THE DISSOCIATION CONSTANT

OF THE

ION-PAIR \( \text{CoSO}_4^+ \)

A THESIS

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INTRODUCTION

The purpose of the present work is to investigate the association of cerous and sulphate ions in aqueous solution. Electromotive force measurements for the cell

\[ H_2 - Pt \mid Ce_2(SO_4)_3, HCl \mid AgCl - Ag \]

\[ P_{H_2} = 1 \text{ atm} \mid m_2 \quad m_1 \]

at various ionic strengths have been used together with a prior knowledge of the dissociation constant of the bisulphate ion, to find the dissociation constant of the ion-pair \( CeSO_4^+ \). By making measurements at varying temperatures derived thermodynamic functions of the ion-pair have been obtained.
Outline of Early Work:

The foundation of electrochemistry was laid by Michael Faraday in the early 19th century when he intensively studied the passage of electric current through solutions of salts, acids and bases. He showed that many substances, non-conductors when solid, conduct well on fusion finding that in practically all such cases decomposition occurs.

The mechanism of electrolytic conduction was however a matter of much speculation. It was not easy to explain why the products of electrolysis only appear at the electrodes. Grotthus\(^1\) supposed that the electric force decomposes the water molecules into positively charged hydrogen and negative oxygen throughout the liquid, but that these very soon meet oppositely charged particles and recombine except at the electrodes. Biot\(^2\) considered that the molecules consisted of positive and negative parts and while without committing himself as to how these parts became separated, he correctly ascribed their motion to the attraction of oppositely charged electrodes. Further he proposed that after depositing their charges at the electrodes, gases were evolved and new chemical species formed. Faraday\(^3\) refused to give an opinion whether or not ions bear electric charges.
Daniell and Miller\textsuperscript{4} showed that anions and cations may travel at different speeds in the same electric field. Hittorf\textsuperscript{5} followed up this discovery with a comprehensive study of the changes in concentration which take place near the electrodes when a measured quantity of electricity is passed. He also proved the existence of complex ions - by showing metals migrated to the anode in such solutions - and showed that there was less conduction in alcoholic than in aqueous solution.

Kohlrausch's\textsuperscript{6} prolonged studies in mid 19th century of the conductivity of electrolytes, using alternating current to avoid polarization at the electrodes, showed Ohm's Law is obeyed with great accuracy. He established the relation showing that the conductivity of salt solutions, if sufficiently dilute is the sum of separate, constant contributions from cations and anions. He studied, in great detail, the variation of equivalent conductivity with concentration, showing that with what have since been called strong electrolytes the equivalent conductivity decreases practically linearly with a fractional power (square or cube root) of the concentration; with weak electrolytes however, the equivalent conductivity decreases very rapidly as the concentration increases. These accurate studies provided much data for the later theoretical developments of electrolytic dissociation, and
interionic attraction in completely dissociated electrolytes.

Clausius\(^7\) suggested that the fact that Ohm's Law is obeyed should prove that none of the energy of the electric field is expended in dissociating the molecules into ions, and that a small fraction of the molecules are always in this form, a little dissociation occurring as a result of thermal agitation.

Between 1880 and 1887 the experimental researches of Raoult and the thermodynamic studies of van't Hoff\(^8\) and Planck\(^9\) showed that solutions of different substances, with the same molar concentration, have the vapour pressure and the freezing point depressed below that of the pure solvent, by the same amount. Salts and strong acids however, usually gave depressions of the freezing-point or of the vapour pressure nearly twice, occasionally nearly three times the normal. These abnormal osmotic effects indicated dissociation into two or three times the number of particles expected from the molecular weight. Arrhenius\(^10\), in the classical paper which inaugurated the theory of electrolytic dissociation, postulated that at extreme dilutions all salt molecules are completely dissociated into ions. The degree of dissociation can be simply found on this assumption by taking the ratio of the equivalent conductivity of the solution in question to
the equivalent conductivity at the most extreme dilution.

\[ \alpha = \frac{\Lambda}{\Lambda_0} \]

For weak electrolytes the degrees of dissociation determined by this method were found to be in good agreement with the values obtained from investigation of the colligative properties of the same electrolyte. By applying the mass-action principle to ionization, Ostwald\textsuperscript{11} obtained a dilution law governing the variation of equivalent conductivity with concentration. This was closely obeyed only for weak electrolytes in dilute solutions.

Many properties of strong electrolyte solutions seemed to vary much less with concentration than one would expect from the predictions by Arrhenius' Theory and Ostwald's Dilution Law. Values for the degree of dissociation obtained from conductance ratios were not in agreement with those from measurements of colligative properties, and dissociation 'constants' were far from constant. Also the study of absorption spectra of solutions of strong electrolytes failed to reveal any evidence for undissociated molecules.

As early as 1902, a possible explanation of many of the deficiencies of the dissociation theory was suggested by van Laar, who called attention to the strong
electrostatic forces that must be present in an ionic solution and their influence on the behaviour of the dissolved ions. In 1912 Milner\textsuperscript{12} gave a method for the statistical evaluation of the effect of the interionic forces on the molal freezing point depression of a 1:1 electrolyte. This gave numerical values at various chosen concentrations which were consistent with a limiting law involving the square root of the concentration, showing (in the light of later work) that his treatment was essentially correct though its merits were largely overlooked due to the arduous and complex nature of the calculations. Ghosh\textsuperscript{13} in 1918 proposed a 'crystal lattice model' for ionic solutions, from which by means of some mathematically dubious assumptions he deduced the result that the equivalent conductivity should be a linear function of the cube root of the concentration. In the same year Bjerrum\textsuperscript{14} proposed an empirical relation for 1:1 electrolytes below 0.1 molar, in that the freezing point data for many salts was consistent with a linear dependence of the osmotic coefficient on the cube root of the concentration. This did give a fair representation of the experimental facts and when Bjerrum allowed for ionic hydration the validity of his expression was extended to several moles per litre.
Debye - Hückel Theory and Extensions:

It was in 1923 that Debye and Hückel succeeded in calculating the activity coefficient of an ion and this marked the beginning of a new era in electrochemistry. They depicted the distribution of positive and negative ions in solution as resulting from a balance between the coulombic potential energy, which would produce a regular lattice arrangement as in a crystal, and the kinetic energy which would produce a completely random distribution. Each positive ion was pictured as inducing a negative charge density in its vicinity with the result that the 'ionic atmosphere' about it would contain on the average more negative and less positive ions than in the bulk of the solution. The existence of this atmosphere leads to a lowering of the energy of the ions as shown by the deviation of the solution from ideal behaviour. The definition of an ideal or perfect solution at constant temperature and pressure in terms of the chemical potential of the species is:

\[ \mu_1 = \mu_1^0 + RT \ln c_i \]

where \( c \) is concentration of species in the solution.

For an electrolyte solution this equation does not hold at ordinary concentrations, and has to be modified by the introduction of an activity coefficient \( f \), thus:

\[ \mu_1 = \mu_2^0 + RT \ln c_i f_i \]

where \( f \) approaches unity as the system tends towards ideal
behaviour. The product $c_i f_i$ is called the activity $a_i$ of the particular component of the solution.

The essential feature of the Debye – Hückel Theory is the calculation of the potential at a point in the solution in terms of the concentration of charges and the properties of the solvent. This is achieved by combining the Poisson equation of electrostatics with the Boltzmann statistical mechanical distribution formula. The Poisson equation, where $\Psi$ is the potential at a point where the charge density is $\rho$, $\varepsilon$ being the dielectric constant of the medium in which the charges are immersed, is written:

$$\nabla^2 \Psi = -\frac{4\pi}{\varepsilon} \rho \quad \cdots (1)$$

In the special case of spherical symmetry where $\Psi$ depends only on the distance $r$ from an origin, i.e., converting from cartesian to polar co-ordinates, $\nabla^2$ becomes

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \quad \cdots$$

and so equation (1) becomes

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Psi}{dr} \right) = -\frac{4\pi}{\varepsilon} \rho \quad \cdots (2)$$

This is a time average value which is necessary to produce spherical symmetry. If $s$ is the number of species of ions present, and $\zeta_i$ is the bulk concentration then by the principle of electrical neutrality,

$$\sum_i n_i z_i = 0 \quad \cdots (3)$$
If we select a certain j-ion as co-ordinate centre then if its charge is \( +z_1e \), the resultant charge of the solution must be \( -z_1e \) by equation (3). This will be found distributed through the remainder of the solution but may be represented as spherical shells of increasing radius. Hence summing all such shells

\[
\int_0^a 4\pi r^2 \rho_j \, dr = -z_1e \quad \ldots(4)
\]

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

Not much can be said about where a certain ion is likely to be found except that the probability is greatest where the potential is least. Hence Debye and Huckel assumed the Boltzmann distribution according to which, since the electrical potential energy of an i-ion is \( z_1e\psi_j \), the average local concentration \( n_i^j \) of i-ions at the point in question is:

\[
n_i^j = n_i \exp \left\{ - \frac{z_1e\psi_j}{kT} \right\} \quad \ldots(5)
\]

Since each i-ion carries a charge \( z_1e \), the nett charge density at the point considered is, summing for all ionic species,

\[
\rho_j = \sum_i n_i z_1 e \exp \left\{ - \frac{z_1e\psi_i}{kT} \right\} \quad \ldots(6)
\]

According to this equation \( \rho \) varies exponentially with \( \psi \). This however contravenes the electrostatic theorem known as the principle of linear superposition of electric fields which predicts that if the charge density \( \rho \) (concentration)
is doubled then the potential is also doubled, not increased exponentially. This dilemma is of fundamental importance in electrolyte theory. If the exponential is expanded the first term is zero by equation (3) and as a first approximation, terms higher than the second may be neglected and hence:

\[ \rho_j = - \sum_{i=1}^{s} \frac{n_{i} z_{i}^{2} e^{2} \psi_{i}}{kT} \]  

This holds only if the thermal energy is large compared with the electrical energy and hence will not be true for ions close to the j-ion, i.e. in more concentrated solutions. This assumption is more valid for symmetrical electrolytes where \( z_{1} = -z_{2} \) and \( n_{1} = n_{2} \) as alternate terms of the exponential expansion disappear. However this means that the Boltzmann distribution has been rejected and replaced by a linear one.

