Berecki-Biedermann,[4] who found that the equilibrium constants for the reactions

$$Cu^{2+} + H_2O \rightleftarrows Cu[OH]^{1+} + H^+$$

and

$$2Cu^{2+} + 2H_2O \rightleftarrows Cu[OH]_2Cu^{2+} + 2H^+$$

correspond to pK values of 8.0 and 10.6, respectively. These results indicate the value of log K_d to be 5.4. Thus there is more extensive polymerization in the case of the aquated copper(II) ion than for the chelates of dipyridyl and *o*-phenanthroline, the ligands having the weakest coördinating tendencies of the ligands studied.

By the use of the equilibrium data of Table I, it is possible to determine species distribution as a function of total metal or ligand concentration and hydrogen ion concentration. A sample plot of $-\log[H^+]$ *vs.* the negative logarithm of the various species concentrations for 1.0×10^{-3} *M* Cu(II) and TMEN at 25° is shown in Fig. 3. Here it may be seen that the concentration of the dihydroxo chelate increases with increasing *p*H, mainly at the expense of the diaquo chelate. In this case, the concentrations of the monohydroxo chelate and dimer remain relatively constant in the $-\log[H^+]$ range 8–10. For many of the other copper(II) chelate systems studied, the concentrations of the dimer and of monohydroxo chelate reach a maximum at $-\log[H^+]$ 8–8.5 and the contributions of these species fall off sharply on either side of this region.

Thermodynamic constants calculated from the data of Table I for reactions 2, 4 and 5 are listed in Tables III and IV. Considerable deviations were observed in some cases because of the lack of accuracy of values of $K_{M[OH]A}$ for chelates of dipyridyl and *o*-phenanthroline (which contain only a small proportion of monohydroxo species in equilibrium with the dimer) and of values of $K_{(M[OH]A)_2}$ for chelates of HEN and 2-HEN (which contain only a small proportion of dimer in equilibrium with the monohydroxo species). Since values of log K_d are determined from the differences of two large quantities according to the equation

$$\log K_d = 2pK_{M[OH]A} - pK_{(M[OH]A)_2}$$

they may be considered to be reliable only to the first decimal place and hence have been rounded off in Table I.

The small, almost negligible values of ΔH^0 in Table III and the relatively large values of ΔS^0 in Table IV indicate that the driving force in the formation of the dimer from the monohydroxo chelate compound is primarily an entropy effect. As is indicated in the equation for this reaction illustrated above, the increase in entropy with dimerization probably is due for the most part to the negative entropy contribution of the coördinated water molecules in the hydroxo chelate, and the entropy increase which results when the restraint on these coördinated water molecules is removed as they are released to the solvent when dimerization occurs.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

A Thermodynamic Study of Some Metal–Amine Coördination Compounds[1]

BY G. H. MCINTYRE, JR., B. P. BLOCK AND W. CONARD FERNELIUS

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A method is presented by which activity formation constants and free energy, enthalpy and entropy changes can be obtained for the coördination of amines to metal ions. Values for these quantities from 10 to 40° in 10° intervals are presented for the reaction of nickel(II) ion with ethylenediamine (en) and N-methylethylenediamine (Meen); copper(II) ion with en, Meen, diethylenetriamine (dien), 4-amino-2-thiabutane (Maes) and 1,8-diamino-3,6-dithiaoctane (diames); and zinc ion with en, Meen and dien. Values for the proton–amine formation constants for these amines also are given. Relations of the enthalpy changes for the different ligand–metal associations are discussed.

Introduction

During the past dozen years many measurements of formation constants have been made.[2]

While the data are very useful, they would be vastly more so if (1) they included values for the heats of reaction as well as free energies and (2) the formation constants were true thermodynamic values instead of *molarity quotients*[3] valid only at a definite ionic strength. The first limitation has been stressed by Bjerrum[4] and by Burkin.[5] The latter points out the need for ΔH values in determining bond strengths. A few investigators have reported calorimetrically measured heats of reaction.[6–9]

Several others have made equilibrium measurements over a limited range of temperatures (0–50° as a maximum) and used these data to calculate ΔH.[10–19] Still others have been concerned with ob-

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taining partial molal entropies of complex ions[20] and with the interpretation of the entropy effect in the formation of complex ions.[21,22]

