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Author

Jolly, William L.

Publication Date

1951-06-15

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UNCLASSIFIED

Berkeley, California

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William L. Jolly

Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

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Introduction

A large literature has developed in the past thirty years on the sub-
ject of ionic solvation effects, but the discussions have been limited mainly
to aqueous systems. In order to test the generality of the various theoreti-
cal and empirical relationships for heats of solvation, entropies of solva-
tion, 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).

$$\bar{H}_2 - \bar{H}_2^0 = -3/2 \; A \; \sqrt{TM_1/D^3 V_1} \cdot \left[\frac{1}{T} + \frac{d \ln D}{dT} + 1/3 \; \frac{d \ln V}{dT} \right] (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$$

For water, $\bar{H}_2 - \bar{H}_2^0 = 258.2 \; (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$ 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 calcu-

late, for liquid ammonia at -33°, $\bar{H}_2 - \bar{H}_2^0 = -200 \; (\Sigma \nu_i z_i^2)^{3/2} m^{1/2}$ 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 $\bar{H}_2 - \bar{H}_2^0$ 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 iden-
tical 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 calcula-
ted 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^o_f	ΔF^o_f(298°K.)	S^o	$\Delta H_{(am)}-H_{(hyd)}$
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 corres-
ponding 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 in-

vestigated 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 ΔH_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, ΔH_s = -20.1 (26) and ΔH_f = -25.3 (2).

Silver

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

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

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

ΔH = - 51.2 for the reaction $Ag^+ + e^-(am)$ = Ag (8).
From this we calculate $\Delta H_f (Ag^+)$ = + 12.

Lithium

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

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

For lithium nitrate, ΔH_s = -10.8 (12) and ΔH_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 ΔH_f = -86.7 (2).

Potassium

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

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

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

Rubidium

Rb^+: For rubidium bromide, ΔH_s = -0.4 (26) and ΔH_f = -95.8 (2). These

data lead to ΔH_f (Rb^+) = -37.2; ΔH_s(Rb) = 0 (28), which yields $\Delta H_f(Rb^+)$=-39.

Cesium

Cs^+: ΔH = 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 ± 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°, ΔF_f = -129.3 (18) and S = 0.083 (9).

Estimating γ = 0.2, we calculate ΔF_s = 4.9.

Chlorine

Cl^-: For ammonium chloride at 25°, ΔF_f = -48.7 (18), S = 24.4 and

γ = .00822 (25). ΔF_s = 1.90.

ClO_3^-: For potassium chlorate at 25°, ΔF_f = -69.3 (18) and S = 0.206 (10).

Estimating γ = 0.1, we calculate ΔF_s = 4.6.

Bromine

Br^-: For silver bromide at 25°, ΔF_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), $S = 3.044 \times 10^{-5}$

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 $\Delta F° = 0$ 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 ΔF_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 ΔF_f $(Ag^+) = 17$.

Lithium

Li^+: For lithium chloride at $0°C$, $S = 0.342$ (16). Estimating $\gamma = .08$, we calculate ΔF_s $(0°) = 3.9$. Using $\Delta H_s = -12$, we find ΔF_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 ΔH_f $(Li^+) = -44$, we correct this to 2.35 v. at $25°C.$ and ΔF_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 ΔF_f $(Na^+) = -43.5$.

At $-50°C.$, the standard potential of the sodium electrode (vs. hydrogen electrode) is 1.84 v. (24). Using ΔH_f $(Na^+) = -38.1$, we correct this to 1.90 v. at $25°C.$ and ΔF_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 ΔF_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 ΔF_s(0°) = 5.4. Using ΔH_s = 1.4, we find ΔF_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 ΔF_s(0°) = 5.4. Using ΔH_s = 1.6, we find ΔF_s(25°) = 5.8. Using ΔF_f = -99.4 (3), we calculate ΔF_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.

Acknowledgement

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 ($E^\circ = 1.64$ v. at -50°), we calculate -133 kcal./mole
for the free energy of formation of Ca^{++}(am) at $298^\circ K$, and -131
cal./deg. for the entropy.

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