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THERMODYNAMIC FUNCTIONS FOR SPECIES IN LIQUID AMMONIA

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May, 1953

Berkeley, California

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ABSTRACT

The heats and free energies of formation and entropies for various species in liquid ammonia at 25° have been calculated from data in the literature. The detailed calculations, as well as a table of oxidation potentials, are presented.

THERMODYNAMIC FUNCTIONS FOR SPECIES IN LIQUID AMMONIA

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I. Introduction

The purpose of this compilation is to extend and revise previous similar compilations[18,19] of the thermodynamic functions (ΔH_f°, ΔF_f° and S°) for species in liquid ammonia. The reader is referred to these previous publications for a general discussion of the methods of calculation. The functions have been calculated mainly from experimental data; the various approximations which have been made are discussed in the following four paragraphs.

(1) Estimated activity coefficients. The only salts whose activity coefficients have been measured in liquid ammonia at 25° are ammonium chloride[38] and potassium iodate.[1] Sedlet and DeVries[42] determined the activity coefficients for NaCl and KCl at -36° and Pleskov and Monoszon[34] determined the activity coefficients for NH_4NO_3 and NH_4Cl at -50°. Even though these measurements were made at greatly different temperatures, all the activity coefficients agree within 50% below 0.01 molal and within 200% below 1.0 molal. It is therefore felt that, in those cases where activity coefficients have been estimated for solutions of ionic strength less than 1.0 molal, errors of no more than 1-2 kcal./mole are made. In the cases of NH_4NO_3, NH_4Br and NH_4I, relative activity coefficients have been measured for the saturated solutions and for concentrations down to about 0.3 molal.[26]

These activity coefficients have been put on an absolute scale using the graphical method of Randall and Vietti.[37] (This method has been described by Latimer[27]).

(2) Estimated entropies. In cases where the heats of formation of solid compounds are known, but no entropy data are available to calculate the free energies of formation, the method of Latimer[28] has been used to estimate the entropies.

(3) Heat capacities. It has been assumed that heats and entropies of reaction are independent of temperature. Some idea of the accuracy of this assumption can be gained from the work of Chall and Doepke.[6] These investigators measured the heat of solution of sodium chloride in ammonia at 20° and found $\Delta H = -2.7$ kcal./mole. This is to be compared with $\Delta H = -5.5$ kcal./mole calculated from data obtained at -33° (cf. Table I) and $\Delta H = -1.5$ kcal./mole measured directly at -33°.[40] The discrepancy between the last two values must be explained by experimental inaccuracies and neglect of heats of dilution. It is apparent that we cannot calculate the sign of ΔC_p for the dissolution of sodium chloride, but at least we can say that the absolute magnitude of ΔC_p is probably not greater than 50 cal./deg.

(4) Simplicity of reactions. In cases of certain liquid ammonia solutions (e.g., solutions of dipositive metal salts and solutions of poly-plumbide, poly-telluride, etc.) where the ions probably are considerably ammonolyzed or associated as ion-pairs, over-simplified equations have been taken to represent certain calorimetric reactions. Such action is justified only by the convenience in tabulation of the heats of formation.

The thermodynamic functions are tabulated in Table I. The free energies have been used to calculate oxidation potentials, and these are presented in Table II.

In Section II, heats and free energies of formation are taken, when possible, from Bichowsky and Rossini[2] or the Bureau of Standards compilation.[31]

Table I

Thermodynamic Functions at 298°K.

	ΔH_f^o kcal./mole	ΔF_f^o kcal./mole	S^o e.u.
H^+	0	0	0
H_2O	-71.6		
F^-		-80.8	
Cl^-	-65.7	-44.1	-30.3
ClO_3^-	-47.7	-17.7	15
Br^-	-59.0	-39.9	-30.3
I^-	-45.3	-29	-25
IO_3^-		-42.2	
$Se_2^=$	-19.0		
$Te_2^=$	-27.8		
$Te_4^=$	-29.7		
NO_3^-	-77.6	-42.8	-5
NH_3	-16.1	- 2.7	24.7
NH_4^+	-16.1	- 2.7	24.7
NH_2^-	10.1	34	-10
NH_2OH	-24.6		
Guanidinium ion	-20.0		
SCN^-	-11.8		
Pb^{++}	21.0	13	11
Pb_9^{----}	64		
Tl^+		5.7	
Zn^{++}		-25	
Hg^{++}	45.2	31	35

Table I
(Page 2)

Thermodynamic Functions at 298°K.

