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"THE THERMODYNAMICS OF COPPER(II) AND NICKEL(II)-  
DIAMINE COMPLEX FORMATION IN AQUEOUS SOLUTION"

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### ABSTRACT

This work describes the accurate measurement of the thermodynamic functions  $\Delta G^\circ$  and  $\Delta H^\circ$  for the step-wise coordination equilibria between each of the ions  $H^+$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and a series of  $C_1$ -substituted 1,2-diaminoethanes in aqueous solution. The study involved

- (a) the construction of a sensitive constant temperature environment calorimeter for measuring the enthalpy changes in the complex-formation reactions,
- (b) the rigorous calibration of an electrode system, incorporating a glass electrode, for the direct potentiometric measurement of equilibrium hydrogen ion concentrations in the solutions containing complex ions.

The thermodynamic functions  $\Delta G^\circ$  and  $\Delta H^\circ$  led to accurate  $\Delta S^\circ$  values for the step-wise complex-formation reactions.

The thesis considers the contribution of the entropy of ligation to the stability of complex ions. The molar entropies of the complex ions have been calculated and their values considered with respect to the coordination number and the possible structure, degree of hydration and steric properties of the ions.

List of Abbreviations

en	ethylenediamine	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
pn	1-methyl 1,2-diaminoethane	$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$
eten	1-ethyl 1,2-diaminoethane	$\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$
i-bn	iso-butylenediamine, (1-dimethyl 1,2-diaminoethane)	$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{NH}_2$
phenen	1-phenyl 1,2-diaminoethane	$\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$
dien	diethylenetriamine, (2,2'-diaminodiethylamine)	$\text{NH}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$
trien	triethylenetetramine, (NN'-di-(2-aminoethyl) 1,2-diaminoethane)	$(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2-)_2$
tren	2,2',2''-triaminotriethylamine	$\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$
tetrameen	1,2-tetramethyl 1,2-diaminoethane	$((\text{CH}_3)_2\text{C}(\text{NH}_2)-)_2$
m-stien	meso-stilbenediamine, (meso-1,2-diphenyl 1,2-diaminoethane)	$\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}_2)\text{CH}(\text{NH}_2)\cdot\text{C}_6\text{H}_5$
bn	symm-butylenediamine, (1,2-dimethyl 1,2-diaminoethane)	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NH}_2$
1,3-pn	1,3-diaminopropane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
(2,2')1,3-pn	2,2'-dimethyl 1,3-diaminopropane	$\text{NH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$
2,2'-dipyr	2,2'-dipyridyl	
1,10-phen	1,10-phenanthroline	
edta	ethylenediamine NNN'N' tetraacetic acid	$(-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2)_2$

## CHAPTER ONE

### INTRODUCTION

While reading Rossotti's article "Thermodynamics of Metal Ion Complex Formation in Solution",<sup>31</sup> the author was impressed by the lack of accurate thermodynamic data ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) for the formation of complex ions in solution. Rossotti wrote "Interpretative speculation has outstripped the precision and quantity of data available, and considerable consolidation is required."

Accurate data is essential for the testing of present theories and the postulation of new and more valid ones concerning the energetics of complex formation. Such important theories as 'Crystal Field' and 'Molecular Orbital' theories as applied to complexes are concerned with small energy differences, and thus require accurate data for their vindication. The entropy changes in like complexing reactions (with similar ions and similar ligands) were once assumed small and equal, but with the accumulation of more accurate data the entropy change is now known to give an indication of the structure, coordination number, degree of hydration and steric properties of complex ions and molecules.

Since the introduction of new experimental techniques by Bjerrum in 1941, an increasing flood of thermodynamic data for complexes has been published. However, most of it

has been too inaccurate to be of theoretical significance. This inaccuracy has not been due to a lack of suitable reliable apparatus. It probably stems from the requirements of time and patience necessary to obtain accurate results.

Ethylenediamine ( $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ ) is an important chelating agent and a simple analogue of many more complex ligands. Other workers have determined the thermodynamic properties for some complexes of the N-alkyl,<sup>56,57</sup> NN'-dialkyl,<sup>35,58</sup> and  $\text{C}_1\text{C}_2$ -dialkyl and diaryl<sup>3</sup> ethylenediamines. For this thesis a thermodynamic study was made of the complex formation reactions between a series of  $\text{C}_1$ -alkyl ethylenediamines  $\text{NH}_2\text{CH}(\text{R})\text{CH}_2\text{NH}_2$ , and the divalent Ni and Cu ions in aqueous solution. The group R was varied to permit a study of the effects of the inductive phenomenon in a ligand and of the bulk of a ligand upon the thermodynamic properties for transition metal coordination compounds in aqueous solution. Because of the lack of fore-knowledge of these effects, it was not possible to a priori predict those amines which could have given the most valuable information. The ligands used had  $\text{R} = \text{CH}_3^-$ ,  $\text{CH}_3\cdot\text{CH}_2^-$ ,  $\text{C}_6\text{H}_5^-$  and  $\begin{smallmatrix} \text{CH}_3 \\ > \\ \text{CH}_3 \end{smallmatrix}$  as in  $\text{NH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\cdot\text{NH}_2$ . In particular, the accurate measurement of entropy changes was sought. The neutralisation reactions between the bases and  $\text{HClO}_4$  were also studied.

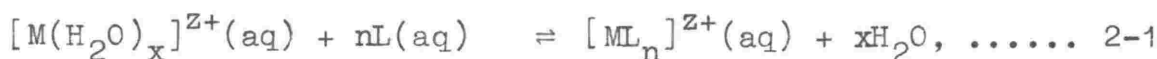
The availability of Infrared spectrometers capable of scanning below  $400\text{cm}^{-1}$  has permitted a study of some metal-

ligand vibration frequencies. A correlation was sought between these frequencies for Ni(II) and Cu(II) diamine complexes and the experimentally determined enthalpies of complex formation.

CHAPTER TWO  
THE STATE FUNCTIONS  $\Delta G$ ,  $\Delta H$  AND  $\Delta S$  FOR  
AQUEOUS COMPLEX ION FORMATION

2-1 The Free Energy Change,  $\Delta G$ :

For a complex-formation reaction between a metal ion  $M^{Z+}$  and a ligand L in aqueous solution,



the free energy change  $\Delta G$  is given by

$$\Delta G = \bar{G}_{[ML_n]^{Z+}(aq)} + x\bar{G}_{H_2O} - \bar{G}_{[M(H_2O)_x]^{Z+}(aq)} - n\bar{G}_{L(aq)}$$

where, for example,

$$\bar{G}_{L(aq)} = \left( \frac{\partial G_{L(aq)}}{\partial n_L} \right)_{T,P,n_{[ML_n]^{Z+}}, n_{[M(H_2O)_x]^{Z+}}}$$

is the partial molar free energy of the hydrated ligand and  $n_L$  is the number of moles of ligand in a given solution.

Partial molar quantities for a given state ( $\bar{X}$ ) are always defined relative to the same quantity for a reference or standard state ( $X^0$ ). The partial molar free energy  $\bar{G}_i$  of a solute i and its standard free energy  $G_i^0$  are related by

$$\bar{G}_i = G_i^0 + RT \ln a_i \dots\dots\dots 2-2$$

where  $a_i$  is the activity of the solute species in the given state. For a solute (or solvent) the standard state is

chosen as that state for which the activity is unity, i.e.,  $\ln a_i = 0$ . The activity is related to the molar concentration by the activity coefficient  $f$ ,  $a_i = c_i f_i$ . At or near infinite dilution a solution approaches ideality and  $f = 1$ . For an infinitely dilute solution  $a_i = c_i$  and for a solute the standard state is conveniently defined as a hypothetical solution of unit molar concentration possessing the properties of a very dilute solution.

For a solvent, the standard state is chosen as that state for which the solvent activity is unity. If the solvent activity is expressed on the mole fraction scale,  $a_s = m_s f_s$ , then the standard state corresponds to that of pure solvent when the mole fraction  $m_s = 1$  and the fugacity  $f_s = 1$ . This state is approached as the concentration of solute becomes infinitely small.

The standard molar quantities  $X^\circ$  for any solute or solvent are a function of temperature and pressure only; they are independent of solute composition.

When the reactants and products in a reaction are in their standard states the free energy change  $\Delta G^\circ$  is given by

$$\begin{aligned}\Delta G^\circ &= \sum_i G_i^\circ(\text{products}) - \sum_j G_j^\circ(\text{reactants}) \\ &= \sum_k G_k^\circ \dots\dots\dots 2-3\end{aligned}$$

where  $\sum_k$  represents a summation over all reactants and products, using appropriate signs. For the ligation



reaction 2-1,

$$\Delta G^{\circ} = G^{\circ}_{[ML_n]^{z+}(aq)} + xG^{\circ}_{H_2O} - nG^{\circ}_{L(aq)} - G^{\circ}_{[M(H_2O)_x]^{z+}(aq)}$$

2-1.1 The relationship between  $\Delta G^{\circ}$  and the formation constant

If  $a_k$ ,  $[k]$  and  $f_k$  are the activity, the molar concentration and the hypothetical ionic activity coefficient of the species  $k$ ,  $n_k$  is the number of moles of  $k$  represented in the equilibrium expression 2-1, and  $K_c$  and  $K_a$  are the concentration and thermodynamic equilibrium (formation) constants for the reaction 2-1 then the following relationships hold:

$$\bar{G}_k = G_k^{\circ} + RT \ln a_k = G_k^{\circ} + RT \ln [k] f_k$$

$$\Delta G = \Delta G^{\circ} + RT \sum_k n_k \ln a_k \dots\dots\dots 2-4$$

$$= \Delta G^{\circ} + RT \ln \frac{\left\{ a_{[ML_n]^{z+}} \right\} \left\{ a_{H_2O} \right\}^x}{\left\{ a_{[M(H_2O)_x]^{z+}} \right\} \left\{ a_L \right\}^n}$$

$$= \Delta G^{\circ} + RT \ln K_a \dots\dots\dots 2-5$$

$$= \Delta G^{\circ} + RT \ln \frac{[ML_n]^{z+} [H_2O]^x}{[M(H_2O)_x]^{z+} [L]^n} + RT \ln \frac{f_{[ML_n]^{z+}} \cdot (f_{H_2O})^x}{f_{[M(H_2O)_x]^{z+}} \cdot (f_L)^n}$$

$$= \Delta G^{\circ} + RT \ln K_c + RT \sum_k n_k \ln f_k \dots\dots\dots 2-6$$

When the reactants and products are in a state of chemical equilibrium, under given conditions of  $T$ ,  $P$ , and  $n_k$ , the

total free energy of the reactants in solution equals the total free energy of the products in solution.

$$\text{i.e.,} \quad \Delta G = \sum_k G_k = 0$$

Therefore, from equation 2-6,

$$- \Delta G^{\circ} = RT \ln K_c + RT \sum_k n_k \ln f_k \dots\dots\dots 2-7$$

$$\text{i.e.,} \quad - \Delta G^{\circ} = RT \ln K_a \dots\dots\dots 2-8$$

As the state of infinite dilution is approached all  $f_k$  tend to unity,

$$\begin{aligned} \text{therefore,} \quad - \Delta G^{\circ} &= \text{Lt} \quad [RT \ln K_c] \\ &\quad (c_k \rightarrow 0) \\ &= \text{Lt} \quad [RT \ln K_c] \\ &\quad (I \rightarrow 0) \end{aligned} \quad 2-9$$

where  $I$  is the total ionic strength in the reaction mixture,

$$I = \frac{1}{2} \sum_k c_k z_k^2$$

Therefore the standard free energy change for a reversible chemical reaction can be obtained by measuring the thermodynamic formation constant  $K_a$ , or by measuring  $K_c$  at a series of finite ionic strengths and obtaining the value of  $K_c$  at infinite dilution by extrapolation of this experimental data to zero ionic strength.

## 2-2 The Enthalpy Change $\Delta H$

Enthalpy is a state function. For a complex formation reaction in aqueous solution (equation 2-1) the enthalpy change is given by

$$\begin{aligned}
\Delta H &= \sum_i n_i \bar{H}_i \text{ (products)} - \sum_j n_j \bar{H}_j \text{ (reactants)} \\
&= \sum_k n_k \bar{H}_k \dots\dots\dots 2-10 \\
&= \bar{H}_{[ML_n]^{z+}} + x\bar{H}_{H_2O} - n\bar{H}_L - \bar{H}_{[M(H_2O)_x]^{z+}}
\end{aligned}$$

where for example,  $\bar{H}_L = \left( \frac{\partial H_L}{\partial n_L} \right)_{T,P,n_{[ML_n]^{z+}}, n_{[M(H_2O)_x]^{z+}}}$

is the partial molar enthalpy or heat content of the aqueous ligand.

## 2-2.1 The relationship between $\Delta H$ and $\Delta G$ :

The partial molar enthalpy  $\bar{H}$  of a substance is related to the partial molar free energy  $\bar{G}$  and the partial molar entropy  $\bar{S}$  by

$$\bar{H} = \bar{G} + T\bar{S} \quad (\text{where } T \text{ is in } ^\circ\text{A}) \dots\dots\dots 2-11$$

and for a reaction,

$$\Delta H = \Delta G + T\Delta S \dots\dots\dots 2-12$$

When the reactants and products are in their standard states,

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \dots\dots\dots 2-13$$

A convenient standard state for the enthalpy is that of a hypothetical solution of unit molar concentration possessing the properties of a very dilute solution, i.e., all  $f_k = 1$ . This standard state is one in which the mutual interactions between all solute molecules or ions are considered negligible.

## 2-2.2 The relationship between $\Delta H$ and $\Delta H^0$ :

From equation 2-6,

$$\Delta G = \Delta G^0 + RT \ln K_c + RT \sum_k n_k \ln f_k$$

But  $(\partial \Delta G / \partial T)_{P, n_k} = -\Delta S$  (see equation 2-21)

$$\begin{aligned} \text{Therefore, } \Delta S = \Delta S^0 - R \ln K_c - RT \left( \frac{\partial \ln K_c}{\partial T} \right)_{P, n_k} \\ - R \sum_k n_k \ln f_k - RT \left( \frac{\partial \left( \sum_k n_k \ln f_k \right)}{\partial T} \right)_{P, n_k} \end{aligned}$$

Multiplying through by  $T$  and substituting in equation 2-7,

$$\begin{aligned} T \Delta S = T \Delta S^0 - \Delta G + \Delta G^0 - RT^2 \left( \frac{\partial \ln K_c}{\partial T} \right)_{P, n_k} \\ - RT^2 \left( \frac{\partial \left( \sum_k n_k \ln f_k \right)}{\partial T} \right)_{P, n_k} \end{aligned}$$

and therefore,

$$\Delta H = \Delta H^0 - RT^2 \left( \frac{\partial \ln K_c}{\partial T} \right)_{P, n_k} - RT^2 \left( \frac{\partial \left( \sum_k n_k \ln f_k \right)}{\partial T} \right)_{P, n_k} \dots 2-14$$

$$\doteq \Delta H^0 - RT^2 \left( \frac{\partial \left( \sum_k n_k \ln f_k \right)}{\partial T} \right)_{P, n_k} \dots \dots \dots 2-15$$

The term  $\left( \frac{\partial \ln K_c}{\partial T} \right)_{P, n_k}$  is zero when concentrations are expressed on the molal scale, because all  $n_k$  are specified as being constant, i.e., the degree of dissociation is invariant. To a first approximation this differential will be zero when concentrations are expressed on the molar scale also.

When the hypothetical ionic activity coefficients  $f_k$  are expressed by the Debye-Hückel equation,

$$-\log f_k = \frac{Az_k^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}}$$

it has been found that

$$\left( \frac{\partial \log f_k}{\partial T} \right)_{P, n_k} = 2 \times 10^{-3} \log f_k \dots\dots\dots 2-16$$

Therefore, from equations 2-15 and 2-16,

$$\begin{aligned} \Delta H &= \Delta H^{\circ} - 2 \times 10^{-3} RT^2 \sum_k n_k \ln f_k \\ &= \Delta H^{\circ} - 352 \sum_k n_k \ln f_k \quad (\text{at } 25^{\circ}\text{C}) \dots\dots\dots 2-17 \end{aligned}$$

The last term in this equation is very small compared with  $\Delta H$  (see chapter six).

For many reactions  $\Delta H$  can be determined directly by calorimetry.  $\Delta H = -q_p$  where  $q_p$  is the heat liberated by the reaction at constant pressure.  $\Delta H$  is then corrected to the standard state by using equation 2-17.

### 2-2.3 The relationship between $\Delta H^{\circ}$ and $\Delta G^{\circ}$ :

From equations 2-8 and 2-21,

$$\begin{aligned} \left( \frac{\partial \Delta G^{\circ}}{\partial T} \right)_{P, n_k} &= -\Delta S^{\circ} = - \left( \frac{\partial (RT \ln K_a)}{\partial T} \right)_{P, n_k} \\ &= -R \ln K_a - RT \left( \frac{\partial \ln K_a}{\partial T} \right)_{P, n_k} \end{aligned}$$

therefore,

$$T \Delta S^{\circ} = RT \ln K_a + RT^2 \left( \frac{\partial \ln K_a}{\partial T} \right)_{P, n_k}$$

i.e., 
$$\Delta H^{\circ} = RT^2 \left( \frac{\partial \ln K_a}{\partial T} \right)_{P, n_k} \dots\dots\dots 2-18$$

and 
$$\frac{\Delta H^{\circ}}{RT^2} = \left( \frac{\partial \ln K_a}{\partial T} \right)_{P, n_k} = - \left( \frac{\partial \ln \frac{\Delta G^{\circ}}{RT}}{\partial T} \right)_{P, n_k} \dots\dots\dots 2-19$$

Therefore  $\Delta H^{\circ}$  can also be obtained from the temperature coefficient of the log of the thermodynamic equilibrium constant,

i.e.,  $\Delta H^{\circ} = RT^2 \times \text{the slope of the graph } \ln K_a \text{ vs. } T.$

### 2-3 The Entropy Change $\Delta S$

For any atom, ion or molecule the entropy is a function of its modes and freedom of motion, internal and external. For a complex formation reaction in aqueous solution (equation 2-1) the entropy change is given by

$$\begin{aligned} \Delta S &= \sum_i n_i \bar{S}_i(\text{products}) - \sum_j n_j \bar{S}_j(\text{reactants}).. 2-20 \\ &= \bar{S}_{[ML_n]^{z+}} + x \bar{S}_{H_2O} - n \bar{S}_L - \bar{S}_{[M(H_2O)_x]^{z+}} \end{aligned}$$

where for example,

$$\bar{S}_L = \left( \frac{\partial \bar{S}_L}{\partial n_L} \right)_{T, P, n_{[ML_n]^{z+}}, n_{[M(H_2O)_x]^{z+}}}$$

is the partial molar entropy of the ligand L in aqueous solution. The entropy change for a reaction is related to the enthalpy and free energy changes by equations 2-12, 2-13, and 2-21. The standard state is defined as for the

enthalpy and free energy.

### 2-3.1 The relationship between $\Delta S$ and $\Delta G$ :

From equation 2-11, for an infinitesimal change of state,

$$dG = dH - TdS - SdT$$

$$= -dq - TdS - SdT \quad \text{at constant pressure.}$$

For an infinitesimal reversible reaction,

$$dS = - \frac{dq}{T}$$

therefore  $dG = -SdT$  and  $\left( \frac{\partial G}{\partial T} \right)_P = -S$  for a reversible process.

Similarly for an equilibrium reaction involving several species,

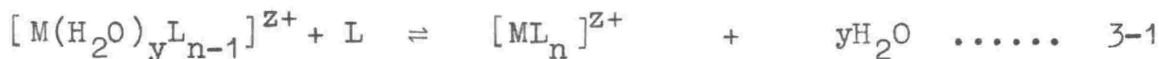
$$\left( \frac{\partial \Delta G^0}{\partial T} \right)_P = - \Delta S^0$$

Therefore the entropy change for an equilibrium reaction can be obtained from the temperature coefficient of the free energy change.

CHAPTER THREE  
LITERATURE SURVEY

3-1 Historical

The study of metal-ammine complex formation in aqueous solution by Jannick Bjerrum<sup>1</sup> (1941) was the first major contribution to research in the field of coordination thermodynamics. His work indicated the co-existence of coordination complexes  $[M(H_2O)_x]^{Z+}$ ,  $[M(H_2O)_{x-y}L]^{Z+}$ , . . .  $[ML_n]^{Z+}$  in step-wise equilibria in solution, (L = ligand):



For each equilibrium step there is an equilibrium constant defined. For example,

$$K_{c_{II}} = [M(H_2O)_{x-2y}L_2^{Z+}] / [M(H_2O)_{x-y}L^{Z+}][L] \quad \text{.....} \quad 3-2$$

where the concentrations are those applying at equilibrium.

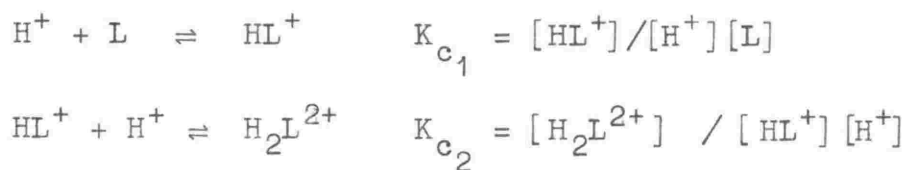
The total concentration of metal ion ( $T_M$ ) and the total concentration of ligand ( $T_L$ ) in solution, are accounted for by

$$T_M = [M(H_2O)_x^{Z+}] + [M(H_2O)_{x-y}L^{Z+}] + \dots + [ML_n^{Z+}], \quad \text{and}$$



$$\begin{aligned}
T_L = & [L] + [M(H_2O)_{x-y}L^{z+}] + 2[M(H_2O)_{x-2y}L_2^{z+}] \\
& + \dots + n[ML_n^{z+}] \\
& + [HL^+] + [H_2L^{2+}] + \dots \dots \dots 3-3
\end{aligned}$$

where  $HL^+$  and  $H_2L^{2+}$  may be protonated forms of the ligand if it is a weak base, in which case the following relationships must also be considered:



etc.

$$\text{and } T_H = [H^+] + [HL] + 2[H_2L] + \dots \dots \dots 3-4$$

= the total concentration of acid present.

Basically the experimental methods which Bjerrum used are those still used for similar determinations. His theoretical treatment of such systems (4-1.1 and 4-1.2) is applicable to all rapidly reversible equilibria in solution. Much work has been done in this field and many results published for systems involving both organic and inorganic ligands with transition metal and 'inert-gas type' cations. A Chemical Society Special Publication by G. Schwarzenbach et al.<sup>2</sup> gives a comprehensive tabulation of results published up to 1955.\*

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\* The publication of a coverage up to 1960 has been announced. (Special Publication No. 17)

Bjerrum's stability constant measurements have led to the subsequent measurement of enthalpy and entropy changes for association and coordination reactions in aqueous solution. However, the usefulness of many of these results is limited. Often it is not possible to compare the results of two workers because of the variety of physical conditions employed.

### 3-2 The Determination of the Free Energy Change $\Delta G$

$\Delta G$  is obtained from the measurement of the thermodynamic equilibrium constant  $K_a$  (equation 2-5) or the concentration equilibrium constant  $K_c$  (equation 2-9).

#### 3-2.1 Potentiometric methods

Most of the common ligands are weak bases, and the equilibrium (formation) constants for metal ion ligation are determined by measuring the equilibrium hydrogen ion concentration and applying the equations 3-2, 3-3, and 3-4. Most measurements in aqueous solution have been made potentiometrically using the glass electrode-calomel electrode system with a pH meter. Often a titration method has been used.

The use of the hydrogen electrode has not been widespread due to its susceptibility to 'poisoning' and the need for frequent regeneration of the Pt-black surface.<sup>5,6</sup> It has been used in the study of metal succinates,<sup>15c</sup>

malonates,<sup>7,8</sup> and oxalates<sup>15a</sup> in aqueous solution. Using the cell  $\text{Pt}, \text{H}_2 / \underset{\text{HCl}}{\overset{\text{(I)}}{\text{NaCl}}} // \underset{\text{HCl}}{\overset{\text{(II)}}{\text{B}, \text{NaCl}}} / \text{H}_2, \text{Pt}$  (B=amine) with half cells I and II of equivalent ionic strength to cancel out activity coefficient terms, Pinsent and Everett<sup>9</sup> were able to measure hydrogen ion concentrations directly rather than hydrogen ion activities. Since the total ionic strength in each half-cell was equal, they assumed that  $f_{\text{HCl}}$  in each half-cell was also equal, and therefore,

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{[\text{H}_{\text{II}}^+](f_{\text{HCl(II)}})^{\frac{1}{2}}}{[\text{H}_{\text{I}}^+](f_{\text{HCl(I)}})^{\frac{1}{2}}} = \frac{RT}{F} \ln \frac{[\text{H}_{\text{II}}^+]}{[\text{H}_{\text{I}}^+]}$$

Knowing  $[\text{H}_{\text{I}}^+]$  and using the relationships 3-4 and

$$T_{\text{B}} = [\text{B}] + [\text{BH}^+] + [\text{BH}_2^{++}] = \text{the total concentration of base in solution,}$$

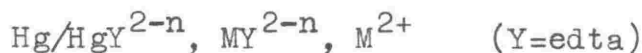
they obtained accurate concentration equilibrium constants  $K_1$ ,  $K_2$  for the systems  $\text{HCl}/1,6\text{-diaminohexane}$  and  $\text{HCl}/1,2\text{-diaminoethane}$  at several ionic strengths.

For systems where a halide or other inorganic anion is the coordinating ligand, an electrode reversible with respect to the anion can sometimes be used, e.g.,  $\text{Ag}, \text{AgX}/\text{X}^-$ , (X=Cl, Br)<sup>8,17</sup>.

Reversible metal or metal-amalgam electrodes have been used for some aqueous metal complex systems, e.g., in cells of the type:<sup>137</sup>

Reference electrode	Metal salt	Metal M or amalgam M-Hg
	Ligand	
	Inert electrolyte	

Bjerrum and Nielson<sup>136</sup> have used the Cu,Hg/Cu<sup>2+</sup> electrode for studies on the Cu(II)--en system. In the above cell the right-hand electrode may be one responding indirectly to the metal ion. e.g., Reilley and Schmid<sup>138</sup> used the electrode system,



to measure the stability of metal (M)-edta complexes, the application depending on the very high stability of the Hg<sup>2+</sup> complex.

### 3-2.2 Activity coefficient assumptions:

For most systems studied potentiometrically, the quantity measured by experiment to determine the solution composition is the activity of one of the equilibrating ions, e.g., commonly the hydrogen ion activity  $a_{\text{H}^+}$  from pH measurements. To be able to apply equations of the form 3-2, 3-3, and 3-4 to the system when deriving formation constants, it is necessary to convert the measured ionic activity  $a_i$  to an ionic concentration  $[i]$  by means of

$$a_i = [i] f_i$$

where  $f_i$  is the hypothetical ionic activity coefficient of the species  $i$ . This is so even if a thermodynamic stability

constant ( $K_a = K_c \text{fn}(f_i)$ ) is being determined because, except in extremely dilute solutions, it is not correct to assume an additivity of activities, e.g.,  $T_H \propto a_{H^+} + a_{HL^+} + 2a_{H_2L^{2+}}$ . It is not possible to work entirely in terms of activities. At some stage in the calculations it is necessary to make an assumption regarding the form of the empirical activity coefficient term.

Dilute solutions: Few workers have used solutions sufficiently dilute ( $\leq 0.005$  molar) to allow the use of the limiting form of the Debye-Hückel equation in calculating activity coefficients.<sup>10,14</sup>

The Davies' Equation:<sup>11</sup> This empirical equation for activity coefficients

$$-\log f_{\pm} = Az_+z_- - \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - \beta I \quad (\beta = 0.2), \quad \dots\dots\dots 3-5$$

has been used frequently for systems with uni- and bivalent ions.<sup>7,8,12,13,15</sup> It has been shown to be a reasonable approximation at low ionic strengths.<sup>8</sup> Davies<sup>11</sup> considered the equation to be accurate to within 2% in solutions up to 0.10 molar ionic strength. Although the equation was derived for solutions of pure electrolytes only, it has in certain systems of mixed electrolytes led to thermodynamic ('activity') equilibrium constants  $K_a$  in good agreement with those obtained by extrapolation of  $\log K_c$  to zero ionic strength<sup>8</sup> (equation 2-9).

Recently it has been shown that the Davies equation

with the empirical constant  $\beta = 0.30$  is a better approximation for most pure electrolytes studied so far.<sup>16</sup>

The Guggenheim Equation: This equation for the activity coefficient of ions in mixed electrolyte systems<sup>18</sup> has had little application. Its use is cumbersome, requiring a knowledge of the activity coefficients of all the component ion pairs when in pure electrolyte solutions of the same total ionic strength.

The presence of inert electrolytes: Most measurements have been made in solutions containing a relatively high concentration of 'inert' electrolyte. Commonly used electrolytes are  $\text{KNO}_3$ ,  $\text{KCl}$ , and  $\text{NaClO}_4$  in the concentration range 0.10 to 3.0m/l. It is assumed that the 'inert' or 'support' electrolyte does not 'interfere' with the species being studied, and that activity coefficients remain constant for different compositions of the equilibrating species. For the purpose of comparison it has been assumed that the term  $RT(\sum_i n_i \ln f_i - \sum_j n_j \ln f_j)$  (equation 2-8) is constant in such systems and that the term  $-RT \ln K_c$  is then a direct measure of the standard free energy change,  $\Delta G^\circ$ .

### 3-2.3 Extrapolation technique

This procedure, using equations 2-8 and 2-9

$$-\Delta G^\circ = RT \ln K_a = \lim_{(I \rightarrow 0)} [RT \ln K_c]$$

has led to the most reliable  $K_a$  and  $\Delta G^\circ$  values when the solutions used contain an inert electrolyte and are not

sufficiently dilute to make valid the use of the Debye-Huckel or Davies equation. However, the extrapolation method is only reliable if  $K_c$  is determined down to low ionic strengths,  $I \leq 0.10\text{m/l}$ .

Curves for the extrapolation of  $K_c$  to zero ionic strength have been found to fit equations of the forms:

$$\log K_a = \log K_c + \alpha I \quad \text{Ref. 9}$$

$$\log K_a = \log K_c + \alpha' I^{1/2} / (1 + I^{1/2}) \quad 9$$

$$\log \beta_n = \log \beta_n^0 + AI + BI^{3/2} + CI^2 \quad 22, 23$$

$$\log \beta_n = \log \beta_n^0 + A'I^{1/2} + B'I \quad 22-25$$

where  $\beta_n = K_{c_1} \cdot K_{c_2} \cdot \dots \cdot K_{c_n}$ ,

$$\beta_n^0 = K_{a_1} \cdot K_{a_2} \cdot \dots \cdot K_{a_n}$$

and all the  $\alpha$ ,  $A$ ,  $B$ ,  $C$  are constants for a given equilibrium system.

### 3-2.4 Spectroscopic methods:

For coloured complexes the concentration equilibrium constant has sometimes been determined by visible absorption spectroscopy. This method has an inherently low accuracy. It has been used to study equilibrium formation constants of the tetraammine complexes of  $\text{Cu(II)}$  and  $\text{Ni(II)}$ .<sup>3</sup> The Job Continuous Variation Technique<sup>4</sup> is very useful in determining the stoichiometric composition of coloured coordination compounds.

### 3-3 The Measurement of the Enthalpy Change $\Delta H$ .

Enthalpy measurements have been limited mainly to the reactions between ligands and protons and the ions Mn(II) - Zn(II), Cd(II), Hg(II) and Ag(I). In particular, reactions involving chelates have been studied, e.g., polyamines: ethylenediamine,<sup>41</sup> diethylenetriamine,<sup>39</sup> triethylenetetramine,<sup>38</sup> etc; dibasic carboxylic acids: oxalate,<sup>15a</sup> succinate,<sup>15b</sup> etc.

$\Delta H$  has been obtained by two methods.

3-3.1 (A) The temperature coefficient of the equilibrium constant: From equation 2-19,

$$\Delta H^{\circ} = 2.303RT^2 \left( \partial \log K_a / \partial T \right)_{P, n_k}$$

$(\partial \log K_a / \partial T)_{P, n_k}$  at 25°C, has been obtained for some systems by measurement of  $K_a$  at temperature intervals of 5-15°C above and below 25°C.<sup>7,9,10,26-29</sup> The temperature coefficient is equal to the slope of the curve  $\log K_a$  vs.  $T(^{\circ}A)$  when  $T=298^{\circ}A$ . When  $\Delta H$  varies appreciably with temperature,<sup>7</sup>  $\log K_a$  can be obtained in terms of parameters  $a$ ,  $b$ , and  $c$  by fitting at least three values of  $K_a$  to the equation

$$\log K_a = a + bT + cT^2.$$

This gives  $\Delta H^{\circ} = 2.303RT^2(b + 2cT)$ .<sup>7</sup>

Nasanen<sup>23</sup> obtained for the copper-1,2-diaminopropane and 1,2-diaminopropane-perchloric acid systems, a relationship  $\log K_a = A_1T^{-1} + A_2 + A_3T$ , whence  $\Delta H^{\circ} = 2.303R(A_1 - A_3T^2)$ .

The accuracy of the stability constants has not



always justified this treatment. Rossotti<sup>31</sup> states that the precision of  $\Delta H$  values obtained this way varies by  $\pm 0.4$  to  $\pm 2$  kcal/mole. Such large errors have rendered  $\Delta H$  values unreliable for comparisons. For the  $[\text{Cu}(\text{tren})]^{2+}$  complex a discrepancy of 4.7 kcal/mole arose between the temperature coefficient value and that obtained calorimetrically.<sup>32</sup> In some cases however, use of a sufficiently large temperature range has yielded  $\Delta H^\circ$  values in good agreement with those obtained by direct heat measurement.<sup>12</sup>

3-3.2 (B) Calorimetry: The use of constant temperature environment calorimeters is now widespread.<sup>3,12,13,19,33-41</sup> Temperature changes are measured accurately with thermistors,<sup>30,33,37,42,43</sup> resistance thermometers (Pt, Cu)<sup>44</sup> and multi-junction thermocouples.<sup>12</sup> Errors of  $\leq 0.5\%$  in the reproducibility of heat measurements, are readily obtained. Isothermal diphenyl oxide calorimeters<sup>45-47</sup> and a t-butyl alcohol calorimeter<sup>48</sup> have been described.

### 3-4 The Measurement of the Entropy Change $\Delta S$

$\Delta S$  has been determined by two methods.

3-4.1 (A) Using the Gibbs-Helmholtz Equation:  $\Delta S$  may be obtained from the experimentally determined free energy and enthalpy change for a reaction according to the Gibbs-Helmholtz equation,

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}.$$

The term  $T \Delta S^{\circ}$  usually occurs as a small difference between the other two experimentally determined quantities. Therefore the accurate determination of  $\Delta S^{\circ}$  requires very accurate  $\Delta H^{\circ}$  and  $\Delta G^{\circ}$  values.

3-4.2 (B) The temperature coefficient method: From equation 2-21,

$$\Delta S^{\circ} = - \left( \partial \Delta G^{\circ} / \partial T \right)_P.$$

When  $\log K_a = (a + bT + cT^2)$ , then  $\Delta S^{\circ} = 2.303R(a + 2bT + 3cT^2)$ .

Only when there is a very large temperature coefficient (for the free energy change) can this lead to more reliable results than those obtained using experimental enthalpy values.

### 3-5 The Relationship of the State Functions $\Delta G^{\circ}$ , $\Delta H^{\circ}$ , $\Delta S^{\circ}$ to the Structure of Complexes in Aqueous Solution

#### 3-5.1 The free energy change

For a metal ion ligation reaction in aqueous solution,  $-RT \ln K_a$  is a measure of the free energy change when water molecules coordinatively bound to the metal ion are replaced by ligand molecules or ions:



For each step-wise equilibrium expression involved, there is a free energy change, a state function, viz.,

$$\Delta G_1^0 = -RT \ln K_{a_1}$$

$$\Delta G_2^0 = -RT \ln K_{a_2}$$

$$\Delta G_n^0 = -RT \ln K_{a_n}$$

$$\begin{aligned} \Delta G_{1-n}^0 &= \Delta G_1^0 + \Delta G_2^0 + \dots + \Delta G_n^0 = -RT \ln K_{a_{1-n}} \\ &= -\lim_{I \rightarrow 0} [RT \ln K_{c_{1-n}}] \quad (\text{see equation 2-9}) \end{aligned}$$

The  $K_a$  values have in several ways been related to the structures of complexes and the nature of the ligands.

(a) The ratio of successive formation constants:

The ratio between  $K_{a_n}$  and  $K_{a_{n+1}}$ , or  $K_{c_n}$  and  $K_{c_{n+1}}$  (see for example equations 3-1 and 3-2) has been expressed statistically in terms of the number of coordination sites 'occupied' and 'free' in each complex.<sup>1,54</sup> If  $N$  is the maximum coordination number of a metal ion with respect to a given ligand, then statistically,

$$K_{c_n} = \text{cst.} \cdot \frac{(n)}{(N-n+1)} = \frac{[ML_n^{z+}]}{[ML_{n-1}(H_2O)_y^{z+}][L]}$$

$$\text{and} \quad \frac{K_{c_{n+1}}}{K_{c_n}} = \frac{(N-n+1)(n+1)}{(N-n)n} \dots\dots\dots 3-6$$

$$\text{Therefore, } \log K_{c_n} = \log K_{c_1} + \log N - \log \frac{(N-n+1)}{n}$$

This equation ignores the orbital symmetry in the ground state of the metal ion, the different bond strengths of the metal-ligand and metal- $\text{OH}_2$  bonds and the increased or

decreased repulsion between adjacent ligand groups as successive water molecules are replaced in the coordination sphere. The equation

$$\log K_{c_n} = \log K_{c_I} - 2 \lambda (n-1)$$

has been shown to be valid<sup>54</sup> for some metal ion complexes with ionic and neutral ligands.  $\lambda$  is an empirical constant characteristic of each system (Ref. 31, p.34).

The relative order of magnitude  $K_{c_I} > K_{c_{II}} > K_{c_{III}}$  is favoured statistically (equation 3-6) and is generally valid. Some reversals have been observed and related to sudden changes of bond type or orbital hybridisation with changes in the coordination sphere. For example,  $[\text{Ni}(\text{tetrameen})(\text{H}_2\text{O})_4]^{2+}$  is an octahedral paramagnetic ion (weak field) while  $[\text{Ni}(\text{tetrameen})_2]^{2+}$  is a square-planar diamagnetic ion (strong field) and therefore  $K_{c_{II}} > K_{c_I}$ .<sup>3</sup> This is because of a change in multiplicity of the ground state and a related increase in bond strength and crystal field stabilisation energy in going from the mono to the bis complex. Similarly for the Fe(II)-2,2'-dipyridyl and 1,10-phenanthroline complexes, the bis salt  $[\text{FeA}_2(\text{aq})]^{2+}$  is spin-free (weak field) while the tris salt  $[\text{FeA}_3]^{2+}$  is spin-paired (strong field) and  $K_{c_{III}} > K_{c_{II}}$ ,<sup>55</sup> because of increased crystal field stabilisation and increased metal  $\rightarrow$  nitrogen  $\pi$ -bonding in the tris salt.

(b) The relationship between complex stability and ligand basicity:  $\Delta G^\circ$  may be expressed in terms of an 'average' formation constant  $K_{av}$ <sup>51</sup> where  $\log K_{av} = \frac{1}{N} \log K_{a_I} \dots \log K_{a_N}$  and  $\Delta G^\circ_{av} = -RT \ln K_{av}$  is the average standard free energy change per ligand for the coordination of N ligands to a given metal ion.

The ratio  $\log K_{av} / \log K_{LH^+}$ , where  $K_{LH^+}$  is the formation constant for the neutralisation reaction



has been found to be approximately constant for a given metal ion with similar ligands, when for each type of complex, the bonding forces and inter-ligand forces are essentially the same.<sup>51</sup>

(c) Inter-ligand forces: The repulsive forces between adjacent ligand groups may, for a given symmetry, increase with the bulk or the charge of the ligand. For example, for a series of metal complexes of N-alkyl ethylenediamines  $RNHCH_2CH_2NH_2$ , the interaction between adjacent ligand groups in a coordination sphere increases with the bulk of the alkyl group R.<sup>56,57</sup> There is also an increasing repulsion between the ligand groups and any water molecules in the coordination sphere. The net effect is to decrease the metal-ligand bond strength and the thermodynamic stability of the complex.

As a result of this steric hindrance and allied effects, it has been found that  $\log(K_{c_I} / K_{c_{II}})$  increases for

the Cu(II) and Ni(II) complexes of some N-alkyl ethylenediamines  $\text{RNHCH}_2\text{CH}_2\text{NH}_2$  <sup>56,57</sup> and some NN'-dialkyl ethylenediamines  $\text{RNHCH}_2\text{CH}_2\text{NHR}$  <sup>35,58</sup> as the bulk of the group R is increased, even though the basicity and therefore the electron donor power of the ligands remains essentially constant within each series. The ratio  $\log K_{\text{av}} / \log K_{\text{LH}^+}$  decreases with increasing bulk of the alkyl group R for each of these series of nitrogen-substituted ethylenediamine-Cu(II) and Ni(II) complexes.

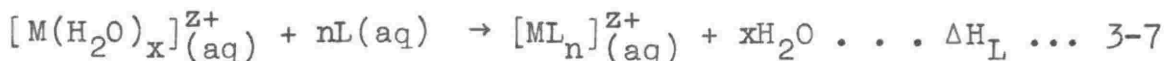
(d) The metal ionisation potential: The stabilities of some complexes in aqueous solution have been related to the gas phase ionisation potentials I of their metal components by

$$\log K_c = p(I - q)$$

where p and q are empirical constants dependent only on the ligand for a given temperature and solvent.<sup>59</sup> Other direct correlations of stability with ionisation potential have also been made.<sup>60-62</sup>

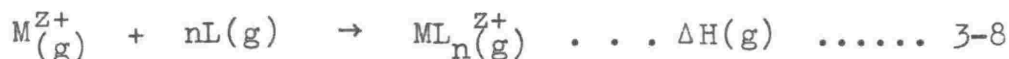
### 3-5.2 The enthalpy change $\Delta H$

The values of the heats of metal ion ligation  $\Delta H_L$  measured for reactions in aqueous solution are the net heat content changes when coordinatively bound water molecules are replaced by ligand molecules or ions; e.g.,



$\Delta H_L$  is a measure of the strength of the metal-ligand bond in the complex relative to the bond strength of the metal- $\text{OH}_2$  bond in the aquo ion.  $\Delta H_L$  also takes into account the relative crystal field stabilisation energies and solvation energies of the complex and aquo ions, and the variation in inter-ligand repulsion forces with substitution (section 3-5.1c). For the amine complexes of the divalent ions  $\text{Mn(II)}-\text{Zn(II)}$ ,  $-\Delta H_L$  has values of the order of 4-6kcal/mole for each metal-nitrogen bond formed,<sup>32,41</sup> These values are very small compared with the 'absolute' enthalpy changes expected for ligation in the gas phase.

Metal-ion ligation in the gas phase: For the reaction in the gas phase,

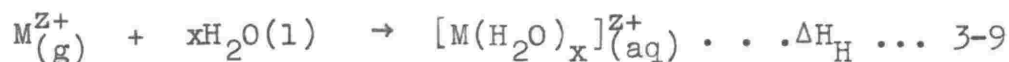


$\Delta H(g)$  is made up of three terms : the coordinate bond energy, the crystal field stabilisation energy for the complex  $\text{ML}_{n(g)}^{Z+}$  and the inter-ligand repulsion energy.

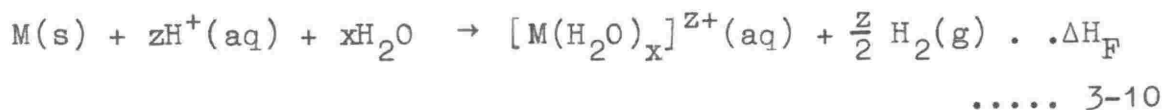
$\Delta H(g)$  can not be measured experimentally.

The enthalpy of hydration of a gaseous metal ion,

$\Delta H_H$  :

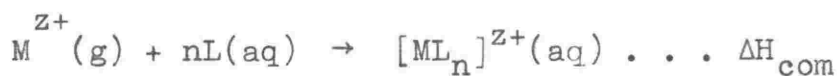


can be obtained experimentally as the summation of two energy terms (Ref. 63, p. 414):



$\Delta H_H = \Delta H_F - H_p^{Z+}$  because, by convention, the standard heat of formation of the hydrated proton (as in equation 3-10) is set equal to zero.<sup>64</sup> Because of this convention the  $\Delta H_H$  value obtained is not absolute.\*

Combination of equations 3-7 and 3-9 gives



and  $\Delta H_{com} = \Delta H_L + \Delta H_H$

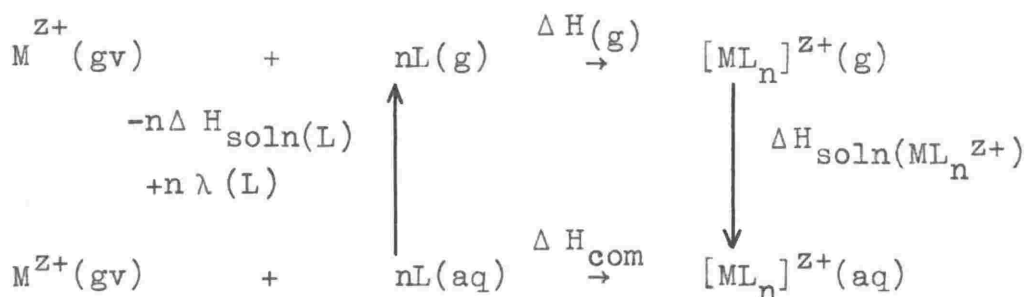
$\Delta H_{com}$  approximates to  $\Delta H(g)$ ,

$$\Delta H_{com} = \Delta H(g) + \Delta H_{soln}(ML_n^{Z+}) - n\Delta H_{soln}(L)$$

For a given metal ion with similar ligands (gaseous), the heats of solution of the ligand and  $[ML_n]^{Z+}$  have been considered approximately invariant. Thus George<sup>65</sup> has used  $\Delta H_{com}$  as a measure of  $\Delta H(g)$  for comparison purposes. These considerations have been summarised in the following energy cycle (after George and McClure<sup>63</sup>):

\* Hydration energies  $\Delta H_H$  can also be estimated from the lattice energies and heats of solution of salts. The heat of solution of the anion plus cation so obtained, is empirically separated into two component terms, one for each ion, by comparison of a series of salts containing a common anion or cation. Here again the determination is not absolute.





$$(\Delta H_{com} = \Delta H_H + \Delta H_L = \Delta H(g) + \Delta H_{soln}(ML_n^{Z+}) + n\lambda(L) + n\Delta H_{soln}(L))$$

where  $\lambda$  is the latent heat of evaporation for a liquid ligand. Alternative ways of formulating this cycle have been adopted in various theoretical discussions.<sup>33,48,94</sup>

Despite their limitations as outlined above, the experimental values of  $\Delta H_L$  give much information about the structure and bonding in coordination compounds. For example,

(a) The structure of complex ions in aqueous solution:

The magnitude of  $\Delta H_L$  depends in part upon the relative number of water molecules endothermically liberated per ligand group coordinated. For example, the aqueous Zn(II) ion is probably six-coordinate in solution,<sup>77</sup>  $[Zn(H_2O)_6]^{2+}$ . In complex formation the Zn(II) ion often adopts a four-coordinate tetrahedral structure in which inter-ligand forces are minimised. Thus two of the water molecules which are endothermically liberated in complex formation, may not be replaced in the coordination sphere by ligand donor atoms. As a result, the  $\Delta H_L$  measured has a low negative value and  $\Delta S$  a high positive value. For example, for the complex ion  $[Zn(trien)]^{2+}(aq)$ , the values -  $\Delta H_L = 8.90 \text{ kcal/mole}$

and  $\Delta S = 25.0 \text{ e.u.}$  have been taken to indicate that  $\text{Zn(II)}$  is probably in four-fold (tetrahedral) coordination.<sup>38</sup>

(b) The donor power of nitrogen atoms: The order of basicities primary nitrogen groups  $\approx 2^\circ > 3^\circ$  is partly a result of their relative heats of neutralisation. For example, the  $-\Delta H_1$  values for the protonation of mono-, di-, and triethylamine are 13.09, 11.86 and 8.81 kcal/mole respectively,<sup>50</sup> and for the diamines 1,2-diaminoethane ( $1^\circ$ ) and piperazine ( $2^\circ$ ) 11.91<sup>41</sup> and 10.17<sup>19</sup> kcal/mole respectively.

For the nitrogen protonation of some polyamines Paoletti et al.<sup>19</sup> found a linear relationship between  $\Delta H_1$  and the ratio (R) of the number of  $2^\circ$  nitrogen atoms to the total number of nitrogen atoms in the amine, viz., 1,2-diaminoethane  $R=0$ ,  $\Delta H_1 = -11.91 \text{ kcal/mole}$ ; <sup>41</sup> diethylenetriamine  $R=0.33$ ,  $\Delta H_1 = -11.20 \text{ kcal/mole}$ ; <sup>121</sup> triethylenetetramine  $R=0.50$ ,  $\Delta H_1 = -11.01 \text{ kcal/mole}$ ,<sup>19</sup> and piperazine  $R=1.0$ ,  $\Delta H_1 = -10.17 \text{ kcal/mole}$ .<sup>19</sup> It was deduced from the relationship that the monoprotonated ions  $\text{Hdien}^+$  and  $\text{Htrien}^+$  exist in two tautomeric forms, one protonated on the primary nitrogen and the other on the secondary, in almost statistical ratio. It was concluded that the basicities of the  $1^\circ$  and  $2^\circ$  amine groups in these polyethylenepolyamines are nearly equal. However, the presence of a  $2^\circ$  or  $3^\circ$  nitrogen atom in a chelating group (e.g., trien, tren respectively) generally lowers the value of  $\Delta H_L$

relative to that for the corresponding ethylenediamine complex with the same total number of nitrogen donors coordinated. For example, in the mono trien<sup>38</sup> and mono tren<sup>32</sup> complexes of Mn(II) - Cu(II), (four nitrogen atoms coordinated) -  $\Delta H_L$  is 3.0 to 4.7 kcal/mole lower than for the corresponding bis ethylenediamine complexes,<sup>40</sup> although Paoletti et al. consider that this effect may be due in part to strain in the additional chelate rings.<sup>32</sup>

### 3-5.3 The entropy change $\Delta S$ :

The entropy of an atom or molecule is a function of its modes and freedom of motion, internal and external.<sup>97</sup>

Any assembly of  $n$  atoms has  $3n$  degrees of freedom (D.F.); three are translational, and for non-linear polyatomic molecules, three are rotational and  $3n-6$  vibrational.

A coordinated water molecule has of itself no translational D.F.; it has three vibrational D.F. and three librational (see p.225). (The three librational D.F. correspond essentially to hindered rotations of a 'free' water molecule.<sup>96</sup>) As a group it also has one vibrational D.F. with respect to the metal ion (M-O stretching mode). When the coordinated water molecule is displaced from the metal ion and 'freed' it loses one vibrational D.F. (M-O stretch) and the librational D.F. with respect to the metal ion. It gains three D.F. of translation and three of rotation.

Upon coordination a ligand loses three D.F. of translation, and in the case of a chelate its vibrational D.F.

are altered and its rotational D.F. (all or some) are lost. One new vibrational D.F. (M-ligand stretch) is gained per metal-ligand bond formed.

The entropy change for a reaction depends on the redistribution of the degrees of freedom within molecules and ions as they combine to form new compounds.

Certain specific factors influence the  $\Delta S$  in complex formation.

(a) The coordination number of the complex: For a reaction of the type



$\Delta S$  generally decreases with increasing values of  $n$ .<sup>40,77</sup> This has been explained statistically by considering the number of sites available for coordination by each successive donor atom.<sup>1,93</sup>

(b) Interactions with the solvent: The entropy can be considered as a measure of the order or disorder in a system. An entropy increase accompanies increased disorder or randomness in a system.

There is evidence that for an aqueous ion of moderate size, the inner coordination sphere is surrounded by a region less ordered than pure water.<sup>84</sup> This region arises from competition between two incompatible structures, those of the primary coordination sphere and the bulk of the liquid.

As the radius of an ion of given charge decreases, its

power to polarise and order the solvent in its vicinity increases. This ordering decreases the entropy of the solvent. The spatial extent of the cloud of ordered solvent molecules about an ion depends on the radius and charge of the ion. For example, the entropies of equally charged ions increase with ionic size because the power to polarise the solvent decreases ( $S_{\text{Li}^+}^0$  3.4e.u.,  $S_{\text{Na}^+}^0$  14.4e.u.,  $S_{\text{K}^+}^0$  24.5e.u.,  $S_{\text{Rb}^+}^0$  29.7e.u.,  $S_{\text{Cs}^+}^0$  31.8e.u.<sup>90</sup>--all relative to  $S_{\text{H}^+}^0 = 0\text{e.u.}$ <sup>89</sup>). Similarly the entropies of ions increase with decreasing ionic charge ( $S_{\text{Al}^{3+}}^0$  -74.9e.u.,  $S_{\text{Mg}^{2+}}^0$  -28.2e.u.,  $S_{\text{Na}^+}^0$  14.4e.u.<sup>90</sup>). A cation has a greater ordering effect on the solvent than does an anion.

In metal ion ligation reactions, both the effective radius of the metal ion coordination sphere and the effective (peripheral) charge of the metal ion may be altered. The resultant change in the ordering of solvent molecules will contribute to the measured entropy change.<sup>93</sup> Entropy changes for addition of ligands beyond the first are smaller; this may arise from a decrease in solute-solvent interaction with decreasing positive charge of the complex ion (e.g.,  $\text{Al}^{3+} + 3\text{F}^-$ <sup>92</sup>), or from increasing size of the solute when large ligand molecules are used, (e.g.,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)} + \text{en}$ <sup>40</sup> or 2,2'-dipyridyl<sup>77</sup>).

However, Eley and Evans<sup>85</sup> in considering the hydration of ions, stated that the effect of coordination on the movement (vibration, libration and lateral translation)

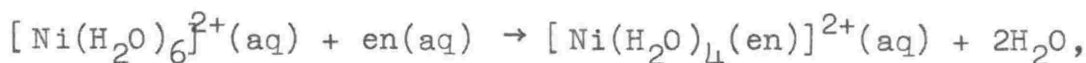
of the ligand ( $\text{H}_2\text{O}$ ) in the primary coordination sphere makes the major contribution to the aqueous ionic entropy. Their argument was based on a calculation of the energy terms involved. They noted a correlation between  $\Delta S$  for the solution of a gaseous ion, and the electrostatic bonding energy between the ion and the fractional charges on the O or H atoms of water in the primary coordination sphere.

Yatsimirskii<sup>94</sup> noted a similar correlation. The entropy of complex formation is primarily determined by the energy of hydration of a central ion.<sup>94</sup>

The contribution of  $T\Delta S^\circ$  to the total free energy change.

For ion-association reactions the  $T\Delta S^\circ$  term is usually very important and may determine both the sign and magnitude of  $\Delta G^\circ$  since  $\Delta H^\circ$  is usually small, cf., Table 3-1. When both the cation and anion donor atoms are readily polarised, the bonding forces and  $\Delta H^\circ$  for ion association increase and  $T\Delta S^\circ$  becomes less significant<sup>13</sup> cf., Table 3-2.

For the reaction of neutral ligands with the ions  $\text{Mn(II)}-\text{Zn(II)}$ ,  $\Delta H^\circ$  values are generally much larger than for ion-pairing reactions and the value of the term  $T\Delta S^\circ$  contributes only slightly to the value of  $\Delta G^\circ$ .<sup>39,41</sup> e.g., for the reaction



$$\Delta G^\circ = -10.50\text{kcal/mole}, \quad \Delta H^\circ = -8.90\text{kcal/mole} \quad \text{and} \\ T\Delta S^\circ = 1.60\text{kcal/mole.} \quad 40$$

TABLE 3-1 <sup>15a,b</sup>

Thermodynamic functions for some transition metal  
dicarboxylate ion pairs, 25°C

<u>Ion pair</u>	<u>-ΔG(kcals/mole)</u>	<u>ΔH(kcals/mole)</u>	<u>TΔS(kcals/mole)</u>
Ni <sup>2+</sup> +C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	7.05±0.02	0.15±0.10	7.20±0.12
Co <sup>2+</sup> +C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	6.54±0.02	0.59±0.07	7.13±0.09
Ni <sup>2+</sup> +succinate	3.20±0.02	2.23±0.2	5.43±0.22
Co <sup>2+</sup> +succinate	3.02±0.02	2.81±0.04	5.83±0.06

TABLE 3-2 <sup>13</sup>

Thermodynamic functions for the reaction Hg<sup>2+</sup>+X<sup>-</sup> ⇌ HgX<sup>+</sup>  
at 25°C

<u>X</u>	<u>-ΔG<sup>0</sup>(kcals/mole)</u>	<u>-ΔH<sup>0</sup>(kcals/mole)</u>	<u>TΔS<sup>0</sup>(kcals/mole)</u>
Cl	10.0	4.8±0.5	5.1±0.9
Br	13.3	10.6±0.5	2.7±0.9
I	18.4	17.6±0.5	0.9±0.9

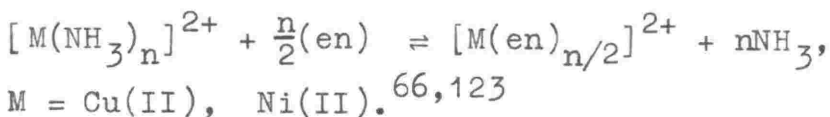
Exceptions to this generalisation arise when a chelate group replaces more or less than its equivalent number of water molecules from metal ion coordination sites. e.g., for the 1:1 reaction of dien with  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ , a large positive  $T\Delta S^\circ$  (+5.55kcal/mole) coupled with a relatively low  $\Delta H^\circ$  (-6.45kcal/mole) indicates<sup>39</sup> that dien may be replacing five water molecules from the  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  ion to give the four-coordinate ion  $[\text{Zn}(\text{H}_2\text{O})(\text{dien})]^{2+}(\text{aq})$ .

The relationship between  $T\Delta S^\circ$  and  $\Delta H^\circ$ . A linear relationship exists between these functions for the hydration of gaseous ions<sup>85</sup> and for many cases of ion-pair formation in aqueous solution;<sup>100</sup> the latter implies that both  $\Delta H^\circ$  and  $\Delta S^\circ$  may vary as the inverse of  $r_{\text{M}^{2+}}$  (e.g., Refs. 7, 156). For reactions involving neutral ligands no such relationship has been observed. For reactions between like metal ions and large polydentate ligands,  $\Delta S$  may remain essentially constant while  $\Delta H^\circ$  varies considerably. e.g., for the mono trien complexes of Mn(II)-Cu(II),  $-\Delta H^\circ$  increases regularly with atomic number from 2.7kcal/mole for Mn(II) to 21.55kcal/mole for Cu(II) while  $T\Delta S^\circ$  remains in the range  $(5.7 \pm 0.9)\text{kcal/mole}$ .<sup>38</sup>

(c) The chelate effect. This is the observation that for the formation of metal ion complexes with bidentate ligands,  $-\Delta G^\circ$  and therefore the formation constant is generally greater than for the complexes containing an equivalent number of the corresponding monodentate ligand



molecules. e.g., this is shown for the pairs of ligands:  
 $2,2'\text{-dipyridyl}^{122} > \text{pyridine},^{2,53} \quad \text{en} > \text{CH}_3\text{NH}_2,^{66}$   
 $\text{en}^2 > \text{NH}_3,^{2,123} \quad \text{oxalate}^2 > \text{formate}^2$  Often this is  
 mainly an entropy effect ( $\Delta S^\circ$  more positive for  
 chelation).<sup>26,53</sup> For the Mn(II) and Zn(II) ions, with no  
 crystal field stabilisation energy in their complexes, it is  
 almost entirely an entropy effect.<sup>53</sup> For other transition  
 metal ions there may also be an enthalpy effect ( $\Delta H^\circ$  more  
 negative for chelation), at times quite significant. e.g.,  
 for the aqueous reactions:



The same observed chelate effect arises between  
 poly- and bidentate ligands. For example, for the formation  
 of the aqueous complexes  $[\text{M}(\text{tren})(\text{aq})]^{2+}$ , M=Mn(II)-Cu(II),  
 $\Delta S^\circ$  is positive and 9-20e.u. greater than  $\Delta S^\circ$  for the  
 corresponding  $[\text{M}(\text{en})_2]^{2+}$  ions,<sup>32,40</sup> although the  $-\Delta H^\circ$   
 values are consistently slightly lower (partly due to the  
 presence of a  $3^\circ$  nitrogen donor in tren).

### 3-6 Bonding Theories for Coordination Complexes

#### 3-6.1 The crystal field theory

This theory assumes that the interactions between a  
 metal ion and its surroundings are purely electrostatic and  
 between point charges and dipoles. The metal ion electrons

are considered to remain in essentially metal ion orbitals.

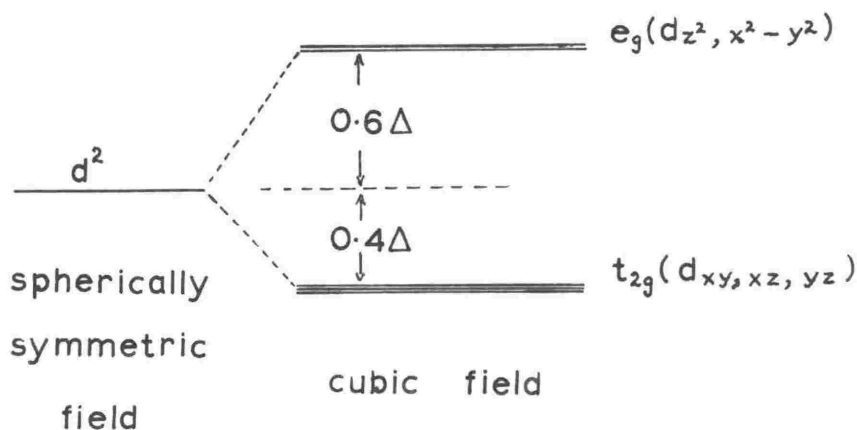
(a) The crystal field stabilisation energy, C.F.S.E.

The approach of say six octahedrally arranged ligand dipoles or charges (cubic field) to a transition metal ion lifts the five-fold degeneracy of the d orbitals. The d electrons can preferentially occupy the lower energy levels formed, with a net gain in stability with respect to the hypothetical ion of the same size and in a spherically symmetrical field. This net gain in stability is the C.F.S.E.

Fig. 3-1 shows the crystal field energy level diagram for a  $d^2$  ion in a cubic field. The crystal field splitting  $\Delta$  equals  $(E_{(e_g)} - E_{(t_{2g})})$  for a cubic field. For any transition metal ion in a cubic field, the C.F.S.E.  $= (0.6n_e - 0.4n_t)$ , where  $n_e$  and  $n_t$  are the numbers of electrons in the  $e_g$  and  $t_{2g}$  orbitals respectively. The value of  $\Delta$  varies with the cubic field component, i.e., with the donor power of the ligand. The relative values of  $\Delta$  for the common ligands are summarised in the spectrochemical series:  $\Delta$  for  $\text{CN}^- \gg \text{NO}_2^- > 1,10\text{-phen} > 2,2'\text{-dipyr} > \text{tren} \approx \text{dien} \approx \text{en} > \text{NH}_3 \approx \text{pyridine} > \text{edta} > \text{H}_2\text{O} > \text{C}_2\text{O}_4^{2-} > \text{HCOO}^- \approx \text{OH}^- > \text{F}^- > \text{NO}_3^- > \text{Cl}^- \approx \text{SCN}^- > \text{Br}^- > \text{I}^-$  (after Fajans and Tsuchida, Ref. 31, p. 266).

For weak fields (poorer donors) the lower and then the upper d orbital energy levels are firstly occupied with electron spins parallel before pairing occurs in the lower energy level (spin-free state). For stronger crystal

Fig. 3-1 The Crystal Field Diagram for a  $d^2$  Ion in a Cubic Field.



fields  $\Delta$  is often large enough to alter the multiplicity of the ground state as found in the gaseous metal ion. This arises if the gain in C.F.S.E. through an electron transferring to a d orbital of lower energy is greater than the electron pairing energy\*  $P$  required for the adoption of a spin-paired state. For example with A=1,10-phenanthroline or 2,2'-dipyridyl,  $[\text{FeA}_2(\text{H}_2\text{O})_2]^{2+}$  is spin-free with four unpaired electrons (paramagnetic) while  $[\text{FeA}_3]^{2+}$  is spin-paired (diamagnetic).<sup>55</sup> A net increase in ligand donor power from the bis to tris complexes, increases the crystal

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\* Electron pairing energies for gaseous ions are obtained from atomic spectra.

field splitting of the d electron energy levels to make  $\Delta > P$ .

For symmetrically 'occupied'  $d^0$  electron configurations ( $\text{Ca}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ),  $d^5$  electron configurations (weak field  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ) and  $d^{10}$  electron configurations ( $\text{Cu}^+$ ,  $\text{Zn}^{2+}$ ), the C.F.S.E.  $= (0.6n_e - 0.4n_t) \Delta = 0$ .

Although a smaller term than the enthalpy of ligation, the C.F.S.E. is often sufficiently significant to determine the structure and/or coordination number of a complex. For example, in a strong ligand field the  $\text{Ni(II)}$  ion may adopt a four-coordinate square planar (spin-paired) configuration; a six-coordinate  $\text{Ni(II)}$  complex would have a higher bonding energy, but this stability would be offset by a lower C.F.S.E. For  $\text{Zn(II)}$  complexes a zero C.F.S.E. term makes inter-ligand repulsion a critical factor determining structure;  $\text{Zn(II)}$  often adopts a tetrahedral coordination configuration although this configuration has a low crystal field strength compared with octahedral or square planar configurations.

(b) The spectroscopic C.F.S.E. ( $\Delta_{\text{spec}}$ ). The energy change  $\Delta$  for an electron transition between the  $e_g$  and  $t_{2g}$  levels in octahedral transition metal complexes can be obtained directly from the visible, near U.V. or near I.R. absorption spectrum ( $\log_{10} \epsilon \approx 0-2$ ), except for  $d^4$  and  $d^9$  ions for which Jahn-Teller distortions must be considered (3-6.1f). This  $\Delta_{\text{spec}}$ , when corrected for electron

pairing energies, is a direct measure of the C.F.S.E.

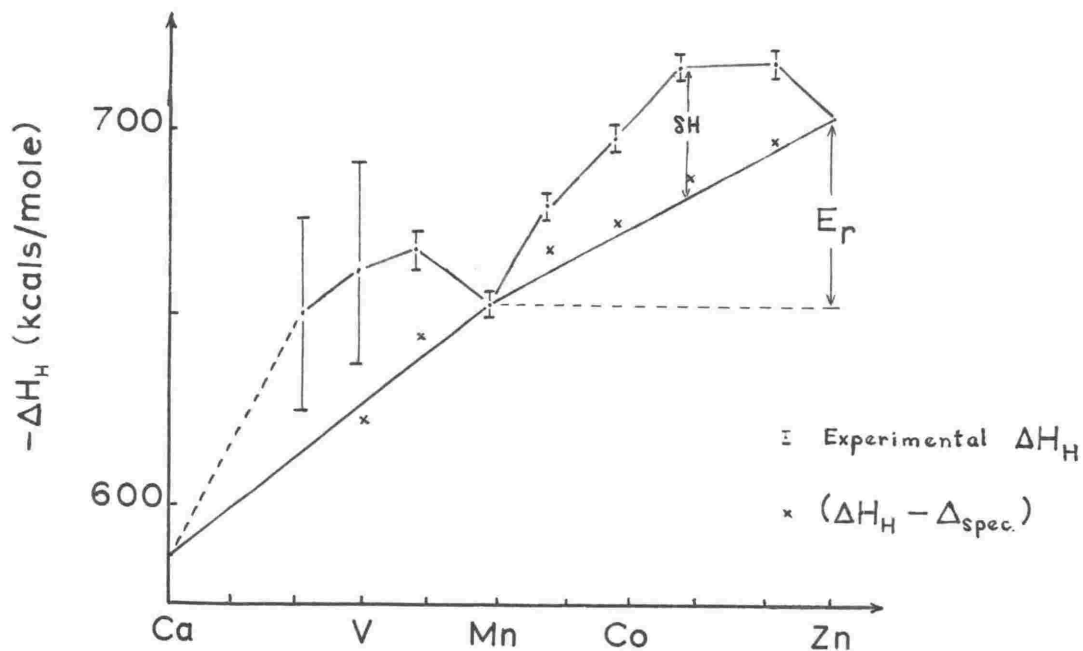
(c) The thermodynamic C.F.S.E. ( $\delta H$ ): This is the enthalpy difference between the  $\Delta H_L$  value observed for a metal ion ligation reaction and that value  $\Delta H_T$  obtained by smooth interpolation of the  $\Delta H_L$  values for Ca(II), Mn(II), and Zn(II).

Ca, Mn and Zn(II) compounds have no C.F.S.E. and the  $\Delta H_L$  values for their formation increase approximately linearly with atomic number. The increase parallels a decrease in ionic radius and an accompanying increase in ionisation energy,  $I_1 + I_2$ .<sup>68</sup> In the absence of crystal field stabilisation, the ligational enthalpies for the ions Ca(II)-Zn(II) would be expected to increase regularly with decreasing ionic radius, and lie on a smooth curve ( $\Delta H_T$ ) through the Ca(II), Mn(II), and Zn(II)  $\Delta H_L$  values. In Fig. 3-2, the  $\Delta H_T$  curve and the heats of hydration  $\Delta H_H$  for the divalent ions of the first-series transition metals are plotted. For each atomic number,  $\delta H = \Delta H_L - \Delta H_T$ .

The crystal field theory does not require that  $-\Delta H_T$  values should lie on a straight line, but that they should increase steadily with decreasing ionic radius. The values ( $\Delta H_L - \Delta_{\text{spec}}$ ) (or e.g., ( $\Delta H_H - \Delta_{\text{spec}}$ ), Fig. 3-2) lie slightly above the interpolated  $\Delta H_T$  values, showing that  $\delta H$  is only an approximate measure of the C.F.S.E. The difference ( $\Delta H_L - \Delta_{\text{spec}}$ ) -  $\Delta H_T$ , has been associated with the small

Fig. 3-2

Hydration Enthalpies for divalent ions of the First Series Transition Metals.



decrease in ionic radius and subsequent increase in  $\Delta H_L$  which accompanies the loss of d orbital degeneracy.<sup>70</sup>

(d) The transition series contraction energy ( $E_r$ )<sup>65</sup>:

For the elements Mn(II) - Zn(II),  $E_r$  is defined by

$$\begin{aligned}
 E_r(\text{Mn(II)-Zn(II)}) &= (\Delta H_L(\text{Zn(II)}) + \Delta H_H(\text{Zn(II)})) - \\
 &\quad (\Delta H_L(\text{Mn(II)}) + \Delta H_H(\text{Mn(II)})) \\
 &= \Delta H_{\text{com}}(\text{Zn(II)}) - \Delta H_{\text{com}}(\text{Mn(II)}) \dots (3-5.2)
 \end{aligned}$$

$E_r(\text{Mn(II)}-\text{Zn(II)})$  is usually in the range  $(55 \pm 10)$  kcal/mole for the coordination of any given number of O- or N- donor ligands (Ref. 63, pp. 431-7), and usually increases slightly with increasing coordinating power of a ligand and with net ligand-field strength in a complex.<sup>63,72</sup>

(e) The Irving-Williams order: When the total spin-quantum number of the divalent metal ion is unaltered by complex formation, the Irving-Williams order of stabilities<sup>62,67</sup>  $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$  is usually followed. The high values for Cu(II) are contributed to by Jahn-Teller distortion.

(f) The Jahn-Teller effect: The Jahn-Teller theorem states that a symmetrical polyatomic molecule in an orbitally degenerate electronic state will distort to a conformation of lower energy (and degeneracy) except when the molecule is linear.<sup>82</sup> This distortion will be larger for a doubly degenerate  $E_g$  state (for example  $t_{2g}^3 e_g^1 (d^4)$  Cr(II), Mn(III);  $t_{2g}^6 e_g^3 (d^9)$  Cu(II)) than for a triply degenerate  $T_{2g}$ , (for example  $t_{2g}^1 (d^1)$  Ti(III);  $t_{2g}^4 e_g^2 (d^6)$  Fe(II)) or  $T_{1g}$  (for example  $t_{2g}^2 (d^2)$  V(III);  $t_{2g}^5 e_g^2 (d^7)$  Co(II)) state.

Because of this effect, the six-fold coordination of ligands around Cr(II), Mn(III) and Cu(II) should be asymmetrical. This has been confirmed by X-ray work.<sup>63,74,75,82</sup>

There is no crystallographic evidence for distortion in triply degenerate molecules. Copper(II) compounds have

four donor atoms coplanar with and relatively close to the metal ion and often two more distant donors above and below the plane. The distortions account for the large C.F.S.E. and ligational enthalpies for compounds of these elements. The relatively high stabilities of Cu(II) complexes are critically dependent upon the tetragonality of the ligand field.<sup>77</sup>

### 3-6.2 The ligand field theory

This is a modification of the C.F. theory to account for small amounts of overlap between ligand and metal ion orbitals. The modifications involve using the parameters of inter-electronic interaction (viz., the spin-orbit coupling constant  $\lambda$  and the Racah parameters B and C) as variable parameters rather than making them equal to the values for the free ion. Values for these parameters can be obtained experimentally from electronic absorption spectra and the amount of covalency (M-L) in a complex estimated by comparing the values for the complex and a free (gaseous) metal ion. With increasing covalency in the metal-ligand bond, the transition metal d electrons became less localised, i.e., their orbitals have increasing ligand orbital character. An ordering of ligands according to their effect upon the parameters for given metal ions gives a series called the Nephelauxetic (cloud expanding) series (after Jorgensen, e.g., Ref. 49).



Satisfactory agreement between experimental ( $\Delta H_L - \Delta_{\text{spec}}$ ) values and predicted ( $\Delta H_T$ ) enthalpies of formation for complex ions of the transition metals appears to justify the interpretation of results in terms of a crystal field or ligand field theory. It is considered that the existence of a crystal field term stabilises transition metal complexes with respect to those of inert gas type ions.

