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A MICROCALORIMETRIC STUDY OF

THE INTERMEDIATE COMPLEXES

$\text{CdBr}^+, \text{CuBr}^+$

IN AQUEOUS SOLUTION.
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I. INTRODUCTION

A. Foreword

Pancinurat has attempted to explain the observed stability trends for a series of halide complexes in solution with a given metal and also for various complexes with a given halide. He concludes that the stabilities relative to one another are dependent upon the relative magnitudes of the standard heat of formation and standard entropy changes but that the data available is inadequate and often subject to factors which make comparison difficult.

In recent years, increasing interest has been shown in the physical chemistry of complex-ion formation. In particular, numerous measurements have been made of the stability constants of complex ions and hence their free energies of formation. If their heats of formation are also known the corresponding entropy changes can, of course, be evaluated. Usually however, either these heats of formation have not yet been determined, or else the only values available are those calculated from stability constant measurements at more than one temperature. The reliability of such values often seems questionable, primarily because the range of temperatures over which the measurements were made has almost always been too small. It is undoubtedly better to measure the heats of formation calorimetrically, preferably under more or less the same conditions of concentration and ionic strength as those used in the measurement of the stability constants.

We here report a microcalorimetric determination of the heats of formation of the complex ions CdBr$^+$ and CuBr$^+$ in
aqueous solution. The apparatus and procedure employed are similar to those used previously in this college in work on the lead halide complexes\(^2\). In the case of the CaBr\(^+\) complex we have extended the method to calculate a value of the equilibrium constant which we shall compare with other values from the available literature.

We shall attempt in conclusion to throw some further light on the nature of complex species in solution and also to further explain the observed stability trends of these complexes.
B. Theory.

**Thermodynamics of solutions**

There follows a brief survey of some aspects of the theory of electrolytic solutions which serve as a theoretical background to the present investigation.

The properties of electrolytic solutions fall naturally into two groups:

(i) those determined by measurements of systems in equilibrium;

(ii) those determined by measurements of systems in disturbed states.

To the first group belong such properties as those derived from measurements of colligative properties, solubility, specific heat, heat content and properties of galvanic cells. It is to this group that we shall confine our attention.

**General Thermodynamic Background**

The first law of thermodynamics has been generally expressed by Gibbs in terms of the energy, \( U \), of a phase as a function of the pressure, \( P \), the volume, \( V \), the temperature, \( T \), the electrical charge \( e \), and the number of moles of each of the \( i \) components, \( n_1, n_2, \ldots, n_i \), in the phase. Providing all other variables are kept constant, the energy of a phase in terms of these variables is

\[
U = f(P, V, T, n_1, n_2, \ldots, n_i, e) + U^0
\]

where \( U^0 \) is the energy in some arbitrary standard state. The first law requires that the increase in energy of a system, of constant composition and mass, is equal to the heat absorbed by the system plus the electrical and mechanical work done on
the system by the surroundings. Mechanical work being
confined to the effect of changes in the volume of the system,
we have

\[ dU = dQ - PdV + dW_{(el.)} \]  \quad \text{(1)}

For a reversible process, \( P \) represents the equilibrium
pressure of the system, and \( dW_{(el.)} \) is the reversible electrical
work. The second law of thermodynamics requires that the
reversible heat absorbed by the system is

\[ dQ = TdS \]  \quad \text{(2)}

where \( S \) is the entropy. The combination of equations (1) and
(2) can be extended\(^3\) to include variations in composition by
introducing the chemical potentials,

\[ \mu_1 = \frac{\partial U}{\partial n_1}, \quad \mu_2 = \frac{\partial U}{\partial n_2}, \quad \text{etc.} \]

representing the rate of change in energy per mole. Our
generalised representation of the first and second laws becomes,
therefore

\[ dU = TdS - PdV + \mu_1 dn_1 + \cdots + \mu_2 dn_2 + \frac{\partial H}{\partial e} de \]  \quad \text{(3)}

for reversible processes, where the term \( \frac{\partial H}{\partial e} de \) is the reversible
electrical work expressed in terms of the charge as independent
variable.

The extensive properties, heat content, \( H \), work content, \( F \),
and free energy, \( G \), are defined

\[ H = U + PV, \quad F = U - TS, \quad G = H - TS \]
The differentials of these quantities may be written

\[ dH = TdS + VdP + \mu_1 dn_1 + \cdots + \mu_2 dn_2 + \frac{\partial H}{\partial e} de \]  \quad \text{(4)}
\[ \frac{dF}{dT} = -SdT + PdV + \mu_1dn_1 + \ldots + \mu_kdn_k + \frac{1}{2} S \partial \theta \partial e \quad \text{(5)} \]
\[ \frac{dG}{dT} = -SdT + VdP + \mu_1dn_1 + \ldots + \mu_kdn_k + \frac{1}{2} D \partial \theta \partial e \quad \text{(6)} \]

consistent with the relations
\[
\mu_1 = \frac{2}{2} \frac{1}{n_1} \sum_{j=1}^{n_1} s_j v_j n_j \quad \text{and} \quad \mu_k = \frac{2}{2} \frac{1}{n_k} \sum_{j=1}^{n_k} s_j v_j n_j \quad \text{for each component}
\]

By considering a system composed of \( p \) phases at constant temperature, pressure, and charge, Gibbs was able to prove by equation (3), that at equilibrium
\[
\mu_1' = \mu_1'' = \ldots = \mu_p' \quad \mu_2' = \mu_2'' = \ldots = \mu_p'' \quad \ldots
\]
\[
\mu_i' = \mu_i'' = \ldots = \mu_i'
\]

where \( \mu_1', \mu_1'', \ldots, \mu_p' \) represent the chemical potentials of the first component, \( \mu_2', \mu_2'', \ldots, \mu_2' \) those of the second component, etc., throughout the \( p \) phases.

The Concept of activities and activity coefficients

The term activity of an electrolyte was first introduced by G.N. Lewis in 1901.

The activity, \( a_i \), of a pure chemical species or constituent of a solution is defined
\[
\mu_i = \mu_i' + RT \ln a_i
\]
where $\mu_1^0$ is the chemical potential in some arbitrary standard state, its value being dependant on the concentration scale in which $a_1$ is expressed. Alternatively since

$$\mu_1 = \overline{G}_1 = \left[ \frac{2G}{n_1} \right]_{T,P,n_1,\ldots}$$

$\overline{G}_1$ being the partial molal free energy of component 1, we have

$$\overline{G}_1 = \overline{G}_1^0 + RT \ln a_1$$

Although the actual ionic constituents are of fundamental importance in determining the properties of a system, their concentrations are not independent variables so that chemical potentials, free energies or activities of individual ionic species cannot be evaluated by thermodynamics. Nevertheless "hypothetical" ionic activities are often used with the strict understanding that only certain ionic activity products, or ratios, have any real physical significance.

Convenient alternative expressions for the activity of an electrolyte are obtained upon consideration of the formal representation of its dissociation in solution. If an electrolyte $C\ \nu_+ A\ \nu_-$, dissociates into $\nu_+ cations and \nu_-$ anions according to

$$C\ \nu_+ A\ \nu_- \rightarrow \nu_+ C + \nu_- A$$

then its activity may be written

$$a = a_+^{\nu_+} a_-^{\nu_-} = a_+^\nu$$

where $\nu = \nu_+ + \nu_-$ and $a_-, a_+$ are the conventional individual activities of the ionic constituents, and $a_+$ is the mean activity of the ions. We may thus write
\[ \mu - \mu^0 = \bar{G} - \bar{G}^0 = RT \ln \left( a^+ a^- \right) = \nu RT \ln a^+ \]

for the chemical potential and partial molar energy of an electrolytic component of a solution.

In solutions of such high dilution that the interaction between solute particles can be neglected it has been shown that the activities of solutes will approach their molalities. On this basis the selected reference state is

\[ \frac{a^+}{m^+} = y^+ = (y^+ y^+ y^-)^{1/2} = 1 \text{ at infinite dilution of the solvent. } \]

\( a^+ \) is the mean ionic molality of the electrolyte and \( y^+ \) the stoichiometric mean ionic molal activity coefficient or practical activity coefficient.

\( y^+ \) describes the departure of real solutes from ideality.

Consider the general reaction

\[ a\,A + b\,B \quad \rightarrow \quad x\,X + y\,Y \quad \rightarrow \]

The total free energy change for the reaction will be

\[ \Delta G - \Delta G^0 = RT \ln \frac{(a_A)^x (a_B)^y}{(a_A)^a (a_B)^b} \]

\[ = RT \ln \Omega \]

where \( \Omega \) is the reaction quotient, \( \Delta G \) the free energy change of the reaction in general and \( \Delta G^0 \) the free energy change when all the products and reactants are in their standard states. When the reaction is at equilibrium at constant temperature, pressure and charge, the composition is fixed. Then from equation (6) it follows

\[ \Delta G = 0 \]
Then
\[ \Delta g^0 = -RT \ln q \]
or if we designate the reaction quotient by \( k \) we have
\[ \Delta g^0 = -RT \ln k \]
where \( k \) is the thermodynamic equilibrium constant.

**Interionic Attraction Theory.**

For many years it was suspected that the behaviour of strong electrolytes in dilute solution could be accounted for by the hypothesis of complete dissociation and an adequate consideration of the effects of interionic attraction. Sutherland, Soyes and particularly Bjerrum were among the first to adopt this point of view. Ghosh attempted to give the effects of interionic attraction mathematical expression but the basis of his treatment proved to be inadequate. Milner successfully analysed the problem, but his mathematical treatment was exceedingly involved and did not yield an entirely satisfactory result. In particular, Milner did not know how ions were distributed with respect to one another in solution.

The main advance towards the solution of the problem came in 1923 when Debye and Hückel advanced their theory. They introduced the concept of the "ionic atmosphere" whereby a particular ion would be surrounded by an atmosphere containing a predominance of oppositely charged ions. Ions were considered as point charges and the forces between them coulombic in nature. Deviations from ideality were ascribed to electrostatic interactions of a given ion with its "ionic..."
atmosphere" and quantitatively described in terms of the activity coefficient which was related to the free energy of electrostatic interaction, $\Delta G_{el}$,

$$\bar{G}_+ = G^0_+ + \gamma_+ RT \ln \gamma_+ + \Delta G_{el}.$$ 

$$\Delta G_{el} = \gamma_+ RT \ln y_+.$$

From a consideration of the Poisson equation and the Boltzmann distribution principle, Debye and Hückel proposed their law to describe the deviations of completely dissociated 1-1 electrolytes from ideality. The limiting form of the law is

$$- \log y_\pm = a z_+ z_- \sqrt{\mu}$$

where $y_\pm$ is the practical activity coefficient, $a$, a parameter dependent on the solvent and temperature, $z_+$, $z_-$, the valencies of positive and negative ions respectively and

$$\mu = \frac{1}{2} \sum m_i z_i^2,$$

the ionic strength, where $m_i$ is the molality of species $i$.

Various extensions of the form

$$- \log y_\pm = \frac{a z_+ z_- \sqrt{\mu}}{1 + b \sqrt{\mu}} + c \mu$$

in some of which either $b$ or $c$ is zero have been proposed. A theoretical form due to Debye in which $c = 0$ regards $b$ as a parameter directly proportional to the distance of closest approach of the ions involved and may be written as $b = a \beta$, where $a$ is the distance of closest approach. Guggenheim, however, considers $b$ best regarded as an empirical parameter.
These formulae have been mathematically extended by Gronwall, La Mer and Sanyel\textsuperscript{12} for the symmetrical type of electrolyte and by La Mer, Gronwall and Grief\textsuperscript{15} for the unsymmetrical type. These extensions do not make the approximations in the solution of the Poisson-Boltzmann equation needed in the simpler Debye-Hückel theory but whereas the approximation leads to a self consistent solution the extended term method leads to results which are not self consistent\textsuperscript{14}.

