ABSTRACT

In the last few years, the stability constants for several hundred systems of complex ions in aqueous solution have been measured. However, few values for heat and entropy changes in the formation of complexes have been reported, although in several published discussions, the need for such information has been remarked. No full realisation of the fundamentals of complex formation may be achieved without this information.

The majority of known heats of formation of complexes have not been measured by direct calorimetry but derived from the variation of stability with temperature, by the thermodynamic relationships,

$$RT \ln K^{\circ} = -\Delta F^{\circ} = -\Delta H^{\circ} - T\Delta S^{\circ}$$

$$\frac{d \ln K^{\circ}}{dT} = -\frac{\Delta H^{\circ}}{RT}$$

As more data are produced, it is becoming increasingly obvious that little reliance may be attached to the results found by this method.

As illustration, the results obtained by independent workers for the formation of the two well defined complexes

of Cu^{2+} with ethylenediamine range from a value of 30% less than the calorimetric value to one 40% in excess of the calorimetric value.

Although it was realised that the method could not yield results with accuracy approaching that of calorimetry, it was felt that they would still be of value if the errors did not exceed $\pm$ 10%. Two of the most accurate and reliable methods of measuring stability constants, viz. the determination of solubilities and the Bjerrum potentiometric method using a glass electrode, were therefore employed at a series of temperatures to find heats of formation of some metal ammines.

The solubilities of silver bromate and iodate in solutions of pyridine and 2:6-lutidine were measured at 0°C, 25°C, and 40°C, and from the calculated stability constants, the heats of formation of the silver ammines were derived. They were found to be $\sim$ 15% lower than the calorimetric values.

The system copper-ethylenediamine was reinvestigated, by the glass electrode method. Stability constants were measured at 20°, 25°, 30°, and 40°C. The derived heats of formation were found to be $\sim$ 14% greater than the calorimetric values in this case.

Considerable care was taken to minimise activity effects, to avoid irregularities in the behaviour of the glass electrode, to exclude carbon dioxide from solution and to reduce other experimental errors as far as possible.

To see whether more accurate results could be obtained for another system, heats of formation were derived for complexes formed by Ni^{2+} and ethylenediamine; here the value for the tris-complex was found to be almost 50% larger than the calorimetric value.

A critical examination of the theoretical assumptions made in the calculation of heat changes from pH measurements leads to the conclusion that there must be experimental errors, as yet undetermined. Although values of ΔH calculated from the temperature coefficients of stability constants are unreliable, (due, principally, to the small temperature range over which it is possible to make stability measurements), measurements of free energy changes by the glass electrode method differ little from the standard free energy changes. When combined with heats of formation measured calorimetrically, the resulting entropy changes do not differ from standard quantities by more than $\pm$ 2 e.u.

Heats of formation were measured directly in a twin micro-calorimeter, in each vessel of which was mounted an all-glass hypodermic syringe actuated by an external

micrometer screw-gauge. Overall heats of formation were measured by observing the heat given out when a small known weight of concentrated metal solution was injected into a large volume of amine solution containing excess ligand.

Several different types of metal ammine systems were studied by calorimetry in conjunction with glass electrode measurements in aqueous solutions of ionic strength 0.10 at 25°C. In the discussion of results, emphasis is laid upon the fact that the interacting ions and molecules are surrounded by sheaths of water molecules. The complete or partial destruction of such sheaths involve changes in energy and entropy which must be taken into account when interpreting the observed overall heat and entropy changes.

Silver Ammines.

The increase of polarity of the nitrogen atoms in the series of methyl-substituted pyridines,

pyridine < 3-picoline < 2-picoline ~ 4-picoline < 2:6-lutidine

is shown by the increasing heats of reaction with hydrogen ion, and corresponding increases in the free energy. Entropy changes are small and nearly the same value for each base (~ + 6 e.u.).

With silver-ion, the stabilities of the bis-complexes are found to increase in the above order.

pK_{AH} (a measure of the affinity of a base for hydrogen ion) varies linearly with $\log \beta_2$ (a measure of the affinity of a base for Ag^+). However, the heats of formation of $Ag(2\text{-picoline})_2^+$ and $Ag(2{:}6\text{-lutidine})_2^+$ are found to be smaller than the heat of formation of the less stable complex $Ag(pyridine)_2^+$. It is suggested that this is due to the fact that the 2-methyl groups interact with the hydration sheath of the silver ion. Some of the heat resulting from the formation of the metal-ligand bonds will be absorbed in the "melting" of hydration sheath. The released solvent particles cause an increase in the entropy of the system. The entropies of formation of the two complexes containing 2-methyl groups are more positive than the entropy of formation of $Ag(pyridine)_2^+$.

The lowering in the heat terms due to hydration is compensated by the increase in the entropy terms, so that stability constants do constitute a more reliable measure of metal-ligand bond strength than do heats of reaction in aqueous solution.

Complexes of Diamines.

The same compensation effect is shown by the tris-ethylenediamine complexes of Zn^{2+} and Cd^{2+}. Zn^{2+}, which is more highly hydrated than Cd^{2+} (as shown by its more negative

entropy of solution) forms the more stable complex. However, the heat of formation of its tris-complex (-15.52 K.cal/g.ion) is smaller than that of the tris-complex of Cd^{2+} (- 19.74 K.cal./g.ion), although there can be little doubt that Zn^{2+} forms the stronger metal-ligand bonds.

The destruction of the larger water sheath around the zinc ion in the formation of its tris-complex results in the entropy change being more positive for Zn^{2+} (+ 2.6 e.u.) than for Cd^{2+} (- 16.9 e.u.).

Five- and Six-Member Rings.

Both heat and free energy changes are larger for 1:3-diaminopropane than for ethylenediamine in the reactions with hydrogen ion. However, complexes of the divalent transition-metals with 1:3-diaminopropane are found to be less stable than those with ethylenediamine. This is an example of the general phenomenon that chelate complexes containing six-member rings are less stable than comparable chelates containing five-member rings. The lower stability of six-member rings has previously been generally attributed to an entropy effect. The present measurements show that for copper complexes, at least, it is the heat term and not the entropy term which changes with size of ring.

Complexes of 1:10-Phenanthroline.

Heats of formation of the tris-phenanthroline complexes of Fe^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}, were determined calorimetrically. The values taken in conjunction with free energy measurements show that the ferrous complex has an abnormally large negative entropy of formation compared with the tris-complexes of the other three cations. The abnormally high stability and the diamagnetism of the ferrous tris-complex have been attributed to "inner type" $3d^2 4s 4p^3$ bonding, and it is suggested that this bonding could cause a high charge density upon the periphery of the complex with an attendant partial "freezing" of solvent particles around it. This hypothesis also accounts satisfactorily for some recently published figures for the entropies of activation in the racemisation of the complex ions $Fe(phenan)_3^{2+}$ and $Ni(phenan)_3^{2+}$.

INVESTIGATIONS ON METAL COMPLEXES

IN SOLUTION.

Thesis submitted for the degree of Doctor of Philosophy.

J. R. Dickens

Keble College,

Oxford.

October 1954.

CONTENTS

NOTE.

All thermochemical data in this thesis are given in terms of the thermochemical calorie, equal to 4.1833 international joules or 4.1840 absolute joules.

INTRODUCTION.

The earliest studies of complex ions in solution were concerned with physical properties such as colour, optical rotary power and conductivity, rather than energies of formation. Werner based his coordination theory, discussed in his book "New Ideas in Inorganic Chemistry", on such semi-qualitative data. Many observations were made on complexes in the solid state, but usually the complex which crystallises out of solution is merely the most insoluble and not the most stable species. In addition the properties of solid complex salts are in part due to the properties of the anion. Measurements of energy changes involve the unknown energy of the lattice.

Some of the first workers who used what may be described as modern methods to study complex ionic equilibria in solution were Euler, Bodländer, Abegg and their coworkers (1) at the turn of the century. They measured the concentration of free metal ion in a complex solution with electrodes of elementary metal though only a limited number, chiefly silver, mercury and zinc, could be studied by this type of potentiometric method. Stability constants so obtained were of doubtful validity because of incomplete knowledge of activity effects and junction potentials.

Although it had been demonstrated that whole series of complexes which could be isolated were formed by successive replacements of one ligand by another, no consideration seems to have been given to solutions in which several species of complex ions were coexisting in dynamic equilibrium until 1920, when N. Bjerrum (2) suggested a series of "reversible step reactions" for such equilibria.

The work of N. Bjerrum and the publication of his book "Metal Ammine Formation in Aqueous Solution" (3), gave great impetus to the chemistry of complex ions in solution. The majority of workers in this field in recent years have adopted J. Bjerrum's technique using the glass electrode.

J. Bjerrum emphasised and developed N. Bjerrum's theory that complex formation takes place in reversible steps.

Consider a solution in which a metal ion, M, is in equilibrium with a complexing agent, L. Electrical charges are omitted for generality.

The following species coexist in solution:-

$$, \; L, \; ML, \; ML_2 \; \ldots\ldots\ldots\ldots \; ML_{N-1}, \; ML_N$$

The reversible step equilibria are represented as follows:-

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2$$

$$\cdot \quad \cdots\cdots\cdots$$

$$ML_{N-1} + L \overset{K_N}{\rightleftharpoons} ML_N$$

Each stage is related to a equilibrium constant, K_n

$$\text{where } K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \cdot \frac{f_{ML_n}}{f_{ML_{n-1}} \cdot f_L} \qquad \ldots\ldots 1.$$

n has integral values from 1 to N, where N is the maximum coordination number of the metal ions.

f_X is the molar activity coefficient of the species X, and the concentration of X, $[X]$, refers to g.mol./l. or g.ion./l.

K_n is termed the thermodynamic stability constant for the species ML_n.

K_n^c is termed the concentration or stoichiometric stability constant and is given by:-

$$K_n^c = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad \ldots\ldots 2.$$

L, the complexing agent, is called generally, the ligand.

A further common notation is that β_n, the overall stability constant is given by:-

$$\beta_n = \prod_{1 \to n} (K_n)$$

e.g. $$\beta_3 = K_1 . K_2 . K_3 .$$

J. Bjerrum introduced the concept of the formation curve which is now the graphical representation of how complex formation takes place which is in current usage.

$\bar{n}$ is plotted against pL.

$\bar{n}$ is the degree of formation of the system.

$$\bar{n} = \frac{[\text{complex-bound ligand}]}{[\text{Total metal}]} = \frac{C_L - [L]}{C_M}$$

C_X is the total concentration of X in all its forms in the solution.

$$p_L = -\log [L]$$

J. Bjerrum showed how values of K_1, K_2 etc. could be calculated from such curves for the complex systems so represented.

J. Bjerrum also emphasised the fact that many ligands are conjugate bases of weak acids, LH^+, LH_2^{2+}, etc.. Stability constants of complex ions of such ligands may be determined by measuring the pH of solutions containing metal ion and ligand. This is the basis of the Bjerrum glass electrode method and may be regarded as the study of the competition between metal ion, M, and hydrogen ion, H^+, for the ligand, L.

Although under the most favourable conditions, concentration of hydrogen ion is most accurately measured by the hydrogen electrode, in most metal-complex systems it proves unsatisfactory (3) and the glass electrode is used almost exclusively by contemporary workers.

At the present time many hundreds of stability constants for widely varying types of metal-ligand systems are known. In some recently published reviews the data have been collected (4), (5), (6), (7). However, different workers have measured stabilities at different temperatures and in different ionic backgrounds, thus rendering impossible direct comparison of results. In addition, most stability constants are not thermodynamic quantities but, more nearly, concentration constants.

For the reaction

$$ML_n + L \longrightarrow ML_{n+1}$$

The free energy change is given by

$$-\Delta F_{n+1} = RT \ln K_{n+1} \quad \ldots\ldots 3.$$

$-\Delta F_{n+1}$ is given in cal./g.ion or cal./g.mol.

where R is the gas constant in cal./g.mol./^{o}C

T is the temperature on the Kelvin scale.

K_{n+1} is the thermodynamic stability constant derived from molar activities.

$$-\Delta F_{n+1} = RT \ln K_{n+1} = -\Delta H_{n+1} + T\Delta S_{n+1} \quad \ldots\ldots 4.$$

$-\Delta F$ is the decrease in free energy of the system.

$-\Delta H$ is the decrease in heat content of the system.

$+\Delta S$ is the increase in entropy of the system.

In several published discussions concerning factors determining the stability of complexes, in the absence of data for enthalpy and entropy changes, ΔF has been assumed to be either negligible or constant (7),(8),(9),(64), and $-\Delta F$, calculated from $RT \ln K^{*}$, where K^{*} is not thermodynamic, has been taken to be a measure of the strength of bonding between metal ion and ligand.

Very few values for enthalpy and entropy changes in the formation of complexes are known and the urgent need for such data has been remarked by a number of workers, (4), (7),(9),(11),(64).

In 1948, in this laboratory, Dr. D. D. Williams measured the stability constants of complexes of ethylenediamine with some divalent metals (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) at several different temperatures.

From eqn. 4,

$$\log K = \frac{-\Delta H}{2.303\ RT} + \frac{\Delta S}{2.303\ R} \qquad \ldots\ldots 5.$$

If $-\Delta H$ is constant over the small temperature range where K's are measured ($\sim 40^{\circ}C$), then a plot of log K against 1/T will give a straight line of slope $-\Delta H/2.303R$.

S is most conveniently calculated from the equation

$$\Delta S = \frac{\Delta H - \Delta F}{T} \qquad \ldots\ldots 6.$$

By this method Williams found enthalpy and entropy changes in the formation of the metal-ammines (10),(11). For the heat of formation of the cupric bis-ethylenediamine complex, Williams obtained the result $-\Delta H_{12} = 35,750$ cal./g.ion. From two stability constants measured by Bjerrum at 18°C and 25°C, using Cu/Hg electrodes, the value $-\Delta H_{12} = 26,100$ cal./g.ion can be calculated (12). Although Bjerrum's result is liable to error because it was derived from only two measurements at a short temperature interval, it did seem the more probable, since William's result gave an entropy of formation of $\Delta S_{12} = -31$, which was much more negative than expected. When in 1952, Basolo (13) published a value, also obtained by the glass electrode method, of $-\Delta H_{12} = 17,200$ cal./g.ion (which gave $\Delta S_{12} = +35$) it was considered that this method could not be relied upon, and it was decided to try other methods of measuring stability constants at different temperatures to find reliable values of ΔH and ΔS.

The Scope of the Present Research.

The present research is described and discussed under the following sections.

Section I. Stabilities of silver-ammines by a solubility method.

Section II. Stabilities of complexes of ethylenediamine and 1:3-diaminopropane with some divalent metals by a glass electrode method.

Section III. Stabilities of silver ammines by a glass electrode method.

Section IV. Heats of formation by calorimetric measurement.

Section V. Enthalpy and entropy changes in the formation of some complexes of divalent metals with 1:10-phenanthroline

Section VI. Discussion of results.

Section VII. Experimental details.

Section I.

The solubility method used was similar to those used by Vosburgh (14,15,16) and Monk (21) for silver complexes. The solubilities of silver bromate and silver iodate were measured in solutions of amines between 0°C and 40°C. Work done in Dr. Bell's laboratory had shown that the method gave good values for ΔH and ΔS. It was decided to study the silver complexes of pyridine and its methyl derivatives. From a knowledge of ΔF, ΔH, and ΔS for the formation of complexes of one metal with a series of closely related ligands, it should be possible to draw conclusions concerning the effect of polar and steric factors upon complex stability.

In the methyl-pyridines the positions of the methyl groups determine the polarity of the nitrogen atom. 2-Methyl groups may be the cause of steric repulsion of both the silver ion (which is a large cation, r = 1.26 Å), and of a second ligand with a 2-methyl group. In the series of methyl-pyridines chosen for investigation, viz. pyridine, 2-picoline, 3-picoline, 4-picoline, 2:6-lutidine, the effects of both steric and polar factors should be detectable. Since with monodentate ligands, silver forms only two types of complex ion, AgL^+ and AgL_2^+, K_1 and K_2 can be calculated easily and unambiguously.

Section II.

It was decided to reinvestigate and improve the glass electrode method used by Williams and Basolo in an endeavour to obtain reliable values for ΔS and ΔH. The apparatus and technique were changed and the copper-ethylenediamine and nickel-ethylenediamine systems were studied at temperatures between 20°C and 40°C. Both copper and nickel have large heats of reaction with ethylenediamine, so that plots of log K against $\frac{1}{T}$ have large slopes.

The stabilities of complexes of zinc and cadmium with ethylenediamine and of copper and nickel with 1:3-diamino-propane at 25°C were also measured in order to study the

effect of chelate ring size upon stability.

Section III.

The acid dissociation constants of the methyl-pyridines were measured by the glass electrode method at 25°C. The stabilities of the silver complexes of the same amines were also measured by the glass electrode at 25°C.

The reactions,

$$A + H^+ \longrightarrow AH^+$$

$$A + Ag^+ \longrightarrow AAg^+$$

(where A represents amine)

are in some ways analogous, and it has been suggested that the affinity of an amine for a proton is proportional to its affinity for a silver ion (as measured by the free energies of the above reactions). The entropy changes in the reactions were calculated from these data and the enthalpy data from Section IV (see below) and the importance of the entropy terms assessed.

Section IV.

Heats of formation of complexes in solution may be measured directly in a suitable calorimeter. Such a calorimeter which had been designed and constructed by Dr. D.F. Evans (22), was kindly loaned by Dr. R.E. Richards to facilitate the production of new data while a substantially

identical apparatus was being constructed in our laboratory. The technique used was to release a small volume of metal solution into a solution containing a large excess of ligand and from the heat generated, the overall heat of reaction was calculated. The results obtained by this method were used, in the first place, as a check on the results from Sections I and II, which were shown to be considerably in error. The overall heats of formation of the silver-ammines and the complexes of ethylenediamine with the divalent metals listed above, were measured in the calorimeter. In addition, by releasing a small volume of acid solution into a large volume of amine solution, heats of neutralisation of the amines used as ligands were measured.

Five and Six Member Rings.

Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}, readily form complexes with ethylenediamine. Stability constants were measured by the glass electrode method and overall heats of formation were measured in the calorimeter.

These complexes contain 5-member rings whereas complexes of 1:3-diaminopropane contain 6-member rings and are of lower stability. It has been suggested by Schwarzenbach (23) that the lowering of stability is primarily an entropy effect.

The stabilities of complexes of Ni^{2+} and Cu^{2+} with 1:3-diaminopropane were measured by the glass electrode method. Only the heat formation of cupric bis-1:3-diaminopropane, which is formed in low amine concentrations, could be measured calorimetrically. Shortage of material made it impossible to measure the heat of formation of nickel tris-1:3-diaminopropane. However, for cupric complexes, the lower stability of the six-member ring is shown to be principally an enthalpy and not an entropy effect.

Section V.

The heats of formation of the tris-complexes of 1:10-phenanthroline with Fe^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} were measured calorimetrically. From the free energies of formation measured by D.H. Mellor (24), the entropies of formation were calculated.

It is well known that Fe^{2+} behaves abnormally when it forms complexes with 1:10-phenanthroline, since it forms an extremely stable complex ($\log.\beta_3 \sim 21$) where $K_3 > K_2 \sim K_1$ (24, 25). The tris-complex is diamagnetic, indicating d^2sp^3 hybridisation (26). The deviation of Fe^{2+} from its normal behaviour is well illustrated when the enthalpy

and entropy of formation of its tris-complex with phenanthroline are compared with those of the tris-complexes of the other three metals.

Section VI.

Complex formation in aqueous solution takes place between hydrated species, the general reaction being represented by:-

$$M^{n+} xH_2O + NL^{m-} yH_2O \longrightarrow M^{(n-m)+}L_N (x + y - z)H_2O + zH_2O$$

where y, z, and to some extent x, are unknown quantities. The values of $-\Delta F$, $-\Delta H$ and ΔS found for the various systems investigated are discussed in this section with particular reference to hydration.

Finally some mention is made of these results in connection with kinetic studies of complex formation, which are rapidly increasing in importance at the present time.

SECTION I

In aqueous solution, the monovalent silver ion forms only two types of complex ion with a monodentate ligand (3).

For the ions AgA^+ + AgA_2^+, the thermodynamic stability constants are given by:-

$$K_1 = \frac{[AgA^+]}{[Ag^+]\,[A]} \cdot \frac{f_{AgA^+}}{f_{Ag^+} \cdot f_A} = K_1^c \cdot \frac{f_{AgA^+}}{f_{Ag^+} \cdot f_A} \quad \ldots\ 7.$$

$$K_2 = \frac{[AgA_2^+]}{[AgA^+]\cdot[A]} \cdot \frac{f_{AgA_2^+}}{f_{AgA^+} \cdot f_A} = \beta_2^c \cdot \frac{f_{AgA_2^+}}{f_{AgA} \cdot f_A} \quad \ldots\ 8.$$

And the overall constant,

$$2 = \frac{[AgA_2^+]}{[Ag^+][A]^2} \cdot \frac{f_{AgA_2^+}}{f_{Ag^+} \cdot f_A^2} = \beta_2^c \cdot \frac{f_{AgA_2^+}}{f_{Ag^+} \cdot f_A^2} \quad \ldots\ 9.$$

where K_1^c, K_2^c, and β_2^c are stoichiometric constants.

In dilute solutions of low ionic strength, f_A, the activity coefficient of the amine, which is an uncharged species, is unity All the ions have unit charge and f_{Ag^+}, f_{AgA^+}, and $f_{AgA_2^+}$ must be very similar in magnitude.

Thus the ratios, $\frac{f_{AgA^+}}{f_{Ag^+} \cdot f_A}$, $\frac{f_{Ag^+A_2}}{f_{AgA^+} \cdot f_A}$, and $\frac{f_{AgA_2^+}}{f_{Ag^+} f_A^2}$

should not deviate appreciably from unity. In solutions of silver ion and monamines, it is thus possible to approximate

closely to thermodynamic stability constants by using concentration stability constants.

The Solubility Method.

This method was developed by La Mer (28) and by Davies (29) and recently it has been used for complexes of silver by Vosburg (14,15,16) and by Monk (21).

When an amine solution is saturated with a sparingly soluble silver salt, a determination of the concentration of the anion of the silver salt in the saturated solution combined with a knowledge of the solubility product of the salt permits the concentration of free silver ion present in solution to be calculated. The difference between the total concentration of silver in solution and that present as the free ion is then the amount of silver which has formed a complex with the amine.

Solutions of different compositions may be prepared by:-

(a) Altering the concentration of the amine.

(b) Using different silver salts so that different solubility products apply.

Advantages of the method.

(1) Stability constants can be measured as accurately by this method as by any other method.

(2) The stability constants so measured are very nearly

thermodynamic quantities, or at least refer to solutions of low and constant ionic strength.

(3) The apparatus used is simple and can be used without modification at any temperature between 0° and 40°C.

The method's special applicability to the silver ammine systems is for the following reasons:-

(1) The two sparingly soluble silver salts used were the iodate and bromate, which can be determined very accurately by iodimetric analysis.

(2) The bromate is about forty times as soluble as the iodate, which allows solutions of all degrees of formation to be prepared.

Theory of the Solubility Method.

The solubility of a sparingly soluble salt at a given temperature in solutions which do not contain species capable of complex-formation, depends upon the solubility product of the salt, on ion-pair formation and the ionic strength of the solution. It is necessary to determine the effect of these factors upon the solubility before the effect of amine concentration upon solubility may be discussed. Firstly, an account will be given of the effect of neutral salt concentration upon solubility.

Solubility Product.

When a silver salt, AgX, in aqueous solution is in equilibrium with the solid salt, the relationship holds:-

$$[Ag^+] \cdot [X^-] \cdot f_{\pm}^2 = S \qquad \ldots. 10.$$

$f_{\pm}$ is the mean activity coefficient of the cation and anion.

S is a constant, the solubility product.

There is also present in solution, the ion-pair $AgX^{\pm}$, which bears a formal charge of zero and is assumed to have an activity coefficient of unity.

For the ion-pair, $AgX^{\pm}$,

$$\frac{[Ag^+]\ [X^-]}{[AgX^{\pm}]} \cdot f_{\pm}^2 = K_{AgX} \qquad \ldots. 11.$$

K_{AgX} is the thermodynamic dissociation constant of the ion-pair.

The relation between mean activity coefficient, $f_{\pm}$, and ionic strength, μ.

When the ionic strength of the solution is increased by adding a neutral soluble electrolyte, the solubility of the silver salt increases, because $f_{\pm}$ is decreased.

The ionic strength, $\mu = \frac{1}{2} \sum_{1 \to i} C_1 Z_1^2 \qquad \ldots. 12.$

where C_1 is the concentration of the i^{th} ionic species of

charge Z_1.

Several equations have been formulated for the relationship between μ and $f_\pm$.

The equation which was tested and used in this work was that of Davies (30).

At 25°C, for a uni-univalent electrolyte,

$$-\log_{10} f_\pm = 0.50\left\{\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.20\,\mu\right\} \qquad \ldots. 13.$$

(At 0°C and 40°C, the parameter 0.50 has the values 0.49 and 0.52 respectively).

To test the applicability of the equation, measurements of the solubility of silver bromate and silver iodate were made in solutions of potassium nitrate at 25°C. If the equation is valid, calculations of solubility product in solutions of different ionic strength will give a constant value for S, the solubility product.

Calculation of Solubility Products.

In an aqueous potassium nitrate solution of concentration C_{KNO_3}, saturated with a silver salt, concentration C_{AgX}, there will be four kinds of ion-pairs present:-

$$KNO_3^\pm, \quad KX^\pm, \quad AgX^\pm, \text{ and } AgNO_3^\pm$$

Having zero charge, the ion-pairs do not contribute to the ionic strength of the solution.

The anion of the silver salt is determined by analysis, and for electroneutrality, $C_{Ag} = C_X$, so for the solution, the total concentrations of the two cations (C_K and C_{Ag}) and the two anions (C_{NO_3} and C_X) are known. It is required to find the concentrations of free ions.

The thermodynamic dissociation constants of the ion-pairs at 25°C have been measured by Monk (21) and Davies (31). The values are given in Table I.

TABLE I

Ion-pair Dissociation Constants at 25°C.

	Silver			Potassium		
Salt	NO_3^-	BrO_3^-	IO_3^-	NO_3^-	BrO_3^-	IO_3^-
log K	1.5	0.5		1.4	2.3	2.0
Ref.	31	21	21	31	31	31

For an ion-pair, $YZ^{\pm}$,

$$K_{YZ} = \frac{[Y^+]\ [Z^-]}{[YZ^{\pm}]} \cdot f_{\pm}^2 \qquad \ldots\ 11.$$

The concentration dissociation constant, K^c_{YZ}, is given by:-

$$K^c_{YZ} = \frac{[Y^+]\ [Z^-]}{[YZ^{\pm}]} \qquad \ldots\ 14.$$

Taking logarithms,

$$\log.\ K_{YZ} = \log K^c_{YZ} + 2 \log f_{\pm} \qquad \ldots\ 15.$$

Applying the Davies equation, 13, at 25°C.

$$\log K^{c}_{YZ} = \log K_{YZ} + \frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\mu \qquad \ldots. 16.$$

The accurate ionic strength of the solution, μ_{Acc}, is given by:-

$$\mu_{Acc} = \frac{[Ag^+] + [X^-] + [K^+] + [NO_3^-]}{2} \qquad \ldots. 17.$$

The ion-pairs are present in very low concentration, so to a close first approximation,

$$\mu = C_{AgX} + C_{KNO_3}$$

Using this value of μ in eqn. 16, the concentration dissociation constants of the four ion-pairs may be calculated.

For the silver solution, the following equations apply:-

$$K^{c}_{AgX} = \frac{[Ag^+][X^-]}{[AgX^{\pm}]} \qquad K^{c}_{AgNO_3} = \frac{[Ag^+][NO_3^-]}{[AgNO_3^{\pm}]} \qquad K^{c}_{KX} = \frac{[K^+][X^-]}{[KX^{\pm}]}$$

$$K^{c}_{KNO_3} = \frac{[K^+][NO_3^-]}{[KNO_3^{\pm}]}$$

And also:-

$$C_{Ag} = [Ag^+] + [AX^{\pm}] + [AgNO_3^{\pm}]$$

$$C_{K} = [K^+] + [KX^{\pm}] + [KNO_3^{\pm}]$$

$$C_{X} = [X^-] + [AgX^{\pm}] + [KX^{\pm}]$$

$$C_{NO_3} = [NO_3^-] + [KNO_3^{\pm}] + [AgNO_3^{\pm}]$$

By substitution in, and rearrangement of, these eight equations, it is possible to arrive at the following expressions for free ion concentrations.

$$[X^-] = \frac{C_X}{1 + \frac{C_{K^+}/K^c_{KX}}{1 + \frac{[X^-]}{K^c_{KX}} + \frac{[NO_3^-]}{K^c_{KNO_3}}} + \frac{C_{Ag}/K^c_{AgX}}{1 + \frac{[X^-]}{K^c_{AgX}} + \frac{[NO_3^-]}{K^c_{AgNO_3}}}} \quad \ldots\ 18.$$

$$[NO_3^-] = \frac{C_{NO_3}}{1 + \frac{C_K/K^c_{KNO_3}}{1 + \frac{[X^-]}{K^c_{KX}} + \frac{[NO_3^-]}{K^c_{KNO_3}}} + \frac{C_{Ag}/K^c_{AgNO_3}}{1 + \frac{[X^-]}{K^c_{AgX}} + \frac{[NO_3^-]}{K^c_{AgNO_3}}}} \quad \ldots\ 19.$$

$$[Ag^+] = \frac{C_{Ag}}{1 + \frac{C_X/K^c_{AgX}}{1 + \frac{[Ag^+]}{K^c_{AgX}} + \frac{[K^+]}{K^c_{KX}}} + \frac{C_{NO_3}/K^c_{AgNO_3}}{1 + \frac{[Ag^+]}{K^c_{AgNO_3}} + \frac{[K^+]}{K^c_{KNO_3}}}} \quad \ldots\ 20.$$

$$[K^+] = \frac{C_K}{1 + \frac{C_X/K^c_{KX}}{1 + \frac{[Ag^+]}{K^c_{AgX}} + \frac{[K^+]}{K^c_{KX}}} + \frac{C_{NO_3}/K^c_{KNO_3}}{1 + \frac{[Ag^+]}{K^c_{AgNO_3}} + \frac{[K^+]}{K^c_{KNO_3}}}} \quad \ldots\ 21.$$

These equations are used for calculations on silver bromate solutions, where $X^- = BrO_3^-$.

The equations become of somewhat simpler form for silver iodate, because of the non-existence of the ion-pair $AgIO_3^{\pm}$.

The equations are of a very convenient form. At the highest ionic strength used (~ 0.10), the whole denominator is less than 1.05. Accurate values of the free ion concentrations are obtained using total ion concentrations, (C_{ION}), instead of free ion concentrations, [ION], in the lower fractions, and no successive approximation is necessary.

Having calculated the concentrations of the free ions, the accurate ionic strength, μ_{Acc}, is calculated by eqn. 17, and $\log f_{\pm}^2$ is calculated from eqn. 13.

Hence the solubility product, S, by eqn. 10.

The Constancy of Solubility Product.

Values of S calculated by this method are not constant but increase slightly with ionic strength of solution (see p.179.). This is due to the fact that the constants of the Davies equation were chosen primarily to give an expression of the widest applicability and for individual salts it is naturally possible to fit the data by changing these parameters.

Vosburgh (14,16) used two such equations in his work on the solubilities of silver iodate and silver bromate in potassium nitrate solutions at 25°C. No allowance was made for ion-pair formation.

$$\underline{\text{Silver Iodate}} \quad -\log f_{\pm}^2 = \frac{1.012\sqrt{\mu}}{1+\sqrt{\mu}} + 0.320\mu$$

$$\underline{\text{Silver Bromate}} \quad -\log f_{\pm}^2 = \frac{1.012\sqrt{\mu}}{1+\sqrt{\mu}} + 0.20\mu$$

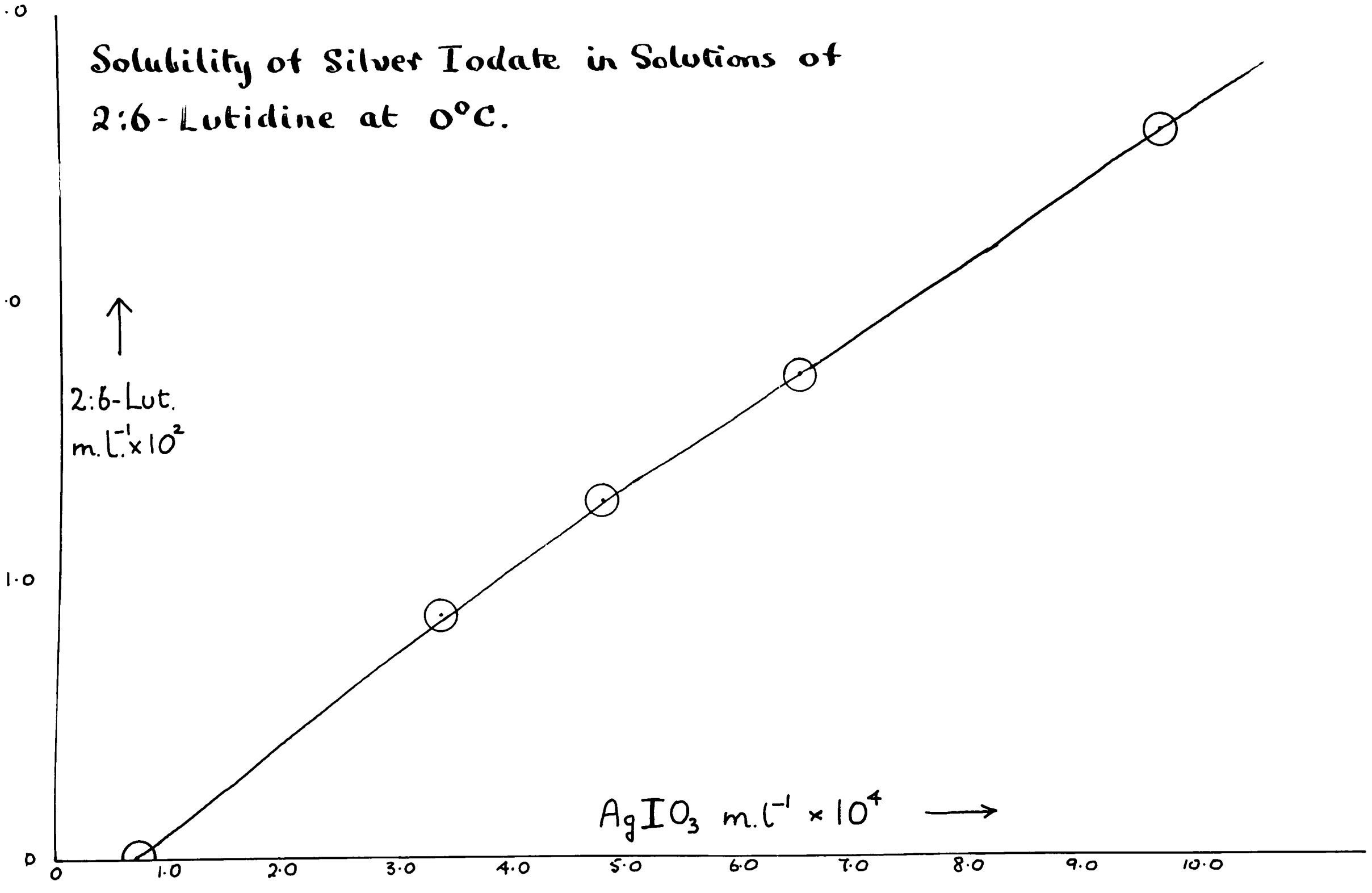
These equations were applied to our results and found to give less consistent values for S than did the Davies equation.

Instead of forming our own empirical equations we preferred to use the Davies equation for two reasons:-

(1) Over the small range of ionic strengths in the amine solutions, (0.003 to 0.017 for $AgBrO_3$ and 0.0001 to 0.0015 for $AgIO_3$), the equation does give constant values of S.

(2) An exact empirical equation for KNO_3 solutions would not necessarily be correct for amine solutions, especially if ion-pair formation were ignored.

Solubility of Silver Iodate in Solutions of 2:6-Lutidine at 0°C.



The Solubility of a Silver Salt in Amine Solutions.

Methyl-pyridines are very weak bases (p.107) and ionise only to a very small extent in aqueous solution. In the weakest solutions used, the percentage of ionised form, AH^+, was only 0.3%. In all cases it was possible to write $C'_A = C_A$, where C'_A is the total amine placed in solution and C_A is total amine available for forming complexes with Ag^+.

A silver salt, AgX, is more soluble in an amine solution than in water, because Ag^+ ions are removed as AgA^+ and AgA_2^+. When the amine solution is saturated with silver salt, the following species are present:-

$$Ag^+,\ X^-,\ AgX^{\pm},\ AgA^+,\ AgA_2^+,\ A.$$

($[Ag^+]$ is less than in water and $[X^-]$ greater.)

From eqns. 10 and 11,

$$[AgX^{\pm}] = S/K_{AgX} \quad \text{(a constant)} \qquad \ldots\ 22.$$

For a given temperature, $[AgX^{\pm}]$ is a constant independent of ionic strength and readily calculated.

The total concentration of the anion, C_X, is determined by analysis of the solution.

The concentration of free anion, $[X^-]$ is given by

$$[X^-] = C_X - [AgX^{\pm}]$$

By electrical neutrality,

$$[X^-] = [Ag^+] + [Ag^+A] + [Ag^+A_2]$$

So, $C_X = [Ag^+] + [Ag^+A] + [Ag^+A_2] + [AgX^-]$

But $C_{Ag} = [Ag^+] + [Ag^+A] + [Ag^+A_2] + [AgX^-]$

..... 23.

So, $C_X = C_{Ag} = C_{AgX}$ (total concentration of silver salt in solution).

The ionic strength of solution is:-

$$\mu = \left\{ [Ag^+] + [AgA^+] + [AgA_2^+] + [X^-] \right\}$$
$$= C_{AgX} - [Ag^+]$$

Using this value of μ, $f_\pm$ is calculated by the Davies eqn. 13,

Since $[Ag^+]\,[X^-]\,f_\pm^2 = S$ ..... 10.

and since $[X^-]$, $f_\pm$, and S are known, $[Ag^+]$ is calculated.

Now

$$C_{Ag} = [Ag^+] + [AgX^\pm] + [AgA^+] + [AgA_2^+] \quad .... 24.$$

$$C_A = [A] + [AgA^+] + 2[AgA_2^+] \quad .... 25.$$

By eqns 7 and 8,

$$C_{Ag} = [Ag^+] + [AgX^\pm] + K_1[Ag^+][A] + K_1K_2[Ag^+][A]^2 \quad .... 24a.$$

$$C_A = [A] + K_1[Ag^+][\ ] + 2K_1K_2[Ag^+][A]^2 \quad .... 25a.$$

In the two equations above, 24a and 25a, there are three unknowns, K_1, K_2, and $[A]$. K_1 and K_2 are constants and, by

taking a series of amine solutions, [A] is varied. K_1 and K_2 are found by a series of successive approximations which are briefly described below:-

Methods of Successive Approximations.

When silver iodate (the less soluble salt) dissolves in the strongest amine solution, conditions are most favourable for the formation of the AgA_2^+ complex. For finding an approximate value of β_2, the assumption is made that the solution contains an unimportant concentration of AgA^+.

$$\text{Then } C_{IO_3} = [Ag^+] + [AgA_2^+]$$

$$[A] = C_A - 2[AgA_2^+]$$

$$= C_A - 2C_{IO_3} + 2[Ag^+]$$

$$\text{Then } \beta_2 = \frac{C_{IO_3} - [Ag^+]}{[Ag^+](C_A - 2C_{IO_3} + 2[Ag^+])} \quad \ldots\ 26.$$

The rough value of β_2 is used for finding K_1 from bromate solubility measurements where the formation of AgA^+ is favoured. Subtraction of eqn. 24a from eqn. 25a gives

$$2[Ag^+][\ ]^2 + [A] - [Ag^+] - C_A + C_{Ag} - [AgA^+] = 0$$

$\ldots\ 27.$

which is a quadratic in [A]. Hence [A] for each bromate

solution. Subtraction of eqn. 24 from eqn. 25 gives :-

$$[AgA^+] = 2C_{Ag} - 2[AX^-] - C_A + [A] - 2[Ag^+] \quad \ldots 25.$$

Now

$$K_1 = \frac{[AgA^+]}{[Ag^+][A]} \quad \ldots 7.$$

So

$$K_1 = \frac{2C_{Ag} - 2[AX^-] - C_A + [A] - 2[Ag^+]}{[Ag^+][A]} \quad \ldots 29.$$

K_1 is calculated for each bromate solution and the average value is used to find β_2 in the solutions of silver iodate. Rearrangement of eqn. 29 gives:-

$$[A] = \frac{C_A - 2C_{Ag} + 2[Ag^+]}{1 - K_1[Ag^+]} \quad \ldots 29a.$$

Hence [A] is found for each iodate solution.

The concentration of $[AgA^+]$ is found by

$$[AgA^+] = K_1[Ag^+][A] \quad \ldots 7.$$

Finally, concentration of AgA_2^+ is calculated by:-

$$[AgA_2^+] = C_{Ag} - [Ag^-] - [AgA^+] - [Ag^+] \quad \ldots 24.$$

All values are known for the calculation of

$$\beta_2 = \frac{[Ag^+A_2]}{[Ag^+][A]^2} \quad \ldots 9.$$

The average value of β_2 for the iodate solutions is found and used to find a more accurate value for K_1.