### 3-6.3 The Molecular Orbital Theory

The Molecular Orbital Theory as applied by Orgel<sup>78</sup> to an octahedrally coordinated transition metal ion considers  $\sigma$ -bonding to occur between the six axial ligand orbitals and six metal ion orbitals of suitable symmetry, e.g.,  $4s$ ,  $4p_{x,y,z}$ ,  $3d_{z^2}$ ,  $3d_{x^2-y^2}$ . The combination of twelve atomic orbitals gives twelve molecular orbitals, six bonding and six anti-bonding. The metal orbitals have a lower stability than those of the ligands and therefore make a smaller contribution to the bonding orbitals. The anti-bonding orbitals have a character predominantly that of the metal orbitals. The metal  $e_g$  and  $t_{2g}$  orbitals approximate

to anti-bonding and non-bonding orbitals respectively in the M.O. model (Fig. 3-3a). The metal ion d electrons can occupy either the lower energy non-bonding orbitals and thereby not affect the bond strength, or the anti-bonding orbitals and thereby destabilise the ion with respect to a corresponding inert gas type ion. For a weak field spin free system, the resulting destabilisations in units of  $\Delta$  (Fig. 3-3a) are for  $\text{Ti}^{2+}$ ,  $\text{V}^{3+}$ ;  $\text{Cr}^{2+} - \Delta$ ;  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $-2\Delta$ ;  $\text{Cu}^{2+} - 3\Delta$ ;  $\text{Zn}^{2+} - 4\Delta$ .

Shuit<sup>79</sup> applied the M.O. theory to the hydration enthalpies for Ca(II) - Zn(II) ions,<sup>79a</sup> the lattice energies of some Ca(II) - Zn(II) complexes with oxygen donors<sup>79b</sup> and the heats of formation of some Mn(II) - Zn(II) complexes containing nitrogen donor ligands.<sup>79c</sup>

For cations with inert gas type structure, there is an empirical relationship between hydration enthalpies and the cation ionisation energy  $I = I_1 + I_2$ .<sup>80,81</sup> (for divalent ions)

$$-\Delta H_H = I + C$$

where  $C$  = a constant for cations of equal

charge, = 180kcal/mole for divalent ions.

For the six coordinate hydrates of the ions Ca(II) - Zn(II), Shuit<sup>79a</sup> has shown the following empirical equation to be valid,

$$-\Delta H_H = I + C - n_e \Delta_t$$

Fig. 3-3a

Molecular orbital energy level diagram for an Octahedral complex (diagrammatic).<sup>69</sup>

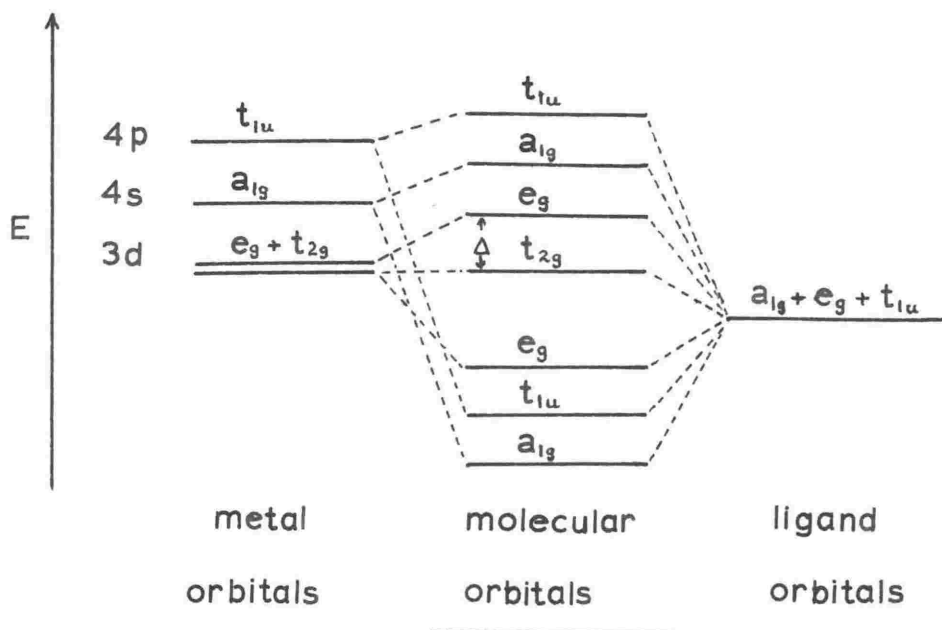
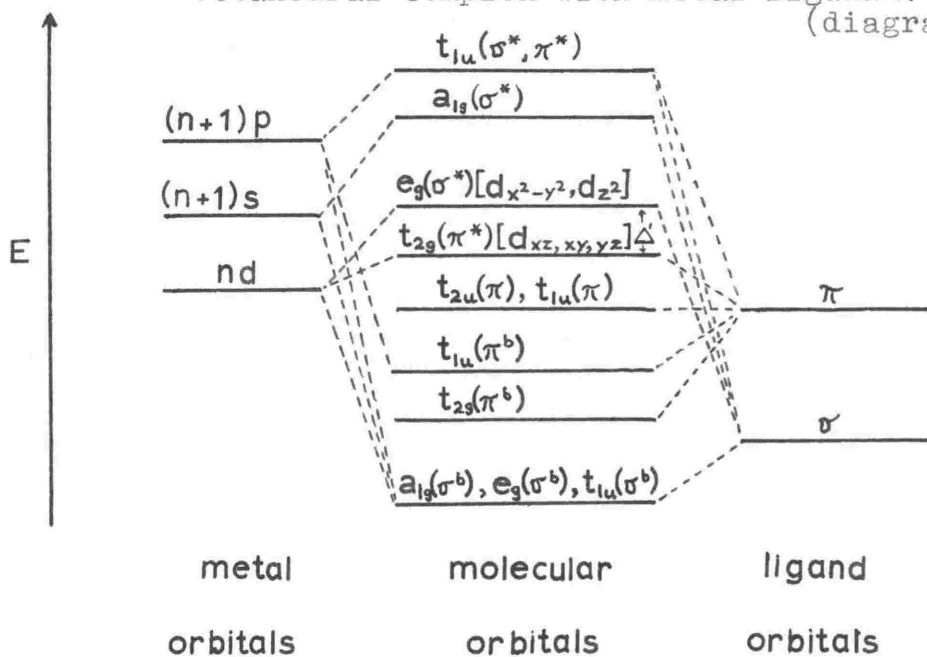


Fig. 3-3b

Molecular orbital energy level diagram for an Octahedral complex with metal-ligand  $\pi$ -bonding (diagrammatic).<sup>83</sup>



where  $n_e$  = the number of d electrons in anti-bonding  $e_g$  orbitals

$\Delta_t$  = the thermodynamic field splitting factor,  
found to be approximately =  $\Delta_{\text{spec}}$ .

This equation illustrated that the M.O. theory gives a satisfactory interpretation of the relative  $\Delta H_H$  for Ca(II) - Zn(II). A modified equation<sup>79a</sup> accounted for the stabilisation of Cu and Cr as  $4s'$  states and for Jahn-Teller distortion in divalent Cr and Cu compounds:

$$-\Delta H_H = I_s + C - n_e^l \Delta_{t(1)} - n_e^h \Delta_{t(h)}$$

where  $I_s$  = the electron affinity of the ion for a pair of s electrons.

$\Delta_{t(1)}$  = the energy difference between the 'lower  $e_g$  level' and the  $t_{2g}$  level.

$\Delta_{t(h)}$  = the energy difference between the 'higher  $e_g$  level' and the  $t_{2g}$  level.

$n_e^l$  = the number of electrons in the 'lower  $e_g$  level'.

$n_e^h$  = the number of electrons in the 'higher  $e_g$  level'.

An extension to N- donor complexes also considered the effects of 'acceptor' and 'donor' pi-bonding upon the spectroscopic field splitting factor  $\Delta'$  (Fig. 3-3b).

CHAPTER FOUR  
THEORY OF ANALYSIS

4-1 The Measurement of Formation Constants

Concentration equilibrium constants  $K_c$  for the metal ion ligation and the neutralisation of some carbon-substituted ethylenediamines have been determined at a series of ionic strengths (0.04 to 0.35m/l).  $\Delta G^\circ$  values were derived from these constants using equation 2-9. All measurements were made at  $25.00 \pm 0.01^\circ\text{C}$ .

$K_c$  values were calculated from experimental data by Bjerrum's method of successive substitution.<sup>1,124</sup>

4-1.1 The protonation of diamines

For the equilibria 3-4 Bjerrum<sup>1</sup> defined 'the degree of formation' for the total system,

$\bar{n}$  = the average number of protons attached per ligand molecule.

=  $\frac{\text{the total concentration of } H^+ \text{ bound to the ligand}}{\text{the total concentration of ligand in the system}}$

=  $\frac{T_H - [H]}{T_L}$ , where  $[H]$  is the equilibrium hydrogen ion concentration,

$$= \frac{[HL] + 2[H_2L]}{[L] + [HL] + [H_2L]} = \frac{K_{c_1}[H][L] + 2K_{c_1}K_{c_2}[H]^2[L]}{[L] + K_{c_1}[H][L] + K_{c_1}K_{c_2}[H]^2[L]}$$

$$= \frac{K_{c_1} [H] + 2K_{c_1} K_{c_2} [H]^2}{1 + K_{c_1} [H] + K_{c_1} K_{c_2} [H]^2}$$

By rearrangement,

$$K_{c_1} = \frac{1}{[H]} \left( \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n})[H]K_{c_2}} \right) \dots\dots\dots 4-1$$

$$\text{and } K_{c_2} = \frac{1}{[H]} \left( \frac{(\bar{n}-1) + \frac{\bar{n}}{[H]K_{c_1}}}{(2-\bar{n})} \right) \dots\dots\dots 4-2$$

If it is considered that to a first approximation the  $n^{\text{th}}$  step-wise equilibrium reaction does not occur until the  $(n-1)^{\text{th}}$  reaction has gone to completion, then

$$K_{c_1} = \frac{1}{[H]\bar{n}=0.5} \quad \text{and} \quad K_{c_2} = \frac{1}{[H]\bar{n}=1.5}$$

and in the general case,

$$K_{c_n} = \frac{1}{[A]\bar{n}=n-0.5} \quad \text{for any coordinating species A..4-3}$$

However, these relationships are only approximate because they ignore the simultaneous existence of more than one equilibrium reaction in this system. Substituting these approximate  $K_{c_1}$  and  $K_{c_2}$  values into the right hand side of equations 4-1 and 4-2, and equating 4-1 for  $\bar{n}=0.5$ ,  $[H]\bar{n}=0.5$ , and 4-2 for  $\bar{n}=1.5$ ,  $[H]\bar{n}=1.5$ , new improved values  $K'_{c_1}$  and  $K'_{c_2}$  are obtained:

$$K'_{c_1} = \frac{1}{[H] \bar{n}=0.5} \left( \frac{1}{1 + 3K_{c_2} [H] \bar{n}=0.5} \right) \dots\dots\dots 4-4$$

and

$$K'_{c_2} = \frac{1}{[H] \bar{n}=1.5} \left( 1 + \frac{3}{K_{c_1} [H] \bar{n}=1.5} \right) \dots\dots\dots 4-5$$

If the constants are not too close together, say  $\log(K_{c_1}/K_{c_2}) > 2$  the term in the bracket [ ] converges rapidly. Alternatively, the improved  $K_c$  values may be resubstituted into the right hand side of equations 4-4 and 4-5, and the process of successive substitution continued until invariant  $K_c$  values result.

The required values of  $[H] \bar{n}=n-0.5$  were obtained by graphical interpolation from directly measured (potentiometric) hydrogen ion concentrations for ligand- $HClO_4$  mixtures of known  $\bar{n}$ . For protonation of the carbon-substituted ethylenediamines the equilibrium hydrogen ion concentration was  $\ll T_H$ , making  $\bar{n} \approx T_H/T_L$ .

Extrapolations of  $K_c$  to zero ionic strength: These were done to obtain values of  $\log K_a = -\Delta G^0/RT$  (equation 2-9). Linear relationships were obtained by plotting  $\log K_{c_1}$  against  $I$  and  $(\log K_{c_2} - I^{1/2}/(1+I^{1/2}))$  against  $I$ . Expressing  $f_i$  by the Davies equation (equation 3-5) in which  $\beta$  is an empirical constant, then to a first approximation,

$$\log K_{a_1} = \log K_{c_1} + \beta' I \quad (\text{from equations 2-5, 2-6})$$

$$\text{and} \quad \log K_{a_1} = \lim_{(I \rightarrow 0)} (\log K_{c_1}) \dots\dots\dots 4-6$$

Similarly,  $\log K_{a_2} = \log K_{c_2} - \frac{2AI^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + \beta''I$

and  $\log K_{a_2} = \lim_{(I \rightarrow 0)} \left( \log K_{c_2} - \frac{2AI^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} \right) \dots\dots\dots 4-7$

It was found that  $\beta'' \doteq 0$ .

#### 4-1.2 The step-wise formation of metal ion coordination complexes

For  $n$  successive step-wise equilibrium reactions (equations 3-1, 3-2),

$\bar{n}$  = the average number of ligands  $L$  coordinated per metal ion  $M$ .

= (the total concentration of  $L$  bound to  $M$ )/

(the total concentration of  $M$  in the system)

$$= \frac{T_L - [L]}{T_M}, \text{ where } [L] \text{ is the equilibrium 'free' ligand concentration}$$

(or in the case where the ligand is a weak acid or the conjugate base of a weak acid,

$$\bar{n} = (T_L - [L] - [HL] \dots\dots\dots [H_n L]) / T_M, \text{ where } L \text{ is } n\text{-basic})$$

$$= [M] (K_{c_I} [L] + 2K_{c_I} K_{c_{II}} [L]^2 + \dots\dots\dots + nK_{c_I} \dots K_{c_N} [L]^N)$$

$$[M] (1 + K_{c_I} [L] + K_{c_I} K_{c_{II}} [L]^2 + \dots\dots\dots + K_{c_I} \dots K_{c_N} [L]^N)$$

(from equations 3-2, 3-3)

$$\text{where } [M] = [M(H_2O)_x^{Z+}] \text{ etc.}$$

For the case when  $n = 3$  it follows, on rearrangement, that

$$K_{c_I} = \frac{1}{[L]} \left( \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n})K_{c_{II}}[L] + (3-\bar{n})K_{c_{II}} \cdot K_{c_{III}}[L]^2} \right) \dots 4-8$$



$$K_{c_{II}} = \frac{1}{[L]} \left( \frac{(\bar{n}-1) + \frac{\bar{n}}{K_{c_I}[L]}}{(2-\bar{n}) + (3-\bar{n})K_{c_{III}}[L]} \right) \dots\dots\dots 4-9$$

and

$$K_{c_{III}} = \frac{1}{[L]} \left( \frac{(\bar{n}-2) + \frac{(\bar{n}-1)}{K_{c_{II}}[L]} + \frac{\bar{n}}{K_{c_I} \cdot K_{c_{II}}[L]^2}}{(3-\bar{n})} \right) \dots\dots\dots 4-10$$

Analogous to the protonation reactions (4-1.1), to a first approximation,  $K_{c_N} = \frac{1}{[L]\bar{n}=N-0.5}$

and improved values of the formation constants ( $K'_{c_N}$ ) can be obtained from:

$$K'_{c_I} = \frac{1}{[L]\bar{n}=0.5} \left( \frac{1}{1 + 3K_{c_{II}}[L]\bar{n}=0.5 + 5K_{c_{II}}K_{c_{III}}[L]^2\bar{n}=0.5} \right) \dots\dots\dots 4-11$$

$$K'_{c_{II}} = \frac{1}{[L]\bar{n}=1.5} \left( \frac{1 + \frac{3}{K_{c_I}[L]\bar{n}=1.5}}{1 + 3K_{c_{III}}[L]\bar{n}=1.5} \right) \dots\dots\dots 4-12$$

and

$$K'_{c_{III}} = \frac{1}{[L]\bar{n}=2.5} \left( 1 + \frac{3}{K_{c_{II}}[L]\bar{n}=2.5} + \frac{5}{K_{c_I}K_{c_{II}}[L]^2\bar{n}=2.5} \right) \dots\dots\dots 4-13$$

in which  $K_{c_I}$ ,  $K_{c_{II}}$ , and  $K_{c_{III}}$  are the approximate  $K_{c_N}$  values obtained from the formation curve. Constant

$K_{c_N}$  were obtained by successive substitution of improved

values in these equations. The bracketed terms converge rapidly when  $\log(K_{c_{N-1}}/K_{c_N}) > 2$ .

Values of  $[L]$  and the formation function  $\bar{n} = (T_L - [L] - [HL] - [H_2L])/T_M$ , were obtained by measuring  $[H]$  for mixtures of varying composition of metal perchlorate, ligand and  $HClO_4$ , and by using the equations:

$$T_H = [H] + [HL] + 2[H_2L] \quad (\text{equation 3-4})$$

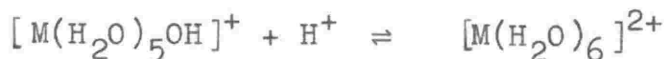
$$T_H - [H] = [L] (K_{c_1} [H] + 2K_{c_1} K_{c_2} [H]^2)$$

where  $K_{c_1} = [HL]/[H][L]$  and  $K_{c_2} = [H_2L]/[HL][H]$ .

The  $K_{c_1}$  and  $K_{c_2}$  values used were those obtained experimentally at the corresponding ionic strengths.

#### 4-1.3 Solution composition:

For metal ion complex formation,  $T_H$  was less than  $0.07T_L$  to minimise the formation of protonated coordination complexes,  $[M(LH^+)(aq)]^+$ , etc. A known concentration of  $HClO_4(T_H)$  was added to each solution so that equation 3-4 could be utilised ( $T_H = [H] + [HL] + 2[H_2L]$ ). For solutions with  $\bar{n} < 1$ , acid buffering suppressed hydrolysis of the metal aquo ions:



For all systems, solutions were made up at ionic strengths 0.04, 0.10, 0.15 and 0.20m/l.  $NaClO_4$  and  $Ba(ClO_4)_2$  were used as inert electrolytes. The

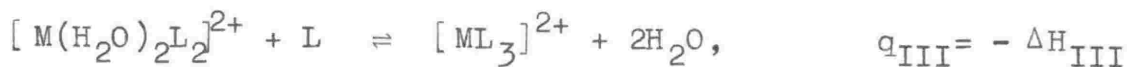
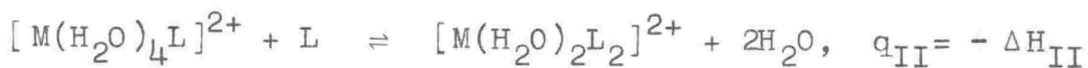
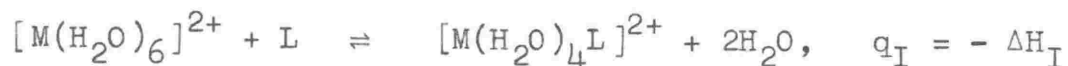
concentrations of  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$  were varied to keep the total ionic strengths of monovalent perchlorates ( $\text{HClO}_4$ ,  $\text{L}(\text{HClO}_4)$ ,  $\text{NaClO}_4$ ) and divalent perchlorates ( $\text{L}(\text{HClO}_4)_2$ ,  $\text{Ba}(\text{ClO}_4)_2$ ,  $[\text{ML}_n(\text{aq})](\text{ClO}_4)_2$ ) in the ratio 2:1 in all solutions. For  $I=0.20\text{m/l}$  separate solutions were made up for each  $\bar{n}$  studied. (This gave a higher inherent accuracy than a titration method.) For each  $\bar{n}$ , solutions at lower ionic strengths were obtained by dilution with distilled water. For the 1-methyl 1,2-diaminoethane (pn)- $\text{HClO}_4$  and pn-M( $\text{ClO}_4$ )<sub>2</sub> systems, solutions with  $I=0.35\text{m/l}$  were also used.

For each system a plot of  $\bar{n}$  vs.  $[\text{L}]$  (metal ligation) or  $[\text{H}]$  (ligand protonation) was made at each ionic strength (a 'formation' curve). Values of  $[\text{L}]\bar{n} = n-0.5$  or  $[\text{H}]\bar{n} = n-0.5$  were obtained by interpolation if necessary. For each equilibrium step studied several solutions (4 to 7) were made up within the composition range  $\bar{n} = (n-0.5)+0.06$  to  $\bar{n} = (n-0.5)-0.06$ . e.g., for  $\text{H}+\text{L} \rightleftharpoons \text{HL}$ , solutions in the range  $\bar{n} = 0.44$  to  $0.56$ ; for  $\text{HL} + \text{H} \rightleftharpoons \text{H}_2\text{L}$ , solutions in the range  $\bar{n} = 1.44$  to  $1.56$ .

#### 4-2 The Measurement of Step-wise Enthalpy Changes

Enthalpy changes were measured calorimetrically.

For each equilibrium step in an aqueous complex formation reaction there is a corresponding enthalpy change, e.g.,



$$\text{where } \Delta H_N = \bar{H}_{[ML_N]^{2+}} + 2\bar{H}_{H_2O} - \bar{H}_L - \bar{H}_{[ML_{N-1}]^{2+}}$$

For a given value of  $\bar{n}$ , the measured heat of ligation

( $-q$  calories per mole of metal ions) will be the sum of the enthalpy terms for the conversion of one mole of  $[M(H_2O)_6]^{2+}$  to a mixture of  $[ML_3]^{2+}$ ,  $[M(H_2O)_2L_2]^{2+}$ ,  $[M(H_2O)_4L]^{2+}$ , and  $[M(H_2O)_6]^{2+}$ . If  $x$ ,  $y$ , and  $z$  are the fractions of  $T_M$  existing as  $[M(H_2O)_4L]^{2+}$ ,  $[M(H_2O)_2L_2]^{2+}$  and  $[ML_3]^{2+}$  respectively in the final equilibrium mixture, then

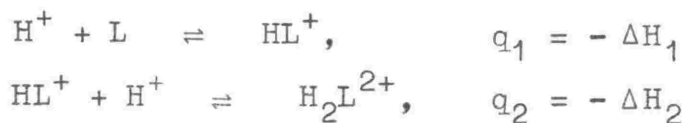
$$\begin{aligned} -q &= (x+y+z) \Delta H_I + (y+z) \Delta H_{II} + z \Delta H_{III} \\ &= a_1 \Delta H_I + b_1 \Delta H_{II} + c_1 \Delta H_{III} \quad \dots\dots\dots 4-14 \end{aligned}$$

where  $a_1$  is the degree of formation of  $[M(H_2O)_4L]^{2+}$ , etc. Addition of a large excess of ligand converted virtually all of  $[M(H_2O)_6]^{2+}$  to  $[ML_3]^{2+}$ ,

$$-q = \Delta H_I + \Delta H_{II} + \Delta H_{III} = \Delta H_{I-III} \text{ (by definition).}$$

The  $\Delta H_N$  values were obtained by the solution of  $N$  (here three) simultaneous equations like 4-14, each corresponding to a different value of  $\bar{n}$ , i.e., each with different values of  $a$ ,  $b$ ,  $c$ , and  $q$ .

For the diamine protonation reactions



$$\text{and} \quad -q' = a'_1 \Delta H_1 + b'_1 \Delta H_2 \dots\dots\dots 4-15$$

where  $a'_1$  and  $b'_1$  are the degrees of formation of  $\text{HL}^+$  and  $\text{H}_2\text{L}^{2+}$  respectively.

To account for the presence of acid ( $\text{HClO}_4$ ) in the metal ion ligation reactions, equation 4-14 was modified to

$$-q_2 = a_2 \Delta H_{\text{I}} + b_2 \Delta H_{\text{II}} + c_2 \Delta H_{\text{III}} + a'_2 \Delta H_1 + b'_2 \Delta H_2 \dots\dots 4-16$$

The numerical value of  $(a'_2 \Delta H_1 + b'_2 \Delta H_2)$  was calculated from previously obtained  $\Delta H_1$  and  $\Delta H_2$  values.

To minimise the effect of experimental errors in the solution of the simultaneous equations, values of  $\bar{n} \leq 1.0$ , approximately 1.8-2.2 and 2.8-3.0 were chosen. These  $\bar{n}$  gave a wide spread of values for  $q$ ,  $b$ , and  $c$ . The errors in  $\Delta H_2$  were greater than in  $\Delta H_1$ , and in  $\Delta H_{\text{III}} > \Delta H_{\text{II}} > \Delta H_{\text{I}}$ .

#### 4-2.1 Analysis of calorimeter reaction mixtures.

Each resultant reaction mixture was analysed potentiometrically to determine its equilibrium composition.

(a) Ligand neutralisation: The coefficients  $a'_1$  and  $b'_1$  in equation 4-15 are related to the formation constants  $K_{c_1}$  and  $K_{c_2}$ , and the equilibrium hydrogen ion concentration  $[\text{H}]$ .

$$b'_1 = [\text{H}_2\text{L}] / ([\text{H}_2\text{L}] + [\text{HL}] + [\text{L}]) = [\text{H}_2\text{L}] / T_{\text{L}}$$

$$a'_1 = ([\text{H}_2\text{L}] + [\text{HL}]) / T_{\text{L}}.$$

$$\text{But } [\text{HL}] = K_{c_1} [\text{H}][\text{L}]$$

$$[\text{H}_2\text{L}] = K_{c_2} [\text{HL}][\text{H}]$$

and

$$T_H - [\text{H}] = [\text{L}](K_{c_1} [\text{H}] + 2K_{c_1} K_{c_2} [\text{H}]^2) \quad (\text{from equation 3-4})$$

and from these relationships we obtain

$$a'_1 = \frac{(1 + K_{c_2} [\text{H}])(T_H - [\text{H}])}{(1 + 2K_{c_2} [\text{H}]) T_L} \dots\dots\dots 4-17$$

and

$$b'_1 = \frac{K_{c_2} [\text{H}](T_H - [\text{H}])}{(1 + 2K_{c_2} [\text{H}]) T_L} \dots\dots\dots 4-18$$

From the relationships 4-15, 4-17, and 4-18 it is seen that the accuracy of the  $\Delta H_n$  values is governed by the accuracy both of the  $K_{c_n}$  values and of the equilibrium hydrogen ion concentration  $[\text{H}]$  determined for each resultant reaction mixture.

(b) Metal ion ligation reactions: The values of  $a$ ,  $b$ , and  $c$  in equations 4-14 and 4-16 are related  $[\text{L}]$ ,  $K_{c_I}$ ,  $K_{c_{II}}$  and  $K_{c_{III}}$  and are limited in reliability by the accuracies of these quantities. From equations 3-1, 3-2, and 3-3

$$a = (1 + K_{c_{II}} [\text{L}] + K_{c_{II}} K_{c_{III}} [\text{L}]^2) / D$$

$$b = (K_{c_{II}} [\text{L}] + K_{c_{II}} K_{c_{III}} [\text{L}]^2) / D$$

$$\text{and } c = (K_{c_{II}} K_{c_{III}} [\text{L}]^2) / D$$

$$\text{where } D = \frac{1}{K_{c_I} [L]} + 1 + K_{c_{II}} [L] + K_{c_{II}} K_{c_{III}} [L]^2 \dots 4-19$$

[L] was obtained from the measured [H] by using equations 3-4.

The accuracy of the experimentally determined coefficients  $a_2$ ,  $b_2$ ,  $c_2$ , and  $a'_2$  in equation 4-16 was checked by their substitution in the following equation:

$$\begin{aligned} T_L &= T_M(a_2 + b_2 + c_2) + T_L a'_2 + [L] \dots 4-20 \\ &= [ML] + 2 [ML_2] + 3 [ML_3] + [H_2L] + [HL] + [L] \end{aligned}$$

An analysis was considered unsatisfactory if the addition of the terms on the right hand side of equation 4-20 did not give a value in the range  $0.97T_L$  to  $1.03T_L$ , i.e., if the 'total' error was  $> \pm 3\%$ . Generally an error of  $< 1.5\%$  was obtained.

#### 4-2.2 Conversion of $\Delta H_n$ to $\Delta H_n^0$

The experimental  $\Delta H_n$  values at various ionic strengths I were corrected to  $\Delta H_n^0$  values (2-2.1) by using equation 2-17. It was assumed that the activity coefficients for the aqueous species  $[M(H_2O)_6](ClO_4)_2$ ,  $[M(H_2O)_4L](ClO_4)_2$ ,  $[M(H_2O)_2L_2](ClO_4)_2$ , and  $[ML_3](ClO_4)_2$  were all equal, and therefore that  $\Delta H_I = \Delta H_I^0$ ,  $\Delta H_{II} = \Delta H_{II}^0$ , and  $\Delta H_{III} = \Delta H_{III}^0$ . By using the approximate form of the Debye-Hückel equation for hypothetical ionic activity coefficients

$$-\log f_i = \frac{Az_i^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}}$$

it was assumed that

$$\log f_{H^+} \approx \log f_{HL^+} \approx 0.25 \log f_{H_2L^{2+}}$$

and therefore

$$\Delta H_1 \approx \Delta H_1^0$$

and

$$\Delta H_2 = \Delta H_2^0 + 8.1 \times 10^2 \times \frac{2AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \dots\dots\dots 4-21$$

for the ligand protonation reactions.



## CHAPTER FIVE

### EXPERIMENTAL

#### 5-1 The Direct Potentiometric Determination of Hydrogen Ion Concentrations

Introduction: The system used in equilibrium measurements had the composition: ligand( $\text{RCH}(\text{NH}_2)\text{CH}_2\text{NH}_2$ );  $\text{NaClO}_4$ ,  $\text{HClO}_4$ ;  $\text{M}(\text{ClO}_4)_2$ ,  $\text{Ba}(\text{ClO}_4)_2$ . The concentrations of  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$  were varied to keep the total ionic strengths of mono- and divalent perchlorates in the ratio 2:1. In determining the equilibrium concentrations of components in such acid/base mixtures it is generally necessary to experimentally determine the equilibrium hydrogen ion concentration (see 3-2.2). Potentiometric analysis of these solutions generally gives acidities in terms of hydrogen ion activities, making it necessary to use empirical activity coefficients to obtain the hydrogen ion concentration (3-2.2). In most cases the coefficients used have been those derived strictly for very dilute solutions of pure electrolytes. Their use for mixed electrolytes at higher ionic strengths introduces unnecessary errors when it is possible to measure hydrogen ion concentrations directly.

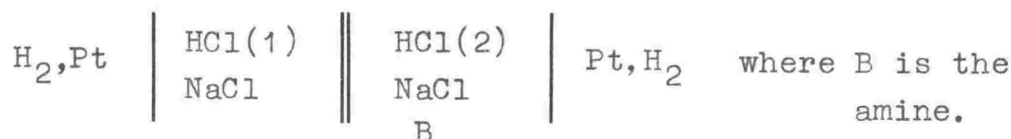
In this work a Glass electrode-Calomel electrode system was rigorously calibrated to give a direct measure of hydrogen ion concentrations rather than activities. To

do this it was necessary to prepare buffer solutions of known  $[H^+]$ . This required accurate  $K_c$  values (e.g.,  $K_c = [BH^+]/[H^+][B]$  where B is a base) at given ionic strengths.

Suitable  $K_c$  values had been determined by Pinsent and Everett.<sup>9</sup> They measured the equilibrium constants for the protonation of 1,2-diaminoethane(en) and 1,2-diaminohexane. The equilibria for en are:



The cell used was:



The ionic strength was kept equal and constant in each half-cell. This was assumed to make the hypothetical hydrogen ion activity coefficients equal for each electrode.

$$\text{the e.m.f, } E = -\frac{RT}{F} \ln \frac{a_{H^+(1)}}{a_{H^+(2)}} = -\frac{RT}{F} \ln \frac{[H^+(1)]}{[H^+(2)]}$$

Knowing  $[H^+(1)]$ , then  $[H^+(2)]$  was calculated from the cell e.m.f. This led to accurate ( $\pm 0.5\%$ ) concentration equilibrium constants  $K_c$  for the buffer systems at ionic strengths in the range 0.07 to 0.30m/l.

Assumptions made in this work: For the equilibrium 5-1,  $K_c$  is related to the thermodynamic equilibrium constant  $K_a$  by

$$K_{a_1} = K_{c_1} \cdot (f_{\text{enHCl}})^{\frac{1}{2}} / (f_{\text{en}})(f_{\text{HCl}})^{\frac{1}{2}}$$

Pinsent and Everett's<sup>9</sup>  $K_{c_1}$  values were invariant with composition at constant ionic strength, showing that Harned and Owen's rule<sup>114</sup> is applicable in this multi-component system;

$$\text{i.e., } \log \frac{f_A}{f_B} = \log \frac{f_A^0}{f_B^0} - a_{12}I, \quad \text{where } f_A^0 \text{ is the}$$

activity coefficient of A in a pure electrolyte system of constant total molality I, and

$$a_{12} = [\partial \log(f_A/f_B) / \partial T]_T.$$

This implies that for the buffer system 5-1,  $(f_{\text{enHCl}})/(f_{\text{HCl}})$  is constant at constant temperature and constant total I.

(It was assumed that  $f_{\text{en}}=1$ , independent of composition and of ionic strength within the ionic strength range studied.)

Therefore the ratio of activity coefficients for this system is independent of composition at constant total I.

Pinsent and Everett<sup>9</sup> also found that  $K_{c_2} = [\text{enH}_2^{2+}] / [\text{H}^+][\text{enH}^+]$  was independent of composition at constant total I.

In this work it was assumed that the  $K_c$  values would be constant for a multi-component system involving perchlorates instead of chlorides; i.e., the  $K_c$  values were assumed independent of solution composition and of the anion at constant total ionic strength. Using these  $K_c$  values interpolated to 25°C and to desired ionic strengths (Table 5-1), the equilibrium hydrogen ion concentrations for

TABLE 5-1

(From the data of Pinsent and Everett<sup>9</sup>)

Concentration equilibrium constants for the step-wise  
protonation of 1,2-diaminoethane at 25°C

<u>Ionic strength, m/l</u>	<u><math>K_{c_1} \cdot 10^{-9} \text{ l m}^{-1}</math></u>	<u><math>K_{c_2} \cdot 10^{-7} \text{ l m}^{-1}</math></u>
0.350	10.8	1.83
0.200	9.93	1.54
0.150	9.35	1.41
0.100	9.12	1.28
0.040	8.67	1.07

en/ $\text{HClO}_4$  buffer systems were found by solving the cubic:

$$K_{c_1} \cdot K_{c_2} \cdot [\text{H}^+]^3 + (2K_{c_1} \cdot K_{c_2} \cdot T_L + K_{c_1} \cdot K_{c_2} T_H) [\text{H}^+]^2 + (K_{c_1} T_L + 1 - K_{c_1} T_H) [\text{H}^+] - T_H = 0$$

This cubic was derived from equations 3-4 and

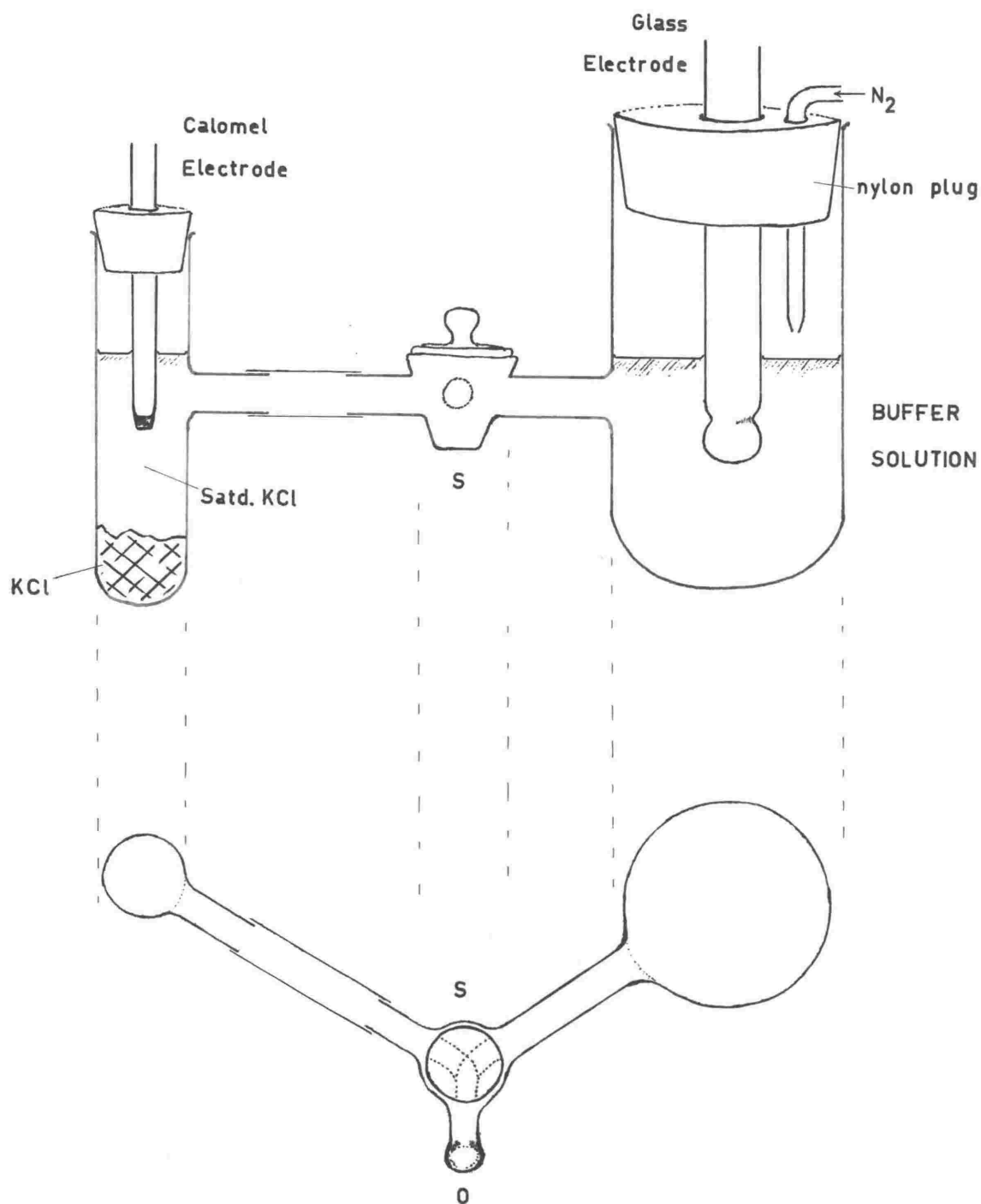
$$T_L = [\text{L}] + [\text{HL}] + [\text{H}_2\text{L}]$$

Experimental: A "Radiometer 22R" pH meter was used with Calomel reference electrode (Radiometer, type K401) and Beckman General Purpose Glass electrode (Hg internals, type 40495). Fluctuations in the main's voltage supply to the meter were suppressed by using a constant voltage transformer. The cell consisted of two compartments, one containing the Calomel electrode in saturated KCl solution, the other the buffer or 'test' solution and Glass electrode. (Fig. 5-1) Electrical contact between the two solutions was made via a non-greased stopcock (S). To bring the 'test' and KCl solutions in to contact at the stopcock, a little of each solution was run through the stopcock to the outlet (O). The use of a stopcock is essential when using a Calomel reference electrode with saturated KCl in solutions of low ionic strength. Both solutions were at  $25.00 \pm 0.01^\circ\text{C}$ .

The sensitivity of the meter reading was increased to  $\pm 0.0005$  pH units by connecting to the meter recorder output a potential divider (200:300  $\Omega$ ) and a PYE potentiometer with a Tinsley Galvanometer (Type AS4/45; 540  $\Omega$ , 2000mm.

FIG. 5-1.

CELL FOR pH MEASUREMENTS.



per microamp deflection) as null-point indicator. The stability was  $\pm 0.001$  pH and the reproducibility  $\pm 0.003$  pH. The magnitude of the reproducibility was mainly due to variations in the liquid junction potential. Reproducibility of this potential was improved by frequent grinding of the stop-cock with fine carborundum. Although the solubility product of  $\text{KClO}_4$  was exceeded at the stop-cock when the KCl and perchlorate solutions were mixed, there was no evidence of its precipitation.

Results: Fig. 5-2 gives the electrode calibration curve for ethylenediamine/ $\text{HClO}_4$  buffers in  $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  media. The data is given in the last two columns of Table 5-2. The values on the voltage axis are proportional to the meter reading (i.e., to  $-\log_{10} a_{\text{H}^+}$ ), and corrected to the scale reading  $V = 1.0700 \text{ v. abs.}$  for 0.05M potassium hydrogen phthalate buffer. The  $-\log_{10} [\text{H}^+] = p[\text{H}^+]$  values were calculated from the data of Pinsent and Everett.<sup>9</sup> Daily variations in the asymmetry potential of the Glass electrode were small and were accounted for by 'zeroing' the instrument with a 0.05M potassium hydrogen phthalate buffer before each series of measurements.

Assuming that the electrode system obeyed the Nerast equation,  $E = E_{\text{calomel}} + 0.0591 p_{\text{H}^+}$ , for the standard phthalate and borate buffers, then the calibration curve was found to obey  $E = \text{const.} + 0.0598 p[\text{H}^+]$ , where 0.0598 is the 'average slope' of the slightly S-shaped calibration curve.

FIG. 5-2

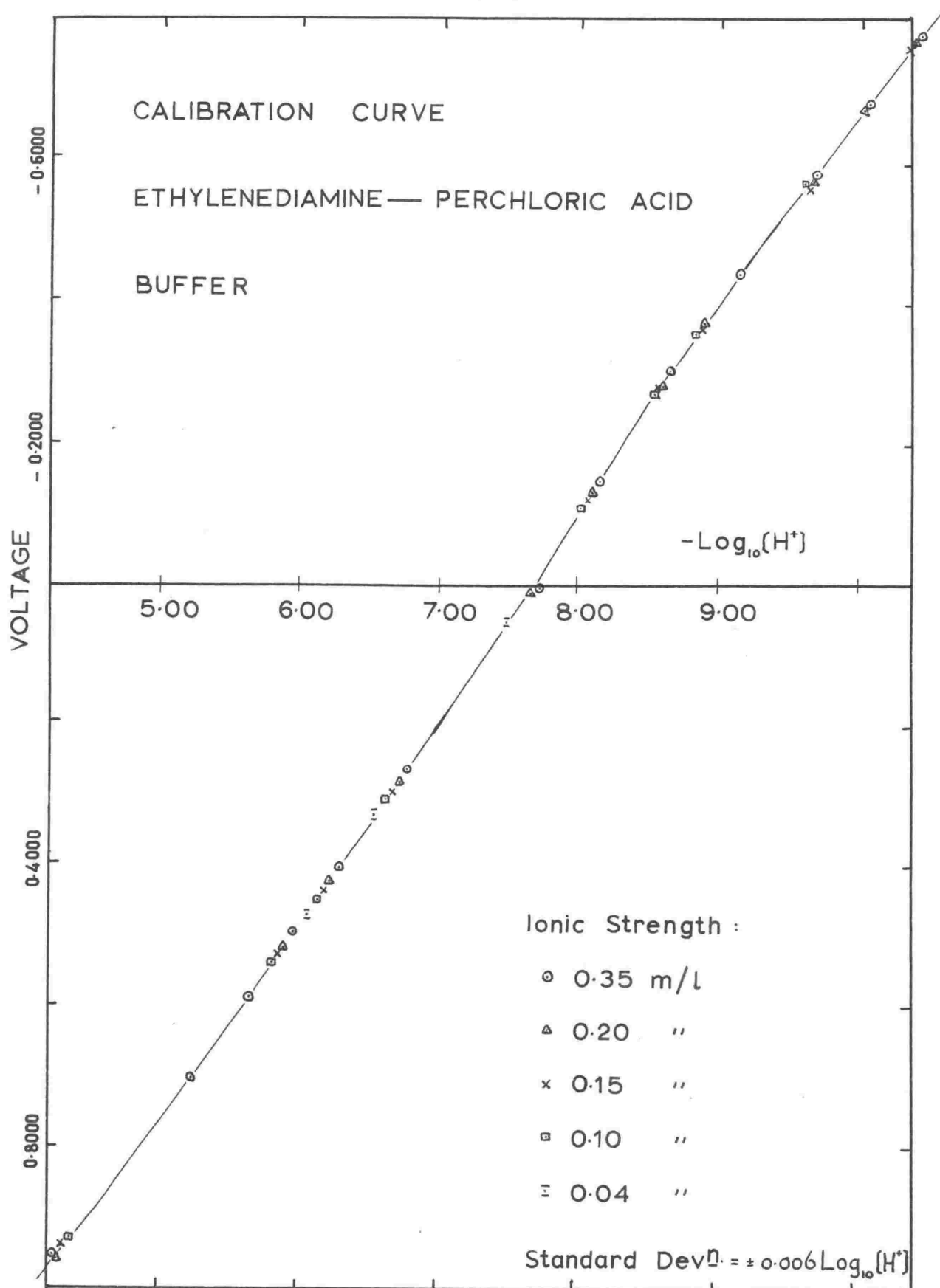




TABLE 5-2

Equilibrium hydrogen ion concentrations ( $p[H]$ ) for ethylene-diamine- $HClO_4$  buffers in  $Ba(ClO_4)_2/NaClO_4$  media,  $25.0^\circ C$

Ionic strength m/l	Total[ $HClO_4$ ] ( $T_H$ ) m/l	Total[en] ( $T_L$ ) m/l	$p[H^+]$ eqbm. (calc)	$V_{corr} \pm 0.0005 v.$ ( $\propto pa_{H^+}$ )
0.350	0.1000	0.0500	4.278	0.9602
"	0.0995	"	5.263	0.7081
"	0.09875	"	5.664	0.5939
"	0.0975	"	5.976	0.5012
"	0.0950	"	6.300	0.4082
"	0.0875	"	6.776	0.2694
"	0.0625	"	7.721	-0.0076
"	0.0550	"	8.150	-0.1450
"	0.0500	"	8.644	-0.3025
"	0.0450	"	9.137	-0.4406
"	0.0350	"	9.671	-0.5852
"	0.0250	"	10.037	-0.6851
"	0.0150	"	10.402	-0.7855
0.200	0.0800	0.0400	4.293	0.9625
"	0.0780	"	5.911	0.5252
"	0.0760	"	6.234	0.4300
"	0.0700	"	6.711	0.2897
"	0.0500	"	7.656	0.0133
"	0.0440	"	8.087	-0.1311
"	0.0400	"	8.593	-0.2800
"	0.0380	"	8.875	-0.3699

Ionic strength	Total[ $\text{HClO}_4$ ] ( $T_H$ ) m/l	Total[en] ( $T_L$ ) m/l	$p[H^+]$ eqbm. (calc)	$V_{\text{corr}} \pm 0.0005 \text{ v.}$ ( $\propto p_{a_{H^+}}$ )
0.200	0.0280	0.0400	9.642	-0.5723
"	0.0200	"	10.000	-0.6764
"	0.0120	"	10.365	-0.7785
0.150	0.0600	0.0300	4.337	0.9487
"	0.0585	"	5.872	0.5344
"	0.0570	"	6.196	0.4429
"	0.0525	"	6.673	0.3006
"	0.0330	"	8.051	-0.1193
"	0.0300	"	8.561	-0.2727
"	0.0285	"	8.846	-0.3645
"	0.0210	"	9.610	-0.5629
"	0.0090	"	10.331	-0.7683
0.100	0.0400	0.0200	4.403	0.9376
"	0.0390	"	5.828	0.5443
"	0.0380	"	6.151	0.4548
"	0.0350	"	6.628	0.3102
"	0.0220	"	8.010	-0.1047
"	0.0200	"	8.533	-0.2710
"	0.0190	"	8.827	-0.3574
"	0.0140	"	9.598	-0.5580
"	0.0060	"	10.328	-0.7596
0.040	0.0152	0.0080	6.076	0.4752
"	0.0140	"	6.553	0.3352
"	0.0100	"	7.499	0.0570

It was assumed that  $-\log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}}$  would be constant at constant ionic strength with the ratio of concentrations of mono- and divalent perchlorates constantly 2:1. However, had  $-\log_{10}(f_{\text{HClO}_4})$  remained constant, then the plot of  $p[\text{H}^+]$  vs.  $V$  ( $\propto pa_{\text{H}^+}$ ) would have been linear since

$$p[\text{H}^+] = pa_{\text{H}^+} - \log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}} \dots\dots\dots 5-3$$

Small deviations from linearity (in the observed direction) are expected above  $pa_{\text{H}^+}=9$  when sodium ion errors become important. Also the  $K_c$  values of Pinsent and Everett may be slightly erroneous because they did not keep the ratio of concentrations of mono- and divalent salts constant in each half cell. From the Guggenheim equation,<sup>18</sup> it is seen that the activity coefficient of any ion in a mixed electrolyte system at constant ionic strength, may vary with the ratio of the concentrations of the other ions due to specific ionic interactions.

The variation of  $-\log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}}$  with  $I$  should, from equation 5-3, lead to parallel calibration curves for different ionic strengths if  $-\log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}}$  is a function of  $I$  only. The curves are parallel and in fact virtually coincident. For 43 points the standard deviation  $S=\pm 0.006 p[\text{H}^+]$  and for 30 points  $S=\pm 0.004 p[\text{H}^+]$  when one curve of best fit is drawn. The deviations from this curve are greatest about  $p[\text{H}^+]=4.2$ , where  $\bar{n}$  is  $= 2.0$ ; the buffer capacity is low in this region, and the  $p[\text{H}^+]$  very

susceptible to small traces of impurity.

Application of the Guggenheim equation<sup>18</sup> predicts a difference between  $\log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}}$  at  $I=0.040\text{m/l}$  and  $I=0.350\text{m/l}$  of approximately  $0.02 \text{ p[H}^+]$ . This should be the separation between the calibration curves at these ionic strengths. Therefore it can be assumed that fortuitously the conditions chosen were such that the variations of the fixed boundary liquid junction potential and the term  $-\log_{10}(f_{\text{HClO}_4})^{\frac{1}{2}}$  with  $I$  were approximately equal in magnitude and opposite in sign.

Discussion: The coincidence of the calibration curves makes this approach a very interesting and useful one. The assumptions made, particularly regarding activity coefficients, were justified by the internal consistency of the results obtained. The method of calibration removed the necessity to use 'absolute' activity coefficient values.

Brannan and Nancollas<sup>8</sup> used a similar method of calibration with malonic acid/sodium malonate buffers in solutions of ionic strengths  $0.03$  to  $0.20 \text{ m/l}$ . The data of Pinsent and Everett<sup>9</sup> was the only data known which would permit a  $[\text{H}^+]$  calibration over the necessary wide range of acidities required for studies on dibasic amines.

A Radiometer Glass electrode (Type G 202B) gave the same calibration curve up to  $\text{p[H}^+]=9.0$ . Unlike the Beckman electrode, which has Hg internals, the Radiometer electrode

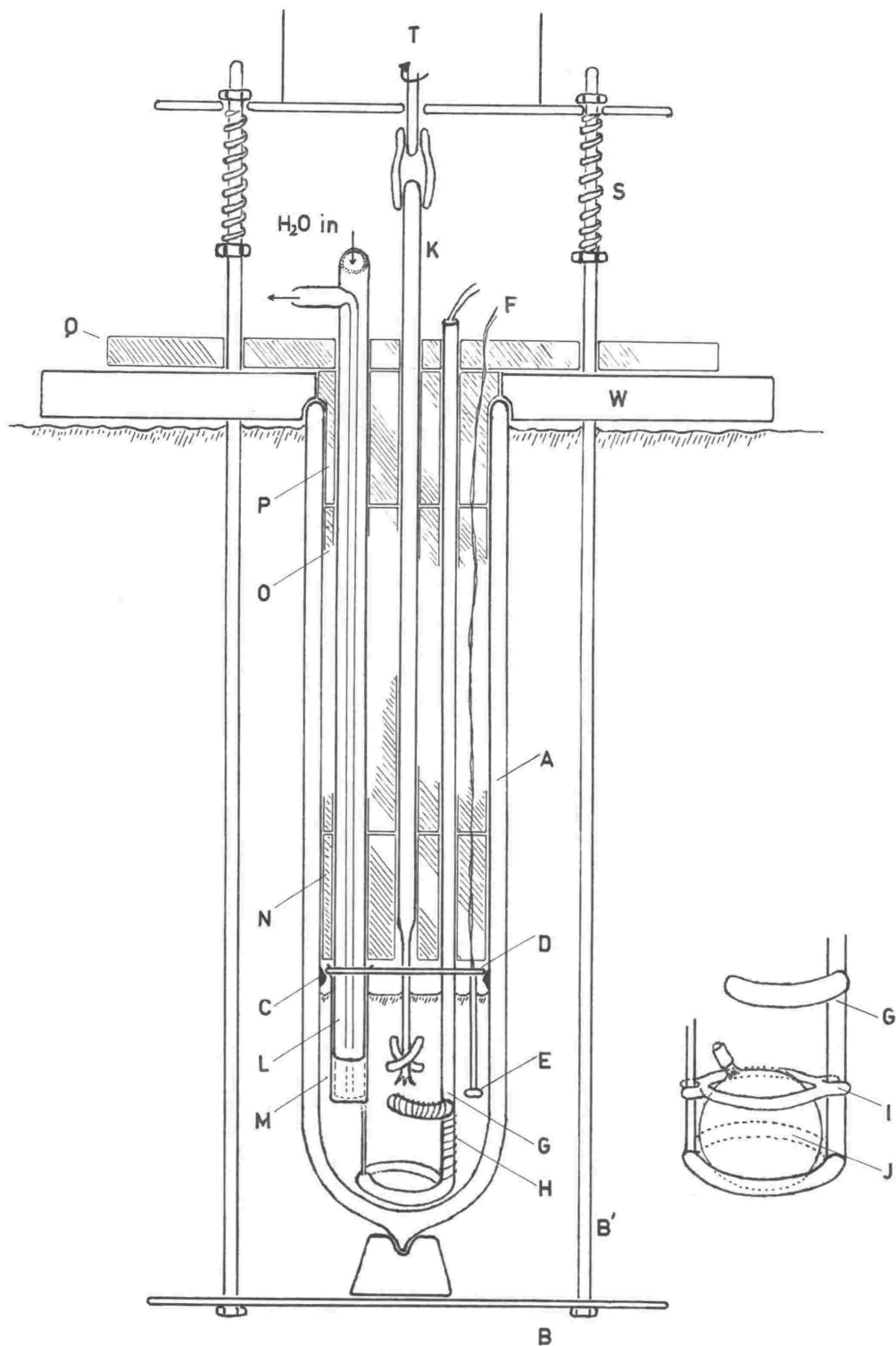
could not be satisfactorily shielded from electrical disturbances, viz., those at the Pt-Hg contact of a Hg-toluene thermostating unit.

## 5-2 The Reaction Calorimeter

The constant temperature environment calorimeter is shown in Fig. 5-3. It consisted of a Dewar vessel (A) 24.5x5cm, fixed in position in a thermostatted water bath (24.8°C to 25°C). The vessel was held by brass rods (B') between a brass plate (B) and a wooden support (W) which was clamped to the water bath. A tufnal disc (D) supported on glass flanges (C) above the reaction compartment, carried the glass mountings for the thermistor (E), resistance heater (H), bulb support (G) and heating finger (M). The reaction compartment had a capacity of 110mls.

The temperature measuring device was a thermistor (E), Philips Type B8 320 03P/~~3~~3 resistor,  $R_{25^{\circ}\text{C}} = 3175 \Omega$ . It was connected into one arm of a D.C. Wheatstone bridge circuit (Fig. 5-4) by 28 guage enamelled copper wire leads (F), ( $R = 0.33 \Omega$ ). The thermistor leads were sealed off from the solution with araldite. The heater (H) was approximately 20  $\Omega$  of cotton wound manganin wire ( $32 \Omega/\text{yard}$ ,  $dR/dT = 0$ ) and was wound on a hollow glass former (G). It was connected to the 'heater circuit' (Fig. 5-5) by 22 guage copper wire (0.016  $\Omega/\text{foot}$ ) and the leads sealed off from the solution

FIG 5-3



THE REACTION CALORIMETER

with araldite. Before mounting the heater wire, its cotton cover was impregnated with araldite; the wire was wound on to the glass former (G) while the araldite was viscous.

The amine solution (4-5mls) was contained in a thin-walled glass bulb (J). The bulb fitted in to the base of the former (G) and was weighted down with a glass ring (I). The bulbs were broken with the spikes on the end of the glass stirrer (K). The stirrer was connected to a synchronous motor (T) mounted on a base supported by springs (S). The bulb could be broken by depressing the whole motor housing. The synchronous motor (T) ( 1 rev/sec) had external gearing to give 209 rev/min.

To attain thermal equilibrium between the reaction compartment and the calorimeter surrounds, water from the thermostatted bath was pumped through the heating/cooling finger (L). The pump was a small centrifugal one, immersed in the bath. The finger (L) fitted snugly in to the thimble (M) which was permanently immersed in the reaction mixture. During a reaction the 'finger' was completely withdrawn from the 'thimble'; when withdrawn it still kept the polystyrene discs (N, O, P, Q) at a temperature close to that of the bath. The air in the calorimeter was flushed by a slow stream of  $N_2$  heated to the bath temperature, saturated with water vapour, and scrubbed of  $O_2$  ( $Cr^{2+}/H^+$ ).

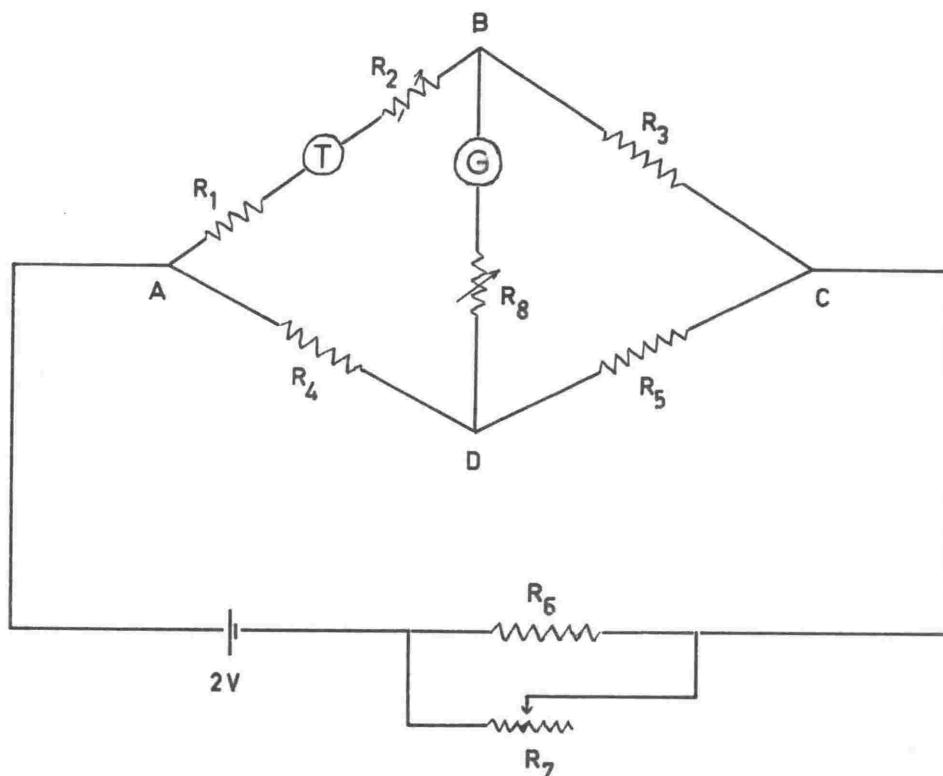
(a) The bridge circuit (Fig. 5-4): The resistance of a thermistor decreases slightly as the applied voltage is increased;<sup>43a</sup> i.e., it does not obey Ohm's Law. To keep the current through the thermistor constant, the decade box  $R_2$  and the thermistor were placed in the same arm of the bridge. The potential across  $R_5$  and hence the current in each arm of the bridge was periodically monitored with a PYE potentiometer (Cambridge, No. 27853). The total bridge current was controlled with the Rheostat  $R_7$ . With a current of  $170.8 \mu\text{A}$  through the thermistor, its resistance changed by approximately  $1 \Omega$  per  $\mu\text{A}$  variation in current. All resistances other than  $R_7$  and  $R_8$  were Armstrong-Sullivan non-inductive manganin resistances, tolerance  $\pm 0.1\%$ . The galvanometer, Tinsley Type AS4/45, ( $R_i$   $540 \Omega$ , 2000mm deflection per  $\mu\text{A}$ ) was shunted with a  $1000 \Omega$  resistance. The power supply was a 2V lead accumulator.

(b) Calibration of the thermistor: The plot of resistance vs. temperature (Fig. 5-6) was linear within experimental error for the temperature range  $24.8$  to  $26.1^\circ\text{C}$ . The graph obeyed the equation  $R=a+bT$ , with  $b=-(102.14 \pm 0.06) \Omega/^\circ\text{C}$ . The current through the thermistor was  $170.8 \mu\text{A}$ ;  $R_{25^\circ\text{C}}=3174.96 \pm 0.03 \Omega$ ;  $(dR/dT)_{25^\circ\text{C}}=-3.218 \%$ . The calibration curve was unchanged after four months. It has been observed that any changes of the thermistor resistance with time are uniform along the calibration curve, not affecting the temperature coefficient of resistance.<sup>43a</sup>



FIG. 5-4

## D. C. BRIDGE CIRCUIT CONTAINING THE THERMISTOR.



$R_1 = 1000\text{ohms } (\pm 0.1\%)$

T = Thermistor

$R_2 = \text{Armstrong Sullivan Decade Box, 0-1000ohms, 4 dial } (\pm 0.03\%)$

$R_3 = 5000\text{ohms } (\pm 0.1\%)$

$R_4 = R_5 = 1000\text{ohms } (\pm 0.1\%)$

$R_6 = 500\text{ohms}$

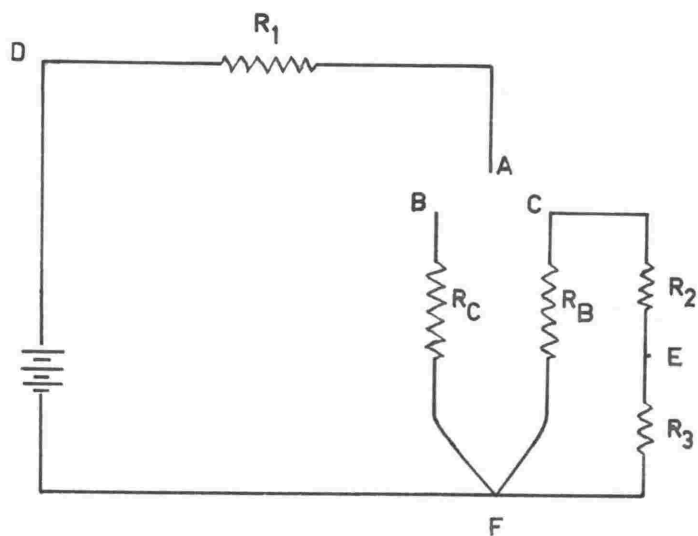
$R_7 = 0-800\text{ohms Rheostat}$

$R_8 = 500\text{K Potentiometer}$

G = Tinsley Galvanometer, Type AS4/45; 540ohms, 2000mm/microamp.

FIG 5-5

## CALORIMETER HEATER CIRCUIT

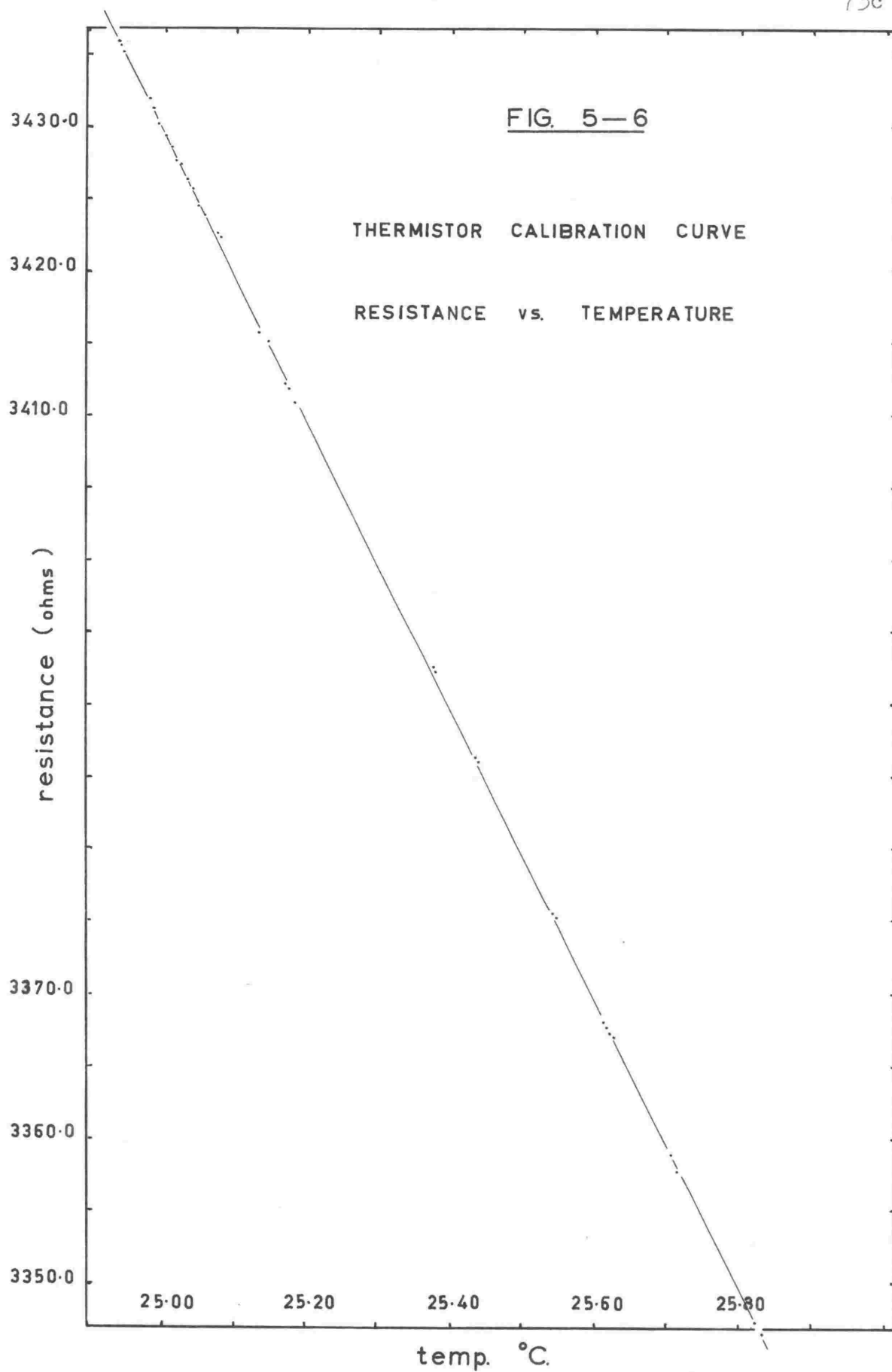


$$R_1 = 2.5 \text{ ohms } (\pm 0.1\%)$$

$$R_2 = 10,000 \text{ ohms } (\pm 0.1\%)$$

$$R_3 = 1,000 \text{ ohms } (\pm 0.1\%)$$

$$R_B = R_C \pm 20 \text{ ohms}$$



The calibration was done by placing the mounted thermistor in a thermostatted water bath. The bath temperature was recorded with a mercury calorimetric thermometer graduated to  $0.01^{\circ}\text{C}$  and read with an eye lens to  $\pm 0.001^{\circ}\text{C}$ .

The current through the thermistor was kept low to prevent excessive heat dissipation during thermal measurements. With  $I=170.8\ \mu\text{A}$ , only  $0.00133\text{ cal/min.}$  were dissipated at  $25.00^{\circ}\text{C}$ . This heat output remained essentially constant during a thermal reaction because the total change in the thermistor's resistance was generally  $< 2\%$  of its initial resistance. The copper leads made a negligible contribution to the temperature coefficient of the thermistor because of their low temperature coefficient and resistance.

A change of  $0.01\ \Omega$  in the decade box gave a  $3\text{ mm}$  galvanometer deflection. The system was sufficiently stable to use the galvanometer deflections to estimate changes in resistance of  $\pm 0.01\ \Omega$  ( $\approx \pm 0.0001^{\circ}\text{C}$ ).

The linearity of the calibration curve for the temperature range  $24.8$  to  $26.1^{\circ}\text{C}$  gave a constant proportionality between changes in temperature and the corresponding changes in thermistor resistance within this range.

(c) The heater circuit (Fig.5-5):  $R_c$  is the calorimeter resistance heater and  $R_B$  a ballast heater of similar resistance immersed in an oil bath at  $25^{\circ}\text{C}$ .  $R_c$  was necessary for experiments to measure the thermal capacity

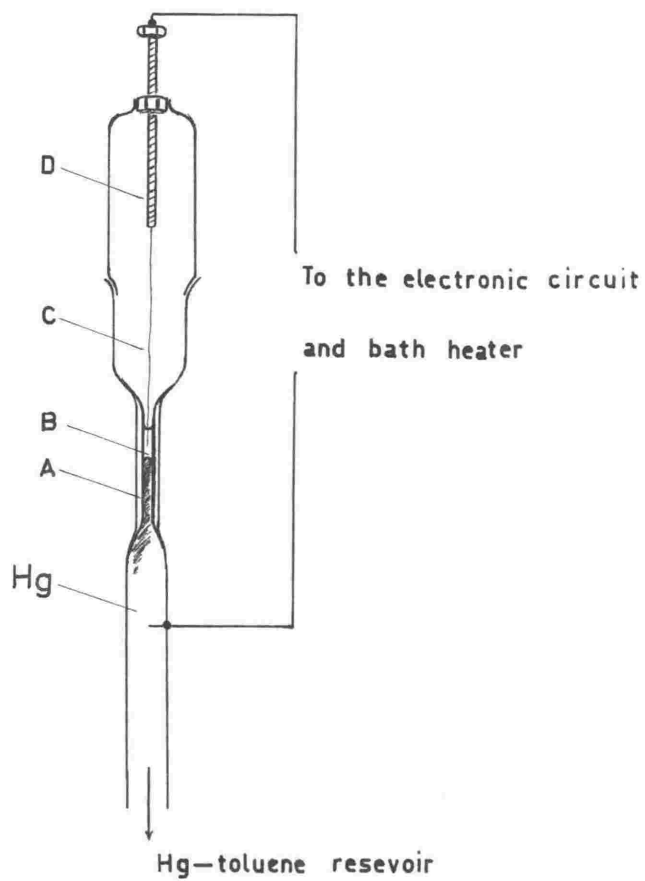
of the reaction mixture/calorimeter assembly after each chemical reaction studied. The power supply was a lead accumulator, 2-12V depending on the heat input required to make  $\Delta T(\text{calibration}) = \Delta T(\text{reaction})$ . To stabilise the voltage supply, the batteries were discharged through  $R_B$  for at least 30 min. before supplying heat to the calorimeter.

A.B.C. is a microswitch operated by a revolving cam attached to a synchronous motor (Venner Type M, 1 rev/120 secs). When the synchronous motor was switched on, the revolving cam depressed the micro-switch for a known period of time and switched the current from  $R_B$  to  $R_C$  and the resistances in parallel with it ( $R_2 + R_3$ ). The cam was allowed to make one revolution only. The period of heating through  $R_C$  ( $62.049 \pm 0.012$  sec) was determined by connecting terminals A.C. on the microswitch to the mains supply via a variac and 10K potentiometer, and counting the main's frequency with a scaler unit while the cam made several revolutions.

(d) The thermostat bath: It was small and well stirred and the temperature controlled with a mercury/toluene regulator. Heat losses were reduced by floating a thin layer of paraffin oil on the water. The sensitivity of the regulator was increased by using a large volume of toluene with a large surface/volume ratio, and by making the bore (A) (Fig. 5-7) very narrow. Good stability was

FIG. 5-7

## MERCURY — TOLUENE THERMOSTAT CONTROL



achieved by floating some non-conducting oil (B) on the surface of the mercury to prevent discharge between, and thus contamination of the Pt wire (C) and the mercury. A fine pitch on the screw (D) gave sensitive control of the bath temperature.

(e) Thin-walled glass bulbs were blown from pyrex or soda glass and were of 5ml capacity. They were filled via a syringe or drawn-out pipette, sealed with a small rubber tube and glass stopper, and their contents determined by weight. When pierced, Pyrex bulbs broke into two or three large pieces with a heat of bulb breaking  $Q_B \leq 0.05\text{cal}$ . Soda bulbs broke into a vast number of small fragments,  $Q_B \approx -0.015\text{cal}$ .

(f) The procedure: The aqueous diamine solution was contained in the bulb (J) (Fig. 5-3). The solution composed of  $M(\text{ClO}_4)_2$ ,  $\text{Ba}(\text{ClO}_4)_2/\text{HClO}_4$ ,  $\text{NaClO}_4$ , made up the bulk of the reaction mixture and was placed in the Dewar by pipettes and a burette with a long nozzle. The volume ratio of the two solutions was kept constant for similar reactions (usually 4 ml:90 ml), so that the heat of dilution of the diamine solution into the perchlorate medium ( $\text{Ba}(\text{ClO}_4)_2/\text{NaClO}_4$ ) had to be determined once only for each series of reactions. The whole internal assembly of the calorimeter, with bulb in place, was lowered in to the Dewar, and the centrifugal pump and stirrer motor started. Equilibration of the interior to bath temperature took 8 to 10 hours

(overnight) by using the heating finger (L). The equilibration time was reduced to approximately four hours by using the calorimeter resistance heater for the initial period of heating.

When the system was at thermal equilibrium, the heating finger was removed from the thimble. A slow fall in the temperature of the reaction mixture followed, (approximately  $0.00015^{\circ}\text{C}/\text{min}$ ). This was recorded for several minutes before breaking the bulb. Mixing of the diamine and perchlorate solutions was complete in 10 to 15 sec, and a cooling (temperature-time) curve plotted for approximately 40 min after 'mixing'.

Before measuring the thermal capacity of the system by input of a known amount of electrical energy, the calorimeter was again equilibrated to bath temperature by using the cooling finger (L). Two temperature-time curves (before and after heating) were plotted for the calibration run.