Expressions of the type (7) have been widely successful in describing data up to $\sqrt{\mu} = 0.1$ for 1-1 electrolytes. Above this ionic strength, individual deviations occur and for certain classes of electrolytes, more especially 2-1, with which we are concerned, much below this figure.

Molecular Species and Ion Pairs.

There are two main lines of thought which seek to explain the deviations of certain electrolytes from the simple Debye-Hückel theory at low concentrations. It must be emphasized that these are not mutually exclusive theories though at present it is uncertain as to whether any sharp line can be drawn between the two\textsuperscript{15}. We shall have cause to return to these theories at a later stage when we consider the nature of the complex ions with which we are at present concerned. It may be here noted that our experimental procedure assumes nothing about the nature of the intermediate ions except that they may be assigned a chemical potential and that equilibria of the type

\[
\text{MX}^+ \rightleftharpoons \text{M}^{++} + \text{X}^- \quad \text{(in solution)}
\]
may be described by the Law of Mass Action.

Various workers\textsuperscript{16} have assumed that deviations from the Debye-Hückel theory at low concentrations can be accounted for by assuming incomplete dissociation. Bates\textsuperscript{17}, for example, has shown that the change of activity coefficient with concentration for cadmium bromide solutions, approaches the limiting Debye-Hückel law above 0.001 m. only when a correction for incomplete dissociation of the intermediate cation, CdBr\textsuperscript{+}, is made. Some doubt however has arisen as to whether the intermediate ions are in fact molecular species or ions which are held together by strong electrostatic forces.

Hoyle\textsuperscript{18} in an early paper suggested that electrostatic attraction produced "molecules" of a particular character.

Bjerrum\textsuperscript{19} went a step further, providing an alternative extension to the Debye-Hückel theory by considering the possibility of ion association, or more particularly, the formation of ion pairs under the influence of coulombic forces. Fuoss\textsuperscript{20} has also postulated the existence of long range ion pairs not considered by Bjerrum and Fuoss and Kraus\textsuperscript{21} have extended the theory to triple ions and quadrupoles.

In the Bjerrum theory, ions are taken to be rigid impolarizable spheres contained in a medium of fixed macroscopic dielectric constant. Non-polar quantum bonds between ions as well as ion-solvent interactions are excluded.

The probability that an i ion is at a distance r from a j ion is given, according to the Maxwell-Boltzmann law by
Probability = \frac{Nc_i}{1000} \exp \left( \frac{U}{kT} \right) \pi r^2 \, dr,

where \frac{Nc_i}{1000} is the number of ions per c.c. of solution, 
\pi r^2 \, dr, is the volume of a spherical shell of thickness dr, 
(radius r, circumscribing the j ion. U is the work done in 
separating an i and j ion from r to infinity. At certain 
distances, U may be replaced by the simple Coulomb law,

U = \frac{z_1 z_2 \varepsilon^2}{Dr},

with the result that the probability is given by

Probability = \frac{Nc_i}{1000} \left[ \exp \left( \frac{-z_1 z_2 \varepsilon^2}{Dr kT} \right) \right] \pi r^2 \, dr.

If the ions are of like sign the probability of ionic 
association is very low. If the ions are of opposite sign, 
the probability can be shown to possess a minimum at a distance 
q, such that,

r (min.) = q = \frac{\varepsilon^2 |z_1 z_2|}{2 kT D}

from which it follows that q is the distance at which the 
energy of separation of ions is 2kT. For values of r less 
than q, the probability increases rapidly as r decreases. At 
values of r greater than q, the probability increases slowly.

Bjerrum assumed that two ions at a distance of r < q would be 
asociated. For 1-1 electrolytes in water at 16°C, q is 
3.52 Å and consequently electrolytes of this type, possessing 
values of the mean distance of approach of ions, a, less than
3.5 Å, will form short range ion pairs. The figure for 2-1 electrolytes is just over 7 Å, although this figure is somewhat arbitrary.

Fajans from a consideration of the variation of apparent molar refraction of a number of 1-1 electrolytes, has given evidence for ion-pairs and non-polar bond types together with all intermediate stages between these two extreme cases.

Thus in solution, we have the possibility of forming either ion-pairs between stable hydrated ions or molecular species in which it is the complex as a whole which may be hydrated. The essential difference is that in one case the hydration shell of the elementary contributing ions (in cases in which these are hydrated) is not disturbed while in the other it is.
G. Previous Work on Cadmium and Copper Bromide Complexes.

Leden\textsuperscript{23} by a method of potentiometric titrations has proved the existence of the following complex ions in cadmium bromide solutions: CdBr\textsuperscript{+}, CdBr\textsubscript{2}, CdBr\textsuperscript{3-}, CdBr\textsubscript{4}\textsuperscript{2-}. We shall be dealing only with the CdBr\textsuperscript{+} complex and will show at a later stage that it is the only complex species present in the solutions under consideration.

As yet no value for the heat of formation of the intermediate complex CdBr\textsuperscript{+} has been recorded though two works have reported values of the dissociation constant $K'$ for the reaction

\[
\text{CdBr}^+ \leftrightarrow \text{Cd}^{2+} + \text{Br}^- \quad \text{(in solution)}
\]

given by

\[
K' = \frac{[\text{Cd}^{2+}][\text{Br}^-]}{[\text{CdBr}^+]}.
\]

Riley and Gallafent\textsuperscript{2h} studied electrolytic dissociation of cadmium bromide solutions by a method of potentiometric titrations using the concentration cell

\[
\text{Cd}/0.01 \text{M} - \text{CdSO}_4/\text{Sat}^d. \quad \text{HNO}_3/0.01 \text{M} - \text{CdSO}_4/\text{Cd}
\]
x being varied from 0 to 0.8. By a method of trial and error they were able to estimate a value of the dissociation constant which is quoted at

\[
K' = 6.8 \times 10^{-3} \text{ at } 25^\circ\text{C}.
\]

Bates\textsuperscript{17} made electromotive force measurements of the cell

\[
\text{Cd} - \text{Mg} (2 \text{ phase})/\text{CdBr}_2 (m)/\text{AgBr} - \text{Ag}
\]
at $5^\circ$ intervals from $5^\circ$ to $40^\circ$C. He calculated values for the
dissociation constant, $K'$, as follows:

$K' = 0.006$ at $5^\circ C$; $K' = 0.0065$ at $10, 15$ and $20^\circ C$;
$K' = 0.007$ at $25, 30, 35$ and $40^\circ C$. As Bates points out
the agreement between his value at $25^\circ C$ with that of Riley and
Ballarient is somewhat fortuitous in view of the fact that they
assumed the presence, simultaneously, of complexes of the type
CdBr$_n^+$ ($n = 1, 2, 3, 4$), whereas he (Bates) used $K'$, as a first
approximation, to account for all incomplete dissociation
effects displayed by solutions more dilute than $0.01$ molal.
He took the agreement to indicate that CdBr$^+$ was the only
incompletely dissociated species present in appreciable
quantities in very dilute solution.

The fact that Bates was unable to detect any variation in
$K'$ over a temperature range of up to $15^\circ C$ leads one to doubt the
accuracy of his method as we have found in this work that the
variation over such a range is of the order of $12\%$ (see later).
Nevertheless, in the absence of more accurate data, we have
used Bates' results together with the Van't Hoff equation, to
calculate a value for the heat of formation of the complex at
$25^\circ C$. This we found to be $-1.5$ kcal.mol.$^{-1}$ though an error
of $\pm 0.7$ kcal. was estimated. The sign and order of
magnitude of $\Delta H$ should, however, be useful for comparative
purposes.

At a constant ionic strength of $3 \, \text{M}$, Eriksen$^{25}$ has found
a value for the equilibrium constant $K_{\text{CdBr}^+} = \frac{1}{K'} = 58 \pm 2$
mol.$^{-1}$ by a polarographic method analogous to Leden's potentiome-
metric method. Although this value is more in keeping with
that which we have found and again with that from spectroscopic
measurements, we are unable to make any real comparison since the latter two determinations have been confined to low ionic strengths (< 0.25). Indeed we cannot place any real significance on Eriksson's value for comparative purposes, since at such a high ionic strength $K_{\text{GdBr}^+}$ will vary considerably with the individual ionic activities which are of course indeterminate.

Results of work on the GdBr$^+$ complex are summarised below:

<table>
<thead>
<tr>
<th>Work</th>
<th>Method</th>
<th>$K_{\text{GdBr}^+}$</th>
<th>$\Delta H$</th>
<th>$t^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riley and Gallasen\textsuperscript{24}</td>
<td>potentiometric titrations</td>
<td>147</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>Bates\textsuperscript{17}</td>
<td>e.m.f.</td>
<td>167</td>
<td>-1.5 kcal.</td>
<td>10, 15, 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>143</td>
<td></td>
<td>25, 30, 35, 40</td>
</tr>
<tr>
<td>Eriksson\textsuperscript{25}</td>
<td>polarographic</td>
<td>58 ± 2</td>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

Kruk\textsuperscript{27} has reviewed the works of Häslin\textsuperscript{28} and Farrington\textsuperscript{29} on the CuBr$^+$ complex and has explained the discrepancies in the values of $K_{\text{CuBr}^+}$ obtained by these workers as being due to the presence of unsuspected higher complex CuBr$_2$ in solutions of low bromide concentration. The three workers all used virtually the same spectroscopic procedure.

Farrington quotes a value of $K_{\text{CuBr}^+} = 2.08 \pm 0.25$ from a study of solutions with the following formal concentrations:
\[ \text{Cu}^{++} = 0.25, 0.21, 0.17, 0.13, 0.1 \text{ mols. per litre} \]
\[ \text{Br}^{-} = 0.005 \text{ mols. per litre.} \]

Mäthnem's value of \( K_{\text{CuBr}^+} = 0.28 \) at the same ionic strength (unity) was calculated from solutions in which the copper concentration never exceeded that of bromide.

Kruk made his calculations at both high and low copper to bromide concentration ratios, the formal concentrations used being as follows:

<table>
<thead>
<tr>
<th>Series</th>
<th>Formal concentrations in mols. per litre</th>
<th>Ionic strength</th>
<th>( {^\circ C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( \text{Cu}^{++} = 0.005; ) Br(- = 0.40, 0.48, 0.64, 0.96 )</td>
<td>1.6</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41.4</td>
</tr>
<tr>
<td>II</td>
<td>Br(- = 0.001; ) Cu(^{++} = 0.20, 0.32, 0.40, 0.48 )</td>
<td>1.6</td>
<td>27.2</td>
</tr>
</tbody>
</table>

Values of \( K_{\text{CuBr}^+} \) calculated from series I differed considerably from that of Farrington and also from that calculated from series II. \( K_{\text{CuBr}^+} \) from series II however, was in quite good agreement with that of Farrington when one makes due allowance for the difference in ionic strength.

Results for \( \text{CuBr}^+ \) are tabulated below:

<table>
<thead>
<tr>
<th>Work</th>
<th>Kruk(^{27})</th>
<th>Kruk ( \text{at 27.2}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 34.4}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 41.4}^\circ \text{C.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.31</td>
<td>0.33</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Work</th>
<th>Kruk ( \text{at 27.2}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 34.4}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 41.4}^\circ \text{C.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.28</td>
<td>2.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Work</th>
<th>Kruk ( \text{at 27.2}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 25}^\circ \text{C.} )</th>
<th>Kruk ( \text{at 22}^\circ \text{C.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.28</td>
<td>2.03</td>
</tr>
</tbody>
</table>
From series I and the Van't Hoff equation, Kruk has calculated the enthalpy change for the formation of CuBr\(^+\) as 
\[ \Delta H = 4.8 \pm 2 \text{ kcal. mol.}^{-1} \]. Unfortunately it is in series I that contributions due to higher complex become apparent and therefore although we should expect the sign of \(\Delta H\) to be correct, the magnitude will probably be much lower than that quoted by Kruk.
II. EXPERIMENTAL

A. Introduction: Microcalorimetry

Swietoslawski and Sturtevant have reviewed advances in, and applications of, calorimetry with particular reference to microcalorimetric methods. The errors and corrections involved in microcalorimetric measurements have been comprehensively treated by White.