It has been the practice of most investigators to determine a so-called concentration formation constant for the stepwise coördination reaction. This constant is determined in a system containing a large excess of neutral salt, 0.1 to 1.0 *M*, to hold activity coefficients constant and *p*H measurements, in general, have been converted directly to hydrogen ion concentration disregarding the effect of the activity coefficient on the value of the hydrogen ion concentration. Carini and Martell[23] have pointed out that the constants so obtained are combination constants containing both concentration and activity terms. Schwarzenbach,[24] one of the first to use 0.1 *M* neutral salt solutions, has attempted to be consistent by using the limiting form of the Debye–Hückel equation to convert hydrogen ion activities (*p*H) to concentrations.

In order to be able to determine activity formation constants from which more reliable values for the thermodynamic quantities could be obtained, dilute solutions with no added neutral salt were used in this investigation. With sufficiently dilute solutions the Debye–Hückel equation can be used to calculate activity coefficients. Thus it becomes as easy to obtain true constants as the less valuable molarity quotients.

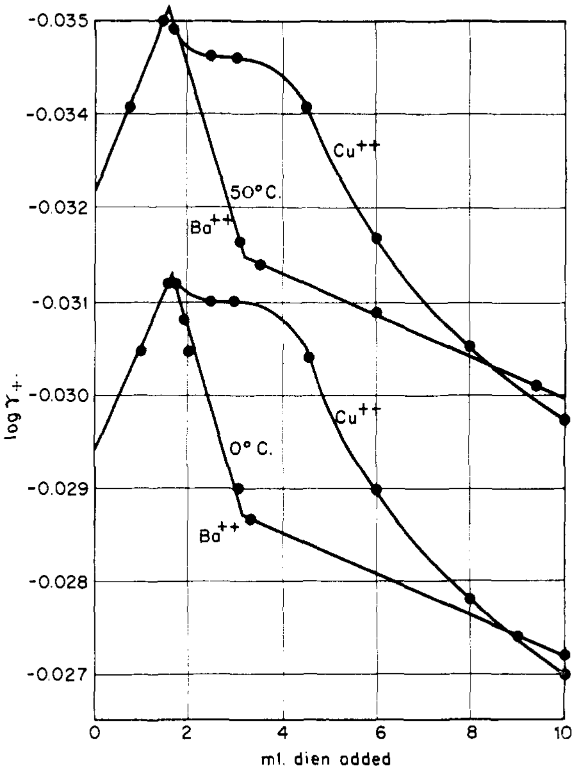

Fig. 1.—Change in log γ_+ on addition of diethylenetriamine.

Preliminary Considerations

In order to minimize the effect of anion coördination, perchloric acid and metal perchlorate salts were used. It was assumed that the coördination reaction takes place between the aquated metal ion and the amine and not between some anion coördination species and the amine. The pertinent equations are (*Q* refers to a concentration constant and *K* to an activity constant)

$$\mathrm{MA}_{n-1}^{++}\,(\mathrm{aq}) + \mathrm{A(aq)} = \mathrm{MA}_n^{++}\,(\mathrm{aq}) + p\mathrm{H_2O} \qquad n = 1 \text{ to } 3 \quad (1)$$

$$\mathrm{AH}_{m-1}^{(m-1)+}\,(\mathrm{aq}) + \mathrm{H^+(aq)} = \mathrm{AH}_m^{m+}\,(\mathrm{aq}) + m\mathrm{H_2O} \qquad m = 1 \text{ to } 3 \quad (2)$$

$$Q_n = [\mathrm{MA}_n^{++}]/[\mathrm{MA}_{n-1}^{++}][\mathrm{A}] \qquad n = 1 \text{ to } 3 \quad (3\text{–}5)$$

$$Q_m^{\mathrm{H}} = [\mathrm{AH}_m^{m+}]/[\mathrm{AH}_{m-1}^{(m-1)+}][\mathrm{H}^+] \qquad n = 1 \text{ to } 3 \quad (6\text{–}8)$$

If it is assumed that the activity coefficient is unity for a neutral species and is the same for each charge type regardless of the character of the specific ion, equations 9–11 are valid

$$K_n = Q_n(\gamma_{\mathrm{MA}_n^{++}}/\gamma_{\mathrm{MA}_{n-1}^{++}}\gamma_{\mathrm{A}}) \approx Q_n \qquad (9\text{–}11)$$