K_1 and β_2 are recalculated until they give mutually consistent values. Then, $K_2 = \beta_{2/K1}$

A Saturator

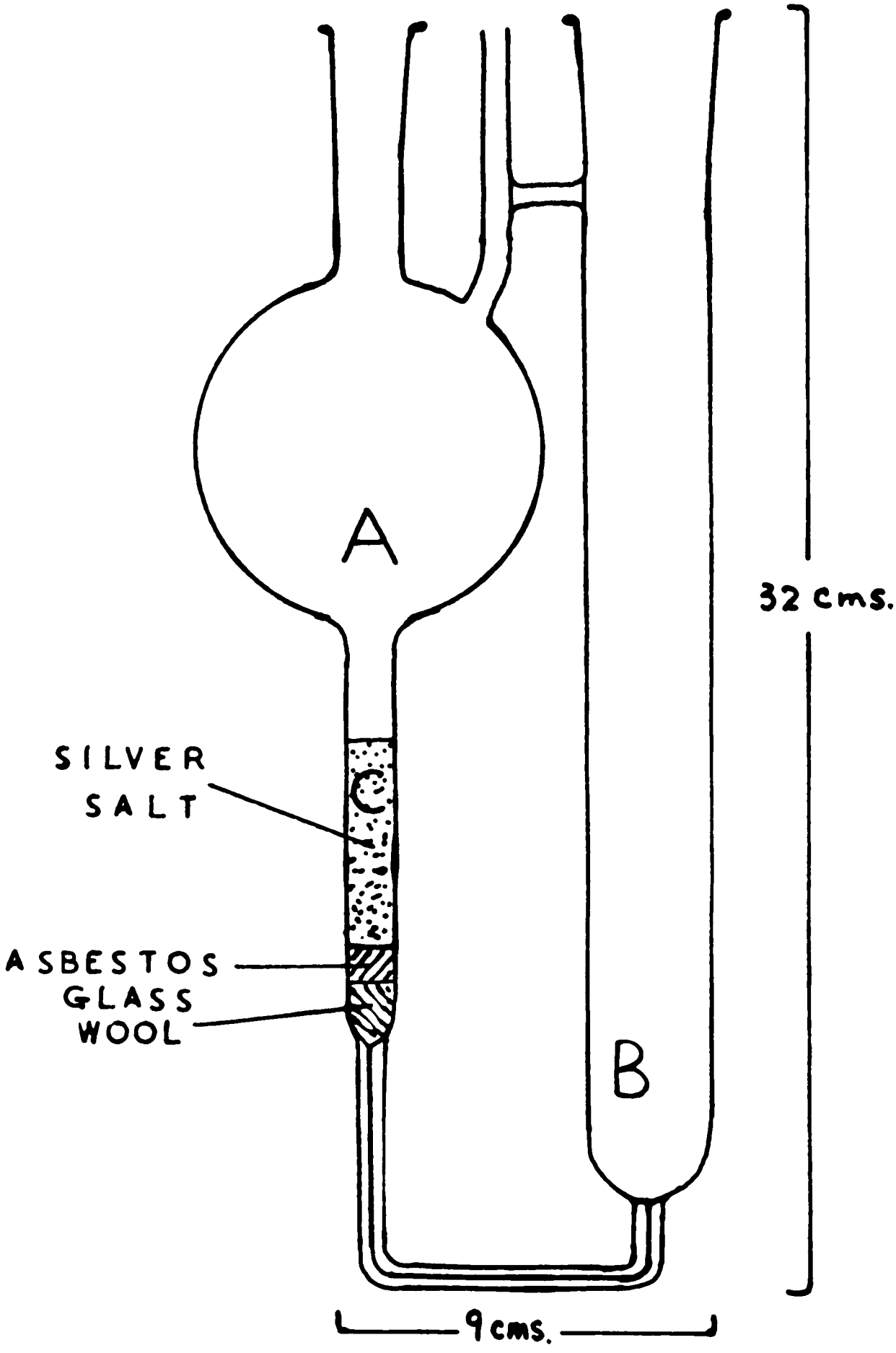


fig. 1.

The Apparatus.

Earlier workers in this field saturated solutions by shaking solvent with excess solid in stoppered flasks for several hours in a thermostat. Samples of solution were filtered off and analysed, but often the results were not consistent and several reasons for this have been suggested.

e.g. The crystals of solid disintegrate and fine particles, in suspension, pass through the filter. (14).

Silver ions exchange with sodium ions in the glass. (32).

In our experiments, saturators of the type used by Monk and Davies (21,29) were used. A diagram of one is given opposite p.28 (fig. 1). It is made of Pyrex glass and fitted with ground-glass stoppers.

Solution is placed in bulb, A. It slowly flows through the column of solid silver salt, C, which rests on a filter pad of Gooch asbestos, which, in turn, rests on a pad of glass wool. Solution collects in limb, B. The solution is withdrawn from B by pipette.

Building the Column.

Small pieces of glass wool were dropped down the tube and tamped down with a glass rod. Secondly, Gooch asbestos was dropped down the tube and tamped down to form a second layer. Each layer was about half a centimetre in thickness.

Dry powdered ~~silver~~ silver salt was placed inside bowl, A, above the column, and distilled water poured in to fill the column and the bottom of the bowl. The bowl was gently agitated so that the solid settled slowly down the tube, forming a regularly packed column, free from channels and air pockets. At least half a litre of water was passed through it to wash out the "fines".

Temperature Control.

At 25°C and 40°C, the saturators were suspended in a thermostat, whose temperature was regulated to ± 0.02°C.

At 0°C, the saturators were placed in a large Dewar vessel, containing a mush of ice and distilled water, stirred by an air jet.

Preparation of Solutions.

Potassium Nitrate Solutions.

Accurately weighed amounts of potassium nitrate were dissolved in accurately weighed amounts of distilled water, (from 1 gm. to 10 gm. of potassium nitrate in 1000 gm. water).

A density correction was applied to express the concentration in terms of moles per litre. In the most concentrated solution, molality and molarity differed only by 0.5%.

Amine Solutions.

Accurately weighed amounts of the amines were placed in standard flasks and made up to 1000 ml. with distilled water. Since the strongest solution was about 5 gm. per litre, no density correction was made, the solutions being assumed to have unit density.

Experimental Procedure.

The procedure is the same whether the solvent is pure water, potassium nitrate solution, or an amine solution.

100 ml. of solvent were placed in bulb, A. The vessel was stoppered and placed as deeply as possible in the water, (or ice), so that the upper surfaces were covered.

At 40°C, this submersion is of great importance, since water vapour rapidly condenses on the inner walls of the vessel above water level, altering the constitution of the solutions.

The column was built to such a depth that 100 ml. of solvent passed through it in an hour. At 0°C, the solvent was more viscous, and a little suction was applied at the mouth of limb, B.

The solution was removed from B by pipette and returned to A. At 40°C, the pipette was preheated, so that crystals of the silver salt were not deposited from the hot solution onto the cold walls of the pipette.

It was found that a solution usually became saturated after passing through the column three times. After the third time, two separate samples of solution were withdrawn from B, by pipette, and analysed. Analysis was by the iodimetric titration described below. The familiar volumetric method was adapted so that weights, and not volumes, of solutions were measured, giving more accurate analyses.

The remaining solution in B was again passed through the column and two more samples were analysed. If the analyses of these latter samples did not agree with those of the former, the solution was again passed through the column and analysed.

Usually, five or six consistent analyses were performed to obtain the best result.

Iodimetric Titration

Samples of bromate and iodate solutions were treated with excess solid potassium iodide and about 10 ml. of 2N sulphuric acid. The iodine liberated was titrated with aged standard $N/_{100}$ sodium thiosulphate solution with starch solution as indicator.

Weight Titration Procedure.

The titrations were performed in light, 100 ml. conical flasks fitted with ground glass stoppers. The flasks were

cleaned with chromic acid and distilled water, rinsed with acetone and dried by compressed air. They were weighed to the nearest milligram on an air damped balance. Each titration required four weighings.

The main volume of sodium thiosulphate solution was run in from a 50 ml. burette. The last half millilitre of sodium thiosulphate solution at the end point was run in from a microburette which read to 0.005 ml.

The weighings were carried out as follows:-

First Weighing.

Stoppered dry empty flask ..... A gm.

The sample of solution to be analysed was run into the flask.

Second Weighing.

Stoppered flask + sample..... B gm.

10 ml. of sulphuric acid and 0.2 gm. of potassium iodide were added to the sample in the flask.

Third Weighing.

Stoppered flask + sample + KI + H_2SO_4..... C gm.

The flask now contained iodine in yellow solution. Standard sodium thiosulphate from the 50 ml. burette was run into the flask until only the last trace of yellow colour remained.

Fourth Weighing.

Stoppered flask + sample + KI + H_2SO_4 + standard thiosulphate..... D gm.

Starch solution was added, whereupon the solution became blue. Standard sodium thiosulphate from the microburette was run in drop by drop until the blue colour just disappeared.

Let the volume of standard solution from the microburette be x ml. No appreciable error is introduced by assuming that this small volume had unit density.

Then (B - A) gm. sample soln. ≡ (B-C + x) gm. standard sodium thiosulphate solution.

The sodium thiosulphate solution is standardised in terms of the number of gm. ions of iodate which are equivalent to 1 gm. of sodium thiosulphate solution.

The number of gm. ions of iodate or bromate ions in the above sample of solution are found from the weight of standard sodium thiosulphate solution used in the titration.

For the purpose of standardising the $N/_{100}$ sodium thiosulphate solution, a solution of potassium iodate of approximate strength $N/_{20}$ was made up accurately. About 2 gm. of dry potassium iodate were weighed to the nearest tenth of a milligram and dissolved in 1000 gm. of distilled water.

The thiosulphate solution was titrated against 5 gm. samples of the prepared iodate solution by the weight method.

The Titration End-Point.

In estimations of silver bromate or silver iodate, silver iodide in fine suspension caused a bluish opalescence which obscured the final disappearance of the starch-blue colour. To sharpen the colour change, a few drops of a yellow dye were added. (Actually, brom-cresol green, which is yellow in acid, was used). The end-point was now the change from blue-grey to yellow solution and occurred over the addition of 0.01 ml. from the microburette.

The excess "AnalaR" potassium iodide, added in each titration, was shown to contain no iodate by blank tests. The weight added was about 0.2 gm. per titration, since larger amounts were found to give a mauve end-point, giving less consistent values for the determination.

Errors in Determination.

The strength of the standard sodium thiosulphate solution altered with time and was standardised against the standard potassium iodate solution each day before use. The estimations were consistent to one part in a thousand. The sodium thiosulphate became steadily weaker by about 1% per week.

In all cases, bromate solutions gave results, on analysis consistent to $\pm$ 0.1%. Iodate solutions could not

be estimated with such precision, especially at 0°C, where some solutions were as weak as $1/_{4000}$ mole/litre. Errors varied from ± 0.1% to ± 0.3%.

Since in no amine solution investigated was the strength of the silver salt greater than 3.5 gms/litre, only a second order error was introduced by setting molarities equal to molalities.

Results of Solubility Product Investigations.

The solubilities of silver bromate and silver iodate were measured at 25°C in aqueous solutions of potassium nitrate. Results are given on, p.179.

Graphs of the increase of solubility with increasing strength of potassium nitrate are given opposite pp.36,37. The results of other investigators have been plotted on the same graphs for purposes of comparison.

The discrepancies lie outside the range of experimental error and this is almost certainly due, not to systematic error, but to real differences in the solubilities of the samples used.

As illustration, the measured solubilities of silver iodate in water at 25°C found by various workers are given below in Table II.

Solubility of Silver Iodate in Potassium Nitrate Solutions at 25°C.

○ Present work.

○ (32)

○ (35)

$AgIO_3$ m.l^{-1} x 10^4

2.50
2.25
2.00
.75

KNO_3 m.l^{-1} x 10^2 →

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0

TABLE II

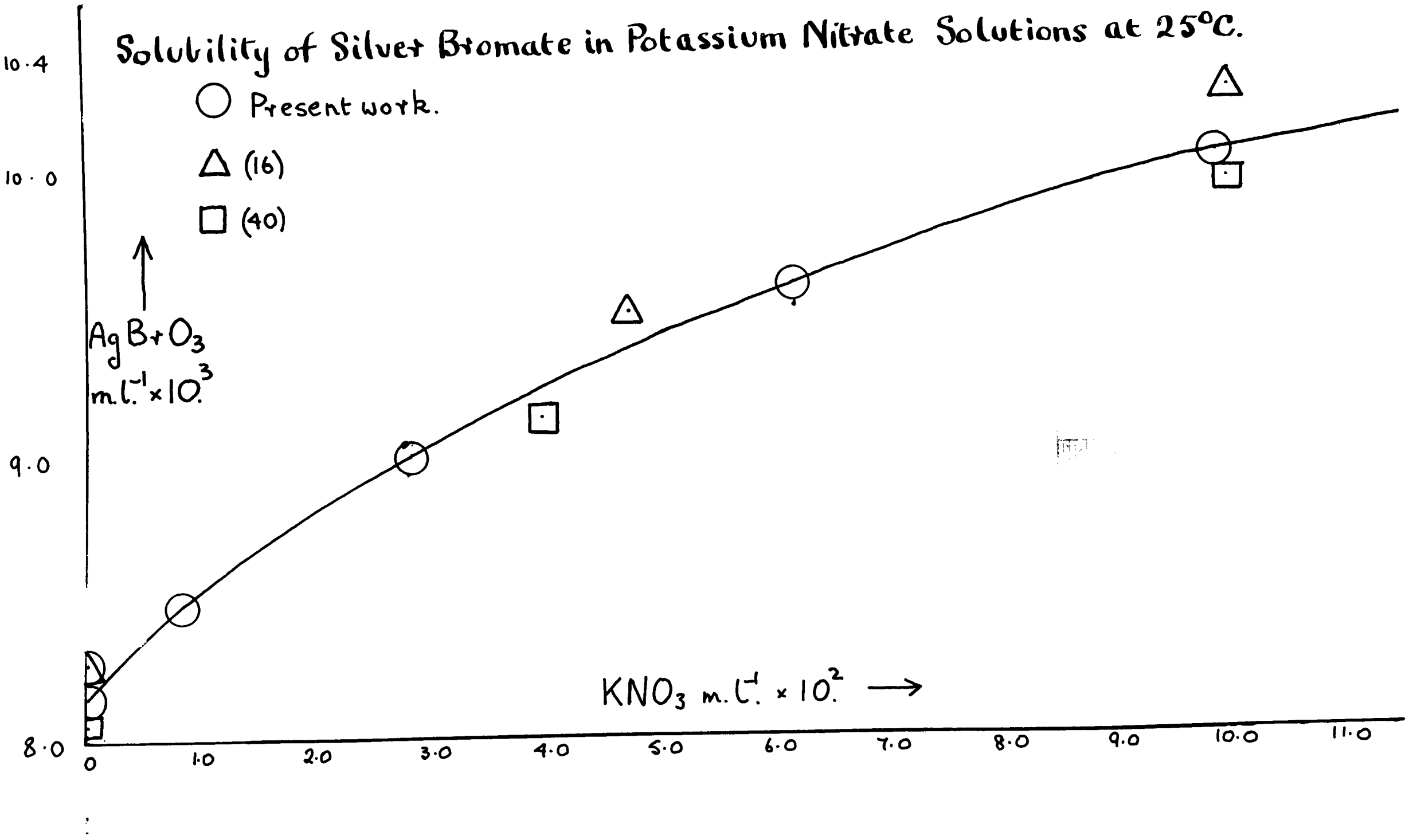
Solubility of $AgIO_3$ in Water at 25°.

Solubility g.mol./l. x 10^4	Workers	Reference
1.79	Kohlrausch	(33)
1.789	Keefer	(34)
1.788	Present work.	
1.787	Vosburgh	(14)
1.785	Li and Lo	(35)
1.78	Monk	(21)
1.776	Kolthoff	(32)

Mean deviation

1.785 $\pm$ 0.005

Solubility of Silver Bromate in Potassium Nitrate Solutions at 25°C.



RESULTS.

From the solubility product investigations, the following results were obtained:-

Solubilities of Silver Salts in Water. g.mol./l.

Salt.	0°C.	25°C.	40°C.
$AgBrO_3$	3.012×10^{-3}	8.155×10^{-3}	$1.3[illegible] \times 10^{-2}$
$AgIO_3$	$6.85(5) \times 10^{-5}$	1.788×10^{-4}	$3.05(5) \times 10^{-4}$

Solubility Products of Silver Salts.

Values of log. S.

Salt	0°C	25°C	40°C.
$AgBrO_3$	$\bar{6}.8941$	$\bar{5}.7310$	$\bar{4}.136$
$AgIO_3$	$\bar{9}.6720$	$\bar{8}.4920$	$\bar{7}.940$

Silver Bromate Ion-Pair.

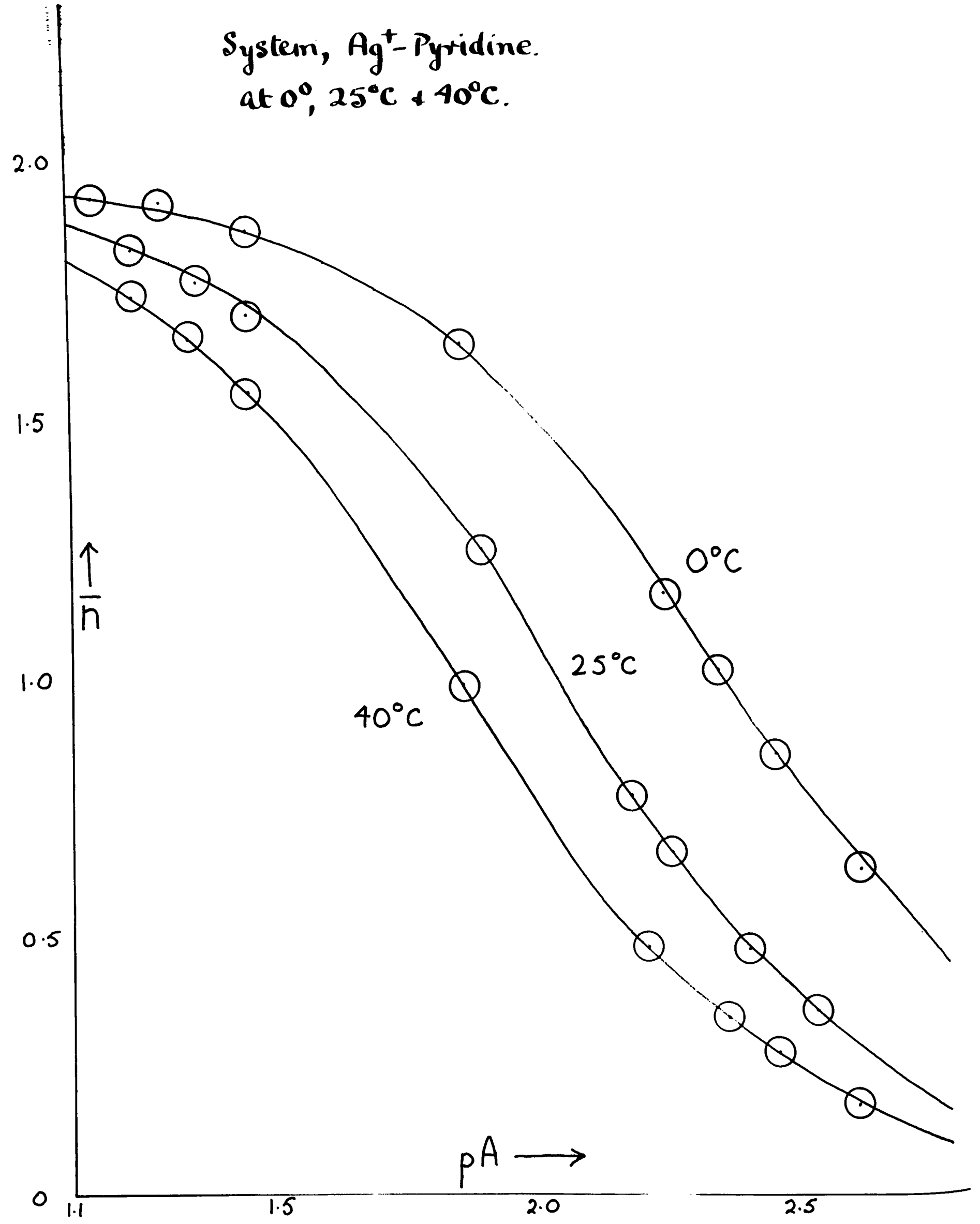
The concentration of $AgBrO_3^{\pm}$ is a constant at a given temperature, given by the equation:-

$$\log [AgBrO_3^{\pm}] = \log S - \log K_{AgBrO_3} \quad \ldots 18a.$$

Found.

g.mol./l.	0°C.	25°C.	40°C.
$[AgBrO_3^{\pm}]$	0.0000147	0.000108	0.000309

System, Ag^+ - Pyridine.
at 0°, 25°C & 40°C.



Silver Ammines.

The stability constants for the complexes of silver with pyridine and with 2:6-lutidine were measured at 0°C, 25°C and 40°C. The results of solubility measurements at these temperatures are given on pp.180-5 . A typical graph of the variation of solubility of silver salt with concentration of amine is given opposite p.24 .

Formation Curves.

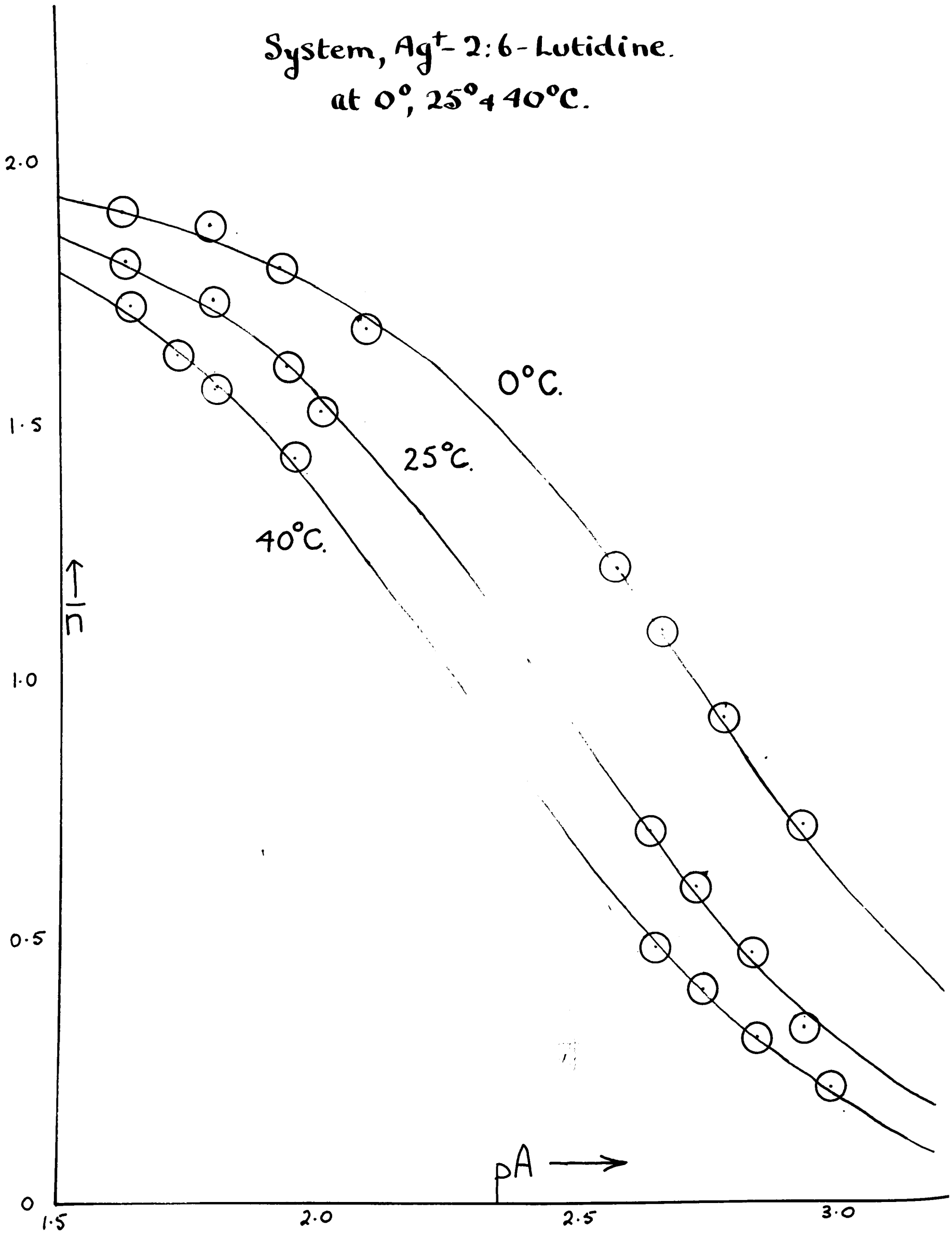
The graphical plot of the degree of formation, $\bar{n}$, against the negative logarithm of concentration of free ligand, pA is the most generally used means of presenting results for systems of complex ions. From measurements by the pH method, pA and $\bar{n}$ are intermediate quantities in the calculation of stability constants, where total metal, total amine, and free amine concentrations are known. In the solubility method, total metal, total amine and free metal concentrations are known.

$$\text{Now } \bar{n} = \frac{[\text{Total ligand}] - [\text{Free ligand}]}{[\text{Total metal}]}$$

In calculating $\bar{n}$ for solutions of silver-ammine, since the ion pair AgX^+, plays no part in complete formation,

$$\bar{n} = \frac{C_A - [A]}{C_{Ag} - [AgX^+]}$$

System, Ag^{+} - 2:6 - Lutidine.
at 0°, 25° & 40°C.



From eqns. 24a and 25a, $\bar{n}$ is given by the familiar expression:-

$$\bar{n} = \frac{K_1[A] + 2\beta_2[A]^2}{1 + K_1[A] + \beta_2[A]^2}$$

Using values of K_1 and β_2 found by the solubility method, and calculating $\bar{n}$ for selected values of pA, formation curves are plotted.

The actual experimental points are plotted on the same graphs.

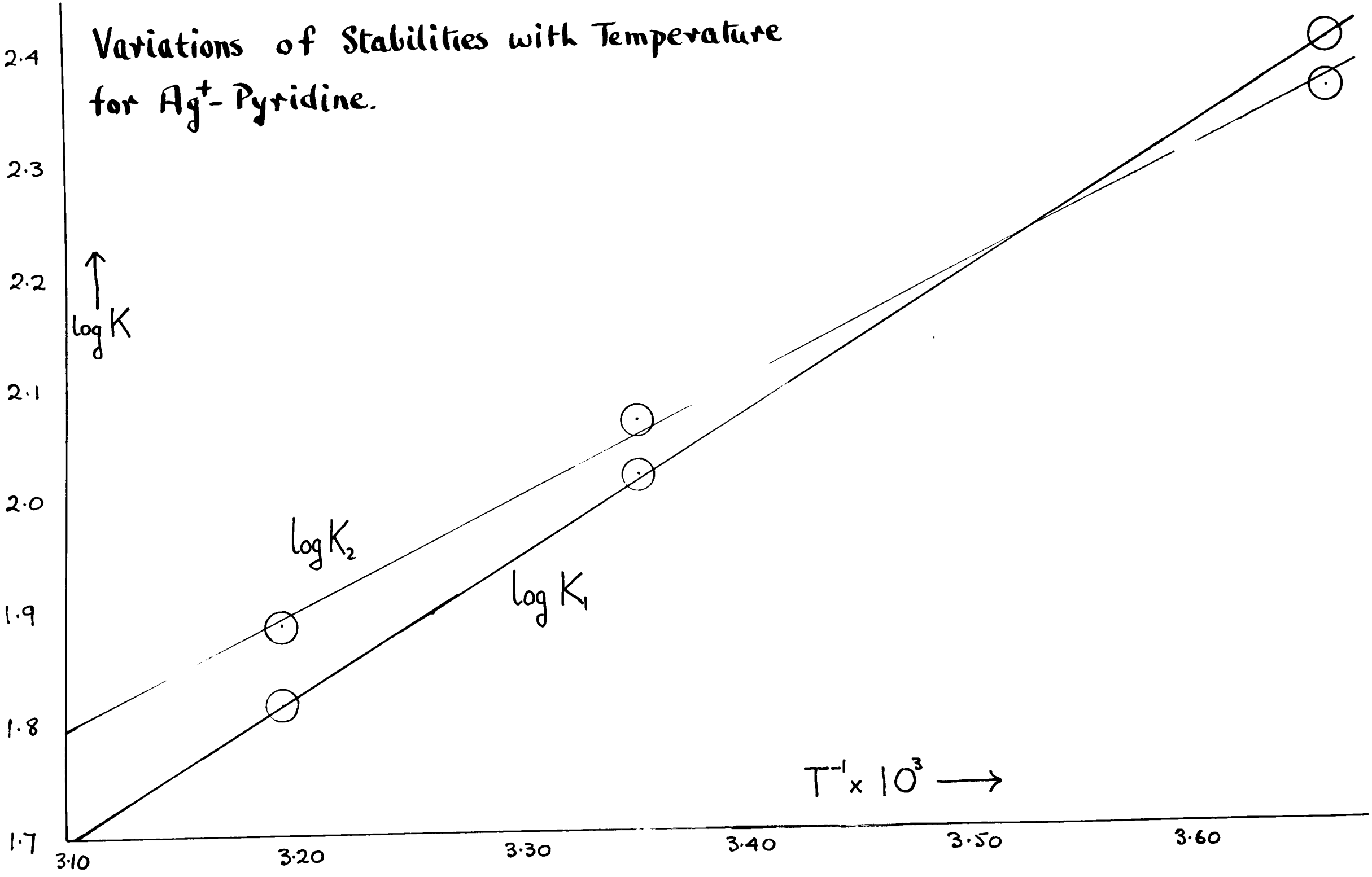
The two graphs are opposite pp.38,39.

From the variation of log K with temperature, the entropy and enthalpy changes in the reactions were calculated. Graphs of log K against $1/T$ are given opposite pp.40,41.

The best straight line for points at the three temperatures at which observations were made, was calculated by the method of least squares. It was assumed that T was a variable measured without error, whereas log K was a variable containing errors. The standard deviations of the values of ΔS and ΔH so calculated were also determined. The results are given in Tables III and IV.

The values of ΔH_{12} were found to be not identical with those found by direct calorimetric measurement, p.97 No other silver-ammines were studied by this method.

Variations of Stabilities with Temperature for Ag^{+}- Pyridine.



Results for Silver-Ammines by the Solubility Method.

Reactions:-

1. $Ag^+ + A \longrightarrow AgA^+$

2. $AgA^+ + A \longrightarrow AgA_2^+$

1.2. $Ag^+ + 2A \longrightarrow AgA_2^+$

Table III

Silver with Pyridine

	Log K			$-\Delta F^{25^\circ}$	$-\Delta H$	ΔS
Reaction	0°C	25°C	40°C	cal./g.ion	cal/g.ion	cal./g.ion
1.	2.393	2.017	1.813	2,750	5,660	- 9.8
2.	2.350	2.065	1.886	2,800	4,500	- 5.7
1.2.	4.743	4.082	3.699	5,550	10,160	- 15.5

Mean deviation.

$\Delta F \pm$ 30 cal./g.ion

$\Delta H \pm$ 20 cal./g.ion

$\Delta S \pm$ 0.15 cal./g.ion/°C

Variation of Stabilities with Temperature for Ag^{+} – 2:6-Lutidine.

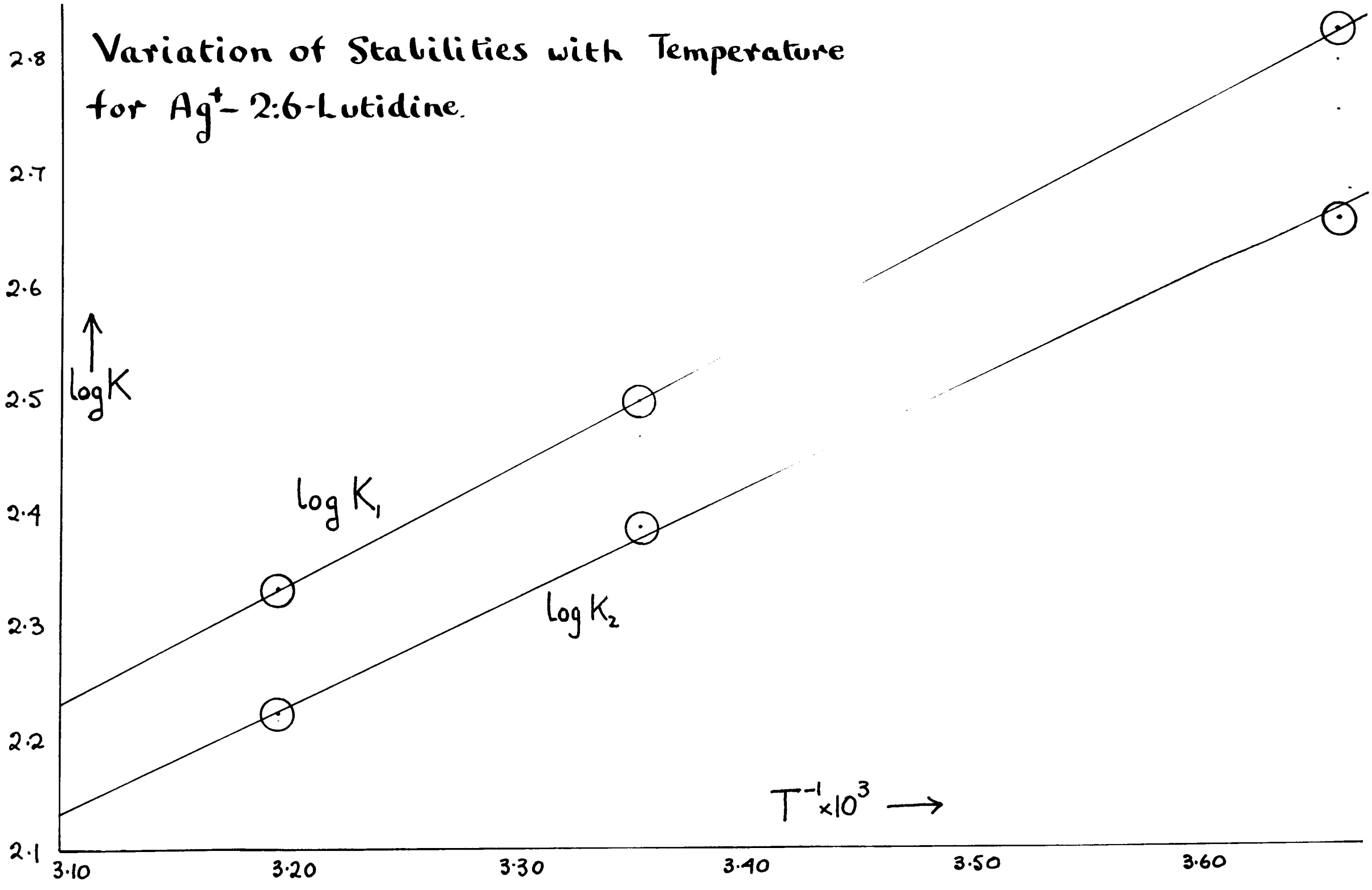


TABLE IV.

Silver with 2:6-Lutidine

Reaction	log K 0°C	log K 25°C	log K 40°C	$-\Delta F^{298}$ cal./g.ion	$-\Delta H$ cal./g.ion	ΔS cal./g.ion
1.	2.822	2.497	2.330	3,400	4,820	- 4.7
2.	2.655	2.384	2.220	3,250	4,225	- 3.3
1.2.	5.477	4.881	4.550	6,650	9,045	- 8.0

Mean Deviation.

$\Delta F \pm 30$ cal./g.ion

$\Delta H \pm 20$ cal./g.ion

$\Delta S \pm 0.10$ cal./g.ion/°C

SECTION II

Determination of Heats of Formation of Ethylenediamine Complexes by a Glass Electrode Method.

Since Williams first measured enthalpy changes in the formation of complexes of ethylenediamine with divalent transition metals of the first long period, by measuring stability constants at different temperatures with the glass electrode, several other independent workers, using essentially the same method have published results for the same systems. The system which has been examined more frequently than any other, is that of cupric ion with ethylenediamine. Reported values for enthalpy changes are given in chronological order in Table V (p.43.) and disagree widely from one another.

Such large discordancies in $-\Delta H$ values are often found when the results of several independent workers on any one system are compared. The discrepancies must be mainly due to systematic errors incidental to the use of the glass electrode and there has been no general or full realisation of the uncertainties of the method. At the same time it must be pointed out that measurements by different workers seldom refer to the same ionic strengths or salt concentrations and an evaluation of such factors must be taken into account.

It was decided to reinvestigate the system, copper-ethylenediamine under the same conditions of ionic strength

TABLE V.

Method.	Background Salt	Ionic Strength	Temp. Range	cal./g.ion $-\Delta H_1$	$-\Delta H_2$	$-\Delta H_{12}$	Worker	Ref.
Cu/Hg Electrode	1.0 M KNO_3	1.40	6°	-	-	26,100	Bjerrum	(12)
Glass Electrode	0.10 KCl	0.13	40°	18,920	16,830	35,750	Williams	(10)
"	0.50 M KNO_3	0.78	25°	8,600	8,600	17,200	Basolo	(13)
"	0.001 M $Cu(ClO_4)_2$	0.005	40°	11,600	11,300	22,900	McIntyre	(36)
"	0.10 KCl	0.13	20°	14,600	14,100	28,700	Present Work	
"	1.80 KNO_3	2.15	30°	14,600	13,800	28,400	Spike & Parry	(37)
Calori-meter	1.0 M KNO_3			13,000	12,100	25,100	Bjerrum	(38)
	0.10 M KCl	0.10				25,160	Staveley	(48)
	0.10 M KCl	0.10				25,080	Present Work	
	0.50 M KNO_3	0.50				24,600	Basolo	(67)

and concentration as those used by R.J.P. Williams to find whether or not the glass electrode method could be used to yield reliable values of ΔH.

The attraction of the method is that it allows the measurement of enthalpy changes in the formation of <u>each</u> complex species present in the solution. It is usually not easy to find such enthalpies by direct calorimetry. The chief shortcoming of the method is that even for reactions where $-\Delta H$ is large, the change of stability constant with temperature is small.

e.g. For a reaction where $-\Delta H$ = 10,000 cal./g.mol.

From the eqn. $$\frac{d \ln K}{dT} = \frac{-\Delta H}{RT^2}$$

it may be calculated that over a temperature interval of 10°C, say 20°C to 30°C, log K will change by $\sim$ 0.25 units.

Although the glass electrode method is one of the most accurate methods for measuring stability constants, the error in log K, even in careful, accurate work is about $\pm$ 0.03 units. It can readily be seen that although this represents a small percentage error in log K, over a small temperature range the resulting error in ΔH can be quite large. However, for some of the many systems for which

stabilities only have been measured, values of enthalpy changes, uncertain even to $\pm$ 10%, would, nevertheless, be of interest.

The theoretical assumptions and points of experimental techniques which could be responsible for errors in ΔH and might account for the wide variations noted in Table V, (p.) for copper-ethylenediamine will be examined critically here, with especial reference to our own measurements on complexes of copper and nickel with ethylenediamine.

The system copper-ethylenediamine was first chosen for investigation for several reasons:-

(1) The two complexes* formed are very stable ($\log \beta_2 \sim 20$)

(2) The Formation curve is symmetrical about $\bar{n} = 1$ (as would be expected for a system where N = 2).

(3) The heats of formation of both $CuEn^{2+}$ and $CuEn_2^{2+}$ are very large.

(En is an abbreviation for ethylenediamine

Tn is an abbreviation for 1:3-diaminopropane).

These three factors are favourable because:-

(1) Two and only two well-defined complexes are formed.

* J. Bjerrum has shown spectrophotometrically, that a tris-ethylenediamine complex of cupric copper does exist; but it is highly unstable (log K_3 = -1.0) and is not present in dilute amine solutions such as those used here (12).

(2) It is relatively easy to calculate values of K_1 and K_2 from a symmetrical formation curve.

(3) Large heats of formation cause the plot of log K against $1/T$ to have an appreciable slope.

Preliminary calorimetric measurements made by J. Bjerrum (38), then available showed

for $CuEn^{2+}$ $\quad -\Delta H_1 = 13{,}000$ cal./g.ion

for $CuEn_2^{2+}$ $\quad -\Delta H_{12} = 25{,}100$ cal./g.ion

---

In the first part of this section the technique of the pH titration method and the apparatus in which the titrations were made will be described with especial reference to the behaviour of the glass electrode at different temperatures, the constancy of liquid junction potential, the standardisation of the electrode system and the accuracy with which pH may be determined.

The Glass Electrode Method.

The principles of the method are well known and have been given in full in several accounts (3, 39, 41). Briefly, by measuring the pH of a solution containing known amounts of metal ion, acid and amine, and from a knowledge of the acid dissociation constants of the amine, the degree of

formation of the system, $\bar{n}$, and the concentration of free amine present, [A], are calculated. From a series of such measurements the formation curve can be drawn for the system ($\bar{n}$ against pA) and from it the stability constants of the metal ammine complexes are calculated. By making measurements at different temperatures, the variation of stability with temperature is found and hence enthalpy changes.

Williams devised a method suitable for amines available only in very small quantity. Amine, metal-ion and acid were mixed in known amounts and the pH of the mixture measured at a series of rising and falling temperatures. A known amount of acid was added and the pH again measured at intervals over the same temperature range. The process was repeated for different concentrations of total acid and in this way curves relating pH to composition of solution could be plotted for each of a number of temperatures. In the course of this work it was found that the glass electrode was subject to "thermal hysteresis". (42).

In the present method, to avoid any irregular behaviour of the glass electrode due to changes in temperature, the apparatus was mounted in a water thermostat and the whole

formation curve for the system was measured at one temperature using the pH titration method. Before readings were taken at a different temperature, the electrode system was allowed to "settle down" for a period of time at that temperature.

A description of the apparatus and of the procedure of standardisation of the glass electrode is given on pp. The accuracy with which K's are determined depends primarily upon how precisely the pH is measured. In the apparatus used, pH could be measured to $\pm$ 0.01 units at temperatures between 20°C and 40°C. Measurements were made at 20°C, 25°C, 30°C, and 40°C.

Titration Procedure.

All solutions were made up in boiled-out distilled water and the intrusion of atmospheric CO_2 was prevented by tubes of "Sofnolite". While a run was in progress, solutions in the reaction cell were protected by bubbling nitrogen, which had been freed from CO_2 through them.

Ethylenediamine solution of strength $\sim$ 1.0 M was added to the solution in the cell from a microburette which could be read to 0.002 ml.

The preparation of materials used in these experiments is described on p. 169.

Acid Dissociation Constants of Ethylenediamine.

After standardising the electrode, the cell was rinsed out several times with distilled water and 25 ml. of standard HCl of accurately known strength (~ 0.10 N) was pipetted into the cell. Successive volumes of ethylenediamine solution were added from the microburette, and after each addition, the solution was stirred and the steady pH which it attained was read on the pH meter. (Solutions, except when very acid or alkaline, gave steady readings almost instantaneously). Curves of pH against volume of amine solution added were plotted and from the point of greatest slope, the amine strength was calculated. The dissociation constants were calculated by the method described on p.79 . Replicate experiments were performed at each temperature and runs were found to be highly reproducible (i.e. to 0.01 pH units).

Stability Constants.

Titrations were performed with 25 ml. of metal-acid solution in the reaction cell. The metal-acid solutions contained:-

0.40 M HCl

0.60 M KCl

0.005 M metal sulphate.

The "AnalaR" grade metal salts used were analysed by standard

Cell for pH Titrations.

