including the figure for 140° and eliminating our first figure for 60°, which is obviously discrepant, are plotted against temperature, a smooth curve is obtained. Dobinski's figures do not extend above 80°. When our figures are plotted by the method of Andrade, the same change in slope is observed as with Dobinski's figures. If, therefore, Andrade's theory is sound, so is Dobinski's deduction, *viz.*, association of liquid phosphorus becomes appreciable below about 45°. If this is so, possibilities 3 and 4 (above) are ruled out. It is very probable that 2 contains the real explanation of our failure to observe positive results.

Summary

1. Experiments have been carried out on the effect of rapid chilling on the viscosity of phosphorus.

2. The viscosity of liquid phosphorus has been determined between the temperature limits 20–140°. The agreement with the prior figures of Dobinski (range 17.5–79.9°) is very good. As most of our work was carried out in ignorance of the very recent work of Dobinski, it appears that the viscosity of phosphorus is now known with a satisfactory degree of accuracy, at least over the temperature range common to both.

3. Association becomes appreciable in liquid phosphorus below 45°. The bearing of this and of the chilling experiments on Smits' theory is discussed.

WINNIPEG, CANADA RECEIVED JUNE 24, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 487]

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

BY CLIFFORD S. GARNER, EMERSON W. GREEN AND DON M. YOST

Introduction

The present investigation was undertaken to determine the suitability of the cadmium amalgam–hexammino cadmium chloride half-cell as a reference electrode for electromotive force measurements in liquid ammonia, and to evaluate the thermodynamic constants of the ammino cadmium chlorides and cadmium chloride.

For the purpose of establishing an electromotive series in the ammonia system it is desirable to refer all half-cells to some half-cell whose potential is taken arbitrarily as zero. Such a half-cell in the aqueous system is the hydrogen electrode. The same half-cell is here adopted for the liquid ammonia system in which the ammonium ion corresponds to the hydrogen ion of the aqueous system.

In this paper are presented the results of measurements on cells of the type Zn(amalg., N_2), $ZnCl_2 \cdot 6NH_3(s)$, NH_4Cl(in NH_3(l), f.), $CdCl_2 \cdot 6NH_3(s)$, Cd(amalg., N_1) together with the thermodynamic constants for the ammino cadmium chlorides and cadmium chloride. Provisional values of known potentials in terms of the standard hydrogen half-cell in liquid ammonia are also presented.

Preparation of Materials and Experimental Procedure

Ammonia.—The gas from a tank was passed over solid potassium hydroxide, condensed into a trap containing metallic sodium, and then fractionated over into an auxiliary vessel.

Mercury.—Mercury was repeatedly sprayed through nitric acid, and washed and dried. It was then redistilled five times in a current of air.

Zinc.—C. P. zinc sticks were scraped free from an oxide coating, placed in a sectioned Pyrex tube and distilled in four fractions in a current of pure dry hydrogen. It was then stored in weighing bottles filled with hydrogen.

Cadmium.—C. P. cadmium sticks were purified and stored in the same manner as for zinc.

Hydrogen.—The gas from a tank was passed through platinized asbestos at 350° to remove oxygen, and then through anhydrous phosphorus pentoxide to dry it.

Zinc Chloride.—Analytical reagent zinc chloride was fused, and immediately upon solidifying it was placed on the zinc amalgam in the cell. A stream of pure hydrogen was passed through the cell during this operation.

Cadmium Chloride.—A nearly saturated solution of recrystallized cadmium chloride (C. P.) was prepared containing a very small amount of hydrochloric acid to prevent hydrolysis. The solution was placed in a desiccator containing sulfuric acid, and the crystals resulting were filtered, pressed dry, and then placed in a flask. The flask was evacuated and at the same time heated to nearly the melting point of the cadmium chloride. Portions of the purified cadmium chloride were then placed on the cad-