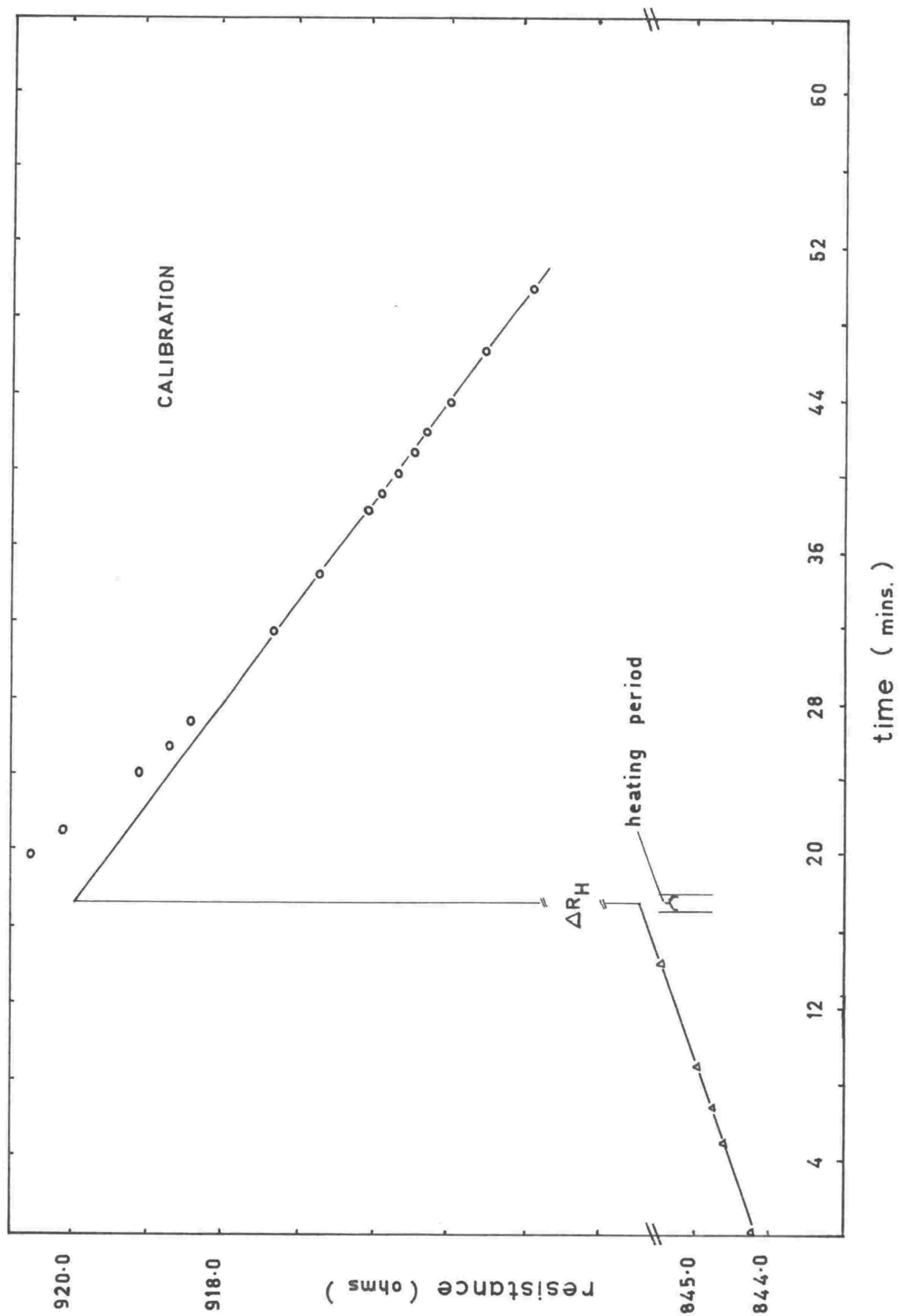
(g) Cooling-curve extrapolations: In making cooling-curve extrapolations to the time of mixing, (see Fig. 5-8), it was assumed that Newton's Law of cooling for heat loss by radiation and conduction was applicable, i.e.,

$$dT/dt = k_1(T_i - T_o),$$

because of the small temperature difference ( $T_i - T_o$ ) between the inside and outside of the calorimeter vessel. For the period of uniform heating during the calibration run, it







was assumed that the average rate of loss of heat was equal to  $k_1 \cdot (T_2 - T_1) / 2$ .  $T_1$  and  $T_2$  were the temperatures at the start and finish of the heating period respectively, as found by cooling-curve extrapolation.

(h) Calculation of the thermal energy of reaction:

During the heating period the potentials  $V_{AD}$  and  $V_{EF}$  (Fig. 5-5) were measured. From these were calculated the current through and potential across  $R_C$ , hence the heat liberated by the resistance heater. If  $I_{tot.}$ ,  $I_{EF}$ ,  $I_{R_C}$ , and  $V_{R_C}$  are the total current through the system, the current through  $R_3$  and  $R_C$ , and the potential drop across  $R_C$  respectively, then

$$I_{tot.} = \frac{V_{AD}}{R_1} \qquad I_{EF} = \frac{V_{EF}}{R_3}$$

$$I_{R_C} = \frac{V_{AD}}{R_1} - \frac{V_{EF}}{R_3}$$

$$V_{R_C} = \frac{V_{EF}}{R_3} (R_2 + R_3)$$

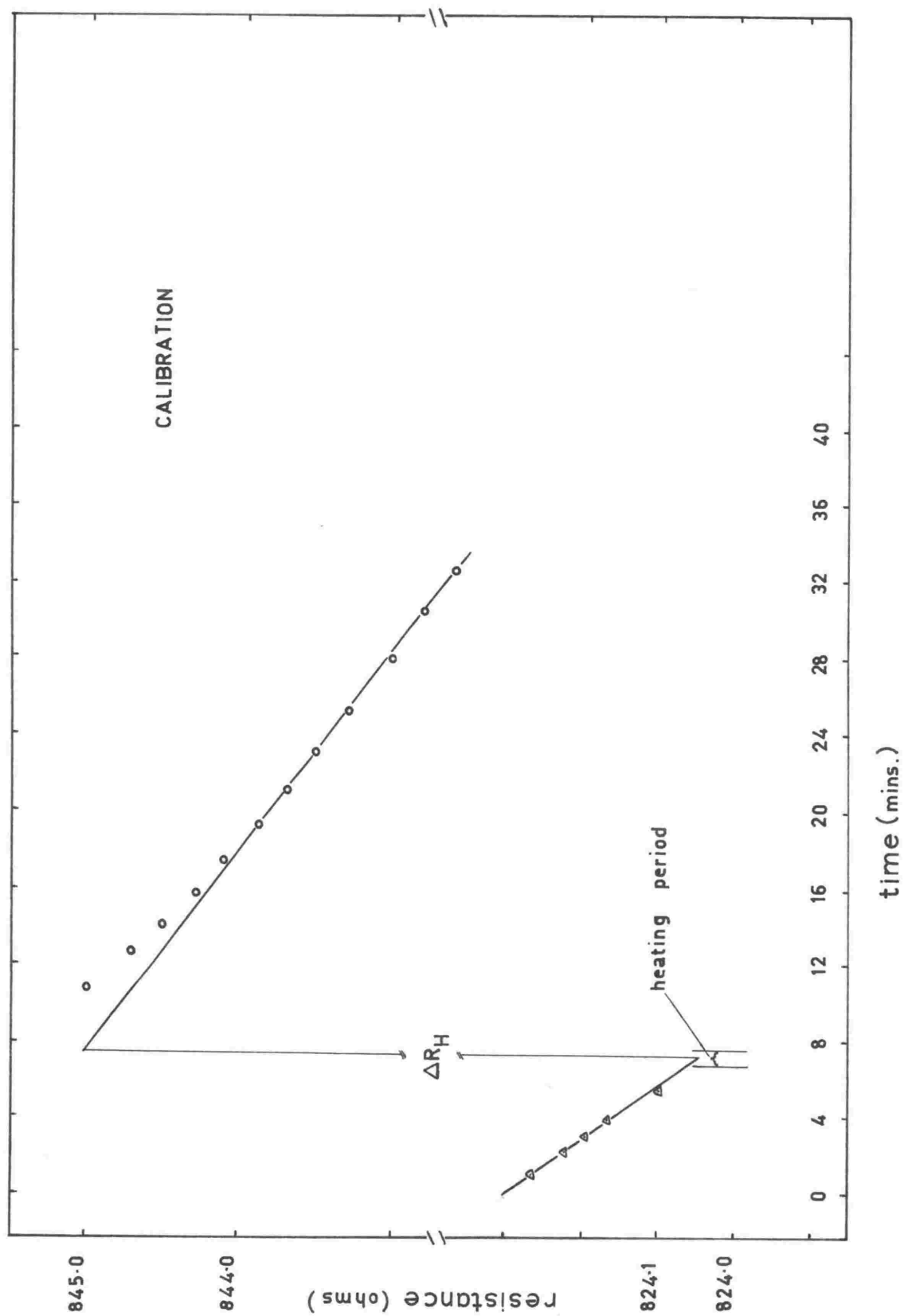
and the thermal energy liberated by the heater in  $\Delta t$  seconds is  $Q_H = V_{R_C} \cdot I_{R_C} \Delta t / 4.1840$

$$= \left( \frac{V_{AD}}{R_1} - \frac{V_{EF}}{R_3} \right) \left( \frac{V_{EF}}{R_3} (R_2 + R_3) \right) \frac{\Delta t}{4.1840} \dots 5-4$$

The thermal energy of reaction  $Q_R$  was equated to the electrical energy input by

$$Q_R = Q_H \cdot \frac{\Delta R_R}{\Delta R_H} \quad (\text{see Fig. 5-8, 5-9}) \dots 5-5$$





### 5-2.1 The heat of neutralisation of aqueous NaOH and HCl:

This was measured to test the reliability of the calorimeter. The concentrated (1.121M) NaOH solution ( $V_{\text{NaOH}} \text{ ml}$ ) was contained in the bulb. A slight excess of 0.04827M HCl solution ( $V_{\text{HCl}} \text{ ml}$ ) was used to ensure a complete reaction. The results are given in Table 5-3.

TABLE 5-3

Run	$V_{\text{NaOH}} \text{ ml}$ (1.121m/1)	$V_{\text{HCl}} \text{ ml}$ (0.04827m/1)	$\Delta Q_{\text{R}}(\text{corr})$ (cals)	$-\Delta H_{\text{R}}$ kc/m	$-\Delta H^{\circ}$ kc/m
1	3.855	89.560	58.59	13.55	13.44
2	3.983	92.500	60.20	13.49	13.38
3	3.361	78.050	50.73	13.47	13.36
4	4.020	93.355	60.93	13.52	13.41
5	3.792	88.075	56.98	13.41	13.30
6	3.986	92.585	59.64	13.36	13.25

$$\Delta H_{\text{av}}^{\circ} = -(13.36 \pm 0.06) \text{ kcal/mole}$$

$\Delta Q_{\text{R}}(\text{corr})$  was the heat liberated in the neutralisation reaction, and was obtained from

$$\Delta Q_{\text{R}}(\text{corr}) = \left( \frac{\Delta R_{\text{R}}}{\Delta R_{\text{H}}} \cdot \Delta Q_{\text{H}} \right) - Q_{\text{B}} \dots\dots\dots 5-6$$

=  $\Delta Q_{\text{R}} - Q_{\text{B}}$ , where  $Q_{\text{B}}$  was the 'heat of bulb breaking'.

$\Delta H_{\text{R}}$  was the enthalpy change per mole for the reaction and was calculated from  $\Delta Q_{\text{R}}(\text{corr})$ :

$$\begin{aligned}\Delta H_R &= \frac{1000 \Delta Q_R(\text{corr})}{V.C} = \frac{1000 \Delta Q_R(\text{corr})}{[\text{NaOH}]V_{\text{NaOH}}} \\ &= \frac{1000 \Delta Q_R(\text{corr})}{[\text{HCl}]V_{\text{HCl}}} \dots\dots 5-7\end{aligned}$$

where  $V = V_{\text{NaOH}} + V_{\text{HCl}}$

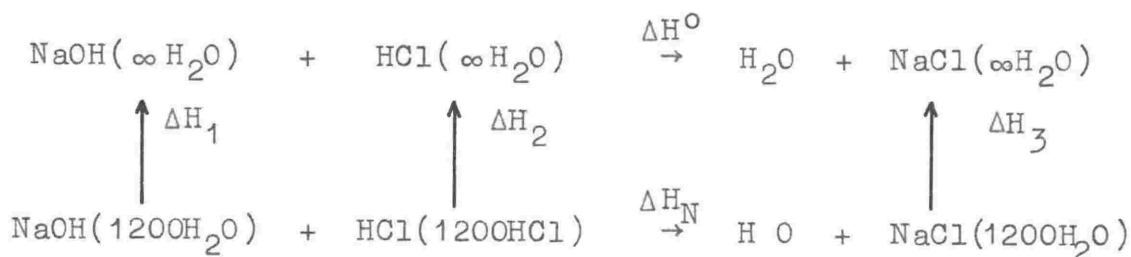
$[\text{NaOH}]$  = the initial concentration of NaOH before reaction, etc.

$$C = \frac{[\text{NaOH}] \cdot V_{\text{NaOH}}}{V_{\text{NaOH}} + V_{\text{HCl}}} = \frac{[\text{HCl}] \cdot V_{\text{HCl}}}{V}$$

$\Delta H_R$  contained a term for the heat of dilution of the NaOH stock from 1.121m/l to 0.04628m/l. ( $\Delta H_{D(\text{NaOH})}$ ) and a smaller term for the heat of dilution of the HCl solution from 0.04827m/l to 0.04628m/l. ( $\Delta H_{D(\text{HCl})}$ ). Thus  $\Delta H_R$  is related to  $\Delta H_N$  the enthalpy change for the neutralisation reaction at an ionic strength  $I=0.0463\text{m/l}$  and mole ratio of reactant to solvent water = 1:1200, by

$$\begin{aligned}\Delta H_R &= \Delta H_N + \Delta H_{D(\text{NaOH})} + \Delta H_{D(\text{HCl})} \\ &\cong \Delta H_N + \Delta H_{D(\text{NaOH})}\end{aligned}$$

$\Delta H^0$  is the enthalpy change per mole when the reactants and products are in the hypothetical standard state of an infinitely dilute solution.  $\Delta H^0$  was obtained from  $\Delta H_N$  by considering the following enthalpy cycle in which, for example,  $\text{NaOH}(1200\text{H}_2\text{O})$  refers to an aqueous NaOH solution with a mole ratio of  $\text{NaOH}:\text{H}_2\text{O} = 1:1200$ .



$\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3$  are enthalpies of dilution and were obtained from N.B.S. data<sup>64</sup> for partial molal heat contents of the aqueous solutes:



also from this data,



$$\Delta H_D(\text{NaOH}) = 14\text{cals/m}$$

$$\begin{aligned}
 \text{Therefore, } \Delta H^\circ &= \Delta H_N + \Delta H_3 - \Delta H_1 - \Delta H_2 \\
 &\doteq \Delta H_R - \Delta H_D(\text{NaOH}) + \Delta H_3 - \Delta H_1 - \Delta H_2 \\
 &\doteq \Delta H_R + 110\text{cals.}
 \end{aligned}$$

The average  $\Delta H^\circ$  value obtained was  $\Delta H_{av}^\circ = -(13.36 \pm 0.06)$  kcals/mole. Values obtained by other workers are in the range  $-(13.34 \text{ to } 13.36) \pm 0.02$  kcals/mole.<sup>41,115-8</sup>

## 5-2.2 Discussion

Slow thermal equilibration has been the main disadvantage in using Dewar vessels for calorimetry. This problem was overcome by incorporating the heating/cooling



finger. The high thermal lag was then an advantage for obtaining cooling curves which could be accurately extrapolated because of their small slope.

Thermistors are most satisfactory devices for measuring small temperature changes near room temperature. They have low thermal inertia and are readily calibrated,  $R$  vs.  $T$ . Because of their large temperature coefficient of resistance, very accurate or sensitive bridge circuits are not required, (cf. Pt resistance thermometers).

Over long periods (up to two days) there was no evidence of evaporation and condensation within the calorimeter vessel.

In subsequent measurements, it was found that a smaller temperature change ( $T_2 - T_1$ ) for a reaction improved the accuracy of the cooling curve extrapolation. The optimum value of  $\Delta Q_R$  was approximately 20 calories.

### 5-3 The Preparation of Diamines

The diamines were prepared and purified by recrystal-

residues filtered off. IV separated from the filtrate on standing. The yield was increased by evaporating the alcohol residues to dryness, taking up the solid in isopropanol and precipitating IV with ether. The product was recrystallised from absolute alcohol by Soxhlet extraction. Yield from 20gm of III, 16.5gm (62.5%). M.pt. 168-9°C, (lit.<sup>128</sup> 186-7°C). The product obtained was recrystallised three times from absolute alcohol, but the M.pt. was invariant.  $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2\cdot 2\text{HCl}$  requires Cl, 44.02. Found Cl, 43.93.

#### 5-3.2 1-Dimethyl 1,2-diaminoethane dihydrochloride

$\alpha$  acetamino isobutyric nitrile  $(\text{CH}_3)_2\text{C}(\text{CN})\text{NHCOCH}_3$  I was prepared on a  $\frac{3}{4}$  mole scale. NaCN (38gm) and  $\text{NH}_4\text{Cl}$  (40gm) were dissolved in 200ml of water, and 55ml of acetone were added. The mixture was left 48 hours at room temperature. The  $\alpha$ -amino isobutyric nitrile formed was liquid-liquid extracted with 400ml of ether (8 hours), and then acetylated by addition to the ether solution of a mixture of 120ml acetic anhydride/120ml glacial acetic acid. The white solid I quickly crystallised and the yield was increased on cooling and addition of ether. I was recrystallised once by Soxhlet extraction into ether. Yield 47gm (50%). M.pt. 102°C (lit.<sup>129</sup> 106°C).

I was converted to 2-methyl 1,2-diacetaminopropane II by catalytic hydrogenation in acetic anhydride solvent.

32gm of I were dissolved in 90ml of acetic anhydride and 0.20gm of  $\text{PtO}_2$  catalyst added; hydrogen uptake was complete in 10 days at 1 atmosphere,  $20^\circ\text{C}$ . The Pt residues were filtered off and the acetic anhydride removed under vacuum. The viscous residue containing II was dissolved in 120cc of 50% alcohol/concHCl, and the mixture refluxed for 24 hours to hydrolyse the acetyl groups off the diamine. 70% of the solvent was distilled off under vacuum to leave a brown viscous solution. From this solution 2-methyl 1,2-diaminopropane dihydrochloride III crystallised on cooling, and was filtered off. The yield was increased by evaporating the filtrate (water bath) until a tarry residue remained; this residue was dissolved in a small volume of methanol. Acetone was added until crystallisation commenced and the solution was cooled. Yield of crude material 29gm. (72% from I). III was extracted with absolute alcohol to remove tarry residues, then twice recrystallised by Soxhlet extraction into 25% aqueous alcohol. M.pt.  $294^\circ\text{C}$ , darkens  $285^\circ\text{C}$ , (lit.<sup>129</sup>  $303^\circ\text{C}$ ). 2-methyl 1,2-diamino propane dihydrochloride requires C, 29.83; H, 8.76; Cl, 44.02. Found C, 29.86; H, 9.19; Cl, 43.43).

An attempt to convert II to 2-methyl 1,2-diaminopropane IV by alkaline hydrolysis in 15% NaOH ( $120^\circ\text{C}$ , sealed tube) followed by ether extraction of IV and conversion to its dihydrochloride gave only a 20% yield.

### 5-3.3 1-Phenyl 1,2-diaminoethane

$\alpha$ -amino phenyl acetonitrile I was prepared by a method based on that of Steiger.<sup>130</sup> NaCN (100gm) and  $\text{NH}_4\text{Cl}$  (118gm) were dissolved in 400ml of water in a 3l. round-bottom flask equipped with a Hershberg stirrer. Benzaldehyde (212gm) in 400ml of methanol was added in one portion and the mixture stirred for three hours at room temperature using a well ventilated hood. The mixture was then diluted with water (1l) and I extracted with benzene (4x100ml). The bulk of the solvents were removed under reduced pressure (rotary evaporator). I was converted to  $\alpha$ -acetamino phenyl acetonitrile II by slow addition of acetic anhydride (200ml) to the ice-cooled mixture. II crystallised immediately, was filtered and washed with ether. Yield 105gm, 62%. M.pt.(crude)  $100-2^\circ\text{C}$ . Benzaldehyde impurities were removed from II by twice recrystallising from benzene. M.pt.  $109^\circ\text{C}$  (lit.<sup>131</sup>  $113^\circ\text{C}$ ).

II was reduced to  $\alpha,\beta$ -diacetamino phenylethane III by catalytic hydrogenation. 34gm of II with 0.30gm  $\text{PtO}_2$  catalyst in 100ml of acetic anhydride, were hydrogenated in nine days at  $20^\circ\text{C}$ , 1 atmosphere. White crystals of III separated during the reaction. The product was dissolved by heating and addition of acetone, the Pt residues filtered off and the filtrate concentrated under vacuum to give a viscous residue containing III.

To hydrolyse III to 1-phenyl 1,2-diaminoethane dihydrochloride IV, 50% concHCl/alcohol (80ml) was added and the solution refluxed for three hours. The bulk of the solvent was distilled off, 40ml of isopropanol added and the azeotrope distilled. The residues were taken up in hot isopropanol and IV crystallised on standing. The product was filtered and the filtrate evaporated to dryness (water bath), the solid residue taken up in hot anhydrous acetone and a further yield of IV crystallised on cooling. M.pt.(crude)  $293-4^{\circ}\text{C}$ . (Three hours of acid hydrolysis was excessive because some tarry residues resulted.)

IV was recrystallised twice by Soxhlet extraction into absolute alcohol. Yield, 17.1gm, 52.5% based on II. M.pt.  $297.5-299.5$ . (lit.<sup>132</sup>  $300-1(d)$ ) 1-phenyl 1,2-diaminoethane dihydrochloride requires C, 45.94; H, 6.75; Cl, 33.91. Found C, 45.75; H, 7.00; Cl, 33.73 .

To obtain the diamine, IV (17.1gm, 0.081moles) was dissolved in 25ml of water and AnalaR NaOH (6.55gm, 0.162 moles) added. 1-phenyl 1,2-diaminoethane was distilled under a  $\text{N}_2$  atmosphere,  $b_{29} 136-8^{\circ}\text{C}$ ,  $b_{33} 141^{\circ}\text{C}$ . (lit.<sup>133</sup>  $b_{19} 135^{\circ}\text{C}$ ) Yield, determined by titration of the aqueous solution obtained, 40%.

#### 5-3.4 1-Methyl 1,2-diaminoethane

A sample (L.Light and Co.) was purified as the sulphate salt and distilled from alkali under reduced pressure,  $\text{N}_2$  atmosphere.

5-4 Chemicals

- a) Potassium hydrogen phthalate: An AnalaR sample, (99.6%) was used as the primary standard in acid-base titrations.
- b) Water: The water used in the preparation of all solutions, other than HCl and  $\text{HClO}_4$ , was distilled, freshly boiled and saturated with  $\text{N}_2$  while cooling.  $\text{p}[\text{H}^+] = 6.4$ .
- c) Sodium hydroxide: Carbonate-free NaOH was made by the method of Vogel.<sup>134</sup> It was standardised against potassium hydrogen phthalate using phenolphthalein indicator.
- d) Acids: HCl and  $\text{HClO}_4$  solutions were prepared by dilution of concentrated AnalaR reagents. They were standardised against a sample of standard alkali by electrometric (pH meter) titration to pH 7.0.
- e) Amine solutions: A sample of the distilled aqueous solution was quantitatively diluted to approximately 0.1m/l. This solution was standardised by running an aliquot into excess standard HCl and back-titrating with standard NaOH to the end-point for amine neutralisation,  $\approx$  pH 4.0-4.4. The electrometric titration was followed graphically.
- f) Barium perchlorate:  $\text{Ba}(\text{ClO}_4)_2$  (B.D.H.) was crystallised from distilled water, removing insoluble residues by filtering the hot solution through 'hyflo super cell'.

The stock solution was analysed for  $\text{Ba}^{++}$  ( $\text{BaSO}_4$  gravimetric) and for  $[\text{H}^+]$  (by  $\text{p}[\text{H}^+]$  measurement,  $[\text{H}^+] < 2.5 \times 10^{-5} \text{m/l}$ ).

- g) Sodium perchlorate:  $\text{NaClO}_4$  (B.D.H.) was recrystallised from distilled water. The stock solution was analysed for  $\text{NaClO}_4$  by density measurement<sup>81</sup> and for  $\text{HClO}_4$  by  $\text{p}[\text{H}^+]$  measurement. ( $[\text{H}^+] < 10^{-6} \text{m/l}$ ).
- h) Nickel perchlorate: This was prepared from  $\text{HClO}_4$  and  $\text{Ni}(\text{CO}_3)_2$ ,  $\text{Ni}(\text{OH})_2$  (B.D.H.), and twice recrystallised from distilled water. The stock solution ( $0.1147 \text{m/l}$ ) was analysed for  $\text{Ni}^{2+}$  using dimethylglyoxime, and for  $\text{HClO}_4$  by  $\text{p}[\text{H}^+]$  measurement ( $[\text{H}^+] = 2.500 \times 10^{-3} \text{m/l}$ ) and by pH titration with very dilute alkali ( $[\text{H}^+] = (2.456 \pm 0.025) \times 10^{-3} \text{m/l}$ ).
- i) Copper perchlorate: This was prepared from  $\text{HClO}_4$  and  $\text{CuO}$ . It was recrystallised from 10% aqueous acetone solution, and  $\text{Cu}(\text{OH})_2$  removed from the hot solution by filtration through 'hyflo super cell.' The stock solution ( $0.3223 \text{m/l}$ ) was analysed for  $\text{Cu}^{2+}$  by electrolytic deposition. It was made acidic ( $1.098 \times 10^{-2} \text{m/l}$ ) by quantitative addition of standard  $\text{HClO}_4$  to prevent precipitation of basic copper salts.



## CHAPTER SIX

### THE PROTONATION OF C<sub>4</sub>-SUBSTITUTED 1,2-DIAMINO ETHANES

#### 6-1 Experimental and Results

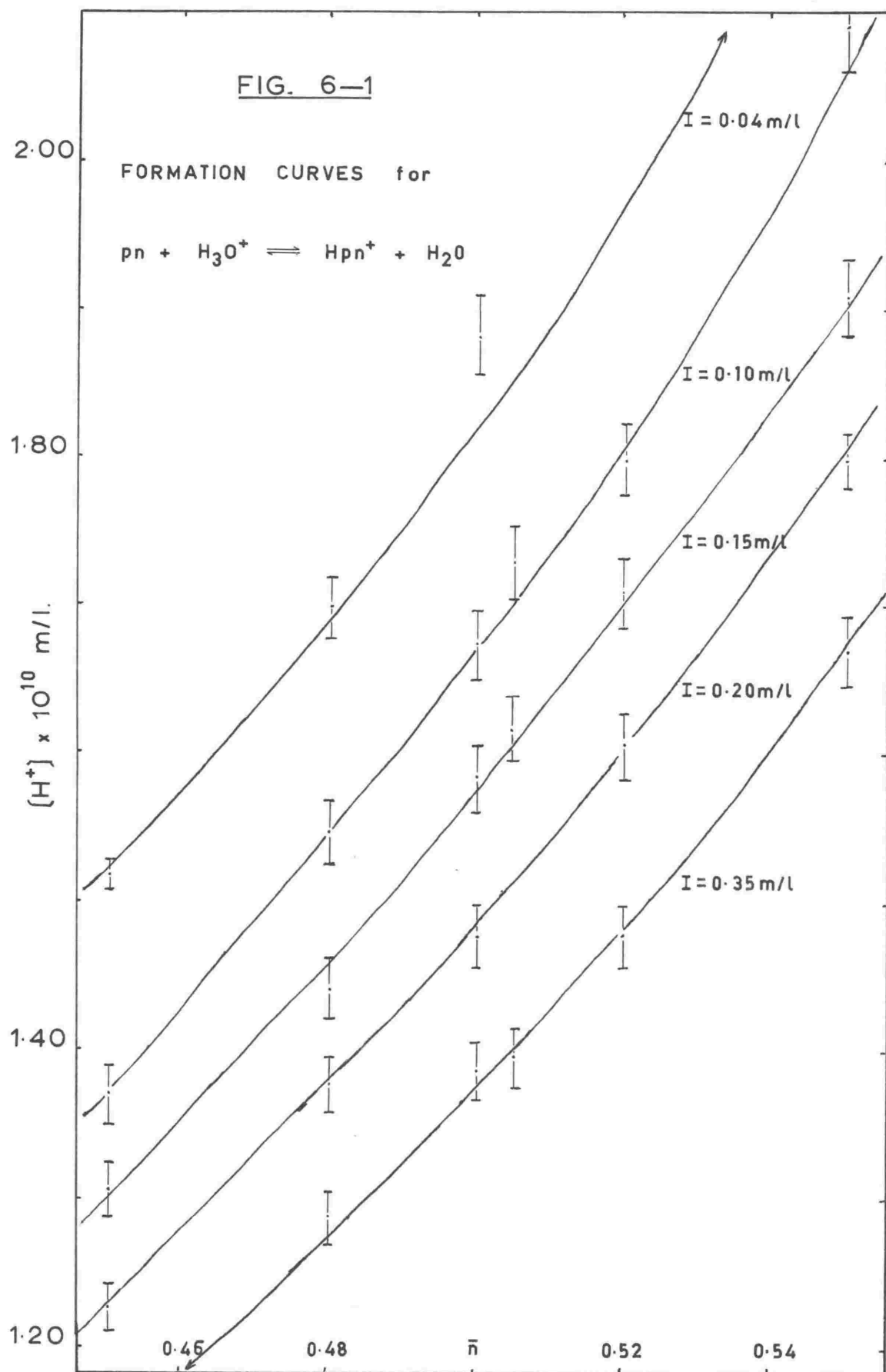
##### 6-1.1 The standard free energy change

$\Delta G^\circ$  was obtained from the thermodynamic equilibrium constant  $K_a$  by the relationship  $\Delta G^\circ = -RT \ln K_a$ , (equations 2-8,9).

For a series of ionic strengths, solutions containing different compositions of acid ( $\text{HClO}_4$ ) and base (L) were prepared. (See formulation in 4-1.3) These solutions were analysed potentiometrically to measure the equilibrium hydrogen ion concentrations at  $25.00 \pm 0.01^\circ\text{C}$  (see 5-1), using the cell:

Calomel	Saturated KCl	Base ( $T_L$ )	Total ionic strength = I	Glass Electrode	
Reference		$\text{HClO}_4$ ( $T_H$ )			
Electrode		$\text{NaClO}_4$			
		$\text{BaClO}_4$			

(see p. 65 and Fig. 5-1). The results for the base 1-methyl 1,2-diaminoethane are given fully in Tables 6-1 and 6-2. From this type of data, formation curves ( $\bar{n}$  vs.  $[\text{H}]$  eqbm.) were plotted (Figs. 6-1, 6-2), and from these curves values of  $[\text{H}]\bar{n} = n - \frac{1}{2}$  were obtained (see 4-1.1). The concentration equilibrium constants  $K_c$  were derived from  $[\text{H}]\bar{n} = n - \frac{1}{2}$  values using Bjerrum's method of successive substitutions



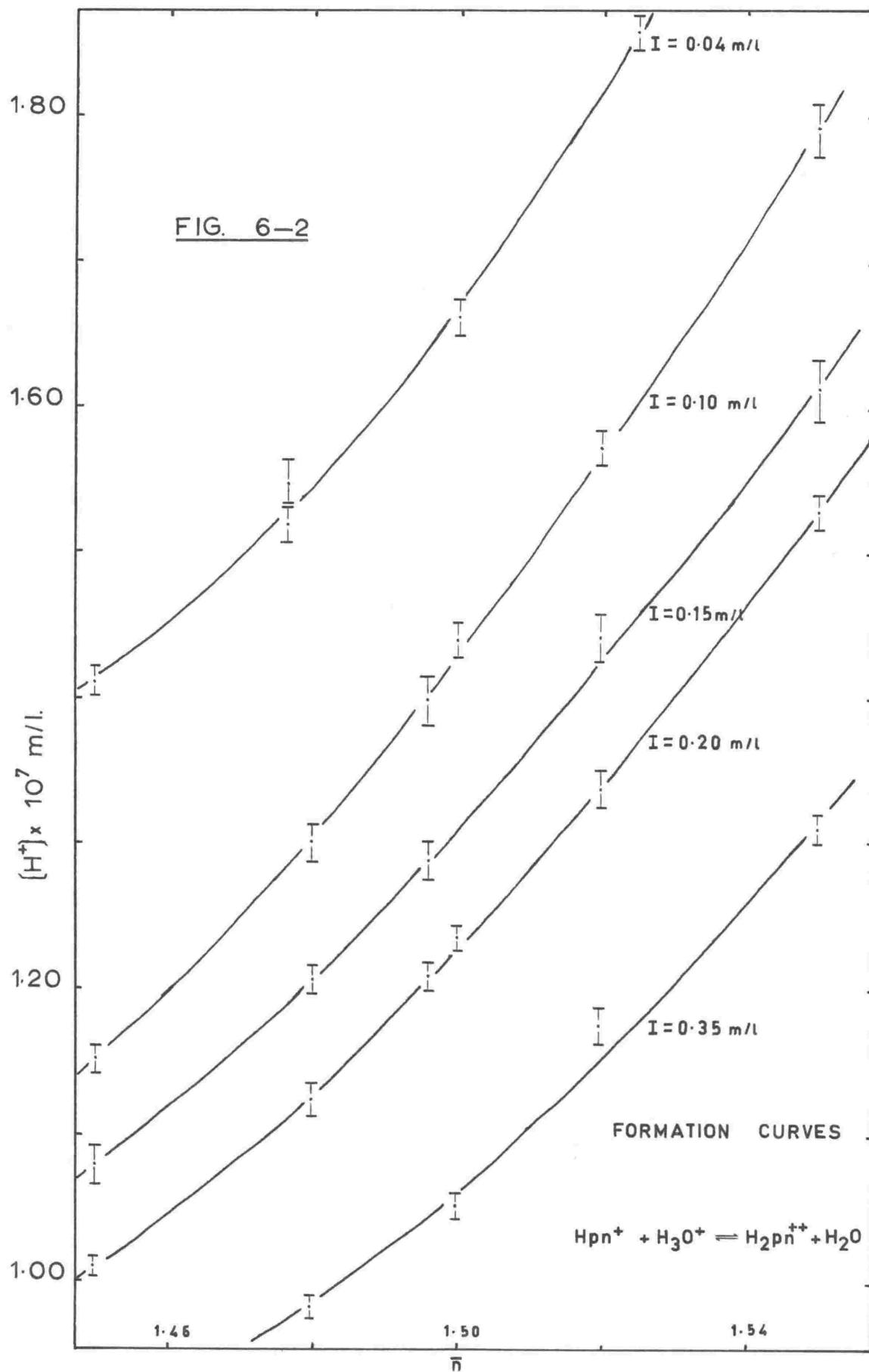


TABLE 6-1

'Formation Curve' experimental data for the protonation of  
1-methyl 1,2-diamino ethane at  $25.00 \pm 0.01^\circ\text{C}$   
The first protonation constant

Ionic strength (m/l)	$\bar{n}$	Equilibrium $[\text{H}^+] \times 10^{10}$ (m/l)		Ionic strength (m/l)	$\bar{n}$	Equilibrium $[\text{H}^+] \times 10^{10}$ (m/l)	
0.350	0.450	$1.127 \pm 0.016$		0.100	0.450	$1.371 \pm 0.019$	
"	0.480	1.288	18	"	0.480	1.549	21
"	0.500	1.387	19	"	0.500	1.675	23
"	0.505	1.396	20	"	0.505	1.730	24
"	0.520	1.479	21	"	0.520	1.799	24
"	0.550	1.671	23	"	0.550	2.094	29
0.200	0.450	$1.227 \pm 0.016$		0.040	0.450	$1.517 \pm 0.010$	
"	0.480	1.377	19	"	0.480	1.698	20
"	0.500	1.479	21	"	0.500	1.884	26
"	0.505	1.503	20	"	0.550	2.239	31
"	0.520	1.607	22				
"	0.550	1.807	25				
0.150	0.450	$1.306 \pm 0.018$					
"	0.480	1.442	20				
"	0.500	1.578	22				
"	0.505	1.618	22				
"	0.520	1.710	24				
"	0.550	1.910	26				

TABLE 6-2

'Formation Curve' experimental data for the protonation of  
1-methyl 1,2-diamino ethane at  $25.00 \pm 0.01^\circ\text{C}$

The second protonation constant

Ionic strength (m/l)	$\bar{n}$	Equilibrium [H <sup>+</sup> ] x10 <sup>7</sup> (m/l)		Ionic strength (m/l)	$\bar{n}$	Equilibrium [H <sup>+</sup> ] x10 <sup>7</sup> (m/l)	
0.350	1.450	0.883 $\pm$ 0.006		0.100	1.450	1.153 $\pm$ 0.008	
"	1.480	0.984	7	"	1.480	1.303	12
"	1.500	1.054	8	"	1.496	1.400	16
"	1.520	1.178	11	"	1.500	1.442	10
"	1.550	1.312	9	"	1.520	1.574	11
"	1.600	1.607	15	"	1.550	1.795	21
0.200	1.450	1.012 $\pm$ 0.007		0.040	1.450	1.413 $\pm$ 0.009	
"	1.480	1.127	11	"	1.475	1.521	17
"	1.496	1.211	8	"	1.475	1.549	18
"	1.500	1.239	8	"	1.500	1.722	16
"	1.520	1.340	12	"	1.525	1.862	15
"	1.550	1.531	11				
0.150	1.450	1.081 $\pm$ 0.013					
"	1.480	1.208	11				
"	1.496	1.291	12				
"	1.500	1.337	12				
"	1.520	1.445	17				
"	1.550	1.614	20				

(see 4-1.1).

The values of  $K_c$  for each of the amines in solutions of various ionic strengths are given in Table 6-3. The values for 1,2-diaminoethane are also given in this Table (from the data of Pinsent and Everett<sup>9</sup>).

$\log K_a$  values were obtained by extrapolation of  $\log K_c$  to zero ionic strength (Figs. 6-3 to 6-6, see p. 51 ). The relationship

$$\log K_a = \lim_{I \rightarrow 0} (\log K_c + f n I)$$

was assumed (equations 2-8, 9). For each equilibrium studied (except  $H^+ + pn \rightleftharpoons Hpn^+$ ) it was found that

$$\log K_a = \log K_c - \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + \beta' I$$

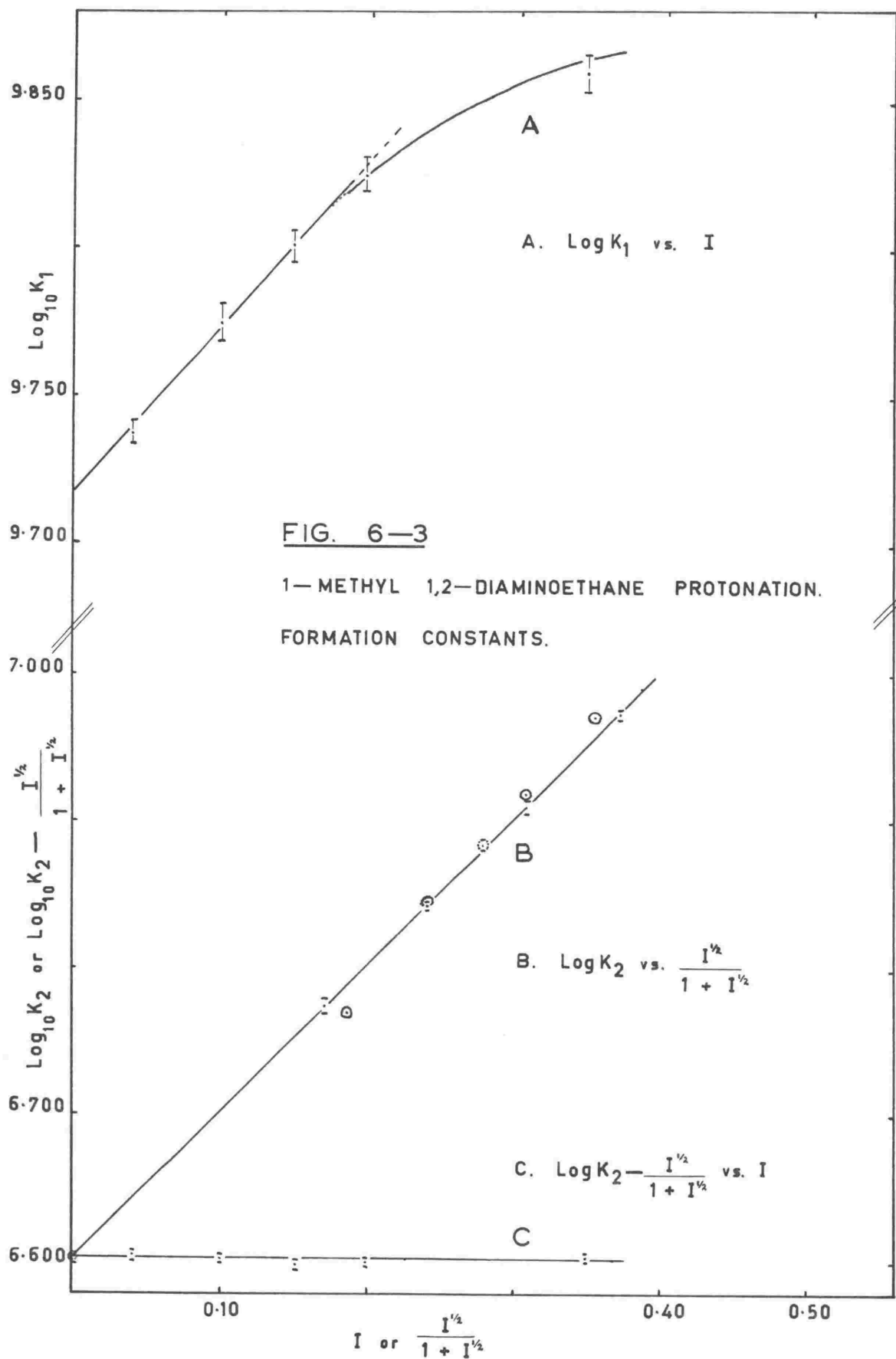
$$\text{where } \beta' \approx 0 \text{ and } \beta' I \ll I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})$$

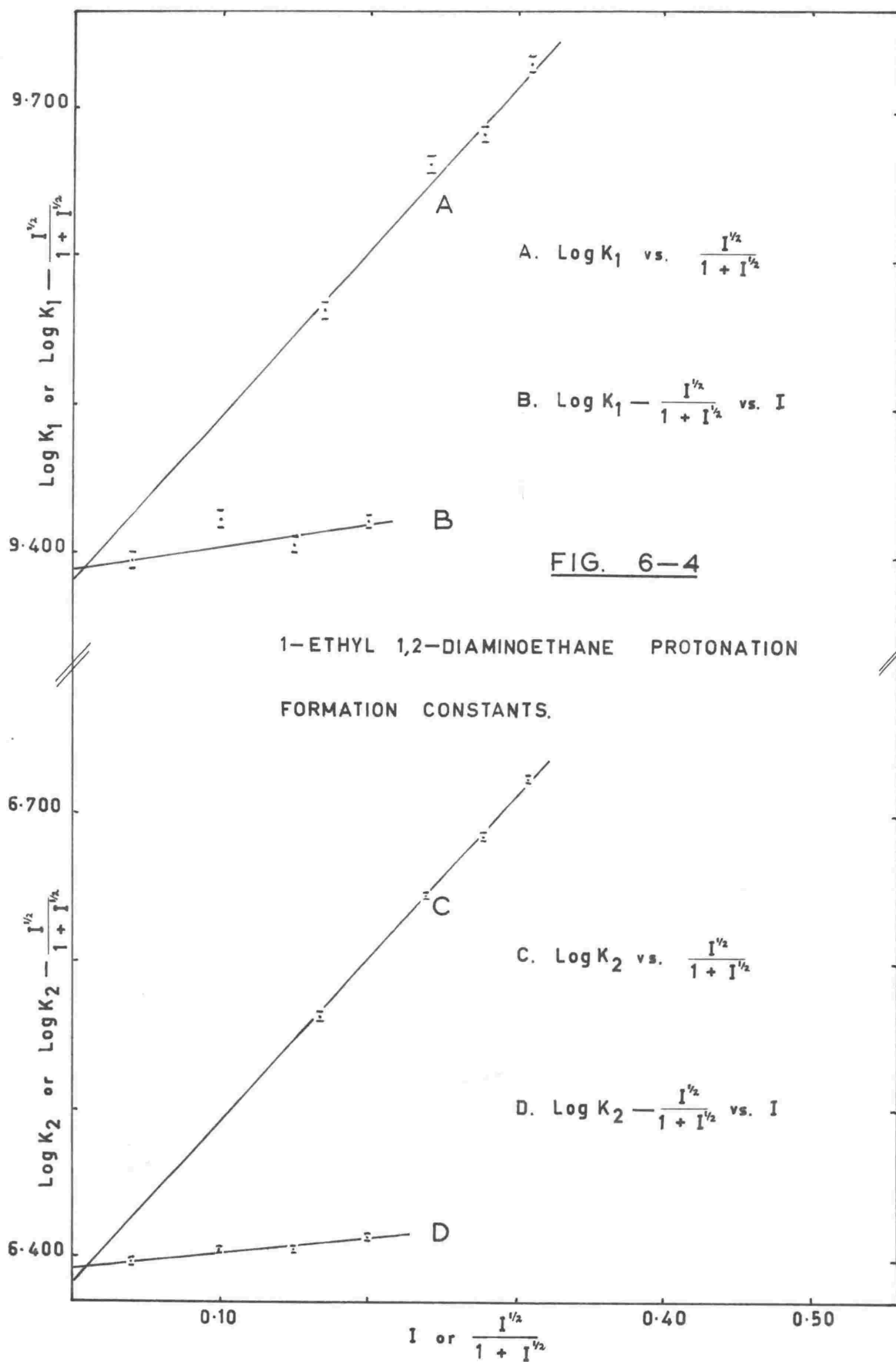
To check the extrapolations of  $\log K_c$  to zero  $I$ , plots of both  $\log K_c$  vs.  $I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})$ , and  $\log K_c - I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})$  vs.  $I$  were made. For a given reaction each plot gave the same intercept on the axis  $I = 0$ . (See Figs. 6-3 to 6-6.)  $\log K_a$  values are given in Table 6-3. Values of

$$\Delta G^0 = -2.303RT \log K_a$$

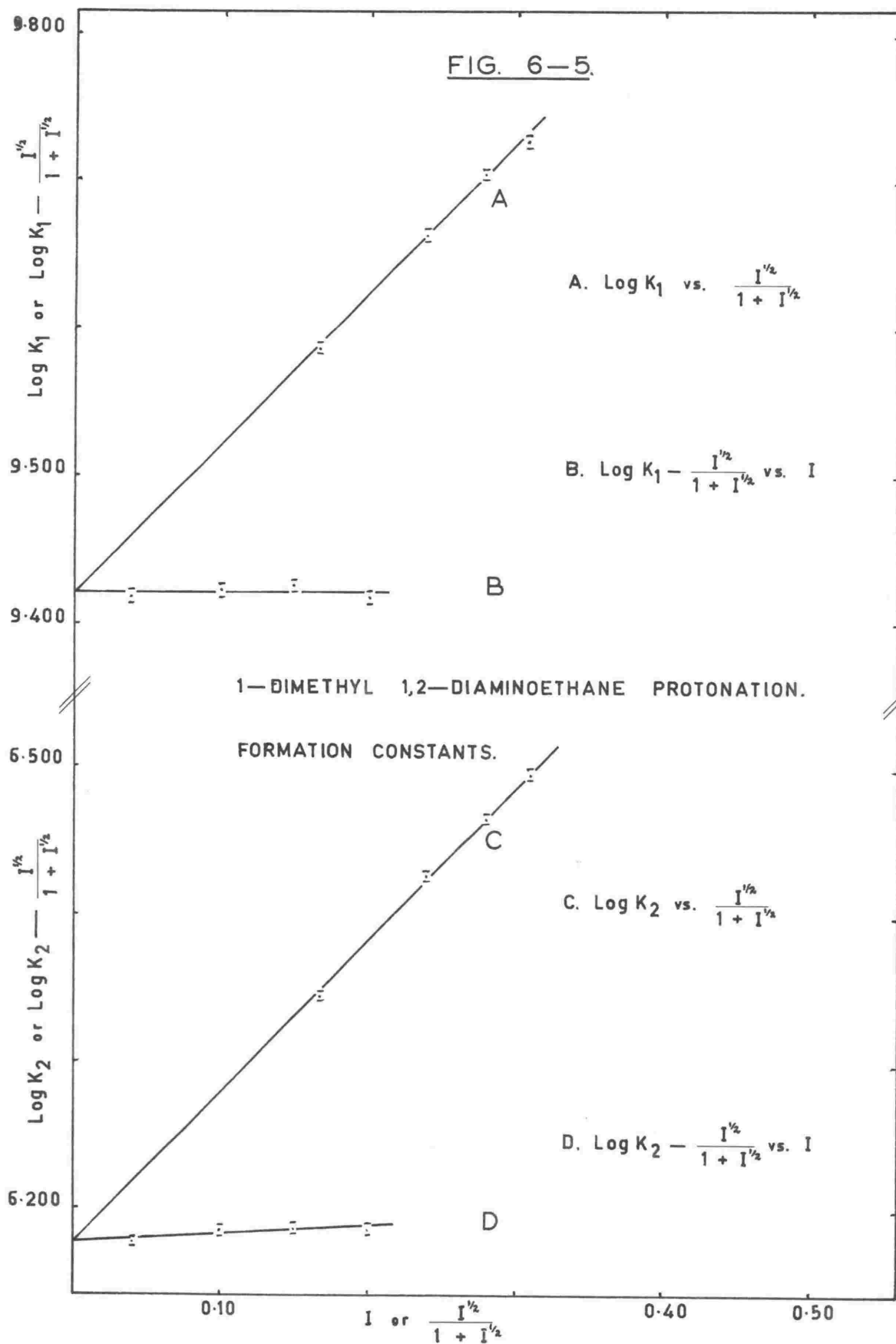
are given in Table 6-6.

Errors: Errors in  $p[H]$  were assessed as  $\pm 0.003$  to  $0.005$  units. Errors in  $K_c$  and  $K_a$  values were assessed as  $\pm(1.0 - 1.5)\%$  for  $K_1$  and  $\pm(0.5 \text{ to } 1.0)\%$  for  $K_2$ .









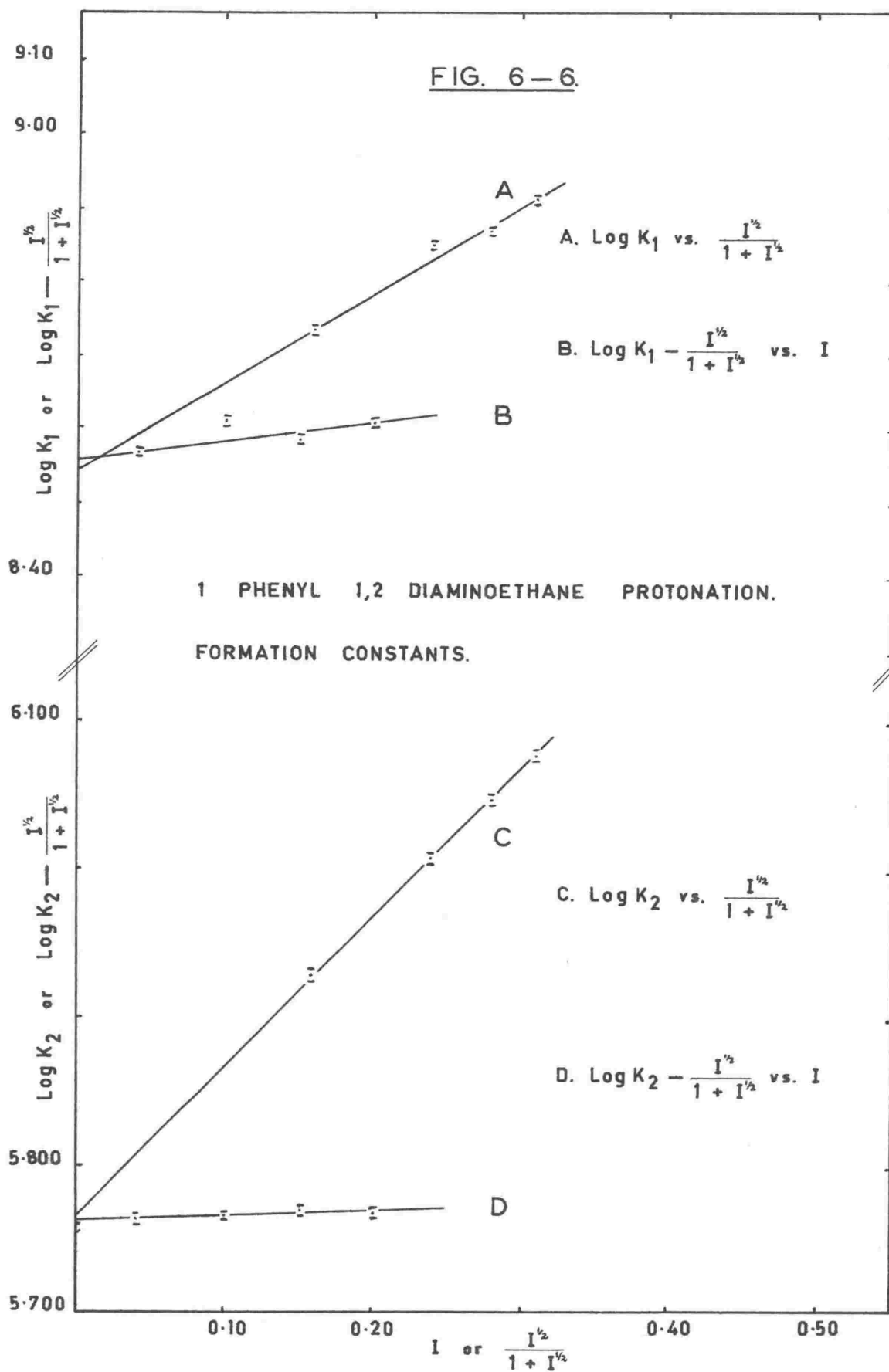


TABLE 6-3

Equilibrium constants for the protonation of  $C_1$ -substituted ethylenediamines at various ionic strengths,  $25.00 \pm 0.01^\circ C$ .  $NaClO_4/Ba(ClO_4)_2$  inert electrolyte

Log Ionic strength (m/l)	1,2-diamino-ethane	1-methyl 1,2-diamino-ethane	1-ethyl 1,2-diamino-ethane	1-dimethyl 1,2-diamino-ethane	1-phenyl 1,2-diamino-ethane
$K_{C_1}$ 0.350	$10.036 \pm 0.003$	$9.860 \pm 0.006$			
" 0.200	$9.997 \pm 0.003$	$9.826 \pm 0.006$	$9.732 \pm 0.006$	$9.728 \pm 0.006$	$8.912 \pm 0.005$
" 0.150	$9.971 \pm 0.003$	$9.801 \pm 0.005$	$9.684 \pm 0.006$	$9.705 \pm 0.005$	$8.865 \pm 0.004$
" 0.100	$9.960 \pm 0.003$	$9.775 \pm 0.006$	$9.664 \pm 0.006$	$9.663 \pm 0.005$	$8.849 \pm 0.004$
" 0.040	$9.938 \pm 0.003$	$9.738 \pm 0.004$	$9.564 \pm 0.006$	$9.586 \pm 0.006$	$8.737 \pm 0.004$
$K_{a_1}$ 0.000	$9.922 \pm 0.003$	$9.720 \pm 0.004$	$9.388 \pm 0.006$	$9.420 \pm 0.006$	$8.55 \pm 0.01$
$K_{C_2}$ 0.350	$7.262 \pm 0.003$	$6.976 \pm 0.003$			
" 0.200	$7.188 \pm 0.003$	$6.912 \pm 0.003$	$6.724 \pm 0.003$	$6.498 \pm 0.003$	$6.079 \pm 0.004$
" 0.150	$7.150 \pm 0.003$	$6.880 \pm 0.004$	$6.686 \pm 0.002$	$6.468 \pm 0.003$	$6.049 \pm 0.004$
" 0.100	$7.106 \pm 0.003$	$6.846 \pm 0.003$	$6.647 \pm 0.002$	$6.428 \pm 0.004$	$6.009 \pm 0.004$
" 0.040	$7.030 \pm 0.003$	$6.776 \pm 0.005$	$6.564 \pm 0.003$	$6.346 \pm 0.004$	$5.930 \pm 0.005$
$K_{a_2}$ 0.000	$6.859 \pm 0.003$	$6.607 \pm 0.005$	$6.399 \pm 0.007$	$6.178 \pm 0.005$	$5.757 \pm 0.007$

### 6-1.2 The enthalpy change

$\Delta H$  was measured calorimetrically (see 4-2, 5-2). The resultant solutions and numerical data from calorimetric runs were analysed according to the methods outlined in 4-2(a) and 5-2(h) respectively.

The experimental data is given in Table 6-4. In this Table,

$$(i) \quad \Delta Q_{R(\text{corr})} = \Delta Q_{R(\text{reaction})} - Q_B$$

where  $Q_B$  was the heat of bulb breaking  
(see 5-2(e) and equation 5-6)

(ii)  $\Delta H_{m(\text{meas'd})}$  is related to the endothermic heat change  $-q$  cal. per mole of metal ions:

$$\begin{aligned} \Delta H_m &= -q - \Delta H_{\text{diln}} = a' \Delta H_1 + b' \Delta H_2 \\ &= a' \Delta H_1^0 + b' \Delta H_2 \quad (\text{see 4-2.2 and Table 6-5}) \end{aligned}$$

(a)  $\Delta H_{\text{diln}}$  was the heat of dilution of the diamine stock solution (from the glass bulb) into a neutral  $\text{Ba}(\text{ClO}_4)_2/\text{NaClO}_4$  medium to give a diamine solution, concentration  $T_L$ . (Table 6-4) The ionic strengths of these diamine solutions were the same as those obtained in all the corresponding neutralisation runs for which  $\bar{n}$  was  $\ll 1$ . With  $\bar{n} > 1$  di-ammonium ions were formed, altering the total ionic strength of the mixture. The effect of this change in ionic strength upon  $\Delta H_1$  and  $\Delta H_2$  was accounted for by applying equation 4-21.

TABLE  
Calorimetric data for the neutralisation re  
diamines and  $\text{HClO}_4$  in aqueous Na

Diamine	Run	Final No. Ionic Strength (m/l)	$T_L$ (final) (m/l)	$T_H$ (final) (m/l)	$[\text{H}^+]$ eq. (m/l)	Total Vol. m
1-methyl 1,2-diamino- ethane	1	0.405	0.05998	0.1349		95.4
	2	0.405	"	0.1200		93.5
	3	0.374	"	0.09542	$1.446 \times 10^{-7}$	95.4
	4	0.335	"	0.08997	$1.069 \times 10^{-7}$	94.3
	5	0.327	"	0.07064	$2.403 \times 10^{-8}$	83.5
	6	0.321	"	0.05664	$1.787 \times 10^{-9}$	101.4
	7	0.329	"	0.03562	$2.017 \times 10^{-10}$	97.8
	8	0.397	0.06037	0.11097	$5.782 \times 10^{-7}$	95.6
	9	0.344	"	0.07070	$2.287 \times 10^{-8}$	101.4

---

\* Calorimeter Heater broke down. Heat capacity data from R<sub>1</sub>

TABLE 6-4(cc)

Diamine	Run No.	Final Ionic Strength (m/l)	T <sub>L</sub> (final) (m/l)	T <sub>H</sub> (final) (m/l)	[H <sup>+</sup> ]eq. (m/l)	Total Vol.m
1-ethyl 1,2-diamino- ethane	10	0.245	0.02300	0.05053		95.2
	11	0.200	"	0.02402	$1.189 \times 10^{-8}$	95.2
	12	0.200	"	0.02248	$4.05 \times 10^{-9}$	96.0
1-dimethyl 1,2-diamino- ethane	13	0.230	0.01500	0.08000		98.8
	14	0.230	0.01500	0.08000		97.9
	15	0.211	"	0.01684	$4.59 \times 10^{-8}$	95.7
	16	0.200	"	0.01460	$4.46 \times 10^{-9}$	95.1
1-phenyl 1,2-diamino- ethane	17	0.051	0.00894	0.01600	$4.415 \times 10^{-6}$	84.7
	18	0.040	"	0.009410	$9.105 \times 10^{-8}$	85.5
	19	0.040	"	0.008940	$4.609 \times 10^{-8}$	85.4
	20	0.040	"	0.00967	$1.685 \times 10^{-7}$	85.0

(b)  $\Delta H_2$  was converted to  $\Delta H_2^0$  by considering equation 4-21, viz:

$$\Delta H_2 \doteq \Delta H_2^0 + 8.1 \times 10^2 2AI^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) = \Delta H_2^0 + \delta ,$$

giving

$$\Delta H_m - b'\delta = a' \Delta H_1^0 + b' \Delta H_2^0$$

and

$$\begin{aligned} \Delta H_1^0 + \frac{b'}{a'} \Delta H_2^0 &= \sum n_i \Delta H_i^0 \\ &= \Delta H_1^0 + b'' \Delta H_2^0 \dots\dots\dots 6-1 \\ &\text{(See Table 6-5)} \end{aligned}$$

The two values of  $\Delta H_{diln}$  listed for 1-methyl 1,2-diaminoethane resulted from using two separately prepared samples of the aqueous amine stock solution. The discrepancy could not be accounted for, the two samples giving comparable results for the neutralisation reactions; cf., runs 5 and 9, Table 6-5.

The  $\Delta H_1^0$  and  $\Delta H_2^0$  values in Table 6-6 were derived from the data in Table 6-5 by two methods:

(a) by solution of pairs of the simultaneous equations

$$\sum n_i \Delta H_i^0 = \Delta H_1^0 + b'' \Delta H_2^0$$

E.g., for the neutralisation of 1-methyl 1,2-diaminoethane, the values obtained from combinations of data for runs 1+5, 2+5, 1+6, 2+6, 3+6, 4+6, 1+7, 2+7, 3+7, 4+7, 8+7, 8+6, 1+9, 2+9, were  $-\Delta H_1^0 = 12.15, 12.12, 11.86, 11.86, 11.86, 11.86, 11.85, 11.85, 11.85, 11.85, 11.85, 11.86, 12.05$  and  $12.02$  kcal/m, and  $-\Delta H_2^0 = 9.44, 9.62, 9.73, 9.88, 9.55, 9.57,$

TABLE 6-5

Calorimetric data continued from Table 6-4

Diamine	Run No.	$\Delta H_m = a' \Delta H_1^O + b' \Delta H_2$			$\sum n_i \Delta H_i^O = a'' \Delta H_1^O + b'' \Delta H_2$		
		a'	b'	$\Delta H_m$	a''	b''	$\sum n_i \Delta H_i^O$
1-methyl 1,2-diamino- ethane	1	1.0000	1.000	-21,277	1.0000	1.0000	-21,591
	2	1.0000	1.0000	-21,425	1.0000	1.0000	-21,739
	3	0.9994	0.5821	-17,235	1.0000	0.5825	-17,424
	4	0.9994	0.5007	-16,492	1.0000	0.5010	-16,650
	5	0.9966	0.1816	-13,767	1.0000	0.1822	-13,870
	6	0.9291	0.0152	-11,161	1.0000	0.0164	-12,016
	7	0.5926	0.0011	-7,035	1.0000	0.0019	-11,870
	8	1.0000	0.8492	-19,778	1.0000	0.8492	-20,043
	9	0.9961	0.1741	-13,614	1.0000	0.1748	-13,720
1-ethyl 1,2-diamino- ethane	10	1.0000	1.0000	-21,105	1.0000	1.0000	-21,374
	11	0.9857	0.0583	-11,917	1.0000	0.0591	-12,105
	12	0.9570	0.0201	-11,088	1.0000	0.0210	-11,591
1-dimethyl 1,2-diamino- ethane	13	1.0000	1.0000	-21,150	1.0000	1.0000	-21,412
	14	1.0000	1.0000	-21,210	1.0000	1.0000	-21,472
	15	0.9967	0.1263	-13,001	1.0000	0.1267	-13,066
	16	0.9600	0.0133	-11,369	1.0000	0.0139	-11,847
1-phenyl 1,2-diamino- ethane	17	0.998	0.7896	-19,321	1.0000	0.7898	-19,454
	18	0.9819	0.0706	-11,671	1.0000	0.0719	-11,896
	19	0.9636	0.0364	-10,893	1.0000	0.0378	-11,309
	20	0.9907	0.1243	-12,328	1.000	0.1255	-12,474



Found between 0.99 & 1.00

TABLE 6-6

Standard thermodynamic functions for the step-wise protonation of C<sub>1</sub>-substituted ethylenediamines in aqueous solution, 25.00±0.01° C. I = 0.00 m/l.

Standard thermodynamic functions	1-methyl 1,2-diamino- ethane	1-ethyl 1,2-diamino- ethane	1-dimethyl 1,2-diamino- ethane	1-phenyl 1,2-diamino- ethane
$\Delta G_1^0$ (Kc/m)	-13.550±0.003	-13.262±0.003	-12.805±0.003	-11.67±0.01
$\Delta G_2^0$ "	-9.360±0.004	-9.015±0.004	-8.717±0.003	-7.855±0.006
$\Delta G_{1-2}^0$ "	-22.91±0.01	-22.28±0.01	-21.52±0.02	-19.53±0.02
$\Delta H_1^0$ "	-11.91±0.12	-11.92±0.14	-11.45±0.10	-11.10±0.10
$\Delta H_2^0$ "	-11.03±0.25	-9.65±0.15	-9.92±0.10	-10.62±0.18
$\Delta H_{1-2}^0$ "	-22.99±0.12	-21.57±0.16	-21.57±0.13	-21.72±0.28
$\Delta S_1^0$ e.u.	+5.5±0.3	+4.5±0.4	+4.5±0.3	+1.9±0.3
$\Delta S_2^0$ "	-5.8±0.8	-2.1±0.4	-4.0±0.3	-9.3±0.6
$\Delta S_{1-2}^0$ "	-0.3±0.4	+2.4±0.4	+0.5±0.3	-7.4±0.8

\*  $\Delta G^0$  values from Ref. 9;  $\Delta H_n^0$  from Ref. 41, the  $\Delta H_2$  value corrected to infinite dilution.

solutions, ±0.3% (5-4(e)).

9.74, 9.89, 9.57, 9.58, 9.65, 9.64, 9.54, and 9.72kcal/m respectively. These results were then averaged and a standard deviation calculated.

(b)  $\Delta H_1^0$  values were obtained graphically by plotting  $\sum n_i \Delta H_i = \Delta H_1^0 + b'' \Delta H_2^0$  vs.  $b''$ , and extrapolating to  $b'' = 0$ . In each case linear graphs were obtained (Figs. 6-7, 8). Substitution of  $\Delta H_1^0$  into equation 6-1 gave a series of  $\Delta H_2^0$  values.

These methods gave comparable  $\Delta H_i^0$  values, e.g., for 1-methyl 1,2-diaminoethane, by method (a)

$$- \Delta H_1^0 = 11.92 \text{kcal/mole}, \quad - \Delta H_2^0 = 9.65 \text{kcal/mole};$$

by method (b)

$$- \Delta H_1^0 = 11.85 \text{kcal/mole}, \quad - \Delta H_2^0 = 9.69 \text{kcal/mole}.$$

$\Delta H_{1-2}^0$  could be obtained directly from measurements for which  $\bar{n} = 2.000$ .

Values of  $\Delta S_i^0$  were obtained by using the equation

$$\Delta G_i^0 = \Delta H_i^0 - T \Delta S_i^0.$$

### 6-1.3 Uncertainties in $\Delta H_i^0$ values

In treating the experimental data, no approximations were made until after the solution of the pairs of simultaneous equations (equation 6-1). The errors quoted on  $\Delta H_1^0$  and  $\Delta H_2^0$  are the summation of two errors:

- (i) the standard deviation on the average  $\Delta H_i^0$  values obtained from equation 6-1.
- (ii) the titration error in analysing the stock diamine solutions,  $\pm 0.3\%$  (5-4(e)).

FIG. 6—7.

PLOT OF  $\Delta H_1^0 + b''\Delta H_2^0$  vs.  $b''$  FOR THE  
 PROTONATION OF A. 1-METHYL 1,2-DIAMINOETHANE  
B. 1-ETHYL 1,2-DIAMINOETHANE

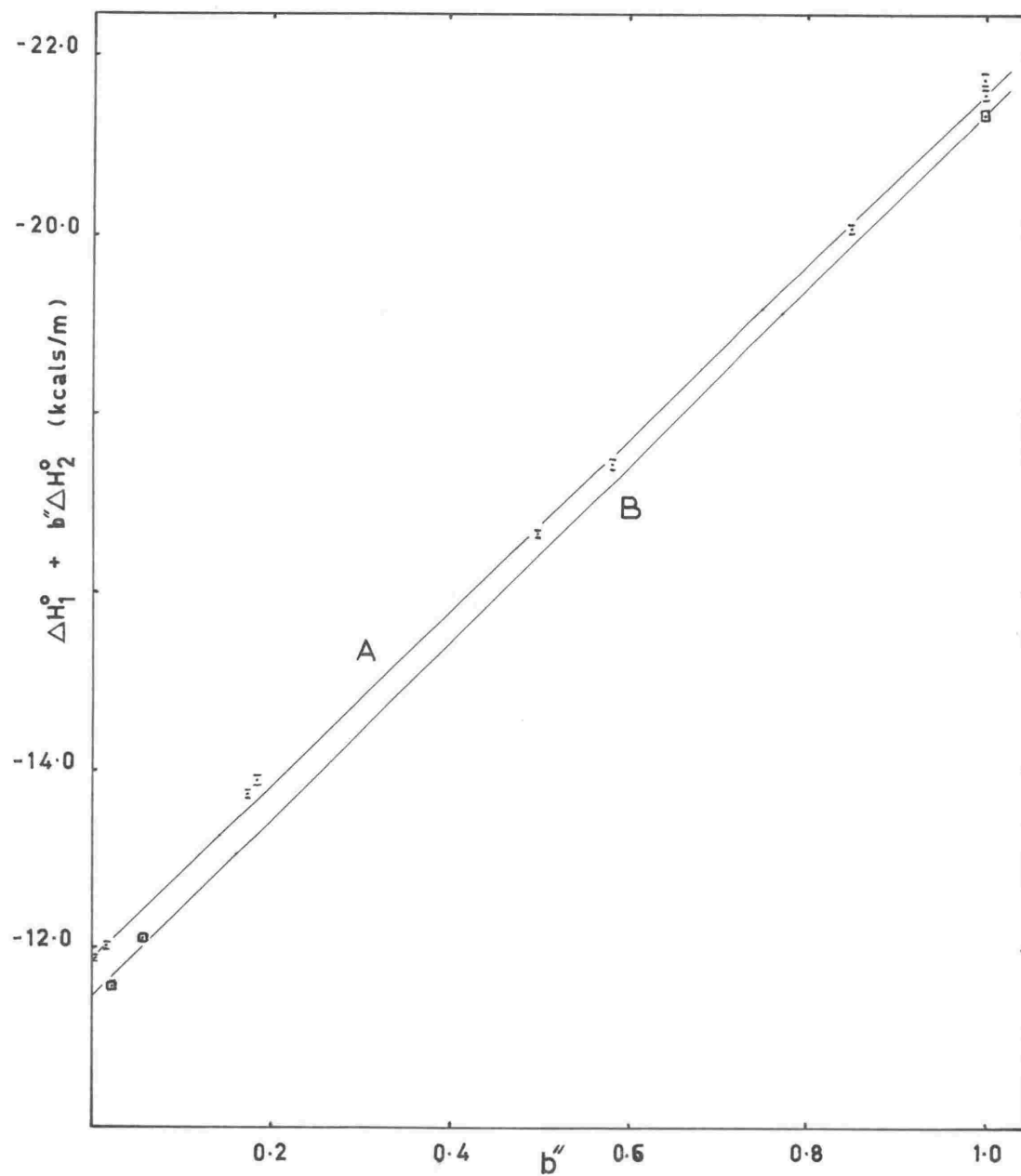
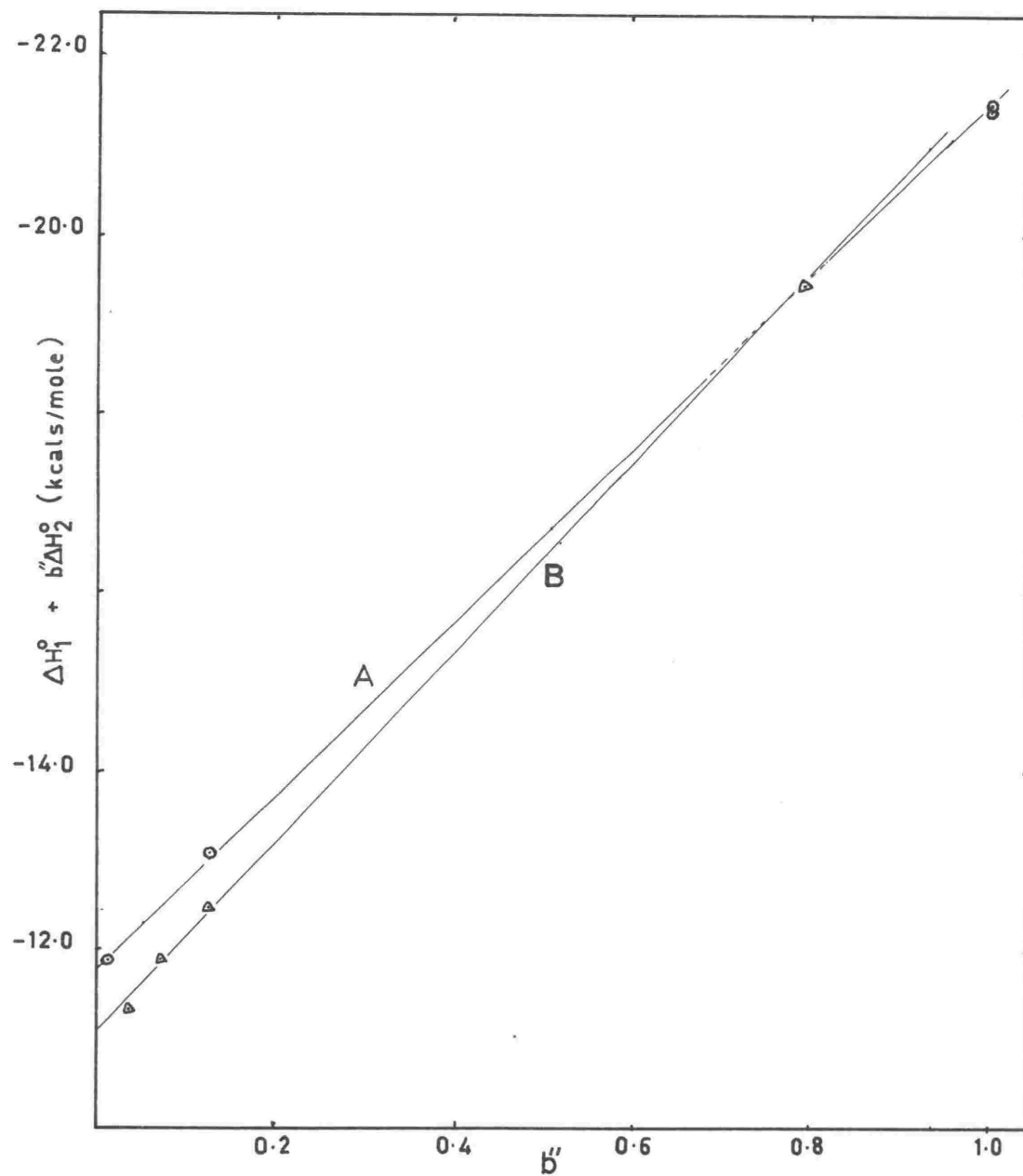


FIG. 6-8.