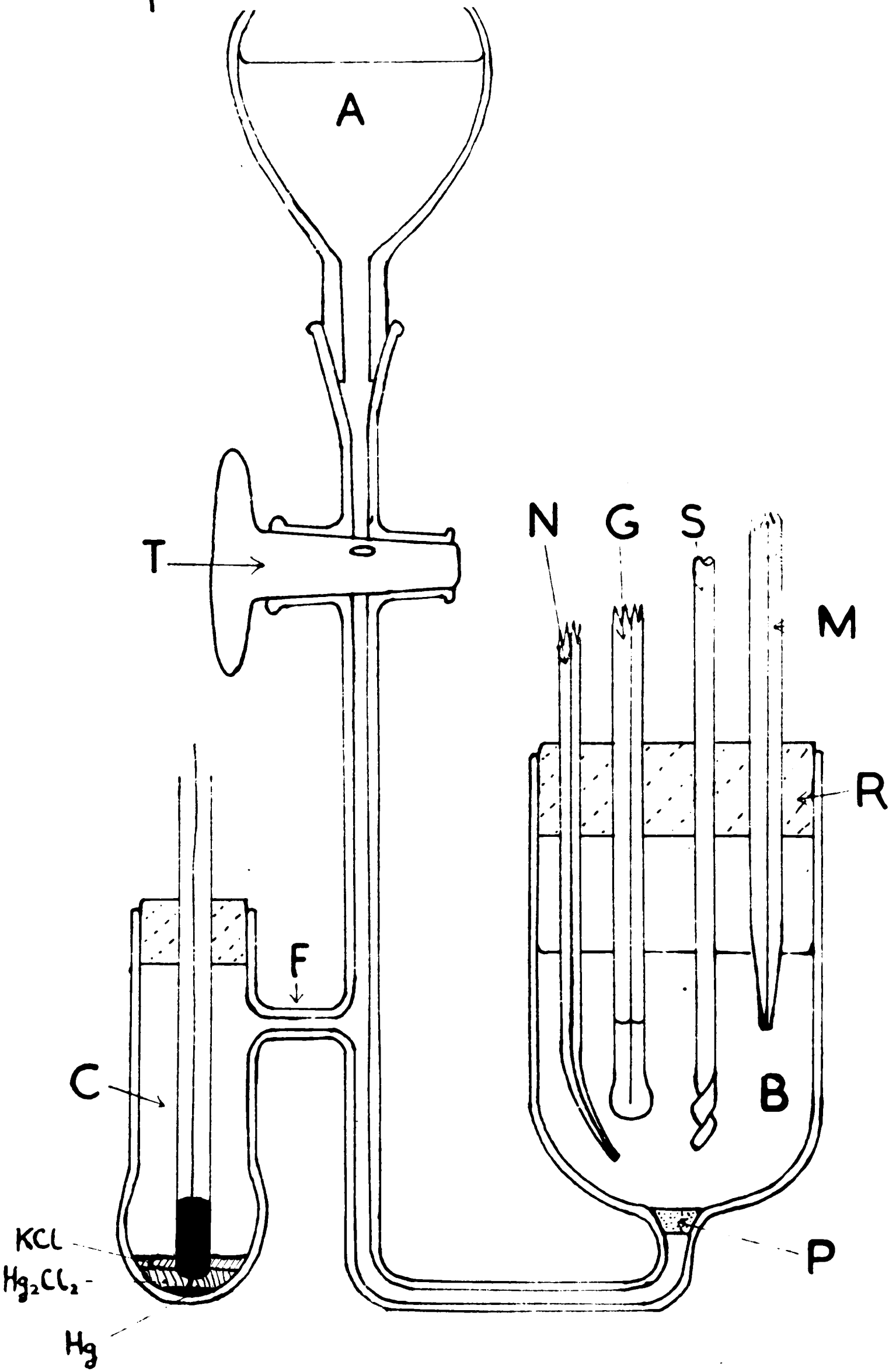


fig .2.

analytical procedures and solutions made up accordingly. Ethylenediamine solution, previously standardised by pH titration, was added in successive increments from the microburette with stirring and the resulting pH values read on the meter. The mean of several runs,(which were again highly reproducible), was taken at each temperature. The calculation of the formation curves is described on p.83. and the calculation of stability constants on p.85

Apparatus.

A diagram of the apparatus used (fig. 2) is given opposite. A cell, B, of about 50 ml. capacity containing 25 ml. of solution is connected with a saturated calomel electrode, C, by capillary tubing filled with saturated KCl solution from the reservoir, A.

The whole cell system is made of pyrex glass.

The saturated KCl solution makes contact with the metal-acid-amine complex solution in B through a sintered glass plug, P.

In the rubber bung, R, are mounted:-

A capillary tube, N, through which nitrogen is passed.

The glass electrode, G.

A small glass stirrer, S, driven by a small electric motor.

The tip of the microburette, M, passes through a closely fitting opening in the bung and dips just below the surface of the solution. The reaction vessel may be drained by removing the microburette and lowering a small suction tube into the cell.

The potential of the cell was measured on a standard "Cambridge" pH meter of the valve electrometer type which gives direct readings of pH. The connections between the pH meter and the electrodes were screened leads of which the copper sheathing was earthed. The cell was mounted in a water thermostat, which could be set at any temperature between 20°C and 40°C to $\pm$ 0.02°C.

The Ionic Strength of Solutions.

Many workers have used "salt backgrounds" of high strength ($\sim$1 M) to keep activities of the species in solution constant. However, in solutions of such high ionic strengths, activity coefficients will deviate considerably from unity. For our solutions, we chose an ionic background of concentration 0.10 MKCl. This was the lowest concentration in which ionic strength, and hence activity coefficients could be kept constant. It was also the highest concentration of KCl at which the pHs of buffer solutions were accurately known, p. 57 .

Hydrochloric acid was used in making up acid solutions. In such solutions, the concentration of KCl was adjusted so that $[HCl] + [KCl] = 0.10$ M. This ensured that $[Cl^-]$ was always the same.

The concentration of M^{2+}, the metal with which complexes were formed, was always 0.005 M, which made the total ionic strength of solution, 0.12. The amine solutions ($[A] \sim 1$ M) were made up in 0.10 M KCl so that when additions of amine (a neutral species) were made from the microburette, the solution in the cell, although diluted slightly, still had an ionic background of $[Cl^-] = 0.10$N.

Junction Potential.

It is impossible to eliminate the junction potential in a cell of this type. It occurs at the dotted line below:-

$$Hg/Hg_2Cl_2 \;|\; \text{Satd. KCl} \;\vdots\; \text{Complex solution} \;|\; \text{Glass Electrode } (N/10\ HCl \;|\; AgCl/Ag)$$

This potential, being unknown, must be kept constant. Saturated potassium chloride is widely used in salt bridges to give small constant junction potentials because:-

(a) The potassium and chloride ions have almost exactly equal mobilities.

(b) Because of its high concentration (~ 4.2 M), almost all the current across the junction will be carried by the K^+ and Cl^- ions.

The potential across such a junction has been estimated to be 1.0 mv., which, in terms of pH, is 0.016 units (43).

Further, to minimise changes in junction potential with changing composition of complex solution, the chloride ion concentration was kept constant at 0.10 M as described above.

Static liquid-liquid junctions deteriorate with time, but by using a sintered glass plug, in which the junction was constrained, it was found that no measurable deterioration took place during a titration run, taking usually about 2 hours.

This was demonstrated in two ways.

(1) At the end of a run, on turning tap T, so that a little fresh saturated KCl solution flowed through the plug, there was no observable change in potential of the cell.

(2) The solution, at the end of the run, was removed from the cell which was then rinsed out with distilled water. The plug was flushed with KCl from the reservoir and the solution replaced in the cell. Exactly the same pH reading was obtained as at the end of the run.

Thus a readily reproducible stable constrained liquid junction was produced at the plug P.

The Electrodes.

Calomel Electrode.

A saturated calomel electrode was made up in compartment C. The saturated KCl solution made direct contact with that from reservoir A by way of the capillary tube, F.

The Glass Electrode.

The glass electrode functions as an electrode reversible to hydrogen ion. The relationship between pH and its measured potential is a straight line of slope $RT/2.303\ F.$ Glass electrodes suffer from certain disadvantages when compared with hydrogen electrodes. These are:-

(1) High Resistance.

The internal resistance of a cell containing a glass electrode lies between 10^5 and 10^9 ohms. Because of this fact, the e.m.f. of the cell must be measured on a valve electrometer which takes no current from the cell. Such electrometers are not as accurate as direct potentiometers which are used with hydrogen electrodes.

(2) The Alkali Effect.

In alkaline solutions of the alkali-metals where $pH > 9$, the glass electrode is not perfectly reversible to hydrogen ion and that ion alone, due to the effect of the alkali-metal ions on the glass bulb.

(3) Asymmetry Potential.

If an Ag/AgCl | $^{N}/_{10}$ HCl type glass electrode is placed in a solution of $N/_{10}$ HCl, it will not have zero potential. This small deviation from zero, which may be positive or negative, is known as the asymmetry potential, Π , and is due to several factors, of which the main one is internal strains in the glass bulb.

Π varies slightly from day to day and alters abruptly if the temperature of the bulb is changed rapidly.

However, it is possible to use hydrogen electrodes in very few metal-ammine systems due to "poisoning" (3) so the glass electrode is always used in such systems. The first disadvantage listed above cannot be overcome, but the other two were minimised.

(2) A recently developed electrode, the "Doran, Universal type", was used which functions reversibly at all pHs from 0 to 13.

(3) The electrode was standardised each day before use with buffers of which the pH was accurately known. When measurements were made at a different temperature, the electrode system was allowed to "settle down" for a day or two at that temperature before readings were taken.

A Note on pH

Originally the definition of pH by Sørensen (44) referred to the concentration of hydrogen ion, $[H^+]$.

$$pH = - \log [H^+]$$

However, electrodes reversible to hydrogen ion measure the activity of hydrogen ion, as given by the Nernst equation,

$$E = E_o + \frac{RT}{F} \ln a_{H^+}$$

The modern meaning of pH is:-

$$pH = - \log a_{H^+} = - \log_{10} [H^+] . f_{H^+}$$

The present concept of pH (or paH, as it is often termed) and the standards by which it is defined are discussed by Bates (43).

Buffer Solutions.

Before any measurement was made in the cell, the electrode was standardised on a buffer solution of known hydrogen ion activity.

Three buffers recommended by the National Bureau of Standards were used. These were:-

TABLE VI

pH of Buffers in $^{N}/_{10}$ KCl at Different Temperatures.

Materials	20°C	25°C	30°C	40°C	Ref.
$^{M}/_{20}$ Potassium hydrogen Phthalate	3.927	3.930	3.940	3.982	(45)
$^{M}/_{20}$ Potassium dihydrogen Phosphate + $^{M}/_{20}$ Disodium hydrogen Phosphate	6.733	6.718	6.702	6.690	(46)
$^{M}/_{100}$ Sodium Borate (Borax)	9.157	9.107	9.068	8.998	(47)

All three buffers contain common substances which are readily obtainable in a high state of purity. The pH values are known very accurately over a range of strengths of potassium and sodium chlorides at all temperatures between 0°C and 50°C.

Buffers with a salt background of $^{M}/_{10}$ KCl were used so that the liquid junction potential should be as closely alike as possible to that which was present during the actual experiment.

The pH range covered by the buffers was that over which experimental pH measurements were made (apart from a few readings between pH 9 and pH 10.).

Procedure of Standardisation.

After standardising the pH meter on one buffer - usually the phthalate - the pH's of the other two buffers were measured in the cell. At all temperatures at which measurements were made, the pHs of the buffers were almost invariably found to be within 0.01 pH units of the appropriate values given in Table VI.

On the one or two occasions when this was not so, it was found that rinsing the glass electrode with acetone, or standing it in $N/_{10}$ HCl rapidly restored its reversibility.

After each pH titration, the buffers were again put into the cell and their pH's remeasured to check the standardisation of the electrode. In the very few cases where correct readings on the buffers were not given, the results of the runs were discarded.

The pH meter.

The meter was of standard commercial design and will not be described here. pH could be read to 0.005 units, but only significantly to 0.01 pH.

From this account of the apparatus, it can be seen that for any solution where $4 \ll pH \ll 10$, it is possible to measure the pH to within $\pm$ 0.01 pH units at any temperature between 20°C and 40°C. It was found that readings for titration runs were reproducible to 0.01 pH units and only very rarely was a difference of 0.02 pH units found for any one reading.

Results for the System of Hydrogen Ion with Ethylenediamine.

The method of calculation of the dissociation constants of onium ions of ethylenediamine is discussed on p. 79. The values of the negative logarithms of the dissociation constants, pK_{AH}, and pK_{AH_2}, found at different temperatures are given in Table VII.

For the reactions,

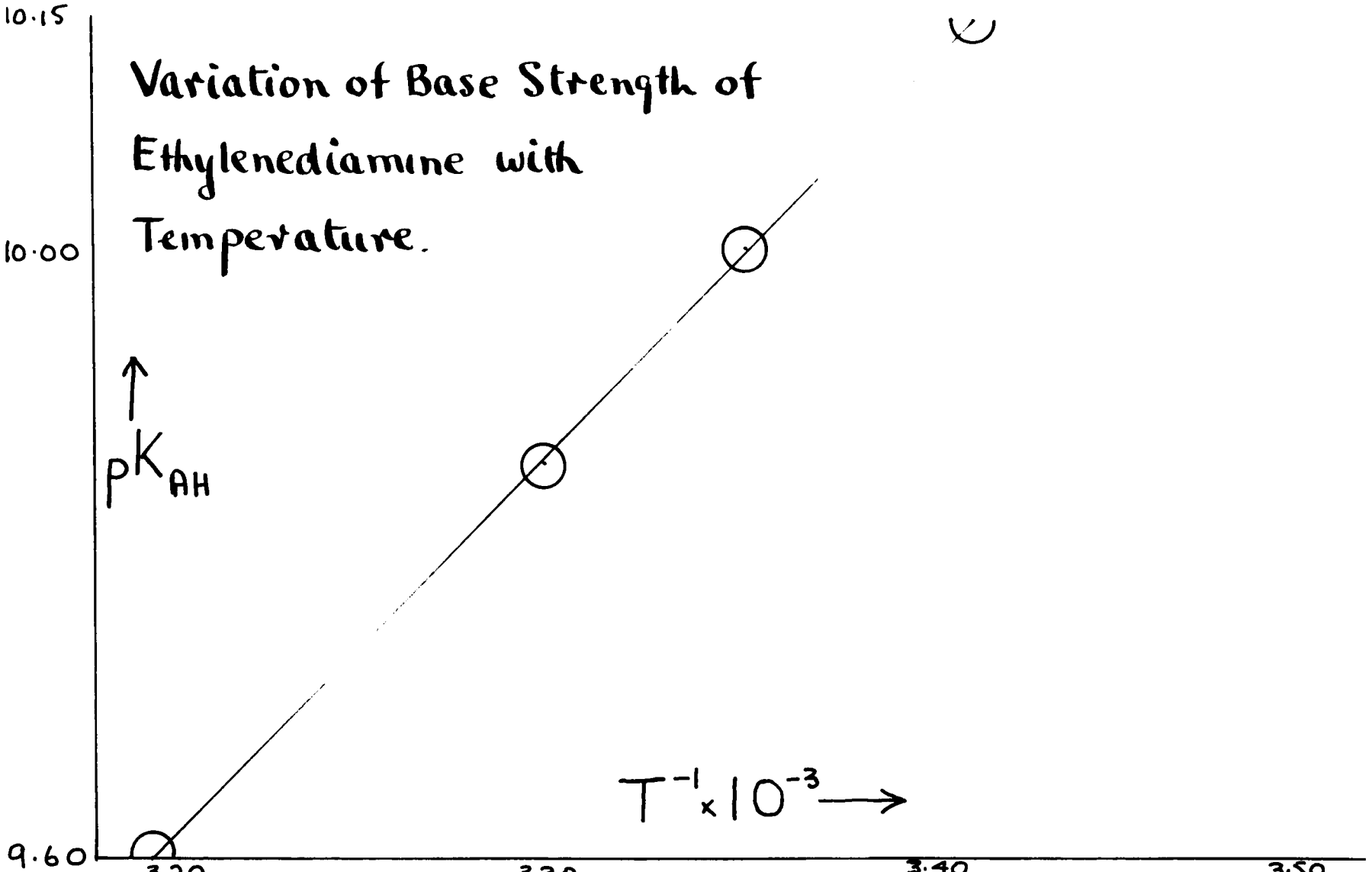
1. $EnH^+ \longrightarrow En + H^+$
2. $EnH_2^{2+} \longrightarrow EnH^+ + H^+$

1.2. $EnH_2^{2+} \longrightarrow En + 2H^+$

Values of ΔF, ΔH and ΔS calculated from the variation of pK with T are given in Table VIII. Plots of pK_{AH} and pK_{AH_2} against $1/T$ are given opposite p. 61 .

For comparison, values for pKs found by independent workers are given in Table IX. Heats of dissociation are given in Table X.

Variation of Base Strength of Ethylenediamine with Temperature.



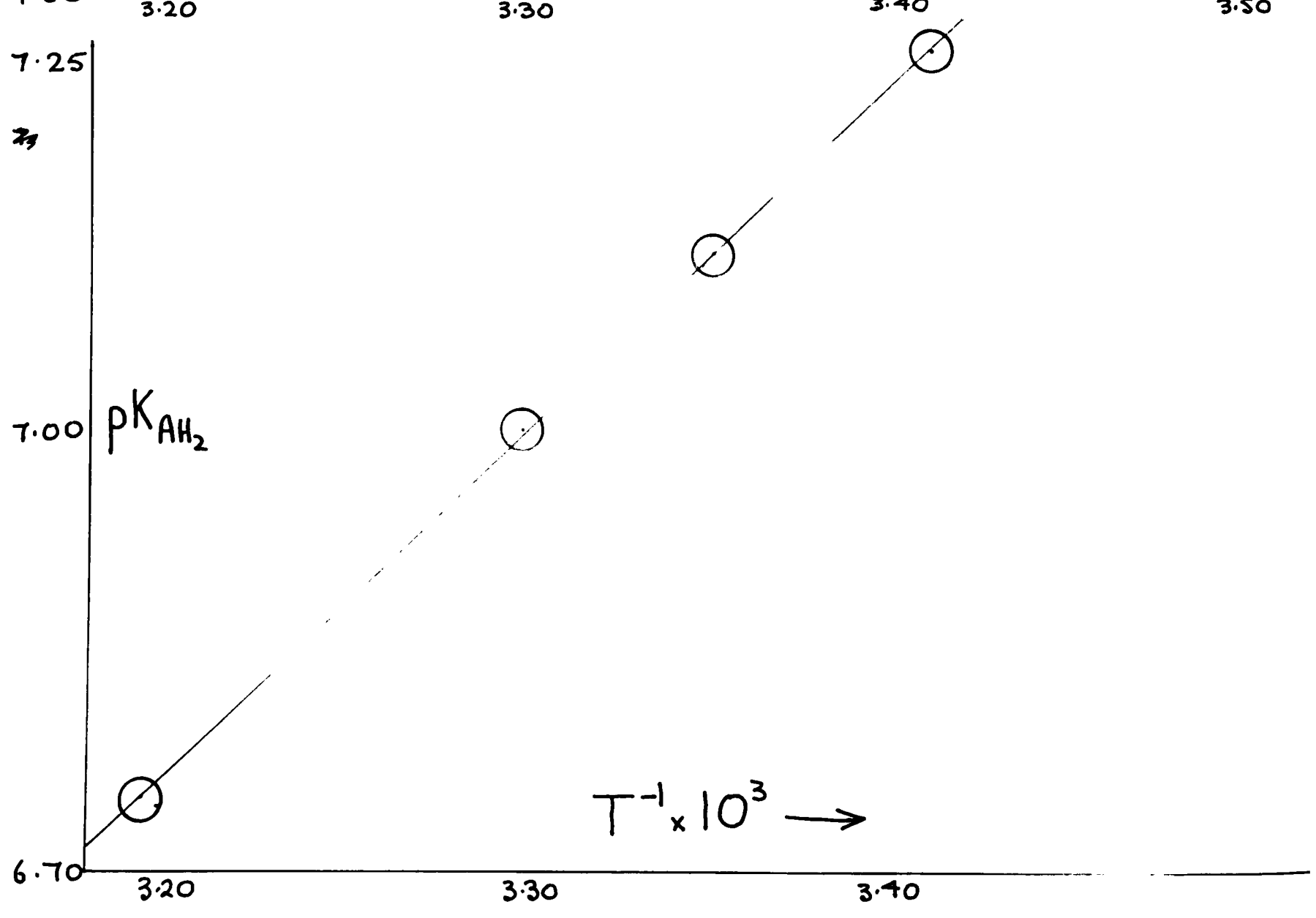


TABLE VII

Dissociation Constants for Ethylenediamine in Aqueous Solutions of Ionic Strength 0.13. $[Cl^-]$ = 0.10 M.

Temp.	20°C	25°C	30°C	40°C.
pK_{AH}	10.15	10.00	9.86	9.60
pK_{AH_2}	7.26	7.12	7.00	6.75

TABLE VIII

cal./g.ion	cal./g.ion	cal./g.ion/°C.
ΔF_1 = 13,660	ΔH_1 = 11,450	ΔS_1 = - 7.3
ΔF_2 = 9,710	ΔH_2 = 10,900	ΔS_2 = + 4.0
ΔF_{12} = 23,370	ΔH_{12} = 22,350	ΔS_{12} = - 3.3

TABLE IX

Dissociation Constant for Ethylenediamine at 25°C.

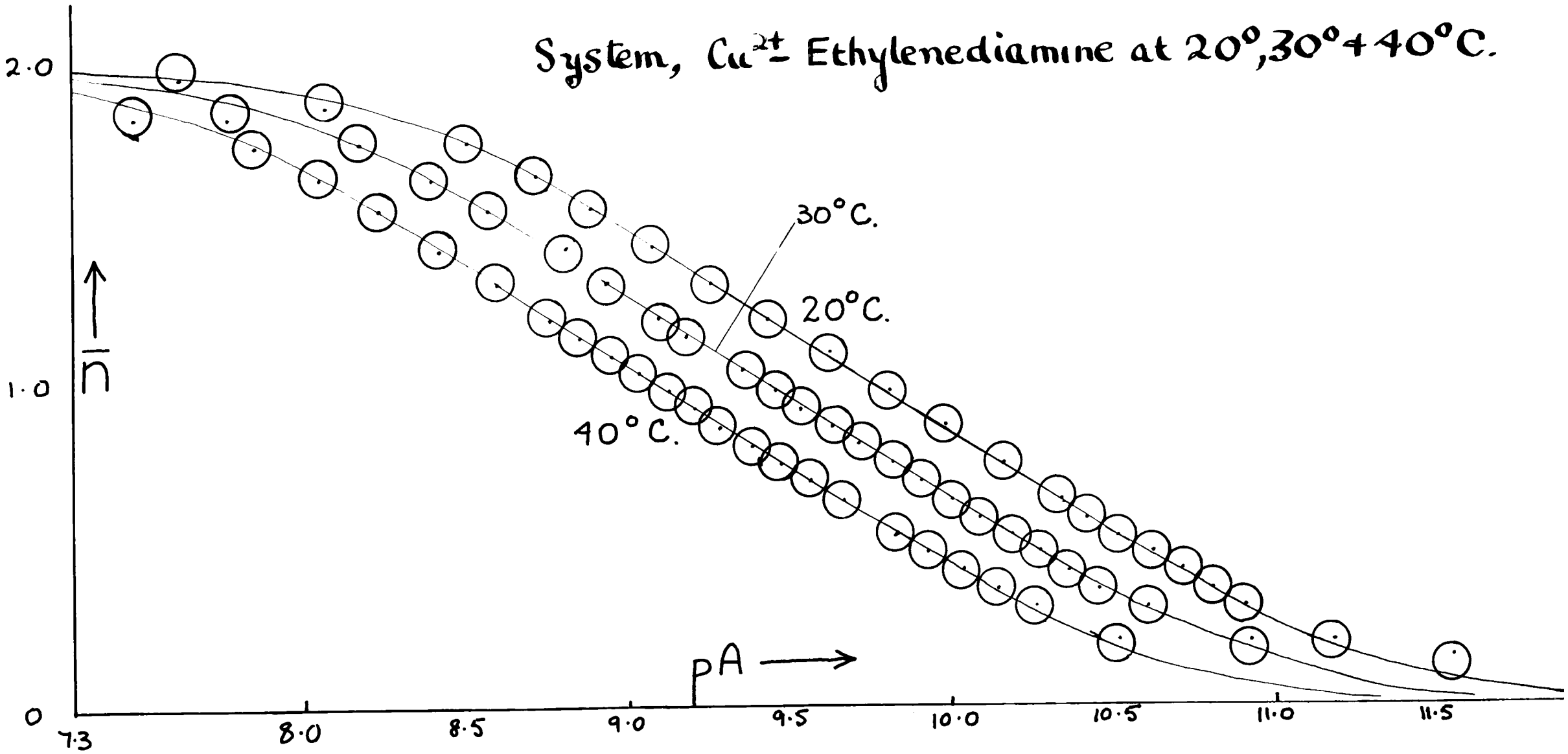
Method	Ionic Strength μ	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$	pK_{AH}	pK_{AH_2}	Workers	Ref.
Hydrogen Electrode	0	0	9.93	6.85	Everett	(55)
Glass Electrode	0.005	.066	9.95	6.87	McIntyre	(36)
"	0.13	.265	9.925	7.13	Williams	(10)
"	0.13	.265	10.00	7.12	Present Work	
"	0.78	.468	10.18	7.47	Basolo	(13)
"	0.78	.468	10.02	7.34	Carlson	(41)
"	1.28	.532	10.17	7.30	Carlson	(41)
Hydrogen Electrode	1.13	.502	10.18	7.47	Bjerrum	(12)
Glass Electrode	1.43	.546	10.19	7.49	Bjerrum	(12)
Hydrogen Electrode	1.55	.552	10.17	7.44	Keller and Edwards	(56)

TABLE X.

The Dissociation of Ethylenediamine at 25°C.

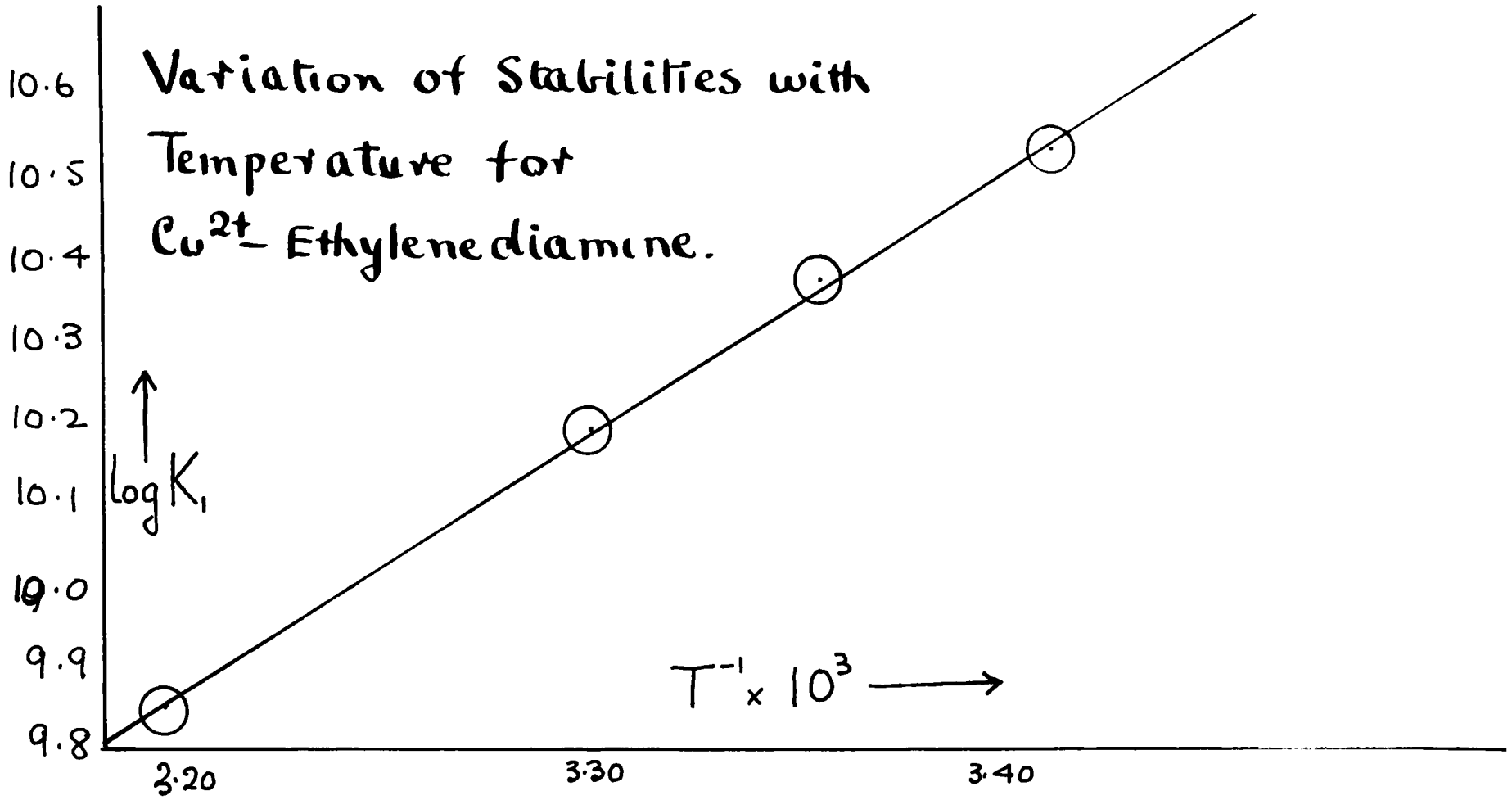
Method	Ionic Strength	Temp. Interval	cal./g.ion ΔH_1	ΔH_2	ΔH_{12}	Workers	Ref.
Gained Cell	0	60°	11,820	10,870	22,690	Everett	(55)
Glass Electrode	0.005	40°	11,200	10,700	21,900	McIntyre	(34)
"	0.13	40°	13,100	10,150	23,250	Williams	(13)
"	0.13	20°	11,450	10,900	22,350	Present Work	
"	0.78	25°	8,180	7,590	15,770	Basolo	(12)
"	1.40	6°	16,500			Bjerrum	(49)
Calorimeter	0.10		11,910	10,940	22,850	Staveley	(48)
"	0.10		11,940		-	Present Work	

System, Cu^{2+} Ethylenediamine at 20°, 30° & 40° C.



Results for the System of copper-ethylenediamine.

The results of the pH measurements are given on pp.190-3 The method of calculation of the formation curve is discussed on p.83 , and the derivation of stability constants from the curve on p.85 . The formation curves are given opposite p.64 , and the stability constants are given below in Table XI. The variation of log K_1 and log K_2 with temperature are shown in the graph opposite p.65 , and calculated values of ΔF, ΔH, and ΔS are given in Table XII. Values of log K_1 and log K_2 at 25°C reported by independent workers are given in Table XIII.


Variation of Stabilities with Temperature for Cu^{2+} Ethylenediamine.
10·6
10·5
10·4
10·3
10·2
10·1
10·0
9·9
9·8
$\log K_1$
$T^{-1} \times 10^3 \longrightarrow$
3·20
3·30
3·40

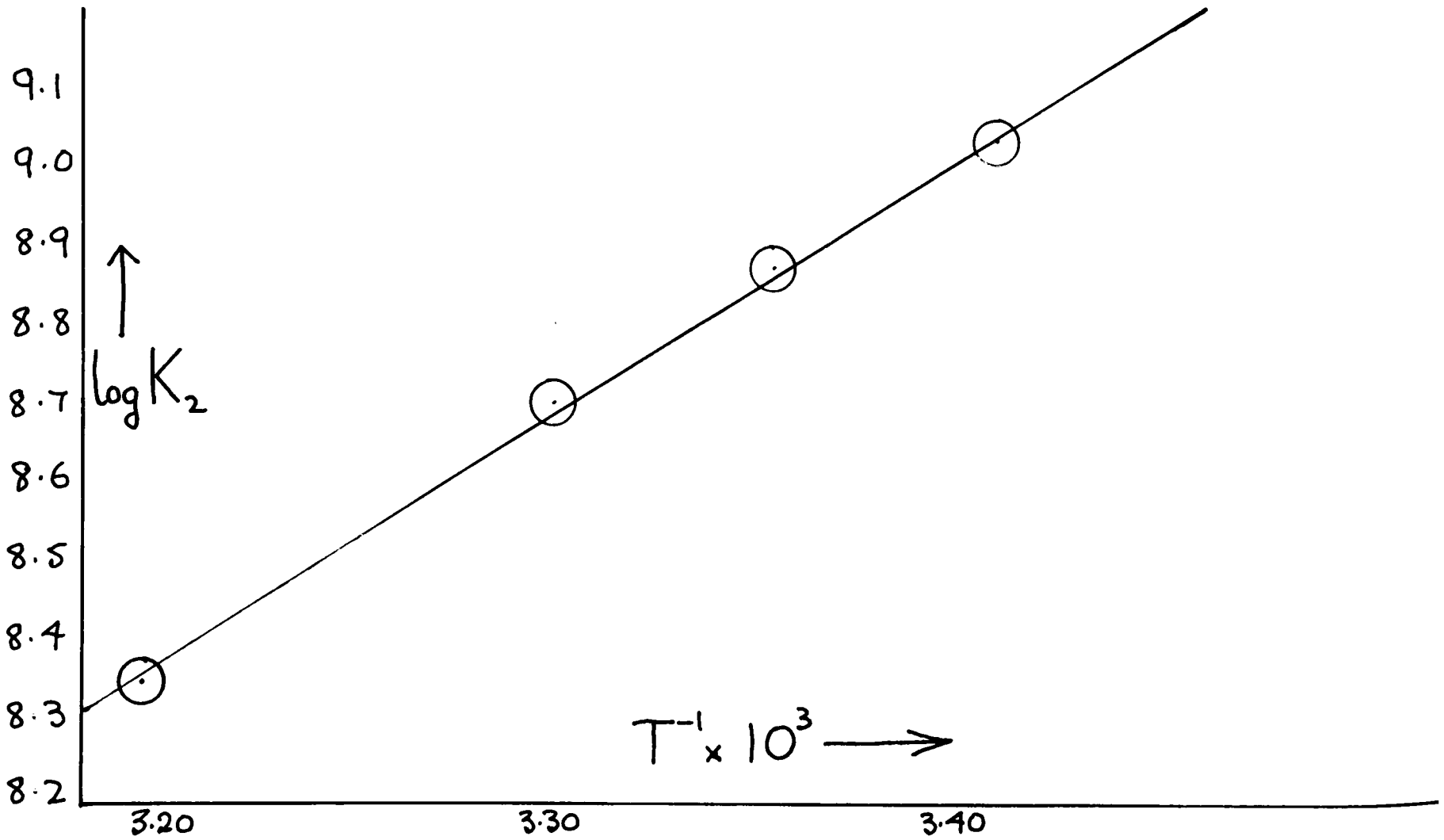

9·1
9·0
8·9
8·8
8·7
8·6
8·5
8·4
8·3
8·2
$\log K_2$
$T^{-1} \times 10^3 \longrightarrow$
3·20
3·30
3·40

TABLE XI

Stabilities of Complexes of Copper with Ethylenediamine in Aqueous Solution of Ionic Strength 0.13. Cl^- = 0.10.

Temp.	20°C	25°C	30°C	40°C
log K_1	10.53	10.37	10.19	9.85
log K_2	9.03	8.87	8.87	8.35
log β_2	19.56	19.24	18.89	18.20

TABLE XII

Formation of Complexes of Copper with Ethylenediamine at 25°C.

cal./g.ion	cal./g.ion	cal./g.ion/°C.
$-\Delta F_1$ = 14,130	$-\Delta H_1$ = 14,600	ΔS_1 = - 1.6
$-\Delta F_2$ = 12,090	$-\Delta H_2$ = 14,100	ΔS_2 = - 6.7
$-\Delta F_{12}$ = 26,220	$-\Delta H_{12}$ = 28,700	ΔS_{12} = - 8.3

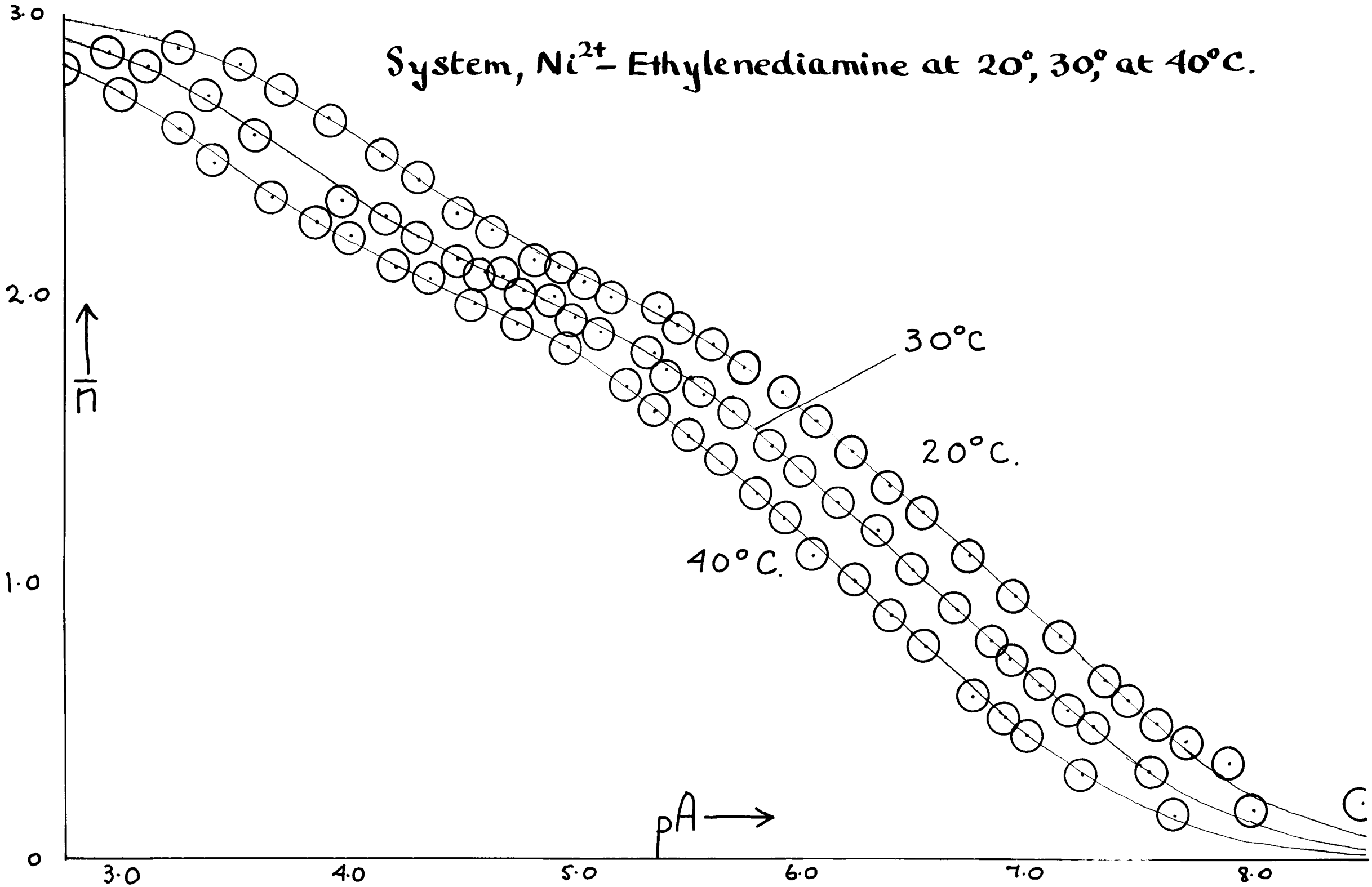
TABLE XIII.

Stabilities of Complexes of Copper with Ethylenediamine at 25°C.

Method	Ionic Strength	log K_1	log K_2	log β_2	$-\Delta F_{12}$ cal./g.ion	$-\Delta H_{12}$ cal./g.ion	Workers	Ref
Glass Electrode	0.005	10.50	9.09	19.59	26,710	22,900	McIntyre	(36)
"	0.13	10.37	8.87	19.24	26,220	28,700	Present Work	
"	0.13	10.50	8.87	19.37	26,420	35,750	Williams	(10)
"	0.78	10.76	9.37	20.13	27,450	17,200	Basolo	(13)
"	0.78	10.71	9.21	19.92	27,170		Carlson*	(41)
Cu/Hg Electrode	1.40	10.75	9.28	20.06	27,360	26,100	Bjerrum	(12)
Glass Electrode	2.15	11.02	9.59	20.61	28,110	28,400	Snike	(37)
Polarograph	0.10			19.72	26,900		Laitinen	(98)

* Estimated from values given at 30°C.

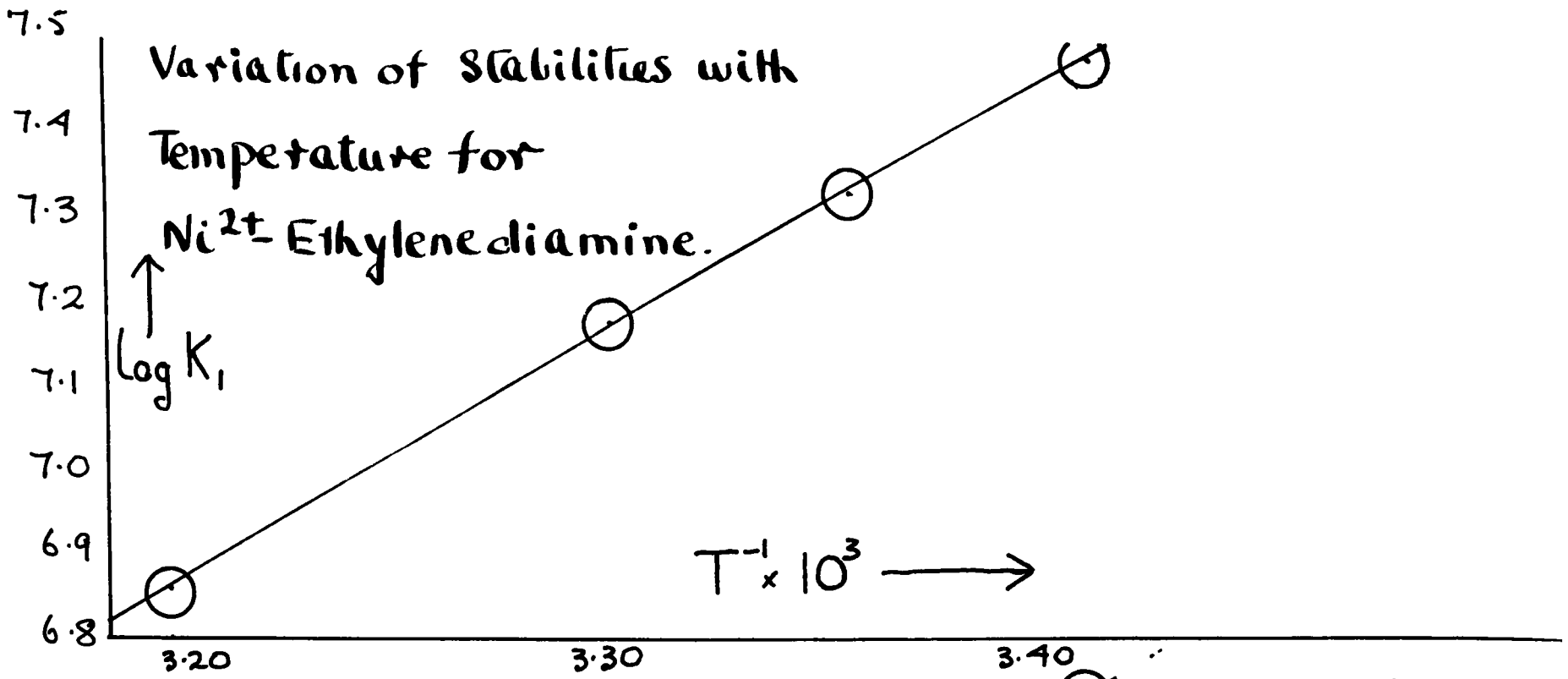
System, Ni^{2+} – Ethylenediamine at 20°, 30° at 40°C.