Inasmuch as the charge type changes for each proton added to the amine, the activity dissociation constants will not be equal to the concentration constants for the amines. The additional assumption that the relationship of the activity coefficients of species with different charges is given by the Debye–Hückel equation leads to equations 12–14

$$K_1^{\mathrm{H}} = Q_1^{\mathrm{H}}\,(\gamma_{\mathrm{AH^+}}/\gamma_{\mathrm{A}}\gamma_{\mathrm{H^+}}) \approx Q_1^{\mathrm{H}} \qquad (12)$$

$$K_2^{\mathrm{H}} = Q_2^{\mathrm{H}}(\gamma_{\mathrm{AH_2^{++}}}/\gamma_{\mathrm{AH^+}}\gamma_{\mathrm{H^+}}) \approx Q_2^{\mathrm{H}}(\gamma^4_+/\gamma^2_+) = Q_2^{\mathrm{H}}\gamma^2_+ \qquad (13)$$

$$K_3^{\mathrm{H}} = Q_3^{\mathrm{H}}(\gamma_{\mathrm{AH_3^{3+}}}/\gamma_{\mathrm{AH_2^+}}\gamma_{\mathrm{H^+}}) \approx Q_3^{\mathrm{H}}(\gamma^9_+/\gamma^4_+\gamma_+) = Q_3^{\mathrm{H}}\gamma^4_+ \qquad (14)$$

At the concentrations used log $\gamma_+ = -0.03 \pm 0.005$ throughout the titration regardless (1) of the change in concentrations caused by dilution on addition of the amine or (2) of change in concentration of different charge types of the protonated amine. An example of the degree and direction of the change in log γ_+ on addition of diethylenetriamine is given in Fig. 1. As this shows the largest change in charge type (0 to 3+) of any amine studied, there will be associated with it the largest change in log γ_+ during a titration.

The method used to determine these constants from experimental data is that reported in a previous paper.[25] Standard equations were used to calculate the desired thermodynamic quantities.

Experimental

Procedure.—The general procedure involved the titration of 100 ml. of solution, 0.00100 *M* in metal ion and 0.00201 to 0.00203 *M* in acid, with 10 ml. of 0.04 to 0.1 *M* amine under nitrogen at 10, 20, 30 and 40°. A Beckman Model G *p*H meter equipped with a saturated calomel electrode and a Beckman Model E No. 1190-80 glass electrode was used to follow the titrations. From 45 min. to 1 hr. was

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required per titration. Measurements were also made at 0 and 50° and the *p*H values calculated by means of the conversion formula supplied with the instrument. When the log *K* values calculated from these values were plotted together with the values from 10–40° against $1/T$, the values at 0° were consistently above the line passing through the points for 10–40° and the values at 50° consistently below this line.

Reagents.—All metal perchlorate salts used were G. F. Smith Chemical Company reagent grade. The stock solutions were standardized by electrodeposition on platinum mesh cathodes and diluted to 0.00200 *M*. The 0.004 *M* $HClO_4$ was prepared by diluting a stock solution which had been standardized with Na_2CO_3 using phenolphthalein-brom cresol as the mixed indicator.

Carbide and Carbon Chemical Company technical grade ethylenediamine was purified by distillation through a 24-inch glass column packed with glass helices. The fraction boiling 118–119° at atmospheric pressure corresponding to the monohydrate was taken. The N-methylethylenediamine was obtained from Dr. F. Basolo of Northwestern University and was distilled through a 6-inch Vigreux column. The fraction boiling at 111° (723 mm.) was taken. Basolo reports the boiling point to be 114–115° at one atmosphere pressure.[12] Technical grade Eastman Kodak diethylenetriamine was distilled through a 6-inch glass column packed with $^3/_{32}$-inch glass beads. The fraction boiling 96–98° at 20–25 mm. was taken.