If equation (7) is combined with equation (2) we obtain:

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = \frac{4\pi e^2}{\varepsilon kT} \sum n_{i} z_{i}^{2} \psi_{j} = k^2 \psi_{j} \]  

where \( k^2 = \frac{4\pi e^2}{\varepsilon kT} \sum n_{i} z_{i}^{2} \)  

Equation (8) is a linear second-order differential equation between \( \psi \) and \( r \) and may be solved by using the substitution \( u = \psi j \) which gives

\[ \frac{d^2u}{dr^2} = k^2u \]
which has the general solution: 

\[ u = Ae^{-Kr} + Be^{Kr} \]

or 

\[ \psi_j = A \frac{e^{-Kr}}{r} + B \frac{e^{Kr}}{r} \]

where A and B are constants of integration. As the potential must remain finite at large values of \( r \), \( B = 0 \). A may be found by substitution in equation (7): 

\[ \rho_j = -\sum_{i} \frac{n_i z_i^2 e^2 \psi_i}{kT} \]

\[ = -A e^{-Kr} \sum_{i} \frac{n_i z_i^2 e^2}{kT} \]

\[ = -A e^{-Kr} \frac{K^2 \varepsilon}{4\pi} \]

Using equation (4) we obtain: 

\[ AK^2 \varepsilon \int_{a}^{\infty} re^{-Kr} \, dr = z_j e \]

which on integration by parts gives: 

\[ A = \frac{z_j \varepsilon}{\varepsilon} \cdot \frac{eKa}{1 + ka} \]

so that the potential \( \psi_j \) is given by: 

\[ \psi_j = \frac{z_j \varepsilon}{\varepsilon} \cdot \frac{eKa}{1 + ka} \cdot \frac{e^{-Kr}}{r} \quad \ldots (10) \]

This is the time average value for the potential\( \psi_j \); at a given distance \( r \) from a reference ion of valency \( \beta_j \); in the absence of external forces. 'a' the distance of closest approach of the ions is taken as the same for all ions but this is rather drastic.
An isolated ion of valency $z_j$ in a medium of dielectric constant $\varepsilon$ gives rise to a field of which the potential at distance $r$ is given by:

$$\psi_j'' = \frac{z_j \varepsilon}{\varepsilon r} \cdots (11)$$

By the principle of linear superposition of fields the total potential at $r$ given by equation (10) may be treated as the sum of that due to the potential $\psi_j''$, due to the central ion and another potential $\psi_j'$, due to all the remaining ions:

$$\psi_j = \psi_j' + \psi_j''$$

From equations (10) and (11):

$$\psi_j = \frac{z_j \varepsilon}{\varepsilon r} \left[ \frac{\varepsilon K a}{1 + K a} e^{-Kr} - 1 \right]$$

This is valid for $r>a$. Within the distance $r<a$, no other ions can penetrate hence the potential due to the spherical distribution of the other ions is constant and equal to the value of that at $r=a$, which is:

$$\psi_j = -\frac{z_j \varepsilon}{\varepsilon} \frac{K}{1 + K a} \cdots (12)$$

If we applied this technique to every ion in the solution we would be counting them twice, once as the central ion and once as the surroundings. Hence the change $\Delta\psi_j$ in electrical energy of a $j$-ion due to ionic inter-
actions is:

\[ \Delta G_j = - \frac{z^2_j e^2}{2\varepsilon} \cdot \frac{K}{1 + Ka} \]

and the corresponding change for a mole of \( j \)-ions is:

\[ \Delta \mu_j = - \frac{z_j^2 e^2 N}{2} \cdot \frac{K}{1 + Ka} \]

assuming the \( j \)-ion behaves as a sphere radius \( a \). If we assume that the solution would behave ideally in the absence of ionic interactions,

\[ \Delta \mu_j = \Delta \mu_j (\text{ideal}) + \Delta \mu_j (\text{el}) \]

* or \( \mu_j^0 + RT \ln f_j = \mu_j^0 + RT \ln N_j + \Delta \mu_j (\text{el}) \)

hence:

\[ \ln f_j = \frac{\Delta \mu_j (\text{el})}{RT} = - \frac{z_j^2 e^2}{2\varepsilon kT} \cdot \frac{K}{1 + Ka} \]

The mean activity coefficient for an electrolyte dissociating into \( n_1 \) cations of valency \( z_1 \) and \( n_2 \) anions of valency \( z_2 \) is:

\[ \ln f_{\pm} = - \frac{e^2}{2\varepsilon kT} \cdot \frac{K}{1 + Ka} \left( \frac{n_1 z_1^2 + n_2 z_2^2}{n_1 + n_2} \right) \]

which upon eliminating the \( n \)'s by means of the relation \( n_1 z_1 = n_2 z_2 \) becomes:

\[ \ln f_{\pm} = - \left( \frac{z_1 z_2}{2\varepsilon kT} \right) \cdot \frac{e^2}{1 + Ka} \]

* \( \mu_j^0 \) refers to a hypothetical standard state, \( N_j \) the mole fraction and \( f_j \) is the activity coefficient of the \( j \)-ions.
Substituting for \( K \) from equation (9) where:

\[
K = \left( \frac{\pi N e^2}{1000 \text{ kT}} \right)^{1/2} I^{1/2}
\]

the result is of the form:

\[
\log I_+ = - \frac{A |z_1 z_2| I^{1/2}}{1 + B a I^{1/2}} \quad \ldots (13)
\]

where \( I \) the Ionic Strength equals \( \frac{1}{2} \sum m_i z_i^2 \)\( I \). A and B are constants as follows:

\[
A = \left( \frac{2 \pi N}{1000} \right)^{1/2} \cdot \frac{e^3}{2.303 k} \cdot \frac{1}{(e T)^{3/2}} = \left( \frac{8.8246 \times 10^6}{(e T)^{3/2}} \right)
\]

\[
B \times 10^3 = \left( \frac{8 \pi N e^2}{(1000 k)} \right)^{1/2} \cdot \frac{1}{(e T)^{3/2}} = \left( \frac{5.022}{(e T)^{3/2}} \right) \times 10^9
\]

\( \delta \) is the distance of closest approach of the ions in solution, which is measurable in order but not in magnitude. Hence the formula for the activity coefficient is not expressible solely in terms of measurable quantities. However at low values of \( I^{1/2} \) i.e. very dilute solutions, the term \( B a I^{1/2} \) will be negligible compared with unity.

\[
\log I_+ = - A |z_1 z_2| I^{1/2} \quad \ldots (14)
\]
This equation is known as Debye-Hückel Limiting Law. This shows that $\log f^+$ approaches linear variation with the square root of the concentration in dilute solutions. But this relation holds at only very high dilution e.g. for a $10^{-3}$ molal solution of a 1:1 the variation is 3% due to neglect of the $B_0^{1/2}$ term. Solutions more dilute are not very practical. The concentrations for which the Debye-Hückel Limiting Law is valid 'have been uncharitably called slightly contaminated distilled water'.

The activity coefficient as expressed in equation (13) is capable of representing experimental data with good accuracy by simply choosing a value of the parameter $\Theta$, independent of concentration and of a physically reasonable magnitude. This often holds up to an ionic strength of about 0.1 when the ions are separated on the average by no more than 20 Å.

The derivation of Debye-Hückel theory is such that the numerator gives the effect of the long-range coulombic forces, while the denominator shows how these are modified by short-range interactions between ions. These are represented by the crudest possible model, the ions all being considered as rigid, non-deformable spheres of equal radii, an assumption which cannot adequately explain any ion-solvent interactions or 'non-electrolyte' interionic forces. Hückel in 1935 dealt with ion-solvent interactions as a salting out effect resulting in the displacement of other ions from the neighbourhood of an ion by solvent.
molecules, and related this to the change in dielectric constant of the solution. He also considered, but dismissed on rather inadequate grounds, the formal thermodynamic effects of ionic solvation. This led to the addition to \( \log f_\pm \) a term linear in the ionic strength.

\[
\log f_\pm = - \frac{A|z_1z_2|I^\frac{1}{2}}{1 + b I} + bI \quad \text{...(15)}
\]

However since no reliable measurements of the dielectric constant of ionic solutions had at that time been made except at extreme dilutions, the coefficient of this term \( b \) had to be evaluated from activity coefficient data. This sometimes leads to negative values of the dielectric constant. Thus Hückel's extension has come to be regarded as a purely empirical modification of the Debye-Hückel theory, as there are two adjustable parameters and hence the activity coefficient curves could be represented quite accurately up to one molar.