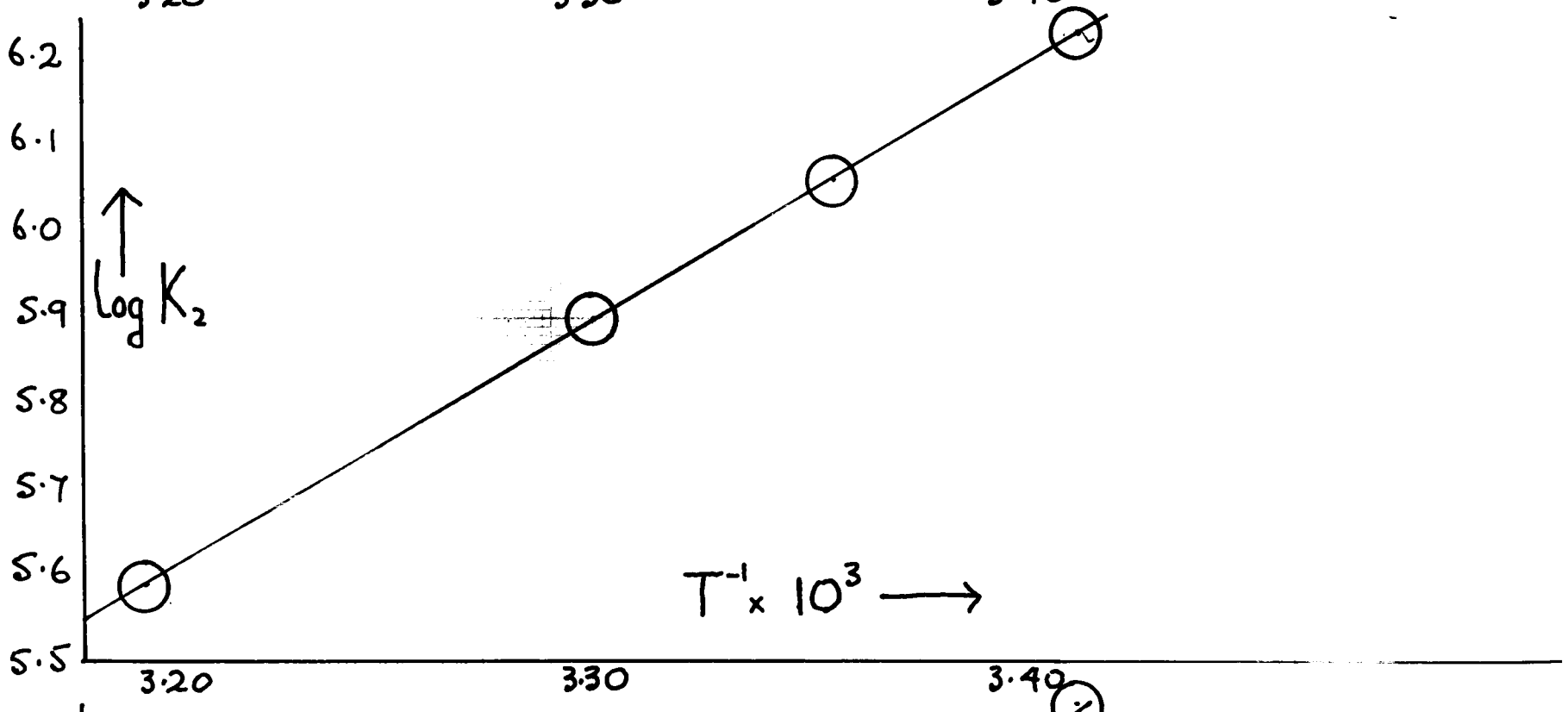


The System of Nickel-Ethylenediamine.

When the present results for enthalpy changes obtained by the glass electrode method for copper-ethylenediamine were compared with those obtained by calorimetric methods, (Table V) the difference of 14% was regarded as unsatisfactory. It was felt that better agreement between values measured by this method and calorimetric values might be obtained for another system. The system chosen was that of nickel with ethylenediamine in which three well defined stable complexes are formed. The heat of formation of each complex is large and the calorimetric values are known (38). The pH titration method was used at 20°C, 25°C, 30°C and 40°C, and the results of the pH measurements are given on pp.194-7. Calculated formation curves on which the experimental points are plotted are given opposite p. 67. The stability constants found are given below in Table XIV and ΔF, ΔH and ΔS for each complex at 25°C are given in Table XV. Plots of log K against $1/T$ are given opposite p. 68. Values of stability constants and heats of formation reported by independent workers are given in Table XVI, p. 69.

Variation of Stabilities with Temperature for Ni^{2+} - Ethylenediamine.





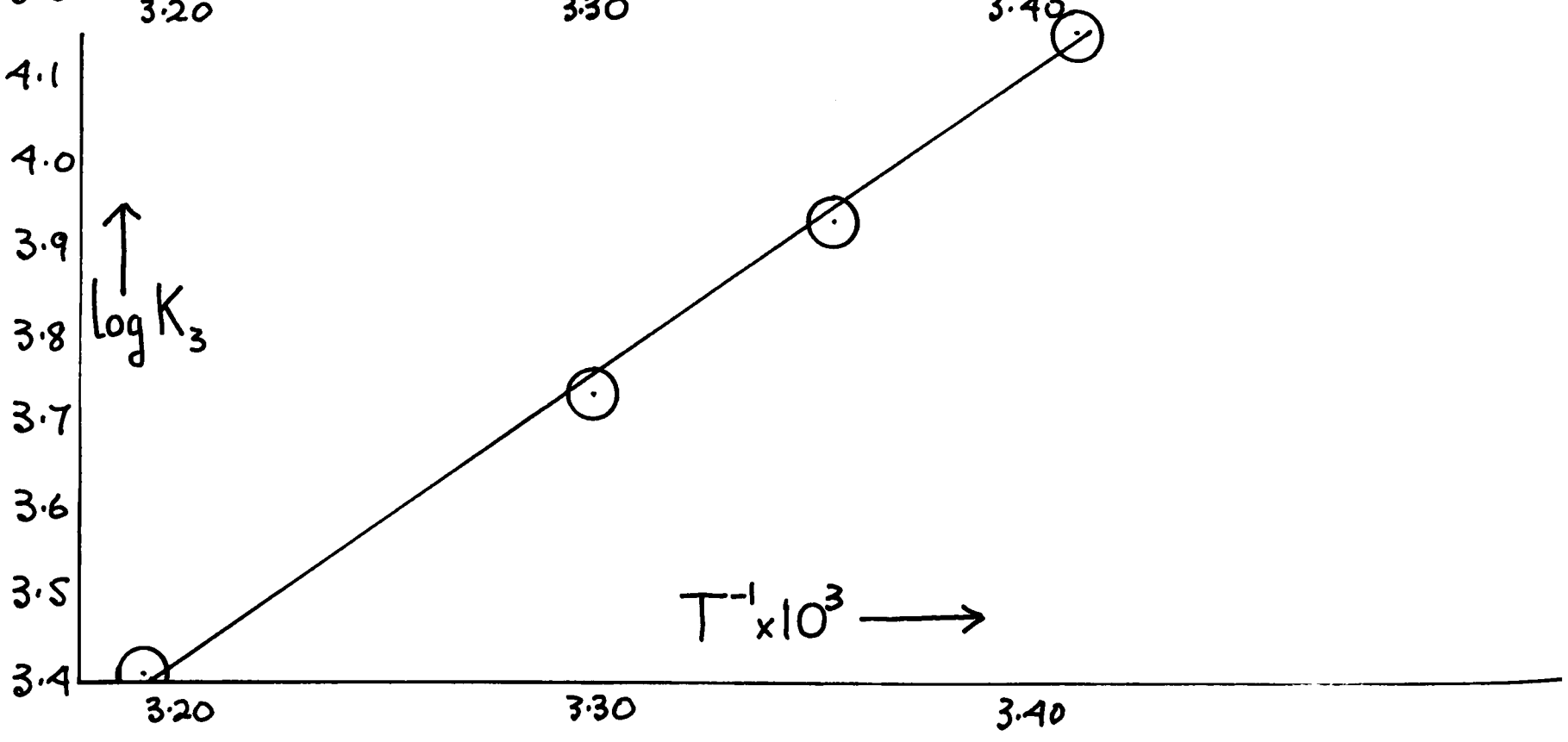


TABLE XIV

Stabilities of Complexes of Nickel with Ethylenediamine in Aqueous Solutions of Ionic Strength, 0.13. $[Cl^-]$ = 0.10 N.

Temp.	20°C	25°C	30°C	40°C
log K_1	7.48	7.32	7.17	6.86
log K_2	6.23	6.06	5.90	5.59
log K_3	4.15	3.93	3.73	3.41
log $_3$	17.86	17.31	16.80	15.86

TABLE XV

Formation of Complexes of Nickel with Ethylenediamine at 25°C.

cal./g.ion	cal./g.ion	cal./g.ion/°C
$-\Delta F_1$ = 9,980	$-\Delta H_1$ = 13,180	ΔS_1 = - 10.6
$-\Delta F_2$ = 8,260	$-\Delta H_2$ = 12,950	ΔS_2 = - 15.6
$-\Delta F_3$ = 5,360	$-\Delta H_3$ = 15,100	ΔS_3 = - 33
$-\Delta F_{123}$ = 23,600	$-\Delta H_{123}$ = 41,230	ΔS_{123} = - 59

TABLE XVI.

Formation of Complexes of Nickel and Ethylenediamine.

Method	Background Salt	Ionic Strength	25°C log K_1	log K_2	log K_3	cal./g.ion $-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$\div \Delta H_{123}$	Worker	Ref
Glass Electrode	0.10 M KCl	0.13	7.26	6.04		13,580	12,580			Williams	(10)
"	0.50 M KNO_3	0.78	7.60	6.48	5.03	4,800	4,300	4,900	14,000	Basolo	(13)
"	0.002 M $Ni(ClO_4)_2$	0.005	7.40	6.21	4.42	8,800	7,500	8,900	25,200	McIntyre	(36)
"	0.10 M KCl	0.13	7.32	6.06	3.93	13,180	12,950	15,100	41,230	Present Work	
"	1.0 M KNO_3		7.72	6.36	4.33						
Calori-meter	1.0 M KNO_3					9,100	8,800	9,300	27,200	Bjerrum	(38)
"	1.10 M KCl	0.10							27,210	Present Work	
"	1.10 M KCl	0.10							28,080	Staveley	(48)
"	0.50 M KNO_3	0.50							24,900	Basolo	(67)

Factors Affecting the Calculation of Enthalpies and Entropies from Stabilities Determined by the Glass Electrode Method.

The serious disagreement between the results obtained for the heats of formation of complexes of nickel with ethylene-diamine and those measured calorimetrically showed that, although care and precautions had been taken in experimental measurements, no reliability could be placed upon values of ΔH and ΔS obtained by the glass electrode method.

Apart from a consideration of methods of minimising experimental error, an enquiry must be made into the assumptions which are made in the calculation of stability constants and into any other factors which could influence the validity of experimental measurements, and in part, at least, account for the discrepancies in the data reported in Tables V and XVI.

Relevant factors are discussed below under the following headings.

Anion interaction.

The variation of ΔH and ΔS with temperature.

The effect of ionic strength upon amine dissociation constants.

The use of "non-thermodynamic" amine dissociation constants in the calculation of a formation curve.

The derivation of stability constants from formation curves.

The variation of stability constant with ionic strength.

Anion Interaction.

If the anion of the background salt interacts in any way with the metal ions or ligand groups of a complex system, the stability constants measured for that system will be different from those measured in solutions in which a different background salt has been used.

Bjerrum (49) has shown that the presence or absence of barium nitrate has no effect on the acid dissociation constants of ethylenediamine (except for that expected from the variation of ionic strength, see p. 81). Verhoek (41) has demonstrated that if the background salt is changed from potassium nitrate to potassium chloride, there is only a very small effect. This occurs in high concentrations of chloride ion when very small concentrations of chloride complexes are formed with copper and cadmium. With nitrate ion no such interaction takes place, and this is the anion most widely employed. There is a growing practice of using perchlorate ion in salt backgrounds, because its tendency to ionic complex formation is extremely small.

The Variation of ΔH and ΔS with Temperature.

The thermodynamic relationship,

$$-\frac{\Delta F_T^\circ}{RT} = \ln K_T^\circ = -\frac{\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R} \quad \ldots\ldots 30.$$

applies rigorously at all temperatures, where:-

ΔH_T° is the standard enthalpy change at T° Kelvin.

ΔS°_T is the standard entropy change at T° Kelvin

ΔF_T° is the standard free energy change at T° Kelvin.

K_T° is the thermodynamic equilibrium constant at T° Kelvin,

for an unspecified reaction in aqueous solution for which the standard change in the specific heats of reactants and products is ΔC_p° .

If ΔH° and ΔS° do not vary with temperature, the plot of log K° against $1/T$ is a straight line.

However, ΔH° and ΔS° are not necessarily constant. Their variations with temperature have been represented by the series:-

$$\Delta H^\circ = A - BT - DT^2 + \ldots\ldots$$

$$\Delta F^\circ = A + BT \ln T - CT - DT^2 \ldots\ldots\ldots$$

$$\Delta C_p^\circ = -B - 2DT + \ldots\ldots$$

$$\Delta S^\circ = (C - B) - B \ln T - 2DT \ldots\ldots\ldots$$

where A, B, C and D are constants.

Everett and Wynne-Jones (50) and Harned (51) have demonstrated that the terms involving D and higher terms are quite unnecessary to represent reactions in solution. The variation of stability constant is adequately represented by the equation

$$-\frac{\Delta F^{o}}{RT} = \ln K^{o} = -\frac{A}{RT} - \frac{B}{R}\ln T + \frac{C}{R} \quad \ldots\ 31.$$

and

$$\Delta H^{o} = A - BT$$

$$+\Delta C_{p}^{o} = -B$$

$$\Delta S^{o} = (C - B) - B \ln T.$$

Thus ΔH^{o} varies linearly with temperature whereas ΔS^{o} varies with ln T. Whether there are appreciable changes in ΔH^{o} and ΔS^{o} for the small temperature range (0 - 50°) over which it is possible to measure stability constant, will depend on the size of the constant B, i.e. on the magnitude of ΔC_{p}^{o}.

The Value of ΔC_{p}^{o}.

It has been found for charge neutralisation reactions in aqueous solution, that ΔC_{p}^{o} is relatively large* (52,76).

* In this context and in future discussion, the words, "large" and "small" refer to the numerical value of the quantity mentioned and not its algebraic value.

e.g. - 2 is said to be "larger" than - 1.

Such is the case in the dissociation of water:-

$$H_2O \longrightarrow H^+ + OH^-$$

where $\Delta C_p^o = -40$ cal./g.mol. (52)

This fact is readily explained, if, as in the treatment of Frank and Evans (53), ionic particles are regarded as having small "icebergs" of water frozen round them.

Thus the ions, H^+ and OH^-, will have molecules of water frozen around them which have to some degree lost, translational, rotational and vibrational energy, so the specific heat of the products of the dissociation will be lower than that of the undissociated molecule.

For the same reason, there will be a decrease of entropy in the dissociation due to freezing and ordering of the water molecules into the ionic "icebergs".

For any uncharged weak acid in aqueous solution, the entropy of the first dissociation, is approximately a constant.

i.e. for the reaction $HA \longrightarrow H^+ + A^-$

$$S \sim -22 \text{ cal./g.mol./}^oC.$$

This generalisation is known as Pitzer's rule (52).

In a dissociation reaction, when there is no change in the number of charged particles, ΔC_p^o will be expected to be small.

For the ammonium ion,

$$H_2O + NH_4^+ \longrightarrow NH_3 + H_3^+O$$

$$\Delta C_p^o = 0.6 \quad (54)$$

From these considerations, in none of the following reactions:-

$$EnH^+ \longrightarrow En + H^+$$

$$MEn^{2+} \longrightarrow M^{2+} + En$$

$$MEn_2^{2+} \longrightarrow MEn^{2+} + En$$

$$MEn_3^{2+} \longrightarrow MEn_2^{2+} + En$$

would a large value of ΔC_p^o be expected.

For the first reaction, a value of $\Delta C_p^o = -9.6$ has been found (55).

The reaction

$$EnH_2^{2+} \longrightarrow EnH^+ + H^+$$

involves a change in the number of ionic particles but not a charge neutralisation. The value of ΔC_p^o for this would be expected to be intermediate between that for EnH^+ (- 9.6) and that for a weak acid ($\sim$ - 40). The value found (55) is - 17.5.

ΔC_p^o has not been determined for any metal ammine system. From the above considerations, ΔC_p^o would be expected to be small. If it were as large as $\Delta C_p^o = -20$ units,

then over a range of 50°C, the variations in enthalpy and entropy changes would be

$$\Delta H^{\circ}_{273} - \Delta H^{\circ}_{323} = -1000 \text{ cal./g.ion}$$

$$\Delta S^{\circ}_{273} - \Delta S^{\circ}_{323} = -3.4 \text{ cal./g.ion/°C.}$$

A graph of log K° against $1/T$ for such a reaction would have a small curvature. However, if the best straight line were drawn through points found between 0°C and 50°C, the values of ΔH° and ΔS° found by applying eqn. 30, would be very close to ΔH°_{298} and ΔS°_{298}. Since ΔC_p° is expected to be small, eqn. 30 should represent experimental data accurately at any given temperature, and it is characteristic of the results in the literature that plots of log K against $1/T$ for the metal ammines give reasonably good straight lines, although the slopes of the lines differ considerably. These differences cannot be due to the variation of ΔH or ΔS with temperature.

The Acid Dissociation Constants of Ethylenediamine and their Variation with Ionic Strength.

The formation curve of a metal ammine cannot be found unless the acid dissociation constants of the amine are known. Although the technique and calculations for finding dissociation constants are generally known, it is proposed here to consider them with especial reference to ionic strength. No such treatment seems to have been published in the literature.

Acid Dissociation Constants of Amines.

For a dibasic amine, such as ethylenediamine, the successive dissociations of the two onium ions may be represented by the equilibria:-

$$AH_2^{2+} \longrightarrow AH^+ + H^+$$

$$AH^+ \longrightarrow A + H^+$$

Thermodynamic dissociation constants are given by the equations

$$K_{AH_2} = \frac{[AH^+]\ [H^+]}{[AH_2^{2+}]} \cdot \frac{f_{AH^+} \cdot f_{H^+}}{f_{AH_2^{2+}}} \qquad \ldots\ 32.$$

$$K_{AH} = \frac{[A]\ [H^+]}{[AH^+]} \cdot \frac{f_A \cdot f_{H^+}}{f_{AH^+}} \qquad \ldots\ 33.$$

where, as before, p.3 , f_X is the activity coefficient of species X.

The concentration dissociation constants of the anilium ions are given by:-

$$K^{C}_{AH_2} = \frac{[AH^+]\ [H^+]}{[AH_2^{2+}]} \quad \ldots\ 34.$$

and

$$K^{C}_{AH} = \frac{[A]\ [H^+]}{[AH^+]} \quad \ldots\ 35.$$

Now $pK = -\log K$.

So:-

$$pK_{AH_2} = pK^{C}_{AH_2} - \log f_{AH^+} - \log f_{H^+} + \log f_{AH_2^{2+}} \quad \ldots\ 36.$$

$$pK_{AH} = pK^{C}_{AH} - \log f_{A} - \log f_{H^+} + \log f_{AH^+} \quad \ldots\ 37.$$

The degree of formation of an amine, $\bar{n}_A$, is defined:-

$$\bar{n}_A = \frac{C_H - [H^+]}{C_A} \quad \ldots\ 38.$$

In the experiments made here, $[H^+]$ is negligible compared with C_H, when $pH \geq 4$.

So above $pH = 4$,

$$\bar{n}_A = C_H/C_A \quad \ldots\ 39.$$

It can readily be shown that $\bar{n}_A$ is related to the concentration dissociation constants by the expressions,

$$K^{C}_{AH_2} = [H^+]\left\{\frac{2 - \bar{n}_A}{(\bar{n}_A - 1) + \frac{\bar{n}_A \; K^{C}_{AH}}{[H^+]}}\right\} \quad \ldots\ 40.$$

$$K^{C}_{AH} = [H^+]\left\{\frac{(1 - \bar{n}_A) + \frac{(2 - \bar{n}_A)\;[H^+]}{K_{AH_2}}}{\bar{n}_A}\right\} \quad \ldots\ 41.$$

These equations reduce to:-

$$pK^{C}_{AH_2} = -\log [H^+] + \log \frac{\bar{n}_A - 1}{2 - \bar{n}_A} \quad \ldots\ 42$$

provided that $1 < \bar{n}_A < 2$.

and

$$pK^{C}_{AH} = -\log [H^+] + \log \frac{\bar{n}_A}{1 - \bar{n}_A} \quad \ldots\ 43$$

provided that $\bar{n}_A < 1$.

The general procedure for measuring dissociation constants is to measure the pH of solutions of known acid and amine concentrations (varying the amount of amine present progressively by titration from a microburette). $\bar{n}_A$ is calculated by eqn. 39. Using whichever of eqns. 42 or 43 applies depending on whether $\bar{n}_A$ is greater or less than unity, and assuming that pH is a measure of hydrogen ion <u>concentration</u>, dissociation constants are calculated which are neither

concentration nor thermodynamic constants. They are, in fact, mixed (Brønsted) dissociation constants (K^B), and will be defined here as follows:-

$$K^B_{AH_2} = \frac{[AH^+]\ a_{H^+}}{[AH_2^{2+}]} = \frac{[AH^+]\,[H^+]}{[AH_2^{2+}]} \cdot f_{H^+} \qquad \ldots\ 44.$$

$$K^B_{AH} = \frac{[A]\ a_{H^+}}{[AH^+]} = \frac{[A]\,[H^+]}{[AH^+]} \cdot f_{H^+} \qquad \ldots\ 45.$$

From eqns. 34, 36, 44.

So,

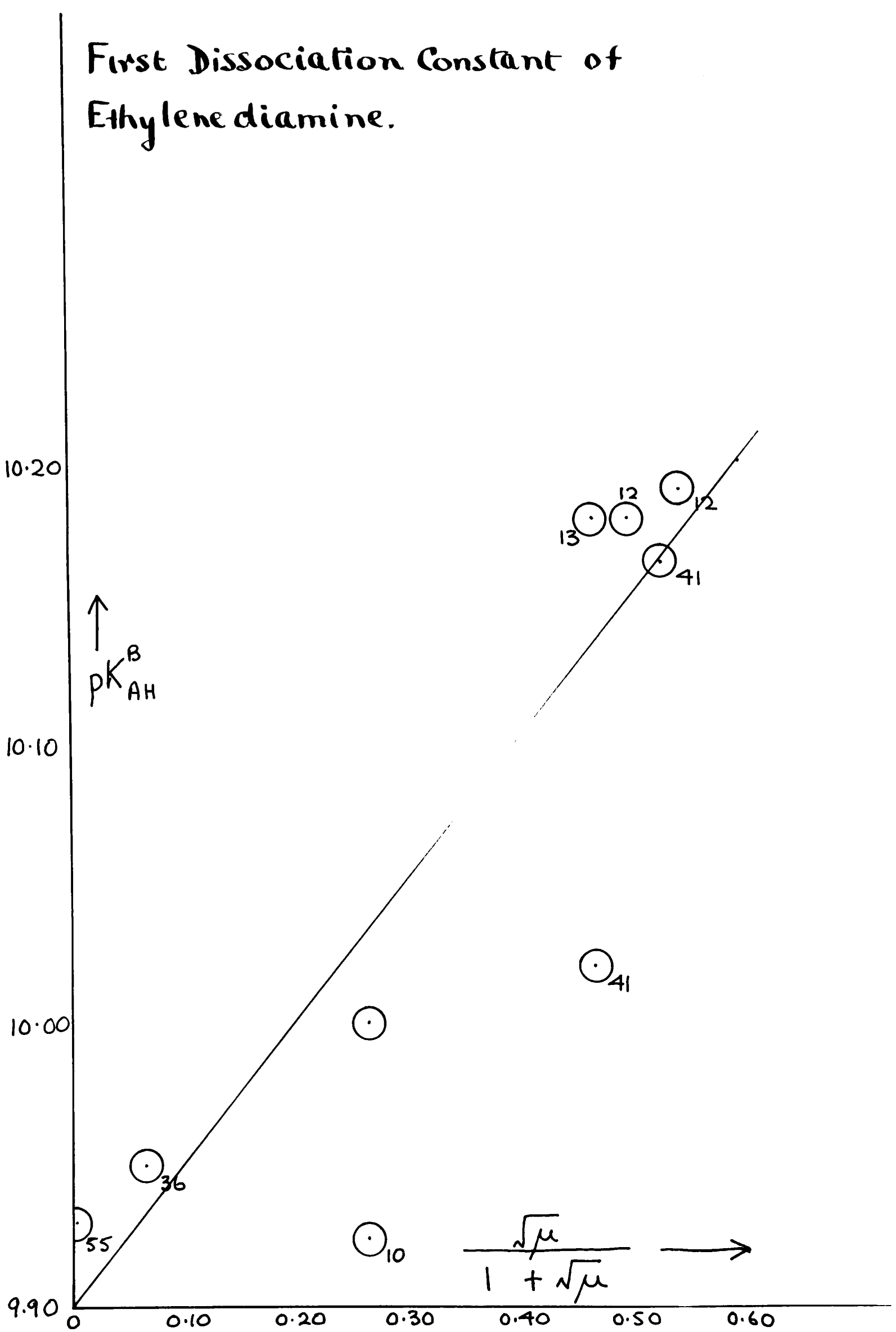
$$pK^B_{AH_2} = pK^C_{AH_2} - \log f_{H^+} = pK_{AH_2} + \log f_{AH^+} - \log f_{AH_2^{2+}} \qquad \ldots\ 46.$$

From eqns. 35, 37, 45,

$$pK^B_{AH} = pK^C_{AH} - \log f_{H^+} = pK_{AH} + \log f_A - \log f_{AH^+} \qquad \ldots\ 47.$$

Since f varies with ionic strength, $K^B_{AH_2}$ and K^B_{AH} are not strictly constants. There are several values for the dissociation constants of ethylenediamine given in the literature, and it is of interest to see if the manner in which they vary with ionic strength is explicable. Values taken from the literature are given in Table IX, p. 62.

First Dissociation Constant of Ethylene diamine.



<u>The First Dissociation Constant, $K^D_{AH^+}$.</u>

$$pK^B_{AH} = pK_{AH} + \log f_A - \log f_{AH^+} \quad \ldots\ 18.$$

A is uncharged, so $\log f_A = 0$, (at least at low ionic strengths).

pK_{AH} is a constant,

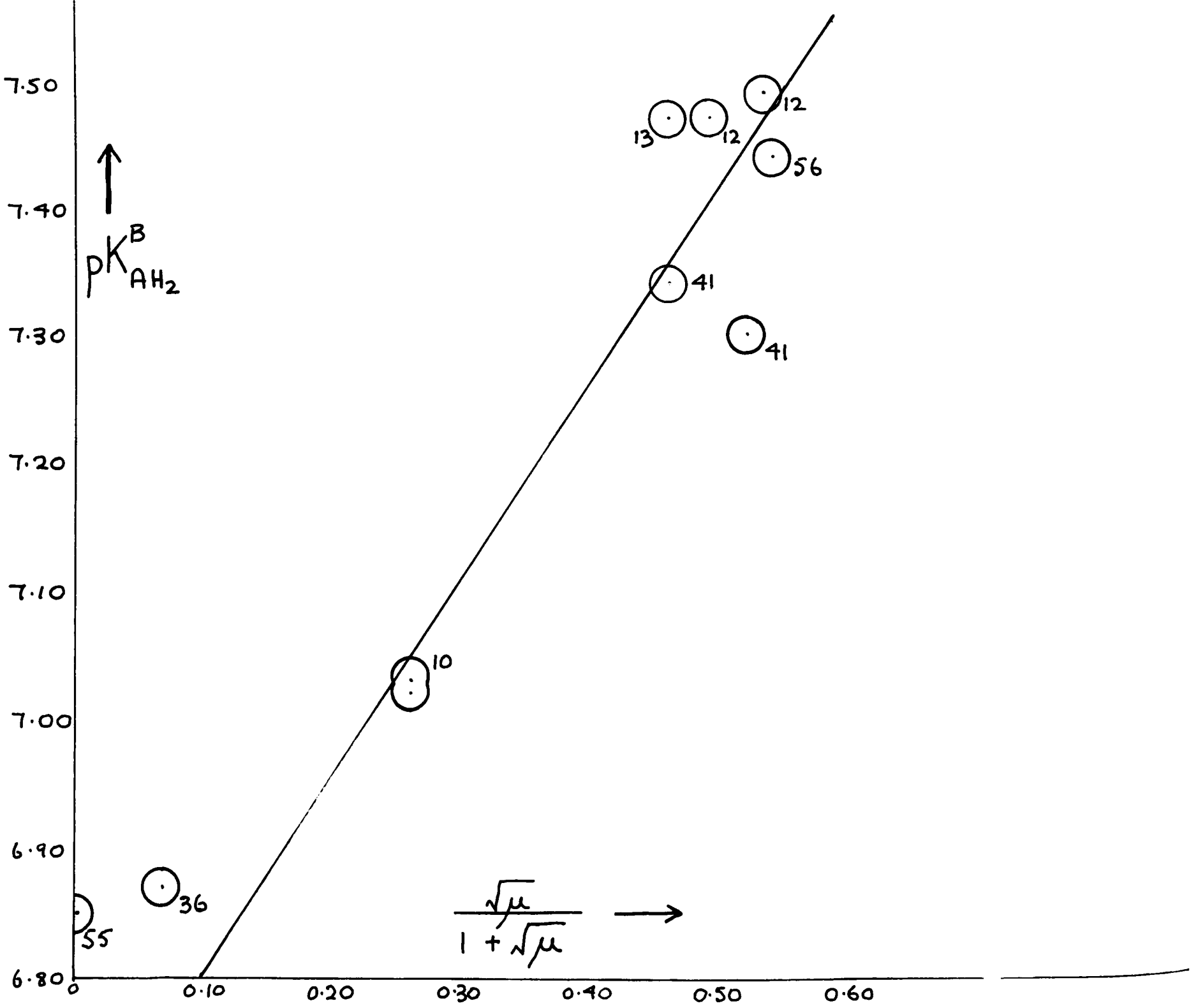
so $pK^B_{AH} = \text{const.} - \log f_{AH^+}$.

Thus pK^B_{AH} will be expected to vary with ionic strength as $-\log f_{AH^+}$. The simplest relationship between ionic strength, μ, and the mean activity coefficient, $f_\pm$, of a single charged body, is

$$-\log f_\pm = \frac{0.5\sqrt{\mu}}{1+\sqrt{\mu}}$$

This equation (see p. 18.) (from which higher terms in μ have been omitted) will not be expected to apply at high ionic strengths. However, a plot of pK^B_{AH} against $(\sqrt{\mu}/1+\sqrt{\mu})$ is given opposite. A line of slope 0.50 is drawn on the graph and it can be seen that the variation of K^B_{AH} with ionic strength is accounted for quite satisfactorily by the rough theoretical treament given above.

Second Dissociation Constant of Ethylenediamine.



The Second Dissociation Constant, $K^B_{AH_2}$.

$$pK^B_{AH_2} = pK_{AH_2} + \log f_{AH^+} - \log f_{AH_2^{2+}} \quad \ldots\ldots 17.$$

AH_2^{2+} is a doubly charged ion, and its activity coefficient is given by

$$-\log f_{AH_2^{2+}} = \frac{2.0\sqrt{\mu}}{1+\sqrt{\mu}}$$

$$\text{So } pK^B_{AH_2} = \text{Const.} + \frac{1.5\sqrt{\mu}}{1+\sqrt{\mu}}$$

Values of $pK^B_{AH_2}$ are plotted against $(\sqrt{\mu}/1+\sqrt{\mu})$ on the graph opposite p.82. A line of slope 1.50 is drawn on it, and again the results of experiment are seen to agree fairly well with theory.

It must be stressed that it is values of K^B_{AH} and $K^B_{AH_2}$ which are used in calculating the formation curve. They are measured in solutions of ionic strength of the same value as that in which the metal ammine is investigated. It will now be shown that correct values of $\bar{n}$ and pA can be calculated using values of K^B_{AH} and $K^B_{AH_2}$ and pH meter readings without additional assumptions concerning the values of individual activity coefficients.

The Use of K^B_{AH} and $K^B_{AH_2}$ in the Calculation of a Formation Curve.

From a measurement of the pH, i.e. the activity of hydrogen ion, a_{H^+}, in a solution containing amine and metal, the degree of formation of the amine is calculated:-

$$\bar{n}_A = \frac{C_H - [H^+]}{C_A} \quad \ldots\ 38.$$

$$C_H = [H^+] + [AH^+] + 2[AH_2^{2+}] \quad \ldots\ 48.$$

$$C_A = [A] + [AH^+] + [AH_2^{2+}] \quad \ldots\ 49.$$

$$\bar{n}_A = \frac{[AH^+] + 2[AH_2^{2+}]}{[A] + [AH^+] + [AH_2^{2+}]} \quad \ldots\ 50.$$

Although $\bar{n}_A$ is defined in terms of <u>concentrations</u> of the various species, it is clear from eqns. 44 and 45, that $\bar{n}_A$ is given exactly by the expression,

$$\bar{n}_A = \frac{K^B_{AH_2} \cdot a_{H^+} + 2a^2_{H^+}}{K^B_{AH_2} \cdot K^B_{AH} + K^B_{AH_2} \cdot a_{H^+} + a^2_{H^+}} \quad \ldots\ 51.$$

Thus the true value of $\bar{n}_A$ can still be calculated from a knowledge of the hydrogen ion activity of the solution and the mixed constants K^B_{AH} and $K^B_{AH_2}$.

The degree of formation of the metal ammine, $\bar{n}$, is given by :-

$$\bar{n} = \frac{C_A - [AH_2^{2+}] - [AH^+] - [A]}{C_M}$$

$$\text{So} \quad \bar{n} = \frac{C_A - \frac{C_H - [H^+]}{\bar{n}_A}}{C_M} \qquad \ldots\ 52.$$

This last expression includes the <u>concentration</u> of hydrogen ions (which is unknown).

But, above pH 4,

$$\bar{n} = \frac{C_A - C_H/\bar{n}_A}{C_M} \qquad \ldots\ 53$$

$\bar{n}$ thus refers completely to <u>concentrations</u> and not to activities.

<u>The Free Amine Concentration, [A].</u>

From eqns. 38 and 49,

$$[A] = \frac{C_H - [H^+]}{\bar{n}_A} - [AH^+] - [AH_2^{2+}]$$

Thus [A] is purely a concentration term.

From eqns. 44 and 45,

$$[A] = \frac{C_H - [H^+]}{\bar{n}_A} \cdot \frac{K^B_{AH_2} \cdot K^B_{AH}}{K^B_{AH} \cdot K^B_{AH_2} + K^B_{AH_2} \cdot a_{H^+} + a^2_{H^+}}$$

The term,

$$\frac{K^{B}_{AH_2} \cdot K^{B}_{AH}}{K^{B}_{AH_2} \cdot K^{B}_{AH} + K^{B}_{AH_2} \cdot a_{H^+} + a^2_{H^+}} = \alpha \qquad \ldots\ 54.$$

Above pH = 4,

$$[A] = {}^{C_H}/_{\bar{n}_A} \cdot \alpha \qquad \ldots\ 55.$$

Exact values of the <u>concentration</u> of A may be calculated from measurements of activity of hydrogen ion by glass electrode and the mixed constants $K^{B}_{AH_2}$ and K^{B}_{AH}.

Thus the Bjerrum pH method is fundamentally sound for solutions of any ionic strength, for although the experimental values of both pH and $K^{B}_{AH_2}$ and K^{B}_{AH} involve activity terms, the derived formation curve refers to complexed and uncomplexed metal ion and ligand in terms of <u>concentrations</u> and not activities.

<u>The Derivation of Stability Constants from Formation Curves</u>.

In some of the papers in the literature where full experimental data have been published, it has been shown that the use of faulty methods of computation have led several authors to give values for stability constants which are not

the "best" values deducible from the experimental curve. In several commonly used methods, only a few of the experimental points (e.g. those about $\bar{n} = \frac{1}{2}$, 1 and 1$\frac{1}{2}$) are used in the computation of K_1 and K_2. A critical survey of the various methods has been made recently by H. Rossotti and H. Irving (57) and their "correction-term" method was used in the present work for systems where N = 2.

For formation curves where N = 3, and where log K_2 - log $K_3 \geq 2$, the curve from $\bar{n} = 0$ to $\bar{n} = 2$ may be treated by the "correction-term" method. From $\bar{n} = 2$ to $\bar{n} = 3$, the eqn. (49) which applies is

$$\log K_3 = pA - \log \frac{\bar{n} - 2}{3 - \bar{n}}$$

in this way the stability constants for nickel and ethylenediamine were calculated.

Faulty computation of stability constants might well be a factor causing some of the discrepancies in Tables V and XVI.

<u>The Stability Constants of Complexes of Metals with Amines and Their Variation with Ionic Strength.</u>

The constants obtained from formation curves are concentration constants and not thermodynamic constants.

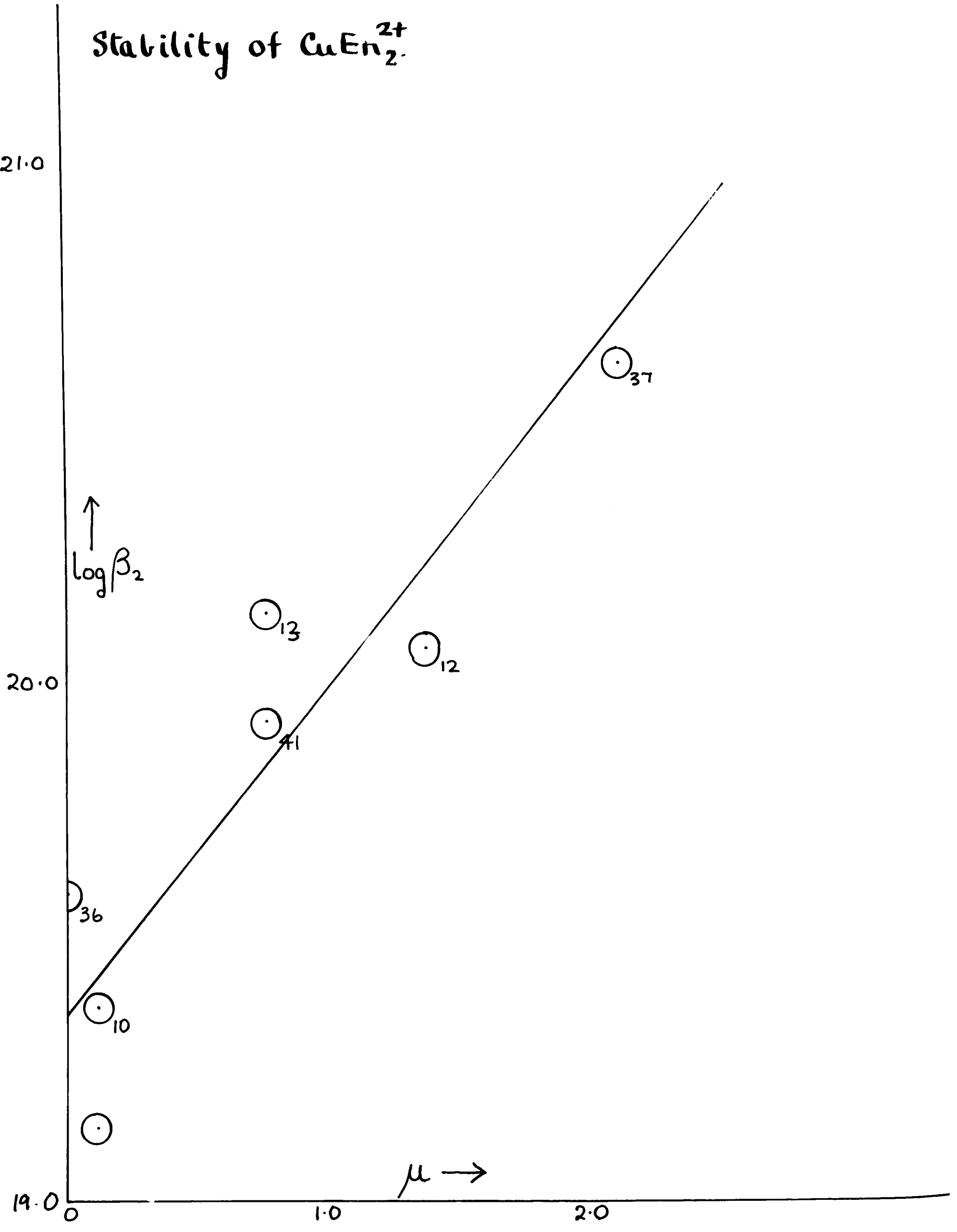
$$K^C_1 = K_1 \cdot \frac{f_{M^{2+}} \cdot f_A}{f_{MA^{2+}}} \qquad \ldots. 7.$$

$$K^C_2 = K_2 \cdot \frac{f_{MA^{2+}} \cdot f_A}{f_{MA_2^{2+}}} \qquad \ldots. 8.$$

The activity coefficients of M^{2+}, MA^{2+}, and MA_2^{2+}, will all be much of the same magnitude in dilute solution and will vary with ionic strength in a closely similar manner. A is an uncharged species and its activity coefficient is assumed to be unity in solutions of low ionic strength. However, in solutions of high ionic strength ($\sim$ 1M), f_A may deviate slightly from unity, (Bjerrum (12), has demonstrated the deviation of f_{En} from unity in high strengths of ethylene-diamine.)

Thus, although the fractions $f_{M^{2+}} \cdot f_A / f_{MA^{2+}}$ and $f_{MA^{2+}} f_A / f_{MA_2^{2+}}$ have values very close to unity (especially at low ionic strengths), concentration stability constants will be expected to vary slightly with ionic strength.

Stability of $CuEn_2^{2+}$



From the data given in Table XIII, p. 66 for Cu^{2+} - En, both log K_1^C and log K_2^C are seen to increase in a fairly regular manner with ionic strength. A plot of log β_2 against μ for the system Cu^{2+} - En is given opposite p.88.

The Variation of Stability Constant with Temperature.

The measured constants, K^C, vary with ionic strength and this variation cannot be expected to be the same at different temperatures, since activity coefficients vary with temperature At two different temperatures, the stability of a complex ion may be represented by fig. 3. ($T_1 > T_2$).