	ΔH_f° kcal./mole	ΔF_f° kcal./mole	S° e.u.
Ag^+	26	17.5	23
Mn^{++}		-26	
BH_4^-	-15.7		
Ca^{++}	-100.0	-100	-21
Li^+	-49	-54	8
Na^+	-38.1	-43.6	15.1
K^+	-40.5	-47.0	21.4
Rb^+	-39	-47.5	29
Cs^+	-40.5	-48	29
$1/2\ e_2^=$ (am)	40.5	44.4	2
e^- (am)	43.5		

Table II

Oxidation Potentials (298°K.)

	E° (volts)
$Li = Li^+ + e^-$	2.34
$Ca = Ca^{++} + 2e^-$	2.17
$Cs = Cs^+ + e^-$	2.08
$Rb = Rb^+ + e^-$	2.06
$K = K^+ + e^-$	2.04

Table II
(Page 2)

Oxidation Potentials (298°K.)

	E° (volts)
$1/2\ e_2^{=} = e^-$	1.93
$Na = Na^+ + e^-$	1.89
$1/2\ H_2 + NH_2^- = NH_3 + e^-$	1.59
$3NH_2^- = 1/2N_2 + 2NH_3 + 3e^-$	1.55
$1/2\ H_2 + NH_2^-(3.6 \times 10^{-14}M) = NH_3 + e^-$ $1/2\ H_2 = H^+\ (3.6 \times 10^{-14}M) + e^-$	0.80
$3NH_2^-(3.6 \times 10^{-14}M) = 1/2\ N_2 + 2NH_3 + 3e^-$ $NH_3 = 1/2\ N_2 + 3H^+(3.6 \times 10^{-14}M) + 3e^-$	0.76
$Mn = Mn^{++} + 2e^-$	.56
$Zn = Zn^{++} + 2e^-$	.54
$1/2\ H_2 = H^+ + e^-$	0
$NH_3 = 1/2\ N_2 + 3H^+ + 3e^-$	-0.04
$Tl = Tl^+ + e^-$	-0.25
$Pb = Pb^{++} + 2e^-$	-0.28
$Hg = Hg^{++} + 2e^-$	-0.67
$Ag = Ag^+ + e^-$	-0.76
$I^- = 1/2\ I_2 + e^-$	-1.26
$Br^- = 1/2\ Br_2 + e^-$	-1.73
$Cl^- = 1/2\ Cl_2 + e^-$	-1.91
$F^- = 1/2\ F_2 + e^-$	-3.50

II. Calculations

ΔH_s = heat of solution in ammonia,

ΔH_f = heat of formation from elements in standard state,

ΔF_s = standard free energy of solution in ammonia,

ΔF_f = free energy of formation from elements in standard state (298°K.),

S = solubility in liquid ammonia (moles per kilogram of ammonia), and

γ = mean activity coefficient for saturated solution.

All energies are given in kilocalories per mole.

Hydrogen:

H^+: By convention we take $\Delta H_f = \Delta F_f = 0$ for the hydrogen ion.

H_2O: For ice, $\Delta H_s = -1.8$[24], $\Delta H_f = -69.8$ and therefore $\Delta H_f = -71.6$ for water in liquid ammonia.

Fluorine:

F^-: For sodium fluoride at 25°, $\Delta F_f = -129.3$ and S = 0.083.[15] Estimating $\gamma = 0.2$, we calculate $\Delta F_s = 4.9$. Using $\Delta F_f(Na^+) = -43.6$, we calculate $\Delta F_f(F^-) = -80.8$.

Chlorine:

Cl^-: For ammonium chloride, $\Delta H_s(\infty) = -6.8$[39] and $\Delta H_f = -75.0$. Using $\Delta H_f(NH_4^+) = -16.1$, we calculate $\Delta H_f(Cl^-) = -65.7$.