A better improvement was suggested by Guntelberg\(^17\) in 1936. He proposed that:

\[
\log f_\pm = - \frac{A|z_1z_2|I^\frac{1}{2}}{1 + I^\frac{1}{2}} \quad \text{...(16)}
\]

which is to say \( \bar{a} = 3.04a \) for all electrolytes at 25°C. This equation has no adjustable parameters, but gives a fair representation of the facts up to concentrations of \( I = 0.1 \); and is vastly superior to the Debye-Hückel Limiting Law. Guggenheim\(^18\) modified the form in a similar manner to Hückel's extension of the original Debye-Hückel form, by
adding a linear concentration term CI, C being empirically determined.

\[
\log f_+ = - \frac{A|z_1 z_2|^{1/2}}{1 + \frac{1}{z_1^2}} + CI \quad \ldots(17)
\]

C may be considered to combine the effects of B^2 and b in equation (15) as both show the same effect, to increase the value of the activity coefficient at higher concentrations. Table 1.^{19} shows how the theoretical predictions of these equations compare with experiment, the data being for sodium chloride at 25°C (C = 0.150)

Table 1

<table>
<thead>
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<th>m</th>
<th>-logf (obs)</th>
<th>-logf Eqn (14)</th>
<th>-logf Eqn (16)</th>
<th>-logf Eqn (17)</th>
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<td>0.1072</td>
<td>0.1607</td>
<td>0.1222</td>
<td>0.1072</td>
</tr>
</tbody>
</table>

Davies^{20}, from results of experimental investigation of electrolyte behaviour, proposed C = 0.2|z_1 z_2| for dilute solutions. This expression was found adequate for the present work.

Various attempts have been made to improve the fundamental mathematical inadequacies of the Debye-Hückel theory, i.e. neglecting terms after the first in the expansion of:

\[
\exp \left\{ - \frac{z_1 e^2}{kT} \right\}
\]

so as to retain a linear relation between \( \rho \) the charge...
density and $\psi_j$ the potential at a point in the solution. Gromwald, La Mer and Sandved\textsuperscript{21} accepted higher terms of the expansion and derived a corresponding expression for the activity coefficient. In a symmetrical electrolyte they found:

$$\ln f_\pm = \frac{e^2 z^2}{2 kT} \cdot \frac{k}{1 + Ka} + \frac{(e^2 z^2)^3}{(kT)^4} \frac{1}{4} X_3(Ka) - 2Y_3(Ka)$$

$$+ \frac{(e^2 z^2)^5}{(kT)^4} \frac{1}{4} X_5(Ka) - 4Y_5(Ka) + \ldots.$$

where $X$ and $Y$ represent complicated functions of $(Ka)$ which they evaluated and tabulated. However the improvement gained by using such an expression is detracted from by the mathematical complexity. Higher terms are more important for ions of higher charge and smaller size as has been shown by experimental results.

More recently Eigen & Wicke\textsuperscript{22} modified the Boltzmann Distribution by defining an upper concentration limit for oppositely charged ions about a given central ion, determined by the physical dimensions of the ions. This amounts to a Fermi-Dirac distribution and though it shows some improvement, it can lead to physically impossible high values of the local concentration of ions of one kind.
FIG. 1. VARIATION OF ACTIVITY COEFFICIENTS WITH CONCENTRATION.
Comparison of Experimental Activity Coefficients with Theory:

From experimental activity coefficient data (as found in the appendices of Robinson & Stokes\textsuperscript{19}) it is found that there are three main types of behaviour as shown by Fig. 1.

Variation with concentration as shown by Type 1 is the most common, where the behaviour is most like that predicted by the Debye-Hückel theory. As expected examples are found in symmetrical electrolytes e.g. hydrochloric acid, because less error incurred as alternate terms are zero in the exponential expansion.

Examples of Type 2 are found among electrolytes containing a small cation with a high field of force which will readily surround itself with a tightly held solvation 'sheath'. This will reduce the amount of 'free water' or solvent in the solution making it effectively more concentrated than indicated by the ionic strength. \( \log f^+ \) will hence increase more rapidly with the ionic strength as plotted. Scatchard\textsuperscript{23} deduced an equation to take into account the effects of ionic solvation. This equation which contains two parameters, \( n \) the solvation number and \( \xi \) the ion size parameter (allowing for solvation) has been extensively tested for aqueous solutions and is remarkably successful for non-associated electrolytes.

Type (3) are electrolytes which tend to associate, i.e. form ion pairs, new kinetic entities in the solution. This will lower the effective ionic strength of the solution.
and the activity coefficient will increase less rapidly than with the plotted ionic strength than for a non-associated electrolyte.

**Bjerrum's Ion Association Theory:**

Bjerrum\(^{24}\) in 1925 (two years after Debye-Hückel theory was first published) envisaged the possibility of ion-pair formation in electrolyte solutions. Such a concept provides a relatively simple and self-consistent method of dealing with the situation which arises when ions of opposite charge are close together. In these circumstances their energy of mutual electrical attraction may be greater than their thermal energy, so that they form virtually a new entity in the solution which is of sufficient stability to persist through a number of collisions with solvent molecules. The conductivity of the solution will be altered, the ion-pair contributing only if it is charged i.e. formed from an unsymmetrical electrolyte.

Two adjacent ions may be considered to be associated when the ion-pair thus formed exists long enough to be a recognisable kinetic entity in the solution. Bjerrum used the idea that the average effects of ion-pair formation may be calculated on the basis that all oppositely charged ions within a certain distance to one another are associated into ion-pairs.
He proposed that the critical distance $q$ should be:

$$q = \frac{|z_1 z_2| e^2}{2\pi k T}$$

in other words the distance at which the mutual electrical potential energy of the two ions:

$$\frac{|z_1 z_2| e^2}{\epsilon q}$$

is equal to $2kT$. This reason for this choice is justified as follows. In discussing the Poisson-Boltzmann equation:

$$\nabla^2 \psi_j = -\frac{4\pi}{\epsilon} \sum_i n_1 z_1 e \exp \left\{ -\frac{z_1 e \psi_i}{kT} \right\}$$

it was shown that no self-consistent solution is possible unless the series expansion of the exponential is stopped at the first power of $\psi$, (or the second in the special case of symmetrical electrolytes), and that pursuing the expansion further, apart from the mathematic complexity, leads to difficulty with the principle of linear superposition of electrostatic fields. Bjerrum's treatment avoids these difficulties. The density of $i$-ions around a selected $j$-ion is given as before by a Boltzmann expression:

$$n'_1 = n_1 \exp \left( -\frac{z_1 e \psi_j}{kT} \right)$$

and the number in a shell of thickness $dr$ at a distance $r$ is:

$$n_1 \exp \left( -\frac{z_1 e \psi_j}{kT} \right) 4\pi r^2 dr$$

-22-
When \( r \) is small, Bjerrum neglects the effect of interionic forces on the reasonable ground that the potential of the central ion will be dominant and writes:

\[
\psi_j = \frac{z_i e}{\epsilon r}
\]

so that the number of \( i \)-ions in the shell is:

\[
4\pi r^2 n_i \exp \left\{ - \frac{z_i z_j g^2}{\epsilon kT} \right\}
\]

Considering a series of shells of equal thickness, \( dr \), the number of ions which on a time average find themselves in each succeeding shell can be calculated. It will be seen that when \( i \) and \( j \) are ions of opposite sign, then with increasing \( r \) there is a decreasing probability of finding an \( i \)-ion in any unit of volume, but the volume of the shell increases and the two opposing effects combine to give a distance at which there is a minimum probability of finding an \( i \)-ion anywhere on a sphere surrounding the central \( j \)-ion at this critical distance. This position is:

\[
q = \frac{z_i z_j e^2}{2kT}
\]

as can readily be shown by differentiating the function:

\[
r^2 \exp \left\{ - \frac{z_i z_j g^2}{\epsilon kT} \right\}
\]

For a 1:1 electrolyte in water at 25°C \( q = 3.67\AA \), the population of oppositely charged ions being greater at smaller and larger distances from the central ion. For higher valence type electrolytes this minimum occurs at successively greater distances from the central ion and is much less pronounced.
Ion-pair formation is only possible if \( \varphi \) is greater than \( \bar{a} \), the effective distance of closest approach of the ions. Thus for a 1:1 electrolyte (whose \( \bar{a} < \varphi \)) all ions closer than 3.57Å may be considered as associated. The degree of association \( (1 - \chi) \) is thus obtained by integrating the number of ions in all shells from the distance of closest approach up to the critical Bjerrum distance:

\[
1 - \chi = 4\pi \rho \int_0^{\varphi} \exp \left( - \frac{|z_1 z_2| e^2}{\varepsilon kT} \right) r^2 \, dr
\]

Put

\[
y = - \frac{|z_1 z_2| e^2}{\varepsilon kT}
\]

so that the integral becomes:

\[
- \left( \frac{|z_1 z_2| e^2}{\varepsilon kT} \right) \int_b^\varphi \frac{e^y}{y^4} \, dy
\]

where

\[
\frac{|z_1 z_2| e^2}{\varepsilon kT_{\varphi}} = b
\]

and

\[
\frac{|z_1 z_2| e^2}{\varepsilon kT_{\bar{a}}} = 2
\]

Thus

\[
(1 - \chi) = \frac{4nNc}{1000} \left( \frac{|z_1 z_2| e^2}{\varepsilon kT} \right)^3 Q(b)
\]

where

\[
Q(b) = \int_2^b y^{-4} e^y \, dy
\]

Values of the integral \( Q(b) \) have been tabulated\(^\text{25} \).