The most critical factors which will determine the type of calorimeter to be used are:

(a) the quantity of heat gained or lost,
(b) the water equivalent of the system,
(c) the time taken in the evolution of the heat.

From the point of view of classification of thermal processes the dilution of electrolytes is a typical phenomenon of short duration. It lasts as long as is required to mix the solution with water. At low concentrations the heat evolved (or absorbed) will be small and hence an apparatus capable of measuring small temperature changes is required. Factor (b) in the present case simply means choosing a convenient size for the calorimeter.

In view of the above requirements several microcalorimeters have been designed to measure the heats of dilution of electrolytes. The most notable contributions are those of Lange and Robinson and Cucker, Pickard and Flank. With this latter apparatus a temperature change of about 0.6 microdegree was detectable.
B. Apparatus

There follows a brief description of the microcalorimeter used in this work, the design being closely similar to that employed by Gucker and his co-workers with the main exception that the adiabatic temperature control between calorimeters and water bath is here absent.

General Description of Apparatus.

A general idea of the apparatus can be gained from the two sections, fig. 1 and fig. 2. Two identical calorimeters, A, A, each containing a stirrer, heater and holder are suspended from the lid of a water-tight submarine jacket, J, immersed in a thermostated water bath. The submarine jacket is supported from a brass plate, B, by means of four brass tubes which accommodate the stirrer and holder shafts.

Two brass columns from the brass plate, B, house two large stirrers for the water bath. The large copper water-bath was lagged with three inches of glass wool and the whole apparatus completely enclosed by a similarly lagged copper lid hinged to the boxing about the water-bath. A sprocket chain driven from a synchronous motor outside the thermostat drives the calorimeter stirrers and bath stirrers. Leakage of heat down the stirrer and holder shafts is reduced by insulating sections of perspex. The brass calorimeter lids are permanently fixed to the top of the submarine jacket and stirrer blades by bakelite sections. The calorimeters are fitted to the machined lids, sealed with Apiezon sealing compound Q and held in place by spring loaded clips.
The temperature difference between the two calorimeters is measured by means of a thermel, $M$, connected to a Paschen astatic galvanometer.

**Submarine Jacket and Lid.**

These were made of sheet brass plated with nickel, the inner surfaces being polished. The jacket is secured to the lid by means of twelve wing-nuts and made water-tight by means of a strip of shaped sheet-rubber.

**Calorimeters and Lids.**

Identical twin calorimeters each of about 500 ml. capacity were constructed of brass and plated on the outside with nickel which was polished to reduce heat transfer across the three centimetre gap between the calorimeters and also between the calorimeters and the submarine jacket. The inner walls of the calorimeters were coated with a thin layer of paraffin wax for chemical inertness and also to reduce adsorption of ions at the surfaces to a minimum. A well of depth 3.5 cm. and cross sectional area $3 \times 4 \text{ cm.}^2$ was welded into the side of each calorimeter to receive the thermel.

**Thermel.**

The difference in temperature between the calorimeters was measured by an 80 junction copper-constantan thermel 10 cm. long and having a resistance of about 12 ohms. It was constructed of no. 20 B and S gauge constantan wire and no. 30 copper wire, the joints being soft-soldered. The thermocouples were mounted in banks of ten on strips of mica notched at the ends to properly separate each junction. The eight banks of ten thermocouples were set in paraffin wax, with the junctions just
outside the wax, so that the final cross-sectional area of the thermal was about 3 x 4 cm.\(^2\). Thin strips of mica were fixed to the walls of the thermal well to prevent contact between them and the thermal.

Shielded copper leads connected the thermal to copper reversing switches and shunts in an oil bath and then to a Paschen galvanometer. The shunts were used to protect the galvanometer system when large deflections were expected. These were made of fine copper wire and had resistances of 0.20 ohm. and 0.53 ohm. respectively.

The Paschen astatic galvanometer which has a resistance of 13.1 ohm. was mounted on a plate which was supported from a concrete ceiling by a special spring made in two halves wound in opposite directions. Vertical vanes from the bottom were dipped into an oil bath to damp rotational vibration. It was housed in a draught-proof pinex cabinet and the scale was fixed outside, two metres from the galvanometer. Under normal conditions it could be read to an accuracy of 1 mm.

This combination of thermal and galvanometer was usually operated at such a sensitivity that 1 mm. galvanometer deflection corresponded to a difference in heat content between the two calorimeters of 0.001 calorie. Since each calorimeter and its contents generally had a heat equivalent of 500 calories, the galvanometer deflection was equivalent to 2 microdegrees per millimeter in terms of the temperature difference between the two ends of the thermal.
Calorimeter Heaters.

Each calorimeter heater having a resistance of about 70 ohms was made of no. 38 manganin wire wound on a flat sheet of glass about half an inch wide. The ends of the manganin wire were soldered to copper wire leads and the whole heater covered with araldite and annealed in an oven at 180°C. for a day. The oven was cooled slowly to prevent cracking of the araldite by too rapid contraction.

For a quantitative heating period the source of current was a 6-volt battery. This battery was checked periodically and maintained at half charge under which conditions the variation in current delivered over a heating period which never exceeded six minutes, was found to be negligible. The potential across the heaters was measured with a Cambridge vernier potentiometer which could be read with an accuracy of 0.00001 volt; the total potential across a heater never exceeded 1.2 volt. Heating periods were timed with a 0.1 second standardized stopwatch and an error of 0.2 seconds was estimated for any one period which was never below 1.5 minutes. Fig. 4 shows the heating circuit.

Temperature Control.

The thermostat water bath was heated by means of four symmetrically spaced heaters supported from the brass plate B. These heaters were connected so as to provide various rates of heating and consisted of 10 ohms of nichrome wire wound on pieces of glass tubing about 12 inches in length. The energy supplied to the heaters came from a 12 volt transformer and was regulated by means of a mercury-acetone regulator in conjunction with a proportioning head and an electronic relay (fig. 3).
fig. 5 The Relay
The relay served to reduce the current at the mercury contact to the order of microamperes and thus eliminated any fouling of the mercury from sparking which would have otherwise taken place. Transmitted vibration from the stirrers reduced sticking of the meniscus in the capillary of the regulator head so much so that the relay in action produced a constant "chattering". The regulator consisted of 25 feet of $\frac{3}{16}$ inch thin walled copper tubing wound into a rectangular coil mounted on the brass plate, $B$, and filled with acetone on account of its large thermal expansion coefficient. The regulator coil completely surrounded the submarine jacket and both heaters and stirrers. It had a large surface to volume ratio and was evenly distributed throughout the thermostat. The regulator head and a thermometer were able to be viewed through a small window in the thermostat-lid. Such an arrangement easily maintained the temperature within the thermostat at 25°C to within $10^{-3}$°C, as observed from a Beckman thermometer.

**Electrical Calibration.**

When a known amount of electrical energy was passed into one of the calorimeters a certain deflection was produced in the galvanometer as read from the scale. We were thus able to calibrate the galvanometer scale in calories per millimeter of deflection. The sensitivity was found to vary from one experiment to the next and also to vary according to which calorimeter was heated in determining the sensitivity. Sensitivity determinations had therefore to be carried out on both calorimeters for each experiment done. Calibration was
carried out as follows:

Fig. 4 shows the layout of the electrical heating circuit. X is a variable resistance to balance the excess in heat of stirring in calorimeter 2 over that in calorimeter 1. R is a standard 50 ohm. resistance and V the potential across it. M is a multiple switch to allow the current from the 6-volt battery C to pass through any one of R1, R2, or R3, the calorimeter heaters and tare (dummy) resistance respectively. R1, R2, R3 all have approximately the same resistance (70 ohm.); V1, V3 are the potentials across R1, R3 respectively.

Suppose that the difference in heat of stirring between calorimeter 1 and calorimeter 2 is balanced by passing a current I1 into calorimeter 1. Then the energy being passed into calorimeter 1 is given by

\[ \text{Energy} = I_1 V_1 \text{ per second} \]

\[ = \frac{V_1 V'}{50.4 \times 10^4} \text{ cals. per second} \]

The current is then switched through the tare resistance and its value raised to I (about 13 mA. as read from A) by means of X. It is then switched back into calorimeter 1 and a stopwatch simultaneously started. Total energy now passing into calorimeter 1 is now given by

\[ \text{Energy} = I V_1 \text{ per second} \]

\[ = \frac{V_1 V}{50.4 \times 10^4} \text{ cals per second} \]

If heating is continued for t seconds, then the energy passed into calorimeter 1 in excess of that needed to balance the difference in heats of stirring is
fig. 4  Calorimeter Heating Circuit
Corresponding to this energy input a deflection of $X$ mm. is observed on the galvanometer scale. The galvanometer sensitivity is then

$$\frac{t}{50 \times 4.184} (V_{1} V - V_{1} V') \text{ cals. per mm.}$$

The galvanometer deflections were in each case corrected for temperature loss by a graphical extrapolation method (see next section).

The following is a sample calibration run carried out on calorimeter 1:

$V_{1}' = 0.33314$ volt. \hspace{1cm} $V' = 0.21872$ volt.

$V_{1} = 0.97878$ volt. \hspace{1cm} $V = 0.62908$ volt.

$t = 120$ sec. \hspace{1cm} $x(\text{corrected}) = 292$ mm.

whence sensitivity

$$= \frac{120}{50 \times 4.184 \times 292} (0.97878 \times 0.62908 - 0.33314 \times 0.21872)$$

$$= 0.00109 \text{ cals. per mm.}$$
C. **Preparation and Purification of Materials.**

**Perchloric Acid:** Hopkin and Williams' "Analar" material was used without further purification.

**Cadmium Perchlorate:** An excess of cadmium oxide ('Baker Ana lysed' Reagent) was boiled with "analar" perchloric acid and the excess oxide filtered off. The solution contained a colloidal precipitate of a hydrated cadmium oxide as had previously been observed by Voeburgh\(^35\) who used a similar preparation. This was dissolved in a minimum quantity of perchloric acid by dropwise addition and constant shaking. A further quantity of cadmium perchlorate was prepared in a similar manner from 'Baker Ana lysed' cadmium carbonate and "analar" perchloric acid. The molality of cadmium perchlorate was determined by gravimetric analysis as dipyrindine cadmium dithiocyanate\(^36\).

**Copper Perchlorate:** A similar preparation from "analar" cupric oxide and "analar" perchloric acid was used. The molality was again determined using the pyridine-ammonium thiocyanate method.

**Potassium Chloride and Bromide:** "Analar" reagents were used without further purification. Both were dried in an oven for eight hours at 120° C before use.

All weighings of less than 100 gm. were performed on a Mettler Analytical Balance with a sensitivity of 0.000002 gm. for a single weighing. A large chemical balance with a sensitivity of 20 mgm. was employed for weighings over 100 gm.

It was found convenient to standardise all solutions on the molal scale mainly for ease of weighing or when making up solutions for particular dilutions.
Wallace and Robinson\textsuperscript{37} showed that no detectable oxidation of chloride or bromide ion takes place in solution and no precautions were taken to eliminate such oxidation.

Distilled water was used throughout and a determination carried out in this laboratory showed it to have a conductance of $1.6 \times 10^{-6}$ mho.

All glassware, including capillary tubing used for manufacturing the small glass bulbs used in dilutions, was thoroughly cleaned with a caustic solution recommended by Willard and Forman\textsuperscript{38}. 
D. Measurement of Heats of Dilution.

