TABLE VI

PARTIAL MOLAL HEATS OF SOLUTION

Concn. m/1000 g. H_2O	n_2/n_1	ΔH	ΔH_2	ΔH_1 Calorimetric
0.040[a]	0.0007	− 3,550	−90,120	+ 1
.100[a]	.0018	− 8,850	−90,000	+ 3
.427	.0077	− 37,910	−89,320	+ 4
.672	.0121	− 59,390	−88,820	+ 5
.905	.0163	− 79,930	−88,330	0
1.127	.0203	− 99,660	−87,870	− 11
1.271	.0229	−111,870	−87,580	− 10
1.702	.0307	−150,010	−86,690	− 45
2.279	.0411	−200,210	−85,490	− 97
2.896	.0522	−253,020	−84,220	−165
3.675	.0662	−318,480	−82,610	−268
4.513	.0813	−386,040	−80,870	−380

[a] Determination of Lange and Robinson.

ΔH_1 values can be calculated also from vapor pressure data. d ln p/dT at 25° for each concentration in Table III was calculated by differentiating equation (1). This differential, substituted in the Clapeyron–Clausius equation for the vapor pressure of liquids, $\Delta H_{\text{vap}} = RT^2 \text{ d ln } p/\text{d}T$, makes possible the calculating of the change in heat content of vaporization of water, ΔH_{w} and ΔH_{s}, from pure water and from solutions, respectively. Since $\Delta H_1 = \Delta H_{\text{w}} - \Delta H_{\text{s}}$, ΔH_1 is at once obtained from vapor pressure data. The only assumption involved is that water vapor behaves as an ideal gas at these low pressures.

The ΔH_1 data, computed by the above two methods, compare as follows at the concentrations at which vapor pressure measurements were made

n_2/n_1	0.0157	0.0300	0.0411	0.0492	0.0595	0.0738	0.0877
(calorimetric), j.	5	−35	−95	−150	−315	−325	−430
(vapor press.), j.	−665	−761	−513	−511	−490	−771	−796

The discordance in ΔH_1 corresponds to a change in slope of the ln p *vs.* $1/T$ curve at 25° which would be caused by errors of 0.1 mm. in the vapor pressures of the most dilute solution at 20 and 30°. For the most concentrated solution, the corresponding error would be considerably less, even if the deviations were the same in the two cases.

Summary

Vapor pressure measurements have been made on solutions, on saturated solutions and on mixed hydrates of the system magnesium nitrate–water at various temperatures.

Heats of solution and of dilution have been determined for the same system.

Heats of hydration and partial molal heats of solution of the salt and of water have been calculated from the calorimetric data. The heat of hydration of the dihydrate to the hexahydrate and partial molal heats of solution of water have been calculated also from vapor pressure data.

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The Potentials of Cells in Liquid Ammonia Solutions. The Thermodynamic Constants of the Ammino Zinc Chlorides and of Zinc Chloride

BY NORMAN ELLIOTT AND DON M. YOST

Introduction

Liquid ammonia has long been known to be an ionizing solvent, and the nature of salt solutions in it has received the careful attention of Franklin, Kraus and other investigators.[1] The few electrode potentials in this solvent which have been investigated were complicated by liquid potentials or were not reversible.[2] A cell free from these objections and one which is also convenient as a reference electrode is highly desirable, especially if the electromotive series in liquid ammonia is to have more than a qualitative basis.[3]

Inasmuch as the thermodynamic constants of thallium amalgams and thallous chloride[4] are accurately known, and since the latter substance is not very soluble in liquid ammonia at 25°, the thallium amalgam–thallous chloride couple was chosen as one half-cell. Moreover, the solid phase consists of thallous chloride alone and not an ammoniated salt.[5] As the other half-cell the zinc amalgam–decammino zinc chloride couple was selected, since the activities of the amalgams[6]

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(1) *Cf.* Kraus, "The Properties of Electrically Conducting Systems," A. C. S. Monograph, The Chemical Catalog Co., New York, 1922. An excellent review of liquid ammonia systems is given by Fernelius and Johnston, *J. Chem. Ed.*, **7**, 2600 (1930). *et ante.*

(2) *Cf. e. g.*, Johnson and Wilsmore, *Trans. Faraday Soc.*, **3**, 77 (1907); Costeanu, *Compt. rend.*, **195**, 778 (1932).

(3) Bergstrom, THIS JOURNAL, **47**, 1503 (1925); Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924).

(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 93, 267, 607.

(5) Stollenwerk and Biltz, *Z. anorg. Chem.*, **119**, 97 (1921).