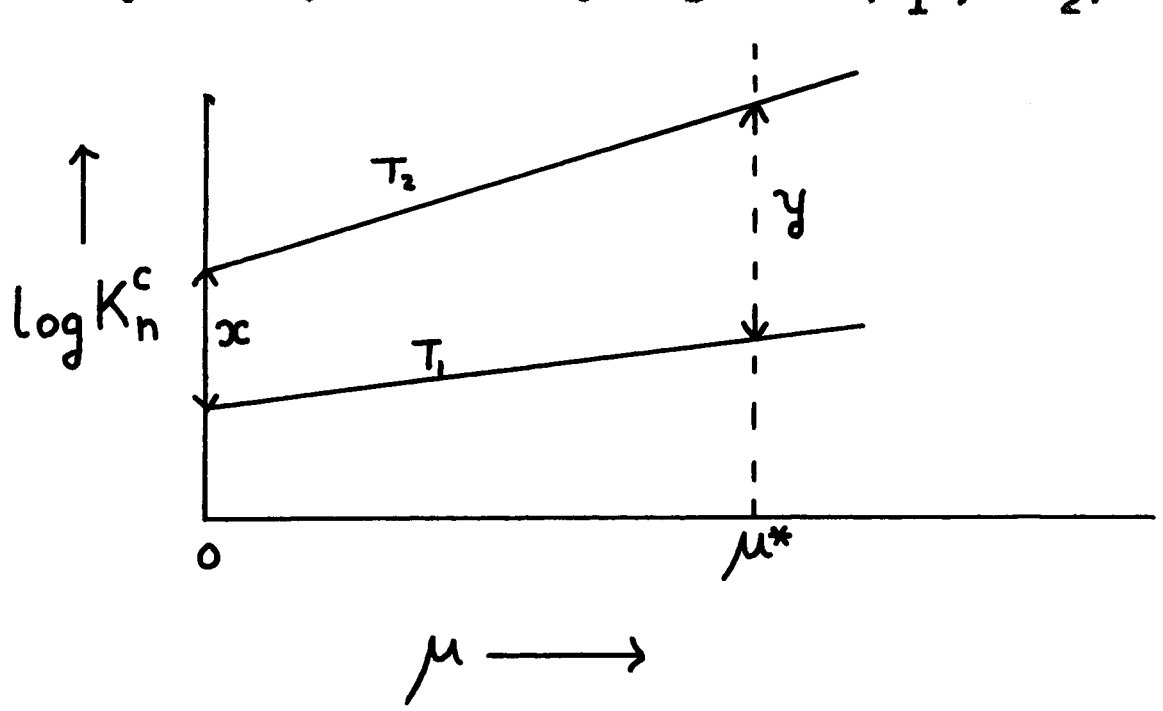


Fig. 3.

The standard heat of formation of the complex, $-\Delta H_n^o$, may be given by the change of log K_n^o at $\mu = 0$ (i.e. where

$K_n^C = K_n$), represented by χ, by the equation,

$$\frac{d \ln K_n}{dT} = - \frac{\Delta H_n^o}{RT^2}$$

$$\text{i.e.} \quad - \Delta H_n^o = \chi \cdot \frac{2.303 \cdot R \cdot T_1 \cdot T_2}{(T_1 - T_2)}$$

When ΔH_n^* is calculated from K_n^C measured in ionic strength, μ^*, the heat of reaction will be given by:-

$$- \Delta H_n^* = y \cdot \frac{2.303 \, R \cdot T_1 \cdot T_2}{(T_1 - T_2)}$$

$- \Delta H_n^*$ will not be the standard heat of reaction. It is not known how the concentration stability constant of any complex of metal and amine varies with ionic strength at different temperatures, so no estimate of how $- \Delta H_n^*$ varies with ionic strength can be given. However, such information is known for amine -proton systems.

Everett and Pinsent, (55) used a double Harned cell with hydrogen electrodes to make accurate measurements of K_{AH}^C and $K_{AH_2}^C$ for ethylenediamine (En) and hexamethylene-diamine (Hn) at various ionic strengths and temperatures.

For the dissociation constant

$$K_{AH}^C = K_{AH} \cdot \frac{f_A \cdot f_{H^+}}{f_{AH^+}} \qquad \ldots\ 34.$$

the fraction $f_A \cdot f_{H^+}/f_{AH^+}$ will be very close to unity.

Everett and Pinsent found that a plot of pK^C_{AH} against μ gave a straight line, and in this way extrapolated to pK_{AH} at $\mu = 0$. (This is a parallel to the way in which log K^C_1 for Cu^{2+} - En varies linearly with μ)

Values of $\Delta H^{\ddagger}$ at each ionic strength have been calculated from the variation of pK^C with temperature. Their results are given below in Table XVII.

TABLE XVII.

The Dissociations of Ethylenediamine and Hexamethylenediamine at 30°C.

	pK^C_{En}	$\Delta H^{\ddagger}_{En}$ cal./g.ion	pK^C_{Hn}	$\Delta H^{\ddagger}_{Hn}$ cal./g.ion
0	9.784	11,820	10.763	13,920
0.10	9.813	11,920	10.795	13,970
0.15	9.827	11,950	10.814	13,980
0.20	9.850	12,020	10.827	13,980
0.25			10.844	14,000
0.30	9.871	12,060		

Thus measurements of pK^C in solutions of ionic strength 0.30 give a result for the enthalpy change 2% greater than the

thermodynamic value, ΔH^{o}, for ethylenediamine. For hexamethylenediamine, the value of ΔH^{*} derived from solutions of $\mu = 0.25$ is only ½% different from ΔH^{o}.

Drawing the analogy between amine-proton reactions and amine metal reactions (p.75.) it is possible to generalise and predict that derived values of ΔH from solutions of several ionic strengths should not differ by more than about 5% for values of μ less than 1.0.

<u>Summary</u>.

From the consideration of factors other than experimental error, it has been demonstrated that, although the glass electrode method is not expected to yield standard heats of formation, it should, in the absence of experimental error, give enthalpy changes which differ by less than 10% from ΔH^{o}_{298}.

In the absence of other explicable reasons, the wide spread of values for ΔH in the Cu^{2+} - En and Ni^{2+} - En systems shown in Tables V and XVI (pp.43,69.) must for the most part be due to some systematic error of method, if not to casual experimental errors.

Errors in pH measurement appear directly in values for the acid dissociation constants of the amine as can be seen

in eqns. 42 and 43. When the enthalpy changes for the reaction of ethylenediamine with hydrogen ion (Table X, p.63.) are studied, the variations among the results are seen to be smaller than those among the metals ammines.

Errors in K^B_{AH} and $K^B_{AH_2}$ will add to errors in pH determination when formation curves and stability constants are calculated for metal ammine systems, so the spread in ΔH values for such systems will be expected to be larger than those in systems of amine with hydrogen ion. It is significant that Basolo and McIntyre who found low values of ΔH for the reactions of ethylenediamine with hydrogen ion, (Table X) also found low heats of formation for both $CuEn^{2+}$, $CuEn_2^{2+}$, and $NiEn^{2+}$, $NiEn_2^{2+}$ and $NiEn_3^{2+}$. (Tables V and XVI). Williams obtained a high heat of formation for EnH^+, and also obtained high heats of formation for $CuEn^{2+}$, $CuEn_2^{2+}$, $NiEn^{2+}$, and $NiEn_2^{2+}$.

In the nickel-ethylenediamine system, the fact that nearly the same results for ΔH_1 and ΔH_2 were obtained in the present work as were found by Williams under the same conditions of ionic strength (Table XVI) is suggestive of some systematic experimental error, as yet undetermined.

In all, it was decided that with ordinary commercial glass electrodes and pH meters it was impossible to obtain

reliable values of ΔH and ΔS, and the method was abandoned.

With hydrogen electrodes, where e.m.f's may be measured with much greater accuracy, the values of log K so determined are correspondingly more reliable. If measurements are made at a series of ionic strengths and extrapolations made to zero ionic strength, log K^{o} may be found at a series of temperatures, and hence ΔH^{o}. The values of ΔH_1^{o}, and ΔH_2^{o} found by Everett and Pinsent (55) for ethylenediamine agree very well with the values found calorimetrically (see Table X). However, there are very few complex solutions in which it is possible to use the hydrogen electrode. Canini and Martell (58) have used it recently for the system Ca^{2+} – ethylenediaminetetraacetic acid in a series of solutions at different ionic strengths and temperatures. It is to be anticipated that their result for ΔH will be found to be very close to ΔH^{o}.

Free Energies by Glass Electrode Method.

When the values of log K^{C} at 25°C for the systems Cu^{2+} – En or Ni^{2+} – En measured by independent workers (Tables XIII and XVI) are compared, it is observed that log K^{C} increases slightly with increasing ionic strength. As

illustration, the values of log β_2 for $CuEn_2^{2+}$ taken from Table XIII have been plotted against ionic strength in the graph opposite p.88 . A straight line may be drawn through the results. Its slope in terms of free energy units is about 1000 cal./g.ion per unit of ionic strength. If stability constants, and hence ΔF^{*}'s, are measured in an ionic strength of 0.10 at 25°C, the results must be within 200 cal. of ΔF°_{298}.

If free energies found in this way are combined with values of ΔH^{*} found by calorimetry at 25°C, the entropies of reactions calculated by the equation:-

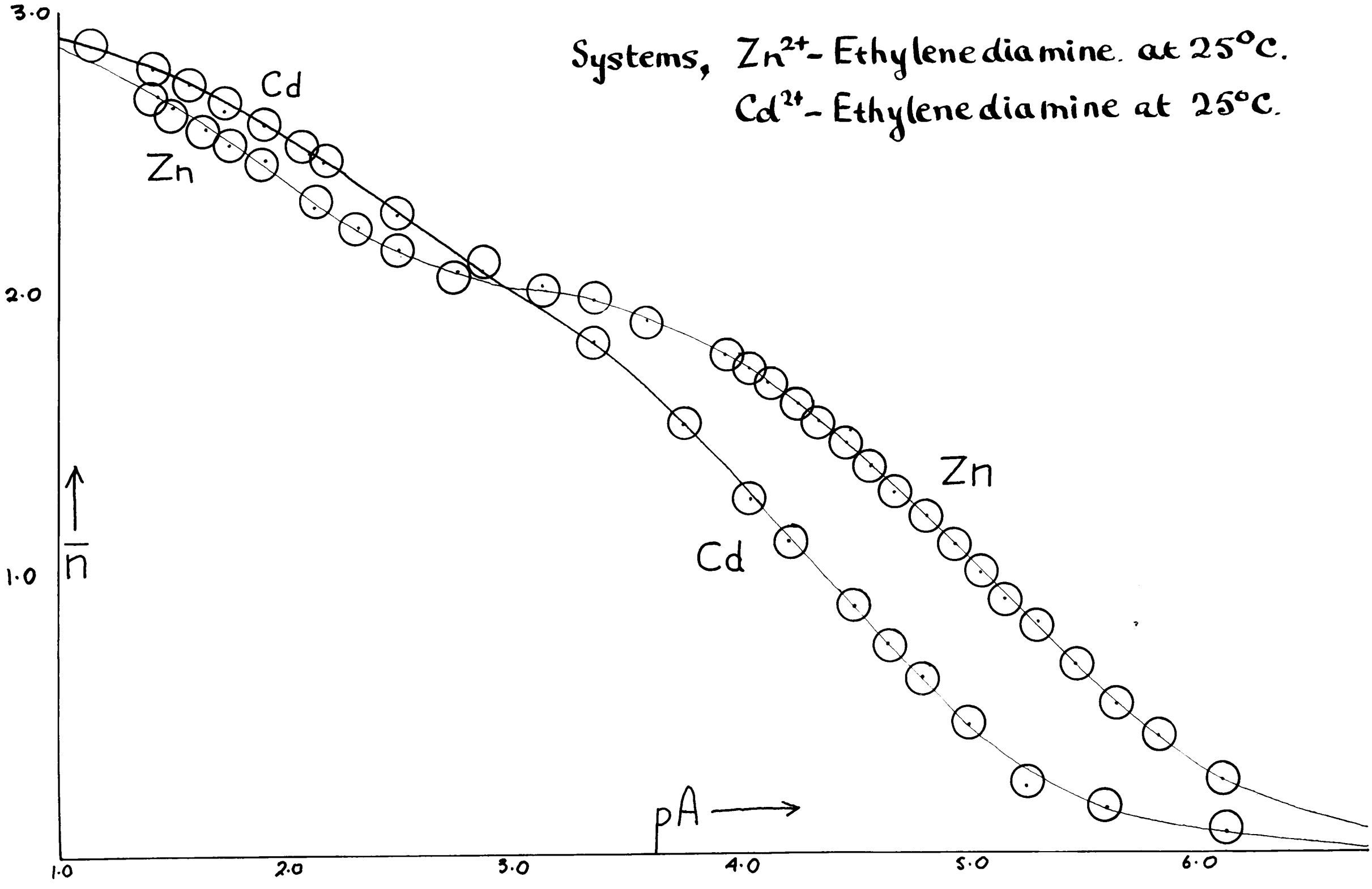
$$\Delta S^{*} = \frac{\Delta H^{*} - \Delta F^{*}}{T} \qquad \ldots. 6.$$

are expected to be within a unit of the standard entropy changes, i.e. ΔS°_{298}.

When it had been shown that the glass electrode method was unsuitable for finding enthalpy changes, it was decided to obtain entropy values by combining free energies, derived from measurements of stability constants with the glass electrode, with values of ΔH measured calorimetrically.

A description of the calorimeter and measurements made with it are given in Section IV, p.108.

Systems, Zn^{2+} - Ethylene diamine at 25°C.
Cd^{2+} - Ethylene diamine at 25°C.



Stability constants, at 25°C, in 0.10 M KCl solution, were measured by the titration method for the following systems:-

Zn^{2+} - ethylenediamine.

Cd^{2+} - ethylenediamine.

Cu^{2+} - 1:3-diaminopropane.

Ni^{2+} - 1:3-diaminopropane.

The dissociation constants of 1:3-diaminopropane were also measured. Calculated formation curves with the experimental points on the plots are given opposite pp.95,96,199. The results from which these curves were derived are given on pp.$\begin{Bmatrix}187-9\\198-9\end{Bmatrix}$. The results for formation constants are given below in Table VIII.

System, Cu^{2+}-1:3-Diaminopropane at 25°C.

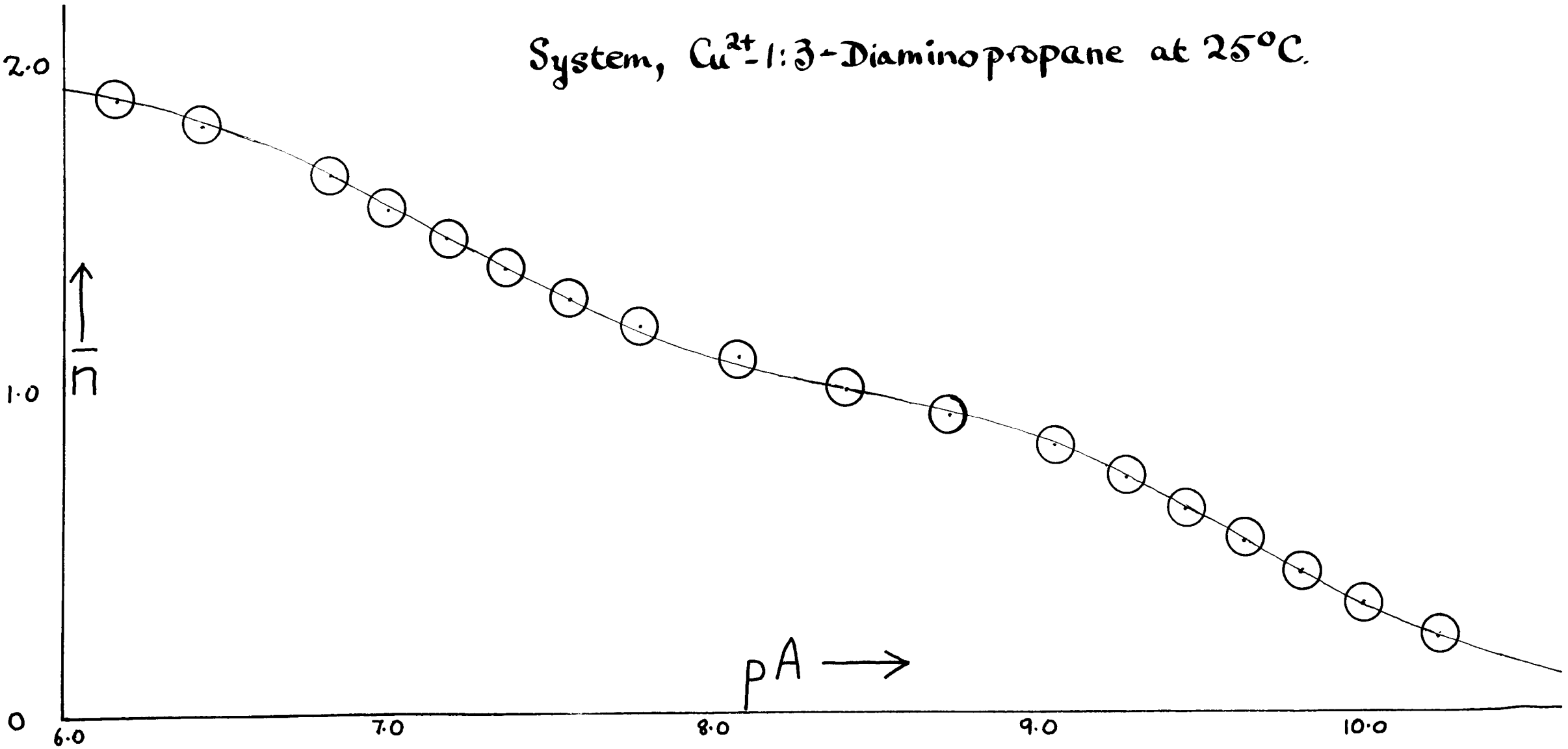


TABLE XVIII

Dissociation Constants and Stability Constants in Aqueous Solution of Ionic Strength 0.13. $[Cl^-]$ = 0.10 N at 25°C.

System	log K_1	log K_2	log K_3	log β_3
Zn^{2+} - En	5.64	4.48	1.81	11.93
Cd^{2+} - En	4.84	3.88	2.03	10.75
Ni^{2+} - Tn	6.26	4.15	1.13	11.54
Cu^{2+} - Tn	9.68	7.14		log β_2 16.82
	pK_{AH}	pK_{AH_2}		
H^+ - En	10.00	7.12		
H^+ - Tn	10.63	8.76		

Silver Ammines.

The heats of formation of the complexes $Ag^+(pyridine)_2$ and $Ag^+(2:6\text{-lutidine})_2$ were measured by direct calorimetry (p.130.) and when compared with the values found by the solubility method they were found to differ markedly. Results are given in Table XIX.

TABLE XIX.

Heats of formation ($-\Delta H_{12}$) of silver ammines at 25°C(cal/g.ion)

Complex	Calorimeter	Solubility
$Ag^+(pyridine)_2$	11,810	10,160
$Ag(lutidine)_2$	10,750	9,050

Several reasons may be put forward to explain why the solubility method does not give the same enthalpy values as those from direct calorimetry.

Firstly, there may be some systematic experimental error, although this error will be expected to be smaller than that in glass electrode methods. Secondly, two of the assumptions made in the calculation of ΔH are not strictly true.

These are:

(1) That log K's are thermodynamic constants.

(2) That ΔH and ΔS do not vary with temperature.

When it became clear that the solubility method did not give reliable values of ΔH, two lines of research were open. One was to try to find a method of measuring stability constants which would give reliable values of ΔH. Some work had already been done with the glass-electrode on some systems of silver with methyl-pyridines (59). The value of $-\Delta H_{12} = 9,250$ cal./g.ion so obtained for $Ag^{+}(pyridine)_2$, is 22% lower than the calorimetric value, which indicated that the glass electrode method might be no more reliable here than it was in the systems Cu^{2+} - En, Ni^{2+} - En. With a silver electrode it would be possible to measure stability constants at different temperatures. However, both the solubility method and the Ag^{+} electrode method are "central-ion methods", i.e. the principal quantity measured is the free metal ion. Some of the same assumptions made in the solubility method would have to be made in the Ag electrode method.

The second line of research was that of using a calorimeter with the object of obtaining definitive heats of formation of silver ammines directly. This latter course was taken. The measurements made and the results are given in Section IV. Heats of formation were combined with free energies to calculate entropies.

Stability constants of the silver ammines were measured at 25°C in 0.10 M KNO_3 by the Glass Electrode method. A full account of the work is given in Section III.

SECTION III

Stabilities of Silver Ammines by the Glass Electrode Method.

It was suggested on p.9. that a knowledge of the free energies, entropies and heats of formation of the complexes of a closely related series of amines with the same metal should lead to a recognition of the part played by polar and steric factors in complex formation. When it was found that the solubility method did not give reliable values for ΔH, it was decided not to use it for measuring stability constants, but to use the glass electrode method instead. There were two reasons for this:-

(1) The solubility method was rather laborious and the glass electrode method, though much quicker, gave results of nearly the same accuracy which agreed well with those obtained by the former method (see p.107).

(2) In connection with the study of polar effects, the acid-dissociation constants of the amines were measured by glass electrode, and it was felt that comparisons between these results and values for silver ammine stabilities would be more applicable if both sets of data had been measured by the same method.

In a constant ionic strength of 0.10 which was always 0.10 M with respect to nitrate ion, the acid dissociation

constants and stability constants with silver were measured for the following amines at 25°C,
NH_3, pyridine, 2-picoline, 3-picoline, 4-picoline, 2:6-lutidine. In addition, the dissociation constant of 2:4:6-collidine was measured, but because it was only slightly miscible with water, it was impossible to determine the stability of its complexes with silver ion.

From the theory of substitution in the benzene nucleus and from calculations such as those made by Coulson and Longuet-Higgins (60) and by Dewar (61), the availability of electrons on the nitrogen atom, i.e. its polarity, is known to increase along the series:-
pyridine < 3-picoline < 2-picoline ~ 4-picoline < 2:6-lutidine < 2:4:6-collidine.
Amines form σ bonds with metal ions by donating the lone pair of electrons from the nitrogen atoms, and from a consideration of the polar effect, the stabilities of silver ammines should increase in the order:-

Pyridine < 3-picoline < 4-picoline

Silver is a relatively large cation (r = 1.26 Å) and when 2-picoline forms a complex with it, there may be some repulsion between the 2-methyl group and the silver ion, thus causing a lowering of stability. When the second

2-picoline molecule interacts with silver ion, there may also be a repulsion between the two 2-methyl groups in the complex.

If such steric factors obtain, then the order of stabilities will be

2-picoline < 4-picoline

since polar factors are nearly equal.

It is impossible to predict what position in the order of stabilities 2:6-lutidine should occupy, since both polar attractions and steric repulsions are greater than for 2-picoline.

There are two further aspects of the stabilities of the silver ammines which are of considerable interest. These are:-

1. The relationship of K_1 to K_2.
2. The ratio of K_1 and K_{AH}.

The Relationship of K_1 to K_2.

Very few cases are known where the successive stability constants for a complex system, K_1, K_2, K_3 etc. do not decrease steadily. In many systems the regular decrease can be explained almost entirely on statistical grounds (3). The statistical calculation involves the assumption that the metal ion has n identical points of attachment for n successive

ligand groups. In actual practice, the attachment of even the first ligand group to the metal ion must alter, though possibly to only a small extent, the distribution of both the electrons in the ion's outermost electronic shell, and the water molecules in the sheath of hydration, so that symmetry is reduced. However, large deviations from the statistically predicted ratio $K_n/K_{(n+1)}$, can indicate appreciable changes in the electronic structure of the ion with successive attachments of ligand groups. This point is further discussed in connection with complexes of 1:10-phenanthroline (p.133).

It has been known for some time that for most complexes of silver, log K_1 is slightly smaller than log K_2, whereas statistically, log (K_1/K_2) = log 4 = 0.60. (4). It has been suggested that this is due to an sp orbital hybridisation (9). It is of interest to observe the effect of polar and steric factors upon the ratio K_1/K_2.

The Ratio of K_1 to K_{AH}.

There is a similarity between the two reactions:-

$$A + H^+ \longrightarrow AH^+$$

$$A + Ag^+ \longrightarrow AAg^+$$

There should be a correlation between the affinity of amine for hydrogen, measured by $RTpK_{AH}$, and the affinity of

Silver Ammines.

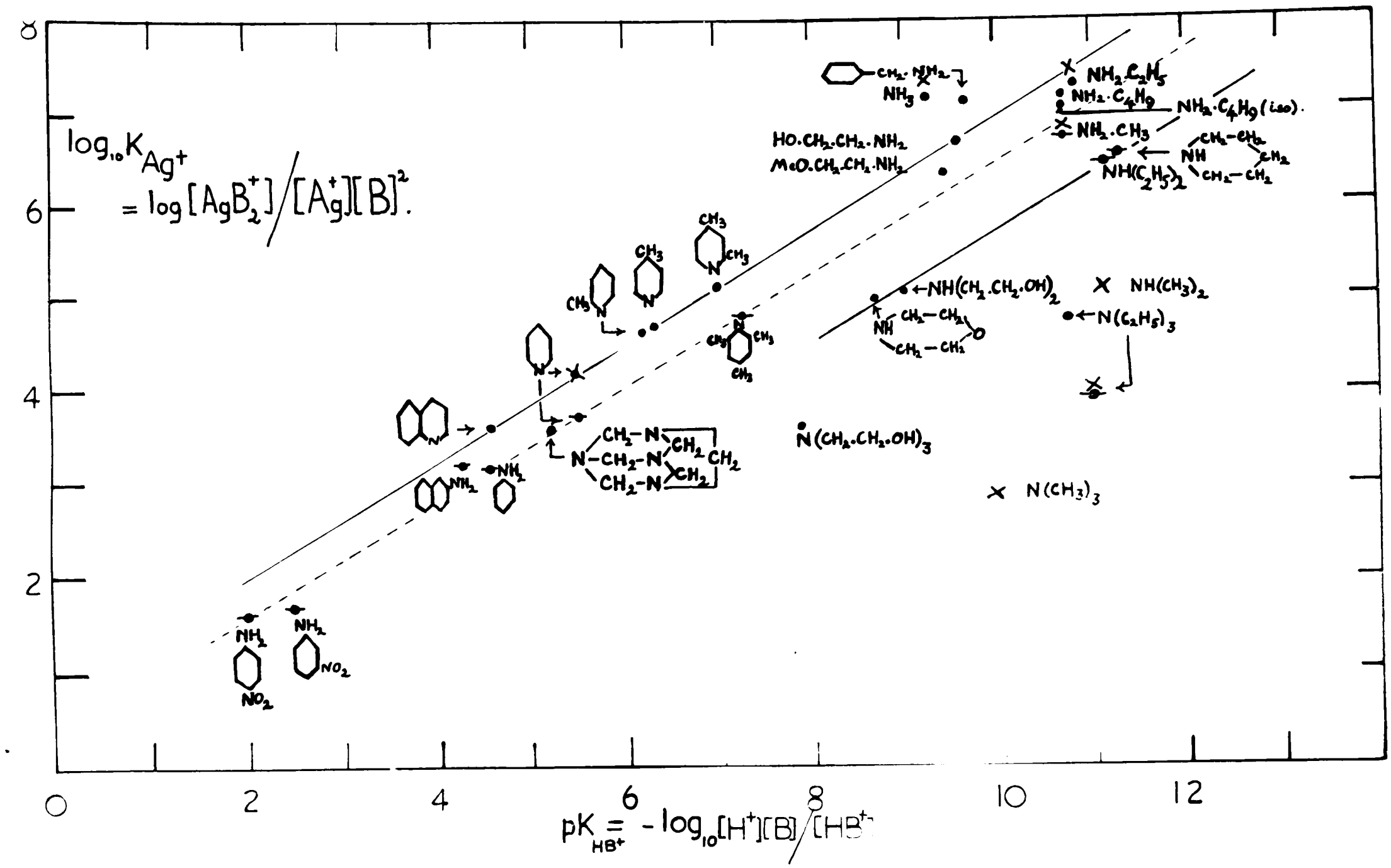


fig. 4.

amine for silver ion, measured by RT log K_1.

For silver amines $K_1 \sim K_2$

So, $RT \log K_1 \sim \frac{1}{2} RT \log \beta_2$

Larsson (62) measured β_2 for about twenty different silver amines in aqueous alcohol and found a rough correlation with basic strength.

Britton and Williams (63) denied the existence of such a relationship.

In 1948, Bruehlman and Verhoek (59) determined stability constants of various silver ammines and using these and other data, established that the ratio log β_2/ log K_{AH} was constant in certain groups of amines. Their experimental results are shown in the graph opposite. (fig. 4.).

It is of interest to determine whether regularities are apparent in ratios of both heats and of entropies of formation for silver ammines and onium ions.

Experimental Procedure.

Apparatus.

The cell used was identical with that described on p.50. apart from the following modification. It was necessary to use saturated potassium nitrate solution instead of saturated potassium chloride solution. A salt bridge of agar-agar-

jelly containing KNO_3 was built, in the tube F, (p.50.), which connects the calomel cell to the rest of the apparatus. The reservoir, A, contained saturated KNO_3 solution, which completely filled the capillary tubing from the agar-bridge to the plug P.

Procedure.

The procedure was that of the standard pH titration method, of which details are given on p.49. All measurements were made at 25°C. Amine solutions of strength ~ 1 M in 0.10 M KNO_3 were run into the reaction cell from the micro-burette. In the determination of base constants, 25 ml. of standard 0.10 M nitric acid was placed in the cell. For stability constants, 25 ml. of acid-metal solution was placed in the cell.

The concentration of metal-acid solution for all amines was:-

$AgNO_3$ = 0.02 M.

HNO_3 = 0.08 M.

In all solutions, the concentration of NO_3^- was constant = 0.10 N to keep the liquid junction potential as constant as possible (see p.53). The preparation of solutions is described on p.171. Results for pH runs are given on pp.200-5.

The calculated formation curves, on which experimental points have been plotted are shown opposite pp.107, 200, 202.

The method of calculation of base constants was that described on p.79 . Stability constants were calculated by the "correction term" method. (see p.86). Results are given in Table XX, p.107.

Results.

The discussion of the results reported in Table XX will be deferred until section VI, p.138

The results from solubility measurements at 25° have been reproduced here for comparison and are in good agreement with those obtained by the pH method.

The stability constants from the solubility method refer to solutions of very low ionic strength, which suggests that for silver amines, K^c varies little with ionic strength; i.e. it implies that the ratios:-

$$\frac{f_{Ag^+} \cdot f_A}{f_{AgA^+}} \qquad \text{and} \qquad \frac{f_{AgA^+} \cdot f_A}{f_{AgA_2^+}}$$

are effectively constant for ionic strengths of values up to 0.10 at least.

Systems, Ag^{+}-Pyridine at 25°C.
Ag^{+}-4-Picoline at 25°C.
Ag^{+}-2:6-Lutidine at 25°C.

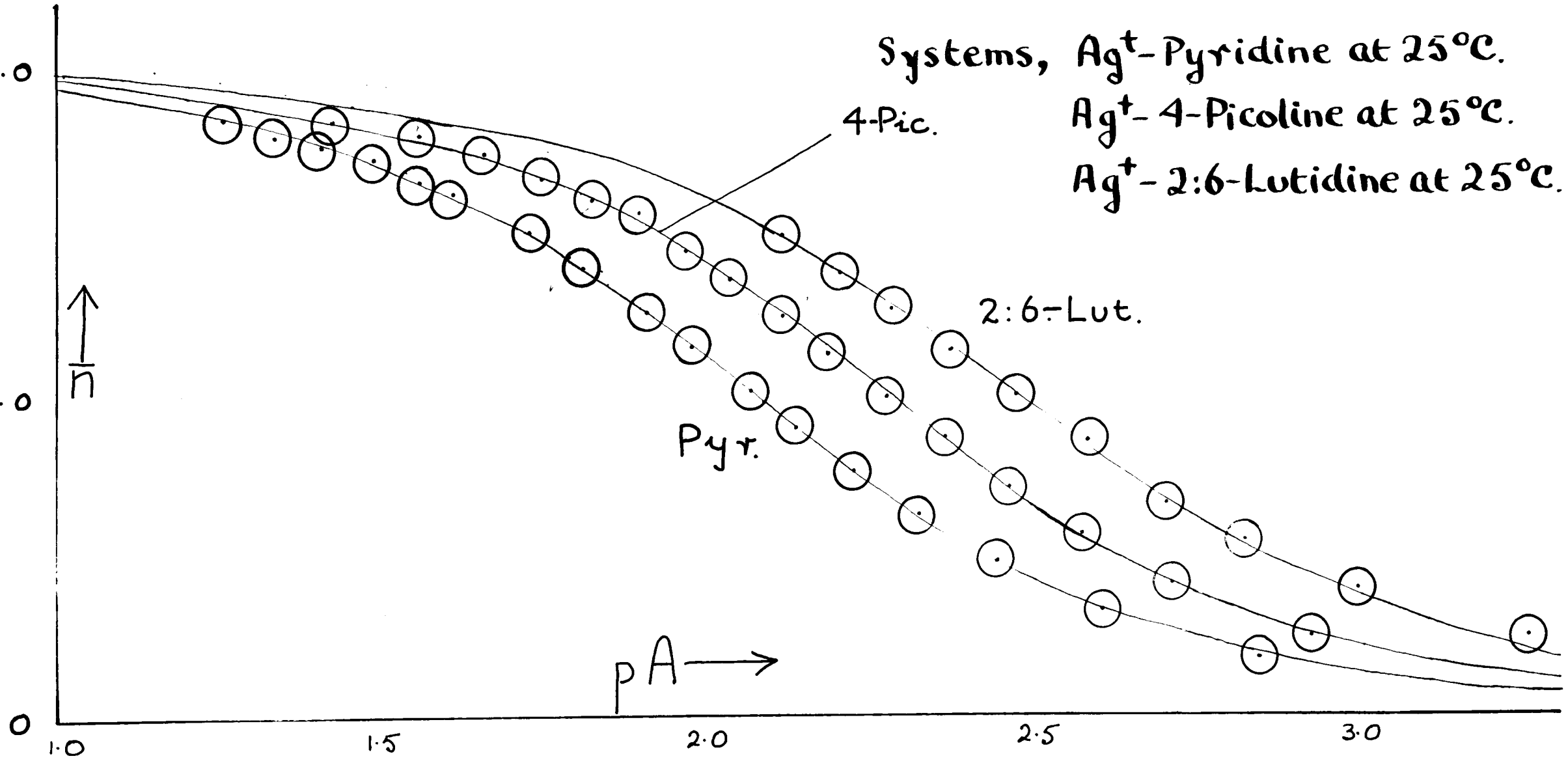


TABLE XX

The Base Dissociation Constants and Stability Constants of Silver Complexes of some Amines at 25°C in 0.10 N Nitrate Solutions.

Ligand	pK_A	log K_1	log K_2	log β_2
Ammonia	9.38	3.48	3.78	7.26
Pyridine	5.30	2.02	2.10	4.12
3-Picoline	5.72	2.10	2.13	4.23
2-Picoline	6.05	2.30	2.22	4.52
4-Picoline	6.09	2.24	2.28	4.52
2:6-Lutidine	6.71	2.49	2.43	4.92
2:4:6-Collidine	7.41			

Solubility Method.

	log K_1	log K_2	log β_2
Pyridine	2.02	2.07	4.08
2:6-Lutidine	2.50	2.38	4.88

SECTION IV

Heats of Formation of Complexes in Solution.

Very few heats of formation of complex ions have been reported in the literature, although the desirability of obtaining such information has been frequently remarked. In most discussions concerning the factors influencing the stabilities of a series of complexes, either heats of reaction have been assumed to be identical (23,37,64), or entropy changes have been supposed to be unimportant, (8). Again, arguments have been based upon enthalpy data obtained by unreliable methods such as those examined in Sections I and II. (9,23,37,53). Only recently have direct calorimetric measurements been made of enthalpy changes in the formation of complexes in solution. (38,48,67,68).

By using solutions containing different concentrations of ligand and measuring the heat of interaction for each one with a solution of metal ion, it is possible to set up a series of simultaneous equations, from which, by using the successive stability constants for the system, individual heats of formation for each complex ion present can be calculated. This technique has been used by Staveley (48) and Latimer (68).

It was considered, however, of more interest to measure the overall heat of formation for as many systems as possible, rather than to measure the integral heats of formation for a small number of systems.

The results so obtained for the reaction of metal ion with a large excess of ligand are unambiguous in that they do not depend upon the knowledge of independent stability constants.

All heat changes were measured in solutions of ionic strength, μ = 0.10 at 25°C, and when combined with the free energies measured at the same temperature in solutions of the same ionic strength by the equation,

$$\Delta S^{*} = \frac{\Delta H^{*} - \Delta G^{*}}{298} \qquad \ldots. 6.$$

the entropy changes so calculated, although not thermodynamic quantities, are directly comparable.

The apparatus used for all the measurements was a twin micro-calorimeter. Concurrently, the construction of a similar twin calorimeter with only minor modifications, was undertaken, with the assistance of two other workers, (Messrs. J. Knight and D. Rutley). Although construction of the second calorimeter has been completed, as yet no heats of formation have been measured with it and no account,

other than that of the first calorimeter and the modifications made to it, will be given here. A detailed description of the twin micro-calorimeter has been already published (22), and so in the description of apparatus, minor constructional details will be omitted. So that small volumes of metal solution could be introduced into a large volume of amine solution, a glass hypodermic syringe, which was actuated by an external micrometer screw gauge was mounted in each vessel of the twin calorimeter.

In the present section, the apparatus will be described, the method of operation and calculation of results will be illustrated with reference to a typical run, and factors affecting the accuracy of the method will be discussed. Results obtained are given in Table XXII, p.129.

Apparatus.

In the drawing of the apparatus, given opposite p. 111 , the syringes and their mountings have been omitted for the sake of clarity.

The twin calorimeter consists, effectively of two calorimeters, which are, as far as is practically possible, identical. Each calorimeter vessel is a Dewar flask, D.

The Twin Micro-Calorimeter.

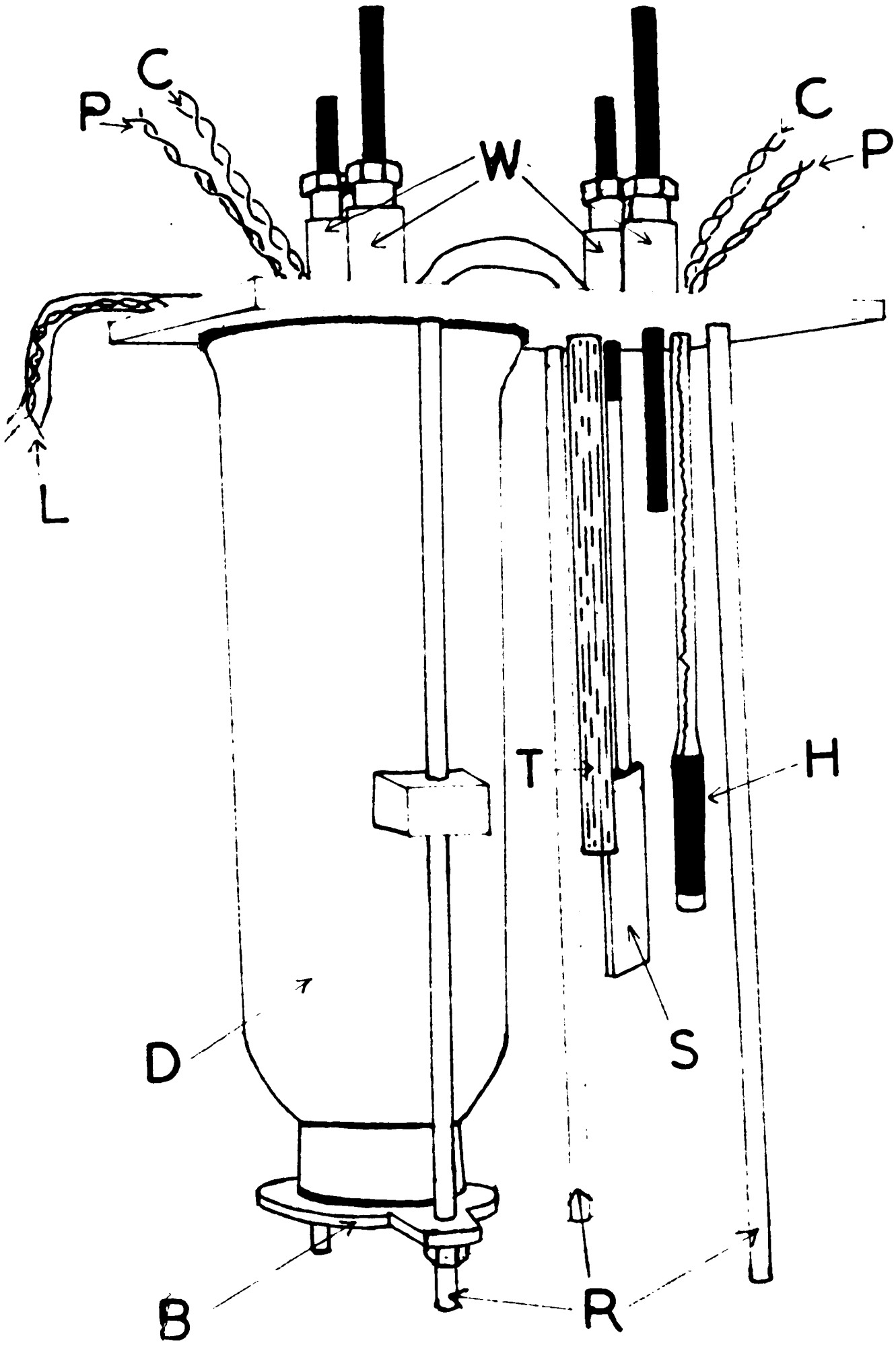


fig. 5.

Both vessels are supported from a common brass plate, from which they are separated by rubber gaskets. Tapped rods (R) project vertically below the top plate, and by means of two sliding padded base plates (R), upon which considerable force may be exerted by thumb screws, each Dewar is pressed against its gasket so that a pressure- and vacuum-tight seal is formed between it and the top plate. Inside each calorimeter is a stirrer, (S), an electrical heater (H), a thermel * (T), and a hypodermic syringe.

The stirrer rods and the rods for actuating the syringes pass through pressure- and vacuum-tight "Wilson seals" (W), in the top plate. Solutions in the calorimeters come in contact with glass surfaces only. The whole apparatus is mounted in a water thermostat at $25^{\circ} \pm 0.003^{\circ}C$.

The Dewar Vessels.

The flasks are of the silvered type, each of 500 ml. capacity and as nearly identical in heat capacity and in thermal leakage coefficient as could be made. The same volume of solution was always used in the calorimeters. This volume, about 300 ml, was run in from a constant volume pipette

* In one calorimeter, there is also a subsidiary thermel

When each contained 300 ml. of water, the difference in heat capacities of the two calorimeters was found to be 0.1%.

The thermal leakage coefficients were found to be very small ($\sim 0.0006^{\circ}/min/^{\circ}C$) and differed by only 2%.

Thermels.

The main thermel, which indicates the temperature difference between the two calorimeters, is constructed of 19 chromel-constantan junctions and one copper-constantan junction so that no external thermal potentials are caused. The junctions are pressed against the flat bottom of the thin glass sheath in which they are mounted, embedded in naphthalene, and insulated from one another by "Bakelite" varnish. The copper output leads, (L) are joined through a resistance network to a photo-electric galvanometer amplifier similar to that described by Preston (69).

At full sensitivity, a difference in temperature of 4×10^{-6} $^{\circ}C$ between the two calorimeters causes a deflection of 1 mm. on the scale of the secondary galvanometer.

A secondary thermel of 4 chromel-constantan junctions is mounted in one of the calorimeters, for measuring the difference in temperature of the contents of the calorimeter

and the water of the thermostat. It is connected directly to a galvanometer; a 1 mm. deflection is equivalent to a temperature difference of 0.001°C.

Stirrers.

