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HEATS, FREE ENERGIES AND ENTROPIES IN LIQUID AMMONIA

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June 15, 1951

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Introduction

A large literature has developed in the past thirty years on the subject of ionic solvation effects, but the discussions have been limited mainly to aqueous systems. In order to test the generality of the various theoretical and empirical relationships for heats of solvation, entropies of solvation, etc., it is necessary to have the appropriate thermodynamic data for solvents other than water. Liquid ammonia is the most extensively studied of the non-aqueous solvents, and sufficient data exist in the literature to calculate heats and free energies for certain ammoniacal species. Makishima (17) calculated electrode potentials and ionic heats of solvation for liquid ammonia, but he employed both empirical generalizations and experimental data in his calculations. Most of the free energy data have been obtained at -50°, -33°, 0°, and 25°C., whereas almost all the heat data have been obtained at -33°. It seemed logical to make 25°C. the standard temperature for liquid ammonia (to permit easy comparison with water) and so, where possible, free energy data were corrected to 25°.

In this compilation, heats of formation have been calculated mainly from experimental heats of solution, the most weight being put on those substances for which heats of dilution to zero concentration have been determined. Heats were not corrected from -33° to room temperature

both because the necessary heat capacities were usually lacking and because the accuracy of the data often did not warrant such corrections. Free energies of formation have been calculated from solubility data and from galvanic cell data. The usual convention was followed: the functions are partial molal quantities for a hypothetical 1 molal solution with unit activity; the 1 molal hydrogen ion was taken as a reference zero.

Heats of Formation

In measuring heats of solution of uni-univalent salts in water, one must carry the dilution to, at most, 0.01 molal in order to agree within 0.05 kcal./mole with the limiting value at infinite dilution. One way of estimating the corresponding dilution in liquid ammonia is by means of the Debye-Hückel expression, (25a).

$$\bar{H}_2 - \bar{H}_2^\circ = -3/2\ A \sqrt{TM_1/D^3V_1} \cdot \left[\frac{1}{T} + \frac{d \ln D}{dT} + 1/3 \ \frac{d \ln V}{dT}\right] (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$$

For water, $\bar{H}_2 - \bar{H}_2^\circ = 258.2\ (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$ cal./mole (25a). Using the data of Cragoe and Harper (4) we calculate d ln V/dt = 0.001819 deg^{-1} for liquid ammonia at -33°C. By plotting and drawing a straight line through the data of Grubb, Chittum and Hunt (7), Palmer and Schlundt (19), Goodwin and Thompson (6) and Latimer (15), we calculate D = 22 and d ln D/dT = -0.0046 deg^{-1} for liquid ammonia at -33°C. Hence we calculate, for liquid ammonia at -33°, $\bar{H}_2 - \bar{H}_2^\circ = -200\ (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$ cal./mole. This figure is very low in precision; in fact the uncertainty in the temperature coefficient of the dielectric constant is sufficient to make the sign of $\bar{H}_2 - \bar{H}_2^\circ$ uncertain. However, the calculation serves to

give the order of magnitude of heats of dilution in liquid ammonia; it appears that one need not be much more cautious in liquid ammonia than in water. Of course, the experimental difficulties in liquid ammonia calorimetry are far greater than in water calorimetry--as a result there are few, if any, heats of solution in liquid ammonia known better than ±0.1 kcal./mole.

Heats of solution and heats of reaction in liquid ammonia were taken from the data of Kraus and Schmidt and their coworkers (8, 11, 12, 13, 26, 27, 28) and Coulter and Maybury (3a). Heats of formation were taken from Bichowsky and Rossini (2). The heat of formation of the ammoniacal electron was calculated by assuming that when an alkali metal dissolves, it ionizes completely into positive metal ions and negative electrons.