PLOT OF  $\Delta H_1^\circ + b'\Delta H_2^\circ$  vs.  $b''$  FOR THE  
 PROTONATION OF A. 1-DIMETHYL 1,2-DIAMINOETHANE  
B. 1-PHENYL 1,2-DIAMINOETHANE



## 6-2 Discussion of Results

For the protonation of the alkyl substituted ethylene-diamines there is no apparent relationship between  $\Delta G_i^0$  or  $\Delta H_i^0$  values and the expected influences of the inductive effects operating from the  $C_1$ -alkyl chains. A '+I' effect operating from an alkyl group would help to stabilise the ammonium ion formed in the protonation reaction: viz.,

$$R \rightarrow \overset{\overset{|}{\text{C}}}{\text{C}} \rightarrow \overset{+}{\text{N}}$$

relative to the case for 1,2-diaminoethane  $H - C - \overset{+}{N}$ . (For all the amines the  $-NH_2$  and  $-\overset{+}{NH}_3$  groups will exhibit a -I effect.) The electron displacement would firstly increase the donor power of the amino nitrogen atom and secondly help to decrease the positive charge which is on or near the most electronegative atom (N). If these '+I' inductive effects make important contributions to the amine basicities, then the series of  $\Delta H_i^0$  values predicted<sup>+</sup> would be  $-\Delta H_i^0$  for  $i\text{-bn} > \text{eten} > \text{pn} > \text{en}$ . \* The same order might be expected for the  $-\Delta G_i^0$  values if no highly specific entropy effects are involved. However, for both these state functions the inverse order is observed. The inductive effects of the alkyl substituents  $R'$  in  $NH_2CH(R')CH_2NH_2$  do not contribute significantly to the amine basicity because  $R'$  is separated from the amino group by a saturated carbon atom. The same applies for the structurally similar mono-

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<sup>+</sup> On the basis of relative +I tendencies of alkyl groups listed in Ingold, Ref. 21, p. 71.

\* For abbreviations see list on p.ii.

amines  $\text{RCH(R')NH}_2$ . e.g.,  $\text{pK}_a = 10.60 \pm 0.04$  when  $\text{R} = \text{H}-$ ,  $\text{CH}_3-$ , or  $\text{CH}_3\text{CH}_2\text{CH}_2-$  while  $\text{R}' = \text{H}$ , and when  $\text{R} = \text{CH}_3-$  or  $\text{CH}_3\text{CH}_2-$  while  $\text{R} = \text{CH}_3-$ . However when the substituents are coordinated directly to the N atom inductive effects may be important, e.g., typical  $\Delta G$  values for protonation of aliphatic amines  $\text{RNH}_2$  and  $\text{RR'NH}$  are  $-14.7$  and  $-15.2$  kcal/mole respectively. <sup>a</sup>

#### 6-2.1 The free energy change

$\Delta G^\circ = -RT \ln K_a$  where  $K_a$  is the thermodynamic equilibrium constant for the amine protonation reaction when all reacting species are in the hypothetical state of infinite dilution.

1-phenyl 1,2-diaminoethane: The relatively low values of  $-\Delta G_1^\circ$  and  $-\Delta G_2^\circ$  for the protonation of 1-phenyl 1,2-diaminoethane (a comparatively weak base) suggest that for this molecule the strong inductive ( $-I$ ) influences of the aryl substituent (operating against the ' $-I$ ' effect of the  $1^\circ$  amino nitrogen,  $\text{Ar} \leftarrow \text{C} \leftarrow \text{N}$ ) may contribute significantly to decrease the basicity. A lowering of electron density about the amino nitrogen renders it less capable of coordinating a proton in the neutralisation reaction. The effect of this aryl ' $-I$ ' influence should be apparent in the enthalpy term, as is the case for  $\Delta H_1^\circ$ . However, the

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a. From data given in Ref. 20, p. 313.

low -  $\Delta G_i^0$  values for 1-phenyl 1,2-diaminoethane protonation are as much a result of low entropy changes as of low enthalpy changes (relative to 1,2-diaminoethane or its  $C_1$ -alkyl derivatives). (See 6-2.2 and 6-2.3(c))

The bulk of the alkyl substituent: In a general sense the basicity of these amines decreases with the increasing bulk of the substituent chain on the basic ethylenediamine unit. This decrease arises mainly from lower entropy changes for the protonation of the larger ligand molecules. These results may be compared with those for the acidities of the methyl- substituted acetic acids. Methyl substitution leads to weaker acids; i.e., the tendency to dissociate into ionic species is in the sequence:  $\Delta G_1^0$  for acetic >  $CH_3CH_2COOH$  >  $(CH_3)_2CH.COOH$  >  $(CH_3)_3C.COOH$ . As pointed out by Ingold,<sup>a</sup> such sequences agree with the recognised electropositivity of the alkyl groups in carboxylic acids, i.e., the greater ease with which, relative to hydrogen, they yield electrons towards an electron-attracting centre ( $-COOH$ ). However, Allan and Wright<sup>52</sup> show that the strengths of these organic acids differ mainly because of differences in their entropies of ionisation which are lower for the more highly substituted acetic acids. Therefore for both these molecular systems the entropy change for formation of an ionic centre close to a non-polar alkyl residue is unfavourable, the magnitude

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a. Ref. 21, p. 734.

depending on the "bulk" of the substituent group.

The relationship  $-\Delta G_2^0 < -\Delta G_1^0$  is typical for the protonation of dibasic amines, and arises from the lower enthalpy and entropy changes for the addition of the second proton (see 6-2.2, 6-2.3).

#### 6-2.2 The enthalpy change $\Delta H_1^0$

Except for en, the values for  $\Delta H_{1-2}^0$  are constant within experimental error (see 6-1.3). Therefore the trends in  $\Delta G_{1-2}^0$  values arise predominantly from decreased entropy changes for the protonation of the larger 1,2-diamino molecules.

The  $-\Delta H_{1-2}^0$  value for 1,2-diaminoethane is  $> 1\text{kcal/mole}$  higher than the values for the C-substituted 1,2-diaminoethanes. This may be due to a solvent shielding effect. For the  $C_1$ -substituted 1,2-diaminoethanes, the substituent R partially shields the solvent from the ammonium ion. This shielding does not occur when  $R = H$  (1,2-diaminoethane), and therefore  $\Delta H_{1-2}^0$  for 1,2-diaminoethane should contain a comparatively larger exothermic term arising from the orientation of solvent molecules about the ammonium ions. Hence the higher value of  $-\Delta H_{1-2}^0$  for 1,2-diaminoethane compared with its C-substituted analogues. However, on this basis a lower  $-\Delta H_{1-2}^0$  value than observed would be expected for 1-dimethyl 1,2-diaminoethane. Also this enthalpy effect is not shown for the ionisation of the C-substituted acetic



acids, although solvent orientation about a negative ion ( $\text{COO}^-$ ) will be much less than that about a positive ion ( $\text{-NH}_3^+$ ).

The relationship  $-\Delta H_2^0 < -\Delta H_1^0$  is typical for the protonation of dibasic amines and arises from two main factors: (i) the high electronegativity of the cationic group  $\text{-NH}_3^+$  lowers the electron density about the second amino group through an inductive electron transmission and decreases its donor power.

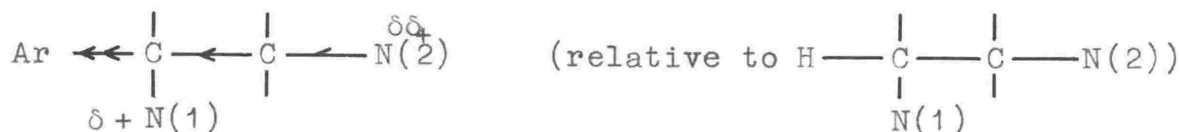
(ii) from the contribution to  $\Delta H_2^0$  of an endothermic term for the intramolecular interaction of the two ammonium ions,  $\text{-NH}_3^+$ .

For the protonation of the  $\text{C}_1$ -alkyl substituted ethylenediamines, both  $-\Delta H_1^0$  and  $-\Delta H_2^0$  are relatively invariant and independent of any inductive effects of the alkyl substituents. The separation of the alkyl groups from the  $\text{-NH}_2$  group diminishes the effect of their +I inductive tendencies on the amine basicity. But for NN'-dimethyl 1,2-diaminoethane,<sup>28</sup>  $-\Delta H_1=12.4\text{kcal/mole}$ . Compared with the value for 1,2-diaminoethane  $-\Delta H_1=11.9\text{kcal/mole}$ , this may\* indicate that at shorter separations, the '+I' effect of an alkyl substituent contributes significantly to the coordinating power of a nitrogen atom.

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\* The  $\Delta H_1^0$  for NN'-dimethyl 1,2-diaminoethane was derived<sup>28</sup> by the  $\frac{1}{T}$  temperature coefficient method (see 2-2.3) and may be subject to a large uncertainty. (see 3-3.1)

1-phenyl 1,2-diaminoethane protonation sequence: For 1-phenyl 1,2-diaminoethane protonation, the low  $-\Delta H_1^0$  value may be a result of the strong '-I' tendency of the phenyl group. The first proton is probably coordinated mainly by the nitrogen atom (N<sub>2</sub>) more remote from the electronegative phenyl group: +



(Substituent inductive effects diminish with distance from the centre of electron induction. Suggested transmission factors range from 0.33 to 0.53 for each atom in the chain.<sup>20</sup>) The second proton will then be coordinated mainly by N<sub>1</sub> which is closer to the phenyl group. The latter then behaves as an electron 'reservoir' (+I), increasing the electron density on the nitrogen atom (N<sub>1</sub>) and stabilising the ammonium ion. This stabilisation accounts for the relatively high value observed for  $-\Delta H_2^0$ . (Note, the phenyl group is empirically assigned electron withdrawing properties relative to the hydrogen atom in a neutral compound, C<sub>6</sub>H<sub>5</sub>-CR<sub>3</sub>, H-CR<sub>3</sub>, and could show marked '+I' effects when situated close to a highly electronegative

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+ This is substantiated by the logK values derived from Perrin and Clark's empirical data.<sup>20</sup> For N(2) protonation, predicted logK=9.17, for N(1), logK=8.57. i.e., the predicted eqbm. constant for the formation of the -N(2)H<sub>3</sub><sup>+</sup> ion is approximately four times greater than that for the formation of -N(1)H<sub>3</sub><sup>+</sup>.

group, e.g.,  $-\text{NH}_3^+$ .) \*

### 6-2.3 The entropy change

(a) Correction for statistical terms: Ethylenediamine has two equivalent amino groups with equal proton affinities. Therefore  $\Delta S_1^0$  contains a statistical term  $+R\ln 2 (=1.4 \text{ e.u.})$ .  $\Delta S_2^0$  for ethylenediamine contains a statistical term  $-R\ln 2$ , because the diprotonated species contains two equivalent ammonium ions each equally capable of losing a proton.

Empirical and experimental data suggest that the two amino groups in 1-phenyl 1,2-diaminoethane do not have similar base strengths. The first proton added to the diamine may be coordinated mainly by the  $-\text{N}(2)\text{H}_2$  group (cf., the  $\log K$  values for protonation of the monoamines;  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ,  $\equiv \text{N}(1)$ , 9.34;  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$ ,  $\equiv \text{N}(2)$ , 9.83.<sup>71</sup>) Therefore  $\Delta S_1^0$  and  $\Delta S_2^0$  for protonation of this amine probably contain negligible statistical terms.

For the amines 1-methyl, 1-ethyl and 1-dimethyl 1,2-diaminoethane, the  $\text{N}(1)$  and  $\text{N}(2)$  amino groups probably exhibit similar, though not equal, basicities. (The relative basicities of these groups are considered in 6-2.3(c)).

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\* This is substantiated by the Taft  $\sigma^*$  values:  $-\text{NH}_2$ , +0.62;  $\text{C}_6\text{H}_5-$ , +0.60;  $(\text{CH}_3)_3\text{NCH}_2-$ , +1.90.<sup>20</sup> These are a measure of the inductive capacity of a group. Therefore  $-I$  of  $\text{C}_6\text{H}_5- \doteq -\text{NH}_2 \ll (\text{CH}_3)_3\text{NCH}_2-$ . It is probable that  $\sigma^*$  for  $\text{H}_3\text{N}^+\text{CH}_2-$  is  $> \sigma^*(\text{CH}_3)_3\text{NCH}_2-$ .

Therefore on addition of the first proton both amino groups will be partially protonated. It is assumed to a first approximation that for each of the amines each amino group has the same proton affinity. Therefore the same statistical corrections are made to  $\Delta S_1^0$  and  $\Delta S_2^0$  as were made for ethylenediamine. The corrected entropy changes left to right in Table 6-6 are:

$\Delta S_1^0$	4.1	3.1	3.1	2.2	1.9 e.u.
$\Delta S_2^0$	-4.4	-0.7	-2.6	-2.7	-9.3 e.u.

(b) The relative values for  $\Delta S_1^0$  and  $\Delta S_2^0$ : For each base  $\Delta S_1^0$  is less than  $\Delta S_2^0$ . This is probably due to

- (i) repulsion between the two ammonium groups in the diprotonated molecule. This repulsion tends to stiffen the intermediate alkyl chain causing a loss in rotational and vibrational entropy.
- (ii) ammonium ions orientating water molecules in their vicinity. This lowers the rotational and translational entropy of the solvent. The volume of solvent affected by an ion depends on the ion-charge. For singly and doubly charged (coincident charge) ions the volume ratio is  $1:2^{3/2}$ , i.e., 1:2.8. As the distance between charges in a doubly charged ion increases, the volume of solvent affected falls from 2.8 to 2.0 times that for the "mono" case. A 1,2-diammonium ion would act essentially as a doubly charged (coincident charge)

species.<sup>9</sup> Therefore  $\Delta S_2^0$  would contain a larger negative 'solvent orientation' term than would  $\Delta S_1^0$ .

(c) Relationship between  $\Delta S^0$  and molecular structure:

Both  $\Delta S_1^0$  and  $\Delta S_2^0$  decrease with increasing bulk of the  $C_1$ -substituent (Fig. 6-9). This decrease may be associated with a repulsion between the non-polar alkyl or aryl chain of low dielectric and the ammonium ions formed on protonation. Formation of an ion (e.g.,  $-NH_3^+$ ) 'freezes' the motions of the solvent molecules in its vicinity.<sup>73,86</sup> There is a radial orientation of the solvent (high dielectric) about an electrostatic charge ( $-NH_3^+$ ). The effect of this orientation is to repel from the charge any region of low dielectric present.<sup>73</sup> Therefore in a protonated amine the alkyl chain is repelled from the ammonium ion; there is an associated chain stiffening<sup>9</sup> or loss of freedom of chain conformation which lowers the rotational and vibrational entropy of the amine molecule. The entropy loss will increase with the 'size' of the  $C_1$  substituent. It has been postulated that a similar chain repulsion phenomenon occurs for the ionisation of the alkyl carboxylic acids.<sup>91</sup>

The large negative  $\Delta S_2^0$  value for 1-phenyl 1,2-diaminoethane may arise because the phenyl group can act as an electron reservoir (see p. 106):

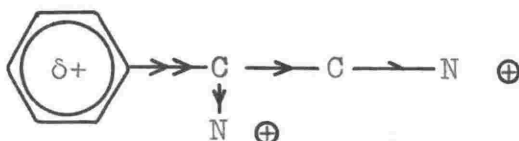
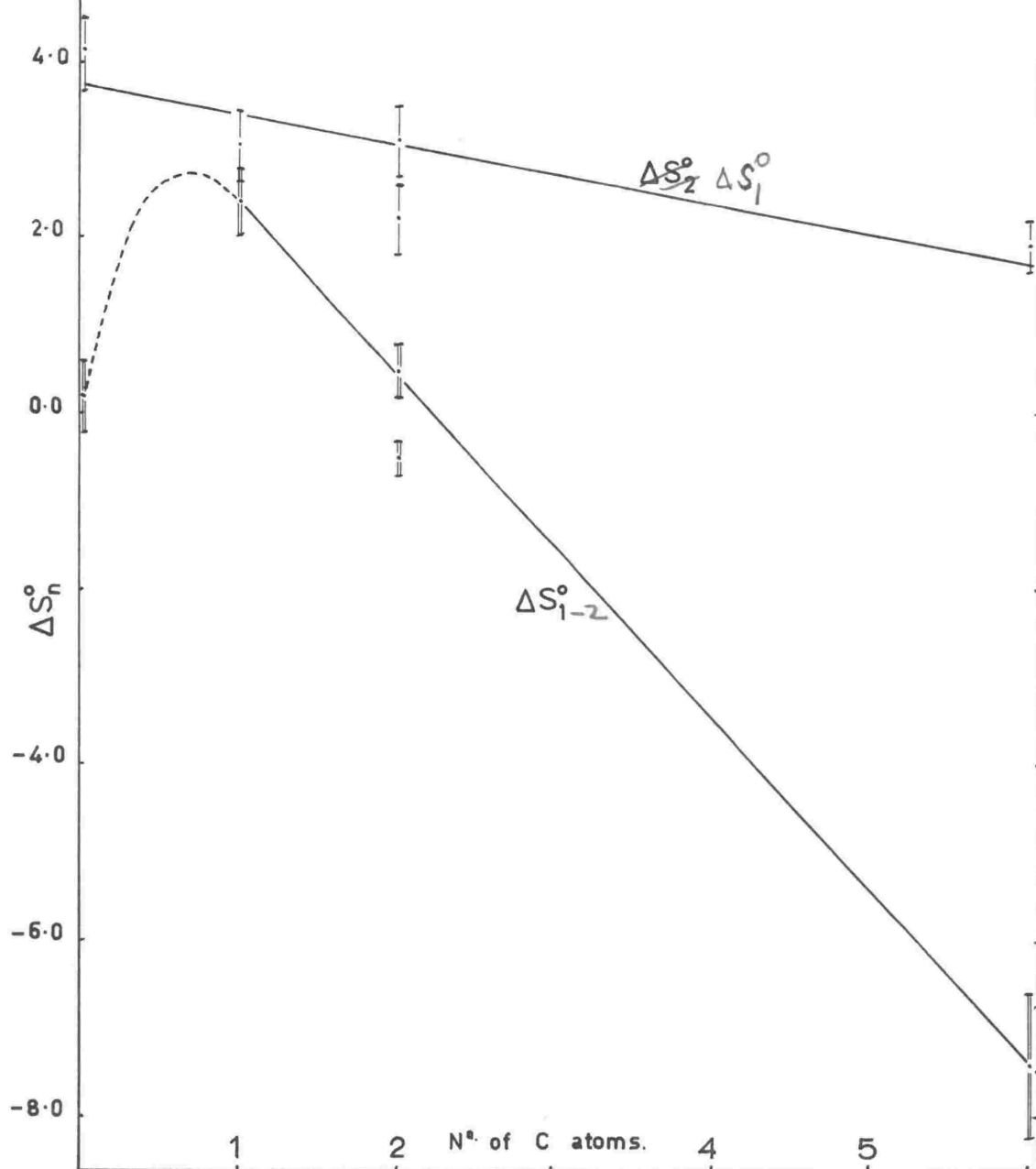


FIG. 6-9

PLOT OF  $\Delta S_n^\circ$  FOR THE PROTONATION REACTION  
 $\text{NH}_2\text{CH(R)CH}_2\text{NH}_2 + n\text{H}^+$ , versus THE NUMBER OF  
 CARBON ATOMS IN THE SUBSTITUENT 'R'



Repulsion between the ammonium and  $\text{C}_6\text{H}_5^{\delta+}$ - groups would further lower the vibrational and rotational entropy of the molecule.

#### 6-2.4 The relative basicities of the amine groups

For the reaction



there will be an equilibrium distribution of protons on N(1) and N(2) (Fig., p.106 ). Ethylenediamine has two equivalent amine groups and therefore the distribution will be equally weighted. On the other hand, 1-phenyl 1,2-diaminoethane has two amine groups which probably exhibit quite different basicities (see pp.106, 107) and it is considered that the first proton added resides mainly on the N(2) amino group. For the alkyl substituted ethylenediamines some evidence (A) suggests that the proton distribution weighting may be equal while other evidence (B) suggests that for addition of the first proton the ratio of N(2) groups protonated to N(1) groups protonated is  $> 1$ . These two possibilities are briefly discussed:

- A. The ratio  $\Delta G_1^0 / \Delta G_2^0$  is approximately constant ( $\pm 2\%$ ) suggesting that very similar factors (e.g., steric, solvation, electronic) contribute to  $K_1$  and  $K_2$ .
- B.1. For ethylenediamine and its  $\text{C}_1$ -alkyl analogues,  $\Delta S_1^0$  and  $\Delta H_1^0$  are approximately constant, suggesting that for each molecule initial protonation occurs

mainly on the similar N(2) basic centres:

$>\text{CH}.\text{CH}_2.\text{NH}_2$ . For each of the N(2) groups similar solvent orientation and electronic effects will be associated with ammonium ion formation.

- B.2. The comparatively high  $-\Delta H_2^0$  and low  $\Delta S_2^0$  values for ethylenediamine. Contributing to the  $\Delta H_2$  and  $\Delta S_2$  values are terms for the effect of solvent orientation about the ammonium ion formed.  $-\Delta H$  will decrease and  $\Delta S$  will increase with decreasing solvent orientation. For protonation at N(1) only could these terms differ markedly for ethylenediamine and its  $\text{C}_1$ -substituted derivatives. Solvent orientation will be greatest about ethylenediamine (see 6-2.2 and 6-2.3(c)) and hence the high  $-\Delta H_2^0$  and low  $\Delta S_2^0$  for this molecule. Therefore it is possible that addition of the second proton occurs mainly on N(1). Proceeding from pn to eten to i-bn the  $\Delta S_2^0$  values decrease with increasing chain-stiffening effects.

Because of the uncertainty in the sequences of  $-\text{NH}_2$  protonation for these diamines, only the overall thermodynamic functions  $\Delta G_{1-2}^0$ ,  $\Delta H_{1-2}^0$ , and  $\Delta S_{1-2}^0$  have any real significance. Solvation effects are apparently important and account for the trend in  $-\Delta G_{1-2}^0$  values,  $\text{en} > \text{pn} > \text{eten} > \text{i-bn}$ .



### 6-2.5 Empirical correlations

The observed sequence of  $\log K$  values was not predicted by Hall's empirical equation for the protonation of aliphatic primary amines:<sup>71</sup>

$$\text{pK}_a = 13.23 - 3.14 \sum \sigma^*$$

In this equation the Taft  $\sigma^*$  values give a measure of intramolecular inductive effects. The lack of correlation suggests that effects other than the electronic inductive effect (viz., solvation, steric) determine the relative basicities.

### 6-3 Comparison with Previous Results

(a) Nasanen et al.<sup>23</sup> have recently published  $\log K$  values for the protonation of 1-methyl 1,2-diaminoethane in aqueous  $\text{NaClO}_4$  media. The values of  $\log K_c$  obtained at various ionic strengths are shown on Fig. 6-3. The thermodynamic functions obtained were  $-\Delta G_1^0 = 13.39 \pm 0.02 \text{ kcal/mole}$ ,  $-\Delta G_2^0 = 9.02 \pm 0.01 \text{ kcal/mole}$  (cf., this work  $13.26 \pm 0.01$ ,  $9.015 \pm 0.005 \text{ kcal/mole}$  respectively),  $-\Delta H_1^0 = 11.8 \pm 0.2 \text{ kcal/mole}$ ,  $-\Delta H_2^0 = 11.1 \pm 0.1 \text{ kcal/mole}$  (by the temperature coefficient method, see 3-3.1; cf. this work,  $11.92 \pm 0.14$ ,  $9.65 \pm 0.15 \text{ kcal/mole}$  respectively).

(b) The effect of  $C_1C_2$ -substitution: It is interesting to note the thermodynamic results obtained by Basalo et al.<sup>28</sup> for some  $C_1C_2$ -substituted ethylenediamines, Table 6-6.

TABLE 6-6

Thermodynamic data for protonation of C<sub>1</sub>C<sub>2</sub>-substituted  
1,2-diamino ethanes, 25.0°C.<sup>28</sup>

Base <sup>a</sup>	- ΔG <sub>1</sub> kc/m	- ΔH <sub>1</sub> kc/m	T Δ S kc/m	- ΔG <sub>2</sub> kc/m	- ΔH <sub>2</sub> kc/m	T Δ S kc/m
dl-bn <sup>+</sup>	13.64	10.3	3.3	9.43	10.3	-0.9
m-bn <sup>+</sup>	13.61	9.8	3.8	9.45	9.4	0.0
dl-stien*	11.02	11.3	-0.3	5.39	9.7	-4.3
m-stien*	10.80	11.0	-0.2	6.52	11.6	-5.1

a for abbreviations see p. ii.

+ Ba(NO<sub>3</sub>)<sub>2</sub>/KNO<sub>3</sub> medium, I=0.65m/1.

\* in 50% H<sub>2</sub>O/dioxan, 0.005m Ba(ClO<sub>4</sub>)<sub>2</sub> medium.

These values show the stilbenediamines to be weak bases because of unfavourable (low) entropy terms which Basalo et al.<sup>28</sup> thought might be attributable to the use of a mixed solvent system. However, the data for 1-phenyl 1,2-diaminoethane in aqueous solution shows that N-protonation in the system C<sub>6</sub>H<sub>5</sub>-C-N is characterised by a low ΔS term (see 6-2.3(c), (d).) For all four amines, ΔH<sub>1</sub> ≈ ΔH<sub>2</sub> (temperature coefficient data). Therefore the typical relationship -ΔG<sub>2</sub> < -ΔG<sub>1</sub> arises mainly because of low entropy values for the second protonation reaction (see p.108). -ΔH<sub>1</sub> for the stilbenediamines is greater than -ΔH<sub>1</sub> for the symmetrical butylenediamines, presumably because the phenyl group acts as a strong intramolecular electron donor when

close to an ammonium ion (see p.106). The relationship  $T \Delta S(\text{stien}) < T \Delta S(\text{bn})$  could arise from stronger repulsion between the ammonium ion and phenyl ( $\delta+$ )- group than between  $-\text{NH}_3^+$  and  $\text{CH}_3^-$  groups (see 6-2.3(c)) and the observed relative basicities stem from these different  $T \Delta S$  terms.

#### 6-4 Conclusions

1. This work has shown that the basicities of  $\text{C}_1$ -alkyl substituted 1,2-diaminoethanes bear no observable relationship to the inductive capacity of the alkyl substituents. This also appears to be true for  $\text{C}_1\text{C}_2$ -symmetrically substituted 1,2-diaminoethanes. e.g., symm-butylenediamines, tetramethylethylenediamine.
2. The basicity of  $\text{NH}_2\text{CH}(\text{R})\text{CH}_2\text{NH}_2$  decreases with increased bulk of the  $\text{C}_1$ -alkyl substituent. This results from a decreasing  $\Delta S$  term which can be related to a solvation effect.
3. C-phenyl 1,2-diaminoethanes are weak bases compared with 1,2-diaminoethane and its C-alkyl derivatives. This is not because of a strong -I effect of the phenyl substituent. (In the system  $\text{C}_6\text{H}_5-\text{C}-\text{N}^+$  the phenyl group shows a '+I' effect which stabilises the ammonium ion.) Their low basicities arise mainly from a low entropy term

for the protonation reaction. It is postulated that this term is low because of repulsion between the  $\text{C}_6\text{H}_5(\delta^+)$ - and  $-\text{NH}_3^+$  ionic centres.

## CHAPTER SEVEN

THERMODYNAMIC DATA FOR AQUEOUS COPPER(II)-DIAMINE COMPLEXES7-1 Experimental and Results

Notation: The equilibrium constants for reactions involving the ligand and metal ion are given Roman numeral subscripts. e.g., for



$$K_I = \frac{[M(H_2O)_4L]^{n+}}{[M(H_2O)_6]^{n+}[L]}, \text{ and } \Delta G_I^O = -RT \ln K_I^O$$

where  $K_I^O$  is the thermodynamic (activity) equilibrium constant consistent with a hypothetical aqueous system containing all reactants at infinite dilution ( $=K_{a_I}$ ).

The equilibrium constants for reactions involving the ligand (base) and acid ( $H^+$ ) only, are given integer subscripts.

e.g., for  $L + H^+ \rightleftharpoons LH^+$

$$K_1 = [LH^+]/[L][H^+], \text{ and } \Delta G_1^O = -RT \ln K_1^O$$

(See Chapter 6)

with reference to the same standard state.

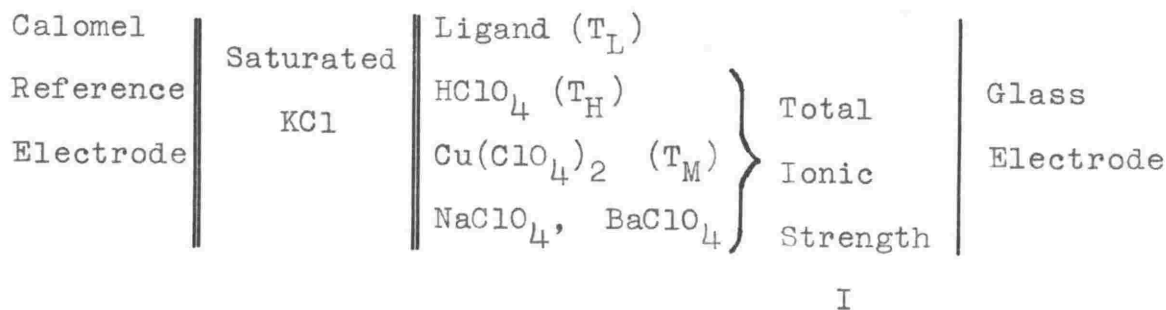
A similar notation is used for enthalpy and entropy changes, viz.,  $\Delta H_I$ ,  $\Delta H_{II}$ ,  $\Delta S_I$ ,  $\Delta S_{II}$ , etc., for metal ion ligation reactions.

To simplify equations charges are generally omitted.

### 7-1.1 The free energy change

$\Delta G^{\circ}$  was obtained from the thermodynamic equilibrium constant  $K_a$  by the relationship  $\Delta G^{\circ} = -RT \ln K_a$ . (See equations 2-8, 9.)

For a series of ionic strengths, solutions were prepared containing different compositions of copper perchlorate ( $T_M$ ),  $HClO_4$  ( $T_H$ ), and ligand ( $T_L$ ). The ionic strength was adjusted by the addition of the inert electrolytes  $NaClO_4$  and  $Ba(ClO_4)_2$ . (See formulation in 4-1.3) The solutions were analysed potentiometrically to measure their equilibrium hydrogen ion concentrations  $[H^+]_{eqbm}$ , at  $25.00 \pm 0.01^{\circ}C$ , (See 5-1) using the cell



(See p. 65 and Fig. 5-1.) By substituting  $[H^+]_{eqbm}$  (designated H) into equation 3-4, the free ligand concentration  $[L]$  and the concentrations of  $HL^+$  and  $H_2L^{2+}$  in each solution were determined. The results for the Cu(II)-1-methyl 1,2-diaminoethane reaction are given fully in Tables 7-1 and 7-2. From this data  $\bar{n}$  was calculated for each solution (see 4-1.2) and formation curves ( $\bar{n}$  vs.  $[L]$ ) were plotted. (Figs. 7-1, 7-2). Approximate  $K_c$  values,

TABLE 7-1

'Formation Curve' experimental data for the 1:1 equilibrium reaction between cupric ions and 1-methyl 1,2-diamino ethane in aqueous solution,  $25.00 \pm 0.01^\circ\text{C}$

Ionic strength (m/l)	$T_L \cdot 10^2$ (m/l)	$T_{Cu} \cdot 10^2$ (m/l)	$T_H \cdot 10^4$ (m/l)	$p[H^+]$	$[HL] \cdot 10^6$ (m/l)	$[H_2L] \cdot 10^4$ (m/l)	$[L] \cdot 10^{11}$ (m/l)	$\bar{n}$
0.350	3.200	6.667	22.72	$4.517 \pm 0.002$	3.889	11.19	$1.765 \pm 0.055$	0.4632
"	"	6.410	21.85	$4.556 \pm 0.001$	4.094	10.77	$2.033 \pm 0.051$	0.4823
"	"	6.300	21.49	$4.567 \pm 0.001$	4.117	10.56	$2.097 \pm 0.052$	0.4925
"	"	6.154	20.99	$4.581 \pm 0.002$	4.166	10.34	$2.191 \pm 0.068$	0.5031
"	"	5.934	20.25	$4.606 \pm 0.001$	4.257	9.976	$2.372 \pm 0.059$	0.5224
"	"	5.714	19.30	$4.636 \pm 0.003$	4.395	9.614	$2.624 \pm 0.092$	0.5430
0.200	1.600	3.333	11.38	$4.672 \pm 0.001$	3.205	5.565	$2.246 \pm 0.053$	0.4633
"	"	3.213	10.92	$4.700 \pm 0.001$	3.283	5.343	$2.454 \pm 0.064$	0.4810
"	"	3.095	10.57	$4.716 \pm 0.001$	3.296	5.173	$2.557 \pm 0.059$	0.5001
"	"	2.963	10.12	$4.752 \pm 0.002$	3.431	4.956	$2.891 \pm 0.087$	0.5230
"	"	2.857	9.766	$4.776 \pm 0.002$	3.499	4.782	$3.115 \pm 0.093$	0.5430

TABLE 7-1 (contd.)

Ionic strength (m/l)	$T_L \cdot 10^2$ (m/l)	$T_{Cu} \cdot 10^2$ (m/l)	$T_H \cdot 10^4$ (m/l)	$p[H^+]$	$[HL] \cdot 10^6$ (m/l)	$[H_2L] \cdot 10^4$ (m/l)	$[L] \cdot 10^{11}$ (m/l)	$\bar{n}$
0.150	1.200	2.500	8.531	4.725 $\pm$ 0.001	2.911	4.157	2.445 $\pm$ 0.066	0.4633
"	"	2.321	7.928	4.778 $\pm$ 0.003	3.059	3.865	2.904 $\pm$ 0.107	0.5001
"	"	2.222	7.592	4.810 $\pm$ 0.001	3.154	3.703	3.222 $\pm$ 0.087	0.5232
"	"	2.143	7.324	4.833 $\pm$ 0.001	3.209	3.573	3.457 $\pm$ 0.093	0.5431
0.100	0.800	1.667	5.687	4.810 $\pm$ 0.001	2.535	2.753	2.745 $\pm$ 0.071	0.4636
"	"	1.607	5.460	4.840 $\pm$ 0.001	2.609	2.644	3.030 $\pm$ 0.085	0.4813
"	"	1.548	5.285	4.868 $\pm$ 0.001	2.696	2.561	3.338 $\pm$ 0.087	0.5002
"	"	1.482	5.062	4.888 $\pm$ 0.002	2.703	2.452	3.504 $\pm$ 0.112	0.5232
"	"	1.429	4.883	4.919 $\pm$ 0.003	2.802	2.367	3.901 $\pm$ 0.140	0.5432
0.040	0.320	6.667	2.274	4.989 $\pm$ 0.003	1.757	1.077	3.129 $\pm$ 0.116	0.4636
"	"	6.427	2.184	5.010 $\pm$ 0.001	1.772	1.035	3.313 $\pm$ 0.091	0.4815
"	"	6.190	2.114	5.053 $\pm$ 0.001	1.898	1.003	3.916 $\pm$ 0.106	0.5004
"	"	5.926	2.025	5.076 $\pm$ 0.001	1.916	0.961	4.169 $\pm$ 0.113	0.5235
"	"	5.714	1.953	5.102 $\pm$ 0.003	1.963	0.927	4.535 $\pm$ 0.159	0.5434



FIG. 7-1.

FORMATION CURVES FOR THE REACTION

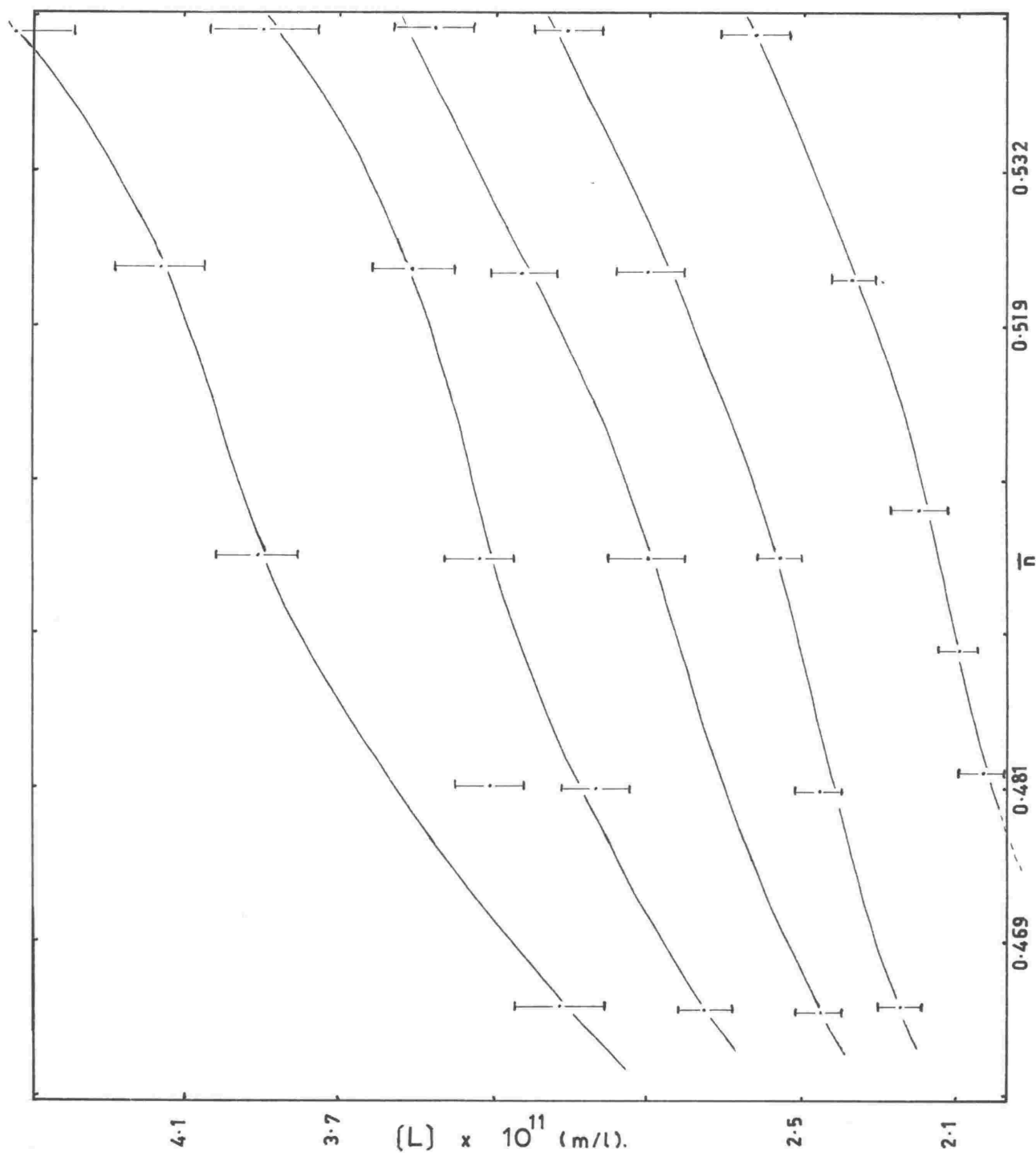
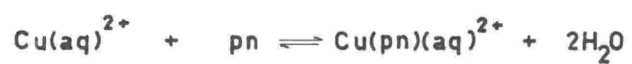


TABLE 7-2

'Formation Curve' experimental data for the 1:2 equilibrium reaction between cupric ions and 1-methyl 1,2-diamino ethane in aqueous solution,  $25.00 \pm 0.01^\circ\text{C}$

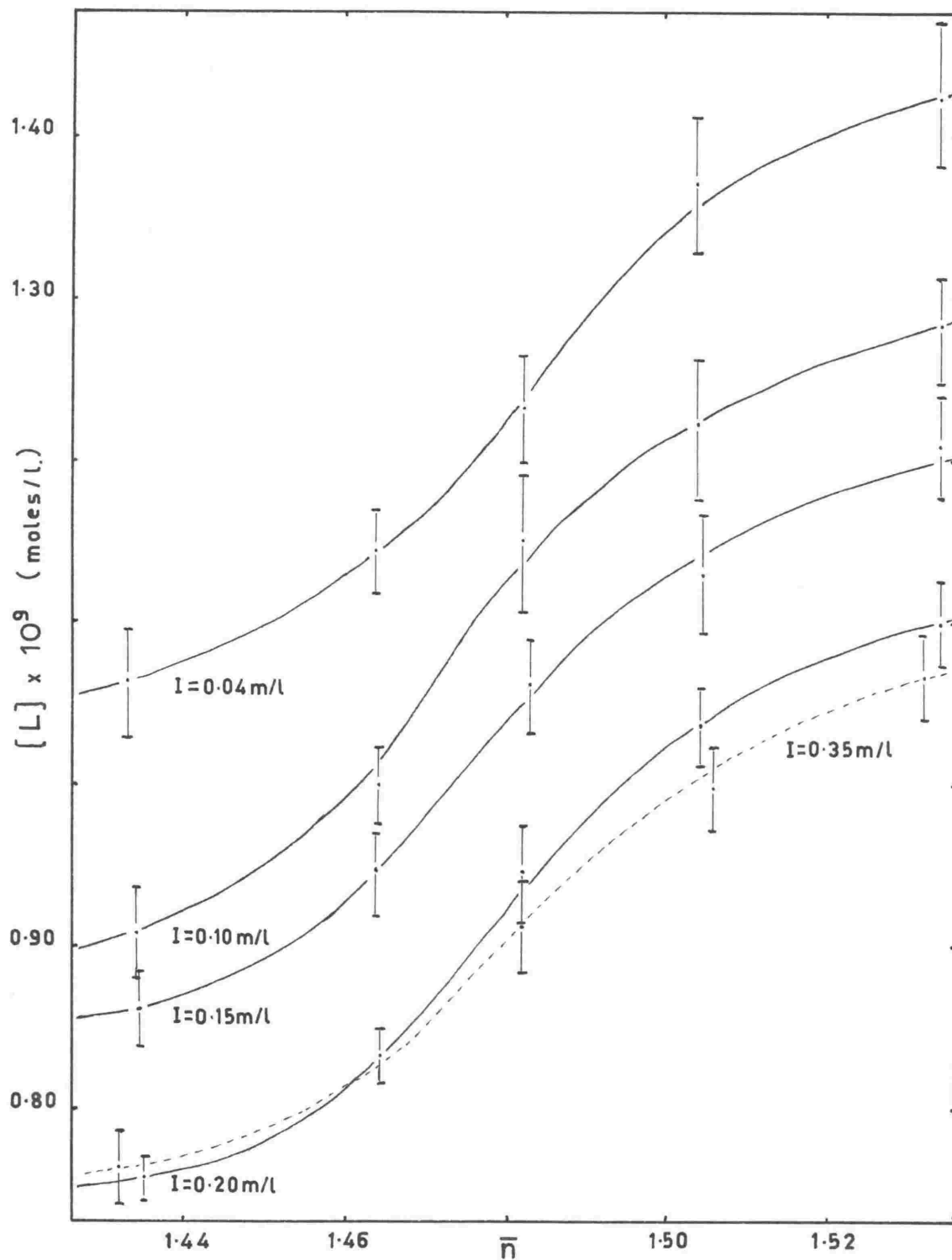
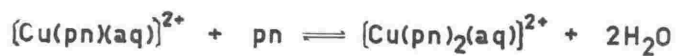
Ionic strength (m/l)	$T_L \cdot 10^2$ (m/l)	$T_{Cu} \cdot 10^2$ (m/l)	$T_H \cdot 10^4$ (m/l)	$p[H^+]$	$[HL] \cdot 10^5$ (m/l)	$[H_2L] \cdot 10^4$ (m/l)	$[L] \cdot 10^9$ (m/l)	$\bar{n}$
0.350	6.000	4.132	16.32	$5.411 \pm 0.002$	2.146	8.034	$0.763 \pm 0.023$	1.430
"	"	4.000	15.97	$5.451 \pm 0.002$	2.343	7.850	$0.913 \pm 0.027$	1.480
"	"	3.935	15.79	$5.473 \pm 0.002$	2.437	7.760	$0.999 \pm 0.027$	1.504
"	"	3.870	15.62	$5.490 \pm 0.002$	2.505	7.670	$1.068 \pm 0.026$	1.530
0.200	4.000	2.759	9.433	$5.477 \pm 0.001$	1.696	4.615	$0.759 \pm 0.018$	1.433
"	"	2.703	99.244	$5.502 \pm 0.001$	1.759	4.518	$0.833 \pm 0.017$	1.463
"	"	2.667	9.134	$5.532 \pm 0.003$	1.860	4.459	$0.944 \pm 0.032$	1.480
"	"	2.632	99.004	$5.555 \pm 0.001$	1.937	4.404	$1.037 \pm 0.025$	1.503
"	"	2.581	8.833	$5.573 \pm 0.001$	1.974	4.305	$1.101 \pm 0.026$	1.532
0.100	2.000	1.379	4.717	$5.611 \pm 0.002$	1.327	2.280	$0.909 \pm 0.028$	1.432
"	"	1.351	4.622	$5.636 \pm 0.001$	1.376	2.231	$0.998 \pm 0.026$	1.463
"	"	1.335	4.567	$5.670 \pm 0.003$	1.467	2.199	$1.151 \pm 0.041$	1.480
"	"	1.316	4.502	$5.686 \pm 0.003$	1.498	2.166	$1.220 \pm 0.049$	1.502

TABLE 7-2(contd.)

Ionic strength (m/l)	$T_L \cdot 10^2$ (m/l)	$T_{Cu} \cdot 10^2$ (m/l)	$T_H \cdot 10^4$ (m/l)	$p[H^+]$	$[HL] \cdot 10^5$ (m/l)	$[H_2L] \cdot 10^4$ (m/l)	$[L] \cdot 10^9$ (m/l)	$\bar{n}$
0.100	2.000	1.291	4.417	5.701 $\pm$ 0.001	1.520	2.122	1.281 $\pm$ 0.033	1.532
0.150	3.000	2.069	7.075	5.539 $\pm$ 0.001	1.572	3.444	0.861 $\pm$ 0.023	1.433
"	"	2.027	6.933	5.564 $\pm$ 0.001	1.630	3.371	0.945 $\pm$ 0.025	1.462
"	"	2.003	6.850	5.592 $\pm$ 0.001	1.715	3.326	1.061 $\pm$ 0.029	1.481
"	"	1.974	6.753	5.609 $\pm$ 0.002	1.759	3.276	1.130 $\pm$ 0.037	1.503
"	"	1.936	6.625	5.628 $\pm$ 0.001	1.799	3.211	1.209 $\pm$ 0.033	1.532
0.040	1.000	0.5517	1.887	5.785 $\pm$ 0.002	0.954	0.935	1.062 $\pm$ 0.033	1.431
"	"	0.5406	1.849	5.817 $\pm$ 0.002	0.955	0.869	1.144 $\pm$ 0.035	1.462
"	"	0.5340	1.827	5.836 $\pm$ 0.001	0.983	0.857	1.231 $\pm$ 0.033	1.480
"	"	0.5263	1.801	5.863 $\pm$ 0.002	1.028	0.842	1.370 $\pm$ 0.042	1.502
"	"	0.5162	1.767	5.876 $\pm$ 0.001	1.038	0.825	1.426 $\pm$ 0.044	1.532

FIG. 7-2.

FORMATION CURVES FOR THE REACTION :



$$K_n = \frac{1}{[L]_{\bar{n}=n-\frac{1}{2}}}$$

were obtained by interpolating  $[L]_{\bar{n}=n-\frac{1}{2}}$  values from the formation curves. Improved  $K_c$  values were obtained by employing Bjerrum's method of successive substitutions. (See 4-1,2)

The  $\log K_c$  values for each of the Cu(II)-diamine systems studied are given in Table 7-3.  $\log K_a$  values were obtained by extrapolation of  $\log K_c$  to zero ionic strength. (Figs. 7-3 to 7-5) For these extrapolations, the relationship

$$\log K_a = \lim_{I \rightarrow 0} (\log K_c + \text{fn.} I) = \lim_{I \rightarrow 0} (\log K_c)$$

was assumed (equations 2-8,9). For 1 = eten and i-bn, it was found that

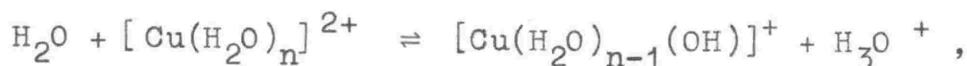
$$\log K_{a_I} = \log K_{c_I} - \alpha I^{\frac{1}{2}} \quad \text{where } \alpha \approx 1.0$$

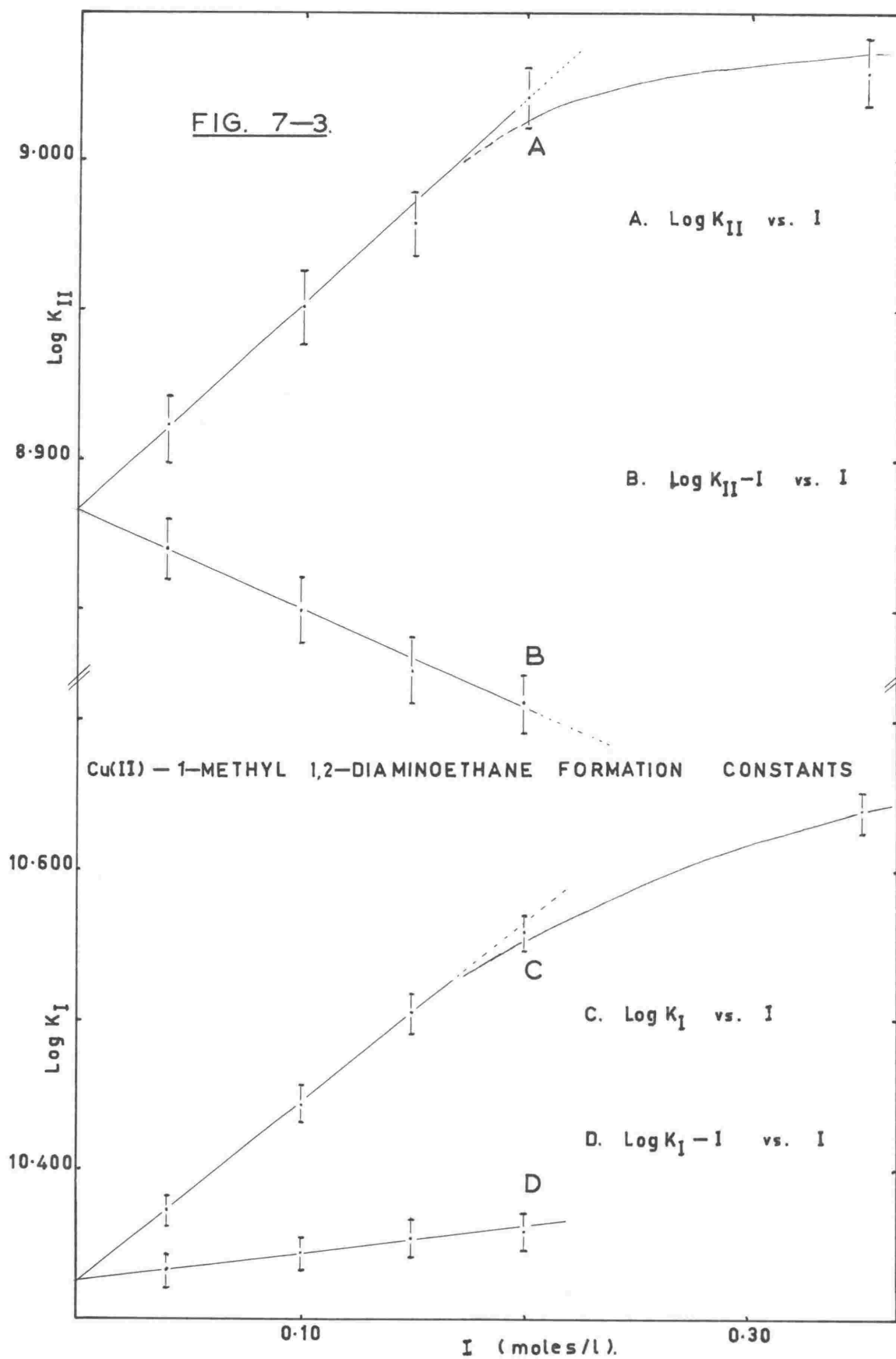
$$\text{and } \log K_{a_{II}} = \log K_{c_{II}} - \beta I \quad \text{where } \beta \approx 0.5$$

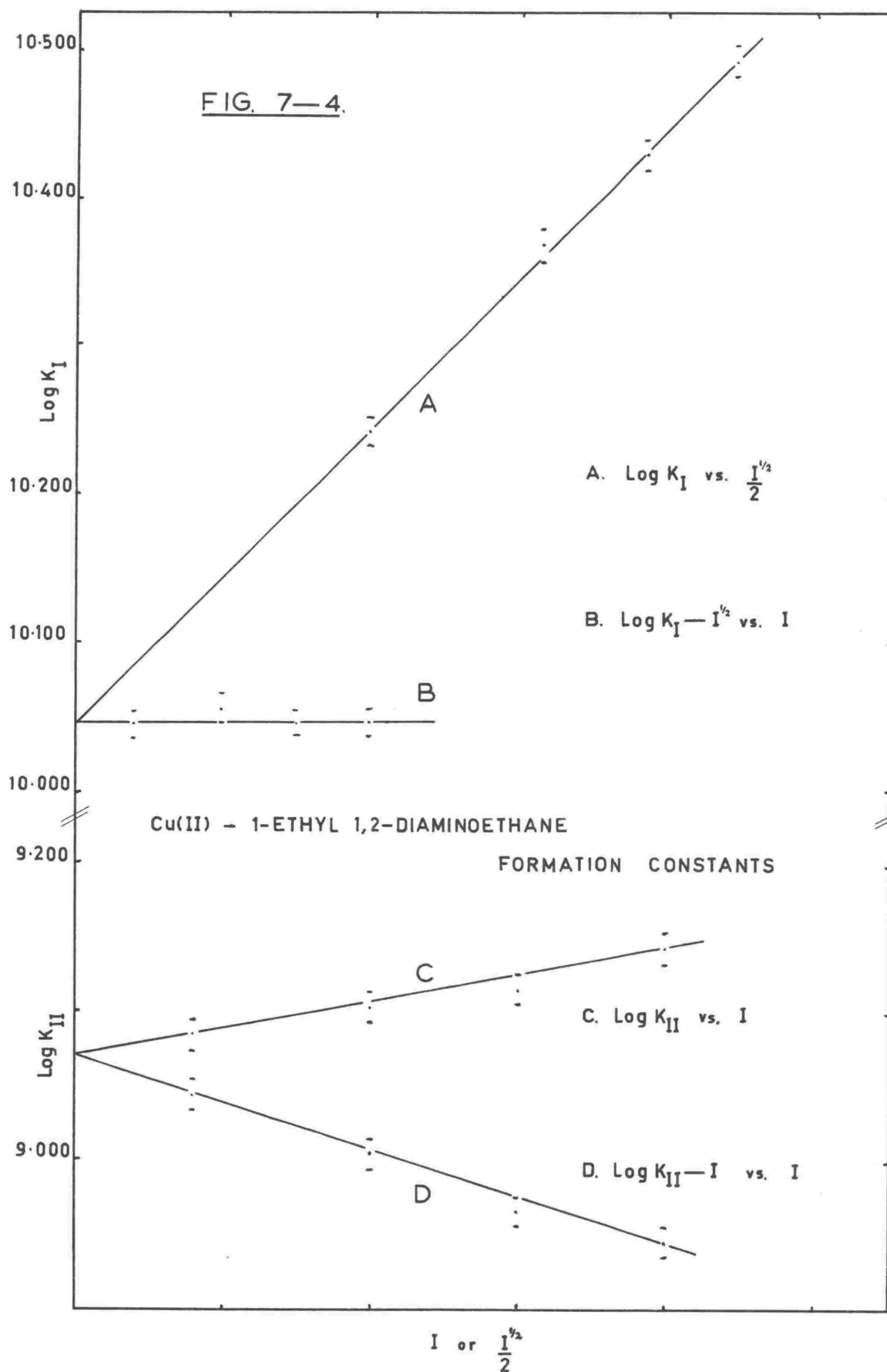
To check each extrapolation of  $\log K_c$  to zero ionic strength, two plots,  $\log K_c$  vs.  $\text{fn.} I$  and  $(\log K_c - \text{fn.} I)$  vs.  $I$  were made. For a given reaction, each extrapolation gave the same intercept on the axis  $I = 0$  (Figs. 7-3 to 7-5).

$\log K_a$  values are given in Table 7-3 and  $G^0$  values in Table 7-5.

Copper ion hydrolysis: For the reaction<sup>99</sup>







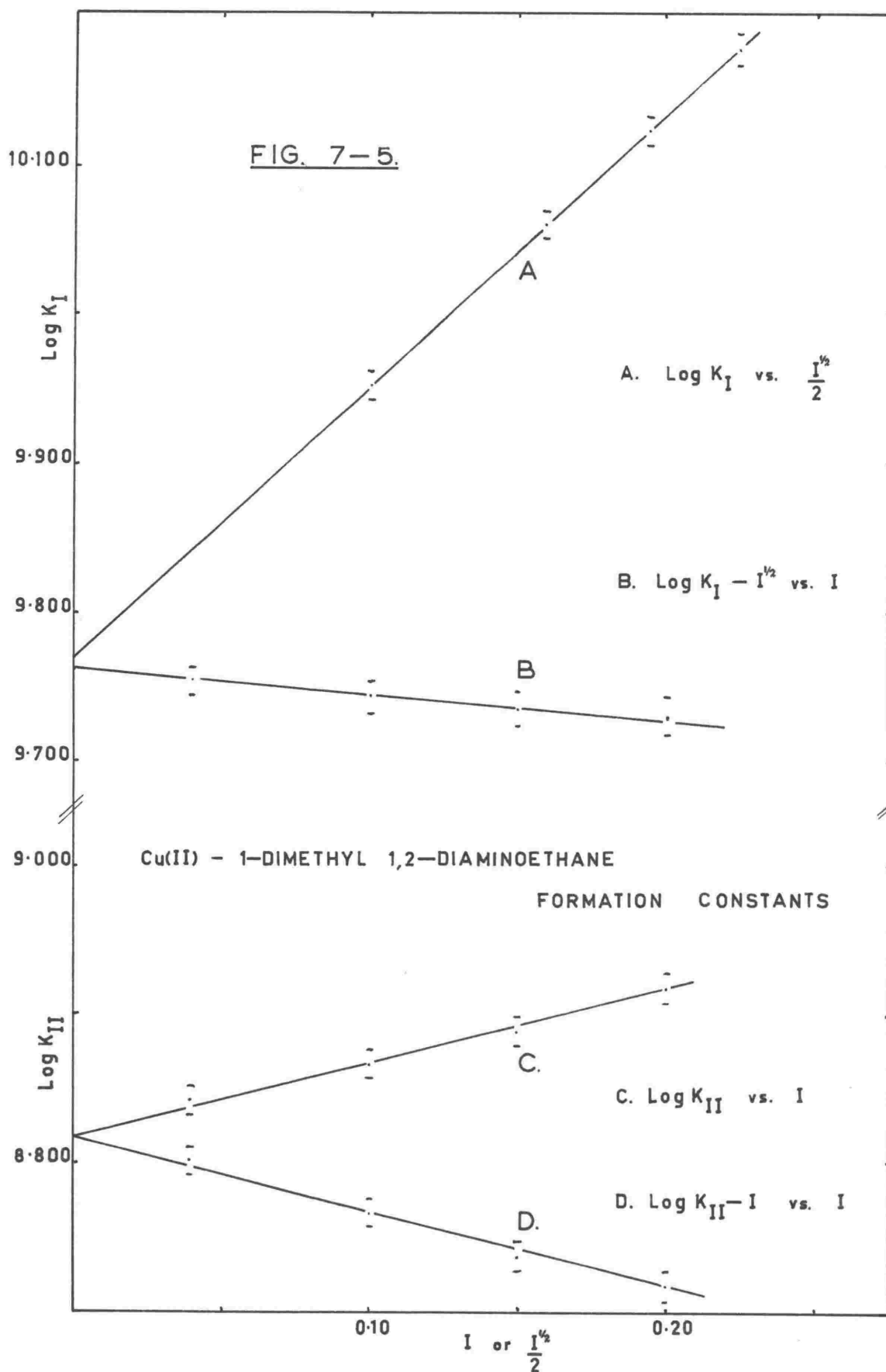




TABLE 7-3

Equilibrium formation constants for the cupric complexes of  
 some C<sub>1</sub>-substituted ethylenediamines in aqueous solution  
 (NaClO<sub>4</sub>/Ba(ClO<sub>4</sub>)<sub>2</sub> medium) 25.00±0.01°C

	Ionic Strength (m/l)	1-methyl 1,2-diamino- ethane	1-ethyl 1,2-diamino- ethane	1-dimethyl 1,2-diamino- ethane
Log K <sub>c<sub>I</sub></sub>	0.350	10.639±0.013		
"	0.200	10.559±0.012	10.494±0.011	10.176±0.011
"	0.150	10.504±0.013	10.430±0.011	10.121±0.010
"	0.100	10.444±0.013	10.369±0.012	10.059±0.011
"	0.040	10.371±0.011	10.244±0.010	9.952±0.010
Log K <sub>a<sub>I</sub></sub>	0.000	10.322±0.012	10.047±0.011	9.765±0.015
Log K <sub>c<sub>II</sub></sub>	0.350	9.030±0.012		
"	0.200	9.021±0.010	9.143±0.012	8.918±0.011
"	0.150	8.980±0.012	9.117±0.010	8.889±0.011
"	0.100	8.951±0.014	9.104±0.011	8.867±0.011
"	0.040	8.911±0.012	9.086±0.011	8.841±0.010
Log K <sub>a<sub>II</sub></sub>	0.000	8.880±0.012	9.070±0.011	8.819±0.011
Log(K <sub>I</sub> <sup>0</sup> /K <sub>II</sub> <sup>0</sup> )		1.44	0.98	0.94

$K_H = 2 \times 10^{-7} \text{ l.m.}^{-1}$ . Metal ion hydrolysis becomes increasingly important at high pH especially when  $\bar{n}$  is  $< 1$  in metal ion ligation systems. Assuming  $K_H$  to be correct, calculation (e.g., from Table 7-1) shows that at a maximum, 3% of the cupric ion in solution would be present as  $[\text{Cu}(\text{H}_2\text{O})_{n-1}(\text{OH})]^+$ . Over a period of days none of the solutions appeared to precipitate hydroxides.

Errors: Errors in  $K_C$  and  $K_a$  values were assessed as  $\pm(2.4-3.0)\%$  for  $K_I$  and  $K_{II}$ . These errors arose from errors in  $p[\text{H}]$  measurement and in  $K_1$  and  $K_2$  values (See 6-1.1).

#### 7-1.2 The enthalpy change

$\Delta H$  was measured calorimetrically (see 4-2, 5-2). The resultant solutions and experimental data from calorimetric runs were analysed according to the methods outlined in 4-2.1(b) and 5-2(h) respectively. The experimental data is given in Table 7-4. The terms  $\Delta R_R$ ,  $\Delta R_H$ ,  $\Delta Q_H$ ,  $\Delta Q_R$ , and  $\Delta H_{\text{diln}}$  in this Table are as defined in 5-2(h) and 6-1.2.  $\Delta H_m$  is related to the endothermic heat change  $-q$  calories per mole of metal ions:

$$\begin{aligned} \Delta H_m &= -q - \Delta H_{\text{diln}} \\ &= a_2 \Delta H_I + b_2 \Delta H_{II} + a'_2 \Delta H_1 + b'_2 \Delta H_2 \quad \text{(from equation 4-16)} \\ &= a_2 \Delta H_I^0 + b_2 \Delta H_{II}^0 + a'_2 \Delta H_1^0 + b'_2 (\Delta H_2^0 + 8.1 \times 10^2 \times \\ &\quad 2AI^{\frac{1}{2}} / (1 + I^{\frac{1}{2}})) \\ &\quad \text{(See section 4-2.2)} \end{aligned}$$

and,

TABLE

Calorimetric data for some Cu(II)-di  
NaClO<sub>4</sub>/Ba(ClO<sub>4</sub>)<sub>2</sub> medi

Run no.	Diamine	T <sub>L</sub> (m/l)	T <sub>Cu</sub> (m/l)	T <sub>H</sub> (m/l)	Total Vol. (mls)	Final I (m/l)
1		0.06037	0.03000	0.001033	95.780	0.350
2	1-methyl	"	0.03092	0.001065	95.370	"
3	1,2-diamino-	"	0.06178	0.002107	94.820	"
4	ethane	"	0.06178	0.002107	94.450	"
5		0.0599	0.06742	0.005684	74.635	0.339
6		"	0.05054	0.00582	90.390	"
7	1-ethyl	0.2300	0.01150	0.000399	89.675	0.192
8	1,2-diamino- ethane	"	0.02706	0.000967	94.630	0.200
9	1-dimethyl	0.01500	0.007159	0.000253	96.395	0.200
10	1,2-diamino-	"	0.02160	0.000741	96.545	0.200
11	ethane	"	0.01543	0.000533	97.160	"

TABLE

Run no.	$-\Delta H_m$ (cals/mole)	$[H^+]_{eqm.}$ (m/l)	$T_L$ (exptl) (m/l)	$\Delta H_m - b_2' \delta = a_2 \Delta H_I^0 + b_2$
1	11765	$6.339 \times 10^{-7}$	0.05899	0.5086 0.482
2	12020	$9.638 \times 10^{-7}$	0.05912	0.5228 0.467
3	12100	$1.146 \times 10^{-5}$	0.05935	0.8845 0.097
4	11990	"	"	0.8845 0.097
5	11785	$2.472 \times 10^{-5}$	0.05688	0.8453 0.055
6	11865	$1.667 \times 10^{-5}$	0.0568	0.8098 0.139
7	12060	$6.27 \times 10^{-7}$	0.02281	0.5041 0.484
8	11975	$1.312 \times 10^{-5}$	0.02272	0.8882 0.093
9	11425	--	--	0.4771 0.477
10	11550	$1.80 \times 10^{-5}$	0.01499	0.9313 0.046
11	11560	$1.09 \times 10^{-5}$	0.01500	0.8980 0.084

$$\Delta H_m - b'_2 \delta = a_2 \Delta H_I^O + b_2 \Delta H_{II}^O + a'_2 \Delta H_1^O + b'_2 \Delta H_2^O$$

(from equation 6-1)

hence

$$\Delta H_I^O + p \Delta H_{II}^O = \sum_i n_i \Delta H_i^O =$$

$$\frac{1}{a_2} [\Delta H_m - a'_2 \Delta H_1^O - b'_2 (\Delta H_2^O + \delta)] \dots\dots 7-1$$

where  $p = b_2/a_2$  (see Table 7-4).

The factors  $a_2$ ,  $b_2$ ,  $a'_2$ , and  $b'_2$  were determined by the methods discussed in 4-2.1(a) and 4-2.1(b). The numerical value of  $a'_2 \Delta H_1^O + b'_2 (\Delta H_2^O + 8.1 \times 10^2 \times 2AI^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}))$  was calculated from previously obtained  $\Delta H_1^O$  and  $\Delta H_2^O$  values (Chapter 6).

The  $\Delta H_I^O$  and  $\Delta H_{II}^O$  values in Table 7-5 were obtained from the data in Table 7-4 by two methods:

(a) by solution of pairs of the simultaneous equations 7-1, viz.,  $\Delta H_I^O + p \Delta H_{II}^O = \sum_i n_i \Delta H_i^O$ , e.g., for the aqueous ligation reaction between Cu(II) and 1-methyl 1,2-diaminoethane, the values obtained from combinations of data for runs 1+3, 2+3, 1+4, 2+4, 1+5, 1+6, and 2+6, were:

$-\Delta H_I^O = 11.97, 11.90, 11.82, 11.76, 11.98, 11.95, 12.13, 12.02$   
 $-\Delta H_{II}^O = 11.37, 11.96, 11.53, 12.03, 11.96, 12.48, 11.80, 12.40$   
 (kcal/mole) respectively. These results were then averaged and a standard deviation calculated.

(b)  $\Delta H_I^O$  values were obtained graphically by plotting

$\sum_i n_i \Delta H_i^O = \Delta H_I^O + p \Delta H_{II}^O$  vs.  $p$ , and extrapolating to  $p = 0$ .  
 In each case linear graphs were obtained (Fig. 7-6).

FIG. 7—6

PLOT OF  $\Delta H_I^\circ + p\Delta H_{II}^\circ$  vs.  $p$  FOR COPPER(II)

LIGATION BY A. 1-METHYL 1,2-DIAMINOETHANE

B. 1-ETHYL 1,2-DIAMINOETHANE

C. 1-DIMETHYL 1,2-DIAMINOETHANE

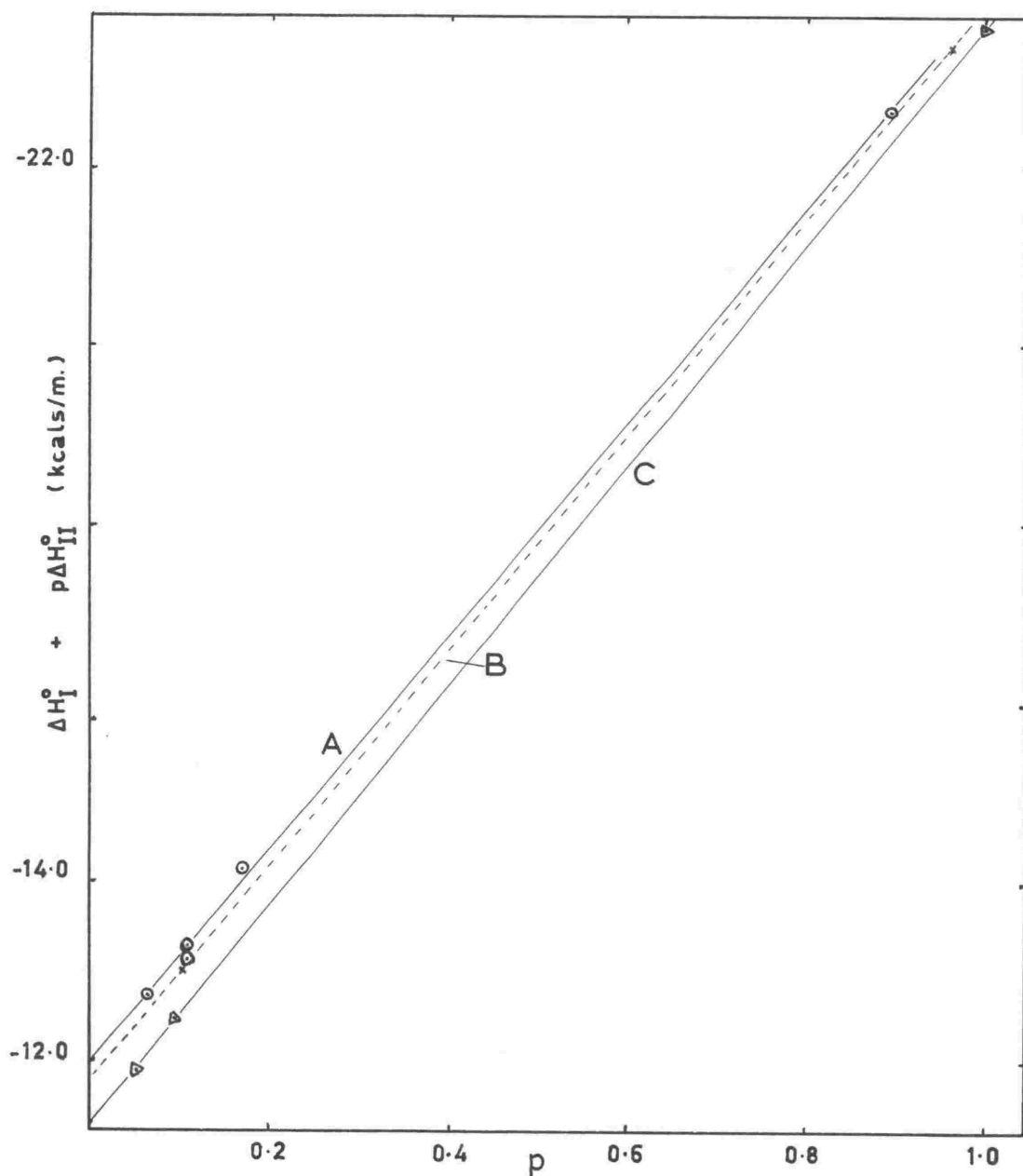


TABLE 7-5

Standard thermodynamic functions for the step-wise equilibrium reactions between Cu(II) and some C<sub>1</sub>-alkyl substituted ethylenediamines in aqueous solution, 25.00±0.01°C, I = 0.0m/1

Standard thermo- dynamic functions	1,2-di- amino - ethane	1-methyl 1,2-diamino- ethane	1-ethyl 1,2-diamino- ethane	1-dimethyl 1,2-diamino- ethane
$\Delta G_I^0$ (Kc/m)	-14.30*	-14.083±0.017	-13.707±0.015	-13.323±0.015
$\Delta G_{II}^0$ "	-12.38*	-12.116±0.016	-12.374±0.015	-12.032±0.015
$\Delta G_{I-II}^0$ "	-26.68	-26.20±0.03	-26.08±0.03	-25.36±0.03
$\Delta H_I^0$ (Kc/m)	-12.6	-11.95±0.15	-11.76±0.13	-11.27±0.08
$\Delta H_{II}^0$ "	-12.6	-11.90±0.25	-12.04±0.13	-12.26±0.08
$\Delta H_{I-II}^0$ "	-25.2 <sup>+</sup>	-23.9±0.4	-23.8±0.3	-23.5±0.2
$\Delta S_{II}^0$ e.u.	+5.7	+7.1±0.3	+6.5±0.7	+6.9±0.2
$\Delta S_{II}^0$ "	-0.7	+0.9±1.1	+1.1±0.4	-0.7±0.2
$\Delta S_{I-II}^0$ "	+5.0	+8.0±1.4	+7.6±1.1	+6.2±0.4
$\Delta S_I^0$ (corr)	+2.9	+3.0±0.3	+2.4±0.7	+2.8±0.2
$\Delta S_{I-II}^0$ "	+3.6	+3.9±1.4	+3.5±1.1	+2.1±0.4

\* Ref. 24b.