The law of mass action gives \( K \) the dissociation...
constant:

\[ K = \frac{x^2 + 2x}{1 - x} \]

where \( f \) is the activity coefficient of the ions while that of the ion-pair is assumed to be unity. The activity coefficient may be found from an appropriate expression:

\[ \log f^+ = \frac{-A (xI)^\frac{3}{2}}{1 + (xI)^\frac{3}{2}} - 0.1 (xI) \]

The degree of association \((1 - x)\) at any value of \( I \) may be calculated by successive approximations.

Investigations show that for a 0.1m solution of a 1:1 electrolyte when \( \beta = 2.0\bar{A} \) about 2.5% of the ions are associated, when \( \beta = 1.4\bar{A} \) about 10% of the ions are associated, and only when \( \beta = 0.6\bar{A} \) does the number of ion-pairs become greater than the number of free ions. Such small ionic radii are unusual and hence we should not look for outstanding examples of ion-pair formation in 1:1 electrolytes. Solvation increases the radii of the ions such that in water they may not be able to approach within the critical distance, but \( q \) may exceed the ordinary ionic diameter if the dielectric constant is lowered. A convincing proof for this is shown by the work of Fuoss & Kraus\textsuperscript{26} using conductivity measurements on tetraisoamy-lammonium nitrate in a series of water-dioxan mixtures covering a wide range of dielectric constants from 2.2 to 79. From the dissociation constants in nine different solutions they calculated the average distance of closest approach as \( 6.4\bar{A} \). They plotted a graph of \( \log K \) as a
function of $\log \varepsilon$, $\log K$ being calculated by Bjerrum's equation for $a = 6.4^\circ$, and on this graph the experimental values of $K$ agreed remarkably well with the predicted curve. This was a severe test of the theory because the dielectric constant varied sixteen fold and the dissociation over a range from $0.29$ to $2 \times 10^{-15}$.

More recently many examples of ion association in aqueous solution have been established, the dissociation constants determined and in some instances thermodynamic data of the ion-pair derived. If the ion-pair formed is charged then in more concentrated solutions triple ion and quadrupole formation are distinct possibilities, and in certain cases - triisooamyllammonium picrate in benzene - these have definitely been established.

On the other hand the behaviour of some electrolytes e.g. potassium nitrate can be explained by postulating a small amount of association, about $3\%$ at $0.1$ molal. However it is not easy to detect such a small quantity except in the special case where the ion-pair has a Raman or ultra-violet spectra. Increasing the concentration, although it will increase the proportion of ion-pairs in the solution, introduces greater uncertainty due to the limitation of the theory used in calculating activity coefficients. Hence care has to be observed when applying this concept.

Many methods are now available for determining the amount of ion-pair formation, all of which demand a high
degree of experimental accuracy. Though the actual type of physical measurement may vary widely, (spectrophotometric, electromotive force, solubility products), all methods are based fundamentally on the same principle; the difference between the expected result and the actual result being due to ion-association.

Much criticism has been directed towards this theory in that it is just an idea invented to explain the behaviour of certain electrolytes. It should be remembered that Bjerrum postulated this concept only two years after the Debye-Hückel theory was first published as means of dealing with ions of opposite charge that approach close together in solution. As Bjerrum said 'the distinction between free and associated ions is not a chemical one, but only a mathematical device making possible an approximate calculation of the effect of interionic forces under conditions where the approximations of Debye and Hückel cannot be used' i.e. when the mutual electrical energy of the ions is large compared with the thermal energy. At this time hardly any activity coefficient data would be available, it was five years before the theory was confirmed in any way.

It may at first appear that with this theory an historical cycle has been completed, returning us to the original Arrhenius concept. There is, however, a real distinction although a somewhat subtle one. Arrhenius presumed that in strong electrolytes there were neutral
molecules which ionized to an extent increasing with dilution. According to the new theory, the solution contains nothing but ions which are electrostatically associated to an extent which increases with the concentration.

Outline of Method:

The thermodynamic dissociation constant of the ion-pair CeSO₄⁺ is by definition:

\[ K_{\text{CeSO}_4^+} = \frac{a_{\text{Ce}^{3+}} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{CeSO}_4^+}} \]

\[ = \frac{m_{\text{Ce}^{3+}} \cdot m_{\text{SO}_4^{2-}}}{m_{\text{CeSO}_4^+}} \cdot \frac{f_{\text{Ce}^{3+}} \cdot f_{\text{SO}_4^{2-}}}{f_{\text{CeSO}_4^+}} \]

where \( m_i \) and \( f_i \) are the molality and activity coefficients of the \( i \) species. To find \( K_{\text{CeSO}_4^+} \) it is necessary to know the concentration of the ion-pair as well as the contributing ions cerous and sulphate. Also required is a knowledge of activity coefficients of the ions and the ion-pair which is assumed to behave in the same manner as a simple ion in that its activity coefficient may be calculated by the same expression:

\[ \log f_i = - Az_i^2 \left( \frac{1}{1 + I} \right) - 0.2 I \]

The concentrations of cerous, sulphate and cerous sulphate can be determined from electromotive force
measurements of the cell:-

\[
\begin{array}{c|c|c|c}
\text{H}_2 & \text{Pt} & \text{HCl}, \text{Ce}_2(\text{SO}_4)_3 & \text{AgCl} - \text{Ag} \\
\text{P}_{\text{H}_2} = 1 \text{ atm} & \text{m}_1 & \text{m}_2 & \\
\end{array}
\]

where \( m_1 \) and \( m_2 \) are respectively the molalities of hydrochloric acid and cerous sulphate. The electromotive force is given by the expression:

\[
E = E^0 - \frac{RT \ln a_{\text{H}^+} a_{\text{Cl}^-}}{2.303 RT (E - E^0) + \log m_1 + \log a_{\text{Cl}^-}}
\]

or

\[
\frac{E}{2.303 \frac{RT}{RT (E - E^0) + \log m_1 + \log a_{\text{Cl}^-}}} = -\log a_{\text{H}^+}
\]

\[
\ldots(18)
\]

The concentration of hydrogen ions in this cell will not be \( m_1 \) because of the equilibria (1) below. Let the concentration of bisulphate ions be \( x \), hence:

\[
x = m_1 - m_{\text{H}^+}
\]

The sulphate ion concentration will be effected by two equilibria:-

(1) as above

\[
\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^{-}
\]

and

(2) \[
\text{Ce}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{CeSO}_4^{+}
\]

If the concentration of the ion-pair \( \text{CeSO}_4^{+} \) is \( y \) then the sulphate ion concentration in the solution will be:

\[
3m_2 - x - y = m_{\text{SO}_4^{2-}}
\]

\[
\ldots(19)
\]
This may be found by knowing the value of the second dissociation constant of sulphuric acid $K_{\text{HSO}_4^-}$.

(See Table 4).

Now

$$K_{\text{HSO}_4^-} = \frac{a_{H^+} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{HSO}_4^-}}$$

$$= \frac{m_{H^+} \cdot m_{\text{SO}_4^{2-}}}{m_{\text{HSO}_4^-}} \cdot \frac{f_{H^+} \cdot f_{\text{SO}_4^{2-}}}{f_{\text{HSO}_4^-}}$$

or

$$\log K_{\text{HSO}_4^-} = \log m_{H^+} + \log m_{\text{SO}_4^{2-}} - \log x$$

$$+ \log \frac{f_{H^+} \cdot f_{\text{SO}_4^{2-}}}{f_{\text{HSO}_4^-}}$$

...(20)

From equation (20) $\log m_{\text{SO}_4^{2-}}$ may be found which when substituted into equation (19) gives a value for $y$.

By definition:

$$K_{\text{CeSO}_4^+} = \frac{a_{\text{Ce}^{3+}} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{CeSO}_4^+}}$$

$$= \frac{(3m_2 - y)(3m_2 - x - y)}{y} \cdot \frac{f_{\text{Ce}^{3+}} \cdot f_{\text{SO}_4^{2-}}}{f_{\text{CeSO}_4^+}}$$

$$\therefore \log K_{\text{CeSO}_4^+} = (3m_2 - y) + \log (3m_2 - x - y) - \log y$$

$$+ \log \frac{f_{\text{SO}_4^{2-}} \cdot f_{\text{Ce}^{3+}}}{f_{\text{CeSO}_4^+}}$$

...(21)

Equations (18), (20) and (21) may only be solved for the required values if the values of the activity coefficients
are known. The Debye-Hückel theory enables activity coefficients to be expressed in terms of the ionic strength of the solution. There are many forms of this relation; the expression applied here was that which gave the most constant values of $K$ with variation of ionic strength:

$$\text{viz. } \log f_i = -A_i Z_i^2 \left( \frac{I^3}{1 + \frac{I}{I_i^3}} \right) - 0.21$$

Successive approximations were necessary because nothing is known about the values of $x$ and $y$ and how they will modify the ionic strength.