For ammonium chloride at 25°, $\Delta F_f = -48.7$, S = 24.4, and $\gamma = 0.00822$.[38] $\Delta F_s = 1.90$. Using $\Delta F_f(NH_4^+) = -2.7$, we calculate $\Delta F_f(Cl^-) = -44.1$.

(From the vapor pressure data of Fowles and Pollard[12] on $NH_4Cl \cdot 3NH_3$ we calculate that the solid phase in equilibrium with the saturated solution at 25° is NH_4Cl. This is confirmed

by the data of Kendall and Davidson.[21])

<u>ClO_3^-</u>: For sodium chlorate, $\Delta H_s = -2.2$[22] and $\Delta H_f = -83.6$. Using $\Delta H_f(Na^+) = -38.1$, we calculate $\Delta H_f(ClO_3^-) = -47.7$.

For potassium chlorate at 25°, $\Delta F_f = -69.3$ and $S = 0.206$.[16] Estimating $\gamma = 0.1$, we calculate $\Delta F_s = 4.6$. Using $\Delta F_f(K^+) = -47.0$, we calculate $\Delta F_f(ClO_3^-) = -17.7$.

<u>Bromine</u>:

Br^-: For ammonium bromide, $\Delta H_3(\infty) = -10.5$[39] and $\Delta H_f = -64.6$. Using $\Delta H_f(NH_4^+) = -16.1$, we calculate $\Delta H_f(Br^-) = -59.0$.

For $AgBr \cdot 3NH_3$ at 25°, $\Delta F_f = -35.05$[4] and $S = .315$.[16] Estimating $\gamma = .085$, we calculate $\Delta F_s = 4.3$. Using $\Delta F_f(Ag^+) = 17.5$, we calculate $\Delta F_f(Br^-) = -40.1$.

From the data of Biltz,[3] we calculate that KBr is not ammoniated at 25°. For KBr at 25°, $\Delta F_f = -90.6$ and $S = 1.135$.[15] Estimating $\gamma = .030$, we calculate $\Delta F_s = 4.0$. Using $\Delta F_f(K^+) = -47.0$, we calculate $\Delta F_f(Br^-) = -40.1$.

NH_4Br is not ammoniated at 25°.[21] For NH_4Br at 25°, $S = 24.8$. From the data of Larsen and Hunt, we estimate $\gamma = .052$, hence $\Delta F_s = -0.3$. For NH_4Br, $\Delta H_f = -64.6$ and we estimate the entropy as 26.9, so $\Delta F_f = -41.8$. Using $\Delta F_f(NH_4^+) = -2.7$, we calculate $\Delta F_f(Br^-) = -39.4$.

For $\Delta F_f(Br^-)$ we shall use the average value -39.9.

<u>Iodine</u>:

<u>I^-</u>: For NH_4I, $\Delta H_s(\infty) = -13.0$[40] and $\Delta H_f = -48.4$. Using $\Delta H_f(NH_4^+) = -16.1$, we calculate $\Delta H_f(I^-) = -45.3$.

At 25°, NH_4I is not ammoniated.[21] S = 25.4 for NH_4I.[16] From the data of Larsen and Hunt,[26] we estimate γ = .63, hence ΔF_s = -3.3. For NH_4I, we estimate an entropy of 28.5, so ΔF_f = -27.2. Using $\Delta F_f(NH_4^+)$ = -2.7, we calculate $\Delta F_f(I^-)$ = -27.8.

From some unpublished data of Jolly on the vapor pressures of KI solutions at 0°, we calculate the free energy of solution of KI at 0° to be ΔF_s = -0.8. Taking ΔH_s = -6.9, we calculate $\Delta F_s(25°)$ = -0.2. Since, for KI, ΔF_f = -77.0 and $\Delta F_f(K^+)$ = -47.0, we calculate $\Delta F_f(I^-)$ = -30.2.

For $\Delta F_f(I^-)$, we shall use the average value -29.

<u>IO_3^-</u>: For potassium iodate at 25°, ΔF_f = -101.7, S = 3.044 x 10^{-5} and γ = 0.891,[1] hence ΔF_s = 12.5. Using $\Delta F_f(K^+)$ = -47.0, we calculate $\Delta F_f(IO_3^-)$ = -42.2.