The methyl 2-aminoethyl sulfide was prepared by combining ethyleneimine with methanethiol in an absolute ethanol medium and distilling off the unreacted reagents and then the product.[26] The fraction boiling 70–71° at 47–50 mm. was taken. The benzoyl derivative melted 57–58°; Schneider[27] reports 57°. The 1,8-diamino-3,6-dithiaoctane was obtained from samples of the dihydrochloride made in this Laboratory by E. Gonick and L. S. Lazar: m.p. of the dihydrochloride 186–188°; Dwyer and Lions[28] report 186–188°. The free amine was recovered by adding slowly a slurry of the dihydrochloride in a minimum of water to a cooled flask containing a large excess of solid KOH and anhydrous ether. The ether was separated and the residue extracted with more anhydrous ether. Most of the ether was boiled off and the free amine then crystallized on cooling; m.p. 39–40°; Dwyer and Lions[19] report 41–43°.

All amines were stored in an air-free atmosphere because of their high reactivity with the carbon dioxide of the air. Standardization of the amine solutions was accomplished by obtaining the end-points directly from the *p*H titrations made to determine the proton–amine formation constants.

Results

Values calculated for log K_n, ΔF_n, ΔH_n and ΔS_n are given in Table I. The ± values are the 95% confidence intervals based on three or more calculations for each constant. The ΔH values were calculated by a standard least-squares method[29] from the slopes of the best straight lines for the log K_n *vs.* $1/T$ systems.

Constants for nickel(II) coördinating with the thiamines and with diethylenetriamine were not obtained due to the extreme slowness with which the reactions reached equilibrium. There was precipitation in the systems involving zinc(II) and the thiamines which made use of the formation function impossible.

Discussion

Because the systems investigated are inherently basic, the possibility of hydroxide formation must be considered. Martell and co-workers[30] have made some estimates of the first hydroxide formation constants for several metal ions, among them those used in this study. These constants are 10^{-7} to 10^{-10} in order of magnitude, which indicates that in this study hydroxide formation can be ignored because the metals coördinated in acidic enough regions to make such species unimportant in the cases for which constants were calculated. The formation of hydroxide species also enters into the consideration of the reaction of copper(II) with diethylenetriamine. Prue and Schwarzenbach[31] report a constant for the reaction of $Cu(OH)^+$ with diethylenetriamine which is of the same order of magnitude as the second constant for copper(II) with diethylenetriamine reported in this work. However, there is a report based on polarographic work that $Cu(dien)_2^{++}$ exists in solutions containing 40–2000 fold excess diethylenetriamine.[32] Such an excess was not present in this work, so the reported second constant may not be real. A reasonable alternative is that the first molecule of diethylenetriamine coördinated fills three positions on the copper while a water molecule fills the fourth. The latter then loses a proton as the *p*H of the medium increases, giving rise to Schwarzenbach's species. Our data, as will be shown later, appear to support association with a second amine molecule.

The ΔH values obtained show, in general, trends that might be expected. Very little difference in the ΔH_1 values for the formation of protonated amines was observed. If ΔH is considered to be a measure of bond strength, it is evident that the proton is bound to the nitrogen with about the same strength in all of the cases studied. In general ΔH_2 is a little smaller than ΔH_1 for the protonated amines. This weakening of the second proton-to-nitrogen bond is probably the result of coulombic repulsion between the positively charged protons. The value of ΔH_3 for diethylenetriamine is substantially lower than the values for ΔH_1 and ΔH_2, indicating that the third proton is not held as strongly as the other two. Again coulombic repulsion probably is responsible for the weakening.

The ΔH values obtained for the metal–amine coordination varied a little going from ethylenediamine to N-methylethylenediamine, but not appreciably except for ΔH_3 for nickel. This indicates that the bonds are of about the same strength for both amines and not appreciably affected by the N-methyl substitution except in the trisamine nickel(II) species. In the latter there appears to be steric weakening of the bonds to the third amine molecule. This is supported by attempts to construct the ion from Fisher–Hirschfelder–Taylor models. The model so constructed is such that the third methyl-substituted nitrogen cannot be firmly fastened to the central atom, indicating substantial steric hindrance toward addition of the third ligand.