TABLE I

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Temp., °C.	Mole fraction Cd. N_1	Cd(amalg. N_1) = Cd(s) E_1, volt	Mole fraction Zn, N_2	Zn(s) = Zn(amalg. N_2) E_2, volt	Formality[a] NH_4Cl, f	E. m. f. observed E, volt	Standard potential E^0, volt
25.00	0.0008234	−0.1132	0.01751	0.0140	0.20	0.4593	0.3601
	.0008234	− .1132	.01751	.0140	.089	.4599	.3607
	.01086	− .0801	.02739	.0087	.28	.4314	.3600
	.0008099	− .1136	.03328	.0066	.22	.4675	.3605
	.0008099	− .1136	.03328	.0066	.045	.4675	.3605
	.05020	− .0568	.03328	.0066	.25	.4111	.3609
	.05020	− .0568	.03328	.0066	.25	.4112	.3610
	.05020	− .0568	.03328	.0066	.089	.4107	.3605
	.05020	− .0568	.03328	.0066	.086	.4107	.3605
						Mean	.3605
3.20	.05020		.03328		.086	.3933	
35.00	.05020		.03328		.086	.4179	

[a] By formality is meant the number of formula weights per thousand grams of solvent.

mium amalgam in the cell. This last operation was carried out in an atmosphere of pure hydrogen.

Ammonium Chloride.—Analytical reagent ammonium chloride was recrystallized several times from water, and after subliming it was stored in a vacuum desiccator.

The Amalgams.—Purified mercury was distilled over into a receiver and a weighed piece of metal added in an atmosphere of hydrogen. The receiver was then partially evacuated, sealed off, and placed in a shaking device for about twenty hours. The receiver with contents was then weighed, the tip was broken off in a stream of hydrogen and the amalgam poured into a hydrogen-filled vessel provided with a number of side tubes. Equal portions were allowed to flow into the small side tubes which were then sealed off under hydrogen at atmospheric pressure. The empty receiver was weighed after these operations had been completed. It was found necessary to evacuate and bake thoroughly all apparatus coming in contact with the amalgams to prevent formation of oxides. The amalgams were always clean and bright.

The cell used was essentially the same as that described by Elliott and Yost.[6] A Leeds and Northrup Type K potentiometer was used in connection with a sensitive null galvanometer for making the electromotive force measurements. The standard cell was carefully calibrated against a new laboratory standard.

Results of the Experiments

Since no data were available on the solubility of cadmium chloride in liquid ammonia, a single rough determination was made using a modified method based on that of Hunt and Boncyk.[1] The value obtained was 0.0011 mole of $CdCl_2$, as such, per 1000 g. of liquid ammonia at 25.0°, but due to the inadequacy of the method for very slightly soluble salts, this is to be regarded as an upper limit. It is probable that the true solubility is not greater than about one-half of this value. The solid phase was $CdCl_2{\cdot}6NH_3$. This follows from the results of Biltz and Mau,[2] on the equilibrium pressures of ammonia above the solid decammino and hexammino cadmium chlorides.

In Table I are presented the results of the electromotive force measurements made on the cell

$$Zn(\text{amalg.}, N_2),\ ZnCl_2{\cdot}6NH_3(s),\ NH_4Cl\ (\text{in } NH_3(l),\ f.),\ CdCl_2{\cdot}6NH_3(s),\ Cd(\text{amalg.}, N_1) \quad (1)$$

for which the reaction is

$$Zn(\text{amalg.}, N_2) + CdCl_2{\cdot}6NH_3(s) = ZnCl_2{\cdot}6NH_3(s) + Cd(\text{amalg.}, N_1) \quad (2)$$

The activities of cadmium in its amalgams have not been calculated, but the electromotive forces of cells at 25.0° in which the following reactions take place are known.

$$Zn(\text{amalg. satd. with pure } Zn) = Zn(\text{amalg.}, N_2)^3 \quad (3)$$

$$Cd(2\text{ phase}) = Cd(\text{amalg.}, N_1)^4 \quad (4), \text{ and } Cd(2\text{ phase}) = Cd(s)^5 \quad (5)$$

In the table E_1 is the electromotive force of the cell whose reaction is

$$Cd(\text{amalg.}, N_1) = Cd(s) \quad (6)$$

and E_2 is that for the cell whose reaction is

$$Zn(s) = Zn(\text{amalg.}, N_2) \quad (7)$$

It is assumed here that the electromotive force of the cell Zn(s) = Zn(saturated amalgam) is zero. In the last column of Table I are presented the values calculated from the relation $E^0 = E_{\text{obsd.}} + E_1 + E_2$, for the standard potential E^0 of the cell

$$Zn(s),\ ZnCl_2{\cdot}6NH_3(s),\ NH_4Cl\ (\text{in } NH_3(l),\ f.),\ CdCl_2{\cdot}6NH_3\ (s),\ Cd(s) \quad (8)$$

for which the reaction is

$$Zn(s) + CdCl_2{\cdot}6NH_3(s) = ZnCl_2{\cdot}6NH_3(s) + Cd(s) \quad (9)$$

and the total pressure is the vapor pressure of the liquid ammonia solution at 25°.

