

# Thermodynamics of Protonation of Aqueous Triethylenediamine

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Calorimetric determinations of heats of solution of solid triethylenediamine in water and in aqueous acid at 25° C. lead to the following:  $\text{NR}_3\text{NH}^+(\text{aq}) = \text{H}^+(\text{aq}) + \text{NR}_3\text{N}(\text{aq})$ ;  $\Delta H^\circ = 7.21$  kcal. per mole and  ${}^+\text{HNR}_3\text{NH}^+(\text{aq}) = 2\text{H}^+(\text{aq}) + \text{NRN}(\text{aq})$ ;  $\Delta H^\circ = 10.18$  kcal. per mole. Combination of these  $\Delta H^\circ$  values with  $\Delta G^\circ$  values from ionization constants leads to  $\Delta S^\circ = -15.2$  and  $\Delta S^\circ = -18.8$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> for the two ionization reactions indicated above.

AS PART of a larger program of thermodynamic investigation of basicities of various organic amines, calorimetric measurements have been made on triethylenediamine to obtain  $\Delta H^\circ$  values for ionization of the mono- and diprotonated species of this substance in aqueous solution. Triethylenediamine is of particular interest because of its chemical and structural relations to such compounds as ethylenediamine and triethylamine, and also because of recent interest in this compound as a ligand in complexes of transition elements.

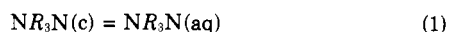
## EXPERIMENTAL

The calorimeter used is patterned after one described previously (3), except that a Leeds and Northrup Mueller G-2 bridge and HS galvanometer were used with a nickel resistance thermometer. Also, the thermometer and calibration heater were contained in a glass spiral filled with mineral oil. All of the work reported here was carried out with 950 ml. of aqueous solution in the calorimeter at 25.0° ± 0.2° C.

Triethylenediamine, given to us by the Houdry Co., was purified by either vacuum sublimation or recrystallization from diethyl ether and stored in a vacuum desiccator with P<sub>2</sub>O<sub>5</sub>. Samples prepared in these ways were thermochemically indistinguishable.

## RESULTS

Heats of solution of triethylenediamine, represented by NR<sub>3</sub>N, were determined in dilute NaOH solution to repress hydrolysis to NR<sub>3</sub>NH<sup>-</sup>. Small corrections (0.01 to 0.05 kcal. per mole to the observed heats were made with the hydrolysis constant and an approximate value for the heat of hydrolysis to yield the results given in Table I for the principal calorimetric reaction as in Equation 1.



A second series of measurements was made in which an excess of NR<sub>3</sub>N(c) was dissolved in dilute aqueous HCl. Part of the NR<sub>3</sub>N(c) dissolved according to Equation 1, and part reacted with H<sup>+</sup>(aq) as in Equation 2:



The experimental results are given in Table II along with the derived values of  $\Delta H_2$ . These derived values of  $\Delta H_2$  were calculated from the experimental heats by means of the equation

$$Q/n = f_1\Delta H_1 + f_2\Delta H_2 + f_4(\Delta H_2 + \Delta H_w) \quad (3)$$

in which  $f_1$ ,  $f_2$ , and  $f_4$  represent the fractions of the NR<sub>3</sub>N(c) that react according to Equations 1, 2, and 4.

Table I. Heats of Solution of NR<sub>3</sub>N(c) in Dilute Base

Moles NR <sub>3</sub> N/950 Ml. <sup>a</sup>	NaOH <sup>b</sup>	-ΔH <sub>1</sub> , Kcal. Per Mole
5.929	2.5	6.22
7.071	2.5	6.24
7.143	0.5	6.20
7.910	2.5	6.26
8.173	5.0	6.21

$$\Delta H_f^\ddagger = -6.23 \pm 0.03 \text{ kcal. per mole}$$

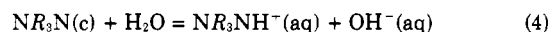
<sup>a</sup> × 10<sup>-3</sup>.

Table II. Heats of Solution of NR<sub>3</sub>N(c) in Dilute Acid

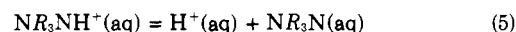
Moles HCl/950 Ml. <sup>a</sup>	n, Moles NR <sub>3</sub> N <sup>a</sup>	-Q/n, Kcal. Per Mole	-ΔH <sub>2</sub> , Kcal. Per Mole
2.315	7.128	8.64	13.46
2.315	3.356	11.27	13.42
3.762	6.862	10.17	13.42
3.810	3.812	13.43	13.43
4.703	5.576	12.26	13.38
5.173	5.505	12.97	13.40
8.935	9.126	13.25	13.40

$$\Delta H_f^\ddagger = -13.44 \pm 0.10 \text{ kcal. per mole}$$

<sup>a</sup> × 10<sup>-3</sup>.



$\Delta H_w$  represents the heat of ionization of water (1, 5). In calculating the  $f$  values,  $\text{p}K = 8.60$  (2) was used for the ionization Reaction 5 with activity coefficients estimated from the extended Debye equation.



The indicated uncertainty in  $\Delta H_f^\ddagger$  includes contributions from the uncertainties in values of  $f_1$ ,  $f_2$ ,  $f_4$ ,  $\Delta H_1$ , and  $\Delta H_w$  used in Equation 3, along with uncertainties in the measured  $Q$  values and the extrapolation by least squares to zero concentration.