The value of ΔH_1 for diethylenetriamine with copper(II) is about 50% greater than that for copper(II) with the diamines, which corresponds to three copper-to-nitrogen bonds in the former and

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TABLE I

VALUES FOR THE THERMODYNAMIC QUANTITIES LOG K_n, $-\Delta F_n$, $-\Delta H_n$ AND ΔS_n INVOLVED IN THE REACTION AT 10, 20, 30 AND 40° OF SEVERAL BIVALENT METAL IONS WITH VARIOUS POLYAMINES

t, °C.	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Ni^{++}
					1,2-Ethanediamine					
		log K_1				log K_2			log K_3	
10	10.39 ± 0.01	11.01 ± 0.03	7.74 ± 0.05	5.85 ± 0.01	7.28 ± 0.04	9.57 ± 0.02	6.44 ± 0.04	5.13 ± 0.03		4.67 ± 0.02
20	10.09 ± .01	10.67 ± .04	7.52 ± .06	5.77 ± .06	7.00 ± .02	9.23 ± .05	6.32 ± .06	5.06 ± .02		4.49 ± .05
30	9.81 ± .01	10.36 ± .03	7.27 ± .02	5.55 ± .09	6.79 ± .03	8.93 ± .01	6.11 ± .03	4.89 ± .05		4.20 ± .03
40	9.53 ± .01	10.06 ± .02	7.04 ± .03	5.51 ± .14	6.50 ± .02	8.66 ± .04	5.89 ± .03	4.76 ± .06		4.05 ± .51
		$-\Delta F_1$ (kcal./mole)				$-F_2$ (kcal./mole)			$-\Delta F$ (kcal./mole)	
10	13.5	14.3	10.0	7.6	9.4	12.4	8.3	6.6		6.1
20	13.5	14.3	10.1	7.7	9.4	12.4	8.5	6.8		6.0
30	13.6	14.4	10.1	7.7	9.4	12.4	8.5	6.8		5.8
40	13.7	14.4	10.1	7.9	9.3	12.4	8.4	6.8		5.8
		$-H_1$ (kcal./mole)				$-\Delta H_2$ (kcal./mole)			$-\Delta H_3$ (kcal./mole)	
10–40	11.5	12.8	9.5	5.0	10.3	12.3	7.5	5.2		8.7
		$-\Delta S_1$ (cal./mole deg.)				$-\Delta S_2$ (cal./mole deg.)			$-\Delta S_3$ (cal./mole deg.)	
10	7	5	2	9	−3	0	3	5		−9
20	7	5	2	9	−3	0	3	5		−9
30	7	5	2	9	−3	0	3	5		−10
40	7	5	2	9	−3	0	3	5		−9
					N-Methylethylenediamine					
		log K_1				log K_2			log K_3	
10	10.44 ± 0.00	10.64 ± 0.03	7.40 ± 0.03	5.47 ± 0.06	7.13 ± 0.02	9.01 ± 0.16	5.75 ± 0.07	4.49 ± 0.09		2.78 ± 0.10
20	10.15 ± .00	10.30 ± .03	7.17 ± .11	5.39 ± .06	6.86 ± .02	8.60 ± .04	5.56 ± 0.08	4.36 ± .16		2.72 ± .48
30	9.90 ± .02	10.06 ± .04	6.97 ± .03	5.29 ± .13	6.63 ± .02	8.38 ± .04	5.40 ± .04	4.23 ± .22		2.68 ± .66
40	9.61 ± .02	9.72 ± .04	6.70 ± .02	5.08 ± .09	6.38 ± .02	8.06 ± .05	5.16 ± .05	4.26 ± .03		2.45 ± 1.07
		$-\Delta F_1$ (kcal./mole)				$-\Delta F_2$ (kcal./mole)			$-\Delta F_3$ (kcal./mole)	
10	13.5	13.8	9.6	7.1	9.2	11.7	7.5	5.8		3.6
20	13.6	13.8	9.5	7.2	9.2	11.5	7.5	5.9		3.7
30	13.7	14.0	9.7	7.3	9.2	11.6	7.5	5.9		3.7
40	13.8	13.9	9.6	7.3	9.1	11.6	7.4	6.1		3.5
		$-\Delta H_1$ (kcal./mole)				$-\Delta H_2$ (kcal./mole)			$-\Delta H_3$ (kcal./mole)	
10–40	11.1	12.2	9.3	5.1	10.1	12.5	7.8	3.4		4.1
		$-\Delta S_1$ (cal./mole deg.)				$-\Delta S_2$ (cal./mole deg.)			$-\Delta S_3$ (kcal./mole deg.)	
10	8	6	1	1	−3	−3	−1	1		−2
20	9	5	1	1	−3	−3	−1	1		−1
30	9	6	1	1	−3	−3	−1	1		−1
40	9	5	1	1	−3	−3	−1	1		−2

