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Correlation of Thermodynamic Properties for Dissociation of Ammines of Divalent Metal Halides

W. E. WENTWORTH, W. M. RALDOW and G. E. CORBETT

Department of Chemistry, University of Houston, Houston, Texas 77004, U.S.A.

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The equilibria between gaseous ammonia and inorganic salts, and the properties of solid ammines formed were extensively studied by Ephraim and co-workers, and by Biltz and co-workers at the beginning of this century. A large part of their results was reviewed in the English language by Clark [1]. In the early forties Hart and Partington performed a comprehensive investigation of solid–gas equilibria with ammonia and trideuterammonia in order to determine isotope effects [2]. Their measurements of dissociation pressures of solid ammines, however, differ somewhat from those reported previously. The discrepancies in data reported in the literature may have been caused by inherent experimental difficulties, *e.g.* the necessity of preparing very dry salts, the long waiting time for the equilibria to be reached, the possible formation of solid solutions, *etc.*

In view of the current interest in the use of ammines as media for thermal energy storage, we feel that correlations of the experimental results for the different ammine systems are of value. The aim of the present note is to call attention to the remarkable constancy of the dissociation entropies and to discuss the dissociation enthalpies for ammines of some first transition series metal dihalides. It will also be demonstrated that the general pattern of the dissociation enthalpies is consistent with thermodynamic calculations on hexammine cations in the gas phase and with spectroscopic measurements on metal dihalides in the solid state.

Ammine equilibria

$$S\cdot nNH_{3(s)} \rightleftarrows S\cdot mNH_{3(s)} + (n\text{-}m)NH_{3(g)}$$

are often characterized by the enthalpy change (ΔH) for the reaction (usually listed per mol of NH_3) and the temperature (T_{100}) at which the vapor pressure of NH_3 reaches a certain value, customarily 100 torr; in other words P = 100 torr is arbitrarily chosen to be the standard state. If entropy changes (ΔS_{100})

TABLE I. Entropy Changes, ΔS_{100} (cal/K mol), for the Dissociation Reactions of Some Transition Metal Ammines. Figures in parenthesis are for the corresponding ΔH (kcal/mol) Values.

a) Hexammines

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Cl^-	35.5 (11.3)	35.8 (12.3)	35.5 (12.9)	35.7 (14.2)	n.a.[a]	36.1 (10.7)
Br^-	35.8 (12.7)	35.6 (13.3)	35.5 (14.0)	35.6 (15.4)	n.a.	36.3 (11.0)
I^-	35.6 (14.2)	35.5 (14.5)	35.5 (14.7)	35.3 (15.9)	n.a.	36.3 (10.9)

b) Diammines

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Cl^-	36.7 (17.0)	36.5 (18.2)	36.5 (18.7)	36.6 (19.0)	n.a.	36.0 (19.2)
Br^-	36.4 (18.4)	36.6 (19.9)	36.6 (20.2)	36.6 (20.4)	n.a.	36.0 (19.9)
I^-	36.5 (19.7)	36.6 (20.5)	36.5 (19.9)	35.9 (19.7)	n.a.	36.0 (19.4)

c) Monoammines

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Cl^-	36.8 (20.1)	36.9 (20.8)	36.8 (21.1)	36.9 (21.5)	–	35.6 (25.0)
Br^-	36.9 (20.0)	36.9 (20.8)	36.8 (21.0)	36.9 (20.8)	–	35.4 (24.0)
I^-	–	–	–	–	–	35.9 (22.0)

d) Additional Ammines

	Zn^{2+}, Tetrammines	Cu^{2+}, Pentammines	Cu^{2+}, 3 1/3-ammines
Cl^-	36.2 (11.8)	36.8 (12.2)	[39.6][b]
Br^-	36.4 (13.6)	38.0 (12.9)	[39.9]
I^-	36.4 (15.4)	38.0 (13.2)	[40.0]

[a] Values are not available. [b] Approximate values of ΔS_{100}.