The solution to be diluted was contained in a thin glass bulb, of about 4 ml. capacity blown from pyrex capillary tubing waxed firmly in position in the holder, (fig. 1). A pin release mechanism and attached spring, operated by a string through the thermostat lid, enabled the bulb to be smashed against the stirrer blade. The bulb remains were then withdrawn from the stirrer path to cut out any heat effects due to friction; the same string enabled this to be done. In this way mixing was found to be both rapid and efficient and the heat effect almost instantaneous except for a small time lag in the apparatus. Several authors have used this method in the past with satisfactory results.

Several blank determinations carried out with bulbs containing water showed no detectable heat effect due to smashing.

Solutions were accurately weighed into the bulbs on a Mettler Analytical Balance using a 5 ml. glass syringes to introduce the solution through the capillaries of the bulb necks: care was taken that no liquid drops were left in the capillaries. The bulbs were sealed as soon as possible after weighing by placing a blob of molten pyrex glass over the capillary openings and then drawing off in an oxygen flame. In this way it was insured that none of the contents escaped by vapourization.

The heat effect on breaking a bulb was determined from the galvanometer deflection produced, the scale having been previously calibrated as described in the last section. Large
heat effects had to be compensated by electrical energy addition to one calorimeter or the other depending on whether the heat effect was positive or negative. In most such cases heat compensation was inexact and the residual heat effect was determined from the resultant galvanometer deflection.
E. Corrections for Heat Exchange.

The argument following is largely that of Van der Waals as presented by Adcock. When a heat change takes place in one of the calorimeters its temperature will be above or below that of the surroundings and heat will flow to or from it accordingly. Again, (for large heat effects) the heat developed in a calorimeter and the electrical energy supplied never simultaneously balance one another, the calorimeter temperature showing small variations from the thermostat temperature with consequent heat transfer between the calorimeter and its surroundings.

If the temperature of the thermostat is \( T_0 \), and that of the calorimeter \( T \), there will be a flow of heat approximately proportional to \( |T - T_0| \) from the surroundings to the calorimeter or vice versa. Since the galvanometer deflection \( G \) is proportional to \( |T - T_0| \), then

\[
\frac{dG}{dT} = -k |G - G_0|
\]

where \( |G - G_0| \) is the deviation of the galvanometer deflection from its value \( G_0 \) at temperature \( T_0 \), \( t \) the time and \( k \) a constant equal to the heat transfer coefficient of the calorimeter divided by its heat capacity. This is represented by the straight lines \( PQ \), \( XY \) in fig. 5.

Fig. 5 shows a typical graph of galvanometer deflection versus time actually obtained in a heat of dilution of potassium bromide (1 molal to 0.009 molal). Heat losses and gains were taken as balanced when the hatched areas \( QBC \), \( XAC \)
were equal as determined by counting squares. The vertical straight line AB then gave the galvanometer deflection corrected for heat exchange (hereafter referred to as the corrected deflection). For this purpose metric graph paper marked in 1 mm. squares was used.

In carrying out runs on heats of solution of potassium chloride and on heats of formation of CaBr⁺ the heat effects were large and electrical compensation had to be used. It was found however that the heat effect became apparent almost immediately — much faster than it could be conveniently compensated for by electrical heating. The method of Van der Waals (which requires that heating and mixing be started simultaneously) for correction for inexact compensation was not therefore applicable in the present case. Correction was made by breaking the bulb at a time equal to half the heating period after heating was started. The straight line portions of the graphs so obtained (see for example fig. 6 which is a typical graph obtained on diluting KBr from 1 molal to 0.009 molal in 0.05 molal Ca(ClO₄)₂) were extrapolated back to the time of breaking the bulb where the corrected deflection was measured. In this way it was assumed that heat losses and heat gains balanced each other which is reasonable provided, as was always the case, the unbalanced residual deflection was not large.
Fig. 6

Time in minutes

Galvo. defln. cms.

-30
-20
-10

Heat calorimeter 1.
Corrected defln. = 5.5 cm.
Break bulb 2
F. Standardization of Apparatus.

We have used as a calorimetric standard the heat of solution of potassium chloride to infinite dilution at 25°C.

A sample of about 20 mg. of dry potassium chloride was accurately weighed into a thin glass bulb which was then sealed as outlined in the last section. The salt was in each case diluted in about 400 gm. of distilled water. Since the bulb and contents were completely dry a small blank heat effect had to be allowed for in each determination due to the heat absorbed in saturating approximately 4 ml. of air with water vapour at 25°C. This was calculated at about 0.006 calorie and several blank determinations using empty bulbs gave a similar result.

The total heat absorbed in a particular determination was about 1.0 calorie which meant that the calorimeter in which the bulb was broken had to be electrically compensated to give a measurable galvanometer deflection. Ideally the electrical energy supplied would exactly compensate the heat absorbed by the potassium chloride in dissolving though in practice this was never quite realised; the difference, due to under- or over-compensation, was measured as the corrected deflection.

The following is a sample calculation of the heat of solution of potassium chloride using calorimeter 2.
weight KCl = 0.01451 gm.

$V_1' = 0.25456$ volt.   $V_3' = 0.16703$ volt.
$V_2 = 0.97968$ volt.   $V_3 = 0.62051$ volt.

$t = 221.5$ seconds.

Electrical energy supplied = 0.66866 calorie.
Corrected deflection = 145 mm. (corresponding to under-compensation)
Sensitivity = 0.00116 cals. per mm.
Total heat absorbed = $(0.66866 + 145 x 0.00116)$
= 0.85086 calorie.
Blank heat effect = 0.006 calorie.

...heat absorbed by 14.81 mg. of KCl in dissolving
= 0.85086 calorie

and heat of solution per mole of KCl is given by

$\Delta H = 0.85086 \times \frac{78.557}{0.01451}$

= 4.283 kcal. per mole.

Results for heats of solution of KCl are given in Table 1.

<table>
<thead>
<tr>
<th>sample weight mg.</th>
<th>$\Delta H$ kcal.</th>
<th>sample weight mg.</th>
<th>$\Delta H$ kcal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.85</td>
<td>4.027</td>
<td>19.41</td>
<td>4.153</td>
</tr>
<tr>
<td>14.81</td>
<td>4.283</td>
<td>17.50</td>
<td>4.047</td>
</tr>
<tr>
<td>17.36</td>
<td>4.286</td>
<td>18.06</td>
<td>4.274</td>
</tr>
<tr>
<td>18.98</td>
<td>4.283</td>
<td>20.00</td>
<td>4.135</td>
</tr>
<tr>
<td>19.15</td>
<td>4.103</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean value $\Delta H = 4.173$ kcal. per mole

Probable error of mean = ±0.024 kcal.

* We shall justify our use of probable errors later in the discussion.
We compare this value with other values available from literature in Table 2.

<table>
<thead>
<tr>
<th>Work</th>
<th>ΔH, kcal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Westrum and Eyring (1)</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>4.18</td>
</tr>
<tr>
<td>&quot;Selected values of Chemical Thermodynamic Properties&quot;</td>
<td>4.17</td>
</tr>
<tr>
<td>Hischenko and Kaganovich (2)</td>
<td>4.194 ± 0.003</td>
</tr>
<tr>
<td>This work</td>
<td>4.173 ± 0.024</td>
</tr>
</tbody>
</table>
G. Experimental Accuracy and Treatment of Errors.

The order of reproducibility of heats of dilution and of formation will depend directly upon the magnitude of the heat effect produced. The main errors involved in a given determination are those due to timing and measurement of the galvanometer deflection produced, the errors due to electrical heating being negligible by comparison.

Strictly speaking, one is not justified in applying statistical treatment to errors unless a very large number of experimental results are available upon which to base such treatment. It was noted however, that in all cases the probable error in a single result as calculated from Bessel's formula, was much less than that expected from purely experimental considerations. Variations were therefore considered random so that calculation of the probable error of the mean is justifiable, and the result calculated from a series of results is expected to be much more accurate than a result calculated from any single one. Probable errors in means were calculated from Bessel's formula as modified by Jeffreys\(^3\) to allow for a limited number of results.

Suspected values were rejected only after application of the Pierce-Chauvenet Criterion.\(^4\)
III. RESULTS AND DISCUSSION OF RESULTS

A. General.

Experimental heats of formation of the complexes under consideration were determined as follows:

The heat effects produced in the following dilutions were measured:

\[ \text{KBr (m)} \xrightarrow{H_2O} \text{KBr (m)}, \text{ heat exchange} = \Delta H_1 \]
\[ \text{KBr (m)} \xrightarrow{M\text{(ClO}_3\text{)}_2} \text{KBr (m)}, \text{ heat exchange} = \Delta H_2 \]

where \( M \) is either cadmium or copper and \( m \), \( m_1 \), and \( m_2 \) are the appropriate molalities of the solutions. Then the heat effect due to formation of complex, \( MX^+ \) is given by

\[ \Delta H_j = \Delta H_1 - \Delta H_2 \]

Experimental accuracy demands that \( \Delta H_1, \Delta H_2 \) and \( \Delta H_j \) should all be large. Further the metal cation to bromide ratio should be large to reduce, as far as possible, association to form higher bromide complexes. Clearly then, the size of the calorimeters will determine the dilutions which will produce optimum heat effects. It was found for example, that in order to obtain a sufficiently large heat effect (\( \Delta H_1 \)) in diluting potassium bromide in water, that the initial bromide molality (\( m \)) have to be at least unity. Hence the lowest possible final molality of bromide (\( m_1 \)), as determined by the capacity of the calorimeters, was 0.009. As pointed out earlier, it is desirable to confine such measurements as these to low ionic strengths and hence it was found necessary to restrict the metal cation molality (\( m_2 \)) to a maximum of 0.08, i.e., to a total ionic strength of 0.249.
The heat of dilution of metal perchlorate was shown to be immeasurably small. It was assumed that the metal perchlorates were completely dissociated in solution.

The above argument is somewhat simplified and the following points must be taken into consideration.

(a) Not all the bromide ions present in solution will be associated as complex, the degree of association being obtained from

$$\begin{align*}
m^{++} + Br^- & \rightleftharpoons MBr^+ \text{ (in solution)} \\
(m_2 - m_1 \alpha) & \quad m_1(1 - \alpha) \quad m_1 \alpha
\end{align*}$$

for which

$$K = \frac{m_1 \alpha}{(m_2 - m_1 \alpha)(1 - \alpha)} m_1$$

where $K$ is the equilibrium constant at the appropriate ionic strength and $\alpha$ the degree of association. If $\Delta H_1$, $\Delta H_2$, and $\Delta H_3$ are expressed in calories per mole of bromide present in solution, then the heat of formation of complex, $\Delta H_f$, is given by

$$\Delta H_f = \frac{\Delta H_2}{\alpha} \text{ cals. per mole.}$$

It is obvious then, that accurate values of the equilibrium constants at the appropriate ionic strengths are required. These have been obtained from the works of Kruh$^{27}$ and Farrington$^{29}$ in the case of the CuBr$^+$ complex while the values for CdBr$^+$ have been made available by Matheson$^{26}$.

(b) The Debye-Hückel Law predicts, and experiment confirms$^{45}$ that the heats of dilution of dilute electrolytes should vary
with ionic strength. Hence it is not correct to carry out the first dilution in water since the final ionic strength will be far less than that in the second dilution. The first dilution was therefore carried out in perchloric acid such that the final ionic strengths in both cases were the same. That is, it was assumed that $\Delta H$ is a function of ionic strength only.

(c) We have assumed up till now that only the mono-bromide complex is present in our solutions. To justify this assumption we have devised the following method of calculating $K_{\text{CdBr}^+}$ at one particular ionic strength.