Each stirrer is a thin rectangular sheet of Pyrex glass, (approx. 6 cm. x 3 cm.) fused to a thin glass tube. Just below the top plate, the glass tube is joined to a stainless steel rod which passes through a "Wilson Seal", lubricated by silicone grease. Both stirrers are driven at the same speed (~150 r.p.m.) by flexible cables attached to the same shaft of a synchronous motor suitably geared down.

Heaters.

Each heater (value ~ 92 ohms) consists of 40 gauge Eureka wire, (which has a very small temperature coefficient of resistance) wound upon a varnished copper former, and inside a closely fitting, thin glass jacket. Both current (C) and potential (P) leads are soldered to the coil. The resistances of the two heaters differ by only 0.03%. Resistances of the heaters were determined when the standard heating current was passing through them, by measuring the potential drop across each, using a "Tinsley" vernier potentiometer.

Syringe Mounting & "Wilson" Seal Detail.

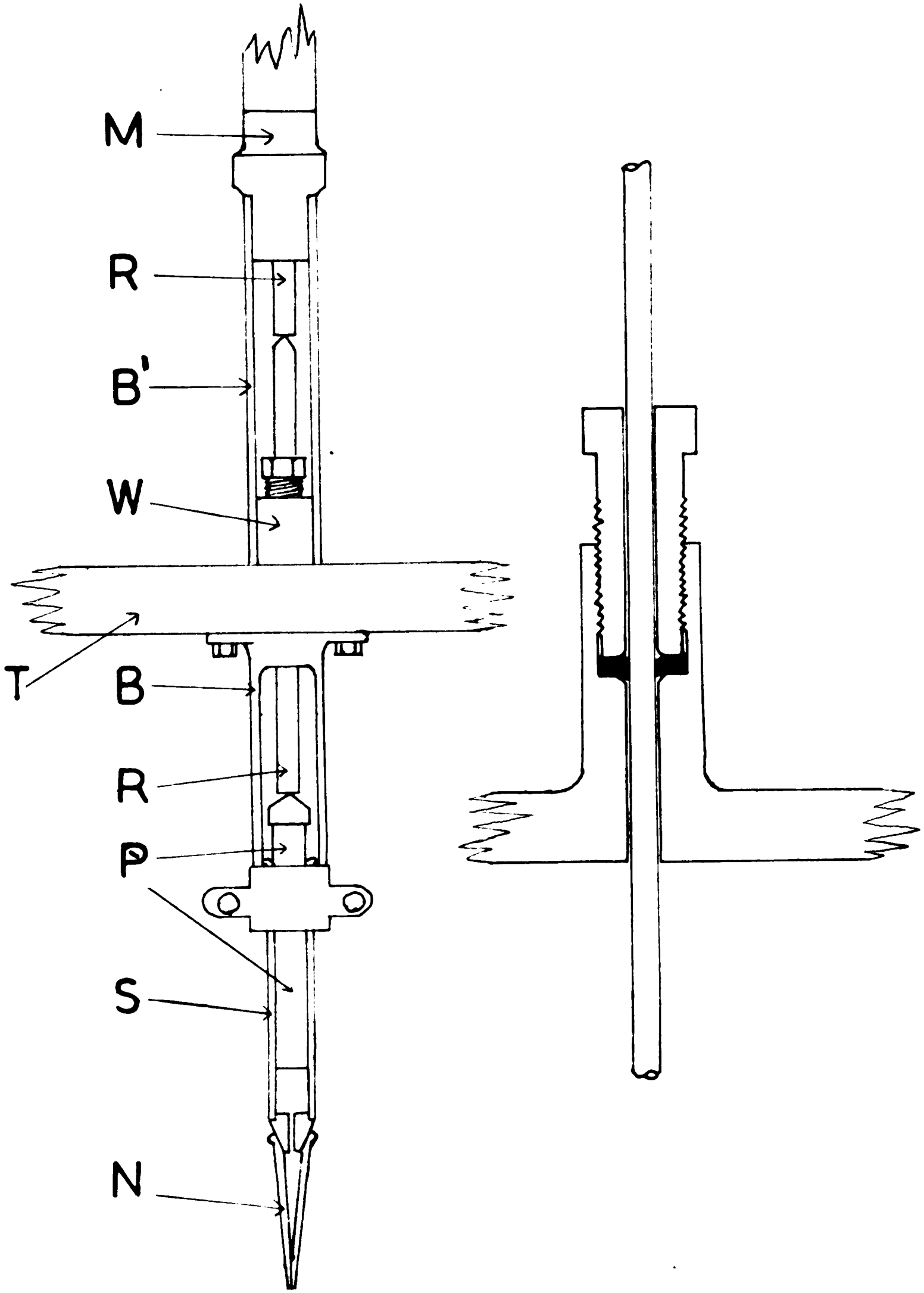


fig. 6.

Electrical Heating.

The heating current is supplied by accumulators. It runs through a standard resistance ($\sim 20\,\omega$) and a dummy heater, which has the same resistance as the heaters in the calorimeter to within 0.05%. The value of the current is kept constant by balancing the potential drop across the standard resistance against a Weston Cell. On switching the current from the dummy heater to either of the heaters in the calorimeter, a stop-watch is simultaneously actuated by an electrical relay. The stop-watch reads to 0.02 secs. The arrangement is similar to that described by Westrum and Robinson (70).

Hypodermic Syringes.

In place of the bulb holders and breakers used formerly, an "Agla" glass syringe was mounted in each calorimeter. The mode of attachment to the top plate (T) is illustrated in the diagram opposite p.114.

The barrel (S) of the syringe is clamped in the lower end of a brass tube (B), which is bolted to the top plate. A micrometer screw gauge (M) is clamped into a brasstube (B') the lower end of which is clamped to the "Wilson" seal.

Syringe Nozzles.

The glass nozzles (N) provided with the syringes were found to allow some diffusion to take place between the solution inside the syringe and that surrounding it. Accordingly the tips of the nozzles were drawn down to very fine jets, from which effectively no diffusion was shown to take place (by the use of very concentrated solutions of dyes).

The position of each syringe is adjusted so that when fully charged with reactant, the face of the piston is just below the level of solution in the Dewar vessel, ensuring that the whole contents of the syringe are at the same temperature as the solution in which reaction took place.

The Capacity of the Syringes.

Each syringe delivers very nearly 0.5 ml. of solution. The movement of the screw gauge is 50 revolutions. For each revolution there are 50 scale divisions. Thus one scale division corresponds to a volume of 2×10^{-4} ml. In all experiments, additions corresponding to only 48 of the 50 scale divisions were made. By filling the syringes with mercury and weighing the successive volumes delivered at scale readings of 12, 24, 36, and 48 units, the bores of the syringe barrels were found to be regular to the extent,

that no one aliquot differed in weight from any other by more than 1.5 parts in a thousand.

For the overall scale reading, 0 - 48 units, the weight delivered was found to be reproducible to two parts in five thousand. The concentrations of solutions were known in terms of weight, see pp.176-7, and so it was not necessary to know the volumes, but only the weights of solution delivered by the syringes. A correction was applied because contents of syringes weighed at 20°C (room temperature) were 0.1% greater than the contents at 25°C (in the calorimeter).

Procedure.

The preparation of solutions and their analyses are described on pp.175-7.

In the following account, the calorimeter in which reaction takes place is referred to as A, and the one containing solution without ligand as B.

Syringe A is filled with metal solution ($\sim$ 1 M), and its contents corresponding to 48 scale divisions are weighed accurately. Syringe B is also filled with the same metal solution.

Ligand solution is run into A from the constant volume pipette. An equal volume of solution of background salt of equal concentration to that in A, is run into B. Both

solutions are preheated to 24.9°C before placing in the calorimeters. The calorimeters are screwed tightly into place against the top plates.

The apparatus is immersed in the thermostat, the stirrers switched on, and using the electrical heaters and the subsidiary thermel, the calorimeters are brought to the same temperature about 0.04°C below that of the bath temperature. For about one hour, the apparatus is allowed to settle down. A linear drift in the temperature difference between the two calorimeters is observed on the scale of the secondary galvanometer of the main thermel. The drift, which is mainly due to differences in heats of stirring, is between 0.1 and 0.5 cm/min. (4 - 20° x 10^{-6}/min.). Readings are taken every minute and the drift plotted. After about ten readings, the gauges on A and B are screwed down from scale reading 0 units to 12 units, and electrical heat switched into B to bring the two calorimeters to the same temperature. Drift readings are taken for the next ten or fifteen minutes. Usually reaction was rapid, and three minutes after injection of reactant solution, the drift was again linear. However, one/reaction took about twenty minutes to reach completion, (see p. 127), and so drift readings were taken for forty minutes.

A further amount of electrical energy,(heating current switched on;about four seconds),is put into B and a third set of drift readings plotted.

A typical trace is given opposite p.120.

Three more sets of measurements are made for reactant injection from the syringes for screw gauge readings 12 to 24, 24 to 36, and 36 to 48.

At the end of the run, current is passed through the heaters wiredin series, and from the resultant small difference in temperature of the calorimeters the difference in heat capacities calculated. A correction for this difference is applied accordingly.

After stripping down the calorimeter, syringe A is refilled with metal solution, and the contents (from 0 to 48) reweighed. This is a precaution taken to ensure that the barrel of the syringe has not altered in alignment since the commencement of the run.

To illustrate the procedure and calculation of results, details of a typical run are given below.

The Heat of Formation of Copper-Bis-Ethylenediamine in Aqueous 0.10 M KCl Solution at 25°C.

Solutions Used.

300 ml. of 0.10 M KCl solution in calorimeter B.

300 ml. of 0.05 M ethylenediamine in 0.10 M KCl solution in calorimeter A.

Syringes filled with a solution of copper perchlorate.

Contents of syringe A at 20°C

before run = 0.5661 g.

Contents of syringe A at 20°C

after run = 0.5659 g.

Mean content = 0.5660 g.

By electrolytic analysis, (see p.176),

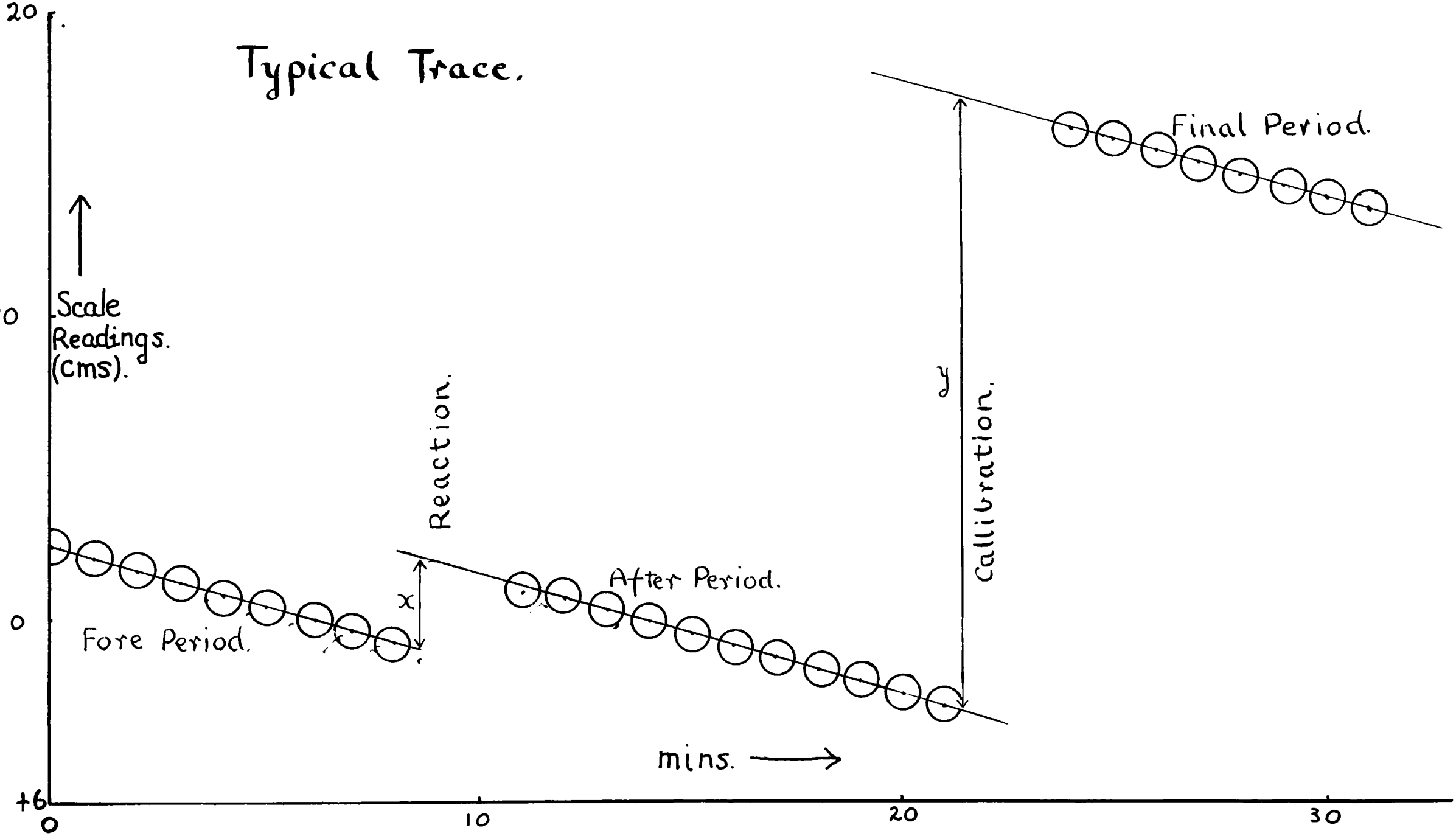
1 g. of copper soln. ≡ 0.04981 g. Cu ≡ 7.833×10^{-4} g.ion. Cu^{2+}.

At 25°C, syringe A delivers 4.430×10^{-4} g.ion Cu^{2+}.

Typical Trace

The trace is plotted opposite p.120, from the following readings:-

Typical Trace.



Time min.	Scale reading cm.	Time min.	Scale reading cm.
0	- 2.42	15	+ 0.51
1	- 2.00	16	+ [illegible].92
2	- 1.61	17	+ 1.28
3	- 1.23	18	+ 1.69
4	- 0.81	19	+ 2.11
5	- 0.40	20	+ 2.50
6	+ 0.01	21	+ 2.91
7	+ 0.43	4.01 sec. heating in A.	
8	+ 0.80	24	- 16.30
0 - 12 units of Cu^{2+} soln. injected.		25	- 15.93
		26	- 15.54
49.58 sec. heating in B.		27	- 15.12
11	- 0.95	28	- 14.72
12	- 0.70	29	- 14.36
13	- 0.32	30	- 13.94
14	+ 0.13	31	- 13.53

Typical Trace

The plot is given in the graph opposite p.120.

Between the 8th and 9th minutes, copper solution was injected from 0 - 12 divisions into calorimeters A and B.

The heating current was run into heater B for 49.58 sec. Between the 21st and 22nd minute heating current in B for 4.01 sec.

It can be seen that at the time of reaction, slightly more heat was put into B than was generated in A.

4.01 sec. in B causes a temperature change of y cm. on scale.

$$x \text{ cm.} \equiv {}^{x}/_{y} \times 4.01 \text{ sec. heating}$$

$$\text{Thus, heat generated in A} \equiv 49.58 - \frac{4.01 \times 3.15}{20.44} \text{ sec. heating in B}$$

$$\equiv 48.96 \text{ sec. heating in B.}$$

It was found that, because there are only very small temperature changes in the calorimeters, the slopes of traces of fore period, after period and final period were usually very nearly equal and no difficulties were found in extrapolation.

The second addition of heat to B, is, in effect, a calibration of the galvanometer scale in terms of heating time.

It was found that it was only necessary to calibrate once during a run.

For the four additions of copper solution in this experiment the heating times were:

	48.96 sec.
	49.12
	49.08
	49.09
Total	196.25

The heat capacity of A was found to be 0.21% less than B.

Corrected total heating time = 195.83 sec.

1 sec. heating in B is known to give 0.05678 cal.

Heat generated in A = 11.119 cal.

All the Cu^{2+} ion added has been converted into $CuEn_2^{2+}$, (as can be calculated from stability constants).

Thus, the heat of formation of :

4.430×10^{-4} g.ion $CuEn_2^{2+}$ = 11.119 cal.

Heat of formation of :

$CuEn_2^{2+}$ = 25,100 cal.g./ion.

General Considerations.

The heat produced by the dilution of the metal salt solution in A is small compared with the heat of reaction. By performing a similar injection of metal salt solution in B, the heats of dilution cancel out one another.

In one sense, each of the four additions of metal ion constitutes a separate experiment. However, it was felt that taking an average of the four results was not justified, since errors in analysis of the metal solution and in the measurement of the difference in heat capacities of the two calorimeters would affect each result in the same way and would not average out. Instead, the consistency of the four results was regarded as confirmation that complete complex-formation was taking place in the reaction.

A second run was always performed with reaction in B, and compensation by electrical heating in A. Usually good agreement between the two results was obtained. When the results differed by more than 0.3%, three, and in some cases, four runs were performed.

It was suggested that the use of syringes might cause heating effects resulting from the flow of solution through an extremely fine jet and from the movement of the piston. When a syringe-full of water was injected into a calorimeter containing 300 ml. of water, no observable alteration of

the linear temperature drift was found, showing that no such heating effects occurred.

Solutions Used.

All solutions used were made up in distilled water from which the carbon dioxide had been boiled out. The solutions injected from the syringes were of such concentrations that 12 unit additions gave heats of reaction corresponding to electrical heating compensation times of about 30 seconds.

Metal Sulphate Solutions.

"AnalaR" sulphates of the divalent metals were used. However, it was found that when nickel and copper sulphate solutions were used, measured heats of formation with ethylenediamine were larger than expected and not reproducible. Solutions of $CuSO_4$ and $NiSO_4$ deteriorated rapidly, becoming cloudy within a few hours. These facts may be explained by postulating the formation of basic-salt type aggregates in aqueous solution, which give rise to a certain acidity. Perchlorates of nickel and copper were used, reproducible results were obtained and no rapid deterioration of the metal solutions took place.

All solutions were made up and analysed on the day on which they were used (see p.175).

Acid solutions.

Hydrochloric acid was used in all experiments upon the heats of neutralisation of amines. The preparation and standardisation of acid solutions are described on p.173.

Amine solutions.

Heats of Mixing.

For the zinc and cadmium complexes of ethylenediamine and for the methyl-pyridine complexes of silver, to ensure complete formation of the highest complex species, it was necessary to use amine solutions of strength ~ 1 M.

It was first observed in the reaction of hydrogen ion with pyridine, that in solutions of pyridine of concentration 0.10 M, high results for the heat of reaction resulted. The extra heat produced was found to be due to the heat of mixing of water with the concentrated amine solution. When a syringe-full of water was injected into 1 M pyridine solution, the heat produced was found to be 0.151 cal. For 2:6-lutidine, the heat produced was 0.159 cal. When these heats were subtracted from the total heats measured in the interaction of hydrochloric acid with molar solutions of pyridine and 2:6-lutidine respectively, the heats of neutralisation so calculated agreed well with those measured in 0.10 M solution. In amine solutions of concentration

0.10 M and less, there is no measurable heat of interaction when water is injected from the syringes.

By making preliminary measurements of the heat changes caused by the interaction of molar solutions of the methylpyridines with water, corrections were calculated which were subtracted from the heats generated when aqueous solutions of silver ion were injected.

With 1.2 M ethylenediamine solution the heat produced by the injection of 48 units of water from a syringe was only 0.048 cal. This correction was applied in the results for $ZnEn_3^{2+}$ and $CdEn_3^{2+}$.

Heat Capacity Effects.

When an amine solution of concentration $\sim$ 1 M was placed in calorimeter A, it was found that the heat capacity of calorimeter A was $\sim$ 1% smaller than that of B. In such cases extra amine solution (about 4 ml.) was added to the contents of A to make its heat capacity approximately equal to that of B ($\pm$ 0.2%).

Slow Reactions.

After an injection of reactant, by following carefully the drift of temperature difference between the two calorimeters, it is possible to estimate at what time after

injection the reaction is complete, i.e. when the drift becomes linear. The slow reactions found are given below in Table XXI.

TABLE XXI.

Complex formed.	Approx. time of complete reaction (min.)
$Ag(2\text{-picoline})_2^+$	4.0 - 4.5
$Ag(2:6\text{-lutidine})_2^+$	5.5 - 6.0
$Ni(ethylenediamine)_3^{2+}$	3.5 - 4.0
$Cu(1:3\text{-diaminepropane})_2^{2+}$	17 - 19
$Ni(1:3\text{-diaminopropane})_3^{2+}$	23 - 25

Degree of Formation of Complexes.

The concentrations of amine solutions used in almost all cases gave complete complex formation. In the few cases where this was not true, a correction was applied, the assumption being made that the heat of overall formation, $\Delta H_{1\ldots N}$ could be calculated to within 0.1% by the relationship

$$\Delta H_{1\ldots N} = \frac{N.\ \Delta H_{1\ldots\bar{n}}}{\bar{n}}$$

provided $\bar{n} > 99.5\%\ N.$

Nickel-(1:3-diaminopropane)$_3$.

It was impossible to obtain sufficient supplies of 1:3-diaminopropane to make up a suitable solution (> 1 M) in which to find the heat of formation of $Ni(Tn)_3^{2+}$. However, measurements in dilute solution showed that a slow reaction took place.

Results.

Measured heats of formation of the complex ions are given on the following pages and discussion of their significance will be deferred until Section VI.

TABLE XXII

Amine - Hydrogen Ion Reactions at 25°C in Aqueous Solution of Ionic Strength 0.10.

Ion Formed	Background Salt	Amine Concentration	-ΔH. cal./g.ion.
NH_4^+	0.10 N KNO_3	0.10 M	12,450 ± 40
EnH^+	0.10 N KCl	0.10 M	11,940 ± 40
TnH^+	0.10 N KCl	0.10 M	12,640 ± 40
Pyridine H^+	0.10 M KNO_3	0.10 M	5,090 ± 20
2-Picoline H^+	0.10 N KNO_3	0.10 M	6,330 ± 20
3-Picoline H^+	0.10 N KNO_3	0.10 M	6,000 ± 20
4-Picoline H^+	0.10 N KNO_3	0.10 M	6,300 ± 20
2:6-Lutidine H^+	0.10 N KNO_3	0.10 M	7,490 ± 30
2:4:6-Collidine H^+	0.10 N KNO_3	0.10 M	8,490 ± 30

TABLE XXIII

Heat of Formation of Silver-amines at 25°C in 0.10 N KNO_3 Solution.

Ion Formed	Amine Concentration	$-\Delta H_{12}$ cal./g.ion
$Ag(NH_3)_2^+$	0.20 M	13,480 ± 50
$Ag(pyridine)_2^+$	1.0 M	11,810 ± 50
$Ag(2:picoline)_2^+$	1.0 M	11,120 ± 50
$Ag(3:picoline)_2^+$	1.0 M	11,820 ± 50
$Ag(4:picoline)_2^+$	1.0 M	12,370 ± 50
$Ag(2:6-lutidine)_2^+$	1.0 M	10,750 ± 50

TABLE XXIV.

Heats of Formation of the Divalent Metal Ammines at 25°C in 0.10 M KCl Solution.

Ion Formed	Amine Concentration	- (Ht. of formation) cal./g.ion.
$Cu(En)_2^{2+}$	0.05 M	25,080 ± 80
$Ni(En)_3^{2+}$	0.10 M	27,210 ± 80
$Zn(En)_3^{2+}$	1.20 M	15,520 ± 50
$Cd(En)_3^{2+}$	1.20 M	19,740 ± 80
$Cu(Tn)_2^{2+}$	0.05 M	22,870 ± 80

SECTION V.

Complexes of 1:10-Phenanthroline.

If the stability constants of complexes of divalent ions of the first transition series are plotted against atomic number of the central ion, there is a monotonic increase, to a maximum at copper. Irving and Williams, who first observed the relationship, have since shown (5) that for over sixty different complexing agents there is a "natural order" of stabilities. It is

$$Mn < Fe < Co < Ni < Cu > Zn$$

Steric factors lead to an all-round lowering of stabilities but do not often cause deviations from the natural order (13).

Irregularities can be caused by "orbital stabilisation", (9) and it is the anomalous behaviour of ferrous iron with large organic aromatic ligands which is considered here.

The successive stability constants of complexes of the divalent metal ions with 2:2'-dipyridyl and 1:10-phenanthroline have been measured in this laboratory (24) by a partition method. The results for phenanthroline are given below in Table XXV.

TABLE XXV.

Stability Constants of Complexes of 1:10-Phenanthroline Measured at 25° in Aqueous Solution of Ionic Strength 0.10.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
log K_1	4.80	5.85	7.02	8.00	8.82	6.30	5.17
log K_2	4.10	5.30	6.70	8.00	6.57	5.65	4.83
log K_3	(5.40)	10.0	6.38	7.90	5.02	5.10	4.26
log β_3	14.30	21.15	20.10	23.90	20.41	17.05	14.26

The first stability constant, K_1, is seen to fall in the natural order for all the elements. For the addition of the second ligand, copper is abnormal. The third constant, K_3, and the overall constant, β_3, show abnormalities for both copper and iron.

With dipyridyl, the same abnormalities and the same stability order is observed.

i.e. For ferrous iron, $K_3 > K_2 \sim K_1$

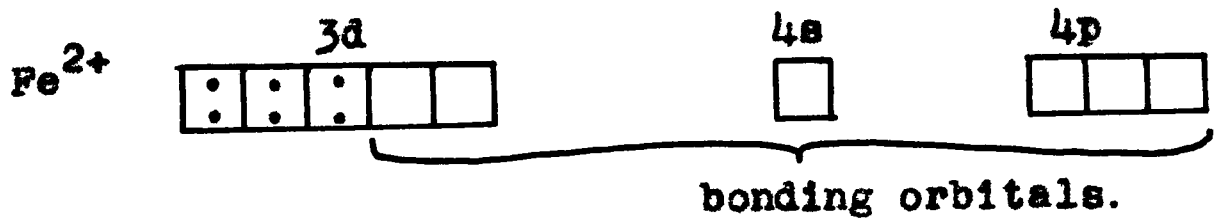
and for β_3 Ni > Fe > Cu > Co > Zn > Cd > Mn

The abnormal behaviour of copper has beeen explained elsewhere (24) and will not be commented upon here.

The outer electronic structure of the ferrous ion is:-

Magnetic susceptibility measurements show that the paramagnetism of the ferrous ion due to the four unpaired 3d electrons is not altered when colourless weak tris-complexes are formed with ligands such as ethylenediamine.

The ferrous tris-phenanthroline complex, which is an intense red colour, has been found to be diamagnetic (26). There can be little doubt that there has been an electronic rearrangement, such that two 3d orbitals become vacant and are available for forming octahedral $3d^2 4s 4p^3$ bond of strong "inner hybrid" type.



Confirmation is provided by the resolution of ferrous tris-phenanthroline complexes into stable optically active antipodal forms (73).

The large increase in stability when the third ligand becomes attached to the ferrous ion, and the usual positions of K_1 and K_2 in the natural order, strongly indicate that

hybridisation does not occur until the attachment of the third ligand. This has been confirmed by recent work of Basolo and Dwyer (72) who find that on heating the solid diamagnetic tris-complex, one molecule of ligand may be eliminated; the bis-complex resulting is found to have the same paramagnetism as the free ferrous ion (5.2 B.M.).

Magnetic susceptibility measurements on the tris-complexes of the other transition metal-ions show that none of them employs inner $3d^2 4s 4p^3$ bonding (27, 73). Vosburgh and Cooper (74) have shown that the addition of complexing agents, ammonia, ethylenediamine and phenanthroline to aqueous solutions of Ni^{2+} ion causes only very slight decreases in its paramagnetism ($< 5\%$) due to quenching of orbital components.

The ions, Zn^{2+} and Cd^{2+}, have full inner d-orbitals and like the transition metal ions (apart from Fe^{2+}), form bonding orbitals of the "outer hybridised" type, $4s 4p^3 4d^2$ (64).

The abnormal stability of $Fe(phenan)_3^{2+}$ is due to "inner orbital" stabilisation and this increase in bond strength is expected to give a large heat of reaction.

The heat of formation of $Fe(phenan)_3^{2+}$ in aqueous solution at 25°C and $\mu = 0.10$, was measured by the calorimetric method described in Section IV.

For purposes of comparison, the heats of formation of the tris-phenanthroline complexes of Ni^{2+}, Zn^{2+} and Cd^{2+} were also measured under the same conditions. The results are given in Table XXVI, p.137, and discussed on p.159.

Experimental.

The ligand solution (300 ml) contained phenanthroline, of concentration 0.01 M, which was 100% in excess of that required for complete complex formation, when 0.5 ml. of metal solutions of strength $\sim$ 0.5 M were injected.

For the ferrous solution, "AnalaR" grade sulphate was used, with the addition of a small amount of hydroxylamine hydrochloride. The solution remained clear for the duration of the experiment but precipitated ferric hydroxide on standing. Ionic background was provided by 0.02 M sodium acetate and 0.08 M potassium chloride. When using cadmium solutions, 0.08 M potassium nitrate was used instead of potassium chloride, since $[Cd(phenan)_3]^{2+}\ Cl_2^-$ is only sparingly soluble.

TABLE XXVI

Heats of Formation of Tris-Phenanthroline Complexes at 25°C in an Ionic Strength of 0.10.

Metal Ion	- ΔH cal./g.ion.
Fe^{2+}	29,970 ± 100
Ni^{2+}	26,800 ± 100
Zn^{2+}	19,470 ± 100
Cd^{2+}	19,300 ± 100

SECTION VI.

Discussion

Although, in previous sections, solvent interaction has not been represented in equations for the formation of complex ions, it is a factor of primary importance in aqueous solutions. Nevertheless, provided the activity of water remains constant, the relationships derived from the Bjerrum treatment of equilibria for successive complex species are still valid (7). All types of solute species, whether ionic, or uncharged, are surrounded by a sheath of water molecules. Frank and Evans (53) have shown that the process of hydration is similar in many ways to the freezing of a patch of water round each species in solution. This formation of microscopic "icebergs" is accompanied by an attendant decrease in heat content and entropy of the water molecules due to their loss of translational freedom, and, to some extent, restriction of rotation (libration). (75,76).

The equilibria to be discussed below are mainly those between ions and uncharged ligand molecules, for which the general reaction is represented:-

$$M^{m+}(xH_2O) + nL(yH_2O) \longrightarrow ML_n^{m+}(3H_2O) + (x + y - z)H_2O$$

Exact values cannot be assigned to x, y and z. For a specific metal ion, different experimental methods of determining x, such as mobility, water transport, dialysis, etc. give results, which although of the order expected, are not completely concordant. (77).

It might be expected that entropies of solution of gaseous metal ions should give a direct measure of x. However, Frank and Evans (53) pointed out that although an ion may have an inner sphere of hydration containing a definite small number of water molecules, immediately outside this sphere will be a region of disorder, since the orientation of water molecules about the ion is such that the ion-water entity cannot "fit" into the tetrahedra of water molecules which characterise the structure of water at room temperature (78,79).

For uncharged bodies, Frank and Evans have shown that entropies of solution are not directly related to polarity of the molecules but are closely related to their sizes.

Monatomic ions have entropies of solution of about the same value as uncharged bodies of the same size. However, because ion-water bonds are far stronger than water-water interactions, the heats of solution of monatomic ions are between seven and ten times as large as those of uncharged bodies of the same size.

In reactions in aqueous solution, the enthalpy and entropy changes due to the "melting" and "freezing" of the sheaths of hydration around the interacting particles obscure those due to the formation of metal-ligand bonds.

Ligand molecules, when forming complexes in aqueous solution, displace water molecules from metal ions, i.e. the patches of frozen water surrounding the ions are "melted". A heat of formation, measured in aqueous solution will be the difference between two terms, viz. the heat produced in the formation of metal-ligand bonds and the heat required to "melt" the water in the ion's sphere of hydration. Entropy changes also will be differences between two terms; viz. the entropy lost by the ligand groups and metal ion on complexing and the entropy gained by the system due to the setting free of water molecules.

The free energy for formation is given by the usual thermodynamic relationship between heat and entropy:-

$$-\Delta F = -\Delta H + T\Delta S$$

A highly hydrated ion may have a small heat of complex formation ($-\Delta H$) with a ligand because of the large amount of energy required to destroy the ion's hydration sheath. However, this liberation of water molecules will result in a large positive entropy, so that the free energy of formation may yet be large.

Another ion, with little hydration, may have large heats of formation with L, but ΔS will be small, or negative, and the free energy of formation not large. This "compensation effect", where, in aqueous solution, a small heat of reaction due to high hydration of the metal ion is balanced by a relatively large entropy of formation, is illustrated by the reactions of ethylenediamine with Ni^{2+}, Zn^{2+} and Cd^{2+}.

The following values, given in Table XXVII, were found for the formation of tris-ethylenediamine complexes at 25°C.

TABLE XXVII

The Formation of Tris-Ethylenediamine Complexes at 25°C in Aqueous Solution of Ionic Strength, 0.13, $[Cl^-]$ = 0.10.

Metal Ion	$-\Delta F$ K.cal./g.ion	$-\Delta H$ K.cal./g.ion	ΔS cal./g.ion/°C.
Ni^{2+}	23.4	27.2	- 12.7
Zn^{2+}	16.3	15.5	+ 2.6
Cd^{2+}	14.7	19.7	- 16.9

Yatsimirskii (80) has calculated the heats of formation of tris-ethylenediamine complexes in the gaseous state. A parallel series of values for the heats of hydration of the gaseous metal ions (81) are also given in Table XXVIII below.

TABLE XXVIII

Reactions:

1. $M^{2+}_{(g)} + 3En_{(g)} \rightarrow M(En)^{2+}_{3(g)}$

2. $M^{2+}_{(g)} + x(H_2O)_{(aq)} \rightarrow M(H_2O)^{2+}_{x(aq)}$

K.cal./g.ion	Fe	Co	Ni	Cu	Zn	Cd
$-\Delta H_1$	342	372	383		372	323
$-\Delta H_2$	468	497	507	507	491	436

It can be seen that the relative affinity of metal ion for ligand, i.e. ability to form strong metal-ligand bonds decreases in the order:-

$$Ni^{2+} > Zn^{2+} > Cd^{2+}$$

However, the heats of formation of the tris-ethylene-diamine complexes in aqueous solution are in the order,

$$Ni^{2+} > Cd^{2+} > Zn^{2+}$$

The anomalous order of Cd^{2+} and Zn^{2+} is probably due to the following reason:-

Zn^{2+} ion is smaller than Cd^{2+} ion and has a larger patch of "frozen" water associated with it (as shown by its more negative entropy of solution)

	r. (Å)	$-\Delta S_{(aq)}$ (91)
Zn^{2+}	0.72	- 25.45
Cd^{2+}	0.96	- 14.60

On forming complexes, although Zn^{2+} forms stronger metal-ligand bonds than Cd^{2+}, more energy is required to destroy the hydration sheath about Zn^{2+} than that surrounding Cd^{2+}, so that the resulting heat given out ($-\Delta H$) for $Zn(En)_3^{2+}$ is smaller than for $Cd(En)_3^{2+}$.

However, the destruction of the large hydration sheath of Zn^{2+} causes $Zn(En)_3^{2+}$ to have an entropy of complex formation about 20 e.u. more positive than that for $Cd(En)_3^{2+}$.

The "compensation effect" is such that for the free energies of formation, the original order of affinities is restored

$$\text{i.e. } Ni^{2+} > Zn^{2+} > Cd^{2+}$$

For the divalent ions of the transition-metals, it has been shown that for over sixty different ligands, the free energies of formation of complexes in aqueous solution fall into a "natural order" (see p.132.) (5).

$$Mn < Fe < Co < Ni < Cu > Zn.$$

This is the order expected from consideration of bond-forming power such as heats of hydration and ionisation potentials

of the gaseous metal ions. No complete series of heats of formation in solution for the complexes of the metals in the "natural order" with the same ligand are known. However, it is very doubtful whether any regular order would be observed. Even for two such closely related ligand groups as ethylene-diamine and 1:3-diaminopropane, irregularities appear. From the data given in Table XXXIII, p.157, it can be seen that when free energies of formation for the complexes of both En and Tn are compared, the natural order is followed:-

viz. $Cu^{2+} > Ni^{2+}$

When heats of formation are compared:-

for Tn, $Cu^{2+} > Ni^{2+}$

but for En, $Ni^{2+} > Cu^{2+}$

Again, the effect of hydration is to obscure one of the fundamental aspects of complex formation. Recognizing the important, and often complex role played by hydration, some consideration will now be given to the systems which have been investigated.

Silver Ammines.

From first principles, it is obvious that one of the principal factors governing the strength of a metal-ligand bond is the availability of electrons at the donor atom, i.e. the negative polarity of the donor atom.

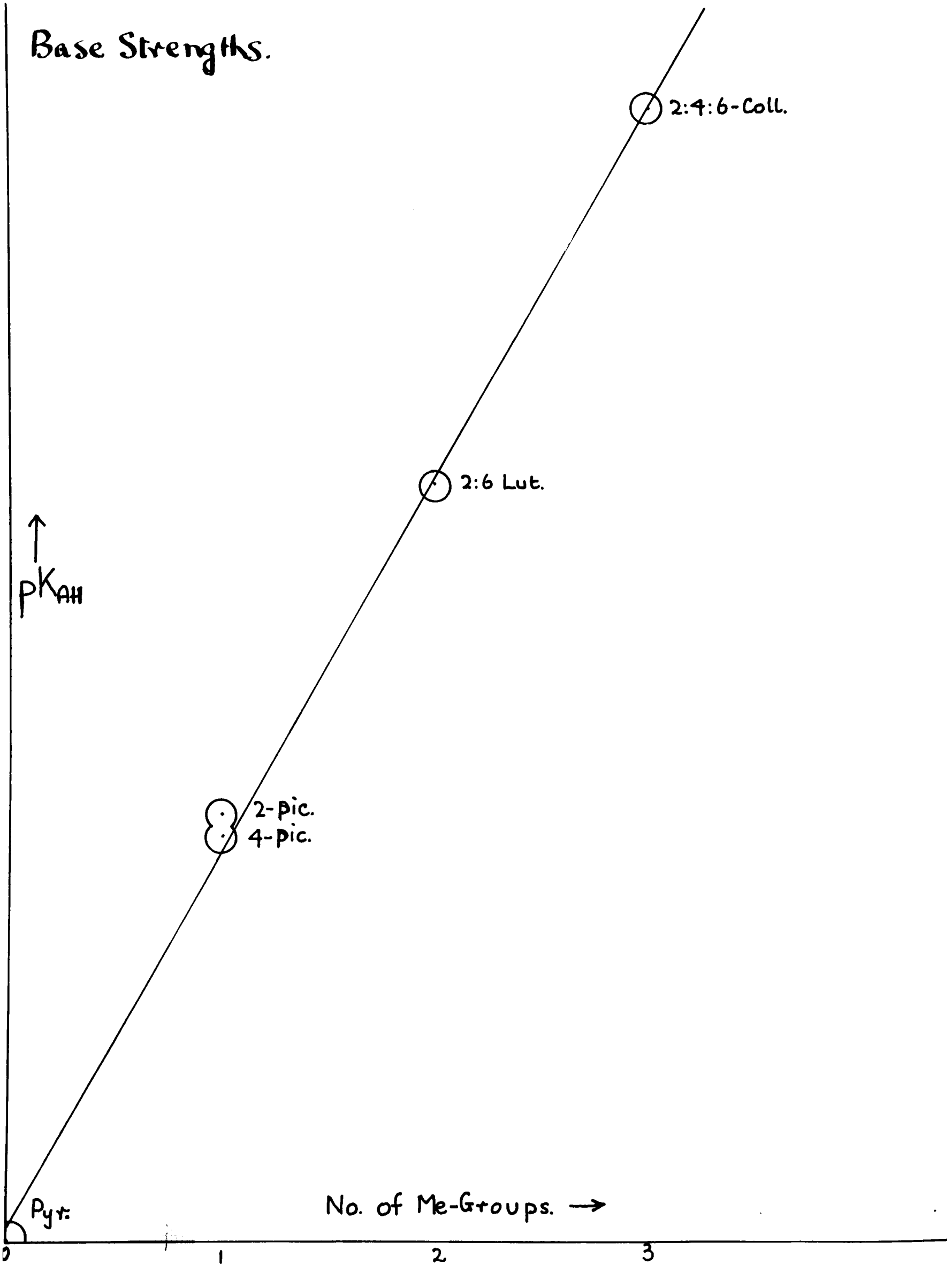
Basicities of Amines.

The polarity of nitrogen atom in an amine is often conveniently measured by the free energy of dissociation of the conjugate acid in aqueous solution. In some cases, hydration effects cause the observed result to be far different from that expected from an assessment of polar factors. One of the most familiar examples is the unexpectedly weak basicity of tertiary amines, compared with the basicity of primary and secondary amines. Brown has suggested that this is due to a Back-Effect, (100), i.e. to the steric repulsion which occurs when, in consequence of onium ion formation, the groups at the back of the amine molecule are forced closer together. Brown has also stated, (101), "the ability of hindered amines to react with aqueous acids is not noticeably affected because of the low steric requirements of the proton". Bell, (85), however, has shown that in non-polar solvents the expected order of basicities applies, i.e.

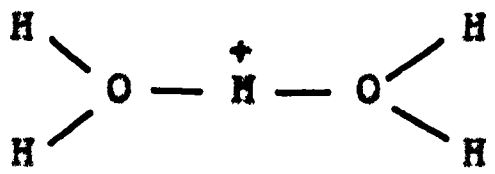
Primary < Secondary < Tertiary

It thus appears that Brown's explanation is not valid, since the Back-Effect should apply equally to non-aqueous solutions.

Base Strengths.



Davies and Hetzer (102) have demonstrated that the basic strengths of some bases in aqueous solution, which are lower than expected from a consideration of the polarity of the nitrogen atom, are explicable in terms of steric hindrance of the hydrated hydrogen ion which they suggest exists in water as



from the infra-red evidence of Rodebush (103).

This ionic entity might be expected to be subject to some steric interference from 2-methyl groups in pyridine derivatives, and the slightly lower basicity of 2-picoline when compared with 4-picoline may be attributed to this effect.

(The stabilisation of onium ions by hydrogen bonding suggested by Trotman-Dickenson (82,83) cannot cause anomalous basicities in a series of closely related series of amines such as the pyridines, where it is found that the correlation between the polarity of the nitrogen atom and the free energy of association with hydrogen ion in aqueous solution is most marked.) The monotonic increase in polarity with substitution of methyl groups (in either the 2- or the 4-position) is shown in the surprisingly regular plot opposite. Results for the amines are given in Table XXIX.

TABLE XXIX

The Formation of Conjugate Acids (Onium Ions) of Bases at 25°C in Aqueous Solutions of Ionic Strength 0.10. $[NO_3^-] = 0.10$ N.