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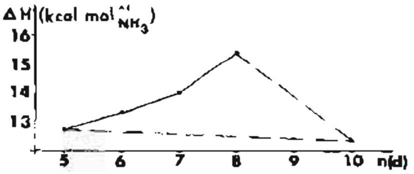

Figure 1. Dissociation enthalpies, ΔH (kcal/mol NH_3), of some $M(NH_3)_6Br_2$ to diammines. The curves for chlorides and iodides are similar. ΔH for zinc is an average value for dissociation of hexa- and tetraammines.

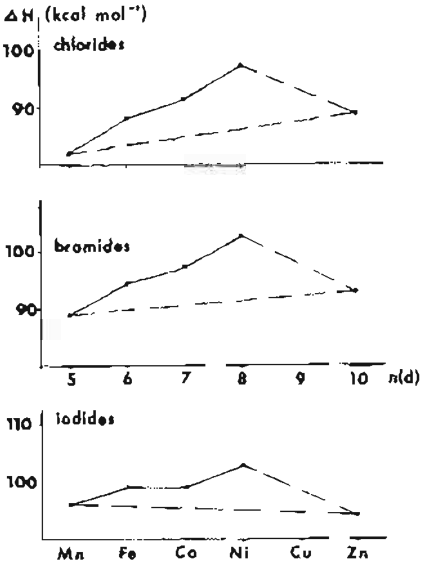

Figure 2. Dissociation enthalpies, ΔH (kcal/mol $M(NH_3)_6X_2$), of hexammines of some transition metal dihalides as a function of the number of d electrons.

were calculated for these particular temperatures, one would expect fairly constant values, since a major part of the change comes from the formation of gaseous ammonia [3]. However, as may be seen from Table 1, the constancy is remarkably greater than anticipated. Table I lists ΔS_{100} values for ammines of chlorides, bromides and iodides of divalent first transition series metals. The corresponding values of ΔH are also shown. The ΔH and T_{100} values for Mn, Fe, Co and Ni complexes were determined by Biltz and Hüttig [4] by a careful nomographic fitting of the experimental data to the Nernst equation:

$$\log P = -\frac{\Delta H}{4.57T} + 1.75\log T + aT + 3.3$$

Observe that ΔS_{100} values for these complexes increase as the number of ammonia molecules decreases. The slightly different values for complexes of zinc and copper may be explained as follows. Firstly, in contrast to Mn, Fe, Co and Ni, zinc forms a stable tetrammine and copper forms stable complexes with 5 and 3 1/3 ammonia molecules. Secondly, the values of ΔH and T_{100} for these complexes [5, 6] were obtained by a simpler procedure and thus their accuracy is expected to be poorer.

It should be pointed out that the values of ΔS_{100} are approximately equal, the variation being from 34 cal/K mol to 39 cal/K mol, for all *ca.* 110 ammines of divalent metal halides listed by Clark [1]. Thus, a quick judgement of the reliability of vapor pressure measurements on ammine systems can be obtained by calculating values of ΔH and T_{100} from the Clausius–Clapeyron equation and comparing the obtained value of $\Delta S_{100} = \Delta H/T_{100}$ with the expected value of approximately 36 cal/K mol (the ΔH values obtained from the Clausius–Clapeyron equation are usually higher than those obtained from the Nernst equation).

Cotton studied the enthalpies of formation in the gas phase of hexammine cations of transition metals [7]:

$$M^{2+}_{(g)} + 6NH_{3(g)} \rightleftarrows M(NH_3)_6^{2+}{}_{(g)}$$

Details of his theoretical calculation can also be found in reference [8]. He showed that ligand field stabilization energies result in a characteristic pattern [9] of dissociation enthalpies of $[M(NH_3)_6]^{2+}_{(g)}$ cations as a function of the number of d electrons. It is interesting to note that a similar pattern is obtained when dissociation enthalpies of hexammine salt complexes in the solid phase, *i.e.*

$$M(NH_3)_6X_{2(s)} \rightleftarrows M(NH_3)_2X_{2(s)} + 4\ NH_{3(g)}$$

are plotted as a function of the number of d electrons, *cf.* Fig. 1. This suggests that the ligand field stabilization in $M(NH_3)_6X_{2(s)}$ has a dominant effect on the trend of the values of ΔH for their dissociation to the diammines.