<sup>+</sup> Ref. 41.

Substitution of  $\Delta H_I^O$  into equation 7-1 gave a series of  $\Delta H_{II}^O$  values.

These two methods gave comparable  $\Delta H_i^O$  values, e.g., for Cu(II) + pn, method (a) gave  $-\Delta H_I^O = 11.87\text{kcal/mole}$ ,  $-\Delta H_{II}^O = 11.95\text{kcal/mole}$ ; method (b) gave  $-\Delta H_I^O = 11.95\text{kcal/mole}$ ,  $-\Delta H_{II}^O = 11.85\text{kcal/mole}$ .

Values of  $\Delta S_i^O$  were obtained by using the equation

$$\Delta G_i^O = \Delta H_i^O - T \Delta S_i^O$$

Uncertainties in  $\Delta H_i^O$  values: These were determined by the method given in 6-1.3. (For "equation 6-1" read equation 7-1.) The uncertainties in  $\Delta H_{II}^O$  are always greater than those in  $\Delta H_I^O$  (see 4-2).

Absorption spectra: These were measured for solutions with 1:1 and 1:2 ratios of metal ion to ligand to determine the C.F.S.E. terms (see 7-3.4). Spectra were determined with a Unicam S.P. 500 or a Hilger Watts 'UVISPEC' spectrophotometer.



## Discussion of Results

### 7-2 The Free Energy Change

#### 7-2.1 The relationship between complex stability and ligand basicity

There is an approximately linear relationship between complex stability and ligand basicity. Comparing the free energy terms for the metal ion-ligation and ligand-protonation reactions, it is found that

$$\Delta G_{\text{I}}^{\circ} / \Delta G_{1-2}^{\circ} = 0.630 \pm 0.006$$

and  $\Delta G_{\text{I-II}}^{\circ} / \Delta G_{1-2}^{\circ} = 1.19 \pm 0.02$

The constancy of these ratios implies that ligand basicity alone significantly determines the relative stabilities of these Cu(II)-diamine complexes. Therefore the forces between bound ligand and water molecules must be uniform in the series of 1:1 and the series of 1:2 copper-diamine complexes. The substituent R in  $\text{NH}_2\text{CH}(\text{R})\text{CH}_2\text{NH}_2$  must make only minor contributions to interligand forces in the coordination sphere.

The results may be compared with those for the N- and NN'-substituted ethylenediamines. Increased length and branching of the N- alkyl substituent has little effect on the amine basicity,<sup>27,28</sup> yet markedly lowers the copper-diamine complex stability<sup>35,56</sup> because of increasing interligand (L-L and  $\text{H}_2\text{O-L}$ ) repulsion forces within the co-

ordination sphere. (NN'-tetramethyl-ethylenediamine<sup>72</sup> probably forms a 1:1 complex only.) \*

### 7-2.2 The average formation constant

Bjerrum<sup>51</sup> defined an 'average' formation constant  $K_{av.}$  for metal ion ligation reactions:

$$\log K_{av.} = \frac{1}{N} \log K_I \cdot K_{II} \cdot \dots \cdot K_N.$$

The ratio  $\log K_{av.} / \log K_1^x$  is approximately constant for a given metal ion with similar ligands when for each type of complex the interligand forces and the bonding forces are essentially the same.<sup>51</sup> The equivalent ratio for the copper-diamine complexes is approximately constant:

$$\Delta G_{I-II}^0 / \Delta G_1^0 = 2 \log K_{av.}^0 / \log K_1^0 = 1.99 \pm 0.02.$$

However, because the ligands (except en) contain two dissimilar basic centres it is preferable (see 6-2.4) to consider the ratio  $\Delta G_{I-II}^0 / \Delta G_{1-2}^0$ , which also is constant ( $1.19 \pm 0.02$ ).

### 7-2.3 The ratio of successive stability constants

For each copper-diamine system,  $\log K_I^0$  is  $> \log K_{II}^0$ . This relationship is favoured statistically and is generally valid for metal ion ligation reactions (see 3-5, 1(a)). The

\* Data is available for Ni(II) only; it gives only a 1:1 complex and Cu(II) is probably analogous. Zn(II) forms a bis complex because steric hindrance is minimised by the ion adopting a tetrahedral configuration.

x  $\log K_1 = \log K_{HL^+}.$

$\log(K_I^0/K_{II}^0)$  values are given in Table 7-3 and may be compared with the literature values for the ligands en 1.41,<sup>24c</sup> dl-bn<sup>+</sup> 1.51, m-bn<sup>+</sup> 1.38, tetrameen<sup>+</sup> 1.39, dl-stien<sup>@</sup> 0.96, and m-stien<sup>@</sup> 0.95.<sup>3</sup> However, for the NN'-di-n-alkyl substituted 1,2-diaminoethanes this ratio is not constant. It increases regularly with substituent size, from 2.84 for the NN'-dimeen complex to 3.83 for the NN'-di-n-Buen complex.<sup>24c,35</sup> This corresponds to an increased steric hindrance between ligands in the bis complexes and a decrease in complex stability.

### 7-3 The Enthalpy Change

#### 7-3.1 The Cu(II)-ethylenediamine system

For this system Davies et al.<sup>41</sup> determined  $-\Delta H_{I-II}^0 = 25.16 \text{ kcal/mole}$ . (Values of 24.6 and 25.4 kcal/mole have also been determined,<sup>34,35</sup> but Davies' result is probably the most reliable.) Several workers<sup>40,41,66,67</sup> have postulated equal  $\Delta H$  for successive step-wise complex formation reactions between the aqueous cupric ion and strain-free dipole ligands, when inter-ligand repulsion forces and metal ion configuration do not vary (appreciably) with metal-ligand ratio. For the Cu(II)-pn reaction and the

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+  $\log(K_I/K_{II})$ , I = 0.65m/l.

@ in 50% dioxane/H<sub>2</sub>O

Cu(II)-2,2'-1,3pn reaction<sup>119</sup>  $\Delta H_I \approx \Delta H_{II}$ . A similar equality could be postulated for the Cu(II)-en reaction, giving  $\Delta H_I^O = \Delta H_{II}^O = -12.6 \text{ kcal/mole}$ .

### 7-3.2 Interligand interactions

For the ligands en, pn, and eten  $\Delta H_I^O / \Delta H_{1-2}^O$  is approximately constant ( $0.551 \pm 0.003$ ) suggesting that the complex bond energies are directly related to ligand donor power. For i-bn the value for this ratio is lower, 0.525, possibly indicating an increase in interligand ( $L-H_2O$ ) repulsion forces within the coordination sphere. (Molecular models show that the gem dimethyl groups of i-bn hinder the free rotation of the fifth or sixth (trans) water molecule in the coordination sphere. However, they do not suggest that the methyl groups would displace the water molecules through steric hindrance.)

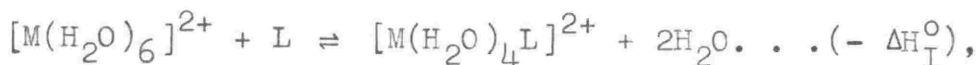
### 7-3.3 Complex stability and ligand donor power

The ratio  $\Delta H_{I-II}^O / \Delta H_{1-2}^O$  is approximately constant,  $1.095 \pm 0.011$ . This constancy indicates that those enthalpy factors which determine the relative stabilities of the Cu(II)-1,2-diamine complexes are the same as those determining the relative stabilities for proton -1,2-diamine complexes. e.g., the solvent shielding effects for any ligand (see 6-2.2 and 6-2.3(c)) have the same relative importance in each complex system. For the copper complexes the interligand repulsion forces must be essentially uniform

and independent of the  $C_1$ -alkyl substituents.

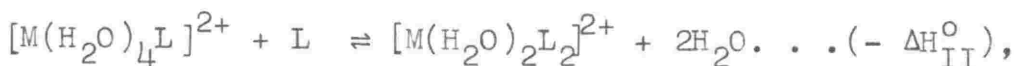
#### 7-3.4 The C.F.S.E. Contribution to $\Delta H_i^0$

The corrected  $\Delta H$  values  $\Delta H_{\text{corr}} = \Delta H_i^0 - \Delta H_{\text{C.F.}}$  are given in Table 7-6. For the reaction



$$\Delta H_{\text{C.F.}}(I) = \text{C.F.S.E.} ([M(H_2O)_2L_2]^{2+}) - \text{C.F.S.E.} ([M(H_2O)_4L]^{2+}).$$

For the reaction



$$\Delta H_{\text{C.F.}}(II) = \text{C.F.S.E.} ([M(H_2O)_2L_2]^{2+}) - \text{C.F.S.E.} ([M(H_2O)_4L]^{2+}).$$

For each aqueous complex the C.F.S.E. was calculated using the equation

$$-\text{C.F.S.E.} = 0.4E_1 + 0.2E_2 + 0.2E_3 \dots \dots \dots 7-2$$

where  $E_1$ ,  $E_2$ , and  $E_3$  are the Cu(II) d-d electron transition energies obtained from the visible-near I.R. absorption spectrum,  $E_1 > E_2 > E_3$ . This equation and the theory are discussed in Appendix I. (The broad single band absorption curve for the cupric ion theoretically resolves into three gaussian curves corresponding to three d-d electron transitions,<sup>125</sup> energies  $E_1$ ,  $E_2$ , and  $E_3$ .)

Each 1:1 complex and each 1:2 complex have the same C.F. stabilisation term  $\Delta H_{\text{C.F.}}$ . The visible-near I.R. absorption spectra for the Cu(II)-bis diamine complexes are energetically identical within experimental error. A broad

TABLE 7-6

Crystal field corrected ligational enthalpies for some  
aqueous Cu(II)-diamine complexes, 25.0°C

Ligand	$-\Delta H_{\text{I}}(\text{corr})$ (kcal/mole)	$-\Delta H_{\text{II}}(\text{corr})$ (kcal/mole)
en	4.4	6.3
pn	3.7	5.6
eten	3.6	5.7
i-bn	3.1	6.0

absorption  $\nu_{\max.} = 18.1 \text{ kK}^*$  graphically resolves into three bands,  $\nu = 19.0, 17.1, 14.8 \text{ kK}$  with  $\epsilon_{\max.} \approx 60, 30, \text{ and } 20$  respectively (e.g., Figs. 7-7, 8). These absorptions correspond to a C.F.S.E. of  $-(40.3 \pm 0.6) \text{ kcal/mole}$ . Similarly the visible-near I.R. spectra for the 1:1 complexes are identical within experimental error. A very broad band,  $\nu_{\max.} = 15.4 \pm 0.2 \text{ kK}$ ,  $\epsilon_{\max.} = 32-43$ , can be considered composed of three absorption bands at approximately 16.6, 14.4 and 11.8 kK. (e.g., Fig. 7-9) These absorptions correspond to a C.F.S.E. of  $-(34.0 \pm 0.5) \text{ kcal/mole}$ .

The visible-near I.R. spectrum for the Cu(II) aqueous ion is reported to have a band at 12.6 kK with a shoulder at 9.3 kK. A further analysis of this broad band has shown that  $\nu_{\max.} = 12.25 \text{ kK}$ . The main band can be graphically resolved into two gaussian absorption curves with  $\nu_{\max.} = 12.6$  and 10.6 kK. The occurrence of three absorption bands at 12.6, 10.6, and 9.3 kK corresponds to a C.S.F.E. of  $-(25.8 \pm 0.5) \text{ kcal/mole}$ .

The resultant C.F. correction terms are

$$\Delta H_{\text{C.F.}}(\text{I}) = -8.2 \text{ kcal/mole}$$

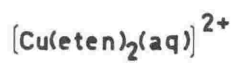
$$\Delta H_{\text{C.F.}}(\text{II}) = -6.3 \text{ kcal/mole}$$

The uncertainty on each of these terms is estimated as  $\geq \pm 1.0 \text{ kcal/mole}$  and arises mainly from the uncertainties

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\* kK or kilokayser =  $1000 \text{ cm}^{-1}$

FIG. 7-7



VISIBLE ABSORPTION SPECTRUM

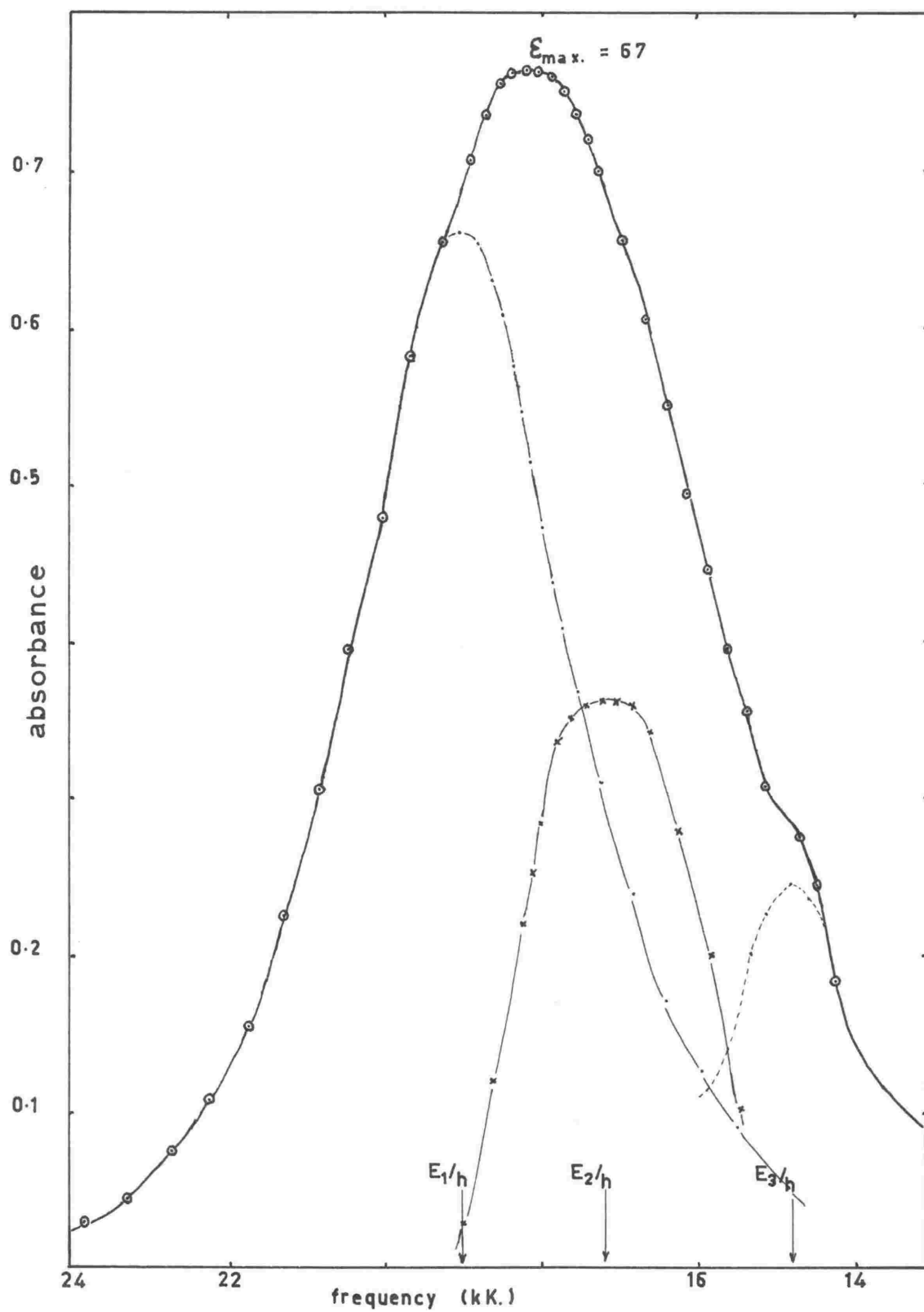
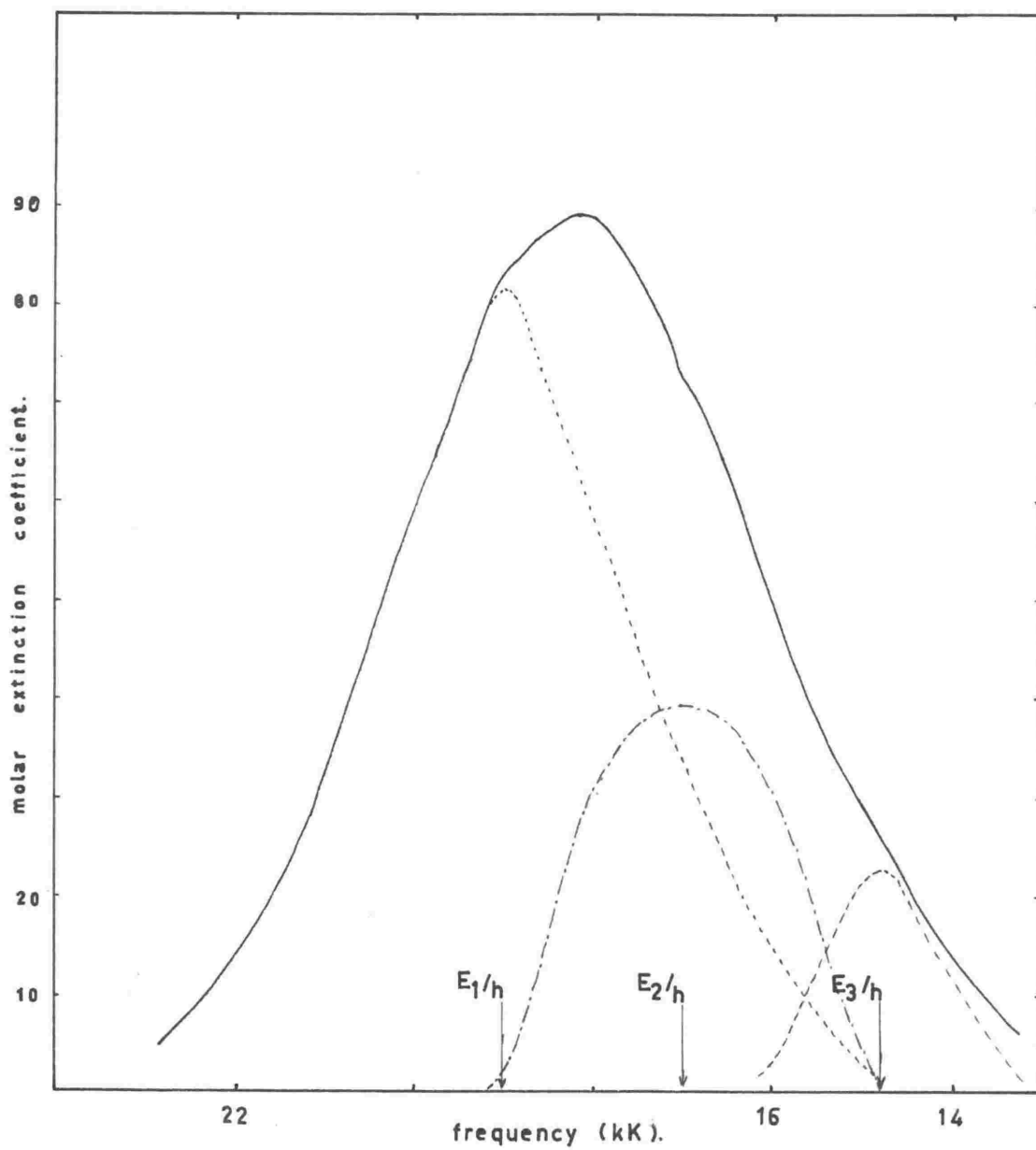
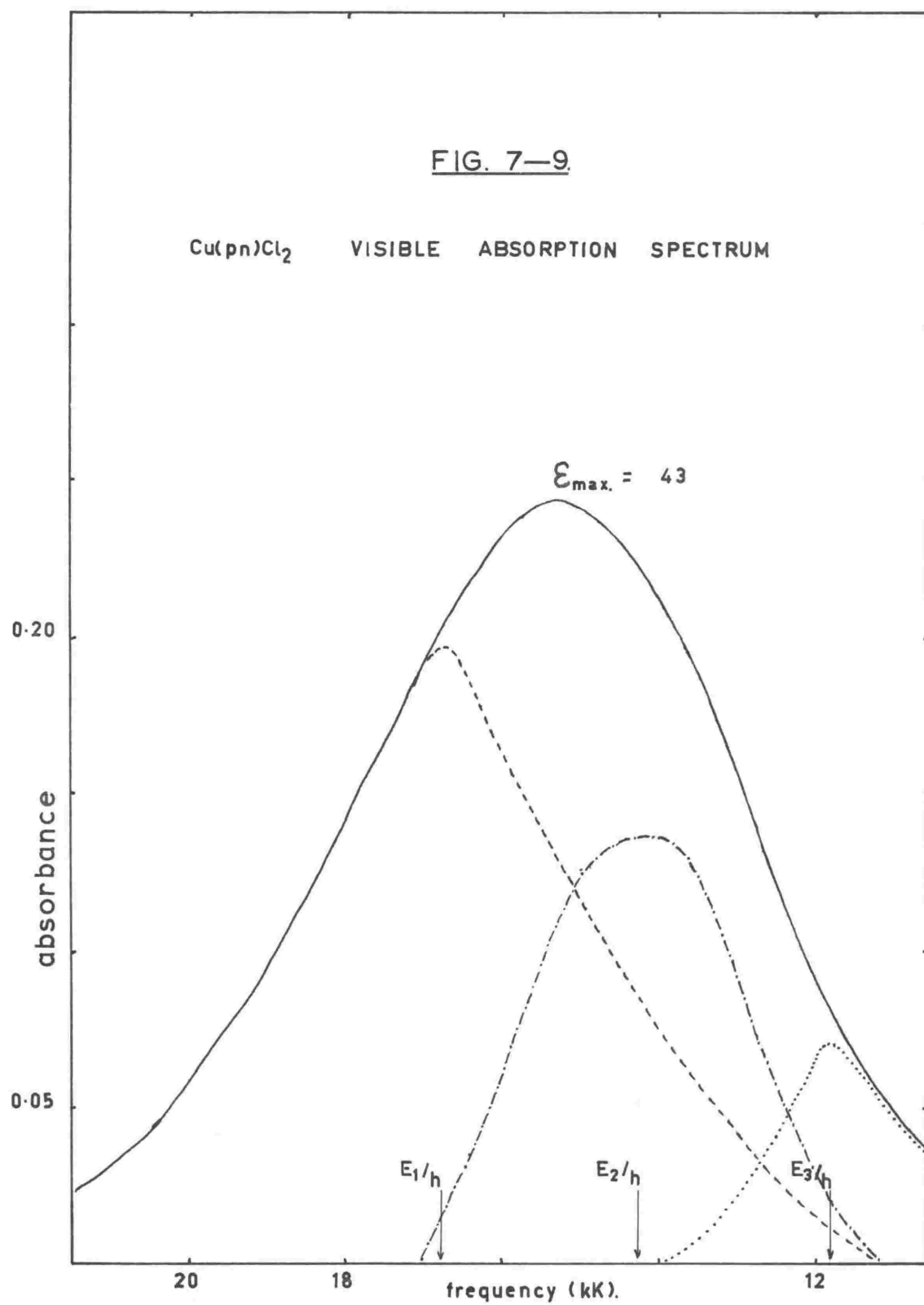




FIG. 7-8.

$[\text{Cu}(\text{i-bn})_2(\text{aq})]^{2+}$  VISIBLE ABSORPTION SPECTRUM.





in graphical resolution of the absorption bands. Therefore, the  $\Delta H_{C.F.}$  are of limited value. The equality of each  $\Delta H_{C.F.}(I)$  and each  $\Delta H_{C.F.}(II)$  is more significant than are their absolute values.

### 7-3.5 The degree of Jahn-Teller distortion

The sequence  $-\Delta H_{C.F.}(I) > -\Delta H_{C.F.}(II)$  may imply that the increase in Jahn-Teller distortion is greater in passing from the hexaquo to mono diamine complex than in passing from the mono to bis diamine complex.

Because the C.F. terms are the same for each of the 1:1 complexes and for each of the 1:2 complexes it follows that within each series

- (1) the Jahn-Teller distortion is approximately constant,
- (2) the M-N bond lengths are approximately equal,<sup>70</sup>
- (3) the average electron densities on the N-donor atoms are approximately equal,\*
- (4) the interligand (L-H<sub>2</sub>O, L-L) repulsions are similar.

### 7-3.6 Complex ion solvation

It follows from 7-3.5 that the variations in ligational enthalpy within the 1:1 or 1:2 series of complexes must arise predominantly from changes in solvent orientation about the complex ion. Solvent orientation will vary with

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\* This supports the deduction (6-2) that the inductive tendency of the C<sub>1</sub>-alkyl substituent has little effect on the ligand basicity (donor power).

the  $C_1$ -substituent according to its tendency to disrupt the solvent lattice and to shield the solvent from the charge on the metal ion. Variations in ligand protonation enthalpies are similarly ascribed chiefly to changes in solvent orientation about the ammonium ion. (see 6-2.2)

#### 7-4 The Entropy Change

Trends in the entropy change can be explained on the basis of

- (1) solvent orientation effects
- (2) interligand ( $L-H_2O$ ) interactions in the 1:2 complexes.

##### 7-4.1 Statistical contributions

$\Delta S_I^O$  contains a statistical term. For the Cu-en complex, it is  $R \ln 4 = 2.8e.u.$  and arises from the fact that the en ligand can probably replace two water molecules from the tetragonally distorted aqueous cupric ion  $[Cu(H_2O)_4(H_2O)_2]^{2+}$  in four different ways. There is only one way for the reverse reaction to occur. Therefore the statistical contribution to  $\Delta S$  is  $R \ln(4/1)$ . For the other 1:1 complexes, the ligand is asymmetric giving eight possible configurations for the complex ion. The statistical contribution to  $\Delta S$  is  $R \ln 8 = 4.1e.u.$

$\Delta S_{II}^O$  contains a statistical term for the  $Cu en_2^{2+}$  complex only,  $\Delta S_{stat} = -R \ln 2 = -1.4e.u.$

The corrected  $\Delta S$  values are given in Table 7-5.

#### 7-4.2 The effect of ligand structure

$\Delta S_{\text{I}}^{\text{O}}(\text{corr}) = \Delta S_{\text{I}}^{\text{O}} - \Delta S_{\text{stat}}$  is constant within experimental error. For L = en, pn and eten  $\Delta S_{\text{II}}^{\text{O}}(\text{corr})$  is also constant within experimental error ( $0.9 \pm 0.2 \text{ e.u.}$ ). The value for L=i-bn is significantly lower ( $-0.7 \pm 0.2 \text{ e.u.}$ ), possibly because the  $\text{C}_1$ -gem dimethyl groups in i-bn hinder the free rotation of water molecules in the fifth and sixth (trans) coordination sites. There is a loss in rotational entropy for the water molecules and for one methyl group on each i-bn molecule. Molecular models (Courtauld) illustrate this phenomenon.

#### 7-4.3 $\Delta S$ values for successive reactions

For each ligand  $\Delta S_{\text{II}}^{\text{O}}$  is greater than  $\Delta S_{\text{I}}^{\text{O}}$ . This is typical for step-wise metal ion ligation reactions, and for neutral ligands\* arises mainly from statistical contributions.<sup>1,40,93,77</sup> On the basis of these contributions alone it is predicted that for each amine,  $\Delta S_{\text{II}}^{\text{O}} = \Delta S_{\text{I}}^{\text{O}} - 4.1 \text{ e.u.}$  For L=en, pn and eten it was found that  $\Delta S_{\text{II}}^{\text{O}} = \Delta S_{\text{I}}^{\text{O}} - (6.3 \pm 0.1) \text{ e.u.}$ ; for L=i-bn  $\Delta S_{\text{II}}^{\text{O}} = \Delta S_{\text{I}}^{\text{O}} - 7.6 \text{ e.u.}$  (The value for i-bn possibly differs because of phenomena discussed in 7-4.2.) Therefore  $\Delta S_{\text{II}}^{\text{O}}$  is approximately 2.2 e.u. lower than predicted statistically. This small discrepancy possibly

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\* For ionic ligands it is partly a charge effect.

arises from a solvation effect. It has been postulated<sup>40,77</sup> that for an aqueous metal ion, solute-solvent interactions decrease rapidly with initial increases in ligand coordination number when large ligand molecules are used, e.g., en, dipyr (see 3-5,3(b)). Replacing two coordinated water molecules on  $[\text{Cu}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_2]^{2+}$  by one chelate group causes a large increase in solvent entropy due to

- (a) increased shielding of the solvent from the metal ion charge, and
- (b) competition between two incompatible structures, those of the primary coordination sphere and the bulk of the solvent.

Replacement by a second chelate group possibly<sup>40,77</sup> causes a smaller increase in solvent randomness, and  $\Delta S_{\text{II}}^{\text{O}}$  contains a smaller positive "solvent-freeing" term than does  $\Delta S_{\text{I}}^{\text{O}}$  (see Fig. 7-10 and p.143).

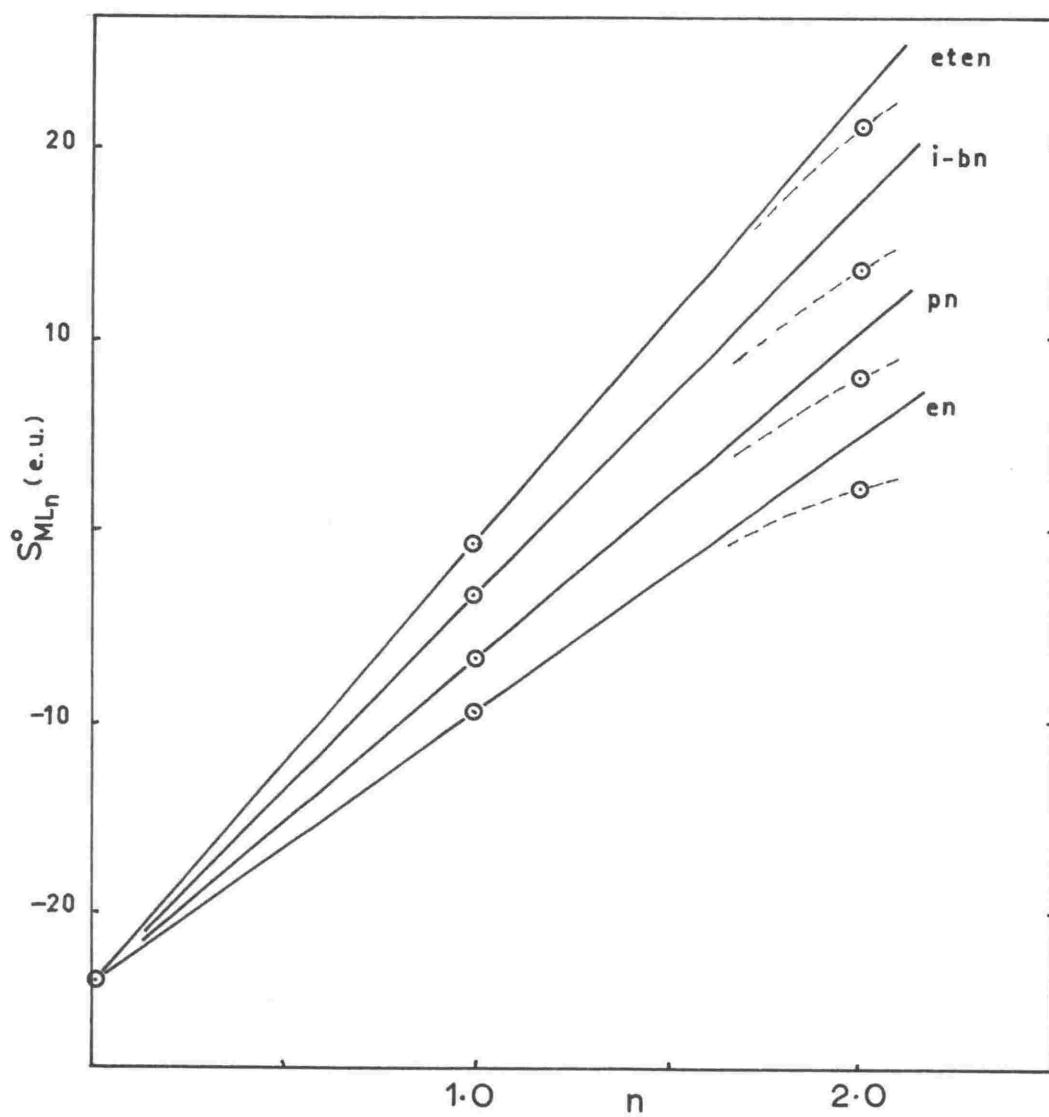
Ciampolini et al.<sup>135</sup> have discussed the 'low second sphere hydration (entropy)' for a complex ammine compared with an aquo ion. They considered it related to the lower entropy of hydration for the  $\text{NH}_3(\text{g})$  molecule (-19.7e.u.) compared with the  $\text{H}_2\text{O}(\text{v})$  molecule (-28.4e.u., entropy of condensation). i.e., the complex aquo ions will be surrounded by more 'frozen' solvent molecules. This argument could be applied to other ligands, e.g.,  $S_{\text{solvation}}^{\text{O}}$  for  $(\frac{1}{2})\text{en} = -15.4\text{e.u.}$ ,  $\frac{1}{3}(\text{dien}) = -13.3\text{e.u.}$ ,  $\frac{1}{4}(\text{trien}) = -12.2\text{e.u.}$ \*

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\* From the Cobble Equation<sup>87c</sup>, Appendix IIb.

FIG. 7—10.

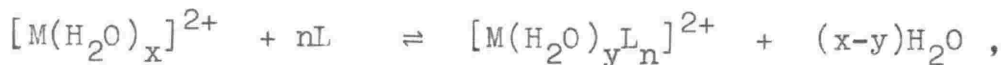
$S_{ML_n}^{\circ}$  vs.  $n$  FOR SOME Cu(II)—DIAMINE COMPLEXES



However, their consideration overlooks the part played by the donor group, O or N, in determining the entropy of hydration.

#### 7-4.4 The molar entropies of aqueous complex ions

For a reaction



$$\Delta S_{n(\text{corr})}^{\circ} = S_{ML_n}^{\circ} + (x-y)S_{H_2O}^{\circ} - nS_L^{\circ} - S_M^{\circ} \dots\dots 7-3$$

From equation 7-3 the standard molar entropy of the aqueous complex ion  $S_{ML_n}^{\circ}$  can be calculated:  $\Delta S_{n(\text{corr})}^{\circ}$  is obtained from the experimental  $\Delta S_n^{\circ}$  value ( $= \Delta S_n^{\circ} - \Delta S_{\text{stat}}$ );  $S_{H_2O}^{\circ}$  the standard molar entropy of solvent ('free') water = 16.7e.u.;<sup>64</sup>  $S_L^{\circ}$  can be calculated approximately by using the empirical Cobble equation<sup>87c</sup> for the partial molar entropies of organic solutes in aqueous solution (Appendix II); the standard molar entropies of many aqueous cations have been measured relative to  $S_{H^+}^{\circ} = 0.0\text{e.u.}$  ( $S_{Cu^{++}}^{\circ} = -23.6\text{e.u.}$ <sup>90</sup>).

$S_{CuL}^{\circ}$  and  $S_{CuL_2}^{\circ}$  values are given in Table 7-7.

The entropies of the complex ions are  $S_{ML_2}^{\circ} > S_{ML}^{\circ} > S_{M(\text{aq})}^{\circ}$ . The entropy of an ion in aqueous solution increases with the amount of non-polar low dielectric medium (in the form of ligand) surrounding it. The ligand shields the solvent from the cationic charge which tends to orientate the solvent molecules and lower their entropy.

$S_{ML_n}^{\circ}$  increases with C-alkyl substitution on the ethylenediamine ligand, i.e., the molar entropies of the



TABLE 7-7

The standard molar entropies of some cupric diamine ions

Ligand	$S_L^{\circ}(\text{e.u.})$	$S_{ML}^{\circ}(\text{e.u.})$	$S_{ML_2}^{\circ}(\text{e.u.})$
en	44.5	-9.6	2.2
pn	47.3	-6.7	8.1
i-bn	51.0	-3.2	13.7
eten	54.0	-0.6	21.1

(cf.,  $S_{Cu^{++}}^{\circ} = -23.6\text{e.u.}$ )

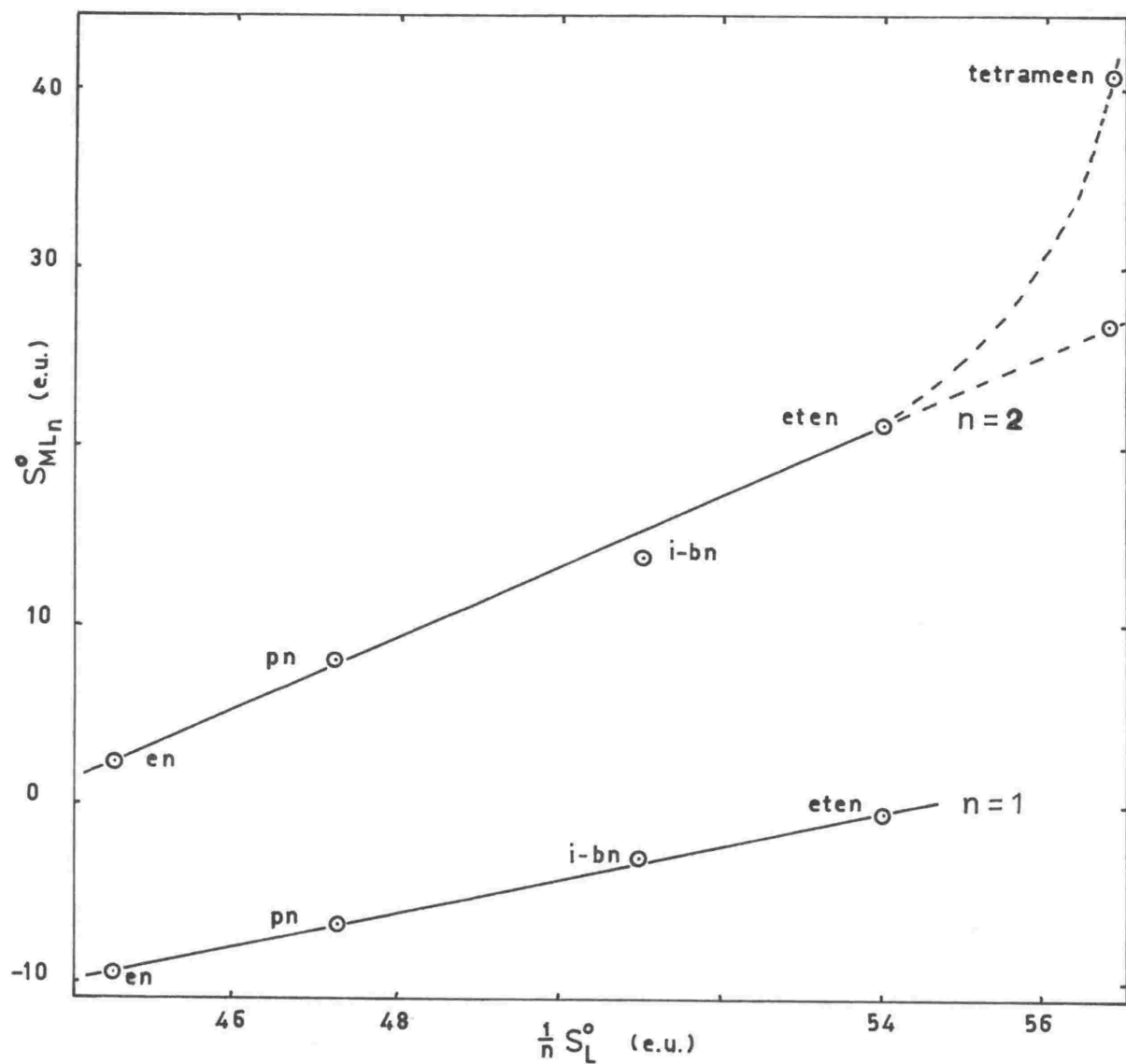
aqueous  $(\text{Cu}(\text{eten})_n \text{ complex ions are } > \text{Cu}(\text{i-bn})_n > \text{Cu}(\text{pn})_n > \text{Cu}(\text{en})_n$  for  $n=1$  and  $n=2$ . The high molar entropy of the  $\text{Cu}(\text{tetrameen})_2$  ion  $(+40.8\text{e.u.})^*$  follows this general sequence. C-alkyl substitution will increase the solvent-shielding capacity and possibly the solvent lattice-breaking capacity of the ligand. It is difficult to estimate the influence of these effects on  $S_{ML_n}^{\circ}$ . The  $S_{ML_n}^{\circ}$  values are linearly related to  $nS_L^{\circ}$  (Fig. 7-11). Therefore the increase in  $S_{ML_n}^{\circ}$  upon C-alkyl substitution on the ligand may result mainly or wholly from the entropy contribution of the 'mobile'  $C_1$ -alkyl substituent. The  $S_{ML_2}^{\circ}$  value for

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\* Calculated from  $\Delta S_{I-II} = 19\text{e.u.}^3(\text{cal})$ ,  $\Delta S_{\text{stat}} = 1.4\text{e.u.}$ ,  $S_L^{\circ} = 56.8\text{e.u.}$  from the Cobble equation (Appendix II), assuming  $d_L = 0.88\text{gm/ml}$ .

FIG. 7—11.

$S_{ML_n}^\circ$  vs.  $\frac{1}{n}S_L^\circ$  FOR SOME Cu(II) DIAMINE COMPLEXES



L=tetrameen does not fit this 1:1 relationship, therefore the other effects discussed above may also contribute significantly in this case.

For each ligand ( $S_{\text{CuL}_2}^{\circ} - S_{\text{CuL}}^{\circ}$ ) is  $2.3 \pm 0.3 \text{ e.u.}$  less than ( $S_{\text{CuL}}^{\circ} - S_{\text{Cu(aq)}}^{\circ}$ ), indicating that substitution of a second chelate group possibly causes a slightly smaller increase in solvent randomness than does substitution of the first, Fig. 7-10 (see 7-4.3).

#### 7-5 Comparisons with Previous Work

Nasanen et al.<sup>24b</sup> have recently published stability constants for the Copper-1-methyl 1,2-diaminoethane reaction at a series of ionic strengths. Their values for  $I=0.00\text{m/l}$ ,  $\log K_{\text{I}}=10.54$ ,  $\log K_{\text{II}}=9.06$ , do not compare well with those in Table 7-3; viz.,  $10.322 \pm 0.012$  and  $8.880 \pm 0.012$  respectively.

$\Delta H_n^{\circ}$  values have been determined for this reaction by the temperature coefficient method<sup>23</sup>(3-3.1A).

$$- \Delta H_{\text{I}}^{\circ} = 13.0 \text{ kcal/mole}$$

$$- \Delta H_{\text{II}}^{\circ} = 13.2 \text{ kcal/mole}$$

cf., this work  $11.95 \pm 0.15$  and  $11.85 \pm 0.15 \text{ kcal/mole}$  respectively.

## CHAPTER EIGHT

THERMODYNAMIC DATA FOR AQUEOUS NICKEL(II)-DIAMINE COMPLEXES

Data has been derived for the ligands 1-methyl 1,2-diaminoethane and 1-dimethyl 1,2-diaminoethane. It is compared with that for 1,2-diaminoethane complexes. Data for the Ni(II)-eten system is discussed in 9-1.

8-1 Experimental and Results

The general notation and experimental method outlined in 7-1 for the copper complexes also applies for the Ni(II)-diamine complexes. Some small differences are briefly outlined:

(a) Formation curve data: This is given fully in Tables 8-1 and 8-2 for the equilibrium system



where  $n=1,2,3$ , and  $\text{L}=\text{pn}, \text{i-bn}$ . The formation curves are given in Figs. 8-1 to 8-6.

(b) Equilibrium constants: For the Ni(II)-pn system it was found that

$$\text{Log}K_{a_N} = \text{Log}K_{c_N} + \alpha I \dots\dots\dots 8-1$$

for  $N=\text{I}, \text{II}$  and  $\text{III}$ . This equation also applied for the Ni(II)-(i-bn) system for  $N=\text{I}$ , but for  $N=\text{II}$  and  $\text{III}$  then,

$$\text{Log}K_{a_N} = \text{Log}K_{c_N} + \beta I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) \dots\dots\dots 8-2$$

TABLE 8-1

'Formation Curve' data for the reaction $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + \text{pn} \rightleftharpoons [\text{Ni}(\text{pn})(\text{H}_2\text{O})_4]^{2+} + 2\text{H}_2\text{O}$ in aqueous solution $(\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2 \text{ medium}), 25.00 \pm 0.01^\circ\text{C}.$									
I (m/l)	$T_L \times 10^2$ (m/l)	$T_{\text{Ni}^{2+}} \times 10^2$ (m/l)	$T_{\text{H}^+} \times 10^4$ (m/l)	$p[\text{H}^+] \pm 0.002$	$[\text{HL}] \times 10^5$ (m/l)	$[\text{H}_2\text{L}] \times 10^4$ (m/l)	$[\text{L}] \times 10^8$ (m/l)	$\bar{n}$	
0.350	3.5115	7.000	14.99	6.277	13.63	6.815	$3.56 \pm 0.10$	0.490	
"	"	6.689	14.33	6.307	13.87	6.47	3.88	"	0.513
"	"	6.503	13.94	6.319	13.83	6.275	3.98	"	0.528
"	"	6.279	13.46	6.345	14.10	6.025	4.31	"	0.5475
"	"	6.054	12.99	6.362	14.09	5.79	4.48	"	0.568
0.200	1.4075	2.815	6.061	6.448	8.89	2.585	$3.72 \pm 0.11$	0.4875	
"	"	2.707	5.832	6.467	8.88	2.47	3.88	"	0.5075
"	"	2.606	5.620	6.505	9.21	2.35	4.39	"	0.5275
"	"	2.513	5.424	6.531	9.34	2.245	4.73	"	0.5475
0.150	1.055	2.111	4.545	6.511	8.01	1.87	$4.11 \pm 0.13$	0.4875	
"	"	2.030	4.375	6.527	8.025	1.81	$4.27 \pm$	"	0.507
"	"	1.955	4.215	6.554	8.055	1.705	4.56	"	0.527
"	"	1.885	4.068	6.567	7.965	1.655	4.65	"	0.547

TABLE 8-1(contd.)

I (m/l)	$T_L \times 10^2$ (m/l)	$T_{Ni2} \times 10^2$ (m/l)	$T_H \times 10^4$ (m/l)	p[H <sup>+</sup> ] ± 0.002	[HL] × 10 <sup>5</sup> (m/l)	[H <sub>2</sub> L] × 10 <sup>4</sup> (m/l)	[L] × 10 <sup>1</sup> (m/l)	$\bar{n}$
0.100	0.7037	1.407	3.030	6.564	6.275	1.20	3.86 ± 0.14	0.487
"	"	1.353	2.016	6.598	6.425	1.135	4.27 "	0.507
"	"	1.303	2.810	6.631	6.565	1.075	4.71 "	0.5265
"	"	1.257	2.712	6.645	6.49	1.03	4.79 "	0.5465
0.040	0.2815	0.563	1.212	6.742	3.83	4.145	3.86 ± 0.13	0.4855
"	"	0.541	1.166	6.754	3.84	3.91	3.98 ± "	0.5055
"	"	0.521	1.124	6.754	3.81	3.62	3.75 "	0.5255
"	"	0.503	1.085	6.811	3.81	3.52	4.51 "	0.5475

FIG. 8—1.

FORMATION CURVES FOR THE REACTION

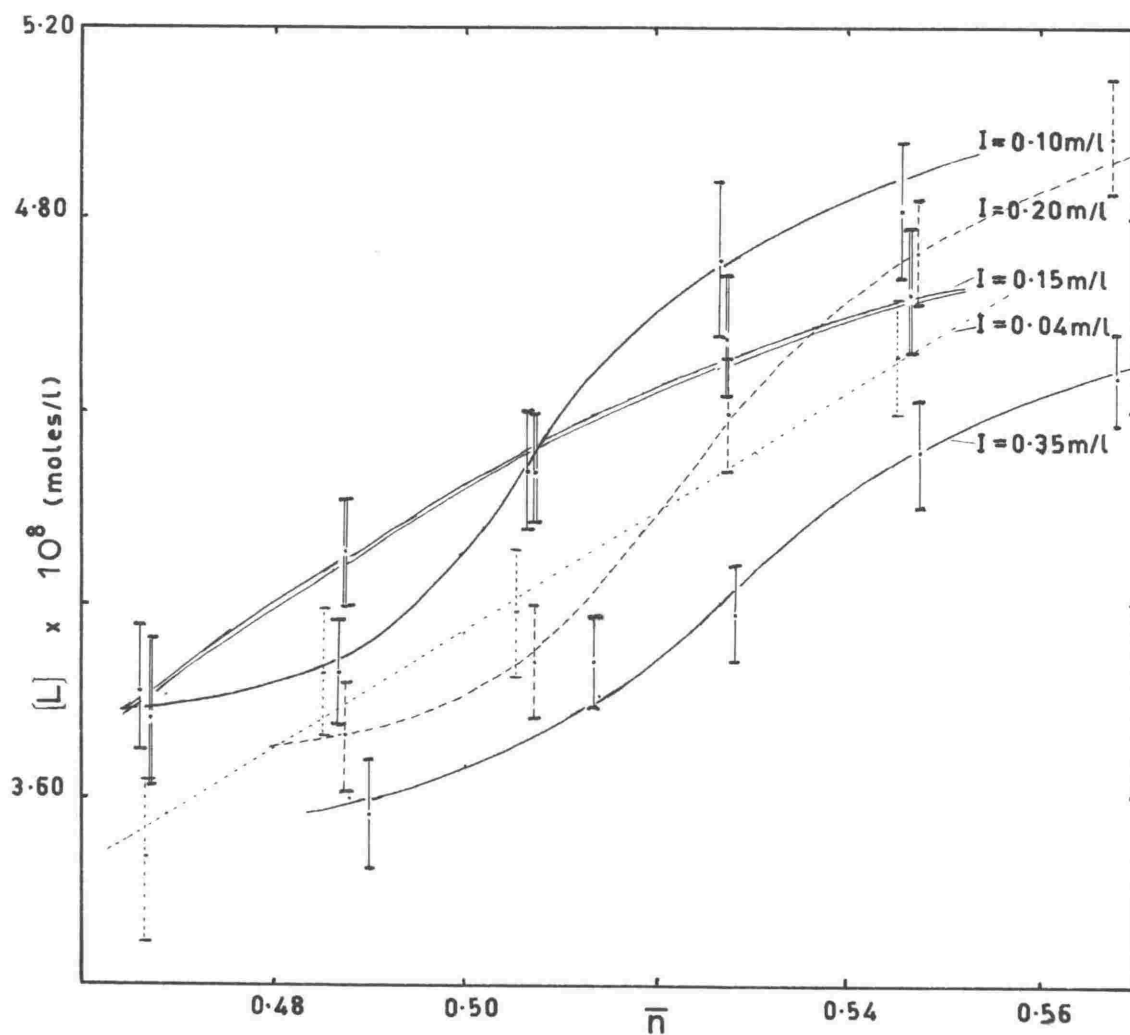


TABLE 8-1(A)

'Formation Curve' data for the reaction $[\text{Ni}(\text{pn})(\text{H}_2\text{O})_4]^{2+} + \text{pn} \rightleftharpoons [\text{Ni}(\text{pn})_2(\text{H}_2\text{O})_2] + 2\text{H}_2\text{O}$ in aqueous solution ( $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$ medium), $25.00 \pm 0.01^\circ\text{C}$									
I (m/l)	$T_L \times 10^2$ (m/l)	$T_{\text{Ni}} \times 10^2$ (m/l)	$T_{\text{H}} \times 10^4$ (m/l)	$p[\text{H}^+] \pm 0.002$ (m/l)	$[\text{HL}] \times 10^4$ (m/l)	$[\text{H}_2\text{L}] \times 10^5$ (m/l)	$[\text{L}] \times 10$ (m/l)	$\bar{n}$	
0.350	3.5115	2.373	5.211	7.157	2.25	14.8	$4.45 \pm 0.13$	1.465	
"	"	2.342	5.147	7.168	2.25	14.45	4.58	1.485	
"	"	2.312	5.083	7.196	2.305	13.9	5.00	1.505	
"	"	2.281	5.018	7.224	2.37	13.4	5.48	1.515	
"	"	2.251	4.954	7.237	2.365	12.95	5.63	1.545	
0.200	3.5115	2.373	5.126	7.172	2.445	13.4	$5.41 \pm 0.15$	1.465	
"	"	2.341	5.060	7.174	2.415	13.2	5.38	1.485	
"	"	2.310	4.995	7.187	2.425	12.85	5.56	1.505	
"	"	2.280	4.932	7.192	2.405	12.6	5.59	1.525	
"	"	2.251	4.870	7.202	2.405	12.3	5.71	1.545	



TABLE 8-1(A)(contd.)

I (m/l)	$T_L \times 10^2$ (m/l)	$T_{Ni2} \times 10^2$ (m/l)	$T_H \times 10^4$ (m/l)	$p[H^+] \pm 0.002$ [HL] $\times 10^4$ (m/l)	$[H_2L] \times 10^5$ (m/l)	$[L] \times 10$ (m/l)	$\bar{n}$	
0.150	2.634	1.780	3.845	7.230	2.03	9.07	5.46 $\pm$ 0.17	1.465
"	"	1.770	3.795	7.236	2.02	8.88	5.50 "	1.485
"	"	1.733	3.746	7.258	2.04	8.53	5.85 "	1.505
"	"	1.710	3.699	7.264	2.025	8.36	5.89 "	1.525
"	"	1.688	3.652	7.285	2.045	8.04	6.24 "	1.545
0.100	1.755	1.186	2.563	7.318	1.53	5.16	5.34 $\pm$ 0.18	1.465
"	"	1.170	2.530	7.341	1.545	4.935	5.68 "	1.485
"	"	1.155	2.497	7.352	1.535	4.795	5.80 "	1.505
"	"	1.140	2.466	7.364	1.535	4.655	5.95 "	1.525
"	"	1.126	2.435	7.399	1.56	4.37	6.00 "	1.54
0.040	0.7023	0.4745	1.025	7.529	0.757	1.34	4.68 $\pm$ 0.18	1.46
"	"	0.4682	1.012	7.572	0.766	1.225	5.23 "	1.48
"	"	0.4502	0.974	7.613	0.754	1.10	5.65 "	1.54

FIG. 8—2.

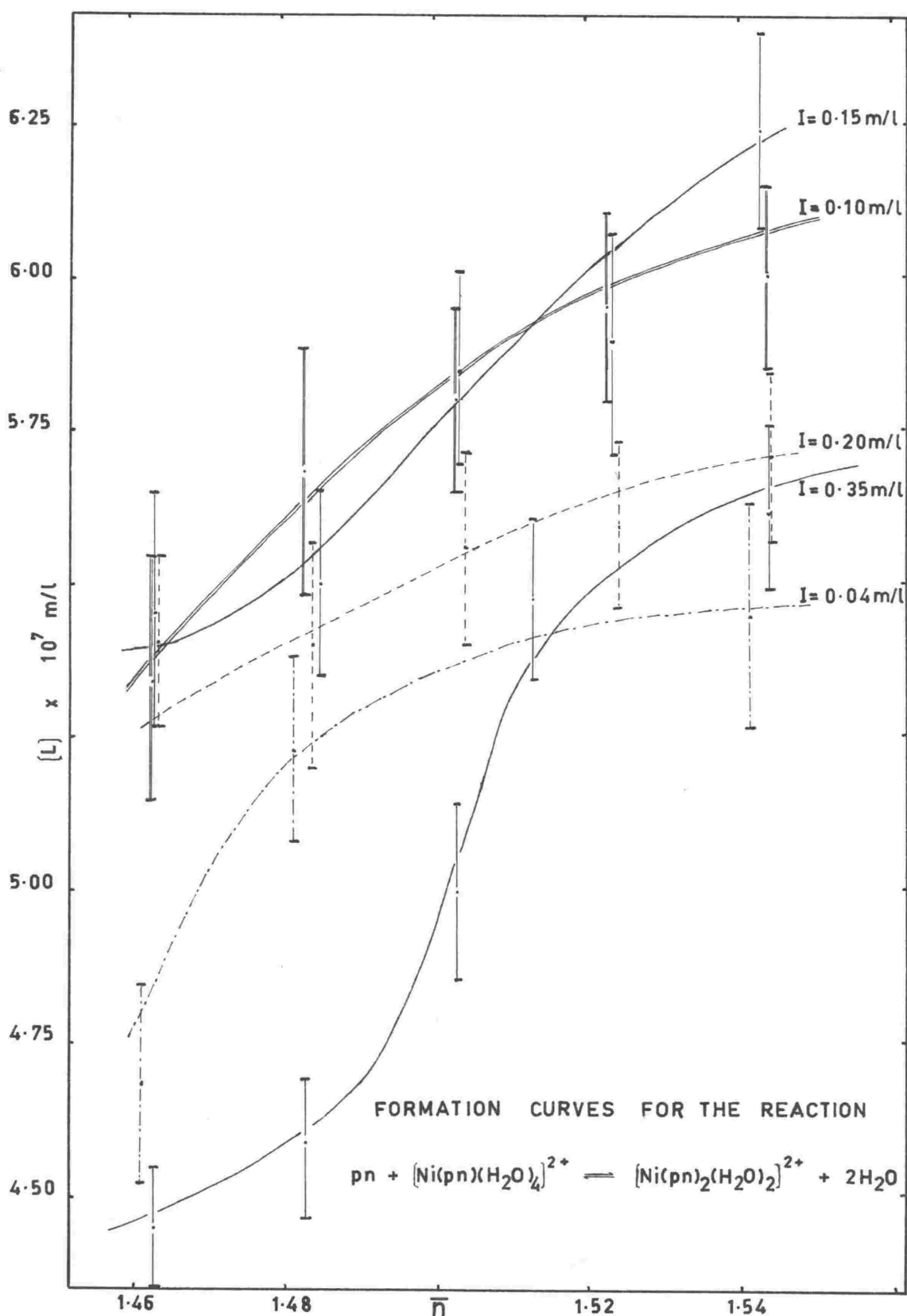


TABLE 8-1(B)

'Formation Curve' data for the reaction  $[\text{Ni}(\text{pn})_2(\text{H}_2\text{O})_2]^{2+} + \text{pn} \rightleftharpoons [\text{Ni}(\text{pn})_3]^{2+} + 2\text{H}_2\text{O}$  in aqueous solution ( $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  medium),  $25.00 \pm 0.01^\circ\text{C}$

I (m/l)	$T_L \times 10^2$ (m/l)	$T_{N_1 2} \times 10^3$ (m/l)	$T_{H^+} \times 10^5$ (m/l)	$p[H^+] \pm 0.002$ [HL] $\times 10^5$ (m/l)	$[H_2L] \times 10^7$ [L] $\times 10^5$ (m/l)	$\bar{n}$		
0.350	3.5115	14.04	31.64	8.624	30.3	68.1	1.76 $\pm$ 0.06	2.48
"	"	13.91	31.37	8.663	30.1	61.9	1.91 "	2.50
"	"	13.83	31.19	8.679	30.0	59.4	1.98 "	2.515
"	"	13.72	30.97	8.719	29.9	54.0	2.16 "	2.535
"	"	13.61	30.74	8.731	29.7	52.2	2.23 "	2.555
0.200	1.4075	5.630	13.03	8.836	12.75	15.15	1.30 $\pm$ 0.04	2.475
"	"	5.585	12.93	8.859	12.65	14.3	1.36 "	2.495
"	"	5.541	12.84	8.868	12.55	13.9	1.38 "	2.515
"	"	5.506	12.75	8.862	12.45	13.95	1.35 "	2.53
"	"	5.455	12.66	8.890	12.4	13.0	1.43 "	2.555

TABLE 8-1(B)(contd.)

I (m/l)	$T_L \times 10^2$ (m/l)	$T_{N_1 2} \times 10^3$ (m/l)	$T_H \times 10^5$ (m/l)	$p[H^+] + 0.002$	$[HL] \times 10^5$ (m/l)	$[H_2L] \times 10^7$ (m/l)	$[L] \times 10^5$ (m/l)	$\bar{n}$
0.150	1.055	4.222	9.77	8.853	9.57	10.15	$1.08 \pm 0.03$	2.475
"	"	4.189	9.70	8.882	9.51	9.46	$1.15 \pm$	2.495
"	"	4.156	9.63	8.924	9.46	8.54	1.26	2.515
"	"	4.129	9.565	8.927	9.40	8.43	1.26	2.53
"	"	4.091	9.495	8.998	9.35	7.12	1.47	2.555
0.100	0.7037	2.815	6.515	9.021	6.43	4.30	$1.13 \pm 0.04$	2.47
"	"	2.793	6.465	9.021	6.38	4.26	1.12	2.495
"	"	2.770	6.42	9.037	6.34	4.08	1.16	2.51
"	"	2.753	6.38	9.070	6.30	3.76	1.24	2.53
"	"	2.728	6.33	9.114	6.26	3.38	1.37	2.55
0.040	0.2815	1.126	2.606	9.105	2.585	1.13	$0.600 \pm 0.025$	2.465
"	"	1.117	2.587	9.134	2.61	1.125	0.638	2.49
"	"	1.108	2.568	9.187	2.55	0.99	0.716	2.51
"	"	1.101	2.511	9.188	2.53	0.98	0.713	2.525
"	"	1.091	2.532	9.253	2.515	0.84	0.823	2.55

FIG. 8-3.

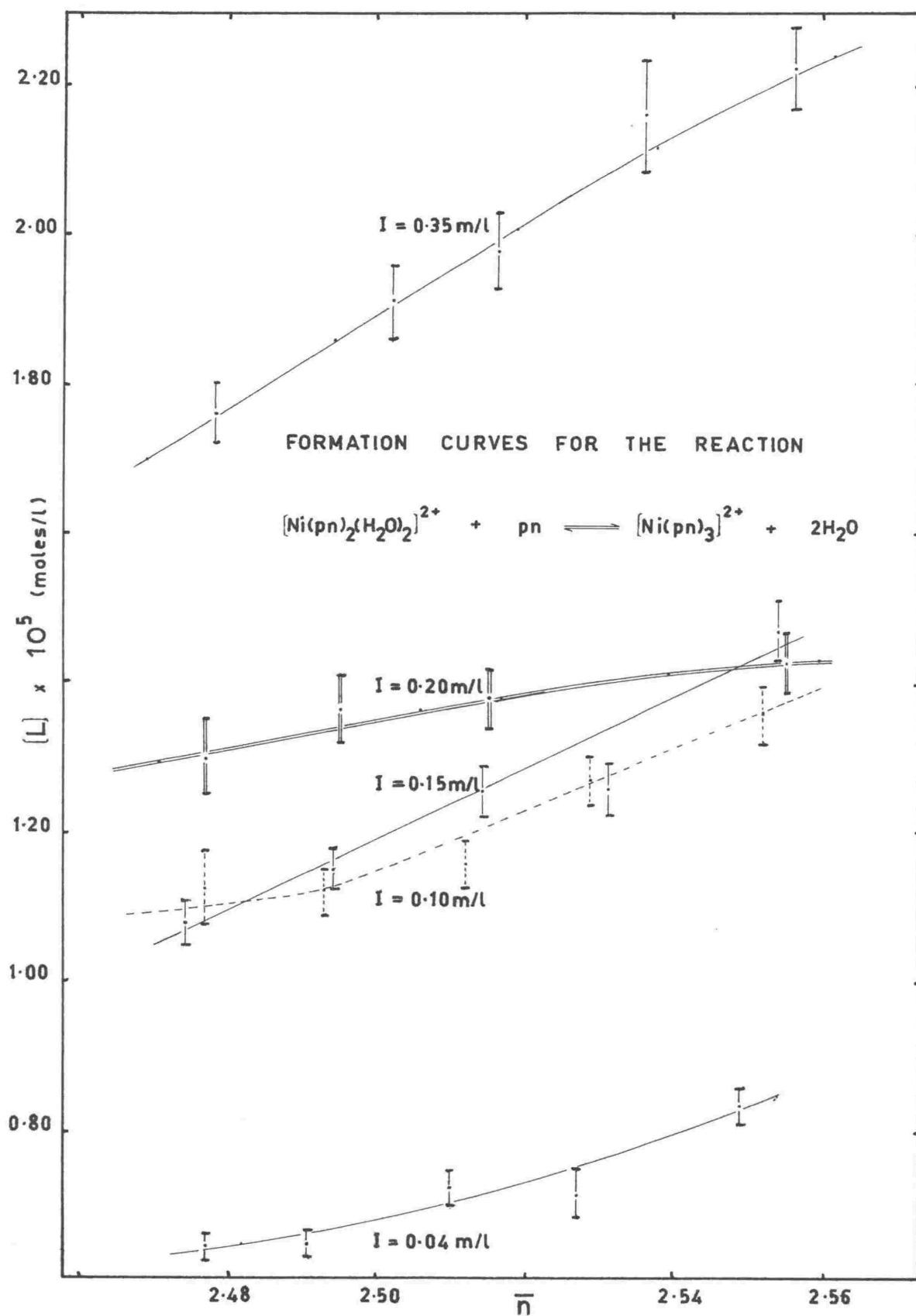


TABLE 8-2

'Formation Curve' data for the 1:1 equilibrium reaction between nickel(II) ions  
and 1-dimethyl 1,2-diaminoethane in aqueous solution  
( $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  medium),  $25.00 \pm 0.01^\circ\text{C}$

I (m/l)	$T_L \times 10^3$ (m/l)	$T_{\text{Ni}^{2+}} \times 10^3$ (m/l)	$T_{\text{H}^+} \times 10^4$ (m/l)	$p[\text{H}^+] \pm 0.003$	$[\text{HL}] \times 10^4$ (m/l)	$[\text{H}_2\text{L}] \times 10^5$ (m/l)	$[\text{L}] \times 10^7$ (m/l)	$\bar{n}$
0.200	8.815	17.99	3.914	6.703	1.74	10.9	$1.63 \pm 0.04$	0.4745
"	"	17.28	3.765	6.727	1.725	10.2	1.70	0.4945
"	"	16.63	3.627	6.752	1.71	9.57	1.78	0.514
0.150	6.612	13.50	2.935	6.766	1.46	7.33	$1.68 \pm 0.04$	0.4735
"	"	12.96	2.823	6.780	1.43	6.95	1.70	0.4935
"	"	12.47	2.720	6.813	1.43	6.43	1.83	0.5135
0.100	4.407	9.000	1.957	6.850	1.12	4.19	1.72	0.472
"	"	8.640	1.882	6.875	1.10	3.90	1.80	0.493
"	"	8.315	1.813	6.905	1.09	3.61	1.90	0.5125
0.040	1.763	3.598	0.7828	7.062	0.564	1.09	$1.67 \pm 0.04$	0.4715
"	"	3.456	0.7530	7.530	0.552	1.00	1.74	0.4915
"	"	3.326	0.7254	7.112	0.539	0.93	1.79	0.511

FIG. 8-4.

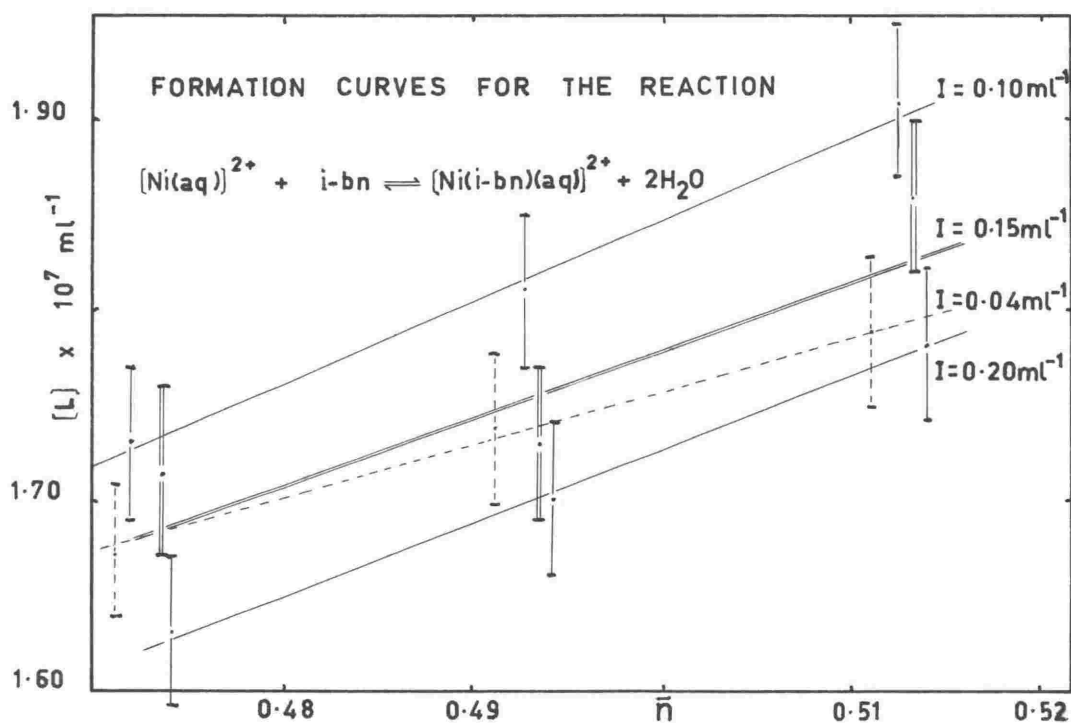


FIG. 8-5.

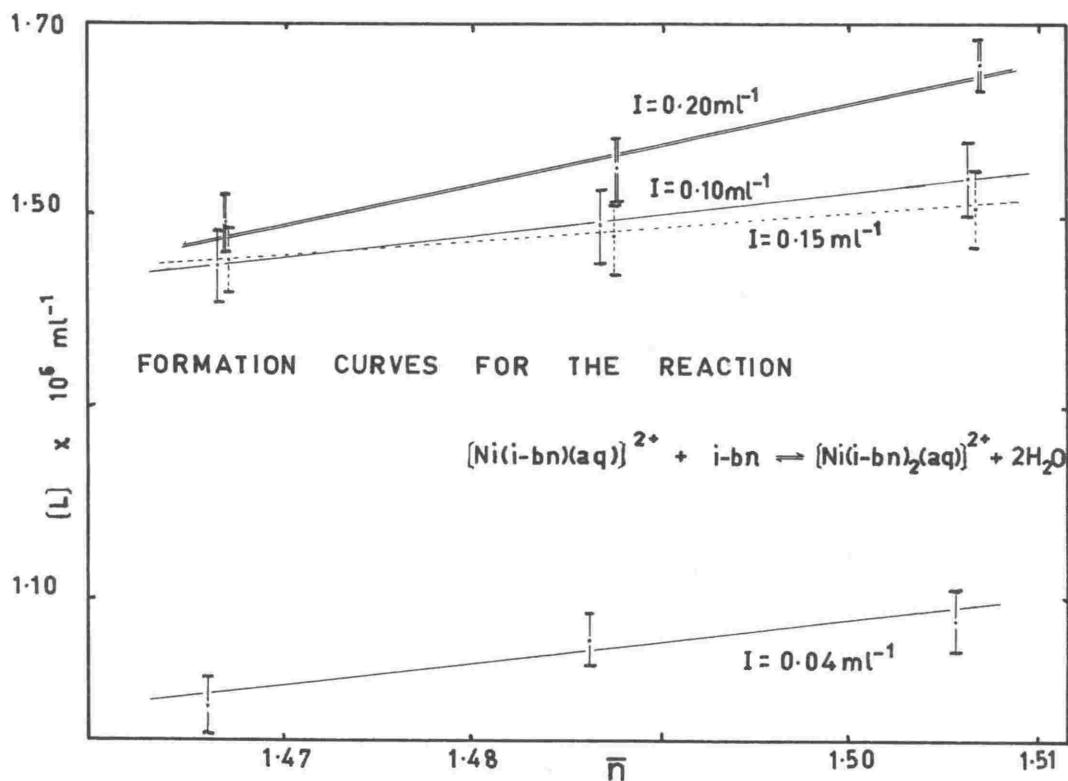


TABLE 8-2(contd.)