<u>Selenium</u>:

<u>$Se_2^=$</u>: ΔH = -100.0[30] for the reaction

$$e_2^= + 2Se = Se_2^=$$

Using $\Delta H_f(1/2\ e_2^=)$ = 40.5, we calculate $\Delta H_f(Se_2^=)$ = -19.0.

<u>Tellurium</u>:

<u>$Te_2^=$</u>: The heats for the following reactions have been measured by Kraus and Ridderhof:[23]

$$2Na^+ + e_2^= + Te = Na_2Te \qquad \Delta H = -86.9$$

$$Na_2Te + Te = 2Na^+ + Te_2^= \qquad \Delta H = -21.9$$

From these data we calculate $\Delta H_f(Te_2^=)$ = -27.8.

<u>$Te_4^=$</u>: ΔH = -1.9[23] for the reaction

$$Te_2^= + 2Te = Te_4^=.$$

We calculate $\Delta H_f(Te_4^=)$ = -29.7.

Nitrogen:

NO_3^-: For sodium nitrate, $\Delta H_s(\infty) = -4.0$[40] and $\Delta H_f = -111.7$. Using $\Delta H_f(Na+) = -38.1$, we calculate $\Delta H_f(NO_3^-) = -77.6$.

For potassium nitrate at 25°, $\Delta F_f = -94.0$ and $S = 1.03$.[15] Estimating $\gamma = .048$, we calculate $\Delta F_s = 3.6$. Using $\Delta F_f(K+) = -47.0$, we calculate $\Delta F_f(NO_3^-) = -43.4$.

For ammonium nitrate at 25°, $\Delta H_f = -87.3$ and we estimate the entropy as 35.6, so $\Delta F_f = -43.7$. At 25°, $S = 48.9$ and from the data of Larsen and Hunt[26] we estimate $\gamma = .056$, hence $\Delta F_s = -1.2$. Using $\Delta F_f(NH_4^+) = -2.7$, we calculate $\Delta F_f(NO_3^-) = -42.2$.

For $\Delta F_f(NO_3^-)$ we shall use the average value -42.8.

NH_3: $\Delta H_f(\text{liquid } NH_3) = -16.07$.[2]

From Kelley[20] we calculate the free energy of vaporization of liquid ammonia at 25° to be -1.3. For ammonia gas at 25°, $\Delta F_f = -4.0$, so ΔF_f for liquid NH_3 is -2.7.

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

$$H^+ + NH_{3(l)} = NH_4^+.$$

NH_2^-: $\Delta H = -26.1$[30] for the reaction $H^+ + NH_2^- = NH_3$; this leads to $\Delta H_f(NH_2^-) = 10.0$.

For potassium amide, $\Delta H_s = -2.0$[30] and $\Delta H_f = -28.3$. Using $\Delta H_f(K+) = -40.5$, we calculate $\Delta H_f(NH_2^-) = 10.2$.

For $\Delta H_f(NH_2^-)$ we shall use the average value 10.1.

We make the assumption that both $NaNH_2$ and KNH_2 are unammoniated at 25°. For $NaNH_2$, $\Delta H_f = -28.4$; for KNH_2, $\Delta H_f = -28.3$. Estimating the entropies to be 13.5 and 15, respectively, we

calculate $\Delta F_f = -12.7$ and -12.1, respectively.

For sodium amide at 25°, the solubilities $S = 0.00103$,[16] and $S = 0.0436$,[43] have been reported. We shall use a value $S = .01$. Estimating $\gamma = .45$, we calculate $\Delta F_s = 6.4$. Using $\Delta F_f(Na^+) = -43.6$, we calculate $\Delta F_f(NH_2^-) = 37.3$

For potassium amide at 25°, $S = 0.65$.[16] Estimating $\gamma = 0.05$, we calculate $\Delta F_s = 4.1$. Using $\Delta F_f(K+) = -47.0$, we calculate $\Delta F_f(NH_2^-) = 39.0$.

At -50°, $\Delta F° = 33.4$ for

$$NH_3 = H+ + NH_2^-.$$ [35]

Using $\Delta H = 26.1$ for the same reaction, we calculate $\Delta F° = 35.85$ at 25°, corresponding to $\Delta F_f(NH_2^-) = 33.2$.