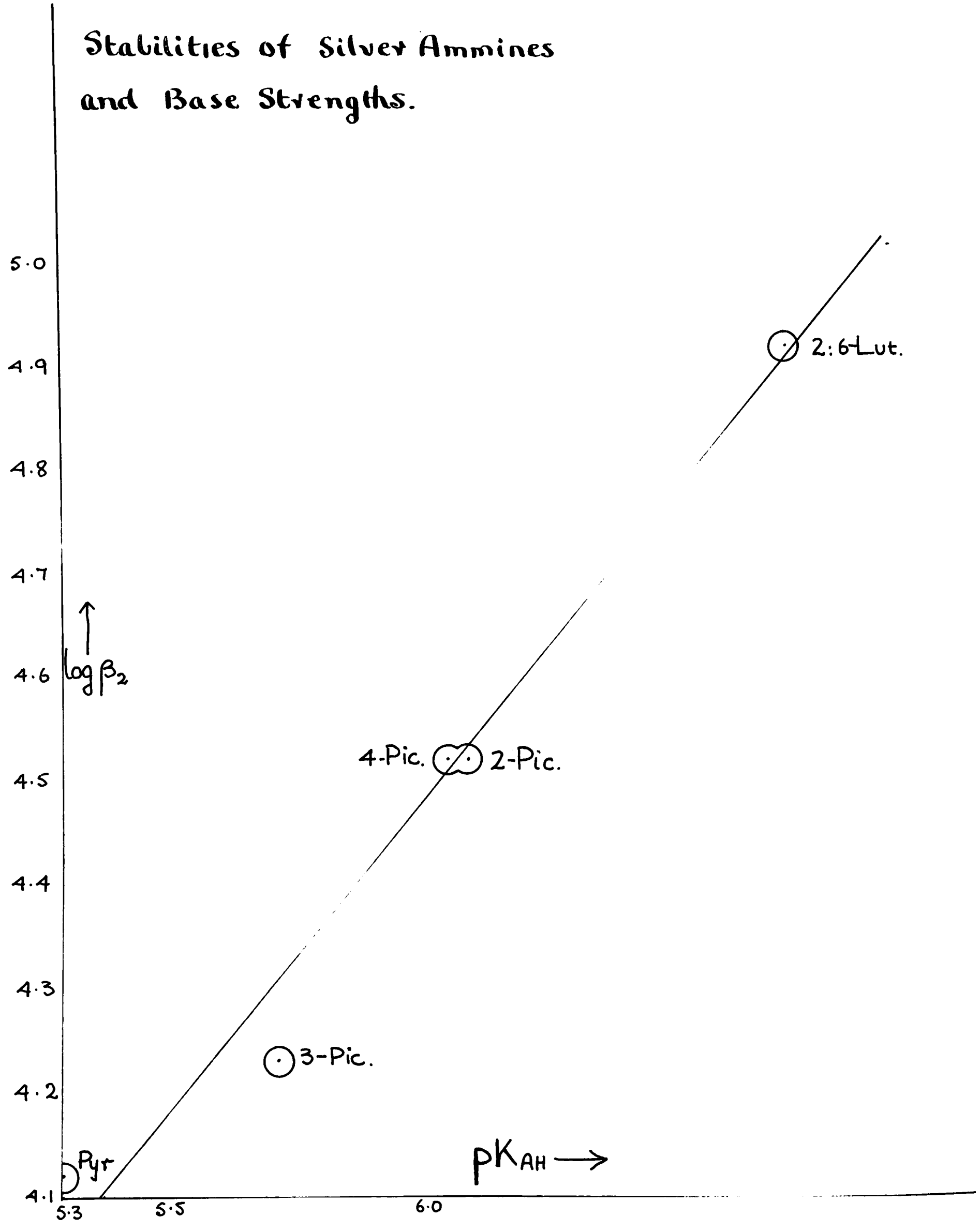
Reaction:-

$$H_3^+O_{(aq)} + A_{(aq)} \rightarrow A^+H_{(aq)} + xH_2O$$

Base	log K_{AH}	$-\Delta F$ K.cal./g.ion	$-\Delta H$ K.cal./g.ion	ΔS cal./g.ion/°C.
Ammonia	9.38	12.700	12.45	+ 0.8
Pyridine	5.30	7.22	5.09	+ 7.1
2-Picoline	6.05	8.24	6.33	+ 6.4
3-Picoline	5.72	7.80	6.01	+ 5.9
4-Picoline	6.09	8.30	6.30	+ 6.7
2:6-Lutidine	6.71	9.15	7.49	+ 5.5
2:4:6-Collidine	7.41	10.01	8.48	+ 5.1

Data for acid dissociation constants in close agreement with the above have been published recently by Gero and Markham (18) and by Herimgton (19). References to earlier and less reliable data are given by Golumbic and Orchin (20). Entropy changes are small and of such a sign as to favour the reaction leading to the attachment of basic ligand to proton, see p.74, and with the variations in $-\Delta F$ from

Stabilities of Silver Ammines and Base Strengths.



reaction to reaction, there are closely corresponding variations in $-\Delta H$. The slight differences in the entropy changes are probably due to the fact that each methyl-pyridine in the series has a different shape, and so will have a different "fit" into the structure of water from each of its neighbours. Ammonium ion has the most negative entropy of formation probably because it is a smaller ion than any other in the table.

The Ratio of pK_{AH} to $\log \beta_2$.

The plot of pK_{AH} against $\log \beta_2$ (shown opposite p.148.) is a straight line for the silver complexes of the pyridines, p. 104. The monotonic increase in polarity of the nitrogen atom per methyl group is accompanied by a proportional increase of stability in each silver-ammine. If there were any appreciable steric hindrance from 2-methyl group interactions, the resultant decreases in $\log \beta_2$ for $Ag(2:picoline)_2^+$ and $Ag(2:6\text{-lutidine})_2^+$ would cause the points for these complexes in the graph opposite to be well below the line drawn. For the overall complex formation reactions, the following results were obtained. Table XXX.

TABLE XXX

Formation of Silver Ammines at 25°C in Aqueous Solution of Ionic Strength 0.10. $[NO_3^-] = 0.10$ N.

Reaction:-

$$Ag^+_{(aq)} + 2A_{(aq)} \longrightarrow AgA_2^+{}_{(aq)} + xH_2O$$

Amine	$-\Delta F$ K.cal./g.ion	$-\Delta H$ K.cal./g.ion	$+\Delta S$ cal./g.ion/°C.
Ammonia	9.90	13.48	- 12.0
Pyridine	5.61	11.81	- 20.8
2-Picoline	6.16	11.12	- 16.6
3-Picoline	5.77	11.82	- 20.3
4-Picoline	6.16	12.37	- 20.8
2:6-Lutidine	6.70	10.75	- 13.6

The large negative entropies which oppose the formation of the silver ammines, are probably due to two complementary factors,

(1) Silver ion is not highly hydrated (91);

(2) Translational and possibly some rotational entropy are lost by the ligand groups on complexing with silver ion.

Ammonia has a much smaller molecular weight than pyridine so losses of translational entropy will be smaller in the formation of $Ag(NH_3)_2^+$ than in the formation of $Ag(pyr)_2^+$.

Pyridine, 3-picoline and 4-picoline, on forming complexes with silver ion may be expected to lose almost equal amounts of entropy due to the restriction of freedom of movement. All three will be expected to alter the hydration sheath of the silver ion to the same extent. The results in Table XXX, show that, as anticipated, the entropies of formation of complexes of silver ion with these amines are virtually identical (~ - 21 e.u.) The silver ammine of 2-picoline has a more positive entropy of formation, (~ - 16.5 e.u.) than those of pyridine and the other picolines. This may be attributed to the interactions of the two 2-methyl groups with the hydration sheath of the silver ion. The steric effect of these groups will be to displace water molecules from the silver ion, and this freeing of solvent particles will result in a positive contribution to the entropy of formation of the complex. With 2:6-lutidine, a larger displacement of water molecules will occur, causing a yet more positive entropy contribution, which is indeed observed (ΔS ~ - 13.5 e.u.).

The polarities of the amines (Table XX) increase in the order

pyridine < 3-picoline < 2-picoline ~ 4-picoline < 2:6-lutidine.

and the strengths of metal-ligand bonds presumably increase in this order. For pyridine, 3-picoline, and 4-picoline the

increase is reflected in the heats of formation of the ammines (although the value of $-\Delta H$ for the complex of 3-picoline seems somewhat low.)

The greater interactions of 2-picoline and 2:6-lutidine with the hydration sheath of the silver ion, cause a greater "melting" of solvent, so that resultant heats of formation are smaller than those of the other ammines. However, by the "compensation effect" (p.141.) the free energies of formation of the amine complexes increase in the order expected from the order of bond-strengths anticipated from the increasing polarities of the donor atoms.

The Relationship of K_1 to K_2.

The fact that $K_1 \sim K_2$ has been suggested to be due to the hybridisation of the orbitals of silver ion to linear sp type and the formation of σ covalent type bonds with the amines (see p.103).

In two recent papers, (85,86), the distinction has been drawn between two types of polarity of the nitrogen atom, viz:-

(1) The polarity as measured by the energy of association with hydrogen ion - i.e. in the formation of a covalent

bond. This is the sense in which the word polarity has been used in the previous discussion.

(2) The polarity as measured by the ability of the nitrogen atom to enter into hydrogen bonding - largely an electrostatic attraction (88). This ability is measured by the change in the O-D stretching frequency when amines are associated with deutero-methyl alcohol and also by the heat of interaction of amines with chloroform in non-aqueous media, (89).

It is found that a primary amine and a pyridine which have similar polarities of type (2), have widely different polarities of type (1). If, for a series of pyridines and primary aliphatic amines, pK_{AH} (polarity type (1)) is plotted against either O-D frequency shift, or heat of interaction with chloroform, (polarity type (2)), a graph such as that shown diagramatically in fig. 7. results.

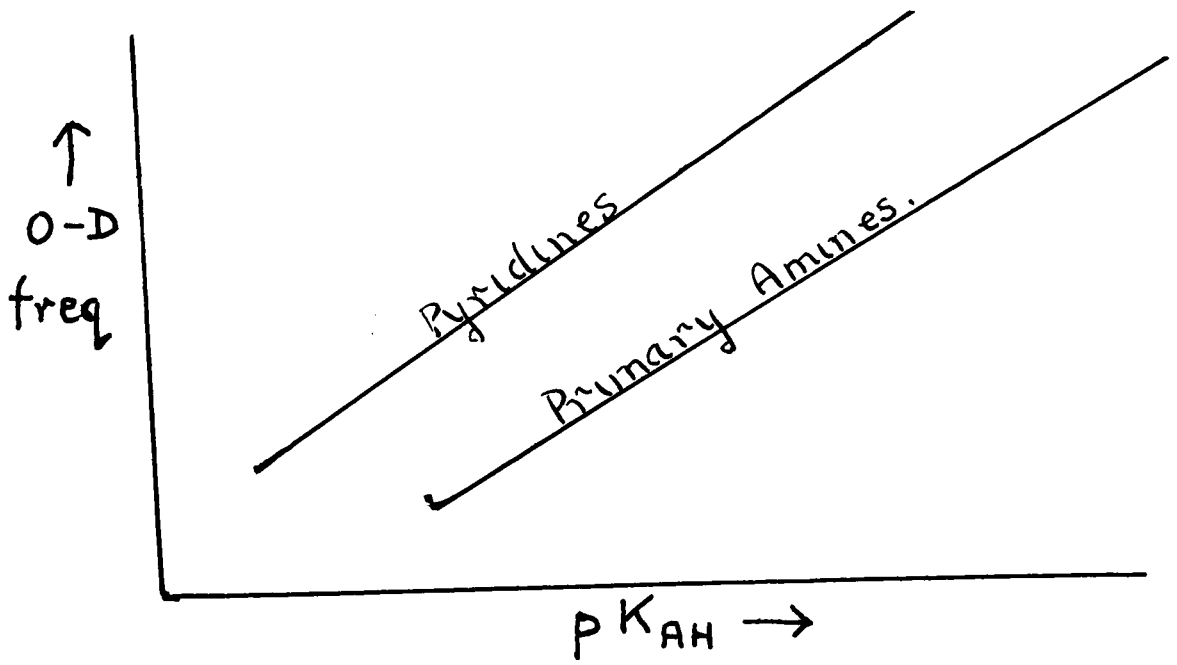


fig. 7.

The position of the pyridine bases relative to the aliphatic amines has been attributed to the fact that the lone pair of electrons on the nitrogen in pyridine nuclei contributes to the stabilisation of the ring by resonance, and on forming a covalent bond by accepting a proton, some of the resonance energy of the ring is lost, resulting in a lowered value of pK_{AH} (87).

In the graph opposite p.104, it was shown that for both primary amines and pyridines, the plot of log β_2 against pK_{AH} was a single straight line, which shows that in bonding of amine to silver ion, polarity of type (1) is displayed by the nitrogen atom. This is strong indication that amine-silver bonds are covalent in character, and further evidence for the postulated sp hybridisation of the orbitals of the silver ion.

In table XXX, p.149, it can be seen that for the complexes of silver with 2-picoline and 2:6-lutidine, K_2 is slightly smaller than K_1. This may be indicative of slight intermolecular repulsion between 2-methyl groups. Alternatively interactions of the methyl groups with the hydration sheath of the silver ion may account for this small effect.

Five- and Six-Member Rings.

The results obtained for the dissociation of the conjugate acids of ethylenediamine and 1:3-diaminopropane are given below in Table XXXI.

TABLE XXXI

Reactions:

(1) $AH^+ \longrightarrow A + H^+$

(2) $AH_2^{2+} \longrightarrow AH^+ + H^+$

			K.cal./g.ion.				cal./g.ion/°C.	
	pK_{AH}	pK_{AH_2}	$+\Delta F_1$	$+\Delta F_2$	$+\Delta H_1$	$+\Delta H_2$	$+\Delta S_1$	$+\Delta S_2$
En	10.00	7.12	13.64	9.70	11.94	10.94*	- 5.6	+ 4.1
Tn	10.63	8.76	14.50	11.94	12.64		- 6.2	

* Staveley (48)

From these figures, it is apparent that 1:3-diaminopropane is a stronger base than ethylenediamine, and that its nitrogen atoms, being more polar, should form stronger metal-amine bonds.

However, stability measurements (Table XXXII) show that it is ethylenediamine which forms the more stable complexes.

TABLE XXXII

Reaction	log K_1	log K_2	log K_3	log β_2	log β_3
Cu and En	10.37	8.87		19.24	
Cu and Tn	9.68	7.17		16.82	
Ni and En	7.32	6.06	3.93		17.31
Ni and Tn	6.26	4.15	1.13		11.54

Chelation by ethylenediamine forms a five-member ring, whereas chelates of 1:3-diaminopropane are six-member rings, see figs. 8, and 9, opposite p.157.

The relatively lower stability of six-member ring chelates compared with five-member ring chelates is a general phenomenon which has been observed in complexes of diamines, amino-acids, dicarboxylic acids, diketones, dioximes, salicylaldehyde derivatives and complex ones. An extensive survey of the data has been made by H. Irving (99).

An explanation of this stability difference between five- and six-member ring complexes has been put forward by Schwarzenbach (23). The theory is based on what would appear to be unreliable data found by the variation of stability constants with temperature. The extra stability of five-member rings is attributed completely to a more positive entropy of formation. The less positive entropy of formation

of six-member rings is calculated statistically from the premise that when a bidentate ligand containing a five atom chain is joined by one end to a metal ion, its other end will have a smaller probability of chelating by forming a second metal-ligand bond than will a ligand having only a four atom chain which is also joined by one end to the metal ion. Heats of coordination are assumed to be the same for all metals and for rings of all sizes, and although some of the inferences of the theory are untenable in the light of recent experimental evidence, the lower stability of six-member chelate complexes compared with five-member chelate complexes is usually attributed to the entropy effect in contemporary discussion.

It is not proposed to criticise this theory in detail but merely to make the following observations:-

(1) For the diamine complexes of copper, and nickel it has been found that differences in stability are principally due to heat terms and not to differences in entropy changes of formation.

(2) In heat and entropy terms for complex formation in aqueous solution, hydration effects may not be ignored completely.

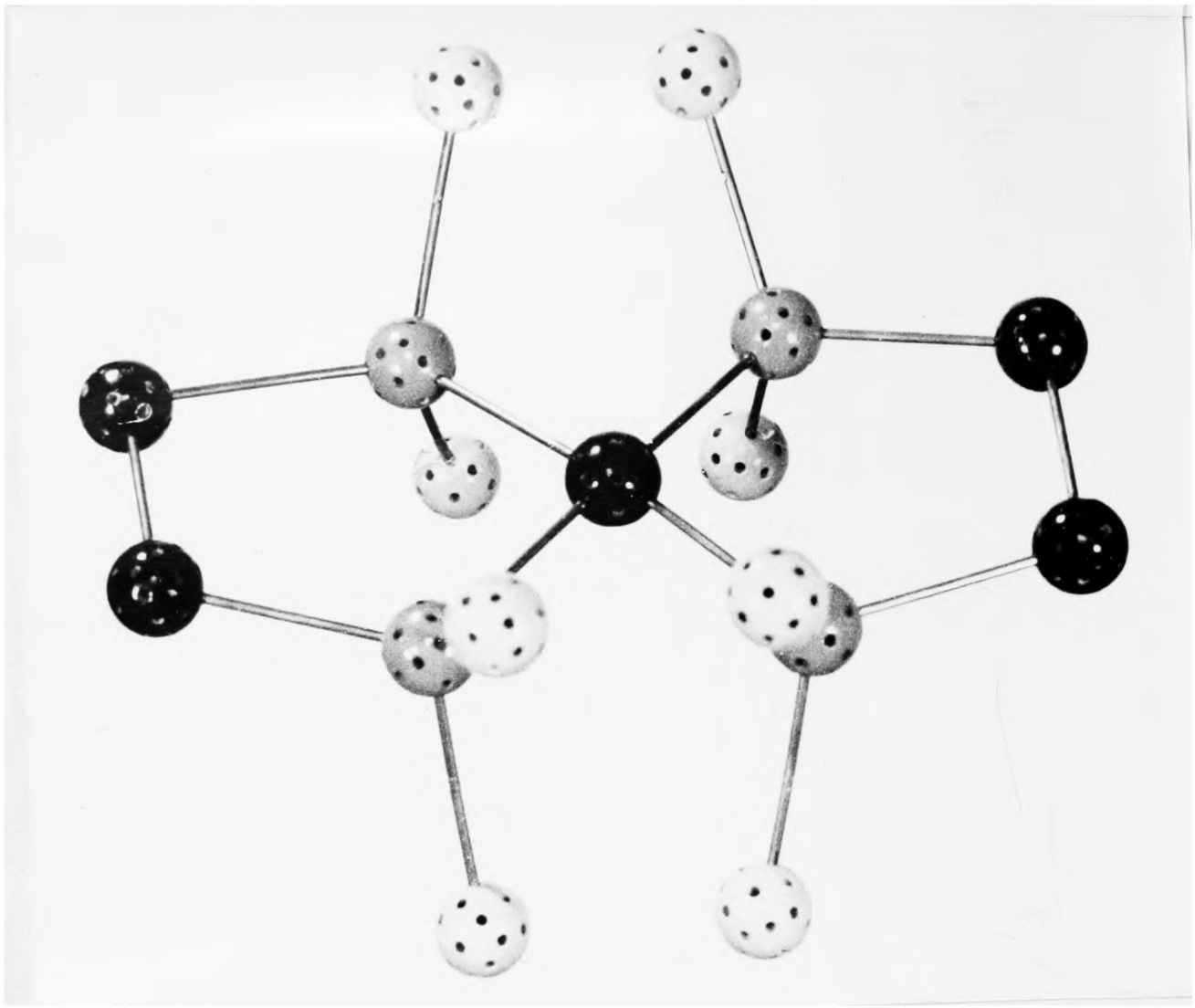


fig. 8.

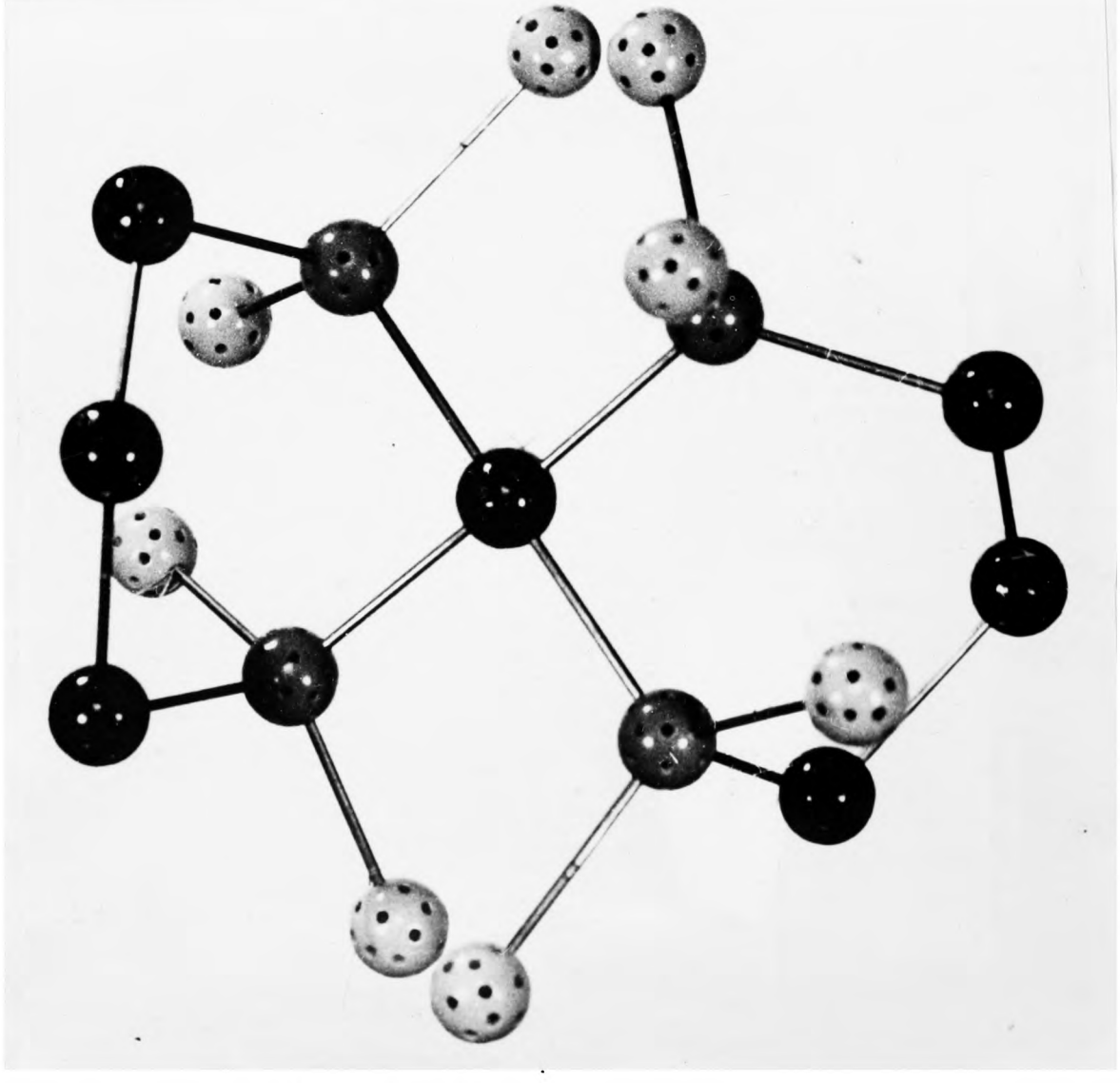


fig. 9.

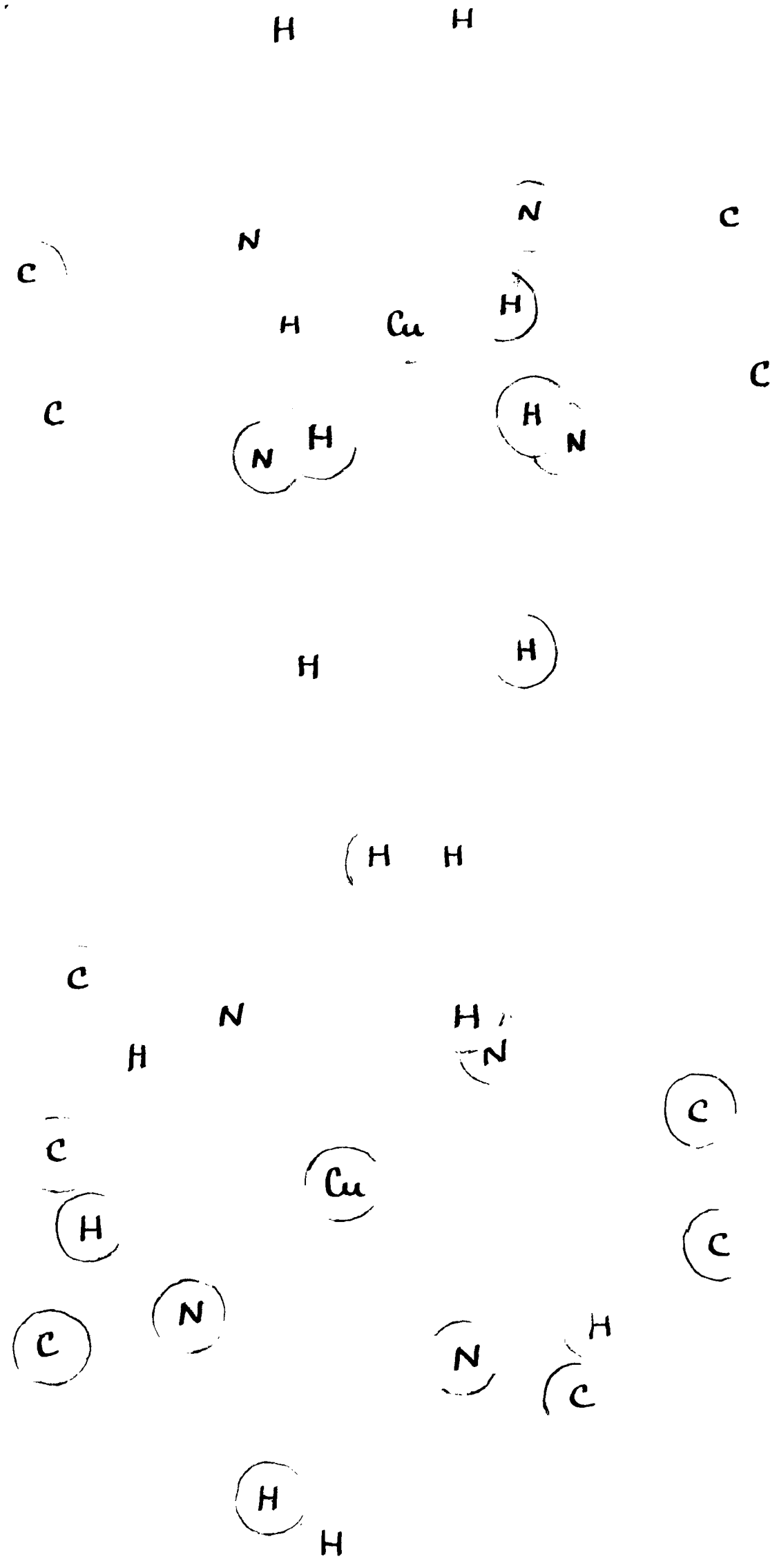


TABLE XXXIII

Reactions:

$$Cu^{2+}_{(aq)} + 2A_{(aq)} \rightarrow Cu\,A^{2+}_{2(aq)} + x\,H_2O$$

$$Ni^{2+}_{(aq)} + 3A_{(aq)} \rightarrow Ni\,A^{2+}_{3(aq)} + y\,H_2O$$

K. cal./g.ion

	Copper			Nickel		
	$-\Delta F$	$-\Delta H$	$T\Delta S$	$-\Delta F$	$-\Delta H$	$T\Delta S$
En	26.2	25.1	1.1	23.4	27.2	- 3.8
Tn	22.9	22.9	0	15.7	21.3[R]	- 5.6
(En-Tn) Diff.	3.3	2.3	1.1	7.7	5.9	- 1.8

[R] Bjerrum (38)

The importance of the heat term and the smaller significance of the entropy term is apparent.

An explanation of limited application has been put forward for the copper complexes (39). Cupric copper forms square planar d sp^2 hybrid bonds (108). From geometrical considerations, there is a probability of steric hindrance between the hydrogen atoms on neighbouring nitrogen atoms in the six-member ring complex. This probability is absent in the five-member ring chelate. The photographs of molecular models opposite p.157, illustrate this argument. (Figs. 8,9,)

Steric hindrance between the six-member rings, with consequential weakening of the metal ligand bonds, accounts satisfactorily for the results obtained for the cupric-complexes of the diamines.

However, for tetrahedral complexes, and for ligands which have no hydrogen atoms attached to the donor atoms, the theory is not applicable.

Neither theory is satisfactory in explaining the lower stabilities of six-member rings compared with five-member rings which have been observed for a large number of chelate complexes. Until many more heats and entropies of formation have been measured, it will not be possible to suggest a general explanation of these phenomena, nor to substantiate it. Many factors must be taken into account, not the least of which is the statistical effect emphasized by Schwarzenbach. Although it is dangerous to draw inferences from rates of formation of complexes (65), the slow rates of formation of $Cu\ Tn_2^{2+}$ + $Ni\ Tn_3^{2+}$, p.127, indicate that the attachment of the second nitrogen atom of 1:3-diaminopropane to the metal ion occurs only after a certain interval of time, as might be expected from the statistical considerations of Schwarzenbach.

A factor which may be of importance but which does not seem to have been recognised, is that the six-member ring is

buckled and in constant transition* between the "chair" and "boat" form, whereas the five-member rings are nearly planar and only slight buckling may take place.

The restriction of movement in five-member rings would cause a release of heat energy. There would also be a loss of entropy for the same reason. Six-member rings, having far less restricted motion, would lose correspondingly less heat energy, and less entropy. The entropy loss on forming a six-member ring will be increased by the statistical effect, and by the fact that the ligand groups, being heavier than those forming five-member rings, will lose more translational entropy. The total effect of the "buckling" factor should be to increase the relative stability of the five-member ring.

Hydration effects such as the loss of water molecules from around the donor groups and the "fit" of the complex ion into the structure of water cannot be assessed and no tentative hypotheses will be put forward.

Complexes of 1;10-Phenanthroline.

If the standard entropies of solution of metal ions, $\bar{S}^{o}_{M}$, are added to the entropy changes of formation of their complexes with a given ligand in aqueous solution, then the

* No racemates have ever been found for these chelates.

values resulting, although not standard entropies of the complexes formed, will all differ from the standard values by the same amount. The difference will be the standard entropy of the ligand. The apparent standard entropies are designated by $\bar{S}$ in Table XXXIV. Figures for $\bar{S}^{\circ}_{M}$ are those given by Latimer (90,91). However, for Ni^{2+}, the most probable figure in the literature (none is given by Latimer) is the one given by Barvinok (92), and this is the one used.

TABLE XXXIV

Metal	$-\Delta F$ K.cal./g.ion	$-\Delta H$ K.cal./g.ion	$-\Delta S$ cal./g.ion/°C	$\bar{S}^{\circ}_{M}$	$\bar{S}$
Fe^{2+}	28.83	29.97	- 3.8	- 27.1	- 30.9
Ni^{2+}	32.58	26.80	19.3	- 29.3	- 10.0
Zn^{2+}	23.23	19.47	12.5	- 25.5	- 13.0
Cd^{2+}	19.50	19.30	0.7	- 14.6	- 13.9

Although the central metal ions have slightly differing ionic radii, because of the large size of the phenanthroline molecules, the tris-phenanthroline complex ions have effectively identical radii. The complexes bear identical charges and should have very similar standard entropies.

The complexes of Ni^{2+}, Zn^{2+} and Cd^{2+}, do have the same values of $\bar{S}$ within limits of experimental error. The significantly more negative value of $\bar{S}$ for the ferrous complex is most probably due to its being more highly hydrated. This would occur if the ferrous complex had a higher distribution of positive charge upon its periphery. From considerations of rates of racemisation in various salt solutions and from studies of redox potentials (93), it has been suggested that considerable fractions of charges borne by complexes of phenanthroline are distributed over their outer surfaces.

Because the metal-ligand bonds in the ferrous complex are of "inner" $3d^2 4s 4p^3$ type, it will be expected to have a higher charge distribution upon its periphery than those of complexes with "outer" $4s 4p^3 4d^2$ bonds for the following reasons:-

(1) By the Pauling principle of electroneutrality of the central ion (96), because of the highly covalent nature of "inner orbital" bonds (64), practically the whole charge of the central ion will be spread over the periphery of the complex, whereas for the "outer orbital" bonds, which are more ionic in character, only partial neutralisation of the central ion takes place.

(2) In complexes in which 4d orbitals are used for bonding, the region of overlap is not equidistant between the

donor atom and the metal ion but relatively closer to the ligand (94). In "outer" complexes, the lone pair electrons will be displaced smaller distances from the nitrogen atoms than in "inner" complexes, so that there will be smaller residual positive charges on the ligand groups in the complexes using $4s4p^3 4d^2$ bonding.

(3) Nyholm has shown that some double bonding takes place between transition metal ions and aromatic ligands containing nitrogen atoms. Besides the lone pair, σ type bond, there is also some π bonding of $d_{\pi} - p_{\pi}$ type, in which the d-electrons of the metal ion are involved. It has been shown that the π bond contribution to the bond strength increases along the series,

$$Fe < Co < Ni$$

as the number of d-electrons of the central ion increases (95).

In the π bond, there is a tendency for the electrons of the metal ion to be displaced towards the ligand so that the residual positive charge on the ligand will be lowered. The effect will be least for the ferrous ion.

The first and second considerations are two different statements of fundamentally the same effect.

From these considerations the more negative entropy of the ferrous complex is readily accounted for.

Superficially, the high heat of formation of the ferrous complex may be attributed to the formation of strong "inner orbital" bonds. However, a considerable fraction of $-\Delta H$ probably results from the "freezing" of water molecules round the complex ion. If it were possible to measure the heat of formation in a non-polar solvent, it is to be anticipated that although $-\Delta H$ would be smaller, ΔS would be more positive, so that by the "compensation effect", the stability of the ferrous complex would still be abnormally high.

Phenanthroline is a weak base ($pK_{AH} = 5.0$) (24) and yet it forms very stable complexes. Like the pyridines, p.153, its affinity for proton is low, probably because with the removal of a lone pair of electrons from one of the nitrogen atoms into a covalent bond, some of the resonance energy of the phenanthroline molecule is lost. The stability of the complexes must be due to partial double bonding. Several canonical structures may be drawn in which a nitrogen atom has an unfilled 2p orbital and with which the 3d electrons of the central atom can interact.

Thus the very factor which causes phenanthroline to have a low basicity (its high aromaticity), is that which enables it to form partial double bonds with transition metal ions. Ethylenediamine, which is strongly basic, is a fully saturated compound and cannot form π bonds. Its complexes have lower stability than those of phenanthroline.

Rates of Racemisation and Dissociation of the Tris-Phenanthroline Complexes of Ni^{2+} and Fe^{2+}.

Several papers have been published recently concerning rates of racemisation and dissociation of complexes of 1:10-phenanthroline. The results for nickelous and ferrous ions are of especial interest in connection with the results for heats and entropies of formation reported in Table XXXIV.

For the ferrous tris-complex, the rate of racemisation is about ten times as great as the rate of dissociation. Thus racemisation must proceed by an intramolecular mechanism in addition to the dissociation mechanism. It has been suggested, by Davies and Dwyer (104) that the intramolecular process could be an expansion of the complex, such that the covalent $3d^2 4s 4p^3$ bonding is destroyed and a labile ionically-bonded aggregate is formed in which the ligand groups may easily rearrange before the complex returns to the non-activated stable state.

It is known that the dissociation of the first ligand group from $Fe(phenan)_3^{2+}$ causes the destruction of the d^2sp^3 hybrid bonding (72), leaving a rather unstable bis-complex (24). Davies (66, 104) has suggested that the activated states for both dissociation and racemisation cannot be very dissimilar.

In the expansion of the ferrous tris-complex from an "inner" complex to a loose ionic aggregate, it may be supposed

that the complex passes through a theoretical intermediate state, corresponding to an "outer" orbital type of complex. The process of activation may be represented,

$$\underset{\text{Bonding Type}}{\text{Fe(phenan)}_3^{2+}} \xrightarrow[S_1^{\ddagger}]{E_1^{\ddagger}} \underset{4s4p^3 4d^2}{\text{Fe(phenan)}_3^{2+}} \xrightarrow[S_2^{\ddagger}]{E_2^{\ddagger}} \underset{\text{"ionic"}}{\left[\text{Fe(phenan)}_3^{2+}\right]^{\ddagger}}$$

Bonding Type: $3d^2 4s4p^3$

The measured energy and entropy of activation, $E_{Fe}^{\ddagger}$ and $S_{Fe}^{\ddagger}$ respectively, will be given by:-

$$E_{Fe}^{\ddagger} = E_1^{\ddagger} + E_2^{\ddagger}$$

$$S_{Fe}^{\ddagger} = S_1^{\ddagger} + S_2^{\ddagger}$$

The racemisation of $Ni(phenan)_3^{2+}$ proceeds solely by dissociation (105), but presumably the activated state is a loose ionic aggregate similar to the activated form of the ferrous complex.

$$\underset{4s4p^3 4d^2}{\text{Ni(phenan)}_3^{2+}} \xrightarrow[S_3^{\ddagger}]{E_3^{\ddagger}} \underset{\text{"ionic"}}{\left[\text{Ni(phenan)}_3^{2+}\right]^{\ddagger}}$$

Reported values for energies and entropies of activation are given in Table XXXV.

TABLE XXXV

The Energy ($E^{\neq}$) and Entropy ($S^{\neq}$) of Activation of Decomposition of Tris-Phenanthroline Complex Ions.

Ion	Dissociation		Ref.
	$E^{\neq}$ K.cal./g.ion	$S^{\neq}$ cal./g.ion/°C.	
Fe^{2+}	32 $\pm$ 0.5	28 $\pm$ 2	(106)
Ni^{2+}	25 $\pm$ 0.5	2 $\pm$ 2	(107)
	25		(107)
	Racemisation		
Fe^{2+}	29 $\pm$ 2	21 $\pm$ 7	(106)
	31		(107)

For the ferrous complex, both the heats and entropies of activation of both racemisation and dissociation are nearly equal and indicate that the two processes may be similar.

The theoretical intermediate "outer" complex of $Fe(phenan)_3^{2+}$ should have a standard entropy comparable to those of $Zn(phenan)_3^{2+}$, $Cd(phenan)_3^{2+}$, and $Ni(phenan)_3^{2+}$, i.e. $\bar{S} \sim -12$ cal./g.ion/°C.

The entropy of activation of the "outer" ferrous complex, $S_1^{\neq}$, is the difference in the standard entropies of the "inner" and "outer" complexes. The standard entropy of the "inner" complex is ~ -31 cal./g.ion/°C., so that,

$$S_1^{\neq} \sim 19 \text{ cal./g.ion/°C.}$$

The expansion of the "outer" ferrous complex to activated ionic state should be accompanied by an entropy change comparable with the entropy of activation of the nickel complex, whose stable form is an "outer orbital" state.

i.e. $$S_2^{\neq} \sim S_3^{\neq}$$

From these considerations it is to be predicted that the difference in entropy of activation of the nickel and ferrous complexes, $dS^{\neq}$, will be given by the following equations:-

$$dS^{\ddagger} = S^{\ddagger}_{Fe} - S^{\ddagger}_{Ni}$$

$$= S^{\ddagger}_1 + S^{\ddagger}_2 - S^{\ddagger}_3$$

$$\sim S^{\ddagger}_1$$

$$\sim 19 \text{ cal./g.ion/}^{\circ}\text{C.}$$

It is seen in Table XXXV, that within the limits of experimental error, the difference in the entropies of activation of the ferrous and nickel complex is ~ 20 cal./g.ion/°C.

The conclusion may be drawn that the large entropy of activation of the ferrous tris-phenanthroline complex ion is due primarily to its abnormally high degree of hydration. In addition, it is to be expected that $Zn(phenan)^{2+}_3$ and $Cd(phenan)^{2+}_3$, which have the same standard entropies as $Ni(phenan)^{2+}_3$, in aqueous solution, will, like the last complex ion, have small entropies of activation.

SECTION VII

Experimental Section.

Preparation of Materials.

Amines.

All the bases used were supplied by Messrs. B.D.H. Ltd., and, with the exception of 1:10-phenanthroline, were purified in the following manner.

The amine was refluxed over freshly ignited barium oxide for several hours and then distilled in an all-Pyrex apparatus through a short fractionating column. The middle fraction, boiling over a range of 0.3°C was collected. Before the purification, air was displaced from the apparatus by flushing it out with nitrogen. Precautions were taken at all stages in the transfer of amine during the preparation of solutions to exclude atmospheric carbon dioxide.

Liquid bases were stored over KOH pellets in dark, tightly stoppered bottles, and distilled when required.

The boiling points of the amines are given in Table XXXVI. 1:10-phenanthroline was purified by recrystallisation.

Ammonia solutions were prepared by dilution of concentrated "AnalaR" grade ammonia solution with boiled out distilled water. The concentrations were determined by titration against standard acid.

TABLE XXXVI

Boiling Points of Amines at a Pressure of 760 mm. Hg, according to Beilstein.

Amine	B. pt. °C.
Ethylenediamine	118.5
1:3-Diaminopropane	135.5
Pyridine	115.3
2-Picoline	129.0
3-Picoline	143.5
4-Picoline	143.1
2:6-Lutidine	142.5
2:4:6-Collidine	171.0

Amine Solutions.

After distillation, the purity of an amine was determined by dissolving a known weight in freshly boiled-out distilled water and titrating with standard hydrochloric acid (see p.173).

Weighed quantities of amines were placed in standard flasks, together with calculated weights of the appropriate back-ground salt, made up to the standard volume with boiled-out distilled water, and their molar concentrations calculated from a knowledge of their previously determined percentage purities (in all cases > 98%).

The pH titration by which base dissociation constants were determined, p.49 , served as a cross-check on the concentration of amine solutions.

Vessels in which amine solutions were stored were protected from atmospheric CO_2 by "Sofnolite" guard tubes. Amine solutions were transferred from one vessel to another, by means of a continuous system of glass tubing through which nitrogen was blown so that any contact with the air was avoided.

Silver Salts.

Silver Bromate.

One gram molecule of "AnalaR" grade potassium bromate was dissolved in three litres of distilled water in a Pyrex

beaker and heated to 60°C. The solution was transferred to a dark-room and continuously agitated by an electrical stirrer while one litre of molar "AnalaR" grade silver nitrate solution was slowly introduced drop by drop. Complete addition took almost two hours.

The fine white suspension of silver bromate so formed was digested on a hot plate for twenty four hours. After standing, the finely crystalline bromate was washed with distilled water by decantation several times. It was collected on a coarse sintered-glass filter and washed with large quantities of distilled water. This washing, besides removing all potassium and nitrate ions, also dissolved the smallest particles of solid present in the aggregate (known as "fines").

Silver Iodate.

This was prepared in molar quantities by the same method as the bromate. (In this case silver nitrate solution was added to hot potassium iodate solution).

The precipitate still remained flocculent, and after digestion settled out very slowly. The silver iodate was collected on a fine glass filter, washed with distilled water, dissolved in the minimum volume of dilute ammonia solution and evaporated to dryness on a water bath in a dark room (21).

The plates of solid produced were broken up, washed in the same way as the bromate and kept in a desiccator with the complete exclusion of light.