'Formation Curve' data for the 1:2 equilibrium reaction between nickel(II) ions and 1-dimethyl 1,2-diaminoethane in aqueous solution ( $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  medium),  $25.00 \pm 0.01^\circ\text{C}$

I	$T_L \times 10^3$ (m/l)	$T_{Ni2+} \times 10^3$ (m/l)	$T_H \times 10^5$ (m/l)	$p[H^+] \pm 0.003$	$[HL] \times 10^5$ (m/l)	$[H_2L] \times 10^6$ (m/l)	$[L] \times 10^6$ (m/l)	$\bar{n}$
0.200	8.815	5.919	13.64	7.815	12.4	6.00	$1.50 \pm 0.04$	1.465
"	"	5.838	13.31	7.836	12.3	5.69	$1.55 \pm 0.04$	1.49
"	"	5.764	13.15	7.861	12.3	5.25	1.66 "	1.505
0.150	6.612	4.438	10.23	7.884	9.50	3.62	$1.44 \pm 0.04$	1.465
"	"	4.378	9.982	7.899	9.41	3.46	1.47 "	1.49
"	"	4.323	9.862	7.911	9.31	3.34	1.49 "	1.505
0.100	4.407	2.959	6.820	8.011	6.48	1.68	$1.44 \pm 0.04$	1.465
"	"	2.919	6.655	8.028	6.42	1.60	$1.48 \pm 0.04$	1.485
"	"	2.882	6.575	8.045	6.35	1.52	$1.53 \pm 0.04$	1.505
0.040	1.763	1.184	2.728	8.165	2.65	0.404	$0.99 \pm 0.03$	1.465
"	"	1.168	2.662	8.197	2.62	0.371	1.06 "	1.485
"	"	1.153	2.630	8.212	2.59	0.355	1.08 "	1.505



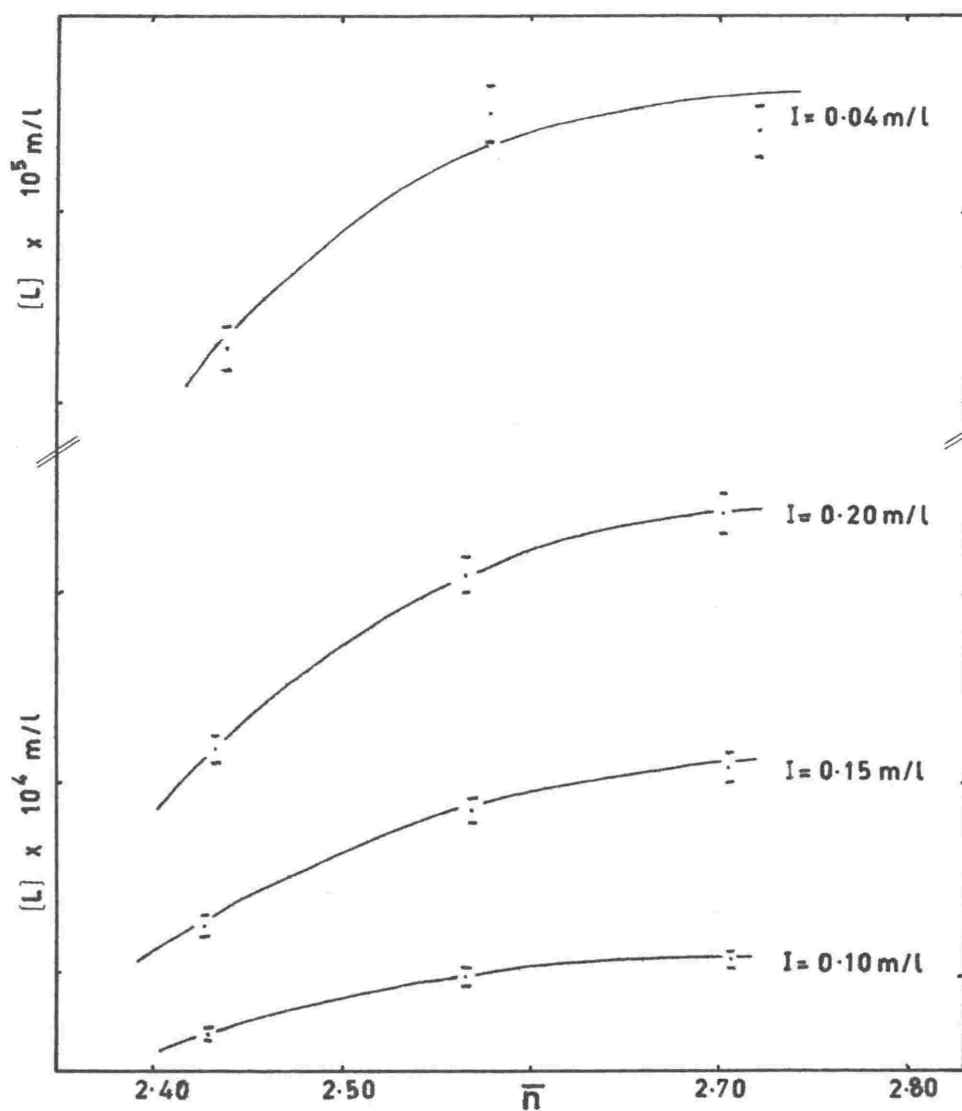
TABLE 8-2(contd.)

'Formation Curve' data for the 1:3 equilibrium reaction between nickel(II) ions and 1-dimethyl 1,2-diaminoethane in aqueous solution ( $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  medium),  $25.00 \pm 0.01^\circ\text{C}$

I (m/l)	$T_L \times 10^2$ (m/l)	$T_{Ni2} \times 10^3$ (m/l)	$T_H \times 10^5$ (m/l)	$p[H^+] \pm 0.003$	$[HL] \times 10^5$ (m/l)	$[H_2L] \times 10^6$ (m/l)	$[L] \times 10^4$ (m/l)	$\bar{n}$
0.200	1.763	7.052	16.03	10.024	16.0	--	$3.18 \pm 0.09$	2.43
"	"	6.653	15.19	10.158	15.2	--	4.02 "	2.565
"	"	6.309	14.46	10.213	14.5	--	4.35 "	2.70
0.150	1.322	5.289	12.02	9.971	12.0	--	$2.23 \pm 0.07$	2.43
"	"	4.989	11.39	10.099	11.4	--	2.82 "	2.57
"	"	4.731	10.84	10.152	10.8	--	3.04 "	2.705
0.100	0.8815	3.526	8.015	9.982	8.01	--	$1.67 \pm 0.05$	2.43
"	"	3.326	7.595	10.082	7.59	--	1.99 "	2.565
"	"	3.154	7.230	10.124	7.23	--	2.08 "	2.705
0.040	0.3526	1.410	3.206	9.808	3.21	--	$0.524 \pm 0.015$	2.44
"	"	1.331	3.038	9.922	3.04	--	$0.646 \pm$ "	2.58
"	"	1.262	2.892	9.937	2.89	--	$0.636$ "	2.72

FIG. 8-6.

## FORMATION CURVES FOR THE REACTION



Log  $K_{c_N}$  values are listed in Table 8-3 for a series of ionic strengths up to 0.35m/l. Log  $K_{a_N}$  values were obtained by graphical extrapolation of Log  $K_{c_N}$  to zero ionic strength using equation 8-1 or 8-2 (Figs. 8-7 to 8-10). Log  $K_{a_N}$  values are listed in Table 8-3, and  $\Delta G_N^0$  values in Table 8-6.

(c) Nickel ion hydrolysis: For  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $K_H = 4 \times 10^{-10} \text{ L.m}^{-1}$  (see 7-1.1). For all the complex equilibria studied, the fraction of the total nickel ion concentration present as  $[\text{Ni}(\text{H}_2\text{O})_5\text{OH}]^+$  was  $\ll 0.01$ .

(d) Uncertainties in  $K_N$  values: These were for  $L=\text{pn}$ ,  $\pm(2.5-3.5)\%$  and for  $L=\text{i-bn}$ ,  $\pm 2.5\%$  in all  $K_{c_N}$  and  $K_{a_N}$ .

(e) The enthalpy change: All experimental calorimetric enthalpy data are given in Table 8-4. The symbols are as explained in 7-1.2. The equation equivalent to 7-1 but applicable to the Ni(II) system is

$$\Delta H_I^0 + p \Delta H_{II}^0 + q \Delta H_{III}^0 = \sum n_i \Delta H_i^0 = \text{etc. ....} \quad 8-3$$

(see 4-2)

The  $\Delta H_I^0$ ,  $\Delta H_{II}^0$ , and  $\Delta H_{III}^0$  values in Table 8-6 were obtained from the data in Table 8-4 by solution of sets of the simultaneous equations 8-3, (see Table 8-5).

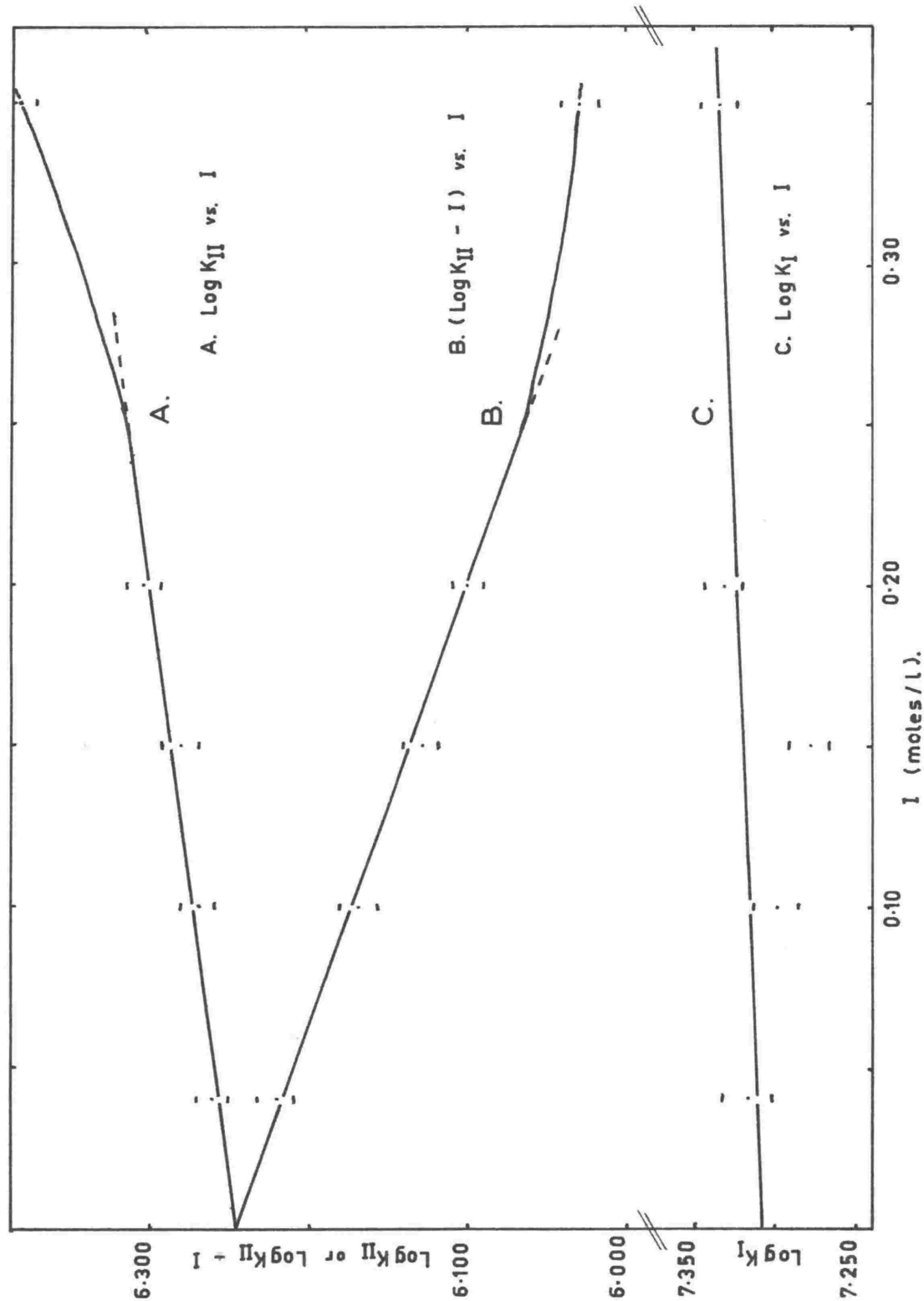
(f) The Ni(II)-1,2-diaminoethane system: Davies et al.<sup>41</sup> quote the step-wise equilibrium constants for this system at  $I=0.015\text{m/l}$ ,  $25.0^\circ\text{C}$ :  $\text{Log} K_I = 7.32$ ;  $\text{Log} K_{II} = 6.06$ ;  $\text{Log} K_{III} = 4.1$ . It is assumed here that these constants closely approximate the thermodynamic equilibrium constants. The corresponding

TABLE 8-3

Formation constants for Ni(II) - 1,2-diamine complexes in aqueous  $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  media,  $25.01 \pm 0.01^\circ\text{C}$

Log	Ionic strength (m/l)	1-methyl 1,2-diaminoethane	1-dimethyl 1,2-diaminoethane
$K_{c_I}$	0.350	$7.333 \pm 0.011$	
"	0.200	$7.330 \pm 0.012$	$6.598 \pm 0.011$
"	0.150	$7.277 \pm 0.012$	$6.567 \pm 0.009$
"	0.100	$7.292 \pm 0.014$	$6.544 \pm 0.010$
"	0.040	$7.316 \pm 0.015$	$6.480 \pm 0.013$
$K_I^O$	0.000	$7.311 \pm 0.021$	$6.465 \pm 0.013$
$K_{c_{II}}$	0.350	$6.380 \pm 0.011$	
"	0.200	$6.301 \pm 0.011$	$5.948 \pm 0.010$
"	0.150	$6.279 \pm 0.013$	$6.011 \pm 0.010$
"	0.100	$6.269 \pm 0.011$	$6.004 \pm 0.010$
"	0.040	$6.260 \pm 0.012$	$6.228 \pm 0.010$
$K_{II}^O$	0.000	$6.247 \pm 0.012$	$6.554 \pm 0.010$
$K_{c_{III}}$	0.350	$4.750 \pm 0.012$	
"	0.200	$4.912 \pm 0.013$	$3.441 \pm 0.012$
"	0.150	$4.985 \pm 0.012$	$3.588 \pm 0.011$
"	0.100	$4.997 \pm 0.015$	$3.738 \pm 0.012$
"	0.040	$(5.269 \pm 0.014)$	$4.250 \pm 0.010$
$K_{III}^O$	0.000	$5.111 \pm 0.015$	$5.25 \pm 0.03$

FIG. 8-7  $\text{Ni(II)} - 1\text{-METHYL } 1,2\text{-DIAMINOETHANE FORMATION CONSTANTS.}$



**FIG. 8-8.** Ni(II) - 1-METHYL 1,2-DIAMINOETHANE FORMATION CONSTANTS

A.  $(\text{Log } K_{\text{III}} + I)$  vs.  $I$ .      B.  $\text{Log } K_{\text{III}}$  vs.  $I$ .

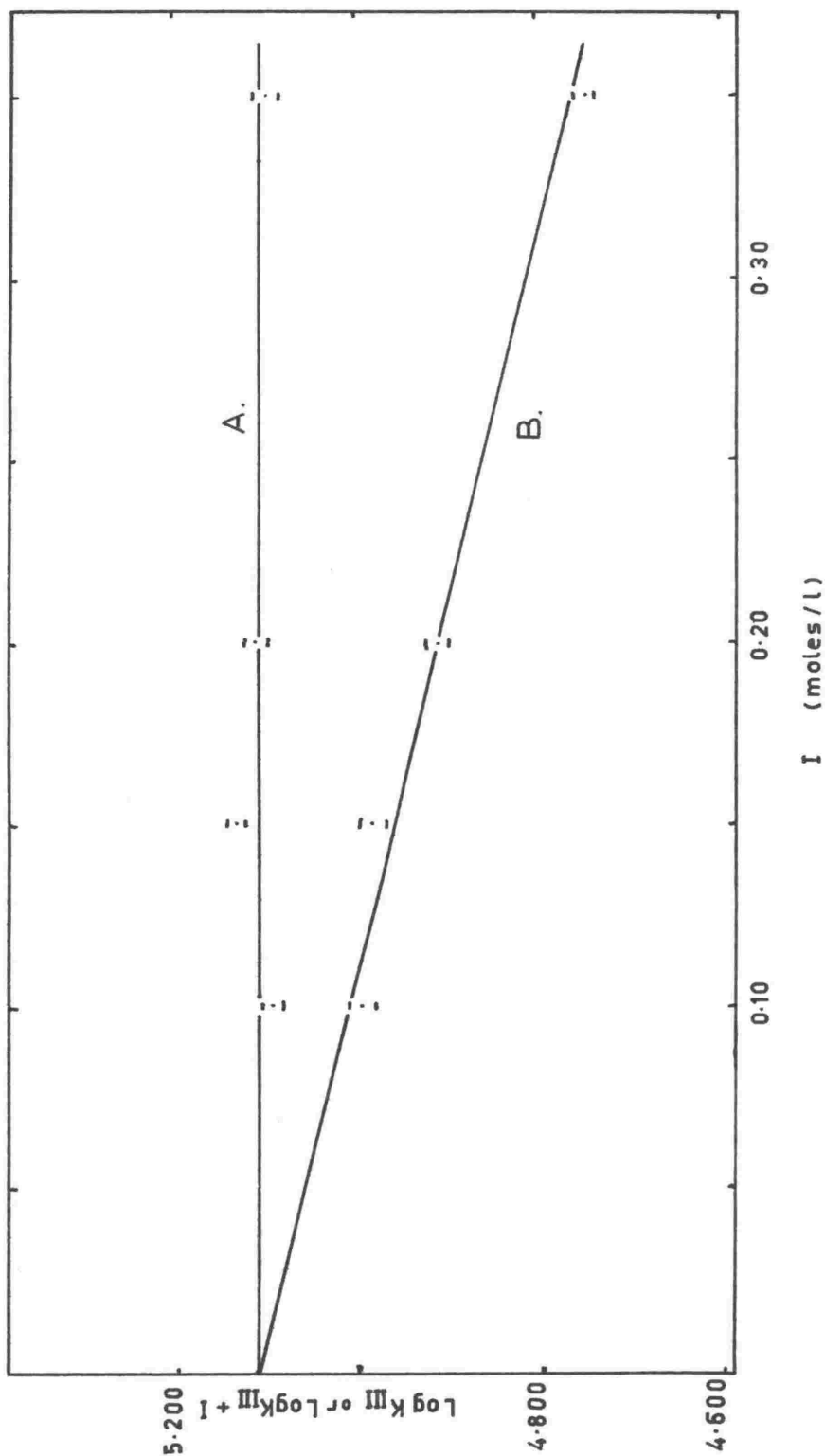


FIG. 8-9.

Ni(II) - 1-DIMETHYL 1,2-DIAMINOETHANE FORMATION CONSTANTS.

A.  $(\log K_{II} + \frac{2I^{1/2}}{1 + I^{1/2}})$  vs.  $\frac{I^{1/2}}{1 + I^{1/2}}$

C.  $(\log K_I + I)$  vs.  $I$

B.  $\log K_{II}$  vs.  $\frac{I^{1/2}}{1 + I^{1/2}}$

D.  $\log K_I$  vs.  $I$

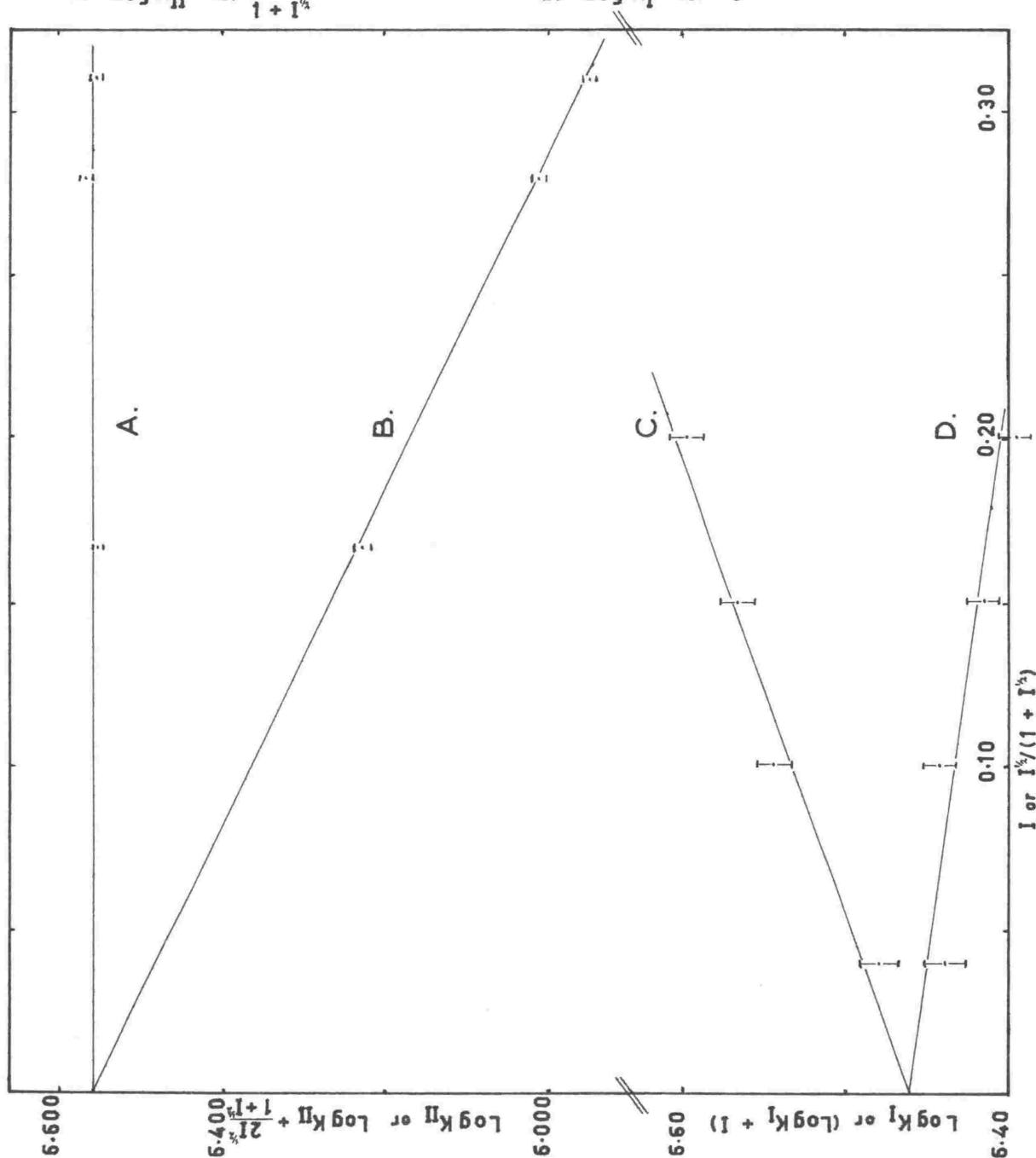
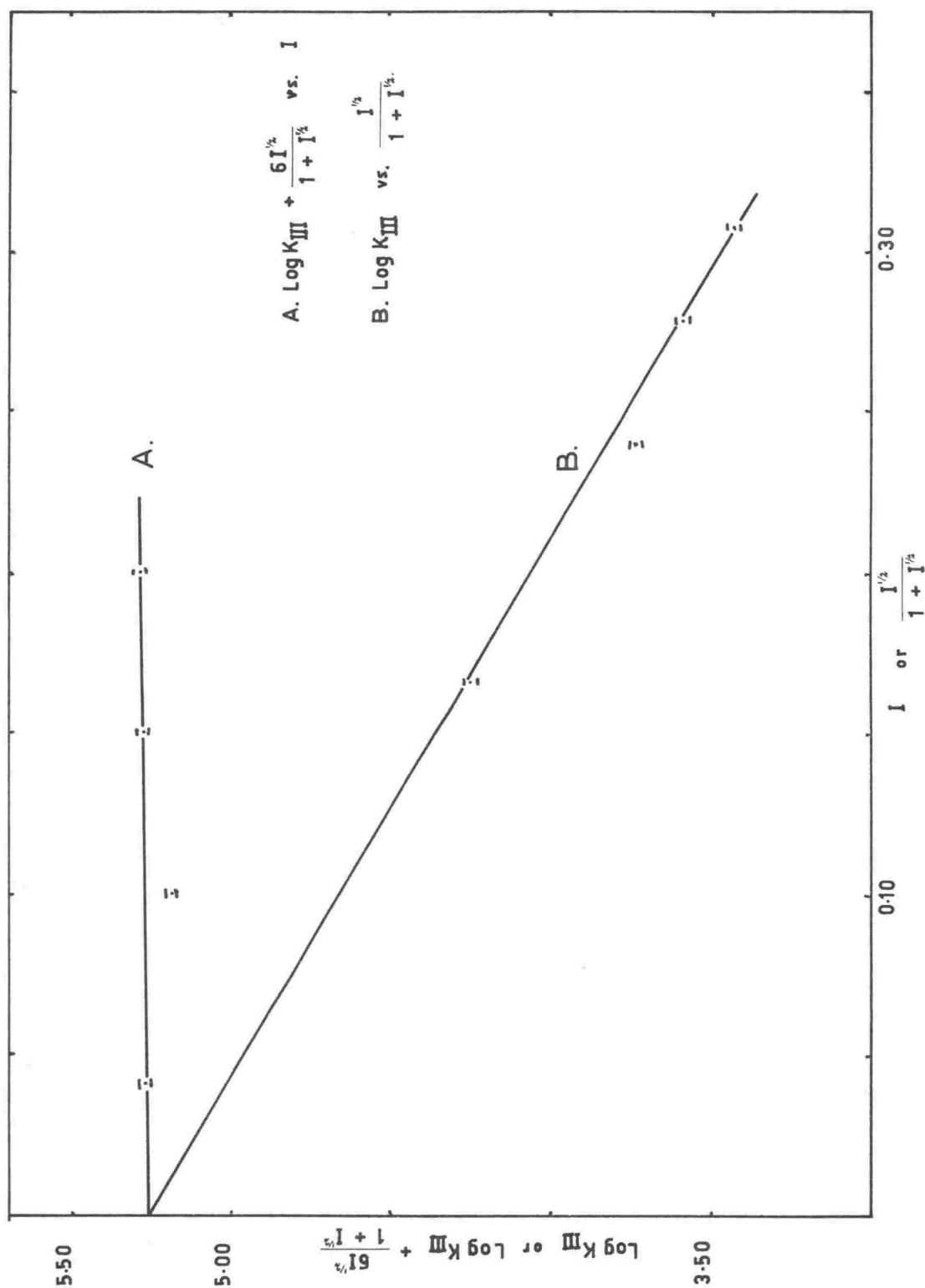


FIG. 8—10. Ni(II) — 1-DIMETHYL 1,2-DIAMINOETHANE FORMATION CONSTANTS.





TABLE

Calorimetric data for some Ni(II)-d:  
 $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  media

Diamine	Run No.	I(m/l)	$T_L$ (m/l)	$T_{\text{Ni}^{2+}} \times 10^2$	$T_{\text{H}^+} \times 10^4$	Vol
1-methyl	1	0.345	0.05977	1.300	2.945	98
1,2-diamino-	2	0.360	"	4.397	9.489	97
ethane	3	0.344	"	3.516	7.966	95
	4	0.344	"	7.000	14.99	95
	5	0.355	"	2.135	4.709	95
	6	0.344	"	7.000	14.99	95
1-dimethyl	7	0.200	0.01500	2.199	4.759	95
1,2-diamino-	8	"	"	1.982	4.169	95
ethane	9	"	"	0.7692	1.739	102
	10	"	0.07519	1.982	4.122	96
	11	"	0.01500	2.199	4.714	98
	12	"	"	0.7144	1.540	96
	13	"	0.07519	2.199	4.714	97

TABLE 8-4

Run No.	$[H^+]_{eqbm.}$ (m/l)	$T_L$ (calc.) (m/l)	$a_2 \Delta H_I^O + b_2 \Delta H_{II}^O + c_2 \Delta H_{III}^O$	$a_2$	$b_2$	$c_2$
1	--	--	0.2175	0.2175	0.2175	0.217
2	$1.146 \times 10^{-7}$	0.06147	0.6696	0.3141	0.006	
3	$5.52 \times 10^{-8}$	0.06123	0.5664	0.4030	0.020	
4	$3.083 \times 10^{-7}$	0.06122	0.8272	0.1585	0.000	
5	$1.167 \times 10^{-9}$	0.05918	0.3607	0.3600	0.271	
6	$3.083 \times 10^{-7}$	0.06122	0.8272	0.1585	0.000	
7	$1.63 \times 10^{-7}$	0.01504	0.8215	0.1553	0.000	
8	$1.32 \times 10^{-7}$	0.01524	0.8027	0.1764	0.000	
9	$4.79 \times 10^{-9}$	0.01452	0.5306	0.4529	0.004	
10	--	--	1.0000	1.0000	0.976	
11	$2.63 \times 10^{-7}$	0.01504	0.8215	0.1553	0.000	
12	$1.167 \times 10^{-9}$	0.01458	0.4898	0.4692	0.028	
13	--	--	0.2925	0.2925	0.281	

TABLE 8-5

Step-wise enthalpy changes from the solution of simultaneous equations (equation 8-3)

Diamine	Data combinations (from Table 8-4 )	$-\Delta H_I^O$ (kcal/m)	$-\Delta H_{II}^O$ (kcal/m)	$-\Delta H_{III}^O$ (kcal/m)
1-methyl 1,2-diaminoethane	1, 3, 4	8.32	8.54	9.85
	1, 2, 4	8.27	8.82	9.63
	3, 4, 5	8.32	8.55	9.68
	2, 4, 5	<u>8.24</u>	<u>8.95</u>	<u>9.26</u>
		<u>8.29<math>\pm</math>0.03</u>	<u>8.71<math>\pm</math>0.18</u>	<u>9.60<math>\pm</math>0.22</u>
1-dimethyl 1,2-diamino- ethane	7, 9, 10	7.38	5.97	4.83
	8, 9, 10	7.26	6.10	4.81
	9, 10, 11	7.48	5.88	4.81
	8, 10, 12	7.18	6.51	4.48
	7, 10, 12	7.30	6.36	4.50
	11, 12, 13	7.48	6.26	4.63
	10, 11, 12	7.40	6.27	4.49
	8, 9, 13	7.26	6.09	5.01
	7, 9, 13	7.38	5.96	4.96
	9, 11, 13	7.48	5.88	4.94
	7, 12, 13	7.37	6.35	4.64
	8, 12, 13	<u>7.18</u>	<u>6.49</u>	<u>4.69</u>
		<u>7.35<math>\pm</math>0.11</u>	<u>6.18<math>\pm</math>0.22</u>	<u>4.73<math>\pm</math>0.18</u>

-  $\Delta G_N^0$  values for the step-wise equilibria are given in Table 8-6.

Ciampolini et al.<sup>40</sup> have calorimetrically measured the step-wise enthalpy changes for this coordination reaction (see Table 8-6).

(g) Solid complexes: To help establish the metal-ligand stoichiometry for some complexes studied in aqueous solution solid complexes were isolated and analysed. Most diamine complexes were also prepared as halide salts for I.R. analysis (Chapter 10).

$[\text{Ni}(\text{pn})_3](\text{ClO}_4)_2$ : A blue-violet solid isolated from aqueous solution and recrystallised from 50% aqueous ethanol. (Found Ni(dmg. gravimetric), 12.23; amine by pH titration, 46.5 46.9.  $[\text{Ni}(\text{pn})_3](\text{ClO}_4)_2$  requires Ni, 12.23; amine, 46.3.)

$[\text{Ni}(\text{i-bn})_2](\text{ClO}_4)_2$ : A yellow-orange solid isolated from aqueous solution and twice recrystallised from the minimum volume of hot water. The solid showed no tendency to hydrate. (Found C, 22.44; H, 6.09; N, 12.55.  $\text{C}_8\text{H}_{26}\text{N}_4\text{Cl}_{12}\text{O}_8\text{Ni}$  requires C, 22.04; H, 6.01; N, 12.85.)

TABLE 8-6

Standard thermodynamic functions for Ni(II)-diamine complexes  
in aqueous solution,  $25 \pm 0.01^\circ\text{C}$ ,  $I = 0.0\text{m/l}$

	1,2-diamino- ethane	1-methyl 1,2-diamino- ethane	1-dimethyl 1,2-diaminoethane	
<u>kcal/s/m</u>			<u>spin-free</u>	<u>spin-paired</u>
$\Delta G_I^\circ$	-9.98Ref41	$-9.97 \pm 0.03$	-8.82	$-8.82 \pm 0.02$
$\Delta G_{II}^\circ$	-8.27 "	$-8.52 \pm 0.02$	-8.99	$-8.88 \pm 0.01$
$\Delta G_{III}^\circ$	-5.59 "	$66.97 \pm 0.02$	-7.11	$-7.22 \pm 0.04$
$\Delta G_{I-III}^\circ$	-23.84 "	$-25.46 \pm 0.07$	-24.92	$-24.92 \pm 0.07$
<u>kcal/s/m</u>				
$\Delta H_I^\circ$	-8.90Ref40	$-8.29 \pm 0.03$	-7.35	$-7.35 \pm 0.011$
$\Delta H_{II}^\circ$	-9.35 "	$-8.71 \pm 0.14$	-7.21	$-4.95 \pm 0.22$
$\Delta H_{III}^\circ$	-10.10 "	$-9.60 \pm 0.18$	-3.70	$-5.96 \pm 0.18$
$\Delta H_{I-III}^\circ$	-28.35 "	$-26.71 \pm 0.05$	-18.26	$-18.26 \pm 0.51$
<u>e.u.</u>				
$\Delta S_I^\circ$	3.6	$5.6 \pm 0.2$	4.9	$4.9 \pm 0.5$
$\Delta S_{II}^\circ$	-3.6	$-0.6 \pm 0.5$	6.0	$13.2 \pm 0.8$
$\Delta S_{III}^\circ$	-15.1	$-8.8 \pm 0.6$	11.4	$4.2 \pm 0.7$
$\Delta S_{I-III}^\circ$	-15.1	$-4.2 \pm 0.4$	22.3	$22.3 \pm 2.3$

$[\text{Ni}(\text{i-bn})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ : A blue-violet solid isolated from aqueous solution. It was recrystallised from solvent alcohol containing a trace of the diamine. The hot alcoholic solution is yellow due to dissociation to the diamagnetic bis complex. (Found C, 27.71; H, 7.01. Requires C, 27.60; H, 6.90.)

$\text{Ni}(\text{i-bn})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ :  $\text{Ni}(\text{i-bn})_2(\text{ClO}_4)_2$  was converted to the chloride salt by passing an aqueous solution through an anion exchange resin in the chloride form. Slow crystallisation of the aqueous solution gave blue crystals of the pentahydrate. (Found C, 24.46; N, 14.43;  $\text{H}_2\text{O}$  by weight loss at  $100^\circ\text{C}$ , 18.6.  $\text{C}_8\text{H}_{36}\text{N}_4\text{Cl}_2\text{O}_5\text{Ni}$  requires C, 24.14; N, 14.08;  $\text{H}_2\text{O}$ , 18.0.)

$\text{Ni}(\text{i-bn})_2\text{Cl}_2$ : A yellow solid obtained by heating the pentahydrate at  $100^\circ\text{C}$  for 24 hours or by recrystallising the pentahydrate from isopropanol.

## 8-2 Magnetic Equilibria for $[\text{Ni}(\text{i-bn})_2]^{2+}$ salts

Many Ni(II) complex salts of suitable stoichiometry exist as a mixture of diamagnetic and paramagnetic forms.

At room temperature the aqueous nickel bis i-bn ion exists as an equilibrium mixture of a yellow-orange diamagnetic form and a light-blue paramagnetic form. The equilibrium constant at  $25^\circ\text{C}$  ( $I=0.20\text{m/l}$ ) is  $K = [\text{D}]/[\text{P}] = 0.832$ , equivalent to 54.5% P, 45.5% D. K increases with temperature

and on addition of acetone or methanol to the solvent. In pure acetone, only the diamagnetic form is present,  $\lambda_{\max.} = 455\text{m}\mu$ ;  $\epsilon_{\max.} = 61.2$ . In dry methanol the equilibrium mixture consists of approximately 95% of the diamagnetic form;  $\lambda_{\max.} = 450\text{m}\mu$ .

The enthalpy change for the  $P \rightleftharpoons D$  reaction in aqueous solution was obtained by the temperature coefficient method:

$$\Delta H_{(P,D)} = 2.303RT^2 \left( \frac{\partial \log K}{\partial T} \right)_{P, n_i} \quad (\text{see 3-3.1a})$$

$K = [D]/[P]$  was obtained at a series of temperatures from spectroscopic measurements. The paramagnetic species has three weak absorptions in the visible spectrum, at 369, 594, and  $980\text{m}\mu$ ,  $\epsilon_{\max.} \leq 10^*$  in each case. The single intense absorption band for the diamagnetic ion occurs between these first two wavelengths; the measured molar extinction coefficient at  $450\text{m}\mu$  is little affected by the presence of the paramagnetic species in solution. It was assumed in calculating  $K$  that  $\epsilon_{\max.}$  for diamagnetic  $[\text{Ni}(\text{i-bn})_2]^{2+}$  is the same in solvent acetone and water.

### 8-2.1 Experimental

Spectra were measured with Unicam S.P. 700 recording spectrophotometer fitted with a thermostatted electric heating block for the absorption cells. Measurements were made at temperatures between 26 and  $62^\circ\text{C}$ . To facilitate

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\* Difficult to assess exactly because of the  $D \rightleftharpoons P$  equilibrium.

rapid thermal equilibrium 0.1cm cells were used. Measurements were made on a solution of ionic strength 0.200m/l; this ionic strength was employed for calorimetric enthalpy measurements also. No inert electrolyte was used. A concentrated (0.066molar) solution of  $[\text{Ni}(\text{i-bn})_2](\text{ClO}_4)_2$  was used to minimise the change in degree of dissociation caused by the effect of temperature on the formation constant for the complex,  $K_I \cdot K_{II}$ .

### 8-2.2 Results

The absorption curves for various solution temperatures are shown in Fig. 8-11. A plot of  $\log K$  vs.  $T^\circ\text{A}$  is shown in Fig. 8-12. The experimental error in  $K$  is approximately  $\pm 8\%$ . From Fig. 8-12,

$$\frac{d\log K}{dt} = \frac{0.01^\circ\text{C}^{-1}}{18}$$

and  $\Delta H_{(P,D)} = 2260\text{cals/mole}$  (for the reaction  $P \rightleftharpoons D$ ).  
 At  $25^\circ\text{C}$   $K = 0.832$  and  $\Delta G_{(P,D)} = -RT\ln K = 109\text{cals}(P \rightleftharpoons D)$ .  
 Therefore

$$\Delta S_{(P,D)} = +7.2\text{e.u.}$$

The electronic multiplicity of the diamagnetic form is one and of the paramagnetic form three. Therefore  $\Delta S_{(P,D)}$  includes a term  $-R\ln 3 = -2.2\text{e.u.}$  arising from the decrease in electronic multiplicity. Therefore  $\Delta S_{(P,D \text{ corr})} = 9.4\text{e.u.}$



FIG. 8-11.

VISIBLE ABSORPTION SPECTRA AS A FUNCTION OF  
SOLUTION TEMPERATURE FOR AQUEOUS  $[\text{Ni}(\text{i-bn})_2(\text{aq})]^{2+}$

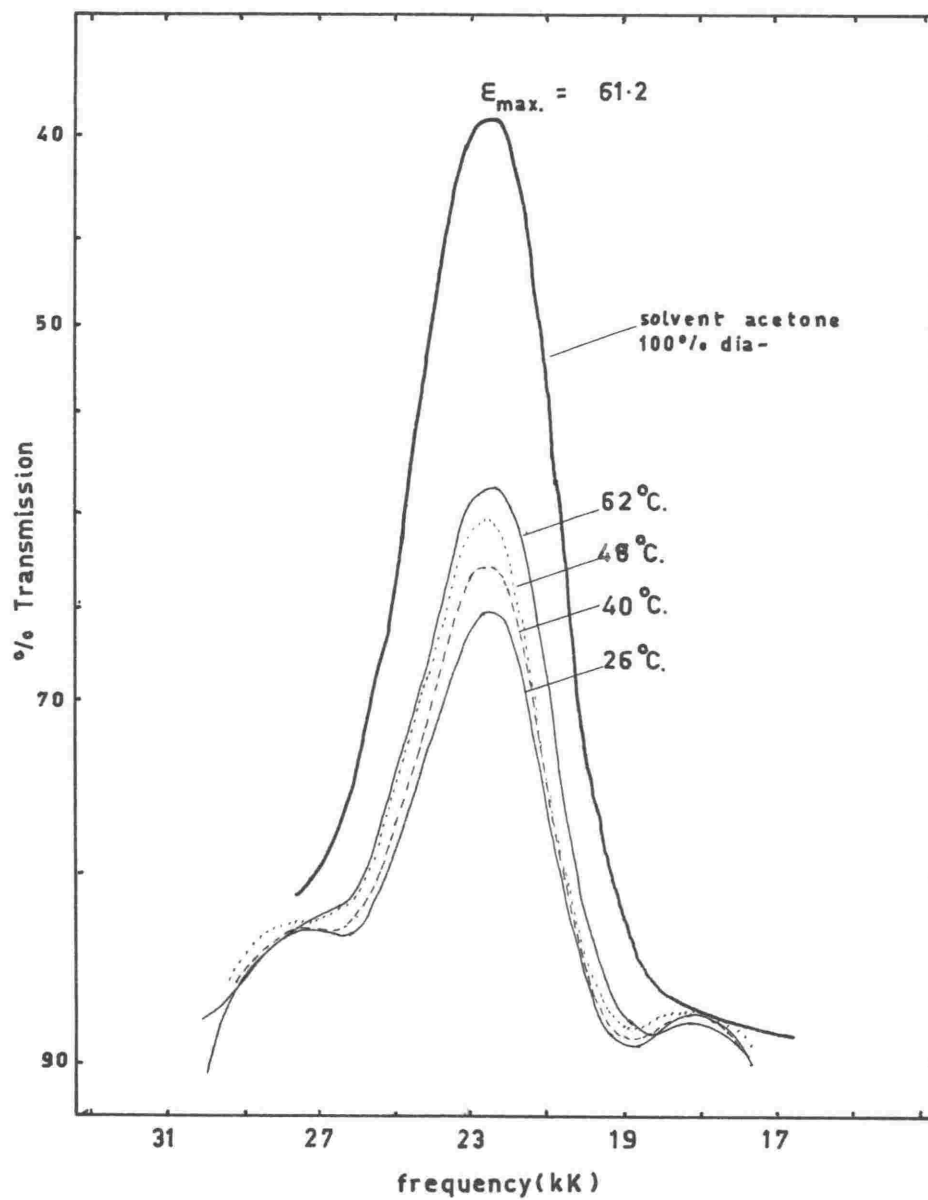
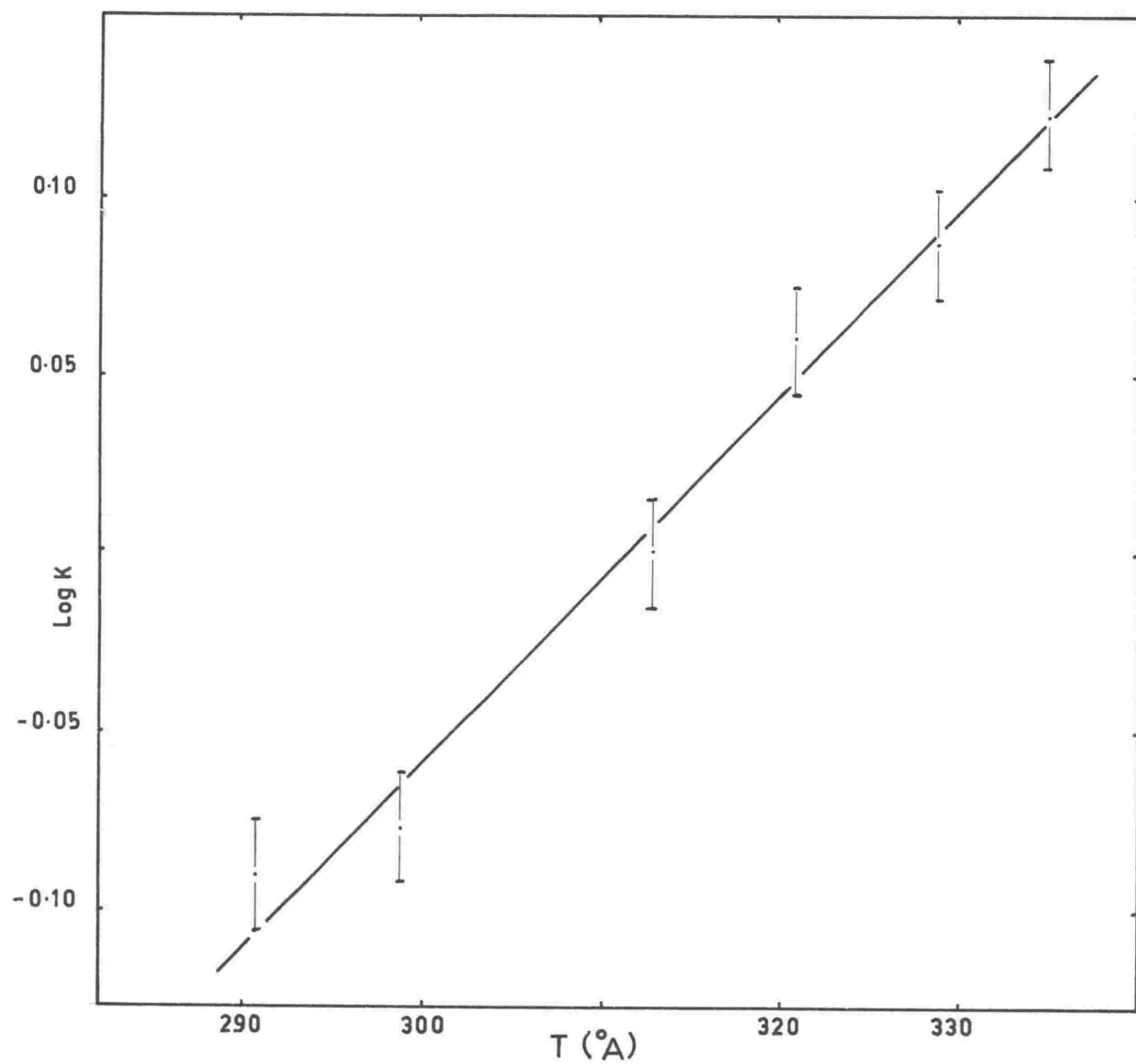


FIG. 8-12.

PLOT OF Log K vs. T (°A) FOR THE EQUILIBRIUM



## Discussion of Results

### Part A

The formation of spin-free nickel(II)-diamine complexes  
(The ligands en, pn and i-bn)

### 8-3 The Free Energy Change

#### 8-3.1 The relationship between complex stability and ligand basicity

There is an approximately linear relationship between complex stability and ligand basicity for the 1:1 complexes, viz:

$$\Delta G_{\text{I}}^{\circ} / \Delta G_{1-2}^{\circ} = 0.432 \pm 0.011$$

This constant ratio implies that interligand forces in the coordination sphere are uniform in each diamine complex.<sup>51</sup>

(See 7-2.1) Therefore C<sub>1</sub>-alkyl substitution on the basic ethylenediamine ligand does not significantly increase interligand interactions in the 1:1 and Ni(II)-diamine complexes.

However the ratios  $\Delta G_{\text{II}}^{\circ} / \Delta G_{1-2}^{\circ}$  and  $\Delta G_{\text{III}}^{\circ} / \Delta G_{1-2}^{\circ}$  increase considerably with increased C<sub>1</sub>-alkyl substitution. i.e., the ratios for en < pn < i-bn. This trend follows the order of decreasing ligand basicity (donor power) and increasing interligand interaction (particularly steric hindrance between the C<sub>1</sub>-substituent on one ligand and the donor atoms of another in the coordination sphere), and arises because the entropy changes,  $\Delta S_{\text{II}}^{\circ}$  and  $\Delta S_{\text{III}}^{\circ}$ , increase markedly with increased C<sub>1</sub>-alkyl substitution.

This entropy effect is discussed in 8-5.2. cf. for the N- and NN'-alkyl substituted ethylenediamines the ratio

$\Delta G_{I-N}^{\circ} / \Delta G_{1-2}^{\circ}$  decreases with increasing substitution and interligand interaction.

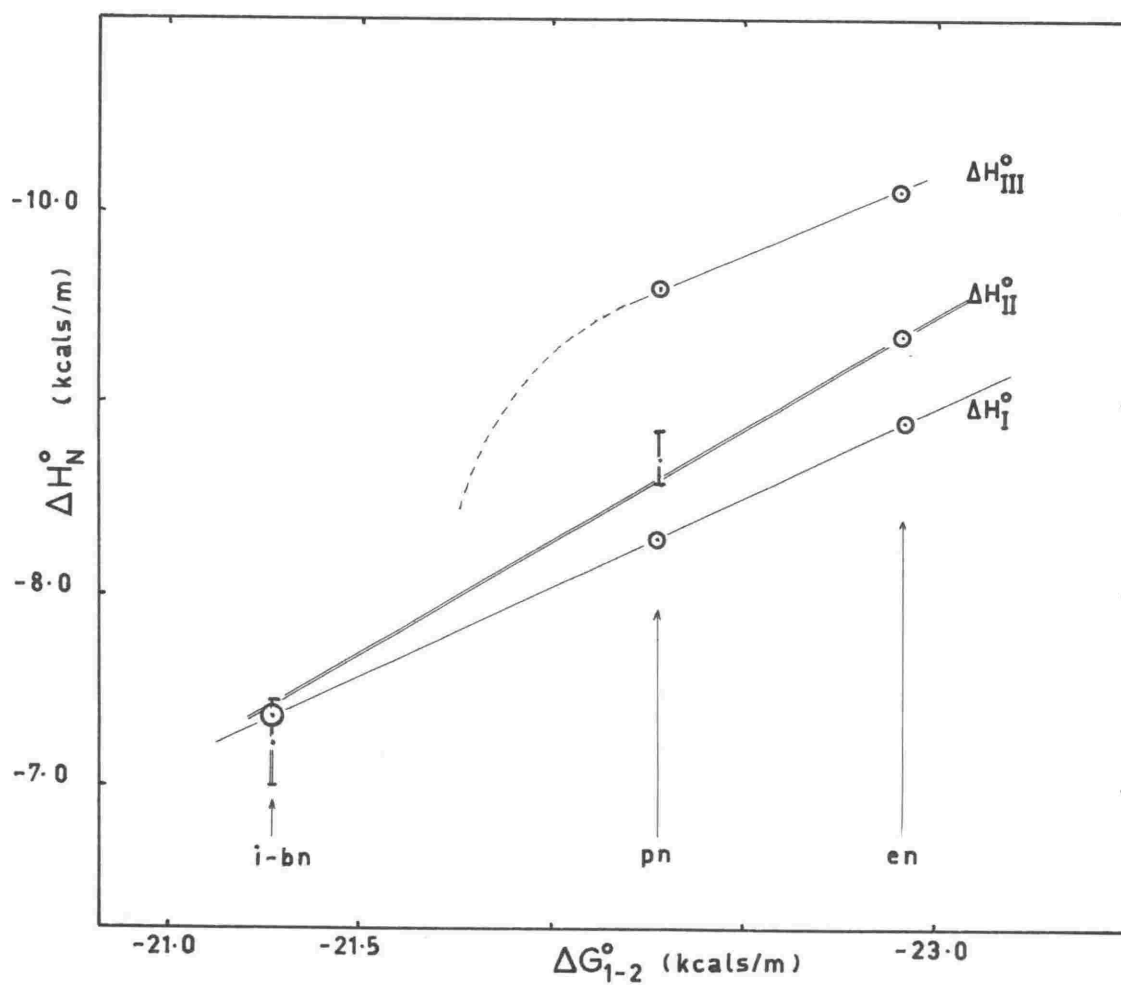
### 8-3.2 The ratio of successive $K_N^{\circ}$ values

The stability constants show the general order  $K_I > K_{II} > K_{III}$ , although for i-bn,  $K_I \approx K_{II}$ . The general decrease of  $K_N$  with increasing N is typical for complex formation reactions (see 3-5-1a). For ex.  $\log(K_I/K_{II}) =$

FIG. 8-13.

$\Delta H_N^\circ$  FOR Ni(II) LIGATION vs.  $\Delta G_{1-2}^\circ$  FOR LIGAND

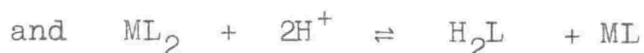
PROTONATION



$$\Delta H_I^O = \Delta G_{1-2}^O + (13.98 \pm 0.04) \text{kcal/s/mole}$$

$$\Delta H_{II}^O = \Delta G_{1-2}^O + (13.73 \pm 0.22) \text{kcal/s/mole}$$

However, because  $\Delta G_{1-2}^O \doteq \Delta H_{1-2}^O$  (see Table 6-6), these relationships imply that the enthalpy changes for the reactions



are both independent of L. Therefore the ligand basicity is giving a direct measure of the metal-ligand bond strength, and the interligand repulsion forces must be approximately the same in each 1:1 and in each 1:2 complex.

For en and pn,

$$\Delta H_{III}^O = \Delta G_{1-2}^O + (12.75 \pm 0.07) \text{kcal/s/mole},$$

probably indicating that  $C_1$ -methyl substitution on three coordinated ethylene-diamine ligands does not affect the interligand repulsion forces. However,  $C_1$ -dimethyl substitution causes considerable steric strain in the tris diamine complex and  $-\Delta H_{III}^O$  for i-bn is very low.

It appears that in the absence of marked strain and interligand interactions in the coordination sphere, the stepwise enthalpy changes for the formation of Ni(II) diamine complexes show the expected linear relationship to ligand basicity.\* However, the available data for dipyridyl<sup>53</sup>

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\*  $\Delta G_{1-n}^O$  for an n-basic amine.

do not fit the relationship (this system complicated by M-L  $\pi$ -bonding), nor do the data for dien,<sup>121,39</sup> or trien,<sup>19,38</sup> although chelation by these may involve ring-strain (see 3-5.2b).

#### 8-4.2 The successive $\Delta H_N^O$ values

For en and pn

$$-\Delta H_{III}^O \text{ is } > -\Delta H_{II}^O > -\Delta H_I^O$$

This order is opposite to that shown by  $\Delta G_N^O$ , and it is interesting to note that  $\Delta G_N^O$  has often been utilised as a measure of  $\Delta H_N^O$  for complex formation reactions. For i-bn  $-\Delta H_I^O$  is  $\approx -\Delta H_{II}^O \gg -\Delta H_{III}^O$ . (The low value for  $-\Delta H_{III}^O$  is discussed above).

For en and pn, the  $\Delta H_N^O$  values when corrected for C.F.S.E. contributions (see 8-4.3),

$$\Delta H_N^O(\text{corr}) = \Delta H_N^O - \Delta H_{\text{C.F.}(N)} \quad (\text{from 7-3.4})$$

still show the order  $-\Delta H_{III}^O > -\Delta H_{II}^O > -\Delta H_I^O$ . (Table 8-7) For i-bn the order becomes  $-\Delta H_I^O > -\Delta H_{II}^O \gg -\Delta H_{III}^O$ .

The increase of  $-\Delta H_N^O$  with N for en and pn is considered to arise at least in part from a solvation effect. It has been noted that  $(S_{ML_n}^O - S_{ML_{n-1}}^O)$  decreases as n increases, and that  $S_{ML_n}^O$  is  $> S_M^O(\text{aq})$ . (See 7-4.4) This has been associated with a progressively smaller release of water molecules from the outer hydration spheres of an aqueous metal ion as successive ligand groups are coordinated<sup>135</sup> (7-4.3 and 7-4.4). The 'freeing' of solvent

TABLE 8-7

Crystal field corrected enthalpy changes  $\Delta H_{N(\text{corr})}^*$  for  
Ni(II)-diamine ligation in aqueous solution, 25°C

<u>Ligand</u> kcal/m	<u>en</u>	<u>pn</u>	<u>spin-free</u>	<u>i-bn</u> <u>spin-paired</u>
$\Delta H_{\text{I}}(\text{corr})$	-4.35	-4.19	-4.86	-4.86
$\Delta H_{\text{II}}(\text{corr})$	-6.97	-4.61	-3.77	+290.5
$\Delta H_{\text{III}}(\text{corr})$	-6.95	-7.70	-2.70	-297
$\Delta H_{\text{I-II}}(\text{corr})$	-11.31	-8.80	-8.63	+285.5
$\Delta H_{\text{I-III}}(\text{corr})$	-18.26	-16.50	-11.33	-11.33

\* Symbols defined in 7-3.4.

water molecules is accompanied by an endothermic enthalpy term which makes a greater contribution to  $\Delta H_{\text{I}}^{\circ}$  than to  $\Delta H_{\text{II}}^{\circ} > \Delta H_{\text{III}}^{\circ}$ .

A similar increase of  $\Delta H_{\text{N}}^{\circ}$  with N has been noted for some other complex formation reactions, viz.,  $M+n(\text{en})$  where  $M=(\text{Mn}, \text{Fe}, \text{Co})\text{II}$  and  $n=1,2,3$ , and  $\text{Co}(\text{II})+n(\text{dien})$ ,  $n=1$  and 2.<sup>135</sup>

#### 8-4.3 The C.F.S.E. contribution to $\Delta H_{\text{N}}^{\circ}$

This was determined spectroscopically (see Appendix III). The C.F.S. energies for some aqueous Ni(II) complexes are listed in Table 8-8. The C.F.S.E. contribution to  $\Delta H_{1-\text{N}}^{\circ} = \text{C.F.S.E. for } [\text{NiL}_n]^{2+}$  minus the C.F.S.E. for



TABLE 8-8

C.F.S.E. for six-coordinate Ni(II) complexes

<u>Ligands</u>	<u><math>\lambda</math> max. (m<math>\mu</math>)</u>	<u>C.F.S.E. (kcal/mole)</u>
+ 6H <sub>2</sub> O	1180	-29.07
x (en).4H <sub>2</sub> O	1020	-33.62
* (en) <sub>2</sub> .2H <sub>2</sub> O	953	-36.0
* (en) <sub>3</sub>	877	-39.15
(pn) <sub>2</sub> .2H <sub>2</sub> O	917	-37.30
(pn) <sub>3</sub>	875	-39.20
(i-bn).4H <sub>2</sub> O	1087	-31.56
(i-bn) <sub>2</sub> .2H <sub>2</sub> O	980	-35.0
(i-bn) <sub>3</sub>	953	-36.0
+ Ref. 120		
x Ref. 76, p. 296		
* Ref. 76, p. 124.		

[Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. The  $\Delta H_N^0$  and  $\Delta H_{1-N}^0$  values corrected for C.F.S.E. are given in Table 8-7.

## 8-5 The Entropy Change

Variations in the entropy change are explained on the basis of

- (a) statistical contributions, and
- (b) solvation effects.

### 8-5.1 Statistical contributions

These were calculated by the method outlined for cupric complexes, 7-4.1. It was considered that the hexaquo Ni(II) ion has six equivalent coordination sites. Account was taken of the asymmetry of the pn and i-bn ligands. The corrected  $\Delta S_N^O$  values,

$$\Delta S_N^O(\text{corr}) = \Delta S_N^O - \Delta S_{\text{stat}}$$

are given in Table 8-9.

If the variation of  $\Delta S_N^O$  with N arises solely from a statistical effect, then for each amine  $\Delta S_N^O$  values should be related by

$$\begin{aligned} \Delta S_{\text{II}}^O &= (\Delta S_{\text{I}}^O - x)\text{e.u.} & \text{where } x = 3.1 \\ \text{and } \Delta S_{\text{III}}^O &= (\Delta S_{\text{II}}^O - y)\text{e.u.} & \text{where } y = 4.0 \end{aligned}$$

The values found for x and y were, for en 7.2 and 11.5, for pn 6.2 and 8.2 and for i-bn -1.1 and -5.5 respectively. For en and pn the observed x and y values are to a first approximation double those predicted statistically. Similar approximate relationships have been observed by other workers.

TABLE 8-9

Entropy data for Ni(II)-diamine coordination equilibria

<u>Ligand</u>		<u>en</u>	<u>pn</u>	<u>i-bn</u>
$\Delta S_I^O$	e.u.	3.6	5.6	4.9
$\Delta S_{II}^O$	"	-3.6	-0.6	6.0
$\Delta S_{III}^O$	"	-15.1	-8.8	11.4
$\Delta S_I^O(\text{stat})$	"	4.95	6.3	6.3
$\Delta S_{II}^O(\text{stat})$	"	1.82	3.2	3.2
$\Delta S_{III}^O(\text{stat})$	"	-2.2	-0.8	-0.8
$\Delta S_I^O(\text{corr})$	"	-1.4	-0.7	-1.4
$\Delta S_{II}^O(\text{corr})$	"	-5.4	-3.8	2.8
$\Delta S_{III}^O(\text{corr})$	"	-12.9	-8.0	12.2
$\Delta S_{I-III}^O(\text{corr})$	"	-19.7	-12.5	13.6

8-5.2  $\Delta S_i^O$  for successive reactions

For en and pn  $\Delta S_N^O$  and  $\Delta S_{N(\text{corr})}^O$  decrease with increasing N. This is typical for complex formation reactions and has been attributed<sup>40,77</sup> to a change in solvent ordering effects with 'degree of ligation'. This is substantiated by the increase of  $\Delta H_N^O$  with N (see 8-4.2).

However, for i-bn  $\Delta S_N^O$  increases with N, and in particular  $\Delta S_{III}^O \gg \Delta S_{II}^O$ . This sequence may arise from (a) a marked incompatibility between the peripheral structure of the complex ion and the 'lattice' of the bulk solvent

when the  $C_1$ -substituent is gem dimethyl

- (b) a small increase in solvent shielding by the ligand and a corresponding decrease in solvent orientation as the amount of non-polar organic matter about the metal is increased.

### 8-5.3 The variation of $\Delta S_N^O$ with the ligand

For  $n=1$ ,  $\Delta S_{(corr)}^O$  appears to be independent of the ligand. For  $n=2$  and  $3$   $\Delta S_{(corr)}^O$  increases in the order  $en < pn < i-bn$ . This sequence may correspond to an increase in the effects (a) and (b) described above (8-5.2). The entropy loss associated with interligand hindrance in the coordination sphere of the  $i-bn$  complexes (see 7-4.2 and 8-4.1) is not apparent, and is probably comparatively small.

### 8-5.4 The standard molar entropies of aqueous nickel(II)-diamine ions

The standard molar entropies of the aqueous complex ions  $[NiL(aq)]^{2+}$ ,  $[NiL_2(aq)]^{2+}$ , and  $[NiL_3]^{2+}$  have been calculated by substituting the experimentally obtained

$\Delta S_N^O(corr)$  values into equation 7-3 (see 7-4.4). The value  $S_{Ni^{++}}^O = -23.0 \text{ e.u.}^{139}$  (relative to  $S_{H^+}^O = 0.0$ ) was used.

$S_{NiL_n}^O$  values are given in Table 8-10.

TABLE 8-10

The standard molar entropies of aqueous Ni(II)-  
diamine complex ions

Ligand	$S_L^{\circ}(\text{e.u.})$	$S_{\text{NiL}}^{\circ}(\text{e.u.})$	$S_{\text{NiL}_2}^{\circ}(\text{e.u.})$	$S_{\text{NiL}_3}^{\circ}(\text{e.u.})$
en	44.5	-13.3	-7.6	-9.4
pn	47.3	-9.8	-0.3	6.4
i-bn	51.0	-6.8	13.6	43.4

(cf.  $S_{\text{Ni}^{++}(\text{aq})}^{\circ} = -23.0\text{e.u.})^{139}$

#### 8-5.5 The variation of $S_{\text{NiL}_n}^{\circ}$ with n

In Fig. 8-14,  $S_{\text{NiL}_n}^{\circ}$  is plotted against n. For each ligand  $S_{\text{NiL}_3}^{\circ} > S_{\text{NiL}_2}^{\circ} > S_{\text{NiL}}^{\circ} > S_{\text{Ni}(\text{aq})}^{\circ}$  (with the exception that  $S_{\text{Ni(en)}_3}^{\circ}$  is slightly low). As for the copper complexes, this sequence corresponds to an increase in ion solvation and therefore to a decrease in solvent entropy (see 7-4.4). For both the copper and nickel complexes ( $S_{\text{ML}_2}^{\circ} - S_{\text{ML}}^{\circ}$ ) is slightly less than ( $S_{\text{ML}}^{\circ} - S_{\text{M}}^{\circ}$ ) when L=en or pn. Also ( $S_{\text{NiL}_3}^{\circ} - S_{\text{NiL}_2}^{\circ}$ ) is less than ( $S_{\text{NiL}_2}^{\circ} - S_{\text{NiL}}^{\circ}$ ) for these two ligands. This order suggests that substitution by a second (third) chelate group is causing a smaller increase in solvent randomness than is substitution by the first (second), (see 7-4.3). When L=i-bn the reverse order is shown for all three terms. This may arise from a rapid increase in the solvent-structure breaking capacity of the complex ion  $[\text{Ni}(\text{i-bn})_n\text{aq}]^{2+}$  as 'n' increases.

FIG. 8-14.

$S_{ML_n}^{\circ}$  vs.  $n$  FOR SOME Ni(II)-DIAMINE COMPLEXES.

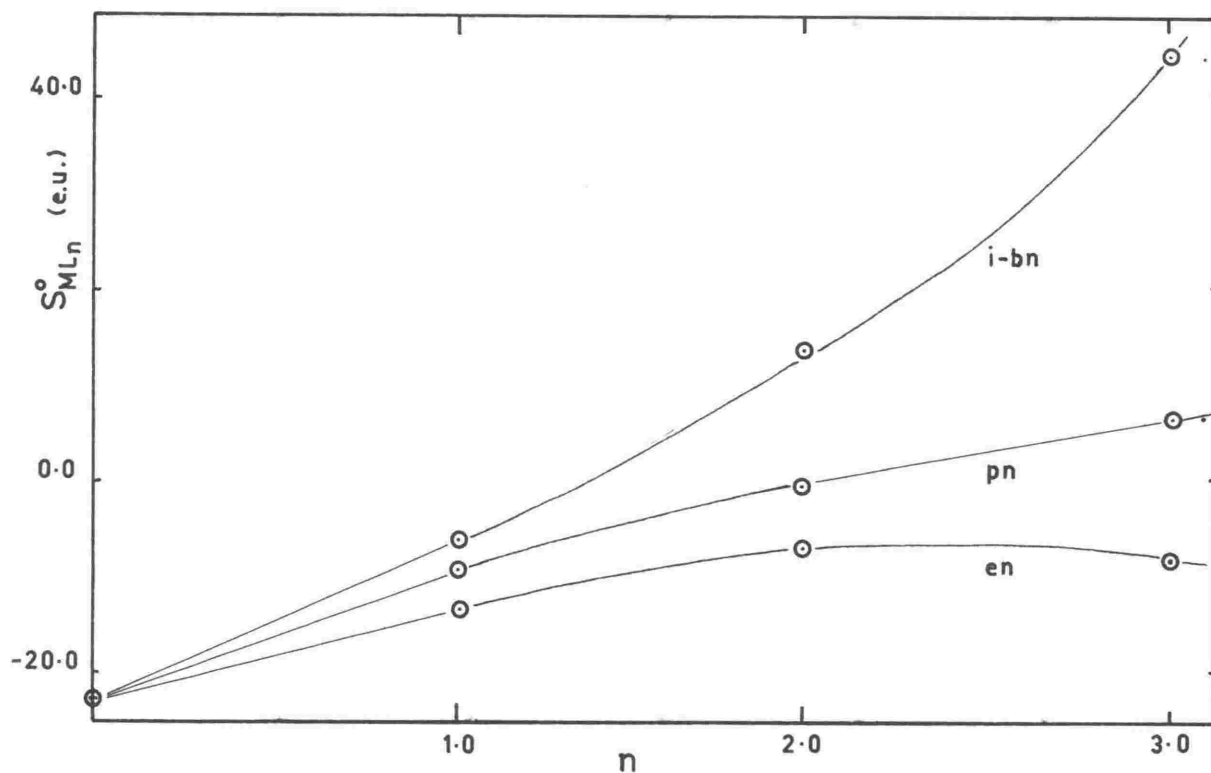
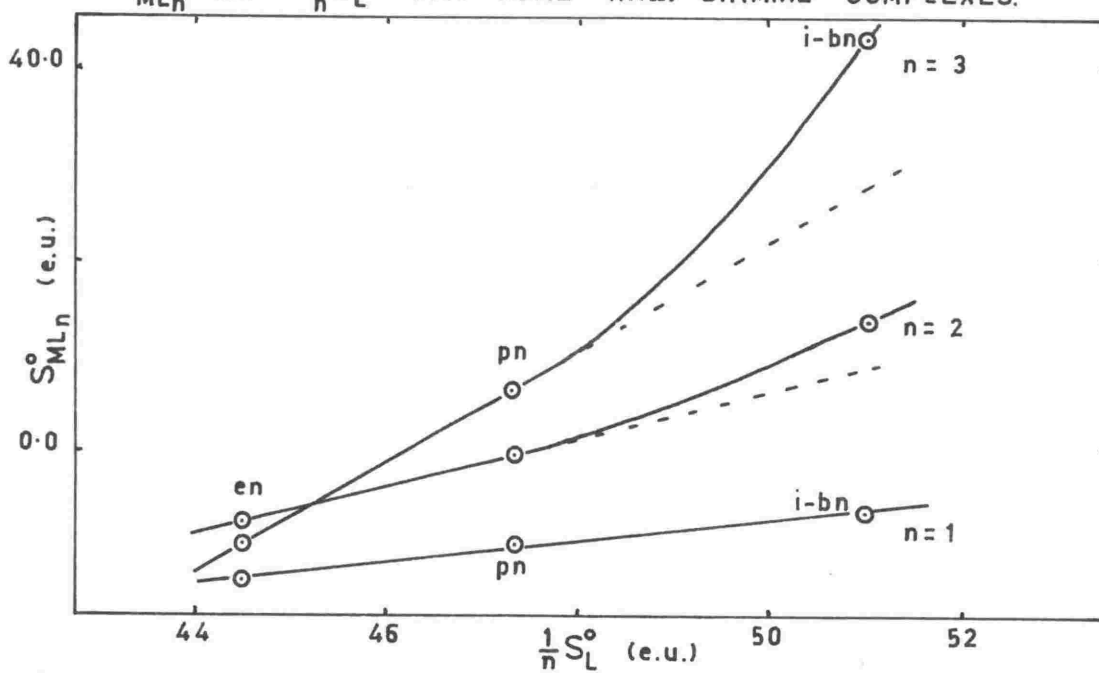


FIG. 8-15.

$S_{ML_n}^{\circ}$  vs.  $\frac{1}{n}S_L^{\circ}$  FOR SOME Ni(II)-DIAMINE COMPLEXES.



# 8-5.6 A comparison with $S_{\text{CuL}_n}^{\text{O}}$ values

The  $S_{\text{ML}_n}^{\text{O}}$  values for the nickel-diamine complexes are lower than those for the corresponding copper ones.

(M(i-bn)<sub>2</sub> is an exception). This appears to be typical for Ni(II) and Cu(II) complexes. e.g., for  $S_{\text{M}(\text{NH}_3)_{2n}}^{\text{O}}$  : \*

n	$S_{\text{Cu}(\text{NH}_3)_{2n}}^{\text{O}}$	$S_{\text{Ni}(\text{NH}_3)_{2n}}^{\text{O}}$
1	-5.4e.u.	-9.9e.u.
2	+5.4e.u.	-1.0e.u.

Also  $S_{\text{Ni}(\text{trien})}^{\text{O}} = 1.7\text{e.u.}$ , whereas,  $S_{\text{Cu}(\text{trien})}^{\text{O}} = 8.9\text{e.u.}$  +

and  $S_{\text{Ni}(\text{tren})}^{\text{O}} = -82.3 + S_{\text{tren}}^{\text{O}}\text{e.u.}$ , whereas,

$$S_{\text{Cu}(\text{tren})}^{\text{O}} = -80.9 + S_{\text{tren}}^{\text{O}}\text{e.u.}$$

This phenomenon may arise from a lesser interligand interaction in the Cu(II) complexes. The Jahn-Teller distortion in copper complexes gives each ligand molecule a greater 'free volume' within the coordination sphere. A ligand coordinated to the copper(II) ion probably retains more of its internal entropy than does one coordinated to a nickel(II) ion. When a ligand forces both cations to adopt

\* Calculated from Fyfe's data<sup>61</sup> when corrected for statistical contributions.  $S_{\text{NH}_3}^{\text{O}} = 26.3\text{e.u.}$ <sup>64</sup>

+ From data of Campiolini et al.,<sup>38</sup> corrected for statistical contributions;  $S_{(\text{trien})}^{\text{O}} = 84\text{e.u.}$ <sup>87c</sup>

the same coordination configuration, the  $S_{ML_n}^O$  values become similar. e.g.,  $S_{Cu(tren)}^O \approx S_{Ni(tren)}^O$ ; both complexes probably have a cis-diaquo octahedral structure.<sup>32</sup>

#### 8-5.7 The variation of $S_{NiL_n}^O$ with the ligand L

For both the copper and nickel complexes  $S_{ML}^O$  is linearly related to  $S_L^O$ ,  $S_{ML}^O = \text{Const.} + S_L^O$  (Fig. 8-15). The differences in  $S_{NiL}^O$  values may arise predominantly from the different internal entropies of the  $C_1$ -alkyl substituents on the coordinated ligand L. (See 7-4.4) A similar relationship  $S_{ML_2}^O = C' + 2S_L^O$  exists for the bis diamine complexes, though  $S_{Ni(i-bn)_2}^O$  is slightly high (Fig. 8-15). For the tris diamine nickel complexes there is no such relationship; effects other than the internal entropy of the ligand substituent must make significant contributions to the relative entropies of these complex ions. These effects probably include the solvent-structure breaking and solvent-metal ion shielding capabilities of the ligand.



PART B

The diamagnetic nickel(II)-bis isobutylene diamine complex.

Thermodynamic data for the formation of this ion in aqueous solution and for its reaction with i-bn to give the paramagnetic tris salt are given in Tables 8-6 and 8-7, and in section 8-2.

### 8-6 The Entropy Change and Complex Ion structure

$$\Delta S_{I(\text{corr})}^{\circ} = -1.1 \pm 0.5 \text{ e.u.} \quad (\text{see } 8-5.1)$$

The value for  $\Delta S_{II(\text{corr})}^{\circ}$  (corrected for statistical and electronic contributions) was calculated from the relationships:

$$\Delta S_{II(D,\text{corr})}^{\circ} = \Delta S_{II(P,\text{corr})}^{\circ} + \Delta S_{(P,D,\text{corr})}$$

and  $\Delta S_{(P,D,\text{corr})} = \Delta S_{(P,D)} + R \ln 3$  (see 8-2.2)  
(where  $\Delta S_{II(D,\text{corr})}^{\circ}$  is the standard molar entropy change for the reaction



corrected for statistical and electronic contributions);

and therefore  $\Delta S_{II(D,\text{corr})}^{\circ} = (10.7 \pm 0.9) \text{ e.u.}$

$\Delta S_{(P,D,\text{corr})}$  is positive, 9.4 e.u. In the reaction  
 $\underline{\text{para}}\text{-}[\text{Ni}(\text{i-bn})_2]_{\text{aq}}^{2+} \rightleftharpoons \underline{\text{dia}}\text{-}[\text{Ni}(\text{i-bn})_2]_{\text{aq}}^{2+},$

the two trans coordinated water molecules are either liberated completely from the coordination sphere to give a square planar four-coordinate diamagnetic ion, or they move

away from the central metal ion to give a highly tetragonal six-coordinate diamagnetic ion.\* In both cases the entropy of the two water molecules will be increased; in the former case each will gain three degrees of freedom of translation. In both cases there will be a loss of vibrational entropy and a gain in librational entropy (see 3-5.3).