(6) Pearce and Eversole, *J. Phys. Chem.*, **32**, 209 (1928).

are known, and the salt is only slightly soluble in liquid ammonia. Ammonium chloride was chosen as the electrolyte. The cells measured were found to have constant and reproducible electromotive forces at 25°.

Attempts were made to construct a hydrogen electrode operating at 25° in liquid ammonia solutions of ammonium chloride. A potential of about 0.42 volt against a 0.0265 *N* thallium amalgam was obtained, but the experimental difficulties were such that its use as a reference electrode did not prove convenient. The ammonium ion in this case corresponds, of course, to the hydrogen ion of the aqueous system.

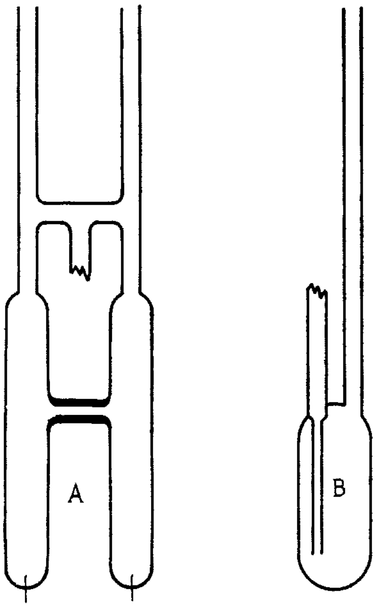

Fig. 1.

Preparation of Materials and Experimental Procedure

Ammonia.—The gas from a tank was passed over solid sodium hydroxide and metallic sodium and then condensed directly into the cell.

Thallous Chloride.—The metal of commerce was dissolved in hot dilute nitric acid, and the resulting mixture was then filtered. After treating the filtrate with hydrogen sulfide, it was again filtered and then boiled. To this solution was added an excess of hydrochloric acid to precipitate thallous chloride. After filtering, and washing repeatedly, the resulting precipitate was dried at 120° for four hours and then stored in a brown glass bottle.

Thallium.—A saturated solution of thallous chloride was electrolyzed between platinum electrodes at 100°. The resulting spongy metal was fused at 300° in a porcelain boat over which was passed a stream of dry hydrogen. The metal was then transferred to a tube containing carefully purified mercury. All operations involving the amalgams were carried out in an atmosphere of dry hydrogen.

Zinc.—The amalgams were prepared as above with purified electrolytic zinc.

Zinc Chloride.—Pure zinc chloride was fused, and, soon after solidifying, a portion was placed on the zinc amalgam in the cell. Oxygen and moisture were carefully excluded.

Ammonium Chloride.—The purest material obtainable was resublimed and stored in a vacuum desiccator.

The cell used is shown in Fig. 1. The auxiliary vessel B was used to fill the cell proper, A, with the liquid ammonia solution of ammonium chloride. After filling and sealing, the cells were placed in a thermostat at 25.00 ± 0.01°.

Results of the Experiments

Since the solubility of thallous chloride in liquid ammonia was not known, a series of measurements using the method of Hunt and Boncyk[7] were made. The results of three representative experiments gave 0.0260, 0.0261 and 0.0257 mole per 1000 g. of liquid ammonia at 25.0°.

In Table I are presented the results of the electromotive force measurements. Functions of the activities of thallium and zinc in their amalgams were plotted, and the values for the concentrations given in the table were obtained from the plot. The reference states for these activities are infinitely dilute solutions. Each cell required about four hours to attain equilibrium and after attaining it, the electromotive force remained constant for days. The thallium electrode was always positive.

The chemical reaction taking place in the cell is the following

$$\mathrm{Zn(amalg.\ }\alpha_2) + 2\mathrm{TlCl(s)} + 10\mathrm{NH_3(l)} = \mathrm{ZnCl_2{\cdot}10NH_3(s)} + 2\mathrm{Tl(amalg.\ }\alpha_1) \quad (1)$$

and the expression for the electromotive force of the cell is

$$E = E^{\circ\prime} - 0.029575 \log (\alpha_1^2/\alpha_2\alpha_3^{10}) \quad (2)$$

where α_2 and α_1 are the activities of zinc and thallium, respectively, in their amalgams at the mole fractions N_2 and N_1, and α_3 is the activity of the liquid ammonia. Since the concentrations of ammonium chloride used were small, as were also those of thallous chloride and zinc chloride, α_3 was taken equal to unity. In doing this, the standard state of liquid ammonia at 25° is assumed to be that state in which the total pressure is the vapor pressure of the liquid, and not one atmosphere. The correction to one atmosphere is probably small but cannot be made at this time since the molal volumes involved are not all known. The values of $E^{\circ\prime}$ given in the table are for the potential of the hypothetical cell

$$\mathrm{Zn(amalg.\ }\alpha_2 = 1),\ \mathrm{ZnCl_2{\cdot}10NH_3(s)},\ \mathrm{NH_4Cl(in\ NH_3(l)},f),\ \mathrm{TlCl(s)},\ \mathrm{Tl(amalg.\ }\alpha_1 = 1);\ E^{\circ\prime} = 0.9016\ \mathrm{volt} \quad (3)$$

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[7] Hunt and Boncyk, THIS JOURNAL, **55**, 3528 (1933).