The large discrepancy between the solubility free energies and the cell free energy may possibly be due to ammoniate formation or to incorrect solubility data. Vaughn, Vogt and Nieuwland[44] have pointed out that the solubility data of Hunt and Boncyk may be low because the latter used commercial sodamide. Vaughn, Vogt and Nieuwland found $S = 1$ at -33°.

Giving more weight to the cell data, we take $\Delta F_f(NH_2^-) = 34$.

<u>NH_2OH</u>: For hydroxylammonium chloride, $\Delta H_s = -16.3$[30] and $\Delta H_f = -74.0$. We presume the net reaction for the dissolution to be:

$$NH_2OH \cdot HCl = NH_2OH + H^+ + Cl^-.$$

Using $\Delta H_f(Cl^-) = -65.7$, we calculate $\Delta H_f = -24.6$ for hydroxylamine in liquid ammonia.

<u>Carbon</u>:

<u>Guanidinium ion</u>: Guanidine is a much stronger base than ammonia and so ammonia solutions of guanidinium salts are

probably very little ammonolyzed. For guanidinium nitrate, $\Delta H_s = -5.5$[30] and $\Delta H_f = -92.1$. Using $\Delta H_f(NO_3^-) = -77.6$, we calculate $\Delta H_f(GH^+) = -20.0$.

<u>SCN^-</u>: For ammonium thiocyanate, $\Delta H_s(\infty) = -9.7$[30] and $\Delta H_f = -18.2$. Using $\Delta H_f(NH_4^+) = -16.1$, we calculate $\Delta H_f(SCN^-) = -11.8$.

<u>Lead</u>:

<u>Pb^{++}</u>: For lead iodide, $\Delta H_s = -27.0$[39], -29.1[22]. We shall assume $\Delta H_s = -29$; taking $\Delta H_f = -41.8$, we calculate $\Delta H_f(Pb^{++}) = 20$.

For lead bromide, $\Delta H_s = -29.8$[23] and $\Delta H_f = -66.3$. Using $\Delta H_f(Br^-) = -59.0$, we calculate $\Delta H_f(Pb^{++}) = 21.9$.

For lead nitrate, $\Delta H_s = -26.9$[22] and $\Delta H_f = -106.9$. Using $\Delta H_f(NO_3^-) = -77.6$, we calculate $\Delta H_f(Pb{+}{+}) = 21.4$.

We shall take the value 21.0 for $\Delta H_f(Pb{+}{+})$.

At -50°, the standard potential of the lead electrode (vs. the hydrogen electrode) is -0.33v.[36] Using $\Delta H_f(Pb{+}{+}) = 21.0$, we correct this to -0.28 v. at 25°. This potential corresponds to $\Delta F_f(Pb{+}{+}) = 13$.

<u>Pb_9^{----}</u>: $\Delta H = -88.0$[23] for the reaction

$$4Na + 9Pb = 4Na^+ + Pb_9^{----}.$$

Using $\Delta H_f(Na+) = -38.1$, we calculate $\Delta H_f(Pb_9^{----}) = 64$.

<u>Thallium</u>:

<u>Tl^+</u>: Thallous chloride is unammoniated at 25°. For TlCl at 25°, $\Delta F_f = -44.2$ and $S = 0.0259$[10]. Estimating $\gamma = 0.3$, we calculate $\Delta F_s = 5.8$. Using $\Delta F_f(Cl^-) = -44.1$, we calculate $\Delta F_f(Tl+) = 5.7$.

Zinc:

Zn^{++}: For $ZnI_2 \cdot 6NH_3$ at 25°, S = 0.0031[16] and ΔF_f = -110.45.[3] Estimating γ = 0.45, we calculate ΔF_s = 10.9. Using $\Delta F_f(I^-)$ = -29, we calculate $\Delta F_f(Zn^{++})$ = -25.

Mercury:

Hg++: For mercuric iodide, ΔH_s = -20.1[39] and ΔH_f = -25.3. Using $\Delta H_f(I^-)$ = -45.3, we calculate $\Delta H_f(Hg^{++})$ = 45.2.