Combination of our  $\Delta H_f^\ddagger$  and  $\Delta H_f^\ddagger$  values leads to  $\Delta H_f^\ddagger = +7.21 \pm 0.10$  kcal. per mole for the ionization reaction represented by Equation 5. From  $\text{p}K = 8.60$  one may calculate  $\Delta G_f^\ddagger = 11.74$  kcal. per mole and, thence, by combination with  $\Delta H_f^\ddagger$ , obtain  $\Delta S_f^\ddagger = -15.2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> for the ionization Reaction 5.

Heats of solution of NR<sub>3</sub>N(c) were also determined in acid of sufficient concentration that the principal solution reaction can be represented by Equation 6:

Table III. Heats of Solution of  $\text{NR}_3\text{N}(\text{c})$  in Excess Acid

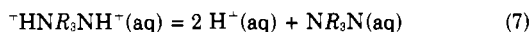
Moles HCl/950 Ml. <sup>a</sup>	n, Moles $\text{NR}_3\text{N}^b$	$-Q/n$ , Kcal. Per Mole	$-\Delta H_6$ Kcal. Per Mole
1.04	3.902	16.61	16.64
1.05	3.568	16.50	16.54
2.12	3.792	16.73	16.76
2.96	3.144	16.94	16.96
3.00	4.330	17.02	17.02
4.23	4.255	17.14	17.14
4.31	3.413	17.24	17.25
4.31	5.027	17.18	17.18

$\Delta H_6^{\circ} = -16.4 \pm 0.3$  kcal. per mole

<sup>a</sup>  $\times 10^{-1}$ . <sup>b</sup>  $\times 10^{-3}$ .



Although most of the  $\text{NR}_3\text{N}(\text{c})$  dissolved according to Equation 6, some dissolved according to Equation 2, so it was necessary to correct the observed heats ( $Q/n$  values in Table III) for this secondary process by means of  $\Delta H_2$  and extent of reaction calculated from  $\text{p}K = 11.55$  (2) for



The derived values of  $\Delta H_6$  are listed in Table III with the experimental data. The estimated uncertainty in  $\Delta H_6^{\circ}$  includes contributions from calculations and extrapolations, along with calorimetric uncertainties.

Combination of our  $\Delta H_6^{\circ}$  and  $\Delta H_2^{\circ}$  values leads to  $\Delta H_7^{\circ} = 10.2 \pm 0.3$  kcal. per mole for the ionization represented by Equation 7. Further combination of  $\Delta G_7^{\circ} = 15.77$  kcal.

per mole from  $\text{p}K = 11.55$  with  $\Delta H_7^{\circ}$  gives  $\Delta S_7^{\circ} = -18.8$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

There are no data in the literature that are directly comparable to the standard state thermodynamic data reported here. Paoletti, Stern, and Vacca (4) have made calorimetric measurements on triethylenediamine in 0.1M KCl as solvent and have reported results that lead to  $\Delta H_6 = 7.30$  kcal. per mole (the authors'  $\Delta H_6^{\circ} = 7.21$ ) and  $\Delta H_7 = 10.31$  kcal. per mole (the authors'  $\Delta H_7^{\circ} = 10.2$ ). The small differences between the present results and those of Paoletti, Stern, and Vacca (4) should probably be attributed mostly to differences in the solvent systems (water vs. 0.1M KCl) used in the two investigations.

#### ACKNOWLEDGMENT

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## Electromotive Force Measurements of the Free Energy of Formation of Molten Lead Chloride

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The e.m.f. of a formation cell of molten  $\text{PbCl}_2$  has been measured at 500° to 620° C. The data obtained may be represented by e.m.f. (volt) =  $1.2471 - 602 \times 10^{-6} (t - 550^\circ \text{C})$ ; agreement with some of the reported e.m.f. data is good. The estimation of the free energy of formation of molten  $\text{PbCl}_2$  given in thermochemical tables has not included values for molten  $\text{PbCl}_2$  obtained by direct e.m.f. methods. A new expression for the free energy of formation of molten  $\text{PbCl}_2$   $\Delta G_f = 86,630 + 94.90 T - 8.860 T \ln T$ , has been obtained by a best fit to the present data for the molten state and the previous data for the solid. These measurements lend support to the previous estimates and show that molten salt formation cells can be a reliable and valuable source of data on free energies of formation.

A LARGE NUMBER of e.m.f. measurements of the formation cell of molten  $\text{PbCl}_2$  have been reported in the literature. References to most of the previous work may be found in a paper by Delimarskii and Roms (2). The agreement among the published data has not been too good, except for the two recent investigations by Lantratov and Alabyshev (7) and Markov, Delimarskii, and Panchenko (8). Attempts to assess the e.m.f. data, however, are beyond the scope of this paper.

The thermodynamic properties for molten  $\text{PbCl}_2$  are estimated in the JANAF tables (4) by using the data

for the solid state, the values for the heat of fusion, the melting point, and a heat capacity value for the liquid. No measurements directly yielding the free energy of formation of the molten salt were included.

The data on pure molten  $\text{PbCl}_2$  presented here are part of a more extensive study of ternary systems consisting of  $\text{PbCl}_2$  and alkali metal chlorides. In order to evaluate the solution properties of the ternary systems, separate e.m.f. measurements have been made of the formation cell