It appears that the diamagnetic bis complex is essentially four-coordinate in aqueous solution:

- (1) Change of solvent or change of state from solution to solid has very little effect on the d-d electron transition energy ( $\nu_{\text{max.}}$  in acetone, methanol, water and the solid state are 22.0, 22.2, 22.4, and 21.6kK respectively).
- (2) The yellow-orange Ni-bis diamine perchlorate isolated from aqueous solution is anhydrous. Similar anhydrous salts,  $\text{NiL}_2\text{X}_2$ ,  $\text{X}=\text{I}^-, \text{NO}_3^-$ , are isolated when L=tetrameen, and in this case it is sterically impossible to coordinate a fifth and sixth water molecule.
- (3) The increase in  $[\text{D}]/[\text{P}]$  with temperature suggests that

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\* The latter probably occurs for the Ni(II)-bis(meso-2,3-diaminobutane) complexes in aqueous solution; addition of electrolyte increases the percentage dia form in solution.<sup>140</sup>  
 Also, dia- $[\text{Ni}(\text{m-stien})_2](\text{Cl}_2\text{CH.COO})_2 \cdot \frac{3}{4}\text{H}_2\text{O}$  has a trans dia-aquo tetragonal structure in the solid state. Addition of water to a solution of this complex in acetone increases the percentage dia form. Water displaces the anion and reduces the L.F. strength in the trans planar positions.

water molecules are being lost from the coordination sphere through increased thermal vibration.

- (4)  $\Delta S_{I-II}^O(\text{corr}) = 9.6 \text{ e.u.}$  cf., for  $[\text{Ni}(\text{tetrameen})_2]^{2+}$ ,  $14.1 \text{ e.u.}$ ,\* and this ion must be four-coordinate (8-8.1).

Assuming that the aqueous  $\text{Ni(II)}$ -bis diamine ion is essentially four-coordinate, the value  $S_{\text{NiL}_2}^O = -11.6 \text{ e.u.}$  results. This value is much lower than those for  $[\text{Cu}(\text{i-bn})_2]^{2+}$  (13.7) and para- $[\text{Ni}(\text{i-bn})_2\text{aq}]^{2+}$  (12.4), and may be due to

- (a) a less effective shielding of the solvent from the charge on the central metal ion, and  
 (b) there being no contribution to  $S_{\text{ML}_n}^O$  from the vibrational degrees of freedom of coordinated water molecules in the diamagnetic ion.

## 8-7 The Enthalpy Change

### 8-7.1 C.F.S.E. Contributions

The C.F. contributions to  $\Delta H_{II}^O$  and  $\Delta H_{III}^O$  have been determined spectroscopically. The C.F.S.E. for  $[\text{Ni}(\text{i-bn})_3]^{2+}$  is given in Table 8-8. For the diamagnetic square planar bis diamine ion, the C.F.S.E. =  $2.456 \Delta'$ , where  $\Delta'$  is the C.F. splitting between the  $d_{xy}$  and  $d_{x^2-y^2}$  orbital energy levels. (Appendix III). The energy change for a transition between these levels in dia- $[\text{Ni}(\text{i-bn})_2]^{2+}$  corresponds to an

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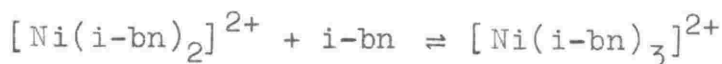
\* From Ref. 3,  $\Delta S_{I-II}$  corrected for statistical contributions.

absorption in the visible spectrum at  $454\text{m}\mu$ . For dia- $[\text{Ni}(\text{i-bn})_2]^{2+}$  the C.F.S.E. =  $-327\text{kcal/mole}$  (see Appendix III) cf. for para- $[\text{Ni}(\text{i-bn})_2\text{aq}]^{2+}$  C.F.S.E. =  $-35.0\text{kcal/mole}$ . For the reaction  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 2(\text{i-bn}) \rightleftharpoons \text{dia}-[\text{Ni}(\text{i-bn})_2]^{2+} + 6\text{H}_2\text{O}$ , the C.F. contribution to

$$\Delta H_{\text{I-II}} = -298\text{kcal/mole} \quad (\text{from } 7-3.4).$$

The corrected  $\Delta H_{\text{N}}^{\text{O}}$  values are given in Table 8-7.

On the basis of bond energies alone, the paramagnetic bis diamine complex is far more stable than the diamagnetic complex. This stability is very nearly offset by the much larger C.F.S.E. for the diamagnetic ion. For the latter ion,  $-\Delta H_{\text{II}}^{\text{O}}$  is very low (highly endothermic) because in the reaction  $[\text{Ni}(\text{i-bn})(\text{H}_2\text{O})_4]^{2+} + \text{i-bn} \rightleftharpoons \text{dia}-[\text{Ni}(\text{i-bn})_2]^{2+} + 4\text{H}_2\text{O}$ , four Ni-O bonds are being endothermically broken while only two Ni-N bonds (of similar strength to Ni-O) are being exothermically formed. On the other hand,  $-\Delta H_{\text{III}}^{\text{O}}$  is very high as it contains no endothermic term for bond-breaking:



#### 8-7.2 The approximate Ni-O and Ni-N bond energies

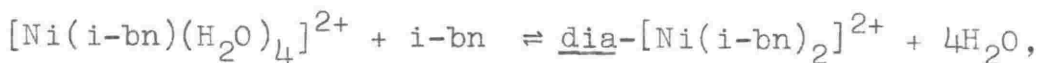
From the  $\Delta H_{\text{N}}^{\text{O}}$  values discussed above it is possible to calculate the approximate Ni(II)-primary N and Ni(II)-OH<sub>2</sub> bond energies for hexacoordinate Ni(II) in aqueous solution at  $25.0^\circ\text{C}$  (ignoring all interligand and solvation effects).

For the reaction



$$\Delta H_{\text{I}}^{\text{O}} \approx 2\Delta H_{\text{Ni-N}} - 2\Delta H_{\text{Ni-O}} = -4.9\text{kcal/mole},$$

and for the reaction



$$\Delta H_{\text{II}}^{\text{O}} \approx 2\Delta H_{\text{Ni-N}} - 4\Delta H_{\text{Ni-O}} = 290.5\text{kcal/mole},$$

from which

$$\Delta H_{\text{Ni-O}} \approx -148\text{kcal/mole}$$

and  $\Delta H_{\text{Ni-N}} \approx -150\text{kcal/mole}.$

From this data the value predicted for  $\Delta H_{\text{III}}^{\text{O}}$ , ignoring solvation, interligand repulsion effects, etc., is -300kcal/mole. (Found, -297kcal/mole.) Considering the drastic approximations made above and the uncertainty in the electron pairing energy assumed in deriving the C.F.S.E. for dia- $[\text{Ni}(i\text{-bn})_2]^{2+}$ , the agreement is quite good.

#### 8-8 The Existence of Dia-Para Equilibria for Ni(II) Complexes

The dia-para equilibrium shown by the Ni(II)-bis isobutylenediamine complex is shown by other nickel complexes also. e.g., the Ni(II)-bis m-stien ion exists as an equilibrium mixture of spin-free and spin-paired forms in aqueous solution,  $K=[P]/[D] \approx 2$  at 20°C, dichloroacetate anion.<sup>141</sup> The effect of solvent composition on this equilibrium has been studied, and X-ray structural determinations made for the hydrated diamagnetic and paramagnetic salts.<sup>142</sup> (See footnote p.177.) The bis dl-stien complexes exist only

as paramagnetic species in aqueous solution.<sup>141</sup>

Some Ni(II)-bis diamine complexes occur as diaquo paramagnetic ions  $[\text{NiA}_2(\text{H}_2\text{O})_2]^{2+}$  at room temperature but at elevated temperatures exist as diamagnetic species in aqueous solution, e.g., A=en, pn. Substances like this can usually be isolated as both anhydrous diamagnetic and hydrated paramagnetic salts, the latter usually being the more stable in air at room temperature. Heating the hydrated salt or controlled crystallisation can produce the anhydrous diamagnetic salt.<sup>143</sup>

Some nickel complexes occur only as a diamagnetic form in aqueous solution and in the solid state, the solid being anhydrous, e.g.,  $\text{K}_2\text{Ni}(\text{CN})_4$ ,  $\text{Ni}(\text{tetrameen})\text{X}_2$ ,  $\text{X}=\text{I}^-$ ,  $\text{NO}_3^-$ .<sup>3</sup> With these two ligands no six-coordinate Ni(II) analogue exists.

The factors influencing the existence of dia- and paramagnetic forms are discussed below.

#### 8-8.1 Steric hindrance vs. ligand field strength

The C.F. splitting  $\Delta'$  increases with ligand field strength, i.e., with ligand donor power. When  $\Delta'$  is greater than the electron pairing energy (Appendix III) then a  $d^8$  system will change from a 'spin-free' state to the more stable spin-paired diamagnetic state. In the reaction between the aqueous Ni(II) ion and  $\text{CN}^-$  this change has occurred when four  $\text{CN}^-$  groups are coordinated,

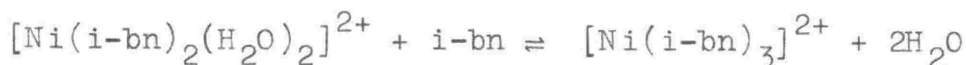
$[\text{Ni}(\text{CN})_4(\text{H}_2\text{O})_2]^{2-}$ ). The change in electronic state is accompanied by the lateral displacement of the two trans coordinated water molecules to give a square planar four-coordinate complex  $[\text{Ni}(\text{CN})_4]^{2-}$ . Although energy is required to liberate the two water molecules, this requirement is more than met by

- (1) a vastly increased C.F.S.E.
- (2) increased strength of the in-plane coordinate bonds due to a bond-shortening
- (3) decreased interligand repulsion.

However, ligand donor power is not the factor responsible for Ni(II) forming diamagnetic square planar complexes with some diamines while giving spin-free six-coordinate complexes with others. If it were, then the expected order of preference for the square planar structure would be the same as the order of basicities, e.g.,  $\text{en} > \text{pn} > \text{eten} > \text{i-bn} > \text{tetrameen} > \text{m-stien}$ . This order is not observed.

The preferential formation of square planar diamagnetic Ni(II)-bis diamino ions results from steric hindrance in the coordination sphere. With the ligand tetrameen it is sterically impossible to form a tris-diamine complex or a bis diaquo bis diamine (paramagnetic) Ni(II) complex. Hindrance occurs between any approaching donor atom and the gem dimethyl groups of ligands in the coordination sphere (of  $[\text{Ni}(\text{tetrameen})_2]^{2+}$ ). For the ligands m-stien and i-bn a similar though lesser hindrance exists

(m-stien < i-bn). With these ligands an equilibrium mixture of spin-free and spin-paired Ni(II) complex ions exists in aqueous solution at 25°C. Because of this steric hindrance -  $\Delta H^\circ$  for the reaction



is very low (3.70kcal/mole). The tris salt has a very low C.F.S.E. implying<sup>70</sup> a slight lengthening of the Ni-N bonds to reduce the interligand repulsions in the coordination sphere.

#### 8-9 Correlations with Previous Work

Basolo et al.<sup>3</sup> have determined the formation constants at I=0.65m/l ( $\text{Ba}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ ) for the equilibrium reactions between the aqueous Ni(II) ion and pn, and i-bn, (also dl-bn, m-bn, tetrameen, dl-stien, m-stien). In general their results compare favourably with those obtained by extrapolation of the data in Table 8-3 to I=0.65m/l.

TABLE 8-11

Ni(II)+C<sub>1</sub>-alkyl 1,2-diaminoethanes, 25.0°C. I=0.65m/l

Ligand	<u>This work:</u>			<u>Literature value:</u> <sup>3</sup>		
	logK <sub>I</sub>	log K <sub>II</sub>	logK <sub>III</sub>	logK <sub>I</sub>	logK <sub>II</sub>	logK <sub>III</sub>
pn	7.36	*	4.46	7.43	6.19	4.27
i-bn	6.90	5.66	1.42	6.77	5.40	2.25



For the Ni(II)-1,methyl 1,2-diaminoethane system Nasanen et al.<sup>144</sup> have obtained the following values at I = 0.00m/l, 25°C:

$\log K_I$  7.29,  $\log K_{II}$  6.14,  $\log K_{III}$  4.18; cf., this work  
7.31, 6.25, 5.11 respectively.

No enthalpy or entropy data has been recorded elsewhere.

## CHAPTER NINE

### GENERAL DISCUSSION

#### 9-1 Relationships between Ligand Structure and Complex Stability

This discussion is confined to aliphatic diamine ligands.

N-substitution: The effect of N-alkyl substitution on the stabilities of Cu(II) and Ni(II) ethylenediamine complexes has been studied and comprehensively discussed by several workers (see 3-5.1c). The stabilities of these complexes are very dependent on the amount of interaction between the N-alkyl substituents and other ligands within the coordination sphere. The basicities of the amines vary little with either the degree of N-alkyl substitution or the nature of the alkyl chain, yet factors such as steric hindrance within a complex and solvation of a complex depend critically on the nature of the substituent.

C-substitution: Regarding C-substitution, Rossotti<sup>31</sup> has written: "The replacement of a diamine by its C-alkyl analogue appears to have little effect on the stability of proton, nickel or copper complexes. The slight increase in stability appears to result mainly from a favourable entropy change which may be ascribed to the increased (solvent) structure-breaking effect of the ligand." Rossotti's

comments were based on temperature coefficient data available at the time.

C<sub>1</sub>-substituted 1,2-diaminoethanes. This work has shown that the stability of the proton complex decreases when 1,2-diaminoethane is replaced by its simple C<sub>1</sub>-alkyl analogues. The decrease appears to arise from a variable solvation energy term (6-2.2), and becomes more marked with increased C<sub>1</sub> substitution.

This change in ligand basicity (or donor power) is reflected by the stabilities of the Cu(II) and Ni(II)-diamine complexes. For the formation of the aqueous complexes  $\text{CuL}^{2+}$ ,  $\text{CuL}_2^{2+}$ , and  $\text{NiL}^{2+}$ , L=en, pn or i-bn, the complex stability is approximately linearly related to the ligand basicity, both decreasing with increasing C<sub>1</sub>-alkyl substitution.

However for the nickel bis and tris diamine complexes the stabilities increase markedly with C<sub>1</sub>-alkyl substitution, the stabilities for L=en < pn < i-bn. This increase arises from an entropy term which is possibly associated with the solvent lattice-breaking capacity of the C<sub>1</sub>-alkyl substituent, and which increases with C<sub>1</sub>-alkyl substitution. For the nickel complexes this entropy effect first becomes significant for  $[\text{Ni}(\text{i-bn})_2\text{aq}]^{2+}$ , for which  $K_{\text{II}} \approx K_{\text{I}}$  (see 8-3.2). This effect is not apparent for the Cu(II) analogue.

The ability of a coordinated diamine ligand to

disrupt the 'lattice' and increase the entropy of the surrounding solvent probably increases with the chain length of the  $C_1$ -alkyl substituent (for small substituents). If so, then 1-ethyl 1,2-diaminoethane which has a similar basicity to 1-dimethyl 1,2-diaminoethane (Table 6-6) should form Ni(II) complexes which are markedly more stable (as a result of a more favourable ligation entropy). Equilibrium constants have been measured for the Ni(II)-eten system and the results are summarised in Table 9-1 and on Fig. 9-1. ( $\Delta H$  and  $\Delta S$  values were not derived because of a lack of the diamine.) The Ni(II)-eten complexes are markedly more stable than the corresponding Ni(II)-i-bn ones, cf. Table 8-3 (and the bis and tris complexes more stable than the corresponding en and pn ones in aqueous solution). Since  $\Delta G_{1-2}^0$  (and  $\Delta H_{1-2}^0$ ) is approximately equal for eten and i-bn protonation (i.e., each diamine has a similar donor power) then the higher stabilities for the Ni(II)-eten complexes probably arise from more favourable entropy terms. For the tris complexes comparison is possibly complicated by the existence of marked steric hindrance in the coordination sphere of the i-bn complex.

For the Cu(II)-diamine complexes, entropy effects are not so apparent. The stabilities of the Cu(II)-bis diamine complexes are approximately linearly related to the ligand basicity. If  $\Delta G_{I-II}^0$  is plotted against  $\Delta G_{1-2}^0$  (Fig. 9-2)

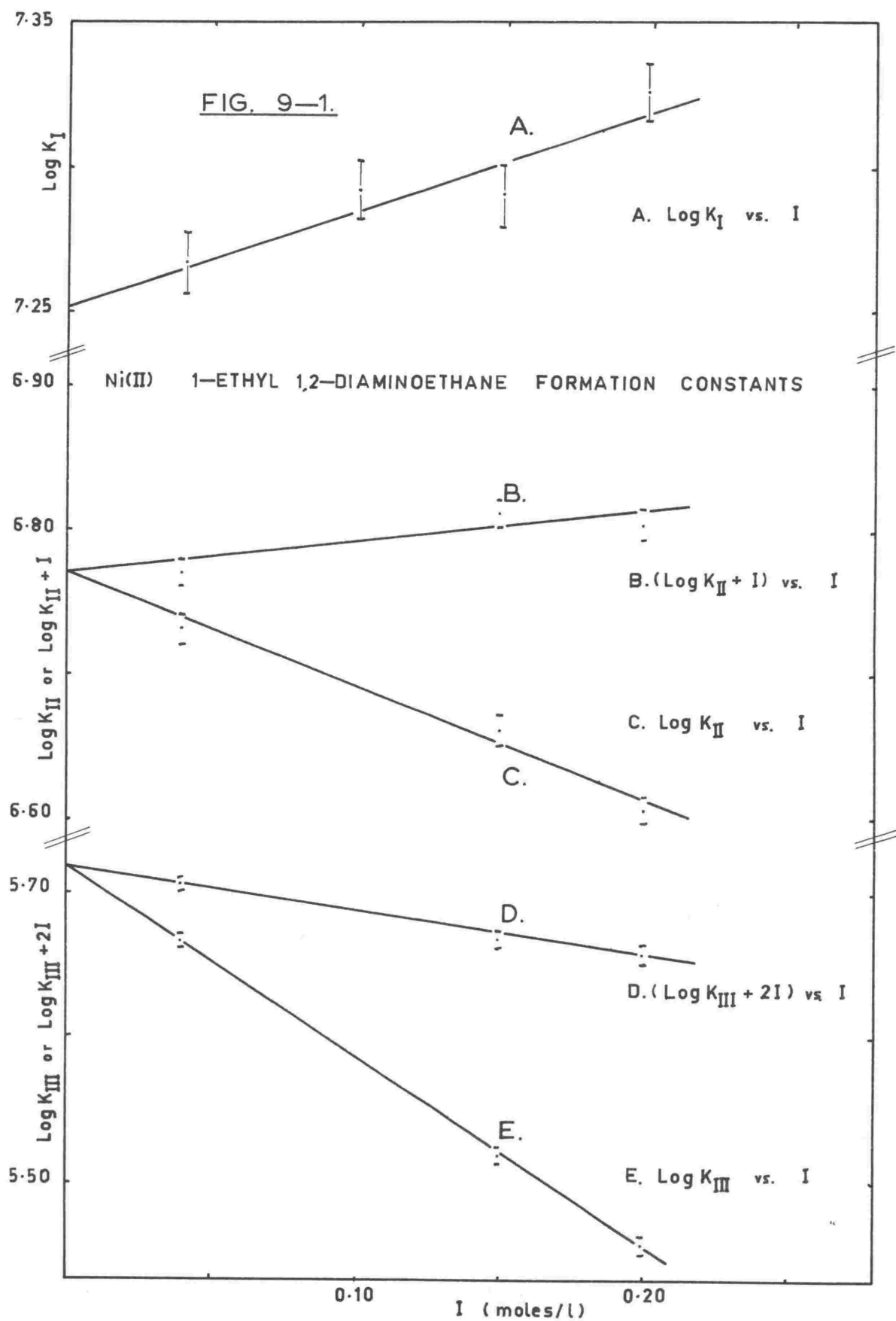


TABLE 9-1

Equilibrium formation constants for the Ni(II)-eten system,  
 $25.00 \pm 0.01^\circ\text{C}$ , aqueous  $\text{NaClO}_4/\text{Ba}(\text{ClO}_4)_2$  media

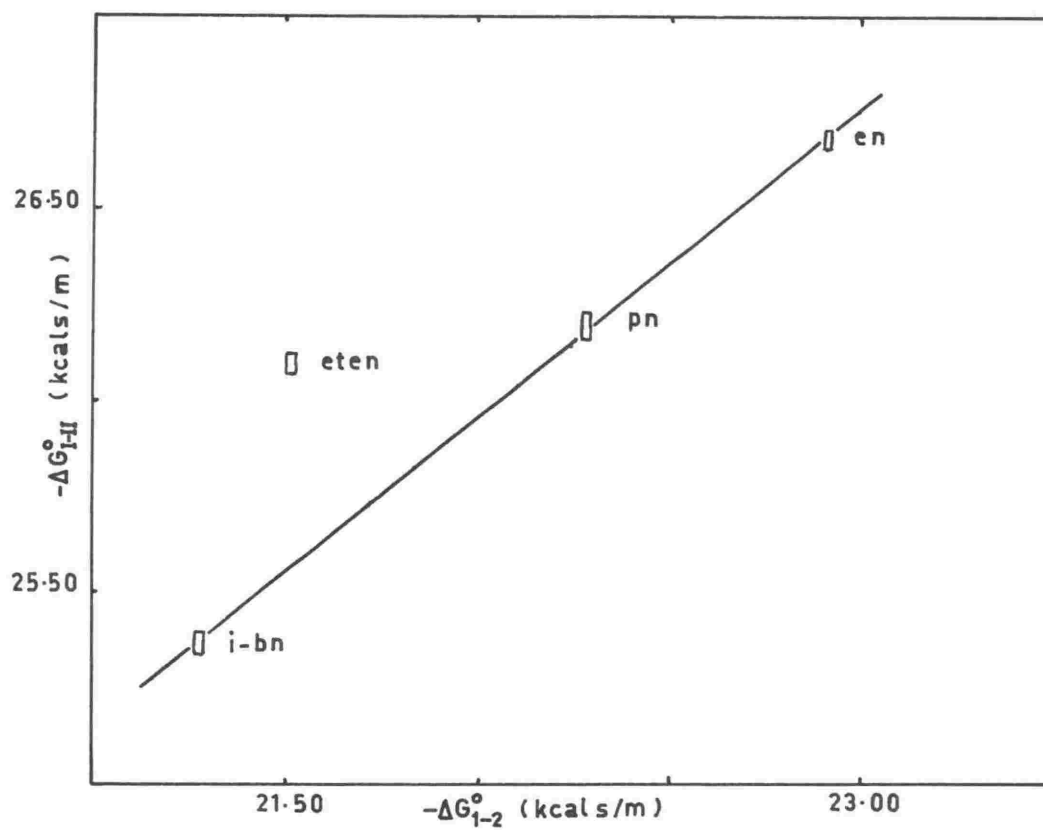
Ionic strength	$\text{LogK}_{\text{c}_I} (\pm 0.011)$	$\text{LogK}_{\text{c}_{II}} (\pm 0.011)$	$\text{LogK}_{\text{c}_{III}} (\pm 0.014)$
0.200m/1	7.326	6.606	5.215
0.150 "	7.290	6.663	5.338
0.100 "	7.292	(6.594)	(5.366)
0.040 "	7.267	6.731	5.631
	$\text{LogK}_I^0$	$\text{LogK}_{II}^0$	$\text{LogK}_{III}^0$
0.000 "	7.252	6.77	5.738

it is seen that  $\Delta G_{I-II}^0$  for the eten complex is anomalously high. However, the high free energy change appears to be as much a result of a high (negative) enthalpy change as of a high entropy change. (Table 7-5)

It follows from these observations that Ni(II) complexes  $\text{NiL}_2^{2+}$ ,  $\text{NiL}_3^{2+}$  (and possibly copper complexes  $\text{CuL}_2^{2+}$ ) may show a marked stability when L is a C-n-alkyl substituted ethylenediamine ligand with a long alkyl substituent, say,  $\text{C}_3$ ,  $\text{C}_4$  . . . On the basis of data in Table 6-6 it can be postulated that the basicity of such a ligand, and therefore its donor power, would not be markedly lower than that for 1-dimethyl 1,2-diaminoethane. Therefore for the Ni-nL equilibrium system both the ligational  $\Delta H$  and  $\Delta S$

FIG. 9-2.

$\Delta G_{1-II}^{\circ}$  FOR Cu(II) LIGATION vs.  $\Delta G_{1-2}^{\circ}$  FOR  
LIGAND PROTONATION



should favour formation of very stable complexes.

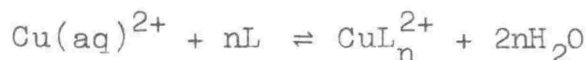
C<sub>1</sub>C<sub>2</sub> symmetrically substituted 1,2-diaminoethanes: The stabilities of the Cu(II) mono and bis diamine complexes increase with the degree of C-substitution, viz., en < dl-bn < tetrameen.<sup>3</sup> This order corresponds to that of decreasing basicity and donor power of the ligands. The order of complex stabilities arises from an increasing entropy of ligation attributable to an increasing solvent structure breaking capacity of the coordinated ligand. For the Ni(II) complexes  $\log K_N(\text{en}) < \log K_N(\text{dl-bn})$  for N=I and II, (as for the Cu(II) complexes). The order of stabilities is reversed for K<sub>III</sub>, probably due to steric hindrance between adjacent ligands in the  $[\text{Ni}(\text{dl-bn})_3]^{2+}$  complex (cf.  $[\text{Ni}(\text{i-bn})_3]^{2+}$ ). The tetrameen complexes are not comparable;  $[\text{Ni}(\text{tetrameen})_2]^{2+}$  is a four-coordinate diamagnetic ion.

1,3-diamines: Although 2,2'-dimethyl 1,3-diaminopropane is a weaker base than 1,3-diaminopropane it forms slightly more stable Cu(II) 1:1 and 1:2 complexes. The higher stabilities arise solely from more favourable entropy terms which can be associated with the breakdown of the solvent 'lattice' structure through the intrusion of the 2,2'-gem dimethyl functional groups. (Table 9-2)



TABLE 9-2

Thermodynamic data for Cu(II)-1,3-diaminopropane  
complexes, 30°C.<sup>119</sup>



L	n	$\Delta G_n$ (kcal/mole)	$\Delta H_n$ (kcal/mole)	$\Delta S_n$ (e.u.)
1,3-pn	1	-13.13	-14.0	-3
"	2	-9.55	-13	-12
(2,2')1,3-pn*	1	-13.57	-12	+7
	2	-10.17	-12	-7

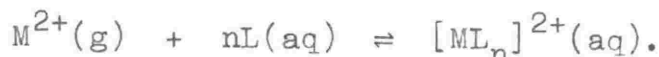
\* 2,2'-dimethyl 1,3-diaminopropane

### 9-2 The Irving-Williams Order of Stabilities.

From 3-5.2

$$\begin{aligned}\Delta H_{\text{com}} &= \Delta H_{\text{L}} + \Delta H_{\text{H}} \\ &= \Delta H_{(\text{g})} + \Delta H_{\text{soln}(\text{ML}_n)} + n(\lambda_{\text{L}} + \Delta H_{\text{soln}(\text{L})})\end{aligned}$$

where  $\Delta H_{\text{com}}$  is the enthalpy change for the reaction



For a given ligand  $n(\lambda_{\text{L}} + \Delta H_{\text{soln}(\text{L})})$  is constant and

$\Delta H_{\text{soln}(\text{ML}_n)}$  will be approximately constant if  $n$  is constant, the metal ions are similar (e.g., divalent transition metal ions), and the complexes  $\text{ML}_n$  have the same or very similar structures. Therefore, to a first approximation  $\Delta H_{\text{com}}$  is directly proportional to  $\Delta H_{(\text{g})}$  the enthalpy change for

ligation in the gas phase. It is advantageous to consider  $\Delta H_{(g)}$  rather than  $\Delta H_L$  because  $\Delta H_{(g)}$  gives a direct measure of the metal-ligand bond energies and does not include terms for the solvation energy of the aquo and complex ions (see 3-5.2).

$-\Delta H_{com}$  for the reactions  $(Mn, Ni, Cu, Zn)(II) + 2en$  are given in Table 9-3, in which  $-\Delta H_L$  and  $-\Delta H_H$  have been corrected for C.F.S.E. contributions by using the data in 7-3.4 and 8-4.3.

TABLE 9-3

Enthalpy data for the hydration and solution ligation of some divalent transition metal ions at 25°C

	$-\Delta H_L$ (kc/m)	$-\Delta H_H$ (kc/m)	$-\Delta H_{com}$ (kc/m)	$(I_1 + I_2)^{\dagger}$ (kc/m)
Mn <sup>2+</sup>	6.00	654	660.0	531.9
Ni <sup>2+</sup>	11.31	686.9	698.2	594.4
Cu <sup>2+</sup>	10.7	691.1	701.8	645.8(633)*
Zn <sup>2+</sup>	13.75	701.1	714.8	630.5
	(Ref.135)	(Ref.63)		(Ref.63)

For this system the Transition Series Contraction Energy  $E_r$  (defined in 3-6.1(d)) is -64.7kcal/mole, which is quite typical for strong coordinating agents (see Ref. 63, pp.431-7).

† The sum of the first two ionisation potentials for the gaseous atoms.

\*  $\Sigma I$  calculated for the loss of two 4s electrons. Ref.79a

Irving and Williams<sup>62,67</sup> drew attention to the parallelism between heats of ligation and ionisation energies. Crystal Field Theory (3-6.1(c)) does not require that a linear relation exist between  $\Delta H_{\text{com}}$  and  $(I_1 + I_2)$  but that  $\Delta H_{\text{com}}$  should increase steadily with  $(I_1 + I_2)$ . These functions are plotted against each other in Fig. 9-3. The striking feature is the anomalously low value of  $-\Delta H_{\text{com}}$  for Cu(II) ( $\cong -\Delta H_{\text{com}}$  for Ni(II)). The same anomaly occurs for the  $-\Delta H_{\text{H}}$  values.

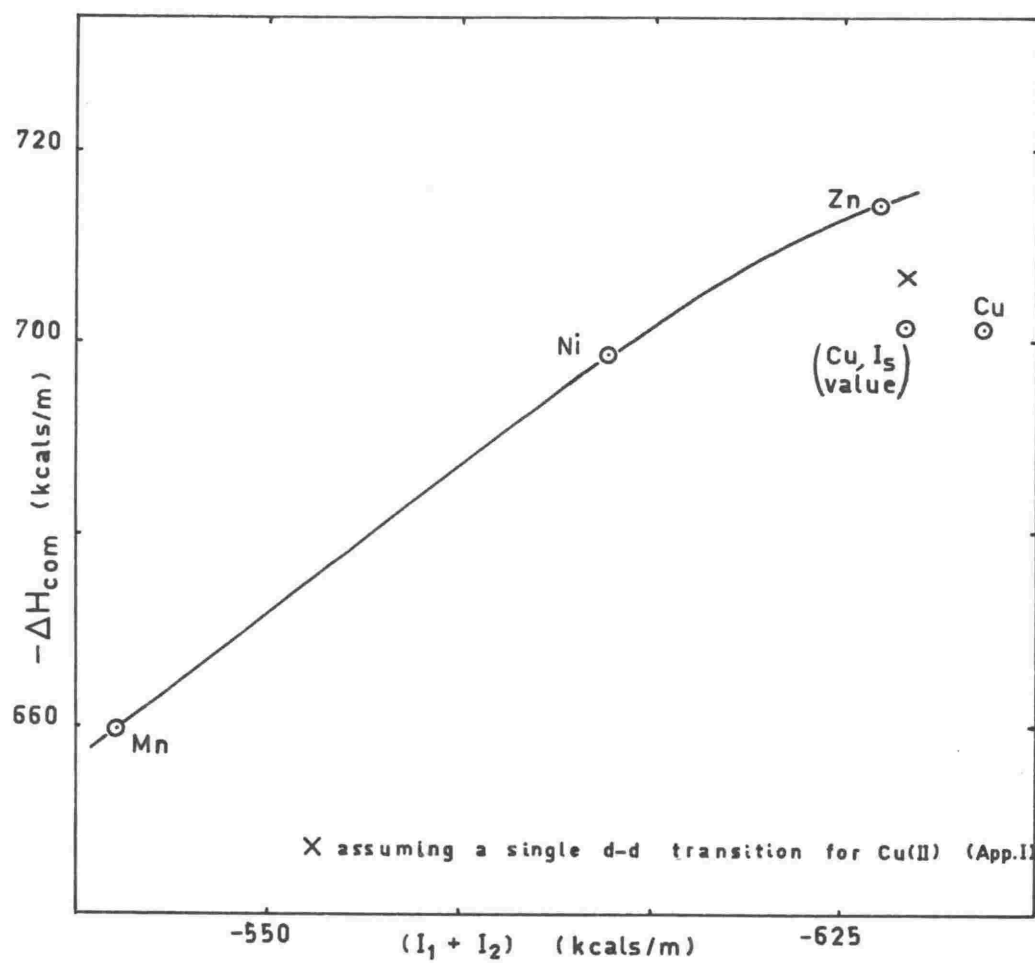
If  $\Delta H_{\text{L}}$  were proportional to  $(I_1 + I_2)$ , then  $\Delta H_{\text{L}}$  for Cu(II) ligation would be approximately the same as for Zn(II). For the reactions between Cu(II) and en, pn and i-bn, the corrected  $-\Delta H_{\text{I-II}}$  values are approximately equal to the respective values for the reactions of the Ni(II) ion (Tables 7-6 and 8-7) and  $\ll$  the values for the Zn(II) ion.\* The low  $-\Delta H_{\text{com}}$  values for Cu(II) complexes are at least in part a result of Jahn-Teller distortion. This distortion involves an elongation along one coordinate axis; water molecules coordinated along this axis are endothermically displaced to an equilibrium position further from the metal ion. The endothermic term causes  $-\Delta H_{\text{L}}$  to be low for Cu(II) ligation. To a first approximation complete removal of two water molecules from an aqueous Ni(II) ion

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\* Data available for Zn(II)-en system only.

FIG. 9—3.

$\Delta H_{\text{com}}$  FOR METAL(II)—bis(EN) LIGATION vs. THE METAL  
IONISATION POTENTIAL ( $I_1 + I_2$ ).



requires 296kcal/mole. Therefore by analogy it is necessary to invoke a small displacement only in the Cu(II) complex to account for the comparatively low enthalpy of ligation.

The Jahn-Teller distortion in the  $[\text{CuL}_n(\text{aq})]^{2+}$  complexes possibly increases as  $n$  increases. This is suggested by the (spectroscopic) C.F.S. increments between  $[\text{Cu}(\text{aq})]^{2+}$  and  $[\text{CuL}(\text{aq})]^{2+}$ , and between  $[\text{CuL}(\text{aq})]^{2+}$  and  $[\text{CuL}_2]^{2+}$  (see 7-3.4 and 7-3.5).

### 9-3 The Chelate Effect

For a definition of this effect and a discussion of examples, see 3-5.3(c).

The phenomenon was first discussed by Schwarzenbach.<sup>123</sup> He considered that, following the formation of a unidentate intermediate  $\text{M-A-A}^*$  in the reaction between a metal ion and a chelate  $\text{AA}^*$ , the probability of a second donor group ( $-\text{A}^*$ ) coordinating is far greater than would be the case for the reaction of the metal ion with two monodentate ligands. Following the formation of  $\text{M-A-A}^*$  there is an increase in the 'apparent activity' of the donor groups ( $-\text{A}^*$ ) in the vicinity of the metal ion. This increase will not occur for monodentate ligands. On this basis the chelate effect should decrease with increasing length of the chelate chain because the 'free volume' of the donor  $-\text{A}^*$  will increase with chain length. i.e., its 'apparent activity' near the metal ion

will decrease. It is well established that there is a decrease in the chelate effect as the chelate chain length is increased<sup>123,147</sup> (Ag(I) and Hg(II) are exceptions).<sup>148</sup>

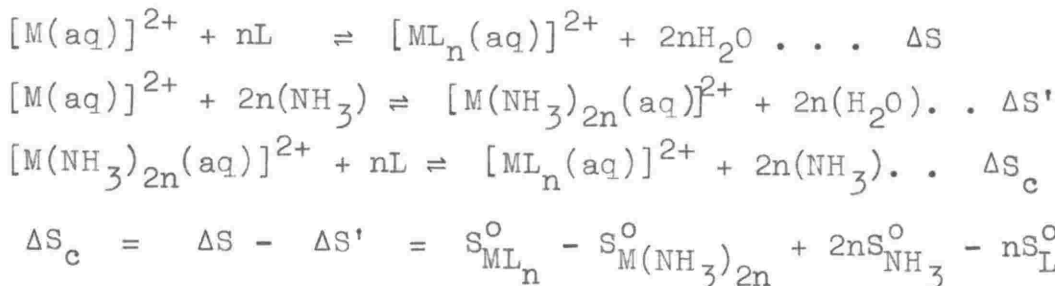
Schwarzenbach's postulate requires that the chelate effect be entirely an entropy effect. For non-transition metal ions it is almost entirely an entropy effect. For  $d^n$  transition metal ions, ( $n \neq 0, 5, 10$ ) it is mainly an entropy effect, but is contributed to by an enthalpy effect.

### 9-3.1 The Ni(II) and Cu(II)- $C_1$ -substituted ethylenediamine complexes

#### A comparison with Ni(II) and Cu(II)-ammonia complexes

When considering the chelate effect for complexes with ethylenediamine-type ligands it would be most appropriate to compare stabilities with those of the equivalent methylamine complexes. However, data are not available for the latter.

For the formation of the  $C_1$ -substituted ethylenediamine complexes of Ni(II) and Cu(II) a measure of the chelate effect is obtained by considering the following reactions:



$\Delta S$  and  $\Delta S'$  are corrected for statistical contributions; the net statistical contribution to  $\Delta S_c$  is small and favours chelation. Values of  $\Delta S_c$  for Ni(II) and Cu(II) complexes with  $n=1, 2$ , and  $3$  are given in Table 9-4. The  $S_{M(NH_3)_{2n}}^0$  values were obtained from Fyfe's data<sup>61</sup> (corrected for statistical contributions):

$S_{Ni(NH_3)_{2n}}^0 = -9.9, -1.0$  and  $3.5$  e.u. for  $n = 1, 2$ , and  $3$ , respectively

$S_{Cu(NH_3)_{2n}}^0 = -5.4$  and  $5.4$  e.u. for  $n = 1$  and  $2$ , respectively.

TABLE 9-4

The chelate (entropy) effect for some 1,2-diamine-metal amine replacement reactions

$n$	Ligand	$(S_{NiL_n}^0 - S_{Ni(NH_3)_{2n}}^0)$ e.u.	$(2nS_{NH_3}^0 - nS_L^0)$ e.u.	$\Delta S_c$
1	en	-3.4	8.1	4.7
1	pn	0.1	5.3	5.4
1	i-bn	3.4	1.6	5.0
2	en	-6.6	16.2	9.6
2	pn	0.7	10.6	11.3
2	i-bn	14.6	3.2	17.8
3	en	-12.9	24.3	11.4
3	pn	2.7	15.9	18.6
3	i-bn	39.9	4.8	44.7

n	Ligand	$(S_{\text{CuL}_n}^{\text{O}} - S_{\text{Cu}(\text{NH}_3)_{2n}}^{\text{O}}) \text{e.u.}$	$(2nS_{\text{NH}_3}^{\text{O}} - nS_{\text{L}}^{\text{O}}) \text{e.u.}$	$\Delta S_{\text{c}}$
1	en	-4.2	8.1	3.9
1	pn	-1.3	5.3	4.0
1	i-bn	2.2	1.6	3.8
1	eten	4.8	-1.4	3.4
2	en	-3.2	16.2	13.0
2	pn	2.7	10.6	13.3
2	i-bn	8.3	3.2	11.5
2	eten	15.7	-2.8	12.9

Within experimental error  $\Delta S_{\text{c}}$  is independent of the central metal ion (Cu(II) or Ni(II))

$\Delta S_{\text{c}} = 4.3 \pm 0.6 \text{e.u.}$  for  $n=1$  (This value also applies for the Zn-NH<sub>3</sub>-en,<sup>29</sup> Cd-NH<sub>3</sub>-en,<sup>66</sup> and Cd-MeNH<sub>2</sub>-en<sup>66</sup> reactions).

$\Delta S_{\text{c}} = 12.6 \pm 1.4 \text{e.u.}$  for  $n=2$  (This value also applies for the Zn-NH<sub>3</sub>-en<sup>29</sup> and Cd-NH<sub>3</sub>-en<sup>66</sup> reactions).

Theories on the entropy contribution ( $\Delta S_{\text{c}}$ ) to the chelate effect require that it be independent of the metal ion.<sup>53,123,149</sup> For  $n=1$  or 2 the effect observed here appears to be independent of the structure of the 1,2-diamino ligand. ( $n=2$ , L=i-bn an exception) For  $n=3$  (Ni(II) complexes)  $\Delta S_{\text{c}}$  is not constant but increases rapidly with the degree of C-substitution on the ligand. This increase



can be related to the increasing solvent-structure breaking capacity of the coordinated ligand; this effect decreases the second-sphere hydration and increases  $S_{\text{NiL}_3}^0$  (see 8-5.5).

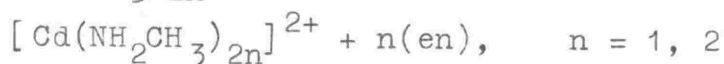
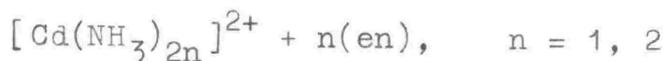
### 9-3.2 The origin of the $\Delta S_c$ term

The component terms of  $\Delta S_c$  for the bidentate-mono-dentate replacement reaction (equation 9-1) correspond to

- (1) A gain of translational entropy by the freed  $\text{NH}_3$  molecules and a loss of translational entropy by the coordinating chelate. The net term will be positive and will favour chelation. (From the Cobble equation,<sup>87c</sup>  
 $S_{\text{trans}}^0 2\text{NH}_3(\text{g}) = 68\text{e.u.}$ ,  $\text{en}(\text{g}) = 38\text{e.u.}$ )
- (2) A small gain in internal entropy by the  $\text{NH}_3$  molecules and a large decrease in internal entropy for the chelate. The chelate will lose its rotational entropy and its vibrational modes will be modified. The net term will probably be small and negative.
- (3) A loss in solvent entropy due to the low solvation entropy of two free  $\text{NH}_3$  ligands in aqueous solution ( $-40\text{e.u.}$ ) compared with a free en ligand ( $-31\text{e.u.}$ ).
- (4) A term resulting from a change in second sphere hydration; probably a small positive contribution due to better shielding of the solvent from the charge on the metal ion when L is a chelate.

### 9-3.3 The enthalpy contribution to the chelate effect

For non-transition metal ions and transition metal ions with  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations the enthalpy effect is approximately zero. e.g., for the reactions



$$\Delta H_{\text{chel}} \doteq 0.$$

For transition metal ions the enthalpy effect contributes approximately 30 to 50% of the energy involved in the chelate effect. This is shown by the data in Table 9-5 which compare the thermodynamic functions for the  $\text{Ni(II)}-n(\text{pn})$  and  $\text{Ni(II)}-2n(\text{NH}_3)$  reactions.

Atkinson et al.<sup>53</sup> have deduced that the enthalpy effect arises predominantly from the higher C.F.S.E. term for chelate complexes, and hence the approximately zero enthalpy terms for non-transition metal ions,  $\text{Zn(II)}$  and  $\text{Mn(II)}$ . The data in Table 9-5 fit this deduction. The C.F. corrected  $\Delta H$  values for the  $\text{Ni(II)}-n(\text{pn})$  and  $\text{Ni(II)}-2n(\text{NH}_3)$  reactions are approximately equal for  $n=1$  and  $n=2$ . Small enthalpy contributions may arise from the relative solvation energy terms for the complex ions and for the free solvated ligands. When polydentate ligands ( $> \text{bi-}$ ) are considered (e.g., dien, trien, tren), chelate ring strain, the presence of weak secondary or tertiary

TABLE 9-5

Thermodynamic data for pn and  $\text{NH}_3$  complexes of  $\text{Ni(II)}$ 

	$-\Delta G$ (kcal/m)	$-\Delta H$ (kcal/m)	$-\Delta H(\text{corr})$ (kcal/m)	$+\Delta S$ (e.u.)	$+T\Delta S(\text{corr})$ (kcal/m)
<u><math>\text{Ni(II)}+n(\text{pn})</math></u>					
n = 1	9.97	8.29	4.19	5.6	0.21
2	8.52	8.71	4.61	-0.6	-1.13
3	6.97	9.60	7.70	-4.2	-2.38
<u><math>\text{Ni(II)}+2n(\text{NH}_3)</math></u>					
n = 1	6.79	7.0	4.4	-0.7	-1.82
2	3.92	7.0	4.4	-10.3	-3.07
3	1.00	7.0	4.3	-20.1	-4.38

( $\Delta H_{\text{corr}}$  is the enthalpy change corrected for C.F.S.E. contributions.\*)

amino donors, and the necessary adoption of less stable configurations by the central metal ion (e.g.,  $\text{Cu}(\text{tren})^{2+}$  is a cis-diaquo distorted octahedron)<sup>32</sup> lower the enthalpy contributions to the chelate effect.

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\* For the ammine complexes, C.F.S.E. calculated from  $\nu_{6\text{NH}_3}=10.8\text{kK}$ ,  $\nu_{4\text{NH}_3}=10.0\text{kK}$ . Ref. 76, p. 296.

CHAPTER TEN  
SPECTROSCOPIC STUDIES

10-1 Introduction

Infrared and charge transfer spectra have been measured for the complexes involved in the thermodynamic studies. It was not considered that the spectral and thermodynamic data obtained would be supplementary. Rather an attempt has been made to characterise some of the important vibrational and electronic quantum transitions involved in these typical coordination compounds. Deuteration studies on some transition metal(II)-diethylene-triamine complexes have facilitated infrared spectral assignments for vibrations within coordinated 1,2-diamines. Studies on some structurally simple amine complexes have led to infrared spectral assignments for the M(II)-primary N vibratory mode. Some infrared absorptions characteristic of coordinated water molecules have been discussed and the characteristic vibratory modes considered group theoretically.

10-2 Infrared spectra for Ni, Cu and Zn(II)-diethylene-triamine complexes and their N-deutero derivatives

The infrared spectra ( $4000-400\text{cm}^{-1}$ ) for mono- and bis diethylenetriamine (dien) complexes of Ni, Cu and Zn(II) were measured. The study was made firstly to facilitate a more complete characterisation of the infrared spectra of transition metal polyamine complexes, and secondly to determine the types of coordination involved in these solid dien complexes. The dien ligand is related to the important basic chelating unit N-C-C-N, and contains the poorly characterised  $2^\circ$  amino group. The Ni, Cu and Zn(II) complexes are of particular interest because

- (a) the salts  $\text{M(dien)}_2 \text{H}_2\text{OX}_2$  are isostructural, and
- (b) thermodynamic data for their formation in aqueous solution (discussed below) suggest that in solution the bis dien salt of Ni(II) is a normal hexamine, while those of Cu(II) and Zn(II) have non-coordinated amine groups.

Deuteration of the complexes has led to assignments for all the fundamental vibrations of the coordinated ligand, and for vibrations and librations of coordinated water. New assignments made are for the  $\text{>N-H}$  deformation mode at  $1480 \pm 10\text{cm}^{-1}$ , the C-N stretch at  $1150 \pm 10\text{cm}^{-1}$ , and the  $\text{-NH}_2$  wagging mode at  $1250 \pm 5\text{cm}^{-1}$ .

The preparations and properties of the new zinc complexes are reported.

### 10-2.1 Historical

In 1948 Breckenridge<sup>151</sup> reported the preparation and properties of the Ni(II) and Cu(II) diethylenetriamine complexes  $M(\text{dien})_2X_2 \cdot H_2O$  and  $M(\text{dien})X_2$ ,  $X = Cl^-, Br^-$ . He considered that

- (1) the bis complexes contain lattice water and not coordinated water because dehydration of the solids is difficult,
- (2) both the Cu(II) and Ni(II) bis complexes are normal hexamines.

Brooks<sup>152</sup> observed that the copper and nickel complexes  $M(\text{dien})_2H_2OCl_2$  are isostructural. Assuming nickel to be hexa-coordinate, he deduced that copper also exhibits six-covalency.

However, the enthalpy changes for the nickel, copper and zinc(II)-dien ligation reactions in aqueous solution<sup>39</sup> suggest that the aqueous Cu(II) and Zn(II) bis complexes have fewer than six amino groups coordinated (see Table 10-1).

The Ni(II) bis dien complex with  $-\Delta H_{I-II} = 25.30 \text{ kcal/mole}$  appears to be a hexamine cf.,  $-\Delta H_{I-III}[\text{Ni}(\text{en})_3]^{2+} = -23.84 \text{ kcal/mole}$ . However, consideration of the thermodynamic data for the aqueous reactions

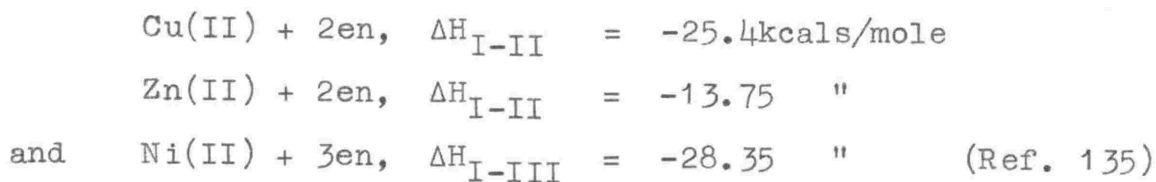


TABLE 10-1

Thermodynamic data for Ni, Cu, and Zn(II) - dien complexes  
in aqueous 0.1M KCl, 25°C

	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
- $\Delta H_I$ (kcal/mole)	11.85	18.00	6.45
- $\Delta H_{II}$ "	13.45	8.15	10.15
- $\Delta H_{I-II}$ "	25.30	26.15	16.60

suggests that the aqueous Cu and Zn bis dien complexes have fewer than six and probably five amino groups coordinated to the metal ion:  $[M(\text{dien})_2\text{H}_2\text{O}]^{2+}$ .

#### 10-2.2 Experimental

All spectra were determined using a Perkin Elmer 221 Spectrophotometer with NaCl/grating, KBr and CsBr optics, and using nujol and hexachlorobutadiene mulls. Amino groups were deuterated by twice crystallising the complexes from  $\text{D}_2\text{O}$  using a vacuum line technique. Deuterated samples were stored in vacuum over  $\text{P}_2\text{O}_5$ . All spectra indicated that at least 94% deuteration was achieved. Wavenumbers are quoted with a tolerance of  $\pm 3\text{cm}^{-1}$ .

#### Preparation of Complexes

$[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$  and  $[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$ : Deep blue crystals prepared by the method of Breckenridge.<sup>151</sup> The complexes could not be dehydrated by prolonged heating in vacuo over  $\text{P}_2\text{O}_5$ . ( $[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$ , found: C, 26.79; H, 8.21; N, 23.02. Calculated for  $[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$ : C, 26.79; H, 7.87; N, 23.42.  $[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$ , found: C, 21.66; H, 6.40; N, 18.34.  $\text{C}_8\text{H}_{28}\text{N}_6\text{OCuBr}_2$  requires C, 21.46; H, 6.30; N, 18.78).

$[\text{Cu}(\text{dien})\text{Cl}]\text{Cl}$ : Prepared by slowly adding a hot ethanolic solution of  $\text{CuCl}_2$  (0.03mole) to a hot solution of dien (0.03mole) in alcohol. Tarry residues formed were dissolved by digestion, then the solution was evaporated to small



volume and crystallisation induced by addition of acetone. The complex was twice recrystallised by Soxhlet extraction into ethanol. (Yield 30%) Blue leaflets, m.pt.  $237.5-238^{\circ}\text{C}$ . A hemihydrate was obtained by evaporation of an aqueous solution (wt. %  $\text{H}_2\text{O}$ , 3.90; required for  $[\text{Cu}(\text{dien})\text{Cl}]\text{Cl}\frac{1}{2}\text{H}_2\text{O}$ , 4.21.) Found: C, 19.94; H, 5.77; Cl, 30.50. Calculated for  $[\text{Cu}(\text{dien})\text{Cl}]\text{Cl}$ : C, 20.28; H, 5.47; Cl, 29.85.

$[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$  and  $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$ : Blue-violet crystals prepared by the method of Breckenridge.<sup>151</sup>

( $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$ , found: C, 27.37; N, 23.32.

$\text{C}_{28}\text{H}_{28}\text{N}_6\text{ONiCl}_2$  requires C, 27.15; N, 23.74. The solid could not be dehydrated under vacuum over  $\text{P}_2\text{O}_5$ .) ( $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$ , found: Br, 36.07. Calculated for  $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$ , Br, 36.08. The solid rapidly dehydrated at  $130^{\circ}\text{C}$ . Wt. %  $\text{H}_2\text{O}$ , by weight loss at  $130^{\circ}$ , 3.8.  $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Br}_2$  requires 4.1.)

$[\text{Ni}(\text{dien})\text{Cl}_2]$ :  $\text{NiCl}_2$  (10g) in alcohol was added with stirring to a solution of dien (10.1mls) in alcohol. Pale green crystals precipitated from a solution of the same colour. The yield was increased by addition of acetone. The crude material contained some  $\text{Ni}(\text{OH})_2$  and was recrystallised from ethanol by Soxhlet extraction (Yield 60%, m.pt.  $300^{\circ}\text{C}(\text{d})$ .) In the atmosphere the compound rapidly formed a pale blue monohydrate which readily dehydrated at  $105^{\circ}\text{C}$ . (Found: C, 20.80; H, 5.99; N, 17.91; Ni, 24.4. Calculated for

$[\text{Ni}(\text{dien})\text{Cl}_2]$  C, 20.62; H, 5.63; N, 18.05; Ni, 25.2).

$[\text{Ni}(\text{dien})\text{Br}_2]$ : The preparation was as for the chloride analogue. Pale green crystals, yield 25%. In the atmosphere it formed a pale blue monohydrate which rapidly dehydrated at  $115^\circ\text{C}$ . (Found for the hydrate: C, 14.23; H, 4.87; N, 12.26.  $\text{C}_4\text{H}_{15}\text{N}_3\text{OBr}_2\text{Ni}$  requires C, 14.13; H, 4.42; N, 12.36.  $\text{H}_2\text{O}$  by weight loss at  $115^\circ\text{C}$ , 5.2; required, 5.3.) The product is very soluble in water and dimethyl formamide, sparingly soluble in iso-propanol and absolute alcohol (blue solutions) and insoluble in acetone. It gives a green solution in n-butanol,  $\epsilon_{\text{max}}$  11.0(980m $\mu$ ), 8.4(630m $\mu$ ), 20(372m $\mu$  , shoulder on charge transfer band).

$[\text{Zn}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$ :  $\text{ZnCl}_2$  (3.4g) in water (10ml) was slowly added to a solution of dien (5.4ml) in alcohol (40ml). Crystallisation was induced by cooling and addition of acetone. The white solid was crystallised from 50% aqueous-alcohol solution (Yield, 55%). M.pt.  $251^\circ\text{C}$ . (Found: C, 26.90; H, 8.08; Zn, 18.05.  $\text{C}_8\text{H}_{28}\text{N}_6\text{OCl}_2\text{Zn}$  requires C, 26.64; H, 7.83; Zn, 18.13. Dehydrated at  $105^\circ\text{C}$ , wt.%  $\text{H}_2\text{O}$ , 4.8; monohydrate requires 5.0).

$[\text{Zn}(\text{dien})\text{Cl}]\text{Cl}$ : The stoichiometric quantity of  $\text{ZnCl}_2$  in the minimum volume of water was added to  $[\text{Zn}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$  in absolute alcohol. The solution was filtered and evaporated to half volume (water bath). Large white crystals separated on standing; the yield was increased by the addition of ether.

The solid was recrystallised from absolute alcohol and dried at 105°C. (Yield, 65% from 0.015 mole). M.pt. 229°C. (Found: C, 20.19; H, 5.80; Cl, 29.15.  $C_4H_{13}N_3Cl_2Zn$  requires C, 20.07; H, 5.47; Cl, 29.61.)

Infrared spectra: Table 10-2 lists assignments of the absorption bands shifted upon deuteration; the amine stretching and deformation modes and the C-N stretching mode. Table 10-3 lists assignments of ligand absorptions unaltered by deuteration; the C-C stretching, methylene group and chelate-ring deformation vibrations. Table 10-4 lists assignments of the bands arising from coordinated water.

### 10-2.3 Discussion

The observed isotopic displacement ratios  $\sigma$ , (Table 10-2) indicate that the assumption of simple harmonic motion is valid for  $-NH_2$  and  $>N-H$  stretching modes, and that the deformation modes have only small anharmonicities.

a) Amine stretching modes (Table 10-2): Coordination of an amine to a metal ion decreases the electron density about the nitrogen atom. The resulting electron drainage from the N-H bonds weakens them and causes a decrease in the N-H stretching frequency. For a non-coordinated amine group the  $-NH_2$  and N-H stretching modes absorb in the  $3500-3300\text{cm}^{-1}$  range.<sup>153,154</sup> Coordination of an amine group lowers the N-H stretching frequency by approximately  $200\text{cm}^{-1}$ ; protonation

TABLE 10-2  
Infrared spectral assignments (cm<sup>-1</sup>)  
(Values in parentheses are

Assignment	[Cu(dien)Cl]Cl	[Cu(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>	[Zn(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>	[Zn(dien) <sub>2</sub> Cl
-NH <sub>2</sub> (free) symm. str.	3448ms (2530) m	3425s (2487) m	3420m	
-NH <sub>2</sub> (free) asymm. str.	3396mw (2496) m	3383m (2466) m	3380vw	
Coord. H <sub>2</sub> O O-H str.	3376mw (2470) m	3349m (2449) s		
-NH <sub>2</sub> symm. str.	3270m (2405) mw	3327, 3312s (2434) m	3268s (2396) s	3268s
-NH <sub>2</sub> asymm. str.	3234s (2368) ms	3240s (2385) m	3237ms (2346) m	3200s
>N-H str.	3143ms (2321) ms	3125s (2313) s	3177, 3159ms (2327, 2297) m	3160, 3
-NH <sub>2</sub> symm. def. (scissors)	1588s (1172) s	1562vs (1167) s	1563ms (1167) s	
>N-H def.		1480vw	1488mw	
-NH <sub>2</sub> twist+ skel. def.	1310, 1295mw (992) w	1320s (1048) s	1323ms (1052) m	
-NH <sub>2</sub> wag.	1255s (970) m	1247ms (944) m	1250mw (931) m	
C-N str.	1150, 1139s (1108, 1100) s	1144, 1128ms (1093, 1082) ms	1143, 1136m (1100) s	
-NH <sub>2</sub> twist	1081s (759) s	1087s (804) ms	1078s (787) s	
-NH <sub>2</sub> rock	620s (435) m	676m (488) w	623, 603s (448, 433) m	

(Abbreviations: vs=very strong; s=strong; m=medium; w=weak)

TABLE 10-3      Infrared spectral assignments

Assignment	$[\text{Zn}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$	$[\text{Zn}(\text{dien})\text{Cl}]\text{Cl}$	$[\text{Cu}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$	$[\text{Cu}]$
$-\text{CH}_2$ -symm. def. $\nu_1$ (scissors)	1473 mw 1450 mw	1475 w 1495 m	1468 1446	1 1
$-\text{CH}_2$ - wag $\nu_2$	1358 mw		1356 mw	
$-\text{CH}_2$ - twist $\nu_3$		1320 w		
		1298, 1266 m		
C-C stretch $\nu_4$	1024 ms 1004 s	1068 w 1034 ms	1075 ms 1044 vs	1 1
( " " ) $\nu_5$	981 ms		983 ms	
$-\text{CH}_2$ - rocking $\nu_6$	890 s	889 s 865 s	895 s 865 w	
Ring deformation modes $\nu_7$	565 s	555 s	567 ms	
C-N-C and C-C-N $\nu_8$	537 w	530 mw	518 m	
angle deformation modes $\nu_9$	494 s	495 s	476 s	

cf., (pn)2HCl: 490, 436 $\text{cm}^{-1}$       (dien)3HCl: 546, 444 $\text{cm}^{-1}$

Abbreviations as for Table 10-2.

TABLE 10-4

Far infrared spectral assignments for Ni, Cu and Zn(II)-  
1,2-diamino coordination compounds

Complex	Assignments ( $\text{cm}^{-1}$ )			
	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}(1^\circ)$	$\nu_{\text{M-N}}(2^\circ)$	$\nu_{\text{M-Cl}}$
[Cu(en)Cl <sub>2</sub> ]		373vs		316vs
[Cu(pn)Cl <sub>2</sub> ]		396vs		311vs
[Cu(pn)Br <sub>2</sub> ]		394s		
[Cu(pn)I]		414m		
[Cu(dien)Cl]Cl		392m	344s, 337sh	313m
[Cu(en) <sub>2</sub> Cl <sub>2</sub> ]		401s		(324s)
[Cu(dien) <sub>2</sub> H <sub>2</sub> O]Br <sub>2</sub>		400m	369, 352m	
[Zn(en) <sub>2</sub> Cl <sub>2</sub> ]		397m		
[Zn(en) <sub>3</sub> ]Cl <sub>2</sub>		397m		
[Zn(dien) <sub>2</sub> Cl]Cl		394m	374m	
[Ni(dien)Cl <sub>2</sub> ] <sub>2</sub>		376ms, 371sh	343w	331s, 326, 318mw
[Ni(dien)H <sub>2</sub> OBr <sub>2</sub> ]		384	358, 352	
[Ni(dien) <sub>2</sub> H <sub>2</sub> O]Br <sub>2</sub> (456s)		406m, 384s	369sh, 351m	
[Ni(dien)(NO <sub>3</sub> ) <sub>2</sub> ]		376m	352m	
[Ni(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub> (497ms)		406m, 386, 374.		

Abbreviations as for Table 10-2.

lowers the frequency by approximately  $800\text{cm}^{-1}$ .

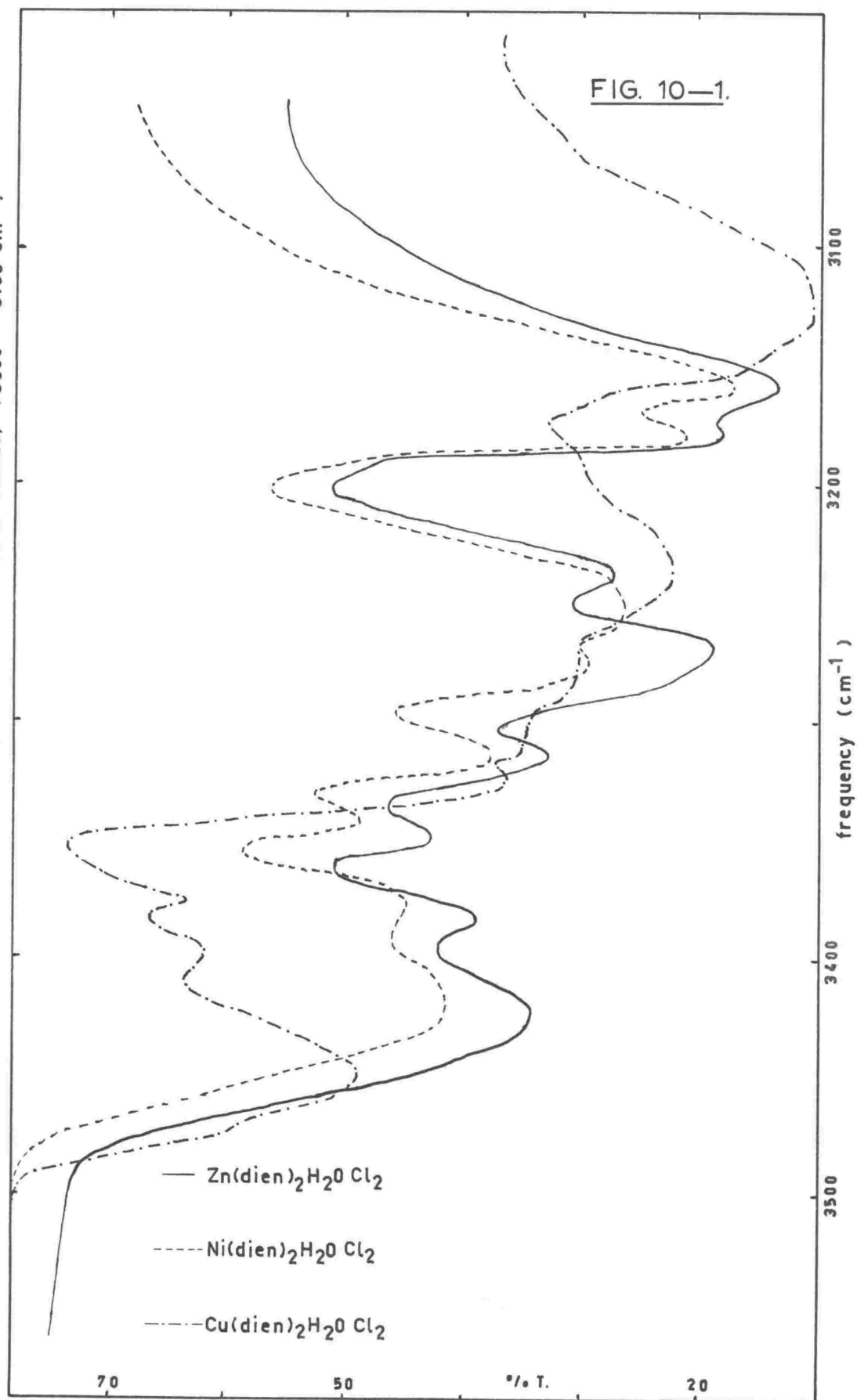
For the dien complexes, absorptions in the  $3320\text{--}3200\text{cm}^{-1}$  region (Table 10-2) arise from symmetric and asymmetric stretching modes of the coordinated primary amino groups. For simple metal(II)-amine compounds these modes each give rise to one well-defined absorption (e.g.,  $\text{Ni}3\text{en}(\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , Fig. 10-4). The frequencies are affected by the nature of the coordination sphere and the anion; an asymmetric environment may cause splitting of the absorption band. Absorptions in the  $3200\text{--}3100\text{cm}^{-1}$  range arise from N-H stretching modes and -NH-H stretching modes in which one H atom remains essentially stationary with respect to the N atom while the other vibrates along its bond axis.

b) Non-coordinated amino groups: The infrared spectrum for solid  $[\text{Ni}(\text{dien})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  shows only bands characteristic of coordinated amine groups and lattice water (Fig. 10-4), and this complex is considered to be a normal hexamine.

The spectra for the hydrated halides  $\text{M}(\text{dien})_2\text{X}_2\text{H}_2\text{O}$  (Fig. 10-1) do not show absorptions characteristic of lattice water,  $3650\text{--}3500\text{cm}^{-1}$  (see 10-5.3). They show complex absorptions in the  $3450$  to  $3320\text{cm}^{-1}$  range. Dehydration of the Ni(II) bromide and Zn(II) chloride causes spectral changes in this latter region, but absorption bands remain at frequencies characteristic of non-coordinated\*  $\text{-NH}_2$  groups

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\* i.e., not coordinated to the metal ion; they are presumably H-bonded to the anion.

FIG. 10-1. I.R. SPECTRA FOR SOME METAL(II)—DIEN COMPLEXES, (3600 — 3100  $\text{cm}^{-1}$ )



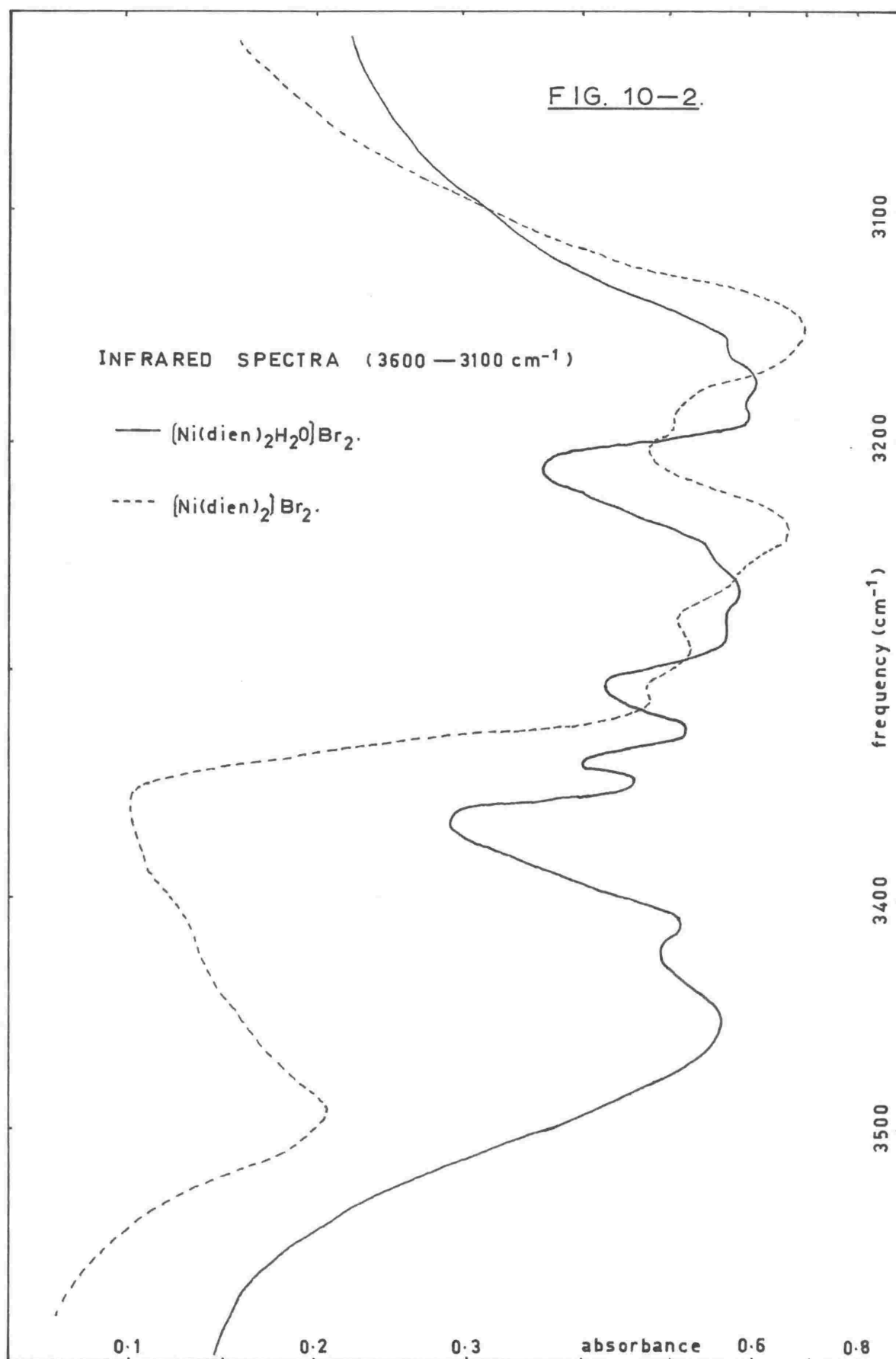
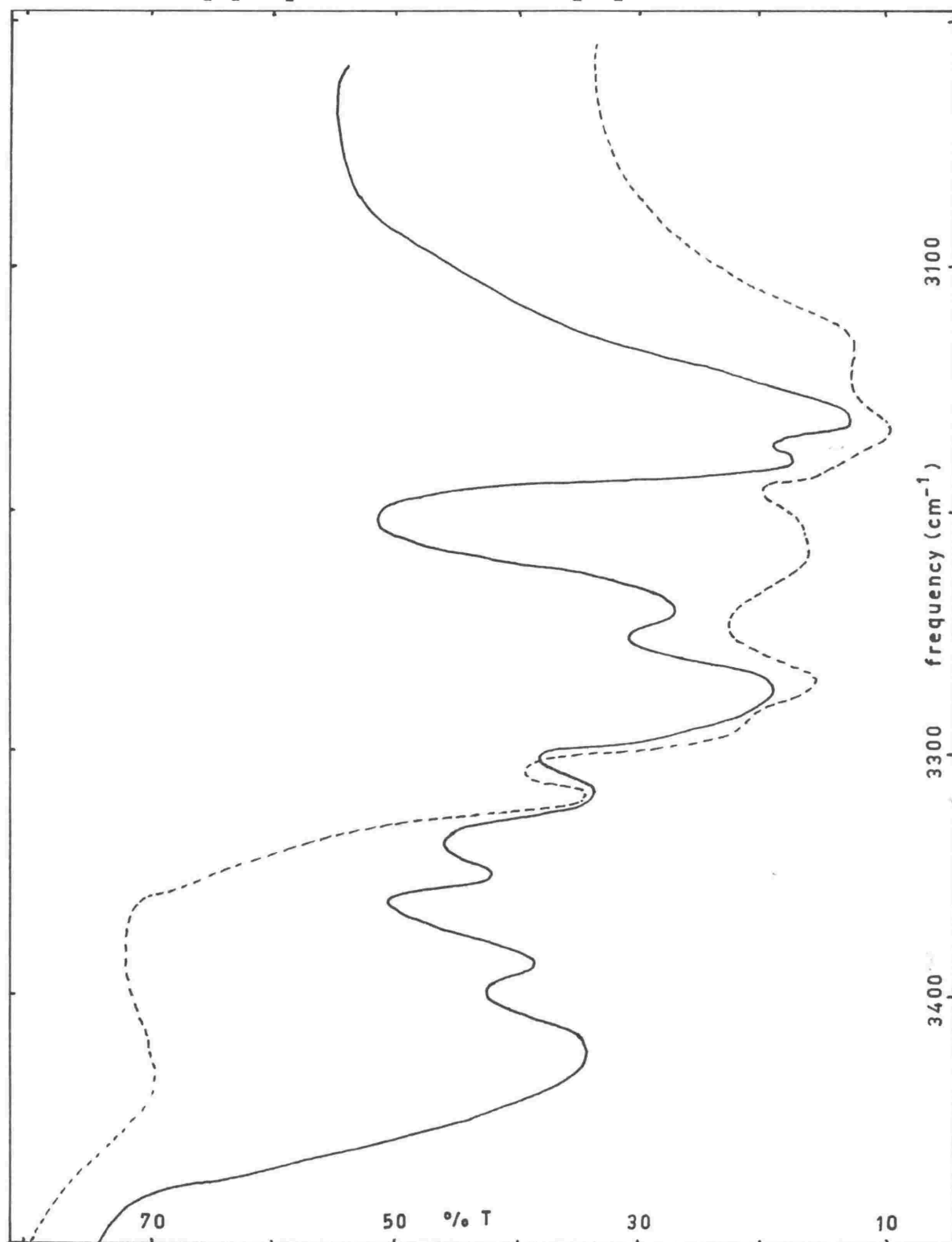


FIG. 10—3. INFRARED SPECTRA ( $3500 - 3000 \text{ cm}^{-1}$ )  
 $[\text{Zn}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$  —  $[\text{Zn}(\text{dien})_2]\text{Cl}_2$  - - - -



(Figs. 10-2 and 10-3). The bands which disappear on dehydration are assigned to coordinated water molecules (see below). These assignments are in reasonable agreement with the spectra for the metal hydrates  $M(H_2O)_6X_2$  (Table 10-6). The spectra for the complexes which do not dehydrate are very similar to the others and bands can be assigned to 'free' amines, coordinated amines and coordinated water (Table 10-2).