Since Rb^+ ion and Br^- ion are isoelectronic and have almost identical hydration energies (3), it is plausible to assume that they have identical ammonation energies. Since $\Delta H = 7.0$ kcal./mole for the process of taking rubidium bromide from ammonia to water, we shall say that 3.5 kcal./mole is the difference in hydration energy and ammonation energy for both the rubidium ion and the bromide ion. Using the data available for the heats of formation of ions and compounds in water (2), we can now calculate the differences between ammonation energies and hydration energies for all the species whose heats of formation in ammonia are known, except the electron and amide ion. (The heats of formation of these in water are unknown). These calculated values are listed in Table I, rounded to kilocalories. It is obvious that the hydrogen ion, ammonium ion, silver ion, lead ion and

Table I

Thermodynamic Functions for Species in Liquid Ammonia

Species	ΔH_f°	ΔF_f°(298°K.)	S°	$\Delta H_{(am)}-H_{(hyd)}$
H^+	0	0	0	-26
H_2O	-72			- 4
F^-		-81		
Cl^-	-65.7	-44.1	-30.3	1
ClO_3^-	-48	-18	16	0
Br^-	-59.0	-41	-26	- 3
I^-	-45.3			- 5
IO_3^-		-43		
NO_3^-	-77.6	-43	- 5	- 1
NH_3	-16.1	-2.7	24.7	3
NH_4^+	-16.1	-2.7	24.7	-11
NH_2^-	3.3	38	-47	
Pb^{++}	21	(13)	11	-31
Tl^+		6		
Hg^{++}	45	(31)	34	-49
Ag^+	26	23(17)	15	-25
Li^+	-44	-43(-54)	4	- 3
Na^+	-38.1	-43.5(-43.8)	15	- 7
K^+	-39	-46.5(-48)	27	- 5
Rb^+	-38	-48.6(-47)	36	- 3
Cs^+	-39	-49.5(-47)	38	- 3
e^-(am)	39	45	- 4	

mercuric ion have ammonation energies greatly in excess of the corresponding hydration energies. Similar results were obtained by Makishima (17) and Pleskov and Monoszon (24), who considered free energies of solvation.

While it is not possible to calculate the difference in ammonation energy and hydration energy for the electron, it is possible to calculate the absolute ammonation energy. We must rely on such data as the absolute potential of the calomel electrode, the absolute entropy of chloride ion in aqueous solution and the free energy change in taking an electron from mercury to the gaseous state. The method of calculation is illustrated below.

	ΔH, kcal./mole	Reference
$H^+_{(aq)} = H^+_{(am)}$	-26	(This paper)
$1/2\ H_{2(g)} = H^+_{(aq)} + e^-(g)$	103.9	(3)
$e^-(am) + H^+_{(am)} = 1/2\ H_{2(g)}$	-39	(This paper)
$e^-(am) = e^-(g)$	39 kcal./mole	

Free Energies of Formation

Solubilities were taken from the data of Hunt and his coworkers (1, 9, 10, 25), Linhard and Stephan (16), Elliott and Yost (5) and Sigetomi (29). Ritchey and Hunt (25) determined the activity coefficient of ammonium chloride for concentrations up to the saturated solution at 25°C. Activity coefficients for the saturated solutions of other salts were estimated from the data for ammonium chloride. Whenever possible,

salts were chosen whose solubiltiy is less than 1 molal, since activity coefficients can be estimated more accurately for low concentrations than for high concentrations. Free energies of formation for compounds at 25° were taken from the National Bureau of Standards table (18).

Pleskov and Monoszon (20, 21, 22, 23, 24) have measured the standard potentials of a number of metallic electrodes relative to the hydrogen electrode in liquid ammonia at -50°. In order to compare the ionic free energies calculated from them with those calculated from solubility data at 25°, it is necessary to know the temperature coefficients of the cells. These can be calculated from the ionic heats of formation of the ions, when known. Unfortunately, the necessary data for all the half-cells investigated by Pleskov and Monoszon are not available. But their data for the alkali metals, silver, lead and mercury have been corrected to 25° and included in Table I. (These cell data may be distinguished by the parentheses). There is fair agreement with the free energies calculated from solubility data except in the cases of silver and lithium. In these cases it is suspected that the solubility data are spurious because silver chloride and lithium chloride (the compounds whose solubilities were used) probably exist as stable ammonates in the presence of liquid ammonia. This would explain why the solubility free energies of both Li^+ and Ag^+ are more positive than the cell free energies.