TABLE I (*Continued*)

t, °C.	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Ni^{++}
					Diethylenetriamine					
		log K_1				log K_2			log K_3	
10	10.22 ± 0.02	16.41 ± 0.02		8.84 ± 0.02	9.20 ± 0.03	5.00 ± 0.10			4.01 ± 0.12	
20	9.94 ± .01	15.84 ± .03		8.79 ± .03	8.88 ± .03	4.79 ± .10			3.70 ± .12	
30	9.66 ± .02	15.43 ± .08		8.57 ± .07	8.59 ± .02	4.68 ± .08			3.58 ± .06	
40	9.40 ± .03	15.00 ± .05		8.38 ± .02	8.29 ± .03	4.52 ± .10			3.46 ± .02	
		$-\Delta F_1$ (kcal./mole)				$-\Delta F_2$ (kcal./mole)			$-\Delta F_3$ (kcal./mole)	
10	13.2	21.3		11.5	11.9	6.5			5.2	
20	13.3	21.3		11.8	11.9	6.4			5.0	
30	13.4	21.4		11.9	11.9	6.5			5.0	
40	13.5	21.5		12.0	11.9	6.5			5.0	
		$-\Delta H_1$ (kcal./mole)				$-\Delta H_2$ (kcal./mole)			$-\Delta H_3$ (cal./mole)	
10–40	11.1	18.9		6.4	12.25	6.3			7.6	
		$-\Delta S_1$ (cal./mole deg.)				$-\Delta S_2$ (cal./mole deg.)			$-\Delta S_3$ (cal./mole deg.)	
10	8	8		18	−1	1			−8	
20	8	8		18	−1	1			−9	
30	8	8		18	−1	1			−9	
40	8	8		18	−1	1			−8	
					4-Amino-2-thiabutane					
		log K_1				log K_2				
10	9.80 ± 0.01	5.74 ± 0.07				5.34 ± 0.04				
20	9.49 ± .03	5.61 ± .12				5.20 ± .06				
30	9.18 ± .01	5.41 ± .03				5.13 ± .03				
40	8.89 ± .01	5.21 ± .07				4.98 ± .05				
		$-\Delta F_1$ (kcal./mole)				$-\Delta F_2$ (kcal./mole)				
10	12.7	7.4				6.9				
20	12.7	7.5				7.0				
30	12.7	7.5				7.1				
40	12.7	7.5				7.1				
		$-\Delta H_1$ (kcal./mole)				$-\Delta H_2$ (kcal./mole)				
10–40	12.3	7.2				4.7				
		$-\Delta S_1$ (cal./mole deg.)				$-\Delta S_2$ (cal./mole deg.)				
10	1	1				8				
20	1	1				8				
30	1	1				8				
40	1	1				8				

Table I (*Continued*)

t, °C.	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Cu^{++}	Ni^{++}	Zn^{++}	H^+	Ni^{++}
1,8-Diamino-3,6-dithiaoctane										
		log K_1				log K_2				
10	9.93 ± 0.01	11.16 ± 0.01			9.00 ± 0.03					
20	9.62 ± .01	10.80 ± .03			8.69 ± .03					
30	9.31 ± .02	10.43 ± .02			8.43 ± .03					
40	9.03 ± .01	10.01 ± .04			8.08 ± .03					
		$-\Delta F_1$ (kcal./mole)				$-\Delta_2$ (kcal./mole)				
10	12.9	14.5			11.7					
20	12.9	14.5			11.7					
30	12.9	14.5			11.7					
40	12.9	14.4			11.6					
		$-\Delta H_1$ (kcal./mole)				$-\Delta H_2$ (kcal./mole)				
10–40	12.2	15.5			12.2					
		$-\Delta S_1$ (cal./mole deg.)				$-\Delta S_2$ (cal./mole deg.)				
10	2	−4			−2					
20	2	−3			−2					
30	2	−3			−2					
40	2	−4			−2					

two in the latter, in each case the contribution of a single copper-to-nitrogen bond being about −6 kcal. Since ΔH_2 for diethylenetriamine has about this single copper-to-nitrogen value, we have support for the assumption that a fourth such bond has been formed. The same pattern does not hold for zinc(II), although ΔH_1 is somewhat larger for the triamine than for the diamines.