Two runs were carried out as outlined above in which the molalities of the species present were

1. $\text{Cd}^{++} = 0.05$, $\text{Br}^- = 0.009$, $\text{HClO}_4 = 0.09$
   \[ I = 0.249 \]

2. $\text{Cd}^{++} = 0.08$, $\text{Br}^- = 0.009$,
   \[ I = 0.249 \]

where $I$ is the total ionic strength. We have then

$$\text{Cd}^{++} + \text{Br}^- \rightleftharpoons \text{CdBr}^+$$

1. $(0.05 - 0.009 \alpha_1)(1 - \alpha_1)0.009 \alpha_1 \; 0.009 \; \Delta H_3'$

2. $(0.08 - 0.009 \alpha_2)(1 - \alpha_2)0.009 \alpha_2 \; 0.009 \; \Delta H_3$

where $\alpha_1$ and $\alpha_2$ are the degrees of association and $\Delta H_3'$, $\Delta H_3$ the heats of formation expressed in calories per mole of bromide present. Now since both determinations were carried out at the same ionic strength we may assume that the equilibrium constant, $K$, and the heat of formation, $\Delta H_f'$, are the same for both cases. That is, the variations in individual ionic activities are assumed negligible. We consider this
assumption will justified in the light of evidence of many works including several at extremely high ionic strengths. (See for example references 25, 27, 29.) We have therefore

\[ K = \frac{\alpha_1}{(0.05 - 0.009 \alpha_1)(1 - \alpha_1)} \times \Delta H_3 \]

\[ = \frac{\alpha_2}{(0.08 - 0.009 \alpha_2)(1 - \alpha_2)} \times \Delta H_3 \]

where \( K \) is the mass action equilibrium constant at an ionic strength of 0.249.

If we now assume a value for \( K \), we may calculate \( \alpha_1 \) and hence \( \Delta H_f \) from

\[ \Delta H_f = \frac{\Delta H_2}{\alpha_1} \]

and since \( \Delta H_f \) is the same in both cases \( \alpha_2 \) may be obtained from

\[ \alpha_2 = \frac{\Delta H_2}{\Delta H_f} \]

This value of \( \alpha_2 \) is then substituted in the second equation and a new value of \( K \) calculated. Thus by repeated approximation we were able to obtain a constant value of \( K \) which agreed favourably with that calculated by Matheson at the same ionic strength. Since this latter determination employed far greater cadmium to bromide ratios than were used here, it seems reasonable to conclude that no higher complexes were in fact present.

Siddhanta has previously reported a calorimetric method for the evaluation of approximate free energies of
imperfect complexes. His theoretical method, we found, was inadequate. In particular he proposed neglecting the heats of dilution of the parent solutions, an assumption which we have shown is not justifiable. In any case he has not, so far as we are aware, published any experimental results. We can not therefore make any comparisons with his work.
Experimental Results at 25°C.

Table 3

Heats of dilution of KBr ($\Delta H_1$) from 1 molal to 0.009 molal at 25°C. $\Delta H_1$ is expressed in calories per mole of bromide present.

(a) Dilution in water. $\mu = 0.009$

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat absorbed Calories</th>
<th>$\Delta H_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003297</td>
<td>0.4078</td>
<td>123.6</td>
</tr>
<tr>
<td>0.003823</td>
<td>0.4631</td>
<td>135.2</td>
</tr>
<tr>
<td>0.003470</td>
<td>0.4109</td>
<td>118.4</td>
</tr>
<tr>
<td>0.003342</td>
<td>0.4194</td>
<td>125.4</td>
</tr>
<tr>
<td>0.003631</td>
<td>0.4816</td>
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<tr>
<td>0.003256</td>
<td>0.3898</td>
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<tr>
<td>0.003403</td>
<td>0.4042</td>
<td>118.8</td>
</tr>
<tr>
<td>0.003651</td>
<td>0.4729</td>
<td>129.5</td>
</tr>
<tr>
<td>0.003599</td>
<td>0.4500</td>
<td>119.5</td>
</tr>
<tr>
<td>0.003722</td>
<td>0.4604</td>
<td>123.6</td>
</tr>
<tr>
<td>0.003497</td>
<td>0.4396</td>
<td>125.7</td>
</tr>
</tbody>
</table>

Mean value $\Delta H_1 = 124.7$ cal per mole of bromide

Probable error of mean = 1.2 cal.
Table 3 (cont.)

(b) Dilution in 0.15 molal HClO₄. \( \mu = 0.159 \)

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>( \Delta H_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003583</td>
<td>0.0686</td>
<td>-26.4</td>
</tr>
<tr>
<td>0.003573</td>
<td>0.0944</td>
<td>-19.4</td>
</tr>
<tr>
<td>0.003339</td>
<td>0.0584</td>
<td>-20.8</td>
</tr>
<tr>
<td>0.003575</td>
<td>0.0673</td>
<td>-22.4</td>
</tr>
</tbody>
</table>

Mean value \( \Delta H_4 = -22.2 \) cals per mole Br.

Probable error of mean = 1.2 cals.

(c) Dilution in 0.25 molal HClO₄. \( \mu = 0.249 \)

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>( \Delta H_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003569</td>
<td>0.6618</td>
<td>-185.4</td>
</tr>
<tr>
<td>0.003508</td>
<td>0.6765</td>
<td>-192.8</td>
</tr>
<tr>
<td>0.003598</td>
<td>0.6708</td>
<td>-187.9</td>
</tr>
<tr>
<td>0.003656</td>
<td>0.6832</td>
<td>-186.9</td>
</tr>
</tbody>
</table>

Mean value \( \Delta H_4 = -188.3 \) cals per mole of bromide.

Probable error of mean = 1.2 cals.
Table 4

Heats of dilution of KBr (\(\Delta H_2\)) from 1 molal to 0.009 molal in various cadmium perchlorate solutions at 25° C.

(a) Dilution in 0.05 molal \(\text{Cd(ClO}_4\text{)}_2\). \(\mu = 0.159\)

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>(\Delta H_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003555</td>
<td>1.5679</td>
<td>-439.8</td>
</tr>
<tr>
<td>0.003441</td>
<td>1.4317</td>
<td>-419.7</td>
</tr>
<tr>
<td>0.003512</td>
<td>1.4811</td>
<td>-421.7</td>
</tr>
<tr>
<td>0.003394</td>
<td>1.3555</td>
<td>-399.4</td>
</tr>
<tr>
<td>0.003380</td>
<td>1.4244</td>
<td>-421.4</td>
</tr>
<tr>
<td>0.003258</td>
<td>1.2914</td>
<td>-396.4</td>
</tr>
<tr>
<td>0.003436</td>
<td>1.4323</td>
<td>-416.9</td>
</tr>
</tbody>
</table>

Mean value \(\Delta H_2 = -416.5\) cal per mole of bromide.

Probable error of mean = 4.0 cal.

(b) Dilution in 0.05 molal \(\text{Cd(ClO}_4\text{)}_2\). \(\mu = 0.259\)

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>(\Delta H_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003615</td>
<td>2.0404</td>
<td>-564.4</td>
</tr>
<tr>
<td>0.003265</td>
<td>1.9204</td>
<td>-588.1</td>
</tr>
<tr>
<td>0.003553</td>
<td>2.0595</td>
<td>-588.0</td>
</tr>
<tr>
<td>0.003334</td>
<td>1.9058</td>
<td>-571.6</td>
</tr>
<tr>
<td>0.003291</td>
<td>1.8930</td>
<td>-575.2</td>
</tr>
</tbody>
</table>

Mean value \(\Delta H_2 = -577.5\) cal per mole of bromide.

Probable error of mean = 3.4 cal.
(c) Dilution in 0.05 molal Cd(ClO₄)₂ and 0.09 molal KClO₄.

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>ΔH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003420</td>
<td>1.8616</td>
<td>-544.9</td>
</tr>
<tr>
<td>0.003480</td>
<td>1.7549</td>
<td>-504.3</td>
</tr>
<tr>
<td>0.003415</td>
<td>1.7680</td>
<td>-523.5</td>
</tr>
<tr>
<td>0.003656</td>
<td>1.9087</td>
<td>-522.1</td>
</tr>
</tbody>
</table>

Mean value ΔH₂ = -523.7 cals per mole of bromide.

Probable error of mean = 6.4 cals.

Table 5

Heats of dilution of KBr (ΔH₂) from 1 molal to 0.009 molal in cupric perchlorate solution at 25°C.

Dilution in 0.05 molal Cu(ClO₄)₂.  

<table>
<thead>
<tr>
<th>No. moles Bromide</th>
<th>Heat evolved Calories</th>
<th>ΔH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003585</td>
<td>0.3552</td>
<td>-99.7</td>
</tr>
<tr>
<td>0.003589</td>
<td>0.3405</td>
<td>-94.9</td>
</tr>
<tr>
<td>0.003560</td>
<td>0.3403</td>
<td>-95.6</td>
</tr>
<tr>
<td>0.003594</td>
<td>0.3608</td>
<td>-100.4</td>
</tr>
</tbody>
</table>

Mean value ΔH₂ = -97.6 cals per mole of bromide.

Probable error of ΔH₂ = 1.1 cals.
C. Calculations

Experimental figures at 25°C are given in tables 3, 4 and 5.

Calculation of $K_{\text{CdBr}^+}$ at $\mu = 0.249$.

According to the method outlined above, the equilibrium constant may be calculated from

$$K_{\text{CdBr}^+} = \frac{\alpha_1}{(0.005 - 0.009 \alpha_1)(1 - \alpha_1)} = \frac{\alpha_2}{(0.08 - 0.009 \alpha_2)(1 - \alpha_2)},$$

where $\Delta H_3' = \Delta H_2$ (table 4 (c)) - $\Delta H_1$ (table 3 (c))

$$\Delta H_3 = -335.4 \text{ cal} \pm 1.9 \%, \quad \lambda = 0.614$$

and $\Delta H_3 = \Delta H_2$ (table 4 (b)) - $\Delta H_1$ (table 3 (c))

$$\Delta H_3 = -389.2 \text{ cal} \pm 1.3 \%, \quad \lambda = 0.724$$

By successive approximations the equilibrium constant was found to be

$$K_{\text{CdBr}^+} = 44.7 \pm 6.2\%$$

Now Davies has suggested that the mean ionic activity coefficient for a 2:1 electrolyte in water at 25°C is

$$-\log f = \frac{2}{1 + \mu} - 0.4 \mu,$$

where $\mu$ is the ionic strength. Accordingly the thermodynamic equilibrium constant, $K^0$, for CdBr$^+$ will be given by

$$\log K^0 = \log K + \frac{2}{1 + \mu} - 0.4 \mu,$$

and using our value of $K = 44.7$ at $\mu = 0.249$ we obtain
\[ \log K^0 = 2.09 \]

or \[ K^0 = 123.0 \]

In Table 6 below we have summarized Matheson's data obtained from spectroscopic measurements over a range of ionic strengths. He suggests that the data is well explained by the relation

\[ \log K^0 = \log K + \frac{2 \mu^{1/2}}{1 + 2 \mu^{1/2}} \text{ at } 20^\circ C \]

The calculated values of \( K^0 \) are given in the last column.