Pleskov and Monoszon (23) measured the ionization constant of liquid ammonia at -50° with cells and found $K = 1.9 \times 10^{-33}$. Using the heats of formation in the table, we correct this to $K = 1.1 \times 10^{-28}$ at 25°. Using the free energies in the table, one obtains $K = 1.6 \times 10^{-30}$ at 25°. The former value is to be preferred.

From the free energies in the table, we calculate $\Delta F = -4$ kcal./mole

for $e^-_{(am)} + NH_3 = 1/2\ H_2 + NH_2^-{}_{(am)}$. This free energy is in agreement with the observed slow decomposition of metallic solutions in liquid ammonia.

Entropies

Where both the heat and free energy of formation of a species in liquid ammonia are known, the corresponding entropy has been calculated and included in Table I. It is noticed that when the entropy of hydrogen ion is arbitrarily taken as zero, the alkali metal ions have positive values and the halide ions have corresponding negative values. The same sort of pattern was observed for ions in methyl alcohol (15a). Since we would expect isoelectronic halide ions and alkali metal ions to have comparable entropies, we conclude that in methyl alcohol and liquid ammonia the hydrogen ion has an absolute entropy much more negative than zero. In water, the absolute entropy of the hydrogen ion is approximately -5(3). The difference between water and both methyl alcohol and ammonia is attributed to a higher degree of "solvent structure" in water. Less structure is broken up when a hydrogen ion enters ammonia or methyl alcohol than when it enters water. Hence the entropies of solvation in methyl alcohol and ammonia are more negative.

It must be remembered that many of the entropy values given in Table I (e.g., the values for the electron and the dipositive metals) are uncertain by ±10 units or more, and only qualitative conclusions can be drawn from the data.

Calculations

A. Calculations for Heats of Formation

ΔH_s = heat of solution in ammonia.

ΔH_f = heat of formation from elements in standard state.

All heats are given in kcal./mole.

Hydrogen

H^+ : By convention we take $\Delta H_f(H^+) = 0$.

H_2O: For ice, $\Delta H_s = -1.8$ (13) and $\Delta H_f = -69.8$ (2).

Chlorine

Cl^- : For ammonium chloride, $\Delta H_s(\infty) = -6.8$ (26) and $\Delta H_f = -75.0$ (2).

ClO_3^- : For sodium chlorate, $\Delta H_s = -2.2$ (11) and $\Delta H_f = -83.6$ (2).

Bromine

Br^-: For ammonium bromide, $\Delta H_s(\infty) = -10.5$ (26) and $\Delta H_f = -64.6$ (2).

Iodine

I^-: For ammonium iodide, $\Delta H_s(\infty) = -13.0$ (27) and $\Delta H_f = -48.4$ (2).

Nitrogen

NO_3^-: For sodium nitrate, $\Delta H_s(\infty) = -4.0$ (27) and $\Delta H_f = -111.7$ (2).

NH_3 : ΔH_f (liq. NH_3) = -16.07 (2).

NH_4^+: We arbitrarily take $\Delta H^\circ = 0$ for the reaction $H^+ + NH_3 = NH_4^+$.

NH_2^-: $\Delta H = -19.4$ for the reaction $NH_4^+ + NH_2^- = 2\ NH_3$ (12).

Lead

Pb^{++}: For lead iodide, $\Delta H_s = -27.0$ (26), -29.1 (11). We shall assume $\Delta H_s = -29$; taking $\Delta H_f = -41.8$ (2) we calculate $\Delta H_f(Pb^{++}) = +20$.