TABLE I

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Temp., °C.	Mole fraction Tl N_1	Activity Tl α_1	Mole fraction Zn N_2	Activity Zn α_2	Formality NH_4Cl. f	E. m. f. observed. E, volt	Standard potential $E^{\circ\prime}$, volt	Standard potential E°, volt
25	0.0265	0.0369	0.0289	0.0255	0.0380	0.9392	0.9016	0.8293
	.0265	.0369	.0289	.0255	.0725	.9396	.9020	.8297
	.0265	.0369	.0289	.0255	.0573	.9395	.9019	.8296
	.0265	.0369	.0289	.0255	.0379	.9392	.9016	.8293
	.0265	.0369	.0301	.0263	.0648	.9393	.9013	.8290
	.428 satd.	3.316	.0289	.0255	.0306	.8231	.9011	.8288
	.0913	0.250	.0289	.0255	.084	.8900	.9015	.8292
						Mean	.9016	.8293
1.75	.0265		.0301		.0648	.9680		
18.50	.0265		.0301		.0648	.9470		

$\alpha_2 = 0.04819$ for a saturated Zn amalgam.

Equation 2 shows that the observed electromotive forces E should be practically independent of the concentration of ammonium chloride when the solutions are dilute and, as the table shows, this was found to be the case. The effect of varying the concentrations of thallium and zinc in the amalgams is also that predicted by equation 2. This is evident from the constancy of the $E^{\circ\prime}$ values. The cell is, therefore, reversible.

In the last column of the table are given the standard potentials E° for the cell

$$Zn(s), ZnCl_2{\cdot}10NH_3(s), NH_4Cl(\text{in } NH_3(l), f), TlCl(s), Tl(s); \quad E^\circ = 0.8293 \text{ volt} \qquad (4)$$

for which the chemical reaction is

$$Zn(s) + 2TlCl(s) + 10NH_3(l) = 2Tl(s) + ZnCl_2{\cdot}10NH_3(s) \qquad (5)$$

and the total pressure is the vapor pressure of the liquid ammonia at 25°. In arriving at the values of E°, account was taken of the fact that the potential of pure thallium is higher than that of the saturated amalgams by 0.0025 volt.[4] The solid phase of the saturated amalgam consists of some mercury dissolved in the thallium.

Discussion

It appears from the results of the measurements of the cell here described that either half-cell could be used as a standard reference electrode. In case very refined measurements were undertaken, account would have to be taken of the appreciable solubility of thallous chloride, if that half-cell were used. If the solubility of the decammino zinc chloride proves to be of the same order of magnitude as calomel or silver chloride in water, then the zinc half-cell would be superior as a reference electrode.

If the hydrogen electrode were measured against the thallium or zinc electrode, then all other half-cells could be compared with either of the two latter, and thus the further use of the troublesome gas cell could be avoided. Direct use of the gas cell could be avoided entirely if the activities and free energies of ammonium chloride solutions in liquid ammonia were known. It is planned to determine these quantities later.

Free Energies and Heat Contents of the Ammino Zinc Chlorides and Zinc Chloride.—The standard free energy change accompanying reaction (5) is given by $\Delta F^\circ_{298} = -NE^\circ F$ and is found to be −38,238 cal. The free energies of formation of thallous chloride and of liquid ammonia are −44,164 cal. and −2570 cal., respectively, at 25°. On combining these values the free energy of formation of $ZnCl_2{\cdot}10NH_3(s)$ at 25° becomes −152,270 cal.

The change in heat content accompanying reaction (5) is −59,500 ± 500 cal. and it was calculated from the temperature coefficient of one of the cells, −0.00121 volt/deg., and the heats of solution of thallium[4] and zinc[6] in their amalgams. The heats of formation[8] of thallous chloride and liquid ammonia are 48,700 cal. and 15,840 cal., respectively. The heat of formation of $ZnCl_2{\cdot}10NH_3$ from the elements becomes, therefore, 315,360 cal., and this is in satisfactory agreement with the less reliable value 327,400 cal. given in the "International Critical Tables."