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>( \mu^{1/2} )</th>
<th>( K )</th>
<th>( \log K )</th>
<th>( \log K^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.249</td>
<td>0.499</td>
<td>35.7</td>
<td>1.55</td>
<td>2.05</td>
</tr>
<tr>
<td>0.159</td>
<td>0.399</td>
<td>43.6</td>
<td>1.64</td>
<td>2.08</td>
</tr>
<tr>
<td>0.128</td>
<td>0.356</td>
<td>50.7</td>
<td>1.71</td>
<td>2.12</td>
</tr>
<tr>
<td>0.094</td>
<td>0.307</td>
<td>58.8</td>
<td>1.77</td>
<td>2.15</td>
</tr>
<tr>
<td>0.091</td>
<td>0.302</td>
<td>52.1</td>
<td>1.72</td>
<td>2.09</td>
</tr>
<tr>
<td>0.070</td>
<td>0.265</td>
<td>61.7</td>
<td>1.79</td>
<td>2.14</td>
</tr>
<tr>
<td>0.049</td>
<td>0.221</td>
<td>63.5</td>
<td>1.80</td>
<td>2.11</td>
</tr>
<tr>
<td>0.031</td>
<td>0.176</td>
<td>71.3</td>
<td>1.85</td>
<td>2.11</td>
</tr>
<tr>
<td>0.022</td>
<td>0.149</td>
<td>77.7</td>
<td>1.89</td>
<td>2.12</td>
</tr>
<tr>
<td>0.016</td>
<td>0.127</td>
<td>78.9</td>
<td>1.90</td>
<td>2.10</td>
</tr>
<tr>
<td>0.010</td>
<td>0.100</td>
<td>87.6</td>
<td>1.92</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Mean value \( \log K^0 = 2.11 \pm 0.01 \)

or \( K^0 = 129.0 \)

Thus neglecting temperature differences our value of \( K \) at \( \mu = 0.249 \) is in excellent agreement with the above quoted value. We consider the agreement as ample proof of the absence of higher complexes in our solutions.
We shall use Netheson's values at $\kappa = 0.249$ and $\kappa = 0.159$ to calculate our heats of formation at those ionic strengths.

**Calculation of $\Delta H_f$ for CdBr$^+$**

At an ionic strength of 0.249, the formation of complex is described by the equilibrium

$$
\text{Cd}{}^{\text{II}} + \text{Br}^- \leftrightarrow \text{CdBr}^+
$$

$$0.08 = 0.009\alpha (1-\alpha)0.009 = 0.009\alpha$$

for which

$$K = \frac{\alpha}{(0.08 - 0.009\alpha)(1-\alpha)}$$

$$= 35.7$$

The heat of formation per mole of bromide present, $\Delta H_3$, is $-389.2$ cal ± 1.3%. Solution of the above quadratic equation for the degree of association, $\alpha$, gives

$$\alpha = 0.724 \pm 5\%$$

whence

$$\Delta H_f = -\frac{389.2}{0.724} = -537.6 \pm 35.0 \text{ calories per mole.}$$

Similarly at an ionic strength of 0.159

$$\Delta H_3 = -394.3 \text{ cal ± 3\%}$$

$$\alpha = 0.652 \pm 5\%$$

$$\Delta H_f = -599.2 \pm 50.0 \text{ calories per mole.}$$

**Variation of $\Delta H_f$ with ionic strength.**

Examination of the above figures shows that $\Delta H_f$ varies considerably with ionic strength. We shall consider this matter further and try and make an estimate of $\Delta H_f^0$, the heat of formation at zero ionic strength. Theoretically the
variation may be predicted as follows:

We have from the Gibbs-Helmholtz equation

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

But

$$\Delta G = \Delta G^0 + RT \ln \frac{a_{\text{CdBr}^+}}{a_{\text{Cd}^{2+}} a_{\text{Br}^-}}$$

and differentiating with respect to temperature

$$\left( \frac{\partial (\Delta G)}{\partial T} \right)_P = -\Delta S^0 + R \ln Q + RT \frac{\partial}{\partial T} \ln Q$$

where Q is the activity quotient. We have therefore

$$\Delta H = (\Delta G^0 + T \Delta S^0) + RT^2 \frac{\partial}{\partial T} \ln Q$$

$$= \Delta H^0 + RT^2 \frac{\partial}{\partial T} \ln \frac{y_{\text{CdBr}^+}}{y_{\text{Cd}^{2+}} y_{\text{Br}^-}}$$

where $\Delta H^0$ is the enthalpy change at zero ionic strength. Now following the method of Harned and Fitzgerald, it is assumed that the activity coefficients of CdBr$^+$ and Br$^-$ are equal and we may write with little error

$$\Delta H = \Delta H^0 + RT^2 \frac{\partial}{\partial T} \ln y_{\text{Cd}^{2+}}$$

Differentiation of the Debye-Huckel limiting law with respect to temperature leads to

$$\frac{\partial}{\partial T} \ln y_{\text{Cd}^{2+}} = -\frac{3}{2} \left( \frac{1}{D} \frac{\partial D}{\partial T} + \frac{1}{T} \right) \ln y_{\text{Cd}^{2+}}$$

where D is the dielectric constant. The value of $\frac{1}{D} \frac{\partial D}{\partial T}$ at 25°C in water is -0.0046. A reasonable value of $y_{\text{Cd}^{2+}}$ was calculated from the relation
\[ K^0_{\text{CdBr}^+} = \frac{K_{\text{CdBr}^+}}{y_{\text{Cd}^{++}}} \]

assuming again \( y_{\text{CdBr}^+} = y_{\text{Br}^-} \). At an ionic strength of 0.249 we have therefore

\[ y_{\text{Cd}^{++}} = \frac{35.7}{12.9} = 2.8 \]

\[ y_{\text{Cd}^{++}} = \frac{43.6}{12.9} \]

We have then

\[ \Delta H_f^0 - \Delta H_f^0 = -\frac{3}{2}RT^2 \left( \frac{1}{D} \frac{\partial P}{\partial T} + \frac{1}{T} \right) \ln y_{\text{Cd}^{++}} \]

465 465 calories \[ \Delta H_f^0 = \Delta H_f + \frac{478 \times 465}{388} = 0.159 \mu \]

and substituting our experimentally calculated value of \( \Delta H_f \)

at \( \mu = 0.249 \) we have \( -57 + 455 \)

\[ \Delta H_f^0 = -95 \text{ calories per mole} \]

A similar calculation at \( \mu = 0.159 \) gives \( -238 \)

\[ \Delta H_f^0 = -99 \text{ calories per mole} \]

The closeness of these two values indicates a remarkable correlation of our heat data with Bitheron's spectrophotometric data.27

We may also make a very rough estimate of \( \Delta H_f^0 \) from our experimental data by assuming \( \Delta H_f \) versus \( \mu \frac{1}{2} \) to be linear, i.e., the normal "Debye-Huckel extrapolation". Our two values of \( \Delta H_f \) would then be connected by the relation

\[ \Delta H_f = 700 \mu \frac{1}{2} - 880 \]

and when \( \mu \frac{1}{2} \) is zero

\[ \Delta H_f^0 = -880 \text{ calories per mole} \]

It will be obvious from the above discussion that values
of $\Delta H_f$ over a range of ionic strengths is desirable in order that $\Delta H_f^0$ may be calculated with reasonable accuracy. This was not possible in the present work as pointed out earlier, though we suppose -900 calories per mole to be a reasonable estimate. In any case a variation of 300 calories in $\Delta H_f^0$ will only cause a difference of 1 entropy unit in the standard entropy change, $\Delta S^0$, and the estimate of $\Delta H_f^0$ should be good enough for our present purposes. The standard free energy, enthalpy and entropy changes associated with the formation of CuBr$^+$ are then

$$\Delta G^0 = -RT \ln K^0 = -2876 \text{ calories per mole.}$$

$$\Delta H^0 = -900 \text{ calories per mole.}$$

$$\Delta S^0 = \frac{-2876}{900} \text{ e.u.}$$

Calculations for CuBr$^+$ at $\mu = 0.159$

From tables 3 (b) and 5 we see that $\Delta H_f$ for CuBr$^+$ is -75 calories per mole of bromide. We have selected a value of 4.6 for $K_{CuBr^+}$ at $\mu = 0.159$ from the data of Kruk and Parrington. This value, it must be pointed out, is somewhat arbitrary in view of the fact that both these works were carried out at high ionic strengths, (see introduction). The degree of association was calculated as before and found to be 0.19 and therefore

$$\Delta H_f = \frac{-44.8}{0.19}$$

$$= -240 \pm 30 \text{ calories per mole}$$

$$\text{Since } \Delta H^0 = -1000 \text{ cal}.$$
IV. GENERAL DISCUSSION

A. The Nature of the Complex Ion.

As pointed out earlier we have two main theories relating to the nature of complex ions of the type $CdX^+$ in solution. That is, they may be ion pairs as defined by Bjerrum\textsuperscript{19} or molecular species (Redlich\textsuperscript{15}). Penckhurst\textsuperscript{1} has discussed the problem at some length and concludes that the complexes with which we are dealing are in fact molecular, the bonding being predominantly covalent.

In this section we shall examine more closely the Bjerrum ion pair concept, its shortcomings and the reasons for its rejection by other workers as a reliable theory for the prediction of the properties of our type of complexes. It will be pointed out that the reasons for its rejection are inadequate in themselves. We shall show however in this, and the following section, that the observed properties are better explained assuming predominantly covalent bonding though it cannot be definitely established that this bonding does in fact exist in the complexes.

According to the Bjerrum theory the equilibrium constant for the ion pair association is given by

$$K = \frac{kTz^2}{1000 \left( \frac{2s^2}{b + T} \right)^3} Q(b)$$

where $Q(b)$ is defined by the integral
\[ Q(b) = \int_{2}^{b} e^y y^{-b} dy \], in which

\[ y = \frac{|z_1 z_2| \varepsilon^2}{r \sigma D k T}, \quad b = \frac{|z_1 z_2| \varepsilon^2}{a D k T} \]

and \( a \) is the distance of closest approach of ions.

James \(^{49}\) has studied the variation of equilibrium constant with dielectric constant for PbCl\(^+\) in water-glycol mixtures using the conductance data of Normal and Garrett \(^{50}\). He has compared this with the variation predicted by the Bjerrum formula showing that the decrease predicted was much greater than that observed and that the distance of closest approach predicted (1.85 Å) was impossibly small as compared with the sum of the crystal ionic radii (Wyckoff \(^{51}\)) of 3.14 Å. Since the Bjerrum treatment assumes that ion association is determined by Coulomb forces James concluded that covalent forces are involved in PbCl\(^+\) formation. Frenchurst \(^{1}\) has analysed his and other data in a similar manner using experimentally determined values for the equilibrium constant, \( K \), together with a large scale plot of the function \( Q(b) \) (as tabulated by Earned and Owen \(^{10}\)) to calculate values for the mean distance of closest approach for a number of complexes. We have carried out a similar calculation for CdBr\(^+\) using Matheson’s \(^{26}\) value of \( K_{\text{CdBr}^+} = 129.0 \). The results of these calculations are summarized below.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Mean distance of closest approach, Å</th>
<th>Sum of ionic radii (Wyckoff)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl⁺</td>
<td>1.85</td>
<td>2.98</td>
</tr>
<tr>
<td>PbBr⁺</td>
<td>1.58</td>
<td>3.14</td>
</tr>
<tr>
<td>CdCl⁺</td>
<td>1.44</td>
<td>2.77</td>
</tr>
<tr>
<td>CdBr⁺</td>
<td>1.39</td>
<td>2.92</td>
</tr>
<tr>
<td>SnCl⁺</td>
<td>3.19</td>
<td>2.82</td>
</tr>
<tr>
<td>SnBr⁺</td>
<td>5.22</td>
<td>2.98</td>
</tr>
</tbody>
</table>

James⁴⁹ has demonstrated that where ion pairs are formed from species which are solvated the critical radii involved in our calculations are the solvated ionic radii. Strictly then, we should be comparing the sum of the effective ionic radii in solution as an estimate of the expected distance of closest approach.  Bernal and Fowler⁵² have indicated that the cations we consider above are hydrated while the chloride and bromide are probably not.  Latimer⁵³ has suggested that since negative ions (if hydrated) have the hydrogens of the water directed in and the positive ions have the hydrogens directed out, the effective radii of the negative ions will be but slightly greater than the crystal radius, while those of the positive ions will be considerably greater.  Latimer⁵⁴ suggests a value of 0.85 Å for this increase in the cation radius.