For lead bromide, $\Delta H_s = -29.8$ (12) and $\Delta H_f = -66.3$ (2). These data lead to $\Delta H_f\ (Pb^{++}) = +21.9$.

For lead nitrate, $\Delta H_s = -26.9$ (11) and $\Delta H_f = -106.9$ (2). These

data lead to $\Delta H_f(Pb^{++}) = +21.4$.

Mercury

Hg^{++}: For mercuric iodide, $\Delta H_s = -20.1$ (26) and $\Delta H_f = -25.3$ (2).

Silver

Ag^+ : For silver bromide, $\Delta H_s = -5.3$ (8) and $\Delta H_f = -23.8$ (2). These data lead to $\Delta H_f\ (Ag^+) = +29.9$.

For silver iodide, $\Delta H_s = -7.4$ (8), -6.7 (12) and $\Delta H_f = -14.9$ (2). Using $\Delta H_s = -7$, we obtain $\Delta H_f\ (Ag^+) = +23$.

For silver nitrate, $\Delta H_s = -21.4$ (11) and $\Delta H_f = -29.4$ (2). These data lead to $\Delta H_f(Ag^+) = +26.8$.

$\Delta H = -51.2$ for the reaction $Ag^+ + e^-(am) = Ag$ (8).

From this we calculate $\Delta H_f\ (Ag^+) = +12$.

Lithium

Li^+: For lithium iodide, $\Delta H_s = -18.1$ (26) and $\Delta H_f = -65.1$ (2). These data lead to $\Delta H_f\ (Li^+) = -37.9$.

For lithium bromide $\Delta H_s = -19.7$ (26) and $\Delta H_f = -83.8$ (2). These data lead to $\Delta H_f\ (Li^+) = -44.5$.

For lithium nitrate, $\Delta H_s = -10.8$ (12) and $\Delta H_f = -115.4$ (2). These data lead to $\Delta H_f\ (Li^+) = -48.6$.

Sodium

Na^+: For sodium bromide, $\Delta H_s(\infty) = -10.4$ (13) and $\Delta H_f = -86.7$ (2).

Potassium

K^+: For potassium nitrate, $\Delta H_s = +0.4$ (12) and $\Delta H_f = -118.1$ (2). These data lead to $\Delta H_f\ (K^+) = -40.1$.

For potassium bromide, $\Delta H_s = -2.9$ (12) and $\Delta H_f = -94.1$ (2). These data lead to $\Delta H_f\ (K^+) = -38.0$.

For potassium iodide, $\Delta H_s = -5.9$ (12) and $\Delta H_f = -78.9$ (2). These data lead to $\Delta H_f(K^+) = -39.5$.

Rubidium

Rb^+: For rubidium bromide, $\Delta H_s = -0.4$ (26) and $\Delta H_f = -95.8$ (2). These data lead to ΔH_f $(Rb^+) = -37.2$; $\Delta H_s(Rb) = 0$ (28), which yields $\Delta H_f(Rb^+) = -39$.

Cesium

Cs^+: $\Delta H = 0$ for the reaction $Cs = Cs^+ + e^-$ (am) (28).

Electron

e^-(am): ΔH_s (K) = 0 (13, 28); this leads to $\Delta H_f(e^-(am)) = 39$. Coulter and Maybury (3a) give as the mean of several direct determinations, $\Delta H_f(e^-(am)) = 40.4 \pm 1$.

B. Calculations for Free Energies of Formation

ΔF_s = standard free enrgy of solution in ammonia.

ΔF_f = free energy of formation from elements in standard state (25°C.).

S = solubility in liquid ammonia (moles per kg. NH_3).

γ = mean activity coefficient for saturated solution.

All free energies are given in kcal./mole.

Hydrogen

H^+ = By convention we take $\Delta F_f(H^+) = 0$.

Fluorine

F^-: For sodium fluoride at 25°, $\Delta F_f = -129.3$ (18) and S = 0.083 (9). Estimating $\gamma = 0.2$, we calculate $\Delta F_s = 4.9$.