At -50°, the standard potential of the mercury electrode (vs. the hydrogen electrode) is -0.75 v.[36] Using $\Delta H_f(Hg^{++})$ = 45.2, we correct this to -0.67 v. at 25°. This potential corresponds to $\Delta F_f(Hg^{++})$ = 31.

Silver:

Ag+: For silver bromide, ΔH_s = -5.3[14] and ΔH_f = -23.8. Using $\Delta H_f(Br^-)$ = -59.0, we calculate $\Delta H_f(Ag^+)$ = 29.9.

For silver iodide, ΔH_s = -7.4,[14] -6.7[23] and ΔH_f = -14.9. Using ΔH_s = -7.0 and $\Delta H_f(I^-)$ = -45.3, we calculate $\Delta H_f(Ag^+)$ = 23.4.

For silver nitrate, ΔH_s = -21.4[22] and ΔH_f = -29.4. Using $\Delta H_f(NO_3^-)$ = -77.6, we calculate $\Delta H_f(Ag^+)$ = 26.8.

ΔH = -51.2 for the reaction $Ag^+ + 1/2\ e_2^= = Ag$.[14] From this we calculate $\Delta H_f(Ag^+)$ = 10.7.

We shall use $\Delta H_f(Ag^+)$ = 26.

For $AgCl \cdot 3NH_3$ at 25°, ΔF_f = -39.4[4] and S = .058.[16] Estimating γ = .24, we calculate ΔF_s = 5.1 and $\Delta F_f(Ag^+)$ = 17.9.

At -50°, the standard potential of the silver electrode (vs. the hydrogen electrode) is -0.83 v.[36] Using $\Delta H_f(Ag^+)$ = 26,

we correct this to -0.74 v. at 25° and $\Delta F_f(Ag+) = 16.8$.

We shall use $\Delta F_f(Ag+) = 17.5$.

Manganese:

Mn++: For MnI_2, Bichowsky and Rossini[2] give $\Delta H_f = -49.8$ and the Bureau of Standards[31] gives $\Delta H_f = -59.3$. Using $\Delta H_f = -49.8$, we estimate $\Delta F_f = -50.4$. Using the data of Biltz[3], we calculate, for $MnI_2 \cdot 6NH_3$, $\Delta F_f = -113.4$. For $MnI_2 \cdot 6NH_3$ at 25°, S = .0006.[16] Estimating $\gamma = 0.7$, we calculate $\Delta F_s = 13.0$. Using $\Delta F_f(I^-) = -29$, we calculate $\Delta F_f(Mn++) = -26$.

Boron:

BH_4^-: For $NaBH_4$, $\Delta H_f = -43.8$ and $\Delta H_s = -10$.[38a] Using $\Delta H_f(Na+) = -38.1$, we calculate $\Delta H_f(BH_4^-) = -15.7$.

Calcium:

Ca++: $\Delta H = -99.3$[45] for the reaction $Ca_{(s)} + 2H+ = Ca++ + H_{2(g)}$.

For calcium iodide, $\Delta H_s(\infty) = -62.8$[45] and $\Delta H_f = -128.5$. Using $\Delta H_f(I^-) = -45.3$, we calculate $\Delta H_f(Ca++) = -100.7$.

We shall use $\Delta H_f(Ca++) = -100.0$.

At 0°, the solubility of $CaBr_2 \cdot 8NH_3$ is S = .00045.[29] Estimating $\gamma = .75$, we calculate $\Delta F_s(0°) = 12.26$. From the data of Hart and Partington[13] we calculate $\Delta H_f = -352.7$ for $CaBr_2 \cdot 8NH_3$, hence $\Delta H_s = 6.6$ and $\Delta F_s(25°) = 12.8$. Using $\Delta F_f = -211.8$ for $CaBr_2 \cdot 8NH_3$ and $\Delta F_f(Br^-) = -39.9$, we calculate $\Delta F_f(Ca++) = -97.6$.

The data of Hüttig[17] on the dissociation pressure of $CaI_2 \cdot 8NH_3$ are somewhat inconsistent, but we calculate from his data that the octammoniate is the stable solid phase in a saturated CaI_2 solution at both 0° and 25°. At 0°, S = .136.[29]

Estimating γ = .070, we calculate $\Delta F_s(0°)$ = 6.8. From the data of Hüttig we calculate ΔH_s = 9.0 and $\Delta F_s(25°)$ = 6.6. Since ΔF_f = -191.1 for $CaI_2 \cdot 8NH_3$ and $\Delta F_f(I^-)$ = -29, we calculate $\Delta F_f(Ca^{++})$ = -104.9.