For 1st approximation:

$$I = \frac{1}{2} \sum \xi m_i Z_i^2 = m_1 + 1.5m_2$$

from which a value for the activity coefficients of all ions can be obtained. By substitution in equations (18), (19), (20) and (21), $m_1^+$, $x$, $y$, $m_{304}^2$ and $K_{\text{ceso}_4^+}$ may be found.

For 2nd approximation:

$$I = m_1 + 1.5m_2 - 2x_1 - 6y_1$$

Thus more accurate values of the activity coefficients may be found, hence more accurate values of $x$, $y$, and $K_{\text{ceso}_4^+}$. This process was repeated until the values of $K_{\text{ceso}_4^+}$ obtained differed by less than the experimental from those of previous approximations.
The value of E.M.F. actually measured can be corrected to the value which would be obtained if the partial pressure of hydrogen was one atmosphere by the equation:

\[ E_{H_2} = 1 = E_{\text{meas.}} - \frac{1}{2} \log \left( \frac{P_{\text{atm.}} - V_{P.}}{760} \right) \]

where \( j = \frac{2.303 \cdot RT}{F} \), \( P_{\text{atm.}} \) is the atmospheric pressure and \( V_{P.} \) is the vapour pressure of the solution at the temperature \( T \). The atmospheric pressure may be written as 760 + \( L \). Thus:

\[ E_{H_2} = 1 = E_{\text{meas.}} - \frac{1}{2} \log \left( \frac{760 - V_{P.}}{760} \right) \]

\[ \quad - \frac{1}{2} \log \left[ 1 + \frac{L}{(760 - V_{P.})} \right] \]

A graph was drawn of the function

\[ \frac{1}{2} \log \left[ 1 + \frac{L}{760 - V_{P.}} \right] \]

for each temperature, and \( E_{\text{atm.}} \) could be read off and applied immediately. The vapour pressure of the solution was taken as equal to that of the solvent i.e. of water.

The following figures were used:

<table>
<thead>
<tr>
<th>( T ) °C</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{P.} ) mm</td>
<td>17.54</td>
<td>23.76</td>
<td>31.82</td>
<td>42.18</td>
<td>55.32</td>
</tr>
<tr>
<td>( -E_{V_{P.}} )</td>
<td>.00029</td>
<td>.00041</td>
<td>.00055</td>
<td>.00075</td>
<td>.0010</td>
</tr>
</tbody>
</table>

Thus the corrected E.M.F.'s were obtained as from the following equation:

\[ E_{H_2} = 1 = E_{\text{meas.}} - E_{V_{P.}} - E_{\text{atm.}} \]
**EXPERIMENTAL METHOD**

**Preparation and Purification of Materials**

**Hydrochloric Acid:**

Constant boiling hydrochloric acid was prepared by the method of Faulk & Hollingsworth\(^{27}\) from Analar acid diluted with distilled water to a density of approximately 1.10 gms/ml. Pinching & Bates\(^{28}\) have emphasised the importance of removing bromide and iodide impurities when using silver-silver chloride electrodes. Hence a few crystals of potassium permanganate were added to the diluted acid. Three litres of this solution were distilled through a fractionating column, the first and last fractions being discarded, the middle fraction redistilled and the third quarter only being used. From the atmospheric pressure the composition of the constant boiling acid was deduced from data in the International Critical Tables. This was independently checked by titration with borax solution which had been standardized against potassium hydrogen phthalate.

**Hydrogen:**

Electrolytic hydrogen from a cylinder was purified by passing through concentrated potassium hydroxide, to remove carbon dioxide, through concentrated sulphuric acid, to dry, over copper and platinised asbestos at 400°C in an electric furnace and through Fieser's reagent\(^{29}\), to remove oxygen, and finally dried by passing through concentrated sulphuric acid. McInnes & Cowperthwaite\(^ {30} \) have stressed
the need for complete removal of oxygen. They showed that differences of up to 50 millivolts could be obtained in readings by using impure hydrogen.

Cerous Sulphate:

It was decided to prepare the actual salt and not to mix two solutions containing the necessary ions, e.g. sodium sulphate and cerous perchlorate. This proved difficult.

Spedding & Jaffe\textsuperscript{51} prepared rare earth sulphates by dissolving the oxides in a slight excess of C.P. sulphuric acid, which was removed by precipitating the sulphate from ethanol. Further re-crystallizations produced no further change in the pH of the solution. However the stable oxide of cerium is cerium (IV) oxide and according to O'Brien, Sneed & Brasted\textsuperscript{32} cerium (III) oxide is spontaneously converted to CeO\textsubscript{2} in air. This would be unexpected from the general stability of cerium (III) salts.

After much preliminary investigation a modified version of the method of Spedding & Jaffe\textsuperscript{51} was used. Analar cerium (III) nitrate was dissolved in a small quantity of distilled water and a slight excess of analar sulphuric acid added. The precipitate was dried, redissolved, recrystallized, filtered and washed with alcohol. This procedure was repeated until the pH of the solution was constant and a spot test from Fiege\textsuperscript{33} (for detection of nitrate ions to 1 part in 10\textsuperscript{6}) gave the same coloration as distilled water when tested with the identical reagents.
Such coloration was probably due to nitrate present in the zinc dust used. Nine recrystallizations were found necessary. The crystals were finally dried at 130°C for four hours to remove all traces of alcohol. A stock solution was prepared and analysed for cerium by oxidation to cerium (IV) by bismuthate, reduction by a known quantity of standardized ferrous ammonium sulphate the excess of which was titrated against potassium permanganate. The sulphate content was found gravimetrically as barium sulphate.

**Preparation of Electrodes**

**Hydrogen Electrodes:**

These electrodes consisted of pieces of platinum foil (1.5 x 1 cms) welded to a platinum wire sealed in the end of a glass tube. The plating procedure found to give reproducible electrodes was that of Popoff, Kunz & Snow\textsuperscript{34} as used in this department by Christensen\textsuperscript{35} and Austin\textsuperscript{36}. The electrodes were cleaned by electrolysis as anodes with a current of 0.5 amps. per pair in concentrated hydrochloric acid until ten minutes after all the old deposit had been removed. A thin coating of gold was deposited on the electrodes as cathodes in a solution of potassium aurocyanide using a platinum anode and a current of 20 milliamps per pair for ten minutes. Such a deposit is necessary to make it possible to remove the subsequent layer of platinum black completely by the method of cleaning described above. Platinum black was then deposited on the
gold from a 2% solution of chloroplatinic acid containing 0.02 gms of lead acetate per 100 ml. with a current of 0.5 amps, passing for four minutes. The electrodes were then hydrogenated to remove any absorbed chlorine by use as cathodes in a 7% sulphuric acid solution at a current of 0.6 amps, per pair for thirty minutes. Even though electrodes prepared by this method did not differ by any measurable amount after use in a cell new electrodes were used for each solution.

**Silver - Silver Chloride Electrodes:**

Many different methods have been used to prepare silver - silver chloride electrodes. Linhart\(^3\) used an electrode made by introducing a platinum wire into a mixture of precipitated silver chloride and silver, prepared by electrolysis of silver nitrate at high current densities. Ellis\(^3\)\(^8\), Roberts\(^3\)\(^9\), and Harned & Ehlers\(^4\) used electrodes prepared by heating silver oxide on a platinum spiral to 500°C. The silver thus formed was coated with silver chloride by electrolysis in hydrochloric acid. The method most commonly employed in recent years is that described by Brown\(^4\)\(^1\) where silver is electrolytically deposited from a solution of potassium argentocyanide. It is difficult to ensure that no cyanide is deposited on the electrode as silver cyanide cannot be completely removed from the solution.

It is necessary to allow electrodes prepared by the above methods a time of 'ageing' to give consistent results.

-36-
A recently published paper of Purlee & Grunwald describes a preparation which eliminates the need for this. The electrodes were of platinum foil (2 x 0.5 cm.) welded to platinum wire and sealed in glass tube. After cleaning with concentrated nitric acid washed in concentrated ammonia and distilled water, silver was deposited on the platinum foil by the Rochelle salts silvering process (sodium tartrate being substituted for Rochelle salts). The platinum foil was suspended vertically in the silvering mixture. Three depositions of silver each requiring one hour were made. By this process Purlee & Grunwald calculated there was approximately 0.8 mgs. of silver per sq. cm. of platinum surface. The silver chloride coating was produced by anodization for four minutes in 0.05 molar hydrochloric acid at a current density of 4 milliamps per pair. These electrodes if carefully prepared were readily reproducible.