Chlorine

Cl^-: For ammonium chloride at 25°, $\Delta F_f = -48.7$ (18), S = 24.4 and $\gamma = .00822$ (25). $\Delta F_s = 1.90$.

ClO_3^-: For potassium chlorate at 25°, $\Delta F_f = -69.3$ (18) and S = 0.206 (10). Estimating $\gamma = 0.1$, we calculate $\Delta F_s = 4.6$.

Bromine

Br^-: For silver bromide at 25°, $\Delta F_f = -22.4$ (18) and S = 0.315 (10).

Estimating $\gamma = .08$, we calculate $\Delta F_s = 4.4$ and ΔF_f (Br^-) = -41. For potassium bromide at 25°, $\Delta F_f = -90.6$ (18) and S = 1.135 (9). Estimating $\gamma = .03$, we calculate $\Delta F_s = 4.0$ and ΔF_f (Br^-) = -40.1.

Iodine

IO_3^-: For potassium iodate at 25°, $\Delta F_f = -101.7$ (18), S = 3.044×10^{-5} and $\gamma = 0.891$ (1). $\Delta F_s = 12.5$.

Nitrogen

NO_3^-: For potassium nitrate at 25°, $\Delta F_f = -94.0$ (18) and S = 1.03 (9). Estimating $\gamma = .03$, we calculate $\Delta F_s = 4.1$

NH_3 : From Kelley (10a) we calculate the free energy of vaporization of liquid ammonia at 25° to be -1.3. For ammonia gas at 25°, $\Delta F_f = -4.0$ (18).

NH_4^+: We arbitrarily take $\Delta F^\circ = 0$ for the reaction $H^+ + NH_3 = NH_4^+$.

NH_2^-: We estimate the entropy of both sodium amide and potassium amide to be 14 cal./deg. Combining this with the known heats of formation (18) we obtain for sodium amide $\Delta F_f = -12.9$, for potassium amide $\Delta F_f = -11.9$.

For sodium amide at 25°, S = 0.00103 (10) and S = 0.0436 (29). Estimating $\gamma = 0.7$ and 0.2, resp., we calculate $\Delta F_s = 8.6$ and $\Delta F_s = 5.6$.

For potassium amide at 25°, S = 0.65 (10). Estimating $\gamma = .05$, we calculate $\Delta F_s = 4.1$.

The above three data lead to ΔF_f (NH_2^-) = 39.2, 36.2 and 38.7.

Lead

Pb^{++}: At -50°C., the standard potential of the lead electrode (vs. hydrogen electrode) is -0.33 v. (24). Using ΔH_f (Pb^{++}) = 21, we correct this to -0.28 v. at 25°C.

Thallium

Tl^+: For thallous chloride at 25°, $\Delta F_f = -44.2$ (18) and S = 0.0259 (5). Estimating $\gamma = 0.3$, we calculate $\Delta F_s = 5.8$.

Mercury

Hg^{++}: At -50°C., the standard potential of the mercury electrode (vs. hydrogen electrode) is -0.75 v. (24). Using $\Delta H_f(Hg^{++}) = 45$, we correct this to be -0.67 v. at 25°C.

Silver

Ag^+: For silver chloride at 25°, $\Delta F_f = -26.2$ (18) and S = 0.058 (10). Estimating $\gamma = 0.2$, we calculate $\Delta F_s = 5.3$ and $\Delta F_f\ (Ag^+) = 23.2$.

At -50°C., the standard potential of the silver electrode (vs. hydrogen electrode) is -0.83 v. (24). Using $\Delta H_f(Ag^+) = 26$, we correct this to -0.74 v. at 25°C. and $\Delta F_f\ (Ag^+) = 17$.

Lithium

Li^+: For lithium chloride at 0°C, S = 0.342 (16). Estimating $\gamma = .08$, we calculate $\Delta F_s\ (0°) = 3.9$. Using $\Delta H_s = -12$, we find $\Delta F_s\ (25°) = 5.5$ Using $\Delta F_f = -92.5$ (3), we calculate $\Delta F_f(Li^+) = -42.9$.