Each cell required between four and five hours to attain equilibrium, after which time the elec-

---

(1) Hunt and Boncyk, THIS JOURNAL, **55**, 3528 (1933).

(2) Biltz and Mau, *Z. anorg. allgem. Chem.*, **148**, 170 (1925).

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

(4) Teeter, THIS JOURNAL, **53**, 3927 (1931).

(5) Parks and La Mer, *ibid.*, **56**, 90 (1934).

tromotive force was constant to 0.1 millivolt or better for days. The cadmium electrode was always positive.

From the results of the measurements of the cell, it appears that the cadmium amalgam–hexammino cadmium chloride half-cell can be used to advantage as a reference electrode in liquid ammonia. Inasmuch as hexammino cadmium chloride is less soluble in liquid ammonia at 25° than thallous chloride, and since cadmium amalgams do not oxidize as readily as thallium amalgams, it would seem that this half-cell is superior to the thallium amalgam–thallous chloride half-cell.

Thermodynamic Constants of the Ammino Cadmium Chlorides and Cadmium Chloride.—The standard free energy increase accompanying reaction (9) was calculated from the relation $\Delta F^0 = -NE^0F$ to be −16,637 cal. The free energy of formation of $ZnCl_2 \cdot 6NH_3(s)$ at 25° is −142,290 cal.[6,7] and hence the free energy of formation of $CdCl_2 \cdot 6NH_3(s)$ at 25° is −125,650 cal.

The increase in heat content accompanying reaction (9) is −8060 cal., and it was calculated from the temperature coefficient of one of the cells +0.000756 volt/deg., and the partial molal heats of solution of zinc[3] and cadmium[4] in their amalgams. The heat of formation of $ZnCl_2 \cdot 6NH_3(s)$ at 25° is 250,840 cal.,[6] and consequently the heat of formation of $CdCl_2 \cdot 6NH_3(s)$ at 25° is 242,780 cal. This is a more reliable value than that given in the "International Critical Tables," namely, 237,000 cal.

From the results of other investigators, taken in connection with the above, the calculation of the free energies and heat contents of the other four ammoniated cadmium chlorides and cadmium chloride itself is possible. From the data of Biltz and Mau[2] the following equations have been derived.

$$CdCl_2 \cdot 10NH_3(s) = CdCl_2 \cdot 6NH_3(s) + 4NH_3(g) \qquad \Delta F^0_{298 \cdot 2} = -6660 \text{ cal.} \quad \Delta H = 32{,}200 \text{ cal.} \tag{10}$$

$$CdCl_2 \cdot 6NH_3(s) = CdCl_2 \cdot 4NH_3(s) + 2NH_3(g) \qquad \Delta F^0_{298 \cdot 2} = 2300 \text{ cal.} \quad \Delta H = 19{,}580 \text{ cal.} \tag{11}$$

$$CdCl_2 . 4NH_3(s) = CdCl_2 \cdot 2NH_3(s) + 2NH_3(g) \qquad \Delta F^0_{298 \cdot 2} = 2350 \text{ cal.} \quad \Delta H = 32{,}660 \text{ cal.} \tag{12}$$

$$CdCl_2 \cdot 2NH_3(s) = CdCl_2 \cdot NH_3(s) + NH_3(g) \qquad \Delta F^0_{298 \cdot 2} = 5681 \text{ cal.} \quad \Delta H = 10{,}800 \text{ cal.} \tag{13}$$

$$CdCl_2 \cdot NH_3(s) = CdCl_2(s) + NH_3(g) \qquad \Delta F^0_{298 \cdot 2} = 10{,}700 \text{ cal.} \quad \Delta H = 23{,}510 \text{ cal.} \tag{14}$$