**Cells, Other Apparatus and Measurements**

**Cells**:–

Two U-tube cells were used. The silver - silver chloride electrodes were contained in a sealed tube A as shown, contact being made by an asbestos fibre B sealed into the glass, as recommended by Purlee & Grunwald. This was to ensure the electrodes were not effected by hydrogen as no such information on this type of silver plated electrode was available. These were completely immersed in the electrolyte. Side arm C was used to bubble hydrogen
through the one half of the cell to degas the solution and displace the air in the compartment. The ground glass stopper D is used to seal off the compartment stopping air entering and keeping the level of the solution constant. The other arm of the cell contained a pair of hydrogen electrodes, the hydrogen entering via side arm at E and escaping up tube F. Tap G controlled the rate of flow such that the bubbling rate in the two cells could be kept the same.

Before entering the cell the hydrogen passed through two saturators as shown in Fig. II which were also immersed in the thermostat. The first contained about 300 mls. of an acid solution of cerous sulphate of approximately the strength used, while the second was filled with 50 mls. of the actual test solution in the cells. These were to ensure that the passage of hydrogen did not alter concentration of the solutions by evaporation. The gas then passed through a three-way tap, a T-tube and into the side-arms of the cell. The three-way tap enabled hydrogen to be used for degassing C. The two cells, in parallel, and the two saturators in series were mounted in a specially constructed copper stand which fitted into the thermostat bath.

The cells were filled until the hydrogen electrodes were half immersed, according to the recommendations of Hamer & Acree⁴⁴. When the temperature was raised the increase in pressure in the side of the cell containing
tube A caused the hydrogen electrode to become flooded. This difficulty was overcome by raising stopper D slightly, blocking outlet tube F until the hydrogen pressure forced liquid back to the proper level, and then quickly closing stopper D and opening tube F.

Other Apparatus:

The thermostat bath was fitted with a stirrer, a cooling coil, an electric heater, a mercury-toluene regulator and a thermometer. The stirrer consisted of a single copper blade 3 ins. in diameter and driven by a synchronous shaded pole motor. This proved to be adequate. Constant temperature was achieved by careful adjustment of the mercury level of the regulator, which operated in conjunction with a Sunvic Relay. The heater connected to this system was 250 watts. The temperature was read on a 0-50°C thermometer graduated in 0.5°, standardized for 100 mm vertical immersion and its reading constantly checked with a laboratory standard thermometer. When the regulator was properly adjusted no noticeable variation of temperature resulted. A 1000 watt booster element was used to raise the temperature. The cooling coil was necessary to keep the temperature of the bath at 20°C.

The e.mfs were measured by a Leeds & Northrup potentiometer capable of reading to 0.01 mV. The galvanometer was a Cambridge Instrument with a sensitivity of 1.7 mm. per/√V at a distance of 1 metre. The potentiometer was standardized against a Weston Normal Cell.
as supplied by the Cambridge Instrument Company. All pairs of leads were of the same length of single copper wire so as not to introduce any error in balancing the potentiometer.

**Cell Measurements:**

The cells and saturators were filled and placed in the thermostat at 20°C. The solutions were degassed, then the hydrogen connected to the hydrogen electrode compartments and the bubbling rates adjusted. The cells were allowed to equilibrate for 9 - 10 hours. Constancy of e. m. f. over a period of thirty minutes (measurements being taken every ten minutes) was considered sufficient to indicate equilibrium. The temperature was then raised to 25°C and allowed to equilibrate for sixty minutes. At higher temperatures times necessary for the cell to reach equilibrium were proportionally shorter.

Measurements were made at concentrations of cerous sulphate over a range of $2.6 \times 10^{-3}$ molal to $5.0 \times 10^{-4}$ molal, the acid concentration remaining approximately constant.
**RESULTS**

Table III is a summary of the results obtained.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>E (v)</th>
<th>$10^3 x$</th>
<th>$10^3 y$</th>
<th>$10^3 I$</th>
<th>$10^4 K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>0.4777</td>
<td>0.793</td>
<td>3.932</td>
<td>2.278</td>
<td>2.03</td>
</tr>
<tr>
<td>(b)</td>
<td>0.4845</td>
<td>0.669</td>
<td>2.851</td>
<td>1.886</td>
<td>1.83</td>
</tr>
<tr>
<td>(c)</td>
<td>0.4851</td>
<td>0.576</td>
<td>1.894</td>
<td>1.698</td>
<td>1.95</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4838</td>
<td>0.436</td>
<td>1.206</td>
<td>1.401</td>
<td>1.92</td>
</tr>
<tr>
<td>(e)</td>
<td>0.4758</td>
<td>0.371</td>
<td>0.655</td>
<td>1.108</td>
<td>2.06</td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>0.4793</td>
<td>0.825</td>
<td>3.955</td>
<td>2.256</td>
<td>1.85</td>
</tr>
<tr>
<td>(b)</td>
<td>0.4859</td>
<td>0.713</td>
<td>2.862</td>
<td>1.970</td>
<td>1.74</td>
</tr>
<tr>
<td>(c)</td>
<td>0.4864</td>
<td>0.618</td>
<td>1.920</td>
<td>1.688</td>
<td>1.83</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4851</td>
<td>0.487</td>
<td>1.225</td>
<td>1.390</td>
<td>1.80</td>
</tr>
<tr>
<td>(e)</td>
<td>0.4770</td>
<td>0.397</td>
<td>0.679</td>
<td>1.087</td>
<td>1.79</td>
</tr>
<tr>
<td>30°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>0.4807</td>
<td>0.871</td>
<td>3.968</td>
<td>2.339</td>
<td>1.79</td>
</tr>
<tr>
<td>(b)</td>
<td>0.4872</td>
<td>0.766</td>
<td>2.870</td>
<td>1.854</td>
<td>1.61</td>
</tr>
<tr>
<td>(c)</td>
<td>0.4877</td>
<td>0.672</td>
<td>1.931</td>
<td>1.662</td>
<td>1.72</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4862</td>
<td>0.543</td>
<td>1.235</td>
<td>1.373</td>
<td>1.72</td>
</tr>
<tr>
<td>(e)</td>
<td>0.4779</td>
<td>0.431</td>
<td>0.690</td>
<td>1.074</td>
<td>1.64</td>
</tr>
<tr>
<td>35°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>0.4818</td>
<td>0.914</td>
<td>3.981</td>
<td>2.222</td>
<td>1.71</td>
</tr>
<tr>
<td>(b)</td>
<td>0.4883</td>
<td>0.812</td>
<td>2.872</td>
<td>1.844</td>
<td>1.58</td>
</tr>
<tr>
<td>(c)</td>
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<td>0.708</td>
<td>1.944</td>
<td>1.647</td>
<td>1.65</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4871</td>
<td>0.591</td>
<td>1.247</td>
<td>1.356</td>
<td>1.62</td>
</tr>
<tr>
<td>(e)</td>
<td>0.4789</td>
<td>0.468</td>
<td>0.707</td>
<td>1.056</td>
<td>1.48</td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>0.4828</td>
<td>0.952</td>
<td>4.003</td>
<td>2.202</td>
<td>1.65</td>
</tr>
<tr>
<td>(b)</td>
<td>0.4893</td>
<td>0.859</td>
<td>2.892</td>
<td>1.823</td>
<td>1.45</td>
</tr>
<tr>
<td>(c)</td>
<td>0.4889</td>
<td>0.746</td>
<td>1.969</td>
<td>1.631</td>
<td>1.50</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4879</td>
<td>0.656</td>
<td>1.253</td>
<td>1.339</td>
<td>1.51</td>
</tr>
<tr>
<td>(e)</td>
<td>0.4797</td>
<td>0.503</td>
<td>0.724</td>
<td>1.039</td>
<td>1.36</td>
</tr>
</tbody>
</table>
The values of the constants used were as quoted in Table IV.

<table>
<thead>
<tr>
<th>Value</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye-Hückel A ( A_{45} )</td>
<td>0.5046</td>
<td>0.5092</td>
<td>0.5141</td>
<td>0.5190</td>
<td>0.5241</td>
</tr>
<tr>
<td>( \frac{2.3032 \text{ RT}^{46}}{F} )</td>
<td>0.058165</td>
<td>0.059158</td>
<td>0.060149</td>
<td>0.061141</td>
<td>0.062133</td>
</tr>
<tr>
<td>( E^0 ) ( 47 )</td>
<td>0.22557</td>
<td>0.22234</td>
<td>0.21904</td>
<td>0.21565</td>
<td>0.21208</td>
</tr>
<tr>
<td>( K_{HSO_4^-} \times 10^{-2} ) ( 48 )</td>
<td>1.20</td>
<td>1.03</td>
<td>0.90</td>
<td>0.78</td>
<td>0.67</td>
</tr>
</tbody>
</table>

As previously explained the method of successive approximations was applied. Five approximations were necessary to obtain values of \( K \) constant within the limits of experimental accuracy. A sample is shown in Table V. (For the convenience of notation the term

\[
\frac{E}{2.303 \text{ RT}} (E_{\text{corr}} - E^0) - \log m_1
\]

is expressed as \( B \)).

Table V

For 1st Approximation

\[
I = m_1 + 15m_2
\]

\[
= 2.22215 \times 10^{-2}
\]

<table>
<thead>
<tr>
<th>E obs</th>
<th>E corr</th>
<th>E corr - E^0</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.48385</td>
<td>0.48425</td>
<td>0.25868</td>
</tr>
<tr>
<td>25</td>
<td>0.4851</td>
<td>0.48557</td>
<td>0.26323</td>
</tr>
<tr>
<td>30</td>
<td>0.4862</td>
<td>0.48661</td>
<td>0.26777</td>
</tr>
<tr>
<td>35</td>
<td>0.4871</td>
<td>0.48797</td>
<td>0.27232</td>
</tr>
<tr>
<td>40</td>
<td>0.4879</td>
<td>0.48895</td>
<td>0.27667</td>
</tr>
</tbody>
</table>
1st Approximation cont.