At -50°C., the standard potential of the lithium electrode (vs. hydrogen electrode) is 2.24 v. (21). Using $\Delta H_f\ (Li^+) = -44$, we correct this to 2.35 v. at 25°C. and $\Delta F_f\ (Li^+) = -54$.

Sodium

Na^+: For sodium chloride at 25°, $\Delta F_f = -91.8$ (18) and S = 0.52 (9). Estimating $\gamma = .06$, we calculate $\Delta F_s = 4.2$ and $\Delta F_f\ (Na^+) = -43.5$.

At -50°C., the standard potential of the sodium electrode (vs. hydrogen electrode) is 1.84 v. (24). Using $\Delta H_f\ (Na^+) = -38.1$, we correct this to 1.90 v. at 25°C. and $\Delta F_f\ (Na^+) = -43.8$.

Potassium

K^+: For potassium chloride at 25°, $\Delta F_f = -97.6$ (18) and S = 0.0054 (9). Estimating $\gamma = 0.5$, we calculate $\Delta F_s = 7.0$ and $\Delta F_f\ (K^+) = -46.5$.

At -50°C., the standard potential of the potassium electrode (vs.

hydrogen electrode) is 1.98 v. (24). Using ΔH_f (K^+) = -39, we correct this to 2.08 v. at 25° and ΔF_f (K^+) = -48.

Rubidium

Rb^+: For rubidium chloride at 0°C., S = 0.024 (16). Estimating γ = 0.3, we calculate $\Delta F_s(0°)$ = 5.4. Using ΔH_s = 1.4, we find $\Delta F_s(25°)$ = 5.8. Using ΔF_f = -98.5 (3), we calculate ΔF_f (Rb^+) = -48.6.

At -50°C., the standard potential of the rubidium electrode (vs. hydrogen electrode) is 1.93 v. (21). Using ΔH_f (Rb^+) = -38, we correct this to 2.03 v. at 25° and ΔF_f (Rb^+) = -47.

Cesium

Cs^+: For cesium chloride at 0°C., S = 0.023 (16). Estimating γ = 0.3, we calculate $\Delta F_s(0°)$ = 5.4. Using ΔH_s = 1.6, we find $\Delta F_s(25°)$ = 5.8. Using ΔF_f = -99.4 (3), we calculate $\Delta F_f(Cs^+)$ = -49.5.

At -50°C., the standard potential of the cesium electrode (vs. hydrogen electrode) is 1.95 v. (22). Using ΔH_f (Cs^+) = -39, we correct this to 2.04 v. at 25° and ΔF_f (Cs^+) = -47.

Electron

e^-(am): Laitinen and Nyman (14) have measured the standard potential of the "electron electrode" in liquid ammonia at -36°C. The average of their reported values is E° = 1.89 v. for $e^-(am) + H^+ = 1/2\ H_2(g)$. Using our value for the heat of formation of the ammoniacal electron, we correct this to E° = 1.94 v. at 25° and find 45 for the free energy of formation of the ammoniacal electron.

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Addendum

Dr. L. V. Coulter has kindly supplied some data recently obtained by himself, S. P. Wolsky and E. Zdanuk. The heat of solution of calcium metal in liquid ammonia solutions of ammonium salts is -100 ± 1 kcal./mole, and in pure ammonia is -20.0 kcal./mole. The heat of solution of CaI_2 in pure ammonia is -63.0 ± 1 kcal./mole. Combining these data with appropriate values from Table I, we obtain a value of -100 ± 1 kcal./mole for the heat of formation of Ca^{++}(am). Employing Pleskov's[21] value for the standard potential of the calcium electrode (E° = 1.64 v. at -50°), we calculate -133 kcal./mole for the free energy of formation of Ca^{++}(am) at 298°K, and -131 cal./deg. for the entropy.

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