The values of ΔH for the thiamine–copper(II) species correspond fairly well to values calculated assuming −6 kcal. per copper-to-nitrogen bond. This indicates that the sulfur-to-copper bonds do not make a substantial contribution to the ΔH values. Calculations of the $\bar{n}$ values in the copper(II)–4-amino-2-thiabutane system indicate the possibility of four amines coördinated per copper(II). However, such coördination is very weak, and values for the third and fourth constants could not be calculated. In any case the nitrogen-to-copper bond is definitely stronger than the sulfur-to-copper bond if the ΔH values are taken as the criterion.

For the most part the ΔS values are not very significant because they have been calculated from the difference between two numbers of about the same magnitude. In these systems, then, the stability of the species formed is primarily a result of the greater strength of the metal-to-nitrogen bonds compared to the metal-to-oxygen bonds in the aquated species. This is in marked contrast to the typical ethylenediaminetetraacetic acid complexes in which the stability is primarily due to a favorable entropy change.[7,18]

In those instances for which there is a substantial value indicated for ΔS the ΔH values appear to be out of line. Since the ΔH value is employed to calculate ΔS, any errors in the former will be reflected in the latter.

One purpose of this investigation was to determine whether reasonably reliable values for ΔH could be determined using the titration procedure in the absence of the neutral salts generally employed in the Bjerrum-type determinations. Comparison of the ΔH values reported for the copper(II)–ethylenediamine system with those determined calorimetrically by Davies, Singer and Staveley[8] and Poulsen and Bjerrum[9] shows agreement well within experimental error. There is not quite as good agreement with the calorimetric values of Basolo and Murmann[15] which are somewhat lower than the others. The values determined by Spike and Parry[17] and by Cotton and Harris[19] by titration in neutral salt media are higher and lower, respectively, than the results reported in this study. The agreement with nickel and ethylenediamine is not as satisfying, but in this case the agreement among the calorimetric determinations is not as good either.[8,9,15] The cause for the poorer agreement in this case may well be the sluggishness with which equilibrium is attained. It does appear that the technique used in this study will give values for ΔH that agree quite well with calorimetric values in favorable situations, *i.e.*, systems in which equilibrium is attained rapidly.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC.]

Complexing of Tantalum Pentachloride by Chloride Ion in Fused Salt Media[1]

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The interaction of $TaCl_5$ with NaCl in their solutions in molten $NaFeCl_4$ was studied at 300 and 400°. The $TaCl_5$ activity, as measured by its vapor pressure, was found to vary with $TaCl_5$ and NaCl concentrations in a manner consistent with the equilibrium reaction $TaCl_5 + Cl^- \rightleftarrows TaCl_6^-$. The corresponding equilibrium constants were found to be log $X_{TaCl_6^-}/a_{TaCl_5}X_{Cl^-} = 2.4 \pm 0.3$ at 300° and 1.7 ± 0.3 at 400°.

The first observation of the $TaCl_6^-$ anion appears to be that of Gutmann,[2] who found the compound $[Pyr{\cdot}POCl_2^+][TaCl_6^-]$ during an investigation of the $POCl_3$ solvent system. More recently, Morozov and his colleagues have studied the phase diagrams of the NaCl–$NbCl_5$ system[3a] and the NaCl–$TaCl_5$ system[3b] and have reported the solid compounds $NaNbCl_6$ and $NaTaCl_6$. These workers have estimated the free energies of formation of these compounds from the $NbCl_5$ and $TaCl_5$ vapor pressures above solid, powdered mixtures of NaCl + $NaNbCl_6$ and NaCl + $NaTaCl_6$, respectively.[4]

In the work described below, the reaction between tantalum pentachloride and sodium chloride in a molten salt solution

$$TaCl_5 + Cl^- = TaCl_6^- \qquad (1)$$

has been studied by measurement of the equilibrium $TaCl_5$ activity as a function of gross $TaCl_5$ and NaCl concentrations. The salt $NaFeCl_4$, was chosen as the solvent for this system because it is low melting, essentially inert to the reactants and dissolves both $TaCl_5$ and NaCl.

