_1/(2n_1 + 3n_2)$, the activity of Cl^-, $2(n_1 + 2n_2)/(2n_1 + 3n_2)$, and the activity of silver chloride, the product of the two, or

$$a_1 = 4n_1(n_1 + 2n_2)/(2n_1 + 3n_2)^2$$

The $-\bar{F}_1$ calculated on this basis would be slightly higher, diverging to about 150 calories

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(7) Lorenz and Höchberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

above the un-ionized curve at a value of 1.000 for log $1/N_1$, thus even on this latter assumption the maximum deviation of the solution from Raoult's law is only 200 calories or about 5%.

Similar results were found for solutions of lead bromide in silver bromide[3] where agreement of the observed free energy of dilution of silver bromide by lead bromide with that calculated on the assumption that Raoult's law is obeyed and that both salts were un-ionized was very good, while assumption of complete ionization of both salts yielded a higher curve which agreed less well with the observed values. The molal volumes of these two solutions were also found to be in essential agreement with those predicted on the assumption of additivity. Moreover, the agreements of the free energies of dilution of silver bromide by lead bromide and of silver chloride by lead chloride with those predicted by Raoult's law were found to be equally as good at the higher temperatures as at lower temperatures. These solutions thus show the partial molal free energies, partial molal entropies and molal volumes of ideal solutions. The slightly poorer agreement of both series of solutions with Raoult's law curves based upon complete ionization is, the author believes, hardly sufficient to be particularly significant.

Summary

E. m. f. measurements of the cells, Ag(s), AgCl in $PbCl_2$(liq.), Cl_2(g), have been measured at mole fractions of silver chloride varying between 1.00 and 0.10 at temperatures from 460 to 620°.

Density measurements have been made upon a fifty mole per cent. solution of silver chloride and lead chloride which may be expressed by the equation $d^t = 5.547 = 0.00128t$ between the temperatures of 428 and 576°.

Calculations of the activity, activity coefficient, free energy of formation, and partial molal free energy of silver chloride have been made at the temperatures 500 and 600°.

The activity of the solvent, a_1, agrees very well with that predicted by Raoult's law throughout the entire range of temperature studied.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Cadmium Sulfate as a Basis for Acidimetry

BY SAMUEL E. Q. ASHLEY AND GEORGE A. HULETT

Upon crystallization from aqueous solution, cadmium sulfate forms large, hydrated crystals ($CdSO_4 \cdot 8/3\ H_2O$) of two sorts—some cloudy from inclusions of mother liquor and others of water clearness. These last possess uniformity of composition rare in salt hydrates and have been used in the determination of the atomic weight of cadmium.[1] In the present paper the authors describe a method of preparing standard sulfuric acid from these clear crystals by weighing them, dissolving in water and then depositing the cadmium in a mercury cathode—thus leaving a precisely known amount of sulfuric acid which may be diluted to a known volume or used to standardize an alkali solution.

Preparation of Material

Our method of preparing clear crystals has been to start with a concentrated filtered solution of chemically pure salt and allow it to evaporate spontaneously in 30-cm. crystallizing dishes closely covered with large pieces of filter paper. The solution is usually added to a depth of somewhat more than a centimeter. After about two weeks, crystals appear on the bottom of the dish; and, after they have reached a convenient size, the clear ones are removed with tweezers and the cloudy ones are redissolved for further crystallization. Although it not infrequently happens that a crop of crystals contains no clear crystals, the average yield of clear crystals is 7–10% by weight. A marked variation in the yields of these crystals made it seem possible that we might discover the conditions which favored their formation. An extensive investigation of the crystallization of the salt has not revealed any means of improving the yield of clear crystals, so we have been forced to rely upon the small yield normally obtained. This is quite sufficient for practical purposes if a large quantity of cadmium sulfate is crystallized.

Purity of Hydrated Cadmium Sulfate

The purity of cadmium sulfate has been disputed chiefly on the basis that the hydrate contains considerable amounts of "dissolved" or "included" water.[2] According to Baxter and Wilson, this water may be present in

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[1] Perdue and Hulett. *J. Phys. Chem.*, **15**, 155 (1911); Baxter and Wilson, THIS JOURNAL, **43**, 1230 (1921).

[2] T. W. Richards, *ibid.*, **33**, 888 (1911).