<table>
<thead>
<tr>
<th>2 logf</th>
<th>$\log_{10} m_{\text{H}^+}$</th>
<th>$m_{\text{H}^+} \times 10^3$</th>
<th>$x_1 \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.12204</td>
<td>2.82735</td>
<td>6.7197</td>
</tr>
<tr>
<td>25</td>
<td>0.12324</td>
<td>2.82886</td>
<td>6.7044</td>
</tr>
<tr>
<td>30</td>
<td>0.12450</td>
<td>2.82537</td>
<td>6.6901</td>
</tr>
<tr>
<td>35</td>
<td>0.12576</td>
<td>2.82440</td>
<td>6.6741</td>
</tr>
<tr>
<td>40</td>
<td>0.12690</td>
<td>2.82353</td>
<td>6.6609</td>
</tr>
</tbody>
</table>

$m_{\text{SO}_4^{2-}} \times 10^3$ $y \times 10^3$ $K \times 10^5$

| 20     | 0.9692         | 1.7513           | 2.3050          |
| 25     | 0.8994         | 1.8058           | 1.9366          |
| 30     | 0.8286         | 1.8718           | 1.2113          |
| 35     | 0.7554         | 1.9195           | 0.7283          |
| 40     | 0.6774         | 1.9839           | 0.3052          |

For 2nd Approximation

$I = m_1 + 15m_2 - 2x_1 - 6y_1$

<table>
<thead>
<tr>
<th>$I \times 10^3$</th>
<th>$B$</th>
<th>2 logf</th>
<th>$m_{\text{H}^+} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.1081</td>
<td>-2.23469</td>
<td>0.09266</td>
</tr>
<tr>
<td>25</td>
<td>1.0733</td>
<td>-2.29683</td>
<td>0.09502</td>
</tr>
<tr>
<td>30</td>
<td>1.0296</td>
<td>-2.29913</td>
<td>0.09378</td>
</tr>
<tr>
<td>35</td>
<td>0.99401</td>
<td>-2.30136</td>
<td>0.09458</td>
</tr>
<tr>
<td>40</td>
<td>0.95683</td>
<td>-2.30337</td>
<td>0.09514</td>
</tr>
</tbody>
</table>

$x_2 \times 10^3$ $m_{\text{SO}_4^{2-}} \times 10^3$ $y_2 \times 10^3$ $K \times 10^4$

| 20     | 0.7603     | 2.1823 | 0.0945          | 122.21  |
| 25     | 0.7959     | 2.0476 | 0.1836          | 57.43   |
| 30     | 0.8312     | 1.8839 | 0.3120          | 29.56   |
| 35     | 0.8691     | 1.7527 | 0.4053          | 19.52   |
| 40     | 0.8982     | 1.6153 | 0.5236          | 10.02   |
For 3rd Approximation

\[ I = m_1 + 15m_2 - 2x_2 - 6y_2 \]

<table>
<thead>
<tr>
<th>I x (10^3)</th>
<th>B</th>
<th>2 (\log f)</th>
<th>(m_{\text{H}^+} x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.0134</td>
<td>0.11846</td>
<td>6.6544</td>
</tr>
<tr>
<td>25</td>
<td>1.9523</td>
<td>0.11802</td>
<td>6.6183</td>
</tr>
<tr>
<td>30</td>
<td>1.8887</td>
<td>0.11758</td>
<td>6.5836</td>
</tr>
<tr>
<td>35</td>
<td>1.9052</td>
<td>0.11722</td>
<td>6.5427</td>
</tr>
<tr>
<td>40</td>
<td>1.7184</td>
<td>0.11662</td>
<td>6.5001</td>
</tr>
</tbody>
</table>

\[ x_3 x 10^3 \quad m_{\text{SO}_4^{2-}} x 10^3 \quad y_3 x 10^3 \quad K x 10^4 \]

<table>
<thead>
<tr>
<th>I x (10^3)</th>
<th>B</th>
<th>2 (\log f)</th>
<th>(m_{\text{H}^+} x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.3319</td>
<td>1.3477</td>
<td>1.3075</td>
</tr>
<tr>
<td>25</td>
<td>0.4130</td>
<td>1.2697</td>
<td>1.3394</td>
</tr>
<tr>
<td>30</td>
<td>0.4527</td>
<td>1.2028</td>
<td>1.3816</td>
</tr>
<tr>
<td>35</td>
<td>0.4936</td>
<td>1.1309</td>
<td>1.4026</td>
</tr>
<tr>
<td>40</td>
<td>0.5362</td>
<td>1.0608</td>
<td>1.4401</td>
</tr>
</tbody>
</table>

For 4th Approximation

\[ I = m_1 + 15m_2 - 2x_3 - 6y_3 \]

<table>
<thead>
<tr>
<th>I x (10^3)</th>
<th>B</th>
<th>2 (\log f)</th>
<th>(m_{\text{H}^+} x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.3613</td>
<td>0.9323</td>
<td>6.5620</td>
</tr>
<tr>
<td>25</td>
<td>1.2349</td>
<td>0.9362</td>
<td>6.3300</td>
</tr>
<tr>
<td>30</td>
<td>1.3017</td>
<td>0.9384</td>
<td>6.2967</td>
</tr>
<tr>
<td>35</td>
<td>1.2319</td>
<td>0.9396</td>
<td>6.2704</td>
</tr>
<tr>
<td>40</td>
<td>1.2509</td>
<td>0.9912</td>
<td>6.2400</td>
</tr>
</tbody>
</table>

\[ x_4 x 10^3 \quad m_{\text{SO}_4^{2-}} x 10^3 \quad y_4 x 10^3 \quad K x 10^4 \]

<table>
<thead>
<tr>
<th>I x (10^3)</th>
<th>B</th>
<th>2 (\log f)</th>
<th>(m_{\text{H}^+} x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.6743</td>
<td>1.9297</td>
<td>0.4331</td>
</tr>
<tr>
<td>25</td>
<td>0.7063</td>
<td>1.3015</td>
<td>0.5193</td>
</tr>
<tr>
<td>30</td>
<td>0.7396</td>
<td>1.6619</td>
<td>0.5356</td>
</tr>
<tr>
<td>35</td>
<td>0.7659</td>
<td>1.5130</td>
<td>0.7582</td>
</tr>
<tr>
<td>40</td>
<td>0.7963</td>
<td>1.3722</td>
<td>0.3686</td>
</tr>
</tbody>
</table>
FIG. III. PLOT OF $\log K_{CeSO_4}$ VS $1/T$.

SHOWS MEAN SQUARE DEVIATIONS OF $\log K$. 
For 5th Approximation

\[ I = m_1 + 15m_2 - 2x_4 - 6y_4 \]

<table>
<thead>
<tr>
<th>( I \times 10^3 )</th>
<th>( B )</th>
<th>( 2 \log f )</th>
<th>( m_{\text{H}^+} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.7274</td>
<td>2.29469</td>
<td>0.11560</td>
</tr>
<tr>
<td>25</td>
<td>1.6593</td>
<td>2.29688</td>
<td>0.11386</td>
</tr>
<tr>
<td>30</td>
<td>1.5929</td>
<td>2.29913</td>
<td>0.11160</td>
</tr>
<tr>
<td>35</td>
<td>1.5141</td>
<td>2.30136</td>
<td>0.11059</td>
</tr>
<tr>
<td>40</td>
<td>1.4417</td>
<td>2.30337</td>
<td>0.10822</td>
</tr>
</tbody>
</table>

\[ x_5 \times 10^3 \] \[ m_{\text{SO}_4^{2-}} \times 10^3 \] \[ y_5 \times 10^3 \] \[ K \times 10^4 \]

| 20   | 0.4365 | 1.3944 | 1.2062 | 1.9159 |
| 25   | 0.4837 | 1.3257 | 1.2247 | 1.7962 |
| 30   | 0.5430 | 1.2583 | 1.2359 | 1.7139 |
| 35   | 0.5912 | 1.1985 | 1.2474 | 1.6213 |
| 40   | 0.6558 | 1.1281 | 1.2532 | 1.5055 |

The values of \( K \) were averaged for each temperature and a plot of \( \log K \) vs \( \frac{1}{T} \) drawn Fig. 3.

\[ T \quad K \text{ (av. values)} \]
| 20 | 1.95 |
| 25 | 1.90 |
| 30 | 1.70 |
| 35 | 1.61 |
| 40 | 1.49 |

From van't Hoff's Isochore:

\[
\int \frac{K_p(T_2)}{K_p(T_1)} \log K_p = -\frac{\Delta H^0}{2.303R} \frac{dT}{T_2}
\]

Thus plotting \( \log K \) vs \( \frac{1}{T} \) the slope will be

\[-\frac{\Delta H^0}{2.303R}\]

where \( \Delta H^0 \) is the heat of ionization of the ion-pair \( \text{CeSO}_4^+ \).