More quantitative results can be obtained when studying the overall dissociation of the hexammines:

$$M(NH_3)_6X_{2(s)} \rightleftarrows MX_{2(s)} + 6NH_{3(g)}$$

The enthalpy changes for the dissociations can be calculated by adding the values listed in Table I. When these ΔH values are plotted as above, once more a characteristic transition metal pattern is obtained, *cf.* Fig. 2. The ΔH values for Fe^{2+}, Co^{2+} and Ni^{2+} are higher than the values obtained by a simple interpolation between values for Mn^{2+} (5 d electrons) and Zn^{2+} (10 d electrons). The differences between the observed values of ΔH and the straight line interpolation values are referred to as "experimental stabilization energies" and are listed in Table II. Notice that the ΔH values (Fig. 2) for zinc chloride and bromide are higher than for the manganese salts, consistently with the generally accepted trend. In addition, a linear extrapolation to Ca^{2+} (0 d electrons) yields for the dissociation of $Ca(NH_3)_6Br_{2(s)}$

TABLE II. Experimental and Calculated Values of the Stabilization Energies (*cf.* text) for Chlorides and Bromides of Divalent Iron, Cobalt and Nickel.

	Ligand Field Stabilization in $M(NH_3)_6^{2+}$ ions (kcal/mol) [8]	Spectroscopic Dq Values for MX_2 (cm^{-1}) [10]	Ligand Field Stabilization	Ligand Field Stabilization Energy in MX_2, kcal/mol	Calculated Stabilization Energy, kcal/mol	Experimental Stabilization Energy from Fig. 2, kcal/mol
$FeCl_2$	11	640–760	4 Dq	7.3–8.7	2–4	4
$FeBr_2$		590–680		6.7–7.7	3–4	5
$CoCl_2$	23	690–764	8 Dq	15.7–17.4	6–7	7
$CoBr_2$		625–697		14.2–15.9	7–9	7
$NiCl_2$	37	692–760	12 Dq	23.7–26.0	11–13	11
$NiBr_2$		680–740		23.2–25.3	12–14	11

($CaCl_2$ does not form a hexammine) a ΔH value of 84 kcal/mol as compared to the experimental value of 82 kcal/mol.

The ligand field stabilization in $M(NH_3)_6X_{2(s)}$ arises primarily from the interaction between cations and ammonia molecules, and can be assumed to be approximately equal to the ligand field stabilization energies as calculated for hexammine cations in the gas phase or in solutions [8]. On the other hand the ligand field stabilization in $MX_{2(s)}$ comes from the interaction between the cations and the halide anions. In this case the stabilization energies can be calculated from the spectroscopic measurements performed on the solid salts by using single crystal absorption or diffuse reflectance powder techniques. The values used in the present work are those listed in a recent review article by Rosseinsky and Dorrity [10]. Consequently, the stabilization energies, as observed from direct vapor pressure measurements, should be equal to the difference between the ligand field stabilization energies caused by interactions with ammonia molecules and halide anions, respectively. This conclusion is tested in Table II for chlorides and bromides of divalent iron, cobalt and nickel. The iodides are not included because spectroscopic data are incomplete.

The agreement between the experimental and calculated stabilization energies is very satisfactory. This validates the assumption of equal ligand field stabilization energies in $M(NH_3)_6^{2+}$ in the solid and gas phases and indicates a relatively weak interaction between metal cations and halide anions in the solid hexammine complexes. Finally, it should be mentioned that Cu^{2+} (9 d electrons) was not included in the present discussion because no reliable data were obtained either from vapor pressure or spectroscopic measurements. In this respect it should be remembered that the octahedral structure of copper(II) compounds is considerably distorted due to a strong Jahn–Teller effect.

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