From these data, combined with those from the cell measurements, the thermodynamic constants of all the ammino cadmium chlorides and cadmium chloride have been computed, and are presented in Table II. In making the calculations, the free energy of formation of ammonia gas at 25° was taken as −3910 cal.[8] and its heat of formation as 10,940 cal.[9] The standard virtual entropies at 25° of cadmium,[8] chlorine,[10] nitrogen,[11] and hydrogen[12] are 11.80, 53.31, 45.79 and 31.23 cal./deg., respectively. The free energy and heat content values are referred to the elements in their standard states of 25° and one atmosphere. These free energy, heat content and entropy values for $CdCl_2(s)$ agree well with those obtained independently by Ishikawa, Kimura and Murooka,[13] namely $\Delta F^0_{298.2} = -81{,}857$ cal., $\Delta H_{298.2} = -92{,}149$ cal., and $S^0_{298.2} = 31.2$ cal./deg.

TABLE II

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

Substance	$\Delta F^0_{298.2}$, cal.	$\Delta H^0_{298.2}$, cal.	$S^0_{298.2}$, cal./deg.
$CdCl_2 \cdot 10NH_3(s)$	−134,633	−318,741	145.1
$CdCl_2 \cdot 6NH_3(s)$	−125,653	−242,781	90.8
$CdCl_2 \cdot 4NH_3(s)$	−115,533	−201,321	56.4
$CdCl_2 \cdot 2NH_3(s)$	−105,363	−146,781	65.7
$CdCl_2 \cdot NH_3(s)$	− 95,772	−125,041	36.7
$CdCl_2(s)$	− 81,162	− 90,591	33.5

$S^0_{298 \cdot 2}$ is the standard virtual entropy.

The Evaluation of the Standard Electrode Potentials Referred to the Standard Hydrogen Electrode.—In a former paper[6] were described briefly the attempts to measure the potential of the thallium amalgam–thallous chloride half-cell against a hydrogen half-cell in liquid ammonia. Due to experimental difficulties a completely satisfactory result was not obtained. It is now possible to calculate a value for the potential of the cell whose reaction is

$$Tl(s) + NH_4{}^+(a = 1, \text{in } NH_3(l)) + Cl^-(a = 1, \text{in } NH_3(l)) \qquad TlCl(s) + {}^1/_2H_2(g, 1 \text{ atm.}) + NH_3(l) \tag{15}$$

The standard free energies for all the substances entering into this reaction are known except that for ammonium chloride. Hunt and Larsen have determined the solubility of ammonium chloride in liquid ammonia as well as the vapor pressures of

---

[6] Elliott and Yost, THIS JOURNAL, **56**, 1057 (1934).

[7] For corrections see *ibid.*, **56**, 2797 (1934).

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 273, 464, 608.

[9] "International Critical Tables," Vol. V, p. 178.

[10] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[11] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[12] Giauque, *ibid.*, **52**, 4816 (1930).

[13] Ishikawa, Kimura and Murooka, *Bull. Inst. Phys. Chem. Research* (Tokyo), **9**, 744 (1930), through *Chem. Abs.*, **25**, 3552 (1924).

ammonia above its solutions over a large range of concentrations.[14] These data permit the calculation of provisional values for the activities of the ammonium chloride by the graphical methods described by Lewis and Randall.[8] In Table III are presented the results of the calculations.[15] The lowest concentration at which Hunt and Larsen worked is 0.4 *f*, and for more accurate activity coefficients it is necessary to go to still lower concentrations.

TABLE III

ACTIVITY COEFFICIENTS OF AMMONIUM CHLORIDE IN LIQUID AMMONIA SOLUTIONS AT 25°

Formality, *f*, of NH_4Cl	Activity coefficient $\gamma = a_{NH_4Cl}/f$
1	0.25
5	.079
10	.068
15	.079
20	.17
24.4 (satd.)	.31

If the provisional values for the activity coefficients given in the table are accepted, and if it is also assumed that the solid phase present in the experiments of Hunt and Larsen is $NH_4Cl(s)$ and not $NH_4Cl \cdot 3NH_3(2)$[16] then there results

$$NH_4Cl(s) = NH_4Cl(a = 1, \text{ in } NH_3(l)) \qquad \Delta F^\circ_{298.1} = -1210 \text{ cal.} \tag{16}$$