Thus allowing for hydration of the ions it will readily be seen that the Bjerrum treatment predicts impossibly small values for the distance of closest approach for the complexes PbCl⁺, PbBr⁺, CdCl⁺ and CdBr⁺ though reasonable values are predicted for SnCl⁺ and SnBr⁺.  Panchhurst¹ however, has pointed out for those complexes which give reasonable, or at
least not impossible values, that the predicted decrease of
K with decreasing dielectric constant is far greater than
that observed as indeed it is for the other complexes we are
considering. James\textsuperscript{49} on this basis has rejected the ion-pair
treatment and postulated that covalent forces are involved in
bond formation. Panckhurst considers this a possibility but
points out that any penetration of the hydration shell of
the cation by the halogen or again any dielectric variation
obtained by adding, say, methanol to water, may well cause a
break-down in the ion-pair theory. However he (Panckhurst)
further considers that the stannous complexes despite their
reasonable values of a are in fact molecular species since
they produce distinct absorption bands\textsuperscript{55}. We shall consider
this point later.

We now consider the influence of dielectric constant on
the distance of closest approach as predicted by the Bjerrum
formula. Again using $x_{\text{CdBr}^+} = 129.0$ and substituting for
the various constants, the Bjerrum formula becomes

$$ Q(b) = 1.524 \times 10^{-5} b^3 $$

where $D$ is the static dielectric constant. The values of $D,$
$Q(b)$ and $a$ are tabulated below and Fig. 7 shows a plot of $a$
versus $D$ together with an exaggerated section over the higher
dielectric range. It is at once obvious that the calculated
value of $a$ increases rapidly with decreasing dielectric
constant especially over the lower dielectric range. We must
accordingly be careful in our choice of a value of $D$ when
making any theoretical calculations from the Bjerrum formula.
The values of $a$ in Table 7 have been calculated using the value
of D in water at 25°C (78.5h) but we will show that this figure is probably far too high though there is considerable doubt as to a correct value. We will consider therefore the effect of addition of ions to water on the dielectric constant.

Table 7.

<table>
<thead>
<tr>
<th>D</th>
<th>Q(b)</th>
<th>a(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>7.803</td>
<td>1.30</td>
</tr>
<tr>
<td>75</td>
<td>6.429</td>
<td>1.39</td>
</tr>
<tr>
<td>70</td>
<td>5.227</td>
<td>1.56</td>
</tr>
<tr>
<td>65</td>
<td>4.185</td>
<td>1.75</td>
</tr>
<tr>
<td>60</td>
<td>3.292</td>
<td>2.02</td>
</tr>
<tr>
<td>55</td>
<td>2.536</td>
<td>2.36</td>
</tr>
<tr>
<td>50</td>
<td>1.905</td>
<td>2.68</td>
</tr>
<tr>
<td>45</td>
<td>1.389</td>
<td>3.58</td>
</tr>
<tr>
<td>40</td>
<td>0.975</td>
<td>4.77</td>
</tr>
<tr>
<td>35</td>
<td>0.653</td>
<td>7.15</td>
</tr>
<tr>
<td>30</td>
<td>0.441</td>
<td>11.12</td>
</tr>
<tr>
<td>25</td>
<td>0.238</td>
<td>16.99</td>
</tr>
<tr>
<td>20</td>
<td>0.122</td>
<td>23.75</td>
</tr>
<tr>
<td>15</td>
<td>0.051</td>
<td>33.90</td>
</tr>
<tr>
<td>10</td>
<td>0.013</td>
<td>53.90</td>
</tr>
</tbody>
</table>

It was first predicted by Sack\textsuperscript{57} that the dielectric constant of an aqueous ionic solution should be considerably lower than that of water. Hasted, Ritson and Collie\textsuperscript{58} have shown that this is an experimentally realisable fact though the magnitude of the lowering effect for a number of aqueous solutions considered was much smaller than that predicted by
fig. 7.

Distance of closest approach

Dielectric constant
Sack. Kitson and Hasted\textsuperscript{59} have modified Sack’s original conception of the electric field of an ion as effectively saturating the surrounding dielectric, to bring it into line with more recent views on the structure of water\textsuperscript{60}. It will readily be seen from figure 1 of Hasted’s paper\textsuperscript{59} that in regions closer than 4 Å to the ion, which is of the order of the first hydration sheath, the dielectric constant is a rapidly varying quantity. The representation of the dielectric as continuous within this region is certainly not valid.

Hasted assumes therefore that a positive ion in solution can be represented as surrounded by a completely saturated first shell and beyond that by a continuous dielectric. He has shown further that the decrease in dielectric constant is described by the expression

\[ D_S = D_W + 2 \delta c \]

where \( D_S \) is the dielectric constant of the solution, \( D_W \) that of water, \( c \) the concentration in moles per litre and \( \delta \) a constant having values between \(-7\) and \(-15\) for various salts in concentrations up to \(2\)M. Theoretical values of \( \delta \) calculated from either of two models compared favourably with those found experimentally. It was therefore concluded that the main contribution to the dielectric lowering comes almost entirely from the first hydration sheath.

Our main point as regards ion-pair formation is that no calculations based on the Bjerrum formula are justified unless we can choose a correct, or at least reasonable, value for the dielectric constant in the near vicinity of the associated ions. At present this does not seem possible and thus
James's basis for rejecting the Bjerrum theory as inadequate becomes itself invalid and certainly no justification for assuming our complexes to be covalent.

We note that the original confirmation of the Bjerrum theory for tetraisocamylammonium nitrate was performed in dioxane-water mixtures in which the dielectric constant never exceeded 10. Presumably in such a case the dielectric constant in the near vicinity of the ions would vary but little from that of the medium. A similar study of our inorganic complexes in solvents of extremely low dielectric constant may well provide valuable information in this direction.

At present it seems desirable to have a reliable criterion for distinguishing between ion pairs and molecular species in aqueous solutions. Redlich and Bigeleisen and Redlich have proposed that the vibration spectrum is both a theoretically significant and experimentally realizable method of distinguishing between ion pairs of the Bjerrum type and molecular species although this criterion does not touch on the nature of the bond. This proposal is supported by a large amount of theoretical and experimental work and in the majority of cases the Raman spectrum is also a sufficient criterion.

Panchhurat proposes that the absorption spectrum is a criterion for the formation of molecular species. That is, the development of a new absorption band in solution which may be attributed to the formation of a complex ion or undissociated molecule is indicative that the species concerned is in fact molecular.

While this appears to be true for many complexes we may
show that it is not necessarily always true. A recent paper by Evans and Mascallos\textsuperscript{62} for example reports the discovery of new bands in the absorption spectrum on adding KK (K = Cl, Br, I) to cobaltic hexamine perchlorate. These must be due to Co(NH\textsubscript{3})\textsubscript{6}\textsuperscript{+++}X\textsuperscript{-} ion-pairs as it would not be possible to form a covalent bond between the two. We note however that in this case we are not dealing with ion-pair formation between normal hydrated ions but rather with a cation in which the first sphere of coordination is taken up with ammonia. It may be that spectra-detectable ion-pairs are not formed from normal hydrated ions but rather the ion-pair as a whole is hydrated. In the absence of experimental evidence we mention this only as a possibility. Such a complex could not however be strictly regarded as a Bjerrum ion pair.

From the point of view of the formation process of complex ions, Pyfe\textsuperscript{63} has noted that the ion-pair concept inadequately describes the observed properties of metal-amine complexes. If it could be assumed (he points out) that the interaction between an ion and a neutral dipolar molecule is purely electrostatic, and that the molecules have rigid unalterable dipoles, then we should expect that water, with a dipole moment much greater than that of ammonia, would not be replaced by the latter from a hydrated cation. This approach is obviously complicated by the different polarizabilities of the molecules. For a series of amines, however, if orders of stabilities of corresponding cations are calculated on the basis of dipole moments, little success is achieved. It seems reasonable that similar considerations should apply to our
halide complexes.

Now Pauling considers that when a metal ion is placed in solution a small definite number of water molecules become firmly bound to the central atom by partially covalent bonds.

If now we may apply Fyfe's idea of metal amine formation to our halide complexes, we should expect that halide ions with electronegativities less than oxygen would displace water from the cation with the formation of a more covalent bond. On this basis chloride, bromide and iodide would displace water but fluoride would not. Obviously this is a rather simplified argument for we have taken no account of the relative sizes of halide ions and water molecules. In addition our conception of electronegativities of species in solution is not at all clear. Qualitatively however the available data seems to agree with this replacement model. Connick for example has shown that to a first approximation the complexing of various metal cations by fluoride appears to be a function of the charge and radius alone. For a number of metal fluoride complexes it was found that at constant radius the equilibrium constant becomes larger with increasing ionic charge while for a constant charge there is a trend towards smaller values as the radius increases. Both these effects are to be expected qualitatively for an ionic type of complex. Quantitative treatment was not possible because of the uncertainty in the dielectric constant in the near vicinity of the ions.

It would appear at this stage that there is no general satisfactory method of distinguishing between molecular entities and ion pairs. However we may tentatively take it,
as Panckhurst\textsuperscript{1} suggests, that in the absence of contradictory evidence the complexes CdX\textsuperscript{+}, SnX\textsuperscript{+}, PbX\textsuperscript{+} (X = Cl, Br, I) are predominantly covalent as are their corresponding halides in the solid and gaseous phase. The complex fluorides on the other hand appear to be almost completely ionic. Whether or not they are ion-pairs in the Bjerrum sense or whether it is the ion-pair as a whole which is hydrated we cannot say. We note however that FeF\textsuperscript{++} produces a definite band in the absorption spectrum\textsuperscript{66}.

We shall go on now to consider the stabilities of complex ions in solutions.
B. The Stability of Complex Ions.

There have been a number of recent discussions on the stability of complex ions in aqueous solution concerned with the relationship between bond type and stability. We shall confine our discussion to the CdX\(^+\), PbX\(^+\), SnX\(^+\) and FeX\(^+\) \((X = Cl, Br)\) for which we have data available.

Fyfe\(^{63}\) has indicated from a study of the halide complexes of cadmium and mercury that in general the iodide is more stable than the bromide which is more stable than the chloride. This trend is also obvious from table 4 of Bjerrum’s paper\(^{67}\) though the complexity constants quoted therein are in most cases doubtful. However, more recent calculations of the complexity constants have indicated that the trend does in general hold though there are exceptions. For example FeCl\(^{2+}\) is more stable than PbBr\(^{2+}\) and SnCl\(^+\) than SnBr\(^+\) though as we shall see later they do fall into a general trend which covers all the complexes for which we have been able to acquire sufficient data.

Fyfe seems to assume that since this general trend in stability is also the order of decreasing electronegativity of the halogen that the more covalent bond is the stronger leading to greater stability. Panckhurst\(^1\) on the other hand from a consideration of bond energies considers that the more covalent bond is in fact the weaker. On this basis we have that the chloride is more stable than the bromide which is more stable than the iodide. Comparison of the bond dissociation energies\(^{68}\) of various metal halide bonds in the gaseous state would also seem to indicate that the more covalent bond is the weaker.
though in most cases these are doubtful.

We will later show that the more covalent bond between a given metal and halide is probably the stronger but first we shall consider Pankhurst's postulate from the point of view of bond energies.