At -50°, the standard potential of the calcium electrode (vs. the hydrogen electrode) has been measured as 1.64 v.[32] Using $\Delta H_f(Ca^{++})$ = -100, we correct this to 1.46 v. at 25° and $\Delta F_f(Ca^{++})$ = -67.4. No explanation is offered for the discrepancy between this value and the solubility values.

We shall use $\Delta F_f(Ca^{++})$ = -100.

Lithium:

Li+: For lithium iodide, ΔH_s = -18.1[39] and ΔH_f = -65.1. Using $\Delta H_f(I^-)$ = -45.3, we calculate $\Delta H_f(Li^+)$ = -37.9.

For lithium bromide, ΔH_s = -19.7[39] and ΔH_f = -83.8. Using $\Delta H_f(Br^-)$ = -59.0, we calculate $\Delta H_f(Li^+)$ = -44.5.

For lithium nitrate, ΔH_s = -10.8[23] and ΔH_f = -115.4. Using $\Delta H_f(NO_3^-)$ = -77.6, we calculate $\Delta H_f(Li^+)$ = -48.6.

ΔH = -9.65[9] for $Li = Li^+ + 1/2\ e_2^=$. Using $\Delta H_f(1/2\ e_2^=)$ = 40.5, we calculate $\Delta H_f(Li^+)$ = -50.1.

We shall use $\Delta H_f(Li^+)$ = -49.

For $LiCl \cdot 5NH_3$ at 0°, S = 0.342.[29] Estimating γ = .075, we calculate $\Delta F_s(0°)$ = 3.96. From the data of Hart and Partington[13] we calculate ΔH_f = -202.6 for $LiCl \cdot 5NH_3$, hence ΔH_s = 7.4. This is in reasonable agreement with the heat calculated from the temperature coefficient of the solubility (ΔH_s = 5.5). We calculate $\Delta F_s(25°)$ = 3.65 and $\Delta F_f(Li^+)$ = -55.3.

At -50°, the standard potential of the lithium electrode (vs. the hydrogen electrode) is 2.24 v.[32] Using $\Delta H_f(Li^+) = -49$, we correct this to 2.28 v. at 25° and $\Delta F_f(Li^+) = -52.5$.

We shall use $\Delta F_f(Li^+) = -54$.

Sodium:

Na^+: For sodium bromide, $\Delta H_s(\infty) = -10.4$[24] and $\Delta H_f = -86.7$. Using $\Delta H_f(Br^-) = -59.0$, we calculate $\Delta H_f(Na^+) = -38.1$.

For sodium chloride at 25°, $\Delta F_f = -91.8$ and $S = 0.52$.[15] Estimating $\gamma = 0.06$, we calculate $\Delta F_s = 4.2$. Using $\Delta F_f(Cl^-) = -44.1$, we calculate $\Delta F_f(Na^+) = -43.5$.

At -50°, the standard potential of the sodium electrode (vs. the hydrogen electrode) is 1.84 v.[36] Using $\Delta H_f(Na^+) = -38.1$, we correct this to 1.90 v. at 25° and $\Delta F_f(Na^+) = -43.8$.

We shall use $\Delta F_f(Na^+) = -43.6$.

Potassium:

K^+: For potassium thiocyanate, $\Delta H_s(\infty) = -4.8$[30] and $\Delta H_f = -47.4$. Using $\Delta H_f(SCN^-) = -11.8$, we calculate $\Delta H_f(K^+) = -40.4$.

For potassium nitrate, $\Delta H_s = 0.4$[23] and $\Delta H_f = -118.1$. Using $\Delta H_f(NO_3^-) = -77.6$, we calculate $\Delta H_f(K^+) = -40.1$.

For potassium bromide, $\Delta H_s = -2.9$[23] and $\Delta H_f = -94.1$. Using $\Delta H_f(Br^-) = -59.0$, we calculate $\Delta H_f(K^+) = -38.0$.