The standard free energy of formation of NH_4Cl (s) at 25° is −47,810 cal.[17] The corresponding value for $NH_4Cl(a = 1, \text{ in } NH_3(l))$ is therefore −49,020 cal. Taking −44,164 cal. as the standard free energy of formation of TlCl(s)[6] and −2620 cal. as that for liquid ammonia,[8] at 25°, we now have for reaction (15), $\Delta F^\circ_{298.1} = 2236$ cal., and $E^\circ_{298.1} = -0.10(00)$ volt. The experimental value becomes, when the differences between the concentrations used in the cell measured and those given for equation (15) are taken into account $E^\circ_{298.1} = -0.15$ volt. The agreement is satisfactory.

In Table IV are given the standard electrode potentials of three known half-cells referred to the standard hydrogen electrode in liquid ammonia as zero. The value for the half-cell involving zinc was derived from the measurements of Elliott and Yost[6] on the cell Zn(amalg.)-$ZnCl_2 \cdot 6NH_3(s)$, $NH_4Cl(\text{in } NH_3(l))$, TlCl(s), Tl-(amalg.), and that for cadmium comes from the results presented above. These values are, of course, to be regarded as provisional.

TABLE IV

STANDARD ELECTRODE POTENTIALS IN LIQUID AMMONIA AT 25°

Half-cell reaction	$E^\circ_{298.1}$, volt
$Tl(s) + Cl^-(\text{liq. } NH_3) = TlCl(s) + E^-$	−0.10(00)
$Zn(s) + 2Cl^-(\text{liq. } NH_3) + 6NH_3(l) = ZnCl_2 \cdot 6NH_3(s) + 2E^-$	+ .7293
$Cd(s) + 2Cl^-(\text{liq. } NH_3) + 6NH_3(l) = CdCl_2 \cdot 6NH_3(s) + 2E^-$	+ .3688

When the solubilities and the activities of the solid substances are known it will, of course, be possible to estimate the molal electrode potentials.

Summary

In liquid ammonia solutions of ammonium chloride at 25° the potentials of the cell Zn(amalg., N_2), $ZnCl_2 \cdot 6NH_3(s)$, $NH_4Cl(\text{in } NH_3(l)$, f., $CdCl_2 \cdot 6NH_3(s)$, Cd(amalg., N_1) have been measured at several concentrations of the dissolved substances. The cell gives accurately reproducible and reversible e. m. f.'s. When zinc and cadmium are present as pure metals $E^\circ_{298.1} = 0.3605$ volt.

From the e. m. f. and the temperature coefficient of the cell, together with the results of other investigators, the standard free energies, heat contents and virtual entropies of the solid ammino cadmium chlorides and cadmium chloride were calculated and are presented in Table II.

Provisional values for the activity coefficients of ammonium chloride in liquid ammonia at 25° were calculated and the results, combined with free energy data, were used to evaluate the standard electrode potentials of three known half-cells with reference to the standard hydrogen electrode in liquid ammonia.

PASADENA, CALIF.

RECEIVED JULY 8, 1935

---

[14] Hunt and Larsen, *J. Phys. Chem.*, 38, 801 (1934).

[15] After the present paper was submitted, an article by Larsen and Hunt, *J. Phys. Chem.*, 39, 877 (1935), has appeared in which relative mean activity coefficients of ammonium chloride are given. Their values are not applicable to the type of calculation made here.

[16] No proof is given by Hunt and Larsen in their paper that the solid phase is $NH_4Cl(s)$. In a private communication Dr. Hunt states that the solid phase does consist of NH_4Cl. Moreover, an extrapolation of the equilibrium pressure data of Troust ("I. C. T.," Vol. VII, p. 240) for the reaction $NH_4Cl \cdot 3NH_3(s) = NH_4Cl(s) + 3NH_3(g)$ gave 6.5 atm. for the pressure of $NH_3(g)$. The vapor pressure of ammonia above a saturated solution of NH_4Cl is 4.13 atm. This confirms the supposition that the solid phase is NH_4Cl.

[17] "International Critical Tables," Vol. VII, p. 240.