Experimental

The vapor pressure of tantalum pentachloride above a mixture containing known quantities of NaCl, $FeCl_3$ and $TaCl_5$ was measured as a function of temperature. The salt mixture was contained in a sealed, evacuated, Pyrex reaction bulb to which was attached a sickle gauge for measurement of the internal pressure. Both bulb and gauge were positioned inside a tube furnace, which was constructed of copper to minimize temperature gradients. The melt was stirred until equilibrium was reached, at which time the bulb temperature and pressure were observed.

Ingredients.—Sodium chloride (Mallinkrodt, Analytical Reagent) was weighed into the Pyrex reaction bulb and dried overnight at 480° under a stream of HCl.

Iron wire (J. T. Baker Analyzed Reagent) was placed in a silica glass side arm attached by a graded seal to the Pyrex reaction bulb. The iron was burned in a stream of chlorine (Matheson Company, Oxygen Free grade), and the ferric chloride product was quantitatively sublimed into the bulb.

Tantalum powder (Fansteel Metallurgical Company, 120–325 mesh) was placed in the silica side arm with the iron wire, chlorinated, and the pentachloride sublimed into the reaction bulb. Traces of iron or tantalum oxides remaining after the sublimation of the chlorides were chlorinated into the bulb by treatment with phosgene. The chlorination gases were dried with $Mg(ClO_4)_2$.

After having been charged with the NaCl, $FeCl_3$ and $TaCl_5$, the reaction bulb was evacuated, backfilled with Cl_2 at approximately 60 mm. pressure, and both side arms fused shut and removed. The bulb and sickle gauge assembly was then placed in the tube furnace and connected to a pressure measuring manifold.

Temperature and Pressure.—The temperature of the molten salt mixture was measured with two chromel-alumel thermocouples held in contact with the surface of the reaction bulb by strips of glass tape. The salt melt was stirred while being held at a constant temperature for approximately 1 hr. before a final pressure–temperature reading was taken. Temperature fluctuations within the furnace due to line voltage changes were eliminated by use of a constant voltage transformer in the power source.

The use of duplicate thermocouples, the stirring of the salt melt and the elimination of sharp temperature gradients in the furnace should reduce error in the measured salt temperatures. This error has been estimated to be less than ±3°.

Pressure measurements were made over a zero to two atmosphere range by the sickle gauge between the reaction bulb and the pressure manifold. The observed pressure was that manifold pressure required to return the gauge pointer to the null position. In the majority of the runs, the gauge sensitivity was greater than ±2 mm.; for the runs made at high $TaCl_5$ concentrations, where the pressures were higher, sturdier gauges of about ±8 mm. sensitivity were used.

Before data were taken, the melt was held at 400° (or the maximum temperature allowed by the pressure limitations of the system) for several hours to bring about complete solution of the NaCl in the solvent. When this precaution was taken, the observed pressures equilibrated rapidly, showed no temperature–pressure hysteresis and underwent no drift with time.

Calculation of $TaCl_5$ Pressure.—The experimental data obtained from any one run consist of a series of observations of total gas pressure inside the reaction bulb as a function of temperature. The $TaCl_5$ pressure at a given temperature is the difference between the total pressure observed at this temperature and the pressure exerted by the Cl_2 initially present in the bulb, *i.e.*, $P_{TaCl_5} = P_{Total} - P_{Cl_2}$. The Cl_2 pressure can be observed directly at low temperatures where $TaCl_5$ pressure is negligible, and P_{Cl_2} at higher temperatures was calculated from the ideal gas law.

Figure 1 shows the data from a typical run and illustrates this treatment. The solid line passes through the experimental points; the dotted line represents the chlorine gas pressure as calculated from a measurement at 25°; the dashed line represents the difference between these two pressures and accordingly is taken as the $TaCl_5$ pressure.

For those runs made at low $TaCl_5$ concentrations, the uncertainty in P_{Cl_2} is a major source of uncertainty in the values calculated for P_{TaCl_5} at 300°, since under these condi-

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[1] Presented at the 11th Summer Symposium of the Division of Analytical Chemistry of the American Chemical Society, Schenectady, N. Y., 6/20/58.

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[4] I. S. Morozov and A. T. Simonich, *ibid.*, **2**, 1907 (1957).