It is concluded that the solid bis dien halide hydrates of Ni, Cu and Zn(II) probably have five coordinated amine groups and one coordinated water molecule; (for  $[Ni(dien)_2H_2O]Br_2$  the Ni(II)-O stretching vibration has been assigned, 10-5.2). Presumably the Cu(II) compound has two long trans bonds, but as the Cu(II) and Ni(II) compounds are isostructural<sup>+</sup> this cannot affect the packing in the crystals.

The spectra for  $Zn(dien)Cl_2$ ,  $Ni(dien)Cl_2$ ,  $Ni(dien)Br_2$ , and  $Cu(dien)Cl_2$  indicate that these salts have all amino groups coordinated.

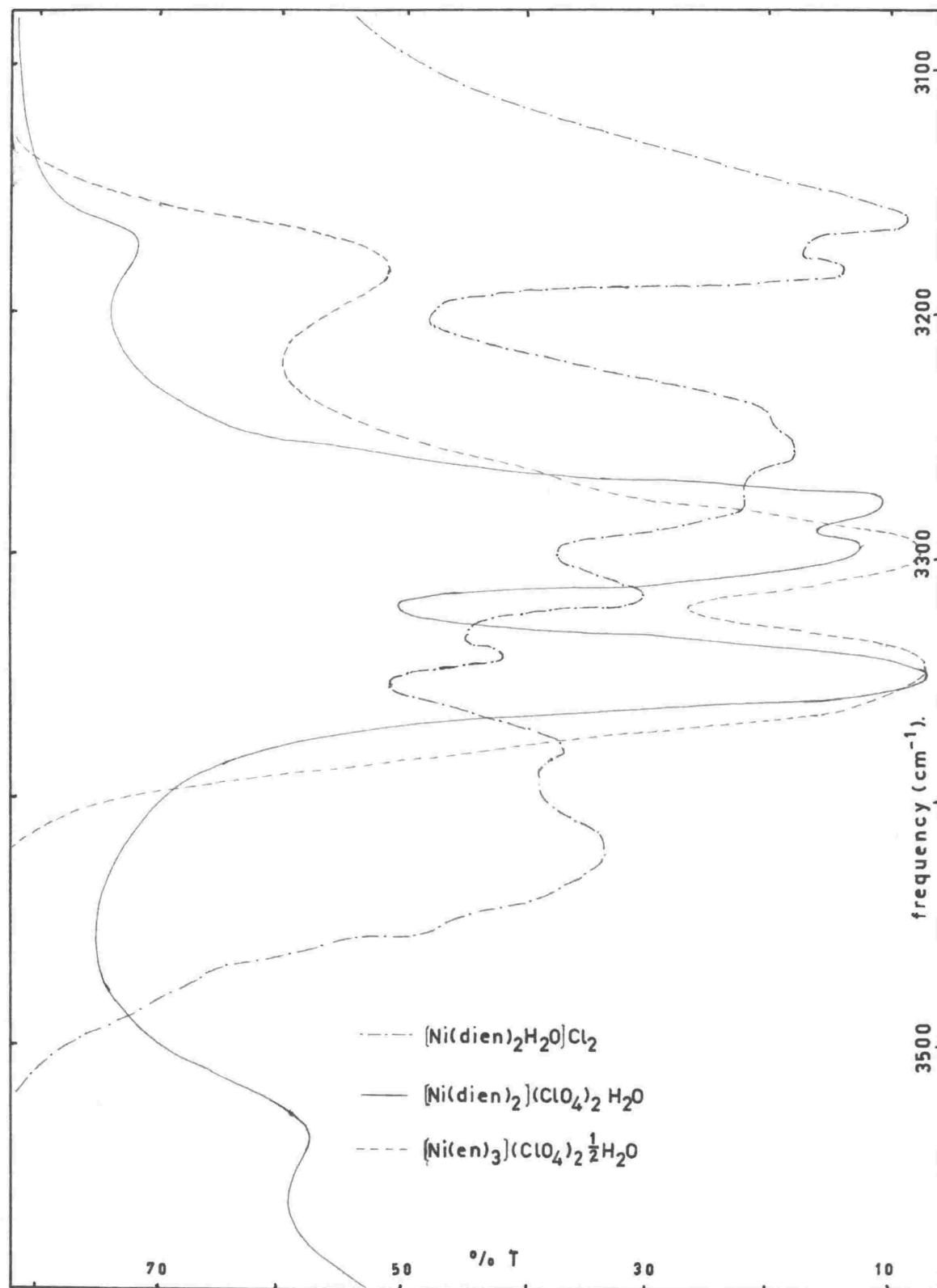
c) Amine deformation modes:

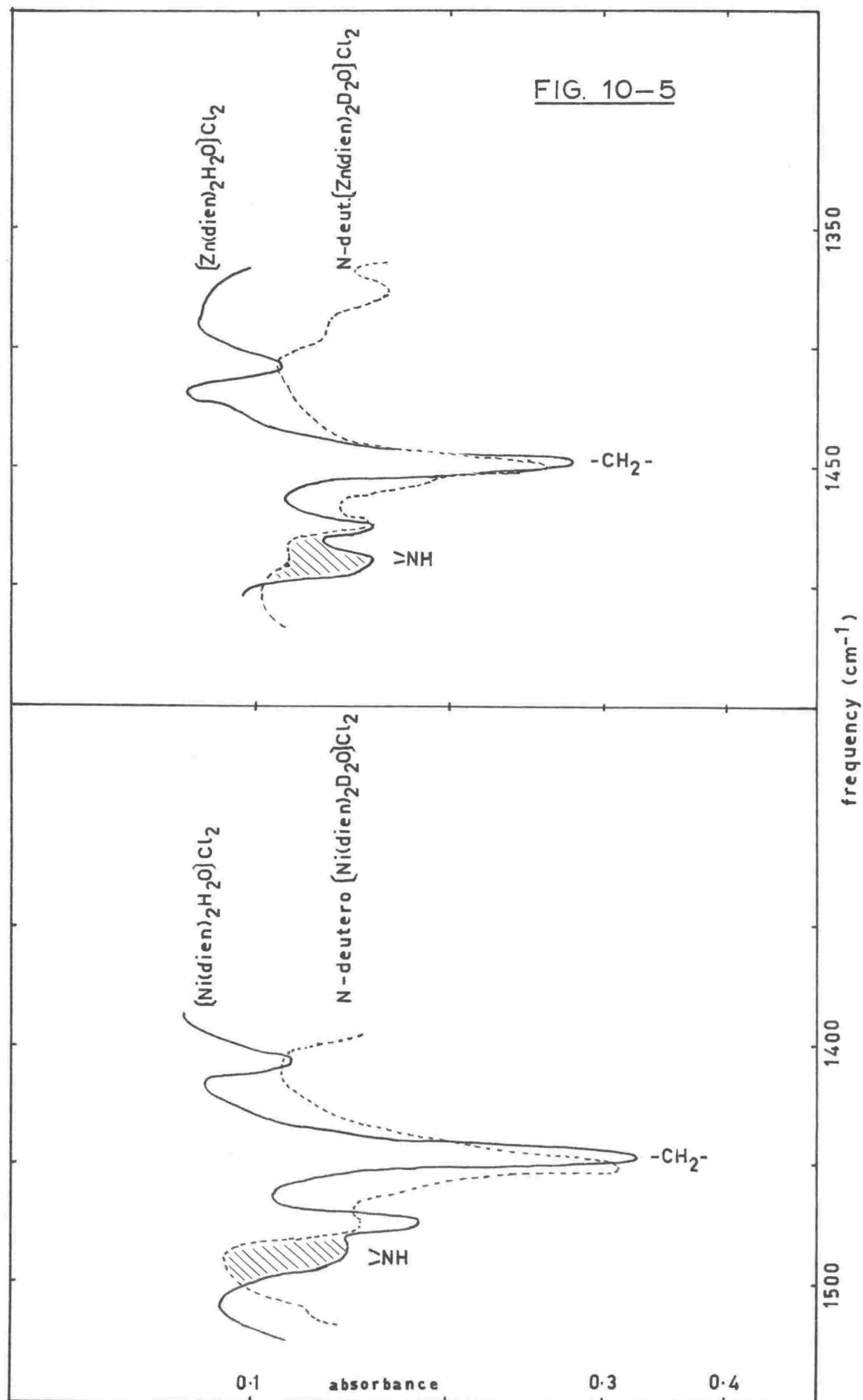
1. The  $2^0$   $>N-H$  deformation mode is assigned to a weak absorption in the  $1500-1475cm^{-1}$  range. This absorption shifts on deuteration (Fig. 10-5). It appears that many transition metal(II) coordination compounds containing RNHR'

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+ X-ray powder patterns have shown the Zn(II) compound to be isostructural with the Ni(II) one.

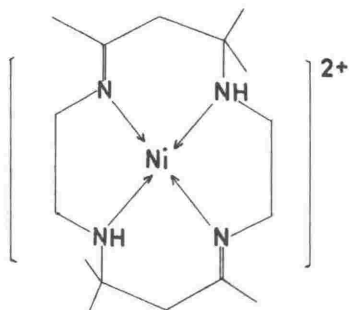
FIG. 10-4. INFRARED SPECTRA ( 3600 — 3100  $\text{cm}^{-1}$  )



I.R. SPECTRA ASSIGNMENTS FOR  $\text{>NH}$  DEFORMATION MODES

groups have a weak absorption in this region. e.g.,

1. The Ni(II) bis-  $\beta\beta'$  diamino dipropylamine complexes,  $1485\text{cm}^{-1}$  (ms).
2. Many of the Schiff Base complexes of the type:



have a mw to w absorption.

Reduction of the azomethine groups increases the absorption intensity.

Ni' di-isopropyl ethylenediamine has a ms absorption at  $1485\text{cm}^{-1}$  ( $\delta\text{-CH}_3$ ,  $1470\text{cm}^{-1}$ ). Dithizone  $\text{C}_6\text{H}_5\text{N}=\text{N}(\text{CS})\text{NHNHC}_6\text{H}_5$ , solid and in  $\text{CHCl}_3$  solution has a mw absorption at  $1483\text{cm}^{-1}$  which is removed by deuteration or by complexing involving loss of one or both protons.\*

In some complexes the absorption is not sufficiently intense to be distinguished from a broad methylene symmetric deformation band at  $1460\pm 15\text{cm}^{-1}$ .

2. The  $\text{-NH}_2$  wagging mode: The ms band at  $1250\pm 5\text{cm}^{-1}$  ( $\sigma=1.33$ ) is assigned to this mode. Apparently many workers have not observed this absorption for amine complexes of divalent metal ions. (Ni, Cu, and Zn(II)) amines have a deformation mode absorbing at  $1245\pm 36\text{cm}^{-1}$ ).<sup>155</sup>

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\* G.R. Burns, unpublished work: these frequencies possibly arise from combination modes,  $\text{>N-H}$  deformation + C-N stretching.

3. A combination  $\text{-NH}_2$  twisting, skeletal deformation mode:

The absorption ( $\nu$ ) in the  $1325\text{-}1295\text{cm}^{-1}$  range ( $\sigma = 1.28\text{-}1.26$ ) is assigned to a mode combining the  $\text{-NH}_2$  twisting mode at  $1080\text{cm}^{-1}$  and a skeletal deformation mode at  $250\text{-}230\text{cm}^{-1}$ .

This assignment accounts for the observed isotopic shift to within  $3\text{-}13\text{cm}^{-1}$ . Absorptions in the  $1350\text{-}1300\text{cm}^{-1}$  range for divalent amine complexes have previously been assigned to the  $\text{-NH}_2$  wagging mode;<sup>110,111,156</sup> anharmonicity has been invoked to explain the low isotopic shift.<sup>110,111</sup>

4. The  $\text{-NH}_2$  twisting mode: When an  $\text{-NH}_2$  group is bound to two other atoms its twisting mode occurs at a lower frequency than does its wagging mode.<sup>157</sup> The absorption bands at  $1088\text{-}1078\text{cm}^{-1}$  ( $\sigma = 1.36$ ) are assigned to the  $\text{-NH}_2$  twisting mode. This assignment agrees with those of Powell et al.<sup>111,156</sup> for M(II) ethylenediamine complexes ( $1180\text{-}1099\text{cm}^{-1}$ ), Allen and Senoff<sup>158</sup> for Ru(II)-tris ethylenediamine complexes ( $1030\text{-}1010\text{cm}^{-1}$ ) and Sacconi and Sabotini<sup>110</sup> for M(II) hydrazine complexes ( $1200\text{-}1150\text{cm}^{-1}$ ).

d) The C-N stretching mode: This is assigned to the strong doublet or singlet absorption in the  $1150\text{-}1128\text{cm}^{-1}$  range. The bands show an isotopic shift  $\sigma = 1.04$  on deuteration; the value expected for a pure C-N stretching mode is 1.028. For Ru(II)-tris ethylenediamine complexes, bands at  $1107\text{-}1102\text{cm}^{-1}$  have been assigned to this mode.<sup>158</sup> For uncoordinated amines the C-N stretching mode has been

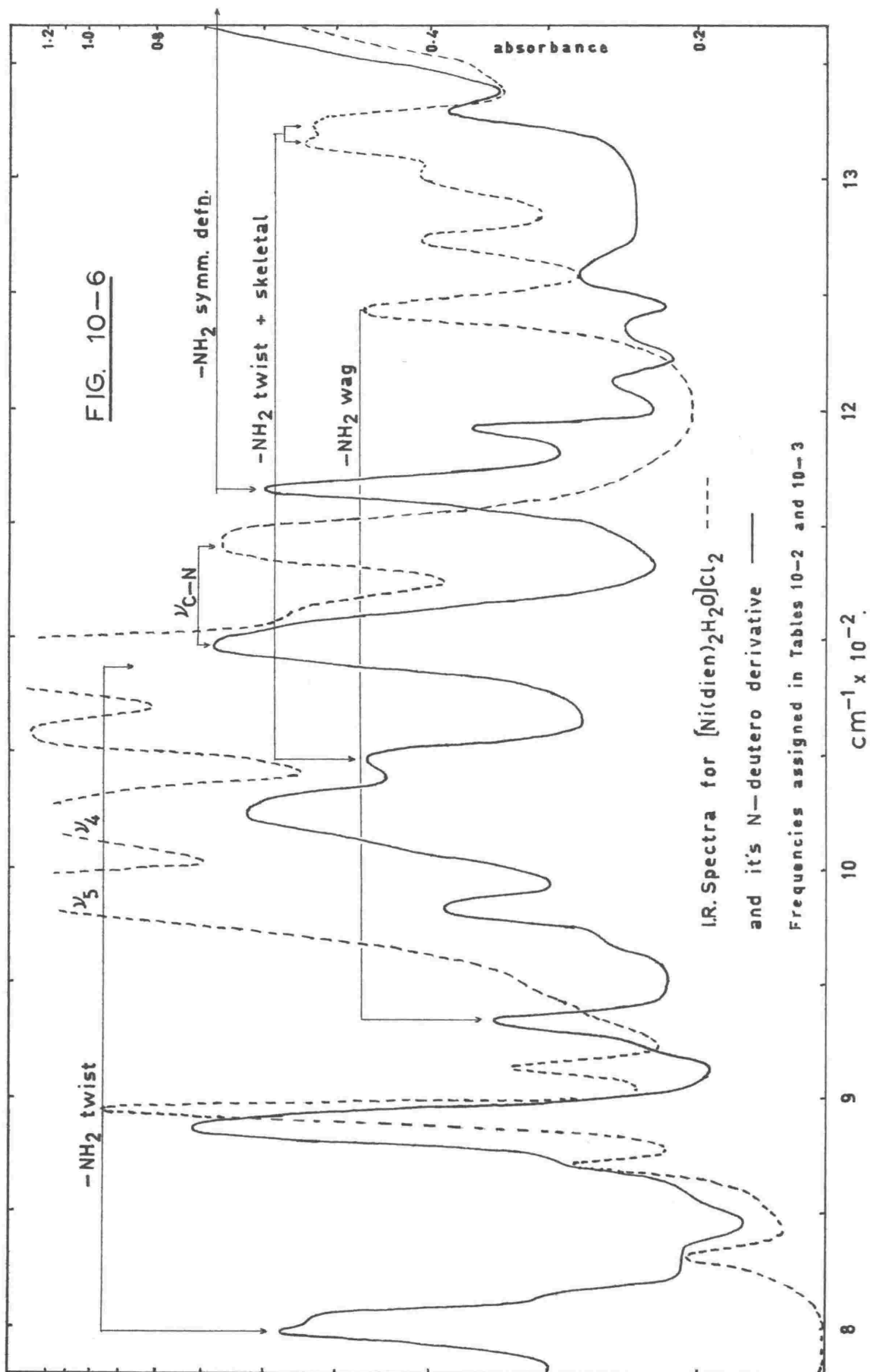
assigned at  $1133\text{cm}^{-1}$  for dien<sup>159</sup> and at  $1065\text{cm}^{-1}$  for en.<sup>160</sup>

e) Other ligand modes (Table 10-3): The assignments  $\nu_1$  to  $\nu_5$  agree with those of Powell and Sheppard<sup>111</sup> who designate  $\nu_4$  a ring skeletal mode. Gover and Murmann<sup>161</sup> characterised the absorptions  $\nu_2$  to  $\nu_4$  by C-deuteration of ethylenediamine dihydrobromide:  $\nu_2$ ,  $-\text{CH}_2$ -wag;  $\nu_3$ ,  $-\text{CH}_2$ -twist;  $\nu_4$ , C-C stretch.  $\nu_5$  ( $983\text{--}972\text{cm}^{-1}$ ) may also arise from the C-C stretching mode. A similar absorption in Ru(II)-tris en complexes has been assigned to the C-C stretching mode.<sup>158</sup> The C-C stretch for uncoordinated ethylenediamine occurs at  $980\text{cm}^{-1}$ .

The absorptions  $\nu_7$  to  $\nu_9$  are assigned to ring deformations which arise predominantly from C-N-C and C-C-N angle deformation modes. The hydrochloride salts of dien, en, pn, and other similar diamines also have two ms absorptions in the regions  $530\text{--}485\text{cm}^{-1}$  and  $470\text{--}440\text{cm}^{-1}$ . Ebsworth and Sheppard<sup>163</sup> found the C-N-C angle deformation frequency at  $460\text{--}420\text{cm}^{-1}$  in methyl ammonium iodides  $(\text{CH}_3)_x\text{NH}_{(4-x)}\text{I}$ . Baldwin<sup>162</sup> observed an absorption at  $590\text{--}570\text{cm}^{-1}$  for Co(III)-en complexes (not assigned).

Fig. 10-6 compares the infrared spectra ( $1350\text{--}780\text{cm}^{-1}$ ) for  $[\text{Ni}(\text{dien})_2\text{H}_2\text{O}]\text{Cl}_2$  and its N-deutero analogue.



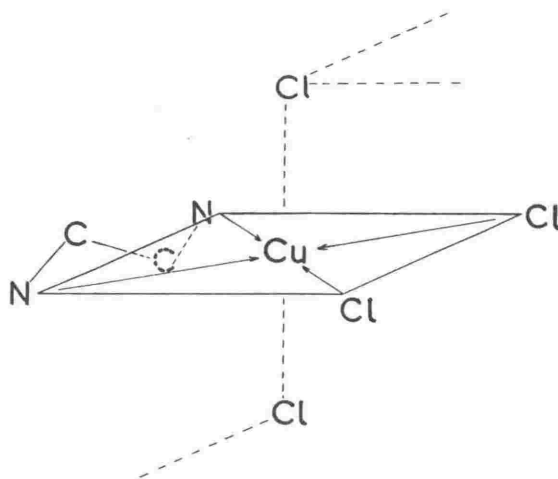


10-3 The Far Infrared Spectra ( $420-290\text{cm}^{-1}$ ) for Ni, Cu, and Zn(II) 1,2-Diamino Coordination Compounds

10-3.1 The Metal(II)-donor stretching frequency

Assignments (Table 10-4) have been possible because of the initial consideration of very simple coordination complexes:

1) The simple system  $[\text{Cu}(\text{diamine})\text{X}_2]^*$ : The crystal structure analysis for  $\text{Cu}(\text{en})\text{Cl}_2$  has shown it to be a simple monomer with the Cu atom in a distorted octahedral environment.



The complexes  $\text{Cu}(\text{pn})\text{X}_2$ ,  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , are considered to have similar monomeric structures (10-6.2b). In these systems the symmetric M-N and M-Hal. stretching modes are I.R. active.

The far I.R. spectral data for these complexes are given in Table 10-4. Very strong absorptions at 316 and  $311\text{cm}^{-1}$  are assigned to the Cu-Cl stretching frequency<sup>101c</sup>

\* Preparations for these complexes are given in 10-6.1.

in  $\text{Cu(en)Cl}_2$  and  $\text{Cu(pn)Cl}_2$  respectively (cf.,  $\text{CuCl}_4^{=}$ , asymmetric Cu-Cl stretch approximately  $267\text{cm}^{-1}$ .<sup>95,101-6</sup>)

The M-N stretching frequency is assigned to m-vs absorptions in the  $414\text{-}373\text{cm}^{-1}$  range. This frequency assignment is considered unambiguous because

a) an upper frequency limit is set by the assignment of all bands above  $430\text{cm}^{-1}$  to ligand vibratory modes in  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ , and  $\text{Zn(II)-1,2-diamino}$  complexes (10-2.3(e)) and b) a lower frequency limit is set by the Cu-Cl stretching mode at approximately  $313\text{cm}^{-1}$ .

2)  $\text{Cu(dien)Cl}_2$ : This complex is considered to be monomeric  $[\text{Cu(dien)Cl}]\text{Cl}$  and is probably square planar (Appendix IV). Its far I.R. spectrum is very similar to that for  $[\text{Cu(pn)Cl}_2]$ , with  $\nu_{\text{M-N}}$  at  $392\text{cm}^{-1}$  and  $\nu_{\text{Cu-Cl}}$  at  $313\text{cm}^{-1}$ . However, for this and most other dien complexes there is a doublet absorption near  $350\text{cm}^{-1}$  which is possibly associated with a mode incorporating metal- $2^{\circ}\text{N}$  stretching.

3)  $\text{Ni(dien)X}_2$ ,  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ : These complexes are considered to have a halogen bridged structure (Appendix IV). Their spectra show  $\nu_{\text{M-N}}(1^{\circ})$  and  $\nu_{\text{M-N}}(2^{\circ})$  in the expected frequency regions (Table 10-4). The chloro compound has complex absorptions in the  $\nu_{\text{Ni-Cl}}$  region:  $331\text{cm}^{-1}(\text{s})$ ,  $326$  and  $318\text{cm}^{-1}(\text{mw})$ . The weaker modes may be associated with the bridging chlorides. The  $\nu_{\text{Ni-Cl}}$  mode has been assigned at  $310\text{cm}^{-1}$  for  $\text{NiCl}_2$ .<sup>164</sup>

### 10-3.2 Conclusions

The Ni, Cu and Zn(II)-1<sup>0</sup> amino stretching mode absorbs in the 400-370cm<sup>-1</sup> range. It generally occurs as a single sharp band. An absorption near 350cm<sup>-1</sup> for dien complexes could be associated with a metal-2<sup>0</sup>N stretching mode.

### 10-3.3 Previous assignments

Few attempts have been made to locate the metal-ligand stretching frequency except for:

1. halide ligands where there are no 'ligand' modes to complicate the spectrum<sup>95,101-106</sup>

2. 2,2'-bipyridyl and 1,10-phenanthroline transition metal complexes<sup>106</sup> for which the ligand conformation is little altered by coordination. The characteristic absorptions of the skeletal modes were found by subtracting the spectrum of the uncoordinated ligand from that of the complex. The metal-nitrogen vibration frequencies in Co(II)-Zn(II) 2,2'-bipyr and 1,10-phen complexes<sup>106</sup> follow the Irving-Williams<sup>62,67</sup> order of stabilities:

2,2'-bipyr:      Co(II) 264cm<sup>-1</sup> — Cu(II) 297cm<sup>-1</sup>

1,10-phen:      Co(II) 288cm<sup>-1</sup> — Cu(II) 300cm<sup>-1</sup>

A similar order is shown by the Mn(II)-Zn(II) hydrazine complexes:<sup>110</sup> Mn(II) 343cm<sup>-1</sup>, Zn(II) 440cm<sup>-1</sup>.

3. A few transition metal ammine complexes.

Frequencies have been assigned: Pt(II) tetra and diammines, 511, 508cm<sup>-1</sup>; <sup>107</sup> Pd(II) tetrammines 498cm<sup>-1</sup>, diammines 496cm<sup>-1</sup>,

(cis and trans) and  $477-63\text{cm}^{-1}$  (cis);<sup>107</sup> Co(III) hexa, penta, and tetrammines  $500-450\text{cm}^{-1}$ ; <sup>108</sup> Cr(III) hexammine  $470\text{cm}^{-1}$  and Ni(II) hexammine  $460\text{cm}^{-1}$ .<sup>109</sup>

#### 10-4 I.R. Spectra for Ni(II) and Cu(II)-C<sub>1</sub>-substituted Ethylenediamine Complexes

In Table 10-5 I.R. spectral assignments ( $4000-400\text{cm}^{-1}$ ) are given for some simple en, pn and i-bn complexes of Ni(II) and Cu(II). Vibrational frequencies for the coordinated ligands were assigned by comparing the spectra with those for the dien complexes (Table 10-2),  $\text{Ni(en)}_2\text{Cl}_2$  and their N-deutero derivatives.

There is little correlation between the  $-\text{NH}_2$  symmetrical stretching frequencies and  $\Delta G^\circ$  per M-N bond for the aqueous ligation reaction:



Some workers<sup>112,113</sup> have noted a degree of correlation between the stabilities of some ammine complexes and the stretching and deformation frequencies of the  $\text{NH}_3$  ligand. However, the force constants for these vibrations are dependent on the structure of the complex and the nature of the anion, as well as on the strength of metal-ligand coordination.

Some tentative assignments are given for the M-N stretching frequencies (see 10-3). The spectrum below

$400\text{cm}^{-1}$  becomes very complex as the symmetry of the complex increases, e.g.,  $[\text{Ni}(\text{pn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , Table 10-5.

10-4.1 Conclusion: There appears to be little or no correlation between the ligand and skeletal vibratory frequencies for solid 1,2-diamino Cu(II) and Ni(II) complexes and the stabilities of the complexes in aqueous solution.

#### 10-5 The Characterisation of the I.R. Spectra ( $4000\text{-}400\text{cm}^{-1}$ ) of Coordinated Water Molecules

Group Theory has been used in analysing the I.R. spectra for some divalent transition metal hydrates. Some assignments have been possible, in particular the metal-oxygen stretching frequency.

##### 10-5.1 Vibrational modes

The neutron diffraction study for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  indicates that the  $\text{H}_2\text{O}$  ligand is coordinated with its two-fold axis collinear with the metal-oxygen bond.<sup>165</sup> It is assumed in this discussion that the system involving a coordinated water molecule  $\text{M}-\text{O} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{H} \end{array}$  is generally planar.

The planar group  $\text{MOH}_2$  belongs to the  $\text{C}_{2v}$  symmetry group. The total reducible representation for the four atoms is

$$\Gamma_T = 4A_1 + A_2 + 3B_1 + 4B_2$$

(Mulliken symbols, Ref. 166, p. 71).

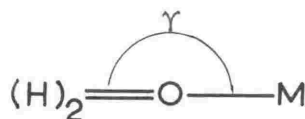
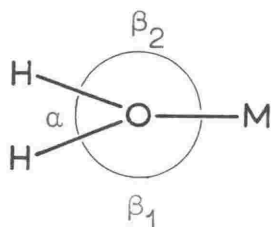
Of the twelve normal modes of displacement, three are

TABLE 10-5 Infrared absorption spectra assign

Assignment	[Cu(pn)I <sub>2</sub> ]	[Cu(pn)Br <sub>2</sub> ]	[Cu(pn)Cl <sub>2</sub> ]	[Cu(en) <sub>2</sub> Cl <sub>2</sub> ]	[Cu(i-bi
-NH <sub>2</sub> str. (symm.)	3275s	3275s	3277s	3290s	332
" (asymm.)					
>NH symm. str.	3200s	3215s	3225s	3190s	327
-NH <sub>2</sub> (scissors)	3095w	3110w	3125s	3120s	315
-NH <sub>2</sub> twist+skel.	1564s	1564s	1570s	1560s	155
-NH <sub>2</sub> wag.	1310w	1307vw	1310m	1320mw	130
C-N str.	1194vw	1203m	1210m	1225vw	121
-NH <sub>2</sub> twist	1163m	1181m	1138s	1155m, b	118
-NH <sub>2</sub> rock	1052s	1065s	1071s	1103mw	--
	676ms	665ms	671ms	665s, b	66
-CH <sub>2</sub> -symm. def.			1445m	1443m	146
-CH <sub>3</sub> symm. def.	1390ms	1390ms	1405)ms 1392)		138
-CH <sub>2</sub> - wag.		1343vw	1346m	1371vs	134
-CH <sub>2</sub> - twist	1270vw	1270vw	1275m	1275m	125
C-C str. }	1017s	1035)vw 1020)	1030m	1030ms	101
skeletal }					
-CH <sub>2</sub> - rock	930w	935vw	935w	960ms	96
Ring	905w	909w	911m		89
		553m	555m	525s	
Deformations					
(see 10-2.3e	434μm	496m 441m	498m 441m	492sh 467m	50 45 41
M-N str.	414μm	394μm	396m	401s 324ms	37

translational  $\Gamma_t = A_1 + B_1 + B_2$ , three are rotational  $\Gamma_r = A_2 + B_1 + B_2$ , and the remaining six, vibrational  $\Gamma_v = 3A_1 + B_1 + 2B_2$ .

Considering the internal coordinates:



the vibration representations obtained are

$$\Gamma_{\text{O-H}} = A_1 + B_2$$

$$\Gamma_{\text{M-O}} = A_1$$

$$\Gamma_{\alpha} = A_1$$

$$\Gamma_{\beta} = A_1 + B_2$$

$$\Gamma_{\gamma} = B_1$$

However, the number of internal coordinates considered is one greater than  $3n-6$ . The redundant condition is

$$\Delta\alpha + \Delta\beta_1 + \Delta\beta_2 = 0$$

and the real vibrational representations obtained are

$$\Gamma_{\text{O-H}} = A_1 + B_2$$

$$\Gamma_{\text{M-O}} = A_1$$

$$\Gamma_{\alpha} = A_1$$

$$\Gamma_{\beta} = B_2$$

$$\Gamma_{\gamma} = B_1$$

and all these coordinate displacements represent I.R. active



modes.  $\Gamma_{\text{O-H}}$  can be considered as composed of two modes,

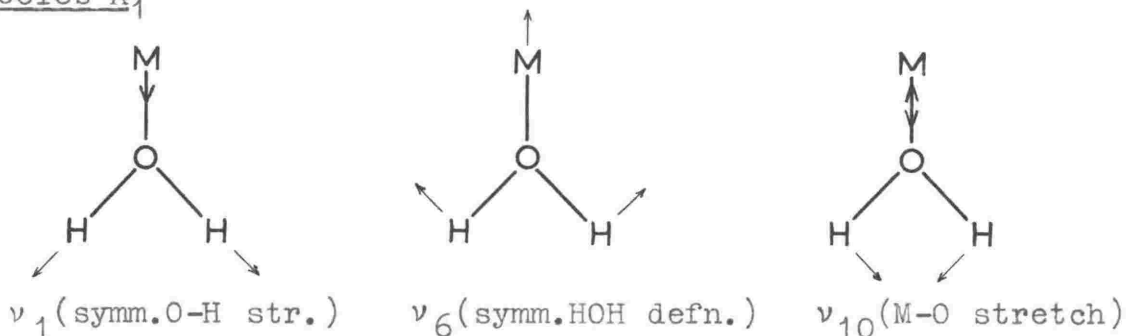
1. a symmetric bond stretching  $A_1$ ; this mode may be partially coupled with the scissors mode.  $\Gamma_\alpha$

2. an asymmetric bond stretching  $B_2$ ; this mode may be partially coupled with the rocking mode  $\Gamma_\beta$ .

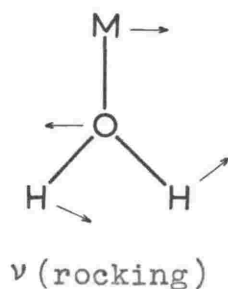
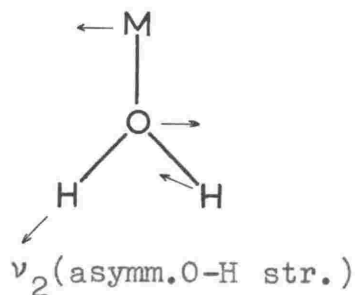
The wagging mode  $\Gamma_\alpha$  will be independent of the other internal vibrations.

The six modes of vibration are represented diagrammatically (after Sartori et al.<sup>167</sup>):

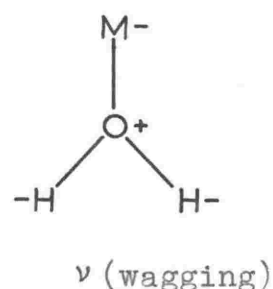
Species  $A_1$



Species  $B_2$



Species  $B_1$



Some assignments are given in Table 10-6 for transition metal(II) hydrates and for dien complexes.

TABLE 10-6 Infrared absorptions

Assignments	Group Represn.	$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$	$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$	$[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	$[\text{Cu}(\text{H}_2\text{O})_6]^{+1}$
$\nu_{\text{O-H}}$ (symm.) $\nu_1$	$A_1$	3520m, sh	3525s		3500w
$\nu_{\text{O-H}}$ (asymm.) $\nu_2$	$B_2$	3400vs	3390s	3365s	3385 $\tau$
$2 \delta \text{H}_2\text{O}$ $\nu_3$	$A_1$	3170m	3180s		3170w
$\nu_4$		2340vw		2350w	2430m
$\nu_{10^+} \nu_6$ $\nu_5$	$A_1$	2050w	2050m	2125w, b	2085 $\tau$
$\delta \text{H}_2\text{O}$ (symm. $\nu_6$ deformation)	$A_1$	1612s (1657m)	1615m (1645sh)	1625s, b (1657sh)	1620 $\epsilon$ (158 $\tau$ )
$\text{H}_2\text{O}$ wag. and $\nu_7$ rock. $\nu_8$	$B_1, B_2$	800m, b 642s, b	800w, b 640b	-- 620m, b	--
Libration $\nu_9$	$B_1, B_2$	520, s, b	550s	450m, b	
$\nu_{\text{M-O}}$ $\nu_{10}$	$A_1$	448s	444s	493vs	

### 10-5.2 The metal-oxygen stretching vibration:

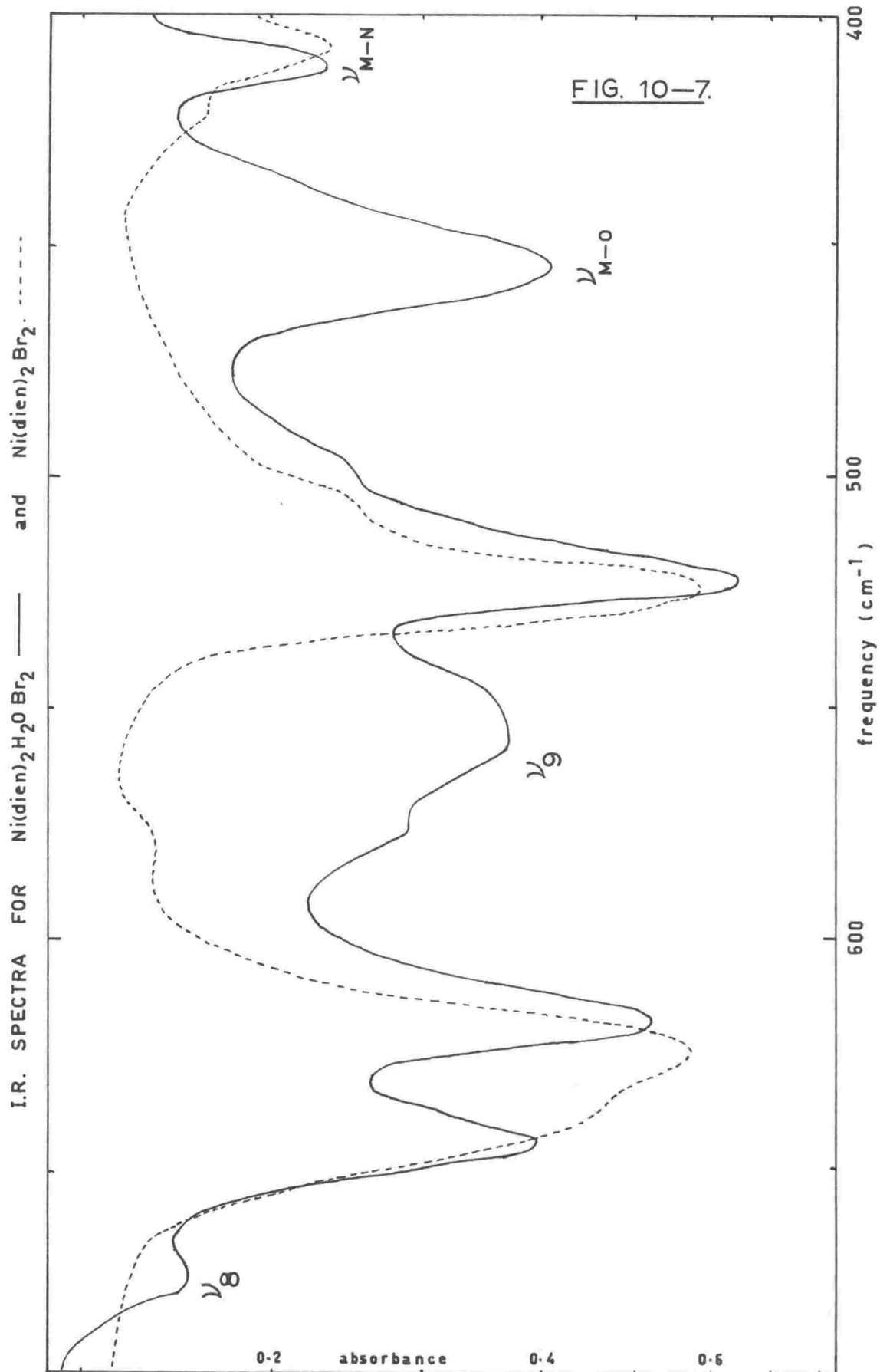
This vibration  $\nu_{10}$  is assigned to absorptions in the  $520-440\text{cm}^{-1}$  range (see Fig. 10-7). This assignment is in the same range as  $\nu_{\text{M-O}}$  for acetylacetonates and oxalates of these metal ions.

This vibration and the  $\hat{\text{H}}\text{OH}$  symmetrical deformation ( $\nu_6$ ) belong to the same symmetry class, and couple to give a combination mode  $\nu_6 + \nu_{10} = \nu_5$ , (assigned in Table 10-5). The additivity of frequencies  $\nu_6 + \nu_{10} = \nu_5$  is good. The mw absorption  $\nu_5$  appears to be characteristic only of hydrated compounds containing coordinated water, e.g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\nu_5 = 2120\text{cm}^{-1}(\text{w})$ ;  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , no absorption. However, some compounds containing lattice water do absorb very weakly in the  $2300-2000\text{cm}^{-1}$  range. This absorption has been assigned<sup>96</sup> to a combination of the symmetrical  $\hat{\text{H}}\text{OH}$  deformation mode and an  $\text{H}_2\text{O}$  librational mode I.R. active because of an asymmetric environment for the water molecule.

Rocking and wagging modes: These probably give rise to  $\nu_7$  and  $\nu_8$ , although no definite assignment is attempted here.

### 10-5.3 Lattice water and coordinated water

There is no definite borderline between these two classes.<sup>168</sup> Coordination denotes water molecules in the primary coordination sphere of the metal; lattice denotes water molecules trapped in the crystal lattice by weak



hydrogen bonds.<sup>168</sup> However, they can often be distinguished by their I.R. spectra.

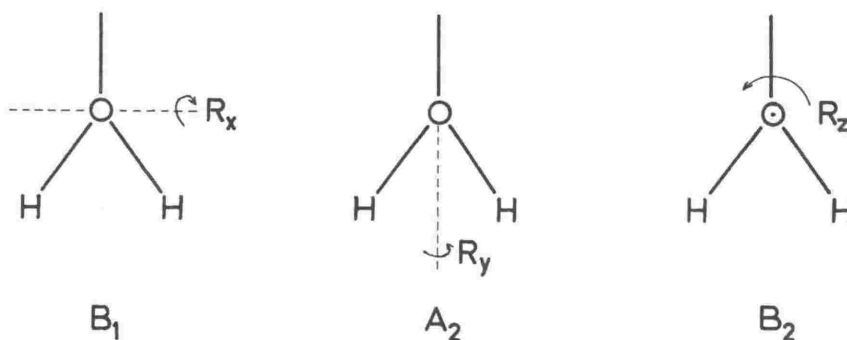
Water vapour has symmetric and asymmetric stretching vibrations at  $3756$  and  $3652\text{cm}^{-1}$  respectively. Coordination of  $\text{H}_2\text{O}$  weakens the O-H bond and lowers the stretching frequencies to approximately  $3520$  and  $3380\text{cm}^{-1}$ . The weak interactions holding 'lattice water' in a crystal lattice generally lower  $\nu_{\text{O-H}}$  to  $3600\text{--}3525\text{cm}^{-1}$  only. e.g.,  $[\text{Ni}(\text{i-bn})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $3625$  and  $3540\text{cm}^{-1}$ . This spectral difference can often be used to distinguish between 'lattice' and 'coordinated' water.

However, very strong H-bonding may lower  $\nu_{\text{O-H}}$  to values similar to those for coordinated water, e.g., ice,<sup>96</sup>  $3400$  and  $3256\text{cm}^{-1}$ ;  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ,<sup>169</sup>  $3340\text{cm}^{-1}$ . This bonding can often be distinguished from coordination by its different effect on the symmetric deformation mode  $\nu_6$ . For a coordinated water molecule the interaction between a proton and both the metal ion and adjacent water molecules increases the restoring force for a deformation vibration compared with that for water vapour.  $\nu_6$  is raised from  $1595\text{cm}^{-1}$  for water vapour<sup>170</sup> to  $1625\text{--}1605\text{cm}^{-1}$ . The restoring force, and therefore  $\nu_6$ , is increased more by H-bonding e.g.,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ,<sup>169</sup>  $1640\text{cm}^{-1}$ ; ice ( $-7^\circ\text{C}$ ),<sup>96</sup>  $1644\text{cm}^{-1}$ ;  $\text{H}_3\text{O}^+$ ,<sup>171</sup>  $1700\text{cm}^{-1}$ ;  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $1657$  and  $1612\text{cm}^{-1}$ .

#### 10-5.4 Libration modes

The rotations normally exhibited by a 'free' water molecule become hindered by H-bonding and/or coordination when the molecule is in a solid compound. The rotational modes are then better termed torsional oscillations or librations.

The coordinated water molecule may oscillate about each of its three axes of inertia:



These modes differ from wagging, twisting, and rocking modes. The M-O bond is now involved in the normal mode; the oxygen electron clouds rotate about the axis of inertia with the same period as the H atoms.

From the  $C_{2v}$  group character table  $\Gamma_r = A_2 + B_1 + B_2$ , and the rotations  $R_x$ ,  $R_y$ ,  $R_z$  have the symmetry representations  $B_1$ ,  $A_2$ , and  $B_2$  respectively. The representations  $B_1$  and  $B_2$  correspond to infrared active modes, i.e.,  $R_x$ ,  $R_z$  (above). Librations about the x and z axis involve similar displacements of the resultant molecular ( $M-OH_2$ ) dipole. These modes may have similar energies. They are jointly assigned to the absorption  $\nu_9$  (Table 10-6).

## 10-6 Charge Transfer Spectra

These were studied to characterise the charge transfer absorptions by Ni(II) and Cu(II)-amine complexes, and to seek possible correlations between the energies of charge transfer transitions in complexes and the symmetry, stability and composition of the complexes. The absorptions by Ni(II) complexes have been located by scanning solid-state spectra below 200m  $\mu$ .

Charge transfer transitions involve molecular orbitals largely localised on different atoms. The very intense absorption bands arising from charge transfers usually occur in the ultra-violet. For coordination compounds they are ascribed to the highly energetic Laporte allowed transfer of electrons from either the donor atoms to the metal ion or vice versa. Charge transfer is essentially a redox process.

For the  $L \rightarrow M$  transition, where all the ligand donors are equivalent, the charge transfer corresponds to an electron being transferred from a delocalised molecular orbital embracing all donor nuclei to a molecular orbital which is localised on the metal ion, has predominantly metal ion atomic orbital character, and which may be non-bonding or anti-bonding,  $\pi$  or  $\pi^*$ ,  $\sigma^*$  (see Fig. 3-3b). The slight delocalisation of the metal ion orbitals means that the electron is not completely transferred from ligand to metal. The transition is from the highest energy filled ligand

orbital to the lowest energy empty or partly filled metal orbital.

When the donor atoms are not equivalent, e.g., in  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ , electron transfer may occur from a specific ligand (viz.,  $\text{Cl}^-$ ) to the central metal ion. For a  $\text{L} \rightarrow \text{M}$  transfer the transition energy will depend upon the electronegativity of the ligand; and in the compounds  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ,  $\text{X}=\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , the absorption wavelength increases in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^-$ .

$\text{M} \rightarrow \text{L}$  transitions occur in complexes which contain ligands with relatively stable, but empty, orbitals ( $\pi$ -acceptor ligands) e.g.,  $\text{CN}^-$ ,<sup>172</sup> pyridine.

Unlike metal ion d-d electron transitions, charge transfer transitions may be influenced by a change of solvent, and this property has been used to distinguish between  $\text{M} \rightarrow \text{L}$  and  $\text{L} \rightarrow \text{M}$  transitions.<sup>173</sup> For a  $\text{L} \rightarrow \text{M}$  transition the energy will be related to the ionisation potential of the ligand and the electron affinity of the metal ion.  $\text{L} \rightarrow \text{M}$  and  $\text{M} \rightarrow \text{L}$  transitions can be distinguished by the effect of metal ion oxidation state on the transition energy.

#### 10-6.1 Experimental

Absorption spectra were measured from 185m $\mu$  into the visible region using a UNICAM SP700 spectrophotometer. The instrument was thoroughly flushed with dry nitrogen for work



in the 185-200m $\mu$  range.

Charge transfer bands are very intense,  $\log \epsilon \approx 3$  and spectral work requires very dilute samples. In aqueous solutions Ni(II) complexes are appreciably dissociated at the required high dilution (approximately  $10^{-4}$ m/l). Therefore solid-state spectra were measured. Cu(II) complexes are approximately 1% dissociated at this dilution, and their spectra were also measured in aqueous solution. (Table 10-7)

Solid samples were prepared as mulls and held in a very thin layer between silica plates. Rice paper was used to space the plates. Of several mulling agents tried\* diglycerol was found to give the best spectra above 200m $\mu$ . Diglycerol is viscous, completely transparent to 220m $\mu$  and has a high refractive index (1.4835) which minimises light scattering ('background') by the solid samples. The solids were ground as finely as possible and very dilute mulls were used. Other workers have used paraffin oil as a mulling agent,<sup>98</sup> or a KBr disc method for preparing samples.<sup>174</sup>

The reliability of the solid-state method was tested by comparing the spectra for a series of  $[\text{CuCl}_4]^{2-}$  salts in the solid-state and in acetone solution. The preparations and properties for these salts are given on the following page.

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\* e.g., Fluorocarb, nujol, paraffin oil.

Preparation of coordination complexes: Some of the preparations are recorded in 8-1 (g) . Others are as follows:

Chlorocuproate salts

Cs<sub>2</sub>CuCl<sub>4</sub>: CsCl (0.337gm) in the minimum volume of 90% ethanol was added dropwise with stirring to a solution of CuCl<sub>2</sub> (0.134gm) in acetone containing a few drops of conc.HCl. Yellow Cs<sub>2</sub>CuCl<sub>4</sub> immediately precipitated; a further crop of crystals was obtained on addition of acetone followed by cooling. Yield 0.35gm, 76%.

A<sub>2</sub>CuCl<sub>4</sub>: A = (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>N<sup>+</sup>, CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, C<sub>5</sub>H<sub>6</sub>N<sup>+</sup>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, N<sub>2</sub>H<sub>5</sub><sup>+</sup>, piperidineH<sup>+</sup>.

ACuCl<sub>4</sub>: A = H<sub>2</sub>en<sup>2+</sup>, H<sub>3</sub>dienCl<sup>2+</sup>, H<sub>4</sub>trienCl<sup>2+</sup>. The amine hydrochloride in solvent S<sub>1</sub> was added dropwise with stirring to a solution of CuCl<sub>2</sub> in solvent S<sub>2</sub> containing a few drops of conc.HCl. The complexes are sparingly soluble and were recrystallised by Soxhlet extraction into S<sub>3</sub>:

Amine	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	Colour	Cl <sup>-</sup> analysis
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> N <sup>+</sup>	abs. alc.	abs. alc.	abs. alc.	yellow	29.99 (30.20)
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	"	acetone	"	yellow-bronze	47.69 (47.37)
C <sub>5</sub> H <sub>5</sub> N	"	"	iso-PrOH	yellow	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>3</sub>	iso-PrOH	iso-PrOH	abs. alc.	"	33.67 (33.37)
N <sub>2</sub> H <sub>4</sub>	alcohol	acetone		yellow-green	51.00 (51.95)
piperidine	iso-PrOH	iso-PrOH	iso-PrOH/ HCl	brown	

[Cu(diamine)<sub>2</sub>X<sub>2</sub>] salts

[Cu(pn)Cl<sub>2</sub>]: 2.9ml of 85% 1-methyl 1,2-diaminopropane in four parts of acetone were added slowly with stirring to a hot solution of 5gm of CuCl<sub>2</sub>·2H<sub>2</sub>O in 25% aqueous alcohol. Pale blue crystals immediately separated from the bright blue solution. The precipitate was digested for 30 minutes and then filtered. The product was recrystallised from 50% aqueous ethanol and crystallisation induced by addition of acetone to the hot solution. Yield 3.4gm, 72%. (Found: Cu(SaO gravimetric), 30.24; Cl (AgCl), 33.94%; amine by pH titration, (see 5-4(e)), 36.07. C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>CuCl<sub>2</sub> requires Cu, 30.47; Cl, 33.98; amine, 35.53.) The product is very soluble in water, sparingly soluble in ethanol and insoluble in acetone.

[Cu(pn)Br<sub>2</sub>]: A concentrated aqueous solution of Cu(pn)Cl<sub>2</sub> was mixed with a slight excess of a saturated aqueous KBr solution. An equal volume of acetone was added to the mixture and pale green crystals separated from the blue solution on ice-cooling. The crude product contained some solid KBr. (Found: Cu(SaO), 18.2; amine by pH titration, 21.43. Ratio Cu: pn=1.009:1. C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>CuBr<sub>2</sub> requires Cu, 21.32; amine 24.93.) The complex is insoluble in alcohol, sparingly soluble in acetone to give a pale green solution, and very

soluble in water to give a blue solution.

[Cu(pn)I<sub>2</sub>]: The dark brown solid separates immediately on mixing hot aqueous solutions of KI and Cu(pn)Cl<sub>2</sub>. It is insoluble in water. and the common organic solvents. On prolonged refluxing with acetone it slowly decomposes to Cu<sub>2</sub>I<sub>2</sub>. (Found: Cu, 16.2. C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>CuI<sub>2</sub> requires Cu 16.2.)

Results: These are listed in Table 10-7.

#### 10-6.2 Discussion

a) The complexes [M(diamine)<sub>2</sub>]<sup>2+</sup>, [M(diamine)<sub>3</sub>]<sup>2+</sup>: The charge transfer absorptions for the Cu(II) complexes all occur at lower frequencies than those for the Ni(II) complexes. This suggests that the charge transfers are L → M, a high transition energy for Ni(II) being related to its low electron affinity.

The Cu(II)-bis diamine complexes have the same C.F.S.E. (see 7-3.4) and it is not surprising that they have the same charge transfer spectrum. The absorption at 235-245mμ is assigned to the N → Cu(II) charge transfer transition.

It is interesting to note that the transition energy is the same for a square-planar diamagnetic Ni(II) complex, [Ni(i-bn)<sub>2</sub>]<sup>2+</sup> and an octahedral paramagnetic Ni(II) complex, e.g., [Ni(i-bn)<sub>3</sub>]<sup>2+</sup>. The transition energy E' can, to a first approximation, be related to the metal ion electron affinity E,

TABLE 10-7

Charge-transfer absorptions for Ni(II) and Cu(II)  
diamine complexes

Complex	$\lambda_{\text{max.}} (\pm 1) \text{ m}\mu$		
$[\text{Ni}(\text{i-bn})_2](\text{ClO}_4)_2$	194		
$[\text{Ni}(\text{i-bn})_3]\text{ClO}_4)_2$	194		
$[\text{Ni}(\text{i-bn})_2\text{Cl}_2]$	194		
$[\text{Ni}(\text{en})_3]\text{Cl}_2$	196		
$[\text{Ni}(\text{en})_2\text{Cl}_2]_2$	193		
$[\text{Ni}(\text{pn})_3](\text{ClO}_4)_2$	196		
$[\text{Cu}(\text{i-bn})_2](\text{ClO}_4)_2$	237		
$[\text{Cu}(\text{eten})_2](\text{ClO}_4)_2$	235, 241		
$[\text{Cu}(\text{eten})_2]\text{Br}_2$	193	232, 242	
$[\text{Cu}(\text{pn})_2](\text{ClO}_4)_2$	232		
$[\text{Cu}(\text{en})_2]\text{Cl}_2$	237		
$[\text{Cu}(\text{en})\text{Cl}_2]$	240		
$[\text{Cu}(\text{pn})\text{Cl}_2]$	196	246	
$[\text{Cu}(\text{pn})\text{Br}_2]$	193	234	336(sh), 394(sh)
$[\text{Cu}(\text{pn})\text{I}_2]$	216	290	363
<u>Aqueous</u> $[\text{Cu}(\text{i-bn})_2]^{2+}$	236 (5,900)		
$[\text{Cu}(\text{i-bn})(\text{aq})]^{2+}$	232 (4,080)		
$[\text{Cu}(\text{eten})_2]^{2+}$	232 (6,800)		
$[\text{Cu}(\text{eten})(\text{aq})]^{2+}$	232 (4,340)		

can to a first approximation be related to the metal ion electron affinity  $E$  and the ligand donor ionisation potential  $I$  by

$$E' = I - E + \Delta$$

where  $\Delta$  gives a measure of solvation effects and the inter electron repulsion involved in transferring an electron from a delocalised ligand molecular orbital to a more localised metal ion molecular orbital. Solvation effects are probably negligible (cf., Cu complexes in aqueous solution and in nujol mulls) because the donor atoms are largely shielded from the solvent by the non-polar alkyl material present. Therefore the solvation term will be approximately constant.

The absorption at 193-196m $\mu$  for the Ni(II) complexes is assigned to a  $L \rightarrow M$  charge transfer. By considering the metal orbital occupance and group theoretical requirements for Laporte allowed electron dipole transitions, the possible  $L \rightarrow M$  transitions for octahedral ( $O_h$ ) and square-planar ( $D_{4h}$ ) Ni(II) complexes, assuming that the ligands have no pi-bonding tendencies are:

Erratum pp 233-4.

Octahedral:  $A_{1g}, E_g \rightarrow T_{1u}(p_x, p_y, p_z)$  i.e.  $\sigma \rightarrow \sigma^*$   
 $T_{1u} \rightarrow A_{1g}(s)$  or  $E_g(d_{x^2-y^2}, d_{z^2})$  " " "

Square planar:  $A_{1g} \rightarrow A_{2u}(p_z)$  i.e.  $\sigma \rightarrow \pi^{nb}$ .  
 $A_{1g} \rightarrow E_u(p_x, p_y)$  or  $E_u \rightarrow A_{1g}(s)$  i.e.  $\sigma \rightarrow \sigma^*$

$\Delta$  is possibly least variant for transitions to the metal ion  $p_x$  and  $p_y$  orbitals and the  $L \rightarrow Ni(II)$  transition is possibly ligand  $\sigma \rightarrow$  metal ion  $\sigma^*(p_x, p_y)$ .

orbital (square planar case) and the  $L \rightarrow Ni(II)$  transition is possibly ligand  $\sigma \rightarrow$  metal ion  $\pi^*$  ( $p_z$ ).

b) Cu(diamine) $X_2$  salts:

The solid state spectra for the chlorides do not contain either of the visible-U.V. absorptions characteristic of the  $[CuCl_4]^{2-}$  ion (approximately 262, 476m $\mu$ ). It is deduced that these salts are monomeric inner complexes  $Cu(diamine)Cl_2$  (see infrared evidence, 10-3.1(1)) and not dimeric salts  $[Cu(diamine)_2]^{2+}[CuCl_4]^{2-}$ . The bromide and iodide compounds have infrared spectra very similar to that for the chloride, suggesting that they are all structurally similar. The bromide does not contain the absorptions characteristic of the  $[CuBr_4]^{2-}$  ion.\* The gradation in colour,  $Cu(pn)Cl_2$  pale blue,  $Cu(pn)Br_2$  pale green, and  $Cu(pn)I_2$  brown, is due to different charge transfer bands in the ultra-violet extending into the visible absorption region. By comparison with the spectra for the Cu-bis diamine complexes, Table 10-7, the absorption at approximately 235-245m $\mu$  for the chlorides and bromide can be assigned to a  $N \rightarrow M$  transition. For  $Cu(pn)I_2$  the separation between the two highest energy absorptions (11.6kK) corresponds approximately to the energy separation between the  $J_{3/2}$  and  $J_{1/2}$  quantum levels (13.15kK) for the iodine atom. This suggests that these two absorptions correspond to transitions involving the  $I^-$  ligands.

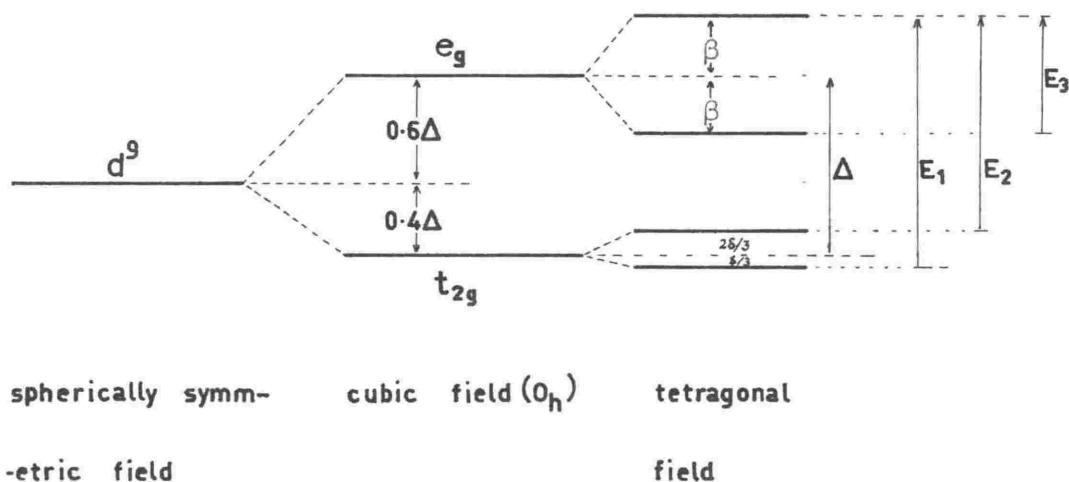
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\* CA. 58, 61d.

# APPENDIX I

## The metal ion spectra for cupric complexes

When in a symmetrical environment (e.g., octahedral coordination) the cupric ion is in an orbitally degenerate electronic state ( $E$ ). Such a system undergoes a Jahn-Teller (tetragonal) distortion to give a system with lower energy and degeneracy (see 3-6.1(f)). The resultant energy levels are shown schematically: \*



The  $d^9$  cupric system in a cubic field will give a single d-d electron transition, energy  $\Delta$ . In a tetragonal field it will give rise to an electronic absorption spectrum with three absorption bands corresponding to the three spin-allowed energy transitions  $E_1$ ,  $E_2$ , and  $E_3$ . These energies

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\* F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, (1962). p. 565.



are for the d-d transitions:

$$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}; d_{xy} \rightarrow d_{x^2-y^2}; d_{z^2} \rightarrow d_{x^2-y^2},$$

respectively.

The cupric ion absorption spectrum actually consists of a single broad asymmetric band, sometimes having a shoulder structure on the low frequency side. To consider that this absorption corresponds to a single electron transition ( $\Delta$ ), i.e., cubic field case, is an obvious approximation. To treat the absorption band as composite of three bands representing three energy transitions, i.e., tetragonal field case, also involves approximations, particularly in the graphical resolution of the absorption curve into component gaussian curves. However, Belford<sup>125</sup> has shown that the single broad absorption band for the cupric (d-d) electronic spectrum can be graphically resolved into three gaussian curves. By studying the solvent effect on the d-d transition energies for a series of copper(II) bis-acetylacetonate complexes Belford proved that of the component absorptions, the highest energy one,  $E_1$ , corresponds to the  $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$  transition, the next,  $E_2$ , to the  $d_{xy} \rightarrow d_{x^2-y^2}$ , and the lowest,  $E_3$ , to the  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition.

The treatment adopted here is that for the tetragonal field. For a  $d^9$  system the C.F.S.E. is given (from figure above) by

$$\begin{aligned}
 \text{C.F.S.E.} &= 4(0.4 \Delta + \delta/3) + 2(0.4 \Delta - 2 \delta/3) \\
 &\quad - 2(0.6 \Delta - \beta) - (0.6 + \beta) \\
 &= 0.6 \Delta + \beta.
 \end{aligned}$$

$$\text{But} \quad \beta = E_3/2$$

$$\begin{aligned}
 \text{and} \quad \Delta &= E_1 - \delta/3 - E_3/2 \\
 &= 2E_1/3 = E_2/3 - E_3/2
 \end{aligned}$$

Therefore,

$$\text{C.F.S.E.} = 0.4E_1 + 0.2E_2 + 0.2E_3.$$

## APPENDIX II

### Empirical entropies for aqueous organic solutes

A. Cobble<sup>87c</sup> derived an empirical equation for the partial molal entropies  $\bar{S}^{\circ}$  of organic solutes in aqueous solution at 25°C, and in a hypothetical one molal ideal solution:

$$\bar{S}^{\circ} = 10 + R \ln M + 9.2(N) - S_{\text{S}}^{\circ} - 0.22V_m$$

where,

$M$  = the molar mass of the solute (in grams)

$(N)$  = the number of 'skeletal' bonded atoms in the compound (total bonded atoms minus hydrogens)

$S_{\text{S}}^{\circ}$  = an empirical term to account for the comparatively low entropies for molecules containing double bonds, rings, and branched chains.

$V_m$  = the molar volume (ccs.) of the solute in the pure liquid state at 25°C, =  $M/d_{25}$ .

From this equation the  $\bar{S}^{\circ}$  values for en, pn, i-bn, and eten are 44.5, 47.3, 51.0, and 54.0e.u. respectively. The densities of en( $d_{20}$  0.899) and pn( $d_{20}$  0.878) were obtained from the Handbook of Chemistry and Physics, 28th Edition. No values were available for the other two amines, but by considering the values for en, pn, and 1,4bn ( $d_{25}$  0.881, Fluka Chemical Catalogue) a density of 0.888 was approximated. An error of 3% in  $d$  would give a discrepancy of

approximately 1e.u. in  $\bar{S}^{\circ}$ .

The approximation was made that  $\bar{S}^{\circ}$  is equal to the standard molar entropy of the ligand  $S_L^{\circ}$  consistent with a standard state of infinite dilution.

B. The Cobble equation<sup>87c</sup> (see part A) in its component parts is

$$S_L^{\circ} = S_{\text{int}}^{\circ} + S_{\text{trans}}^{\circ} + \Delta S_{\text{soln}}^{\circ}$$

where,

$S_{\text{int}}^{\circ} = 9.2(N) - S_S^{\circ}$  is the internal entropy of the gaseous molecule

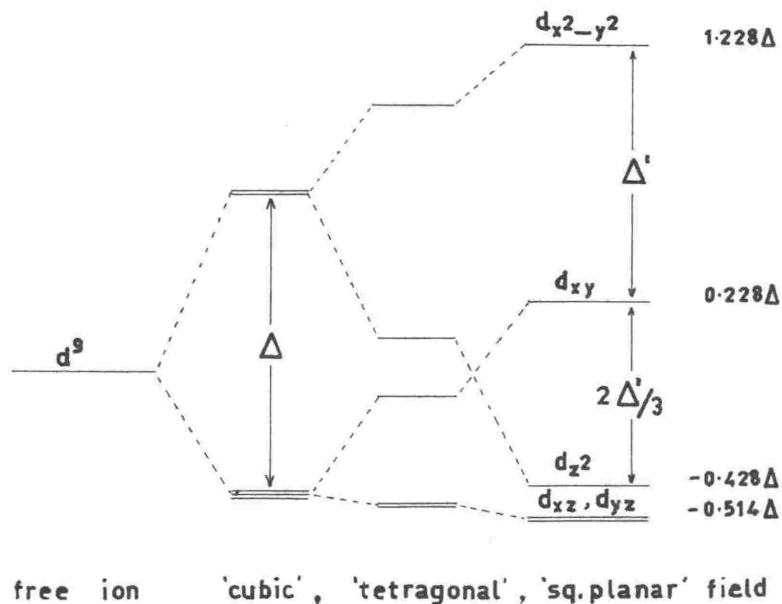
$S_{\text{trans}}^{\circ} = R \ln M + 26.00$  is the translational entropy

and

$\Delta S_{\text{soln}}^{\circ} = -16.00 - 0.22V_m$  is the entropy of solution of the gaseous molecule.

### APPENDIX III

The Crystal Field energy level diagrams for a transition metal ion in spherically symmetrical, cubic, tetragonal, and square-planar fields are shown below.<sup>145</sup>



#### Spin-Free Ni(II) Complexes

For a  $d^8$  transition metal ion in octahedral coordination (cubic field) the C.F.S.E. is  $1.2\Delta$  where  $\Delta$  is the C.F. splitting factor. For Ni(II) ions in six-fold coordination  $\Delta$  can be determined directly from the visible-near I.R. absorption spectrum. The spectrum has three weak absorption bands corresponding to the three Laporte

forbidden transitions from the ground state:



The energy change for the lowest energy transition,

$A_{2g} \rightarrow T_{2g}(F)$  is equal to the C.F. splitting factor  $\Delta$ .

Values for  $\lambda_{\max.}$  and C.F.S.E. are given in Table 8-8.

$$\text{C.F.S.E.} = 1.2\Delta = 1.2 \times 2.859 \times 10^7 / \lambda_{\max.} (\text{m}\mu).$$

### Spin-Paired (Diamagnetic) Ni(II) Complexes

In a square planar ligand field the  $d^8$  Ni(II) ion is diamagnetic with the high energy  $d_{x^2-y^2}$  orbital unoccupied. The C.F.S.E. is then  $2.456 \Delta'$ , where  $\Delta'$  is the C.F.

splitting ( $d_{xy} - d_{x^2-y^2}$ ). Electronic transitions occurring from the  $d_{xy}$  to the  $d_{x^2-y^2}$  orbital require an energy absorption  $\Delta' - P$ , where  $P$  is the energy required to pair two electrons in a Ni(II)  $d$  orbital. The energy requirement  $\Delta' - P$  corresponds to a light absorption in the visible region for the  $[\text{Ni}(\text{i-bn})_2]^{2+}$  ion. For spin-paired Ni(II)  $P$  has been estimated as 70kcal/mole.<sup>146</sup>

Therefore for dia- $[\text{Ni}(\text{i-bn})_2]^{2+}$  with  $\lambda_{\max.} = 454\text{m}\mu$

$$\Delta' - P = 62.96\text{kcal/mole}$$

$$\Delta' = 133\text{kcal/mole}$$

and the C.F.S.E. = 327kcal/mole.

APPENDIX IVM(dien)X<sub>2</sub> complexes

A. Cu(dien)Cl<sub>2</sub> is a 1:1 electrolyte in anhydrous methanol (Table I). A band at  $313\text{cm}^{-1}$  in the infrared spectrum is assigned to the Cu-Cl stretching frequency.<sup>101c</sup> Therefore the complex is considered to be monomeric [Cu(dien)Cl]Cl. It has a sub-normal magnetic moment, 1.18B.M. (Table I). This moment could arise from an anti-ferromagnetic interaction between adjacent Cu atoms. This interaction could be  $\delta$ -bonding<sup>150</sup> between  $d_{x^2-y^2}$  orbitals of Cu(II) atoms in parallel assemblies of planar complex groups, or super-exchange<sup>150</sup> through a dichloro bridge system (dimer). Another possibility is spin-pairing in a molecular orbital embracing three Cu atoms in a trimeric structure (theoretical magnetic moment=1.00B.M.). However, dimeric and trimeric structures are probably precluded by the conductivity datum.

B. Zn(dien)Cl<sub>2</sub> is a 1:1 electrolyte in anhydrous methanol. It is probably monomeric [Zn(dien)Cl]Cl with tetrahedrally coordinated Zn(II).

TABLE I

Complex magnetic susceptibilities ( $294^{\circ}\text{A}$ ); conductivities  
in anhydrous methanol (0.001M)

Complex	$\chi_g \times 10^6$ (cgsu)	$\chi_D \times 10^6$ (cgsu)*	$\mu(\text{BM})\dagger$	$\Lambda_m^{\circ}$ (mho)	Ratio of ions**
[ZndienCl]Cl	-	-	-	85	1:1
[CudienCl]Cl	$3.08 \pm 0.10$	142	$1.18 \pm 0.03$	103	1:1
[NidienBr <sub>2</sub> ]	$12.71 \pm 0.05$	163	$3.05 \pm 0.01$	146	1:2
[NidienH <sub>2</sub> OBr <sub>2</sub> ]	$12.12 \pm 0.10$	173	$3.06 \pm 0.01$	-	-
[NidienCl <sub>2</sub> ]	$17.47 \pm 0.10$	143	$3.05 \pm 0.01$	123	partly disso- ciated
[NidienH <sub>2</sub> OCl <sub>2</sub> ]	$16.55 \pm 0.05$	153	$3.08 \pm 0.01$		-
[Cu(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>	-	-	-	136	1:2
[Ni(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>	-	-	-	144	1:2
[Zn(dien) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>	-	-	-	139	1:2

\*  $\chi_D$ =diamagnetic correction.

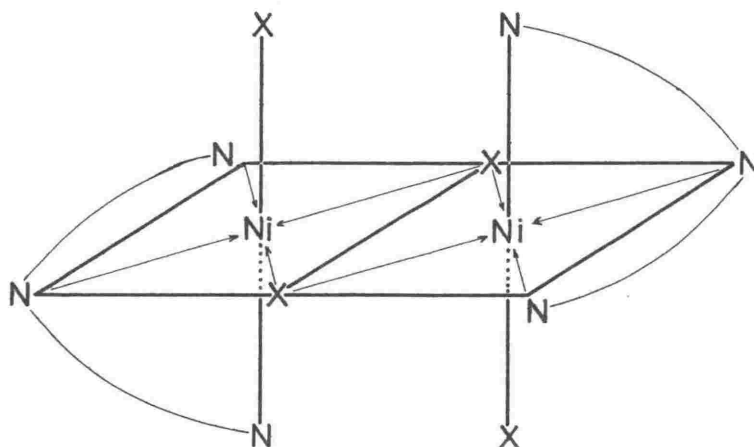
$\dagger$  Calculated from  $\mu = 2.84(\chi_m T)^{\frac{1}{2}}$

\*\* For KCl,  $\Lambda_m^{\circ} = 98 \pm 2(\text{mho})$ ; NaCl,  $\Lambda_m^{\circ} = 90 \pm 1(\text{mho})$ ;

BaCl<sub>2</sub>,  $\Lambda_m^{\circ} = 167 \pm 1(\text{mho})$ ; [NiZen]Cl<sub>2</sub>·2H<sub>2</sub>O,  $\Lambda_m^{\circ} = 144 \pm 1(\text{mho})$



C.  $\text{Ni}(\text{dien})\text{X}_2$ .  $\text{X}=\text{Cl}^-, \text{Br}^-$ . These complexes are considered to have dimeric (or polymeric) structures with halide bridges and with each Ni(II) ion in an 'octahedral' environment:



Their magnetic moments are typical for six-coordinate paramagnetic Ni(II) compounds (Table I). I.R. spectra indicate that all amino functional groups are coordinated. Absorptions at  $331(\text{s})$ ,  $326$ , and  $318\text{cm}^{-1}$  are assigned to the Ni-Cl stretching modes, Table 10-4 (cf., Ref. 164).

The hydrates  $\text{Ni}(\text{dien})\text{H}_2\text{OX}_2$  also have normal magnetic moments characteristic of six-coordinate Ni(II). Visible reflectance spectra are also typical:  $\text{Ni}(\text{dien})\text{H}_2\text{OBr}_2$ ,  $\lambda_{\text{max.}} = 1069, 634, 388\text{m}\mu$ ).

Electrolytic conductivities indicate that these Ni(II) complexes are dissociated in anhydrous methanol(S):

$$[\text{Ni}(\text{dien})\text{X}_2]_2 + 2\text{xS} \rightleftharpoons 2\text{Ni}(\text{dien})\text{S}_\text{x}^{2+} + 4\text{X}^-.$$

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