For potassium iodide, $\Delta H_s(\infty) = -7.8$[30] (this is to be compared with $\Delta H_s = -5.9$[23]) and $\Delta H_f = -78.9$. Using $\Delta H_f(I^-) = -45.3$, we calculate $\Delta H_f(K^+) = -41.4$.

We shall use $\Delta H_f(K^+) = -40.5$.

For potassium chloride at 25°, $\Delta F_f = -97.6$ and $S = .0054$.[15] Estimating $\gamma = 0.55$, we calculate $\Delta F_s = 6.9$ and $\Delta F_f(K+) = -46.6$.

At -50°, the standard potential of the potassium electrode (vs. the hydrogen electrode) is 1.98 v.[36] Using $\Delta H_f(K+) = -40.5$, we correct this to 2.055 v. at 25° and $\Delta F_f(K+) = -47.4$.

We shall use $\Delta F_f(K+) = -47.0$.

Rubidium:

Rb^+: For rubidium bromide, $\Delta H_s = -0.4$[39] and $\Delta H_f = -95.8$. Using $\Delta H_f(Br-) = -59.0$, we calculate $\Delta H_f(Rb+) = -37.2$.

For rubidium metal, $\Delta H_s = 0$[41], which yields $\Delta H_f(Rb+) = -40.5$.

We shall use $\Delta H_f(Rb+) = -39$.

We shall assume that rubidium chloride is unammoniated at 0°. For RbCl at 0°, $S = 0.024$.[29] Estimating $\gamma = 0.3$, we calculate $\Delta F_s(0°) = 5.4$. Using $\Delta H_s = 0.4$, we calculate $\Delta F_s(25°) = 5.9$. Using $\Delta F_f = -98.5$[5] for RbCl, we calculate $\Delta F_f(Rb+) = -48.5$.

At -50°, the standard potential of the rubidium electrode (vs. the hydrogen electrode) is 1.93 v.[32] Using $\Delta H_f(Rb+) = -39$, we correct this to 2.01 v. at 25° and $\Delta F_f(Rb+) = -46.4$.

We shall use $\Delta F_f(Rb+) = -47.5$.

Cesium:

Cs+: For cesium metal, $\Delta H_s = 0$;[41] hence $\Delta H_f(Cs+) = -40.5$.

We assume that cesium chloride is unammoniated at 0°. For CsCl at 0°, $S = 0.023$.[29] Estimating $\gamma = 0.3$, we calculate $\Delta F_s(0°) = 5.4$. Using $\Delta H_s = 0.1$, we calculate $\Delta F_s(25°) = 5.9$. Using $\Delta F_f = -99.4$[5] for CsCl, we calculate $\Delta F_f(Cs+) = -49.4$.

At -50°, the standard potential of the cesium electrode (vs. the hydrogen electrode) is 1.95 v.[33] Using $\Delta H_f(Cs^+) = -40.5$, we correct this to 2.02 v. at 25° and $\Delta F_f(Cs^+) = -46.5$.

We shall use $\Delta F_f(Cs^+) = -48$.

Electron:

1/2 $e_2^=$: Coulter and Maybury[8] give $\Delta H = 40.4$ as the mean of several determinations for the reaction

$$1/2\ H_{2(g)} = 1/2\ e_2^= + H^+.$$

$\Delta H = 0$[24,41] for the reaction

$$K = K^+ + 1/2\ e_2^=,$$

yielding $\Delta H_f(1/2\ e_2^=) = 40.5$.

We shall use $\Delta H_f(1/2\ e_2^=) = 40.5$.

Laitinen and Nyman[25] have measured the standard potential of the "electron electrode" in liquid ammonia at -36°. The average of their reported values is E° = 1.89 v. for $1/2\ e_2^= + H^+ = 1/2\ H_{2(g)}$. Using our value for the heat of formation of the ammoniacal electron pair, we correct this to E° = 1.93 v. at 25° and $\Delta F_f(1/2\ e_2^=) = 44.4$.

e^-: Coulter and Candela[7] measured the heat of solution of potassium to extreme dilution. From the heat of dilution, they calculate $\Delta H = 6$ for the process

$$e_2^= = 2e^-,$$

yielding $\Delta H_f(e^-) = 43.5$.

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