Solutions of Standard Acid.

Approximately 0.1 N solutions of hydrochloric and nitric acids were prepared by dilution of the concentrated "AnalaR" grade solutions with boiled-out distilled water. They were standardised by titration against weighed quantities of borax (sodium borate) whose preparation is described below. The indicator used was brom-cresol green. Results were reproducible to one part in a thousand and were identical with those obtained by titration against roasted sodium carbonate.

Borax (Sodium Tetraborate Tetrahydrate).

"AnalaR" grade borax was recrystallised from distilled water below 50°C. It was collected on a sintered glass filter and washed with distilled water, and placed in a desiccator over a solution saturated with sucrose and sodium chloride. Borax is practically non-hygroscopic and could be kept indefinitely in this manner.

Buffer Solutions.

Borax prepared by the above method and "AnalaR" grade potassium hydrogen phthalate, potassium dihydrogen phosphate, disodium phosphate and potassium chloride without further purification were dissolved in boiled-out distilled water to give solutions of the concentrations given in Table VI, p.57.

Metal Solutions for pH titrations.

Solutions except those containing silver ion were prepared by dissolving weighed quantities of "AnalaR" sulphates of the metals, potassium chloride and standard hydrochloric acid in distilled water so that all resulting solutions had the following composition:-

MSO_4 = 0.005 g.mol./l.

HCl = 0.04 g.mol./l.

KCl = 0.06 g.mol./l.

The following "AnalaR" grade salts were used.

$CuSO_4 . 5H_2O$

$NiSO_4 . 6H_2O$

$ZnSO_4 . 7H_2O$

$3CdSO_4 . 8H_2O$

The exact water content of each salt is not known so each salt was analysed before making up solutions. In some cases, check analyses of the concentration of metal ion in the prepared solutions were performed.

Solutions of Silver Nitrate.

"AnalaR" grade silver nitrate has a specified purity of at least 99.9%; this was confirmed by electrolytic analysis, p.176. The silver solution was prepared by dissolving a weighed quantity of "AnalaR" grade silver nitrate and a volume of standard nitric acid in boiled-out distilled water so that the composition of the resulting solution was,

$$Ag\,NO_3 = 0.02\ M$$
$$H\,NO_3 = 0.08\ M$$

Metal Solutions for Calorimetric Experiments.

The solutions used were of various concentrations between 0.5 and 1.0 M. No back-ground salt was added and solutions were made up by dissolving weighed quantities of "AnalaR" grade sulphates, (whose exact cation content had been determined by standard analytical procedures) in known weights of boiled-out distilled water. "AnalaR" grade silver nitrate was used for preparing solutions of silver ion. Each solution was freshly prepared on the day on which it was used.

The reasons for using the perchlorates of copper and nickel instead of the sulphates have been given on p.124 . Because of their great solubility and extreme hygroscopicity, the crystalline perchlorates were not prepared.

Copper Perchlorate Solution.

17 or 18 ml. of 70% "AnalaR" grade perchloric acid were diluted to 50 ml., and excess "AnalaR" grade cupric oxide added. The mixture was warmed gently until neutral to litmus. The solution was filtered first through a filter-paper and secondly through a coarse sintered-glass filter, this latter to remove fine fibres of paper which could block the fine jets of the syringes. The resulting solution, diluted with boiled-out distilled water to a volume of 100 ml. was $\sim$ 1 M, and was analysed by electrolysis (see below).

Nickel Perchlorate Solution.

No "AnalaR" grade nickel oxide was available. Nickel nitrate was roasted, first gently and finally strongly to dull red heat. At higher temperatures, ($>$ 700°C) a grey form of the oxide is formed which is insoluble in acids. The oxide was broken up and washed well with distilled water to remove any remaining nitrate ions. The oxide was dissolved, filtered and diluted as described above, although it was found necessary to boil the mixture for a few minutes to reach complete neutralisation.

Electrolytic Analysis.

The modern technique of electrodeposition provides a rapid and highly accurate method of analysis for solutions of

metal ions. Complete deposition is achieved rapidly by using rotating platinum electrodes (~ 700 r.p.m.), hot solutions and high electrolysing currents (5 - 10 amps.)

Weights of solutions from a weight burette were electrolysed with original type Sand's electrodes under conditions which are fully described in the book by J.S. Sand on gravimetric electrolytic analysis (17). From the measured weight of metal deposited on the cathode, the concentrations of solutions in terms of gram mols. per 1000 g. of solution were calculated. The period of electrolysis was between a quarter of an hour and half an hour. Analyses were found to be consistent to one part in two thousand and agreed very well with those by standard gravimetric procedures. For example, analyses of samples of a nickel solution by precipitation of the dimethyl glyoxime complex gave a result 0.1% lower than that obtained by electrolytic deposition.

When cadmium and zinc solutions were analysed, the cathode was first plated with copper to prevent any alloying of the platinum. In all cases, at the end of the analysis, exhaustion of the electrolyte solution was confirmed by addition of standard colorimetric reagents, or by increasing the depth of the electrolyte solution by addition of a little distilled water and looking for any dulling of the freshly immersed cathode surface.

In the following tables of solubilities, the column headings have the following significance.

C_{KNO_3}	total concentration of potassium nitrate.
C_A	total concentration of amine taken.
C_{AgBrO_3}, C_{IO_3}	total concentration of silver bromate (or silver iodate) found by analysis of the saturated solution.
$[Ag^+]$	Concentration of free silver ions.
$[A\ ]$	Concentration of free amine molecules.
$[AgA^+]$	Concentration of free 1:1 complex
$[AgA_2^+]$	Concentration of free 1:2 complex.
μ	Ionic strength.
pA	$-\log [A]$
$\bar{n}$	Degree of complex formation.
K_1	Calculated value of the first stability constant.
β_2	Calculated value of the overall stability constant.
S	the solubility product.

All concentrations are given in g.mol. x 10^4 per litre
or g.ion. x 10^4 per litre.

Solubilities of Silver Iodate and Silver Bromate in Potassium Nitrate Solutions at 25°C.

IODATE

C_{KNO_3}	C_{AgIO_3}	μ_{ACC}	$[Ag^+]$	$[IO_3^-]$	$-\log_{10} f_\pm^2$	log S.
0	1.788	1.788	1.788	1.788	0.01285	$\bar{1}$.4919
82.2	1.941	84.12	1.932	1.934	0.08233	$\bar{1}$.4903
283.9	2.109	285.9	2.081	2.088	0.13692	$\bar{1}$.4990
623.9	2.300	626.2	2.242	2.256	0.18705	$\bar{1}$.5168
1021	2.432	981.8	2.340	2.363	0.21895	$\bar{1}$.5239

BROMATE

C_{KNO_3}	C_{AgBrO_3}	μ_{ACC}	$[Ag^+]$	$[BrO_3^-]$	$-\log_{10} f_\pm^2$	log S.
0	81.55	80.47	80.47	80.47	0.08071	5.7306
82.2	84.69	165.5	83.26	83.39	0.11068	5.7308
283.9	89.85	372.1	87.54	87.95	0.15439	5.7323
623.9	95.90	716.8	92.44	93.25	0.19685	5.7386
999.2	101.6	1054.6	96.82	98.09	0.22405	5.7535

Silver - Pyridine Complexes at 0°C.

IODATE

$C_{pyridine}$	C_{AgIO_3}	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	β_2
141.3	2.700	0.1771	136.9	0.6063	1.949	1.864	1.648	5.88×10^4
366.2	6.238	0.0781	354.6	0.6920	5.478	1.450	1.865	5.56×10^4
536.7	8.770	0.0569	519.8	0.7396	7.974	1.284	1.929	5.20×10^4
729.3	12.09	0.0411	706.0	0.7451	11.32	1.151	1.931	5.50×10^4

BROMATE.

$C_{pyrdine}$	C_{AgBrO_3}	$\mu_{ACC.}$	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	K_1
49.05	41.11	40.96	21.82	23.44	12.67	6.64	2.630	0.623	248
72.73	46.85	46.70	19.29	33.56	15.66	11.89	2.474	0.845	242
97.05	53.23	53.08	17.12	43.54	18.43	17.68	2.361	1.006	247
126.4	61.18	61.03	15.03	55.45	21.03	25.14	2.256	1.159	252

Silver - Pyridine Complexes at 25°C.

IODATE.

$C_{Pyrdine}$	C_{AgIO_3}	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	β_2
129.5	3.750	0.8647	124.8	1.124	1.761	1.904	1.252	1.32×10^4
369.2	8.160	0.4055	355.2	1.497	6.257	1.450	1.705	1.22×10^4
485.5	10.34	0.3224	467.2	1.566	8.451	1.330	1.770	1.20×10^4
623.6	13.00	0.2585	599.7	1.612	11.235	1.222	1.831	1.21×10^4

BROMATE.

$C_{Pyrdine}$	C_{AgBrO_3}	$\mu_{ACC.}$	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	K_1
62.4	96.8	95.7	68.74	28.63	20.19	7.79	2.543	0.349	103
82.7	103.3	102.2	65.74	38.50	24.76	9.72	2.414	0.466	98
122.6	112.9	111.8	60.03	53.46	34.44	17.35	2.272	0.612	107
129.5	115.0	113.9	58.69	53.83	34.83	20.52	2.269	0.658	110
157.4	121.7	120.6	55.74	64.53	36.87	28.00	2.190	0.764	102

Silver - Pyridine Complexes at 40°C.

IODATE.

$C_{Pyridine}$	C_{AgIO_3}	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	β_2
141.3	5.098	1.8010	136.3	1.596	1.701	1.865	0.982	5.18×10^3
369.1	9.384	0.9921	354.6	2.283	6.109	1.450	1.550	4.95×10^3
485.4	11.78	0.7962	465.9	2.407	8.598	1.332	1.660	5.00×10^3
623.6	14.61	0.6465	598.2	2.510	11.455	1.223	1.740	4.95×10^3

BROMATE.

$C_{Pyridine}$	C_{AgBrO_3}	$\mu_{ACC.}$	$[Ag^+]$	$[Pyr]$	$[Ag^+Pyr]$	$[Ag^+Pyr_2]$	pA	$\bar{n}$	K_1
49.06	146.8	1.437	1.221	23.93	18.12	3.48	2.621	0.169	62.4
72.73	152.9	1.499	1.176	33.77	23.38	7.79	2.471	0.273	60.2
97.05	159.7	1.566	1.131	43.03	33.06	10.49	2.366	0.338	67.5
14.14	171.7	1.686	1.060	59.80	43.67	18.94	2.223	0.475	68.5

Silver - 2:6-Lutidine Complexes at 0°C.

IODATE.

$C_{Lutidine}$	C_{AgIO_3}	$[Ag^+]$	[Lut.]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	β_2
85.74	3.372	0.1427	79.49	0.7768	2.452	2.100	1.680	2.85×10^5
126.2	4.814	0.1005	117.5	0.8031	4.011	1.930	1.800	2.90×10^5
172.2	6.584	0.0740	159.8	0.8045	5.705	1.796	1.885	3.13×10^5
256.7	9.783	0.0504	238.0	0.8161	8.916	1.623	1.910	3.11×10^5

BROMATE.

$C_{Lutidine}$	C_{AgBrO_3}	$\mu_{ACC.}$	$[Ag^+]$	[Lut.]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	K_1
43.46	44.27	44.12	20.35	11.44	15.53	8.24	2.942	0.724	670
63.95	51.52	51.37	17.64	16.08	19.59	14.14	2.794	0.929	662
85.74	58.93	58.78	15.56	21.08	21.69	21.48	2.676	1.097	661
106.8	66.56	66.41	13.40	25.85	24.11	28.40	2.587	1.215	666

Silver - 2:6-Lutidine Complexes at 25°C.

IODATE.

$C_{Lutidine}$	C_{AgIO_3}	$[Ag^+]$	[Lut]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	β_2
106.8	6.020	0.5448	97.46	1.646	3.748	2.011	1.519	7.45×10^4
126.2	7.013	0.4696	113.7	1.656	4.806	1.944	1.608	7.85×10^4
172.2	8.966	0.3701	157.3	1.805	6.912	1.803	1.741	7.50×10^4
256.7	12.94	0.2596	233.2	1.876	10.81	1.632	1.855	7.83×10^4

BROMATE.

$C_{Lutidine}$	C_{AgBrO_3}	$\mu_{Acc.}$	$[Ag^+]$	[Lut]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	K_1
43.46	95.99	94.91	68.56	11.42	22.82	3.53	2.942	0.334	242
63.95	103.5	102.5	64.00	14.45	29.59	8.91	2.840	0.478	318
85.74	111.4	110.3	59.89	18.48	26.29	14.11	2.733	0.603	327
106.8	118.9	117.9	56.44	23.42	40.65	20.81	2.649	0.710	319

Silver - 2:6-Lutidine Complexes at 40°C.

IODATE.

$C_{Lutidine}$	C_{AgIO_3}	$[Ag^+]$	[Lut]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	β_2
126.2	836.0	1.110	109.7	2.558	4.692	1.960	1.431	3.51×10^4
172.2	1072	0.8723	155.3	2.828	7.838	1.808	1.570	3.69×10^4
201.8	1219	0.7698	181.9	2.941	9.025	1.740	1.630	3.54×10^4
256.7	1501	0.6299	228.4	3.022	11.36	1.641	1.730	3.48×10^4

BROMATE.

$C_{Lutidine}$	C_{AgBrO_3}	$\mu_{ACC.}$	$[Ag^+]$	[Lut.]	$[Ag^+Lut]$	$[Ag^+Lut_2]$	pA	$\bar{n}$	K_1
43.46	151.0	146.9	119.1	10.20	24.46	3.34	2.991	0.220	203
63.95	158.8	154.7	113.7	14.04	33.99	6.96	2.852	0.314	213
85.74	167.2	163.2	108.5	17.90	43.24	11.47	2.747	0.406	221
106.8	175.1	171.0	104.1	22.11	51.14	15.71	2.655	0.483	221

Results of pH Titrations.

The data obtained by glass electrode measurements were somewhat extensive. A typical fully detailed table is given for the system Zn - En at 25°C. Data have been condensed and reported in the standard manner employed in the literature i.e. experimentally determined values of $\bar{n}$ and pA have been tabulated and these values have been plotted on formation curves calculated by the "Difference Method", p. 86 . The good agreement between the experimental points and the theoretical curves demonstrate the validity of method of calculation of stability constants employed. Some of the curves are presented in the relevant sections; the remainder are shown opposite the appropriate tables.

System, Zn^{2+} - Ethylenediamine.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution	$ZnSO_4$	.	0.005 M
	HCl	.	0.040 M
	KCl	.	0.060 M

Titrant.

Ethylenediamine solution, 0.704 M.

pH Range. 6.3 to 10.0.

pH	C_A g.mol x 10^2/l.	$\bar{n}_A$	pA	$\bar{n}$
6.33	2.222	1.847	6.110	0.253
6.53	2.345	1.803	5.844	0.411
6.63	2.446	1.760	5.658	0.518
6.72	2.575	1.715	5.473	0.674
6.80	2.690	1.675	5.329	0.814
6.88	2.787	1.635	5.186	0.900
6.95	2.884	1.597	5.063	0.996
7.02	2.987	1.557	4.943	1.093
7.09	3.092	1.518	4.824	1.187
7.16	3.202	1.476	4.708	1.278
7.24	3.332	1.428	4.579	1.375

Zn^{2+} - En (cont.)

pH	C_A g.mol. x 10^2/l.	$\bar{n}_A$	pA	$\bar{n}$
7.31	3.439	1.391	4.469	1.465
7.38	3.551	1.352	4.362	1.545
7.44	3.641	1.321	4.272	1.600
7.53	3.771	1.276	4.141	1.675
7.60	3.869	1.246	4.042	1.730
7.68	3.974	1.212	3.933	1.780
7.95	4.284	1.120	3.587	1.902
8.15	4.476	1.071	3.350	1.973
8.42	4.706	1.027	3.048	2.037
8.69	4.962	0.979	2.762	2.091
8.92	5.317	0.932	2.492	2.163
9.10	5.690	0.891	2.309	2.236
9.29	6.357	0.833	2.118	2.307
9.42	6.871	0.780	1.978	2.403
9.53	7.607	0.723	1.849	2.475
9.64	8.413	0.668	1.741	2.540
9.74	9.310	0.615	1.644	2.595
9.88	11.222	0.524	1.490	2.677
9.94	12.078	0.490	1.434	2.710

System, Cd^{2+} - Ethylenediamine

Temrerature 25°C.

Contents of Cell

25 ml. of solution

$CdSO_4$	0.005 M
HCl	0.040 M
KCl	0.060 M

Titrant. Ethylenediamine solution, 1.153 M.

pH Range. 6.3 to 10.0.

$\bar{n}$	pA	$\bar{n}$	pA
0.070	6.125	1.824	3.364
0.166	5.615	2.082	2.846
0.244	5.250	2.279	2.491
0.456	4.953	2.472	2.160
0.623	4.801	2.615	1.804
0.744	4.636	2.663	1.729
0.883	4.493	2.749	1.573
1.118	4.205	2.800	1.408
1.265	4.062	2.883	1.137
1.545	3.741		

System, Cu^{2+} - Ethylenediamine

Temperature 20°C.

Contents of Cell.

25 ml. of solution, $CuSO_4$ 0.005 M.
HCl 0.0395 M.
KCl 0.0605 M.

Titrant. Ethylenediamine Solution, 0.696 M.

pH Range. 3.8 to 5.8.

$\bar{n}$	pA	$\bar{n}$	pA
0.152	11.551	0.992	9.810
0.204	11.189	1.105	9.631
0.313	10.909	1.216	9.441
0.367	10.810	1.328	9.261
0.422	10.720	1.442	9.082
0.481	10.629	1.558	8.893
0.536	10.539	1.666	8.722
0.593	10.429	1.776	8.485
0.650	10.349	1.876	8.071
0.762	10.169	1.955	7.623
0.878	9.989		

System, Cu^{2+} - Ethylenediamine

Temperature 25°C.

Contents of Cell

25 ml. of Solution, $CuSO_4$ 0.005 M
HCl 0.0395 M
KCl 0.0605 M

Titrant. Ethylenediamine Solution, 0.696 M.

pH Range. 3.7 to 5.7

$\bar{n}$	pA	$\bar{n}$	pA
0.205	11.110	0.991	9.635
0.314	10.758	1.046	9.534
0.368	10.631	1.107	9.460
0.423	10.546	1.158	9.362
0.482	10.452	1.216	9.271
0.537	10.361	1.327	9.100
0.593	10.263	1.440	8.917
0.650	10.180	1.555	8.733
0.706	10.085	1.660	8.498
0.762	9.994	1.768	8.321
0.821	9.893	1.852	7.919
0.878	9.814	1.931	7.722
0.932	9.712		

System, Cu^{2+} - Ethylenediamine.

Temperature 30°C.

Contents of Cell.

25 ml. of Solution	$CuSO_4$	0.005 M
	HCl	0.0395 M
	KCl	0.0605 M

Titrant. Ethylenediamine Solution, 0.696 M.

pH Range. 3.8 to 5.8.

$\bar{n}$	pA	$\bar{n}$	pA
0.206	10.931	0.990	9.460
0.315	10.608	1.045	9.360
0.369	10.460	1.100	9.290
0.424	10.371	1.160	9.191
0.482	10.280	1.217	9.100
0.538	10.186	1.326	8.938
0.594	10.091	1.438	8.752
0.650	10.010	1.553	8.574
0.706	9.910	1.654	8.392
0.762	9.820	1.760	8.156
0.821	9.720	1.838	7.768
0.878	9.640	1.914	7.215
0.932	9.540		

System, Cu^{2+} - Ethylenediamine

Temperature 40°C.

Contents of Cell .

25 ml. of Solution	$CuSO_4$	0.005 M
	HCl	0.0395 M
	KCl	0.0605 M

Titrant. Ethylenediamine Solution, 0.696 M.

pH Range. 3.6 to 5.6.

$\bar{n}$	pA	$\bar{n}$	pA
0.164	10.948	0.988	9.133
0.208	10.520	1.043	9.042
0.315	10.270	1.098	8.951
0.369	10.151	1.158	8.852
0.424	10.040	1.212	8.760
0.480	9.929	1.325	8.594
0.536	9.830	1.431	8.415
0.650	9.672	1.546	8.234
0.706	9.571	1.652	8.046
0.760	9.480	1.751	7.837
0.817	9.392	1.842	7.480
0.874	9.291	1.890	6.907
0.930	9.212		

System, Ni^{2+} - Ethylenediamine

Temperature 20°C.

Contents of Cell. 25 ml. of Solution

$NiSO_4$	0.00486 M
HCl	0.0392 M
KCl	0.0608 M

Titrant. Ethylenediamine Solution, 1.035 M.

pH Range. 5.3 to 8.5

$\bar{n}$	pA	$\bar{n}$	pA
0.202	8.488	1.906	5.453
0.349	7.891	1.968	5.308
0.421	7.713	2.013	5.166
0.492	7.574	2.061	5.044
0.570	7.455	2.108	4.923
0.648	7.336	2.138	4.805
0.793	7.139	2.170	4.706
0.938	6.942	2.213	4.617
1.072	6.746	2.302	4.452
1.208	6.571	2.432	4.300
1.330	6.396	2.555	4.112
1.451	6.223	2.644	3.905
1.565	6.070	2.725	3.711
1.667	5.918	2.823	3.515
1.759	5.749	2.880	3.237
1.836	5.600		

System, Ni^{2+} - Ethylenediamine.

Temperature. 25°C.

Contents of Cell.

25 ml. of Solution	$NiSO_4$	0.00486 M
	HCl	0.0392 M
	KCl	0.0608 M

Titrant. Ethylenediamine Solution, 1.035 M.

pH Range. 5.3 to 8.5

$\bar{n}$	pA	$\bar{n}$	pA
0.193	8.225	1.854	5.407
0.332	7.768	1.927	5.205
0.482	7.426	1.975	5.082
0.554	7.301	2.034	4.971
0.632	7.194	2.068	4.850
0.782	6.996	2.110	4.734
0.918	6.810	2.135	4.637
1.047	6.623	2.181	4.553
1.191	6.460	2.258	4.377
1.301	6.285	2.361	4.288
1.415	6.112	2.451	4.046
1.510	5.960	2.550	3.842
1.637	5.820	2.651	3.643
1.702	5.750	2.773	3.445
1.793	5.603	2.851	3.170

System, Ni^{2+} - Ethylenediamine.

Temperature 30°C.

Contents of Cell.

25 ml. of Solution	$NiSO_4$	0.00486 M
	HCl	0.0392 M
	KCl	0.0608 M

Titrant. Ethylenediamine Solution, 1.035 M.

pH Range. 5.3 to 8.5.

$\bar{n}$	pA	$\bar{n}$	pA
0.185	8.003	1.886	5.110
0.316	7.543	1.940	4.999
0.472	7.286	2.008	4.896
0.532	7.148	2.031	4.778
0.617	7.050	2.080	4.663
0.720	6.932	2.095	4.567
0.773	6.854	2.150	4.488
0.896	6.677	2.218	4.305
1.022	6.502	2.290	4.158
1.174	6.347	2.345	3.976
1.273	6.174	2.455	3.777
1.380	6.001	2.580	3.576
1.470	5.851	2.721	3.375
1.604	5.701	2.824	3.115
1.646	5.553	2.870	2.870
1.743	5.406	2.910	2.910
1.804	5.362		

System, Ni^{2+} - Ethylenediamine.

Temperature 40°C.

Contents of Cell.

25 ml. of Solution

$NiSO_4$	0.00486 M
HCl	0.0392 M
KCl	0.0608 M

Titrant. Ethylenediamine Solution, 1.035 M.

pH Range. 5.3 to 8.6.

$\bar{n}$	pA	$\bar{n}$	pA
0.159	7.653	1.691	5.232
0.301	7.236	1.821	4.968
0.439	7.000	1.905	4.731
0.506	6.882	1.985	4.536
0.577	6.764	2.079	4.349
0.752	6.588	2.115	4.171
0.863	6.414	2.228	4.041
0.988	6.240	2.268	3.838
1.078	6.086	2.360	3.658
1.210	5.934	2.485	3.450
1.292	5.801	2.600	3.252
1.415	5.652	2.728	3.008
1.506	5.504	2.832	2.752
1.627	5.357		

System, Cu^{2+} - 1:3-Diaminopropane.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution	$CuSO_4$	0.00475 M
	HCl	0.040 M
	KCl	0.060 M

Titrant. 1:3-Diaminopropane Solution, 0.586 M.

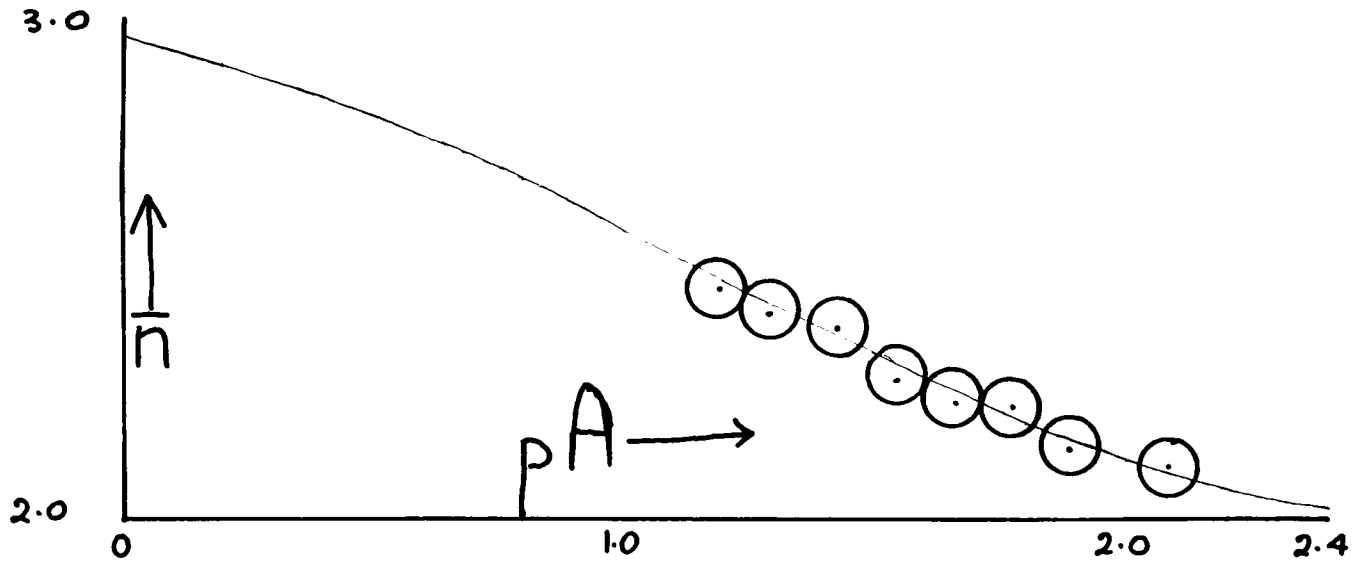
pM Range. 5.1 to 7.5.

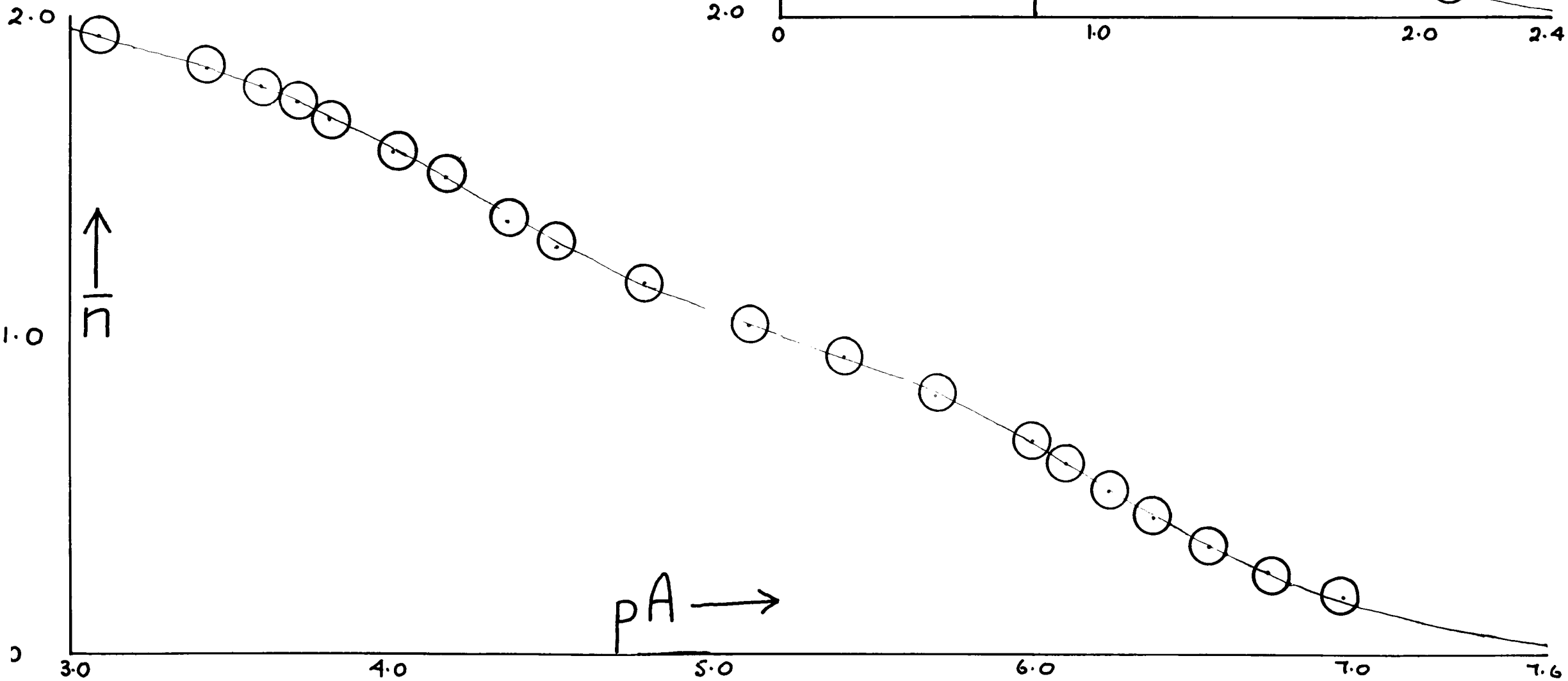
$\bar{n}$	pA	$\bar{n}$	pA
0.061	10.944	1.108	8.069
0.230	10.223	1.202	7.770
0.328	9.986	1.298	7.550
0.424	9.805	1.389	7.351
0.525	9.626	1.478	7.172
0.624	9.446	1.570	6.993
0.723	9.266	1.667	6.814
0.822	9.047	1.748	6.626
0.917	8.727	1.830	6.418
1.012	8.408	1.902	6.161

System,

Ni^{2+} - 1:3 - Diamino propane

at 25°C.





System, Ni^{2+} - 1:3-Diaminopropane.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution,

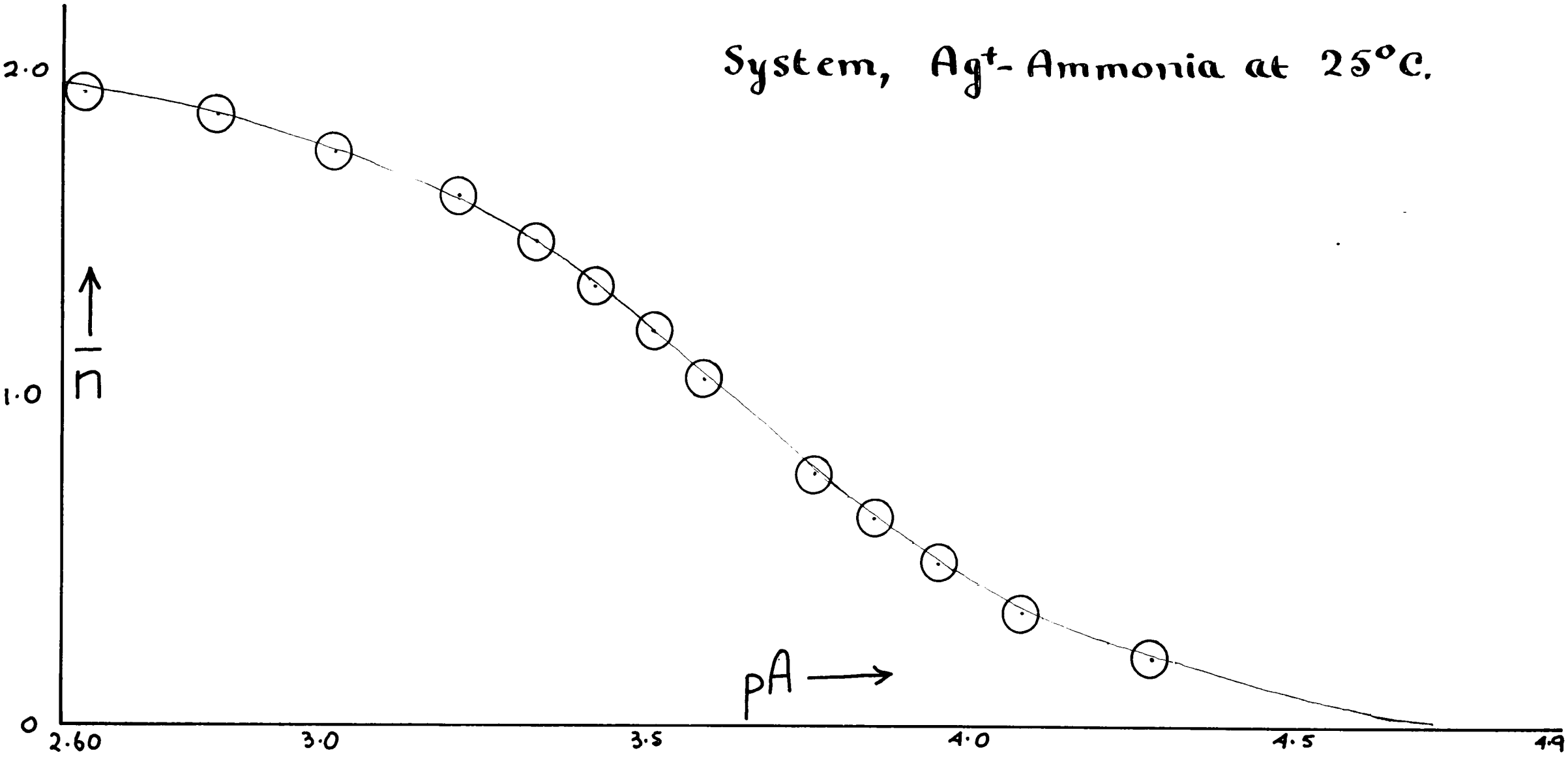
$NiSO_4$	0.00492 M
HCl	0.040 M
KCl	0.060 M

Titrant. 1:3-Diaminopropane, 0.586 M.

pH Range. 7.0 to 10.80.

$\bar{n}$	pA	$\bar{n}$	pA
0.186	6.969	1.580	4.000
0.266	6.731	1.684	3.803
0.346	6.552	1.793	3.596
0.429	6.374	1.814	3.558
0.507	6.236	1.849	3.420
0.590	6.098	1.944	3.095
0.671	5.981	2.102	2.081
0.807	5.686	2.140	1.892
0.936	5.414	2.203	1.768
1.032	5.106	2.238	1.661
1.169	4.784	2.277	1.539
1.280	4.506	2.327	1.423
1.363	4.361	2.410	1.292
1.497	4.164	2.460	1.190

System, Ag^{t}- Ammonia at 25°C.



System, Ag^+ - Ammonia.

Temperature. 25°C.

Contents of Cell.

25 ml. of Solution

$AgNO_3$, 0.020 M.

HNO_3, 0.080 N.

Titrant. Ammonia Solution, 1.450 M.

pH Range. 6.2 to 8.0

$\bar{n}$	pA
0.210	4.27
0.355	4.07
0.498	3.94
0.641	3.84
0.785	3.75
0.928	3.66
1.071	3.58
1.214	3.50
1.355	3.41
1.495	3.32
1.633	3.20
1.761	3.01
1.876	2.83
1.940	2.63

System, Ag^+ - Pyridine.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution

$AgNO_3$ 0.020 M

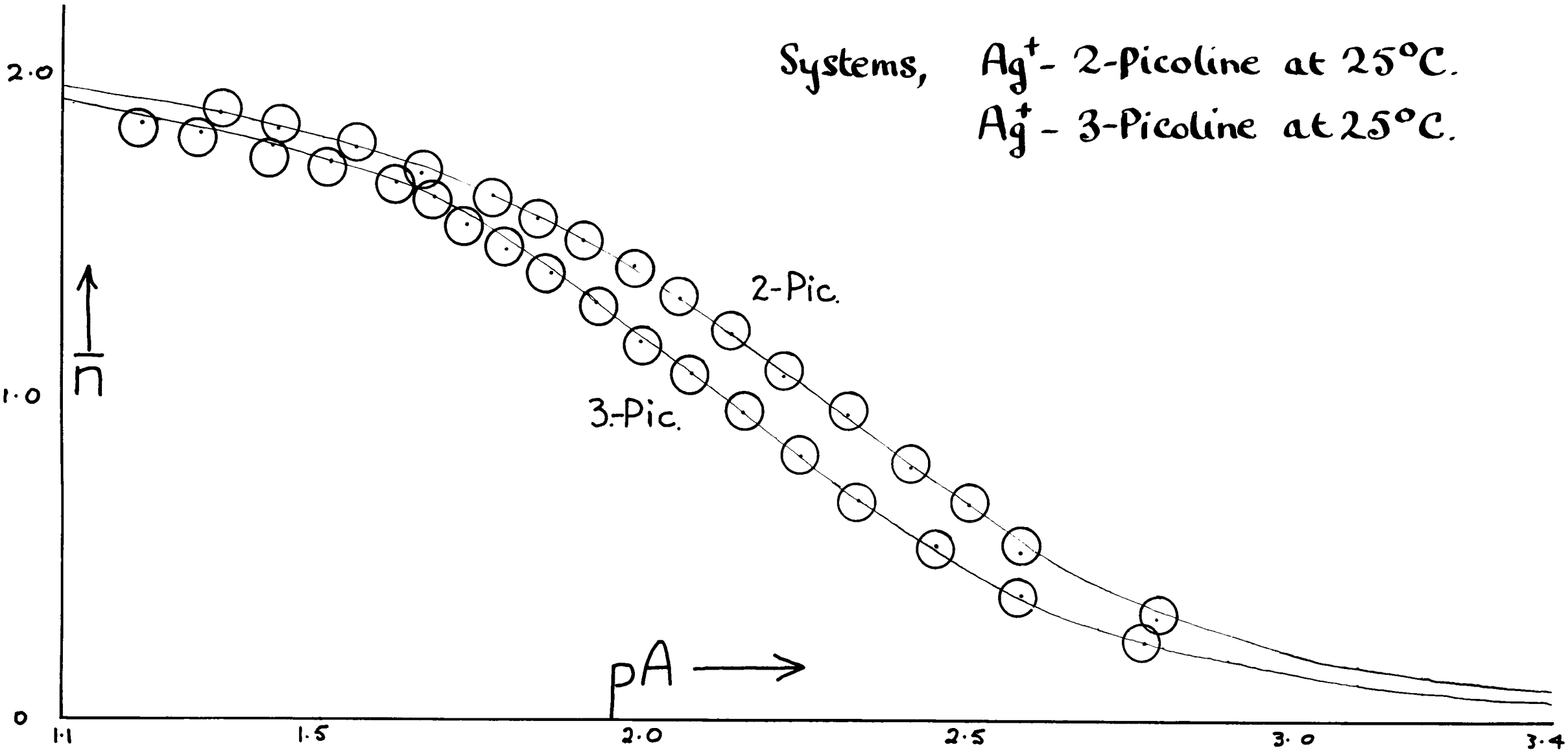
HNO_3 0.080 M

Titrant. Pyridine Solution, 1.060 M.

pH Range. 3.1 to 5.2.

$\bar{n}$	pA	$\bar{n}$	pA
0.161	2.84	1.337	1.84
0.312	2.60	1.429	1.78
0.465	2.44	1.503	1.72
0.613	2.32	1.619	1.60
0.757	2.22	1.663	1.55
0.893	2.13	1.732	1.48
1.012	2.06	1.770	1.40
1.146	1.97	1.795	1.33
1.246	1.90	1.856	1.25

Systems, Ag^+ - 2-Picoline at 25°C.
Ag^+ - 3-Picoline at 25°C.



System, Ag^+ - 2-Picoline.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution

$AgNO_3$ 0.020 M

HNO_3 0.080 M

Titrant. 2-Picoline Solution, 0.967 M.

pH Range. 4.4 to 5.9.

$\bar{n}$	pA
0.311	2.79
0.518	2.62
0.673	2.50
0.785	2.41
0.953	2.31
1.077	2.21
1.202	2.13
1.313	2.05
1.408	1.98
1.483	1.90
1.553	1.83
1.621	1.76
1.697	1.65
1.781	1.55
1.836	1.43
1.885	1.34

System, Ag^+ - 3-Picoline.

Temperature. 25°C.

Contents of Cell.

25 ml. of Solution, $AgNO_3$ 0.020 M; HNO_3 0.080 M

Titrant. 3-Picoline Solution, 0.983 M.

pH Range. 4.0 to 5.6

$\bar{n}$	pA	$\bar{n}$	pA
0.240	2.77	1.388	1.85
0.390	2.58	1.461	1.78
0.541	2.45	1.535	1.72
0.681	2.33	1.625	1.67
0.824	2.24	1.665	1.61
0.955	2.15	1.735	1.51
1.079	2.07	1.781	1.42
1.190	1.99	1.818	1.31
1.297	1.92	1.844	1.22

System, Ag^+ - 4-Picoline.

Temperature 25°C.

Contents of Cell.

25 ml. of Solution — $AgNO_3$ 0.020 M; HNO_3 0.080 M

Titrant. 4-Picoline Solution, 0.977 M.

pH Range. 4.3 to 5.9.

$\bar{n}$	pA
0.235	2.92
0.390	2.71
0.546	2.57
0.700	2.47
0.846	2.36
0.981	2.27
1.117	2.19
1.240	2.11
1.350	2.03
1.442	1.96
1.530	1.89
1.600	1.82
1.668	1.74
1. 752	1.65
1.801	1.55
1.828	1.42
1.850	1.33

System, Ag^+ - 2:6-Lutidine.

Temperature 25°C.

Contents of Cell. 25 ml. of Solution

$AgNO_3$	0.020 M
HNO_3	0.080 M

Titrant. 2:6-Lutidine Solution, 0.924 M.

pH Range. 4.6 to 5.8.

$\bar{n}$	pA
0.220	3.25
0.380	2.99
0.538	2.82
0.645	2.70
0.845	2.58
0.988	2.47
1.125	2.37
1.256	2.28
1.375	2.20
1.488	2.12

precipitation

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ACKNOWLEDGEMENTS.

The author would like to thank,

Dr. Lee's Professor of Chemistry for laboratory facilities.

Dr. H.M.N.H. Irving for his constant encouragement and advice.

Drs. R.E. Richards and D.F. Evans for the loan of the calorimeter and advice concerning its use.

Mr. D.H. Mellor, B.A., for his stability measurements.

The Department of Scientific and Industrial Research for a grant.