In discussing bond strengths we should strictly be concerned with dissociation energies but since reliable figures are not available we will take it that bond energies will be sufficient for our purposes. Now it has been shown taking force constant as a measure of bond energy that for the halogen series with a given metal the bond energy decreases from fluorine to iodine. Cordy has established an empirical relationship between the force constant of a bond and the product of the electronegativities of the atoms, of the form

\[ k = a \left( \frac{x_A x_B}{d^2} \right) + b \]

where \( k \) is the bond stretching force constant, \( d \) the equilibrium bond length, \( N \) the bond order, \( x_A \) and \( x_B \) the electronegativities of the bonded atoms and \( a \) and \( b \) are constants for a given broad class of molecules. For a given metal the bond strength increases with electronegativity of the anion giving us that the chloride is more stable than the bromide which is more stable than the iodide if bond strength is the main stability determining factor, as in the gas phase. (We shall in fact see later that this is not always the case.) We note however that if these ideas are to be applied to our type of complexes in aqueous solution, we must assume that force constant is unchanged by hydration.
Now Warhurst\textsuperscript{71} has shown that solvation by non-ionizing solvents of hydrogen halides containing partial ionic bonds has the effect of decreasing the force constants of the bonds. This decrease becomes greater with decreasing electronegativity of the halogen. The effect of hydration would presumably be even greater and may well give misleading results if we consider force constant as a measure of bond strength in our aqueous complexes.

We conclude therefore that it is not possible at present to predict relative stabilities of complexes on theoretical considerations alone.

Let us now consider the available thermodynamic data for a number of metal halide complexes. Table 8 shows the free energy, enthalpy and entropy changes associated with the formation of a number of these complexes. It will be noted that these quantities have in most cases been determined at widely differing ionic strengths but their relative magnitudes should be good enough for our present comparative purposes.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Complex</th>
<th>$\Delta G$</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>CdCl$^+$</td>
<td>2670</td>
<td>625</td>
<td>11.1</td>
</tr>
<tr>
<td>This thesis</td>
<td>CdBr$^+$</td>
<td>2876</td>
<td>-900</td>
<td>6.6</td>
</tr>
<tr>
<td>73</td>
<td>SnCl$^+$</td>
<td>1570</td>
<td>2600</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>SnBr$^+$</td>
<td>995</td>
<td>1380</td>
<td>8.0</td>
</tr>
<tr>
<td>66</td>
<td>FeCl$^{2+}$</td>
<td>2000</td>
<td>8500</td>
<td>35.2</td>
</tr>
<tr>
<td></td>
<td>FeBr$^{2+}$</td>
<td>800</td>
<td>6100</td>
<td>23.2</td>
</tr>
<tr>
<td>1</td>
<td>PbCl$^+$</td>
<td>2046</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>PbBr$^+$</td>
<td>2850</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>PbI$^+$</td>
<td>2618</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
Examination of these figures shows that although no general trend is apparent in the free energy changes there is a definite trend in the heat and entropy changes. We note that the heat change favours the greater stability of the bromide in each case while for the entropy changes the reverse is true. This trend appears to hold for quite a large class of halide complexes including those with two or more halogens attached to the metal ion\(^7\). Preliminary measurements\(^2\) indicate that the same is true of the lead halide complexes.

Now we propose (cf., Davies\(^7\)) that the enthalpy change associated with the formation of complex is a measure of the strength of bonding in the complex. In this case, since the bromide complexes are associated with the more negative heat change their formation will be energetically more favourable than will be the corresponding chloride complexes. Or, if we may state it differently, the bond between the metal and the bromide is of lower energy than that between the metal and the chloride. It is clear then that it is the more covalent of the two bonds which is the stronger. There are, so far as we are aware, no exceptions to this general rule. We note however that bond strength is not always the main stability determining factor. The entropy changes must also be considered.

The relative stabilities of complex ions in solution then are determined by the relative magnitudes of the standard heats of formation and the standard entropy changes. As Fanshawe\(^1\) has noted, these changes are determined by relatively small differences in the heats and entropies associated with a number
of theoretical steps involving the formation of the complex in the gaseous phase and its subsequent hydration.

Let us return now to the formation process. As indicated earlier we consider the formation of a complex ion as the replacement of a coordinatively bound water molecule by a less electronegative halide ion. The formation of the complex in solution would then be formulated (cf., Cobble\textsuperscript{76}).

\[
\text{M(H}_2\text{O)}_{n}^{++} \text{aq.} + X^- \text{aq.} \rightleftharpoons \text{MX(H}_2\text{O)}_{n-1}^{+} \text{aq.} + \text{H}_2\text{O} \quad (1)
\]

How Frank and Evans\textsuperscript{60} have suggested that ions in aqueous solution order the water molecules around them so as to form an "iceberg", the process being similar to the partial freezing of the liquid. On this picture the removal of ions from solution, as in the process of complex formation between oppositely charged ions, will lead to a breakdown of the "icebergs" and a resulting entropy change favouring complex formation. Qualitatively the data in table 8 agree with this picture.

A semi-quantitative approach has been provided by Cobble\textsuperscript{76}. The entropy change for reaction (1), he considers, is given by

\[
\Delta S = \overline{S}^0 + \overline{S}^0_{\text{H}_2\text{O}} - \overline{S}^0_{\text{M}^{++}} - \overline{S}^0_{X^-} \quad \text{---------(2)}
\]

where \(\overline{S}^0_{\text{H}_2\text{O}}\), \(\overline{S}^0_{\text{M}^{++}}\) and \(\overline{S}^0_{X^-}\) are the partial molal entropies of water and of the aqueous ions respectively and \(\overline{S}'\) is the "corrected" partial molal entropy of the aqueous complex.

Rearranging (2) we have
Cobble has shown that the "corrected" entropies for a large number of complexes are a linear function of the change to radius ratio. No such correlation is evident when the replacement of water is not allowed for.

How Nancollas has suggested that the entropy of association in aqueous solution, \( \Delta S^0 \), may be evaluated from the entropy cycle:

\[
\begin{align*}
\text{Cd}^{2+}(g) + \text{Br}^-(g) & \rightleftharpoons \text{CdBr}^+(g) \\
\downarrow \Delta S_1^0 & \quad \downarrow \Delta S_2^0 & \quad \uparrow \Delta S_4^0 \\
\text{Cd}^{2+}(aq) + \text{Br}^-(aq) & \rightarrow \text{CdBr}^+(aq)
\end{align*}
\]

where \( \Delta S_1^0 = \Delta S \) (hydration) of gaseous \( \text{Cd}^{2+} \) ions,
\( \Delta S_2^0 = \Delta S \) (hydration of gaseous \( \text{Br}^- \) ions, \( \Delta S_3^0 = \Delta S \) (dissociation) in the gas phase and \( \Delta S_4^0 = -\Delta S \) (hydration) of the gaseous complex.

\[-\Delta S^0 = \Delta S_1^0 + \Delta S_2^0 + \Delta S_3^0 + \Delta S_4^0\]

The values of \( \Delta S_1^0 \) and \( \Delta S_2^0 \) are given by Latimer as
\[\Delta S_1^0 = -52.0 \text{ e.u.}, \quad \Delta S_2^0 = -11.2 \text{ e.u.}\]

\( \Delta S_3^0 \) was obtained by summing the translational and rotational contributions to the entropies of the gaseous ions. That is
\[\Delta S_3^0 = s^0_{\text{tr}}(\text{Cd}^{2+}) + s^0_{\text{tr}}(\text{Br}^-) - s^0_{\text{tr}}(\text{CdBr}^+) - s^0_{\text{rot}}(\text{CdBr}^+)\]

These figures were calculated from the Sackur-Tetrode equation in the appropriate forms, i.e.,
\[ S^0_{\text{tr}} = 6.86 \log M + 26.03, \]

where \( M \) = molecular weight, and
\[ S^0_{\text{rot}} = 4.606 \log IT + 177.7 \]

where \( I \) is the moment of inertia given by
\[ I = \mu r^2, \]

\( \mu \) being the reduced mass and \( r \) the internuclear distance. \( r \) was taken as 2.39 Å from the work of Lister and Sutton\(^7\) in the gas phase. The following values were then calculated
\[ S^0_{\text{tr}} (\text{CdBr}^+) = 41.70 \text{ e.u.} \]
\[ S^0_{\text{tr}} (\text{Cd}^{2+}) = 40.10 \text{ e.u.} \]
\[ S^0_{\text{tr}} (\text{Br}^-) = 39.09 \text{ e.u.} \]
\[ S^0_{\text{rot}} (\text{CdBr}^+) = 17.04 \text{ e.u.} \]

and hence
\[ \Delta S_3 = 20.45 \text{ e.u.} \]

The value of \( \Delta S_4 \) was calculated using the empirical relation suggested by Cobble\(^6\):
\[ \overline{S}' = 49 - 99(\frac{z}{r}) \]

where \( \overline{S}' \) is the "corrected" partial molal entropy of the complex and \( z \) its charge. Again using \( r = 2.39 \) Å we have
\[ \Delta S_4 = S^0_{\text{rot}} (\text{CdBr}^+) + S^0_{\text{tr}} (\text{CdBr}^+) - \overline{S}' \]
\[ = 17.04 + 41.70 - 7.55 \]
\[ = 51.16 \text{ e.u.} \]

The entropy of formation, \( \Delta S^0 \), of the aqueous complex is now
\[ \Delta S^0 = -52.0 - 11.2 + 20.45 + 51.16 \]
\[ = 8.4 \text{ e.u.} \]

This figure is in reasonable agreement with our experimental value of 6.6 e.u. and lends further support to our postulate.
of a predominantly covalent complex formed by the replacement of a water molecule by a halide ion.

The observed trends in the heat changes on the formation of complexes between a given metal and halide may also be qualitatively explained on this replacement model. We have already noted that we expect those halides with electronegativities less than oxygen to replace water from the metal cation and it is not unreasonable to suppose that this tendency will increase with decreasing electronegativity provided the differences in anion radii are unimportant. It is perhaps not surprising therefore that complex formation is always energetically in favour of the greater stability of the bromide over that of the chloride.

Finally we might expect the heat changes associated with the formation of complexes between various metal cations and a given halide to depend on the strength of bonding of the water molecules to the metal cations. We note for example that the ferric complexes are formed with a far greater heat absorption than are the corresponding stannous and cadmium complexes; CdBr⁺ is in fact formed endothermically. This is what might be expected if the water molecules were more strongly bound to the ferric ion than to the cadmium or stannous ions. Now the third ionization potential for iron is in the vicinity of 30 e.v. while the second ionization potentials of tin and cadmium are 14.5 e.v. and 16.3 e.v. respectively. The ferric ion is also more positively charged than the other two. If we neglect the differences in cation radii it is obvious that water molecules will be more tightly bound to the ferric ion than to the cadmium or stannous ions and their replacement
should be correspondingly more difficult.

Obviously before we can make any wide generalizations on the relative stabilities of complexes we need more heat and entropy data for a far greater range of metal complexes. It is desirable that this data should all be referred to the same standard state.
V. SUMMARY

1. A microcalorimeter has been described for accurate measurement of the heats of formation of complex ions in solution.

2. The heats of formation of the intermediate complexes CdBr$^+$ and CuBr$^+$ have been determined.

3. A method has been devised for a calorimetric determination of the free energy of formation of the intermediate complexes and the method applied to CdBr$^+$.

4. The nature of complex ions in solution has been discussed.

5. The stability of complex ions and the relationship between stability and bond type has been discussed.

6. The experimental thermodynamic data for a number of complexes has been discussed in the light of a proposed formation process.
REFERENCES.
3. "The Scientific Papers of J. Willard Gibbs".


G.M. Slansky, ibid, 62, 2430, (1940).
R.B. Williams, ibid, 64, 1935, (1942).
44. T.B. Crompler and J.H. Yoe, "Chemical Computations and Errors", Wiley and Sons, New York, 1940,
p.188.
    16, 1, (1948).
60. R.S. Frank, ibid., 13, 478, (1945).
    R.S. Frank and M.W. Evans, ibid, 12, 507, (1945).
64. L. Pauling, ibid., 59, 1467, (1946).
    Burkin, Quart. Rev., 2, 1, (1951).
68. T.L. Gottrell, "The Strengths of Chemical Bonds",
    Butterworths Scientific Publications, London,
    C.E. Vanderzee, ibid, 74, 4806, (1952).
75. T. Davies, S.S. Singer and L.A.V. Stevels,