Sufficient data are available for calculating the free energies of the other four ammoniated zinc chlorides. From the data given in "International Critical Tables"[8,9] the following equations have been derived.

$$ZnCl_2{\cdot}10NH_3(s) = ZnCl_2{\cdot}6NH_3(s) + 4NH_3(g) \qquad (6)$$
$$\Delta F^\circ_{298} = -2200 \text{ cal.} \quad \Delta H = 28{,}390 \text{ cal.}$$

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(8) "International Critical Tables," Vol. V, pp. 184, 178, 185.

(9) "International Critical Tables," Vol. VII, p. 252.

$$ZnCl_2 \cdot 6NH_3(s) = ZnCl_2 \cdot 4NH_3(s) + 2NH_3(g) \qquad (7)$$
$$\Delta F^\circ_{298} = 2240 \text{ cal.} \quad \Delta H = 22{,}080 \text{ cal.}$$

$$ZnCl_2 \cdot 4NH_3(s) = ZnCl_2 \cdot 2NH_3(s) + 2NH_3(g) \qquad (8)$$
$$\Delta F^\circ_{298} = 4550 \text{ cal.} \quad \Delta H = 23{,}700 \text{ cal.}$$

$$ZnCl_2 \cdot 2NH_3(s) = ZnCl_2 \cdot NH_3(s) + NH_3(g) \qquad (9)$$
$$\Delta F^\circ_{298} = 13{,}240 \text{ cal.} \quad \Delta H = 19{,}450 \text{ cal.}$$

The heat of the reaction $ZnCl_2 \cdot NH_3(s) = ZnCl_2(s) + NH_3(g)$ has not been determined accurately, and the value given for it appears to be a rough estimate.[10] The more reliable value of −11,600 cal. was obtained by combining equations (6) to (9) with the heat of formation of zinc chloride[8] and that of $ZnCl_2 \cdot 10NH_3(s)$ derived above. In making the calculation the heat of formation of ammonia gas was taken to be 10,940 cal.[8] The "International Critical Tables" gives an experimentally determined dissociation pressure for the monoammino zinc chloride at only one temperature. This was used in connection with the heat of dissociation just given to calculate the free energy change at 25°. The following equation expresses the results of the calculations.

$$ZnCl_2NH_3(s) = ZnCl_2(s) + NH_3(g) \qquad (10)$$
$$P_{298.1} = 0.0088 \text{ atm.} \quad \Delta H = 11{,}590 \text{ cal.} \quad \Delta F^\circ_{298} = 7350 \text{ cal.}$$

It is now possible to construct a table of the thermodynamic constants for all of the ammino zinc chlorides and zinc chloride. In making the calculations the free energy of formation of ammonia gas at 25° was taken to be −3910 cal.[4] and the standard virtual entropies at 25° of zinc[4] chloride,[11] nitrogen[12] and hydrogen[13] to be 9.83, 53.31, 45.79 and 31.23 cal./deg., respectively. The results are presented in Table II. The free energy and heat content values are referred to the elements in their standard states of 25° and one atmosphere.

TABLE II

THE THERMODYNAMIC CONSTANTS OF THE AMMINO ZINC CHLORIDES AND ZINC CHLORIDE AT 25°

Substance	$ZnCl_2 \cdot 10NH_3$	$ZnCl_2 \cdot 6NH_3$	$ZnCl_2 \cdot 4NH_3$	$ZnCl_2 \cdot 2NH_3$	$ZnCl_2 \cdot NH_3$	$ZnCl_2$
ΔF°_{298} cal.	−152,270	−138,830	−128,770	−116,400	− 99,250	−87,990
ΔH°_{298} cal.	−314,200	−242,040	−198,070	−152,480	−112,080	−99,550[8]
S°_{298} cal./deg.	217.4	134.8	109.6	81.5	53.0	24.3

S°_{298} is the standard virtual entropy.

Summary

With liquid ammonia as the solvent, the cells Zn (amalgam N_2), $ZnCl_2 \cdot 10NH_3(s)$, NH_4Cl (in NH_3-(*l*), *f*), TlCl(s), Tl (amalgam N_1) were measured at 25°. The cells are reversible and give constant and reproducible electromotive forces. When the zinc and thallium are present in the amalgams at unit activity the standard potential is $E^{\circ\prime}_{298} = 0.9016$ volt. When zinc and thallium are present as the pure metals the standard potential is $E^\circ_{298} = 0.8293$ volt.

From the cell potential and its temperature coefficient, together with the results of other investigators, the free energies, heat contents and virtual entropies for five ammoniated zinc chlorides and zinc chloride itself were calculated and are presented in Table II.

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(10) Biltz and Messerknecht, *Z. physik. Chem.*, **129**, 161 (1923).

(11) Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

(12) Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

(13) Giauque, *ibid.*, **52**, 4816 (1930).