-45-
Slope = 500 (dimensions of T)

\[ \therefore \Delta H^0 = -500 \times 2.303 \times 1.987 \]

\[ \Delta H^0 = -2.28 \text{ K. cals/mol.} \]

Now \( \Delta G^0 = -2.303 \text{ RT log } K \)

Hence at \( 25^{\circ} \text{C or } 298^{\circ} \text{K} \)

\[ = -2.303 \times 1.987 \times 298 \times (-3.73373) \]

\[ \therefore \Delta G^0 = 5.11 \text{ K. cals/mol.} \]

From the definition

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

\[ \therefore \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \]

\[ = \frac{-2.28 - 5.11}{298} \]

\[ \therefore \Delta S^0 = -24.8 \text{ cals/mol/deg.} \]
DISCUSSION

The Cell:-

The test the preparing and reproducibility of electrodes and the accuracy to which solutions could be prepared the standard electrode potential of the cell:-

\[
\begin{align*}
\text{H}_2 - \text{Pt} & \quad | \quad \text{HCl} & \quad | \quad \text{AgCl} - \text{Ag} \\
P_{\text{H}_2} = 1 \text{ atm} & \quad | \quad 0.1 \text{ m} & \quad |
\end{align*}
\]

was measured. Instead of the usual extrapolation method of Lewis and Randall - which in the past has proved only fairly satisfactory - a new technique as suggested in a paper by nine of the world's leading authorities in this field was employed. These workers after extensive investigations find there is considerable difficulty in establishing the \(E^0\) value of this cell with a certainty to better than 0.2 mv. The uncertainty is most probably due to small differences in the structure of the solid phases. In contrast to this the value of the activity coefficient \(f_{\text{HCl}}\) at 0.01 molality is uncertain to only about 0.0005 which corresponds to an uncertainty of only 0.03 mv.

Hence they recommend that for measurements of high precision each worker should determine the \(E^0\) value for his own set of electrodes by standardization at 0.01 molality, taking the value of \(f_{\text{HCl}} = 0.904\) at 25°C. This method was applied and found satisfactory.

Three independently prepared solutions were used and twelve pairs of electrodes. Two pairs yielded inconsistent
results - to be explained - while the remaining varied by not more than 0.001 mv giving a mean value of 0.2223 volts for electrode potential the silver-silver chloride electrode at 25°C. This compares favourably with the quoted value 0.22234 volts as determined by several workers, e.g. Bates & Bower.  

**Electrodes:**

The consistency of the hydrogen electrodes, if properly prepared and subject to a constant stream of hydrogen, leaves little to be desired. Johnson found that an incomplete coating of platinum black made no difference to the readings. The present work showed however that no steady, consistent reading could be obtained under these conditions. The solution of chloroplatinic acid become more dilute with use and it was necessary to modify plating times to ensure a complete even covering.

The silver-silver chloride electrodes were found to be satisfactory. An incomplete coating of silver on the platinum foil did not appear to effect readings in any way. The conditions for preparation were not found critical. Purlee & Grunwald found equilibration times varied with surface area and thickness of silver-silver chloride coating, and that in 95% methanol-water mixture 10-15 minutes was all that was necessary. Austin found that for electrolytically prepared silver-silver chloride electrodes, a considerably longer equilibration period was necessary in non-aqueous solvents. With the solutions used, shorter equilibration
times would be necessary. All cells were left over-night to reach equilibrium, thus explaining why the preparation conditions were not found to be critical, as such times would be sufficient to allow the electrodes to equilibrate even if a longer time was necessary than found by Purlee & Grunwald.

Some electrodes however gave widely inconsistent results. No cause for this could be discovered though considerable investigation was carried out. The colour of the silver-silver chloride coating varied from medium-grey to a light purple to a darker grey. It was noticed that a smaller proportion of the dark grey electrodes was reliable. This method of preparation appears to be more straightforward than alternative methods and produces electrodes whose time of ‘ageing’ is small and that do not drift noticeably throughout a series of measurements. If an electrode gave incorrect readings they were usually so incorrect as to be easily detected. In only two of the twenty runs recorded could small inconsistencies be possibly due to the silver-silver chloride electrodes.

Solutions:-

All solutions prepared were molal so their concentration did not change with temperature. The accuracy to which they could be prepared, only 3%, was due to the multiple weighings required.

The hydrochloric acid after two fractionations and distillations careful removal of bromide and iodide - by
addition of permanganate - was considered sufficient. An independent check by titration against a standard solution of alkali agreed within 0.02% of the value obtained by comparing the atmospheric pressure at which the acid boiled with that in the International Critical Tables.

The cerous sulphate however presented difficulties. A first sample of ten grams was prepared as described but the salt was dehydrated by heating for 12 hours in a furnace at 450°C. This procedure is recommended by Spedding & Jaffe31 and by O'Brien, Brasted & Sneed32 who report there is no oxidation of cerium III to cerium IV below 500°C.

The crystals were a light ochre colour, and though only a 0.3% solution was prepared - solubility at 25°C is 5% - they did not dissolve readily.

Experimental runs with this solution proved unsatisfactory; great difficulty was experienced in obtaining real, positive values of x and y. This could be due to two factors,

(1) all the excess acid not removed from the crystals;

(2) during the heating some of the cerium could have been oxidised.

It is unlikely that (1) would be the cause as all nitrate had been removed as shown by the spot test, and the pH of the solution was constant.

As explained the crystals were an ochre colour and only sparingly soluble, whereas cerous sulphate is white
and soluble to about 5 gms in 100 gms of water at 25°C. Ceric (Ce IV) salts are a characteristic yellow orange colour. This suggests some cerium IV was present, probably as the oxide in these conditions, which is insoluble. Unfortunately the remainder of the crystals were inadvertently lost so they could not be analysed.

The second preparation yielded clean, white crystals which were dried only at 120°C to remove any remaining alcohol. A stock solution was prepared and analysed as described; the analysis proving the crystals were the octahydrate Ce₂(SO₄)₃ · 8H₂O within 0.25%. J. Koppel as reported by Mellor prepared the octahydrate by crystallization from a solution between 30°C and 70°C. The evaporation was carried out at approximately 60°C, as at any higher temperature was impractical due to bumping of the solid phase settling on the bottom of the flask. Results, using this solution - a selected number are recorded here - were more satisfactory. It would thus seem inadvisable to heat Ce III salts to a high temperature due to the possibility of oxidation to Ce IV, which is the more stable valency state of cerium.

Results:

The method for calculating the dissociation constants though rather lengthy and tedious is straightforward. The tendency is for the approximations to alternately over and under correct the values of K, the over correction being more pronounced. Values of K obtained after the 7th
approximation varied by less than the experimental error from those of the previous approximation, while applying this method to spectrophotometric data the same occurs at the 4th approximation.

The experimental errors involved in making the measurements were not very large. Weighings for larger solutions were correct to $\pm 0.01$ gms, incurring an error of not more than 3%. All electromotive force measurements were $\pm 0.00005$ volts or $\pm 0.01\%$. Analyses showed materials to be pure within 0.25%. The total experimental error attributable to physical measurements is not more than 3.25%. However the values of $K$ obtained from different strength solutions at the same temperature vary widely (see Fig. IV) e.g., by a margin of 8.72% at 20°C. Calculations show that a difference of 0.00005 volts may alter the value of $K$ obtained by $6 \times 10^{-6}$. In other words a 0.01% difference in reading could produce a value of $K$ which differs by 3%. This illustrates the accuracy required and helps to explain the large distribution of $K$ values obtained.

Newton and Arcand\textsuperscript{55} have used spectrophotometric measurements to study the $\text{CeSO}_4^2-$ ion-pair. From their results it can be calculated that the thermodynamic dissociation constant $K = 4.18 \times 10^{-4}$ at 25°C. These workers calculated from some solubility measurements of Chloupek, Danes and Danesova\textsuperscript{56} that $K_{\text{CeSO}_4^2-} = 4.26 \times 10^{-4}$ at 25°C, a value not significantly different from the
spectrophotometric result. Spedding and Jaffé from conductivity measurements also calculated $K_{\text{CeSO}_4}$, but their value at 25°C, $2.6 \times 10^{-4}$ is considerably lower than those quoted above. From the present work a value of $K = 1.80 \times 10^{-4}$ at 25°C was obtained, an even greater difference from the other results.

Newton & Arcand attack the problem from a quite different angle to that employed here. Instead of using a solution of cerous sulphate they mixed solutions of sodium sulphate and cerous perchlorate, assuming that the only ions which tend to associate in the solution are cerous and sulphate. Using the perchlorate of the cation required is quite a general method of approach because perchlorate ions due to their high electronegativity and low field of force, apparently show no tendency to associate. But there is definite evidence to show that sodium sulphate is not completely dissociated in aqueous solution. Its activity coefficient behaviour is of Type 3 (Fig. 1).

Davies, Jones & Monk\textsuperscript{43} in determining the value of the second dissociation constant of sulphuric acid showed how previous values obtained by Hamer\textsuperscript{57} using the cell:

$$
H_2 \mid \text{NaHSO}_4, \text{Na}_2\text{SO}_4, \text{NaCl} \mid \text{AgCl} - \text{Ag}
$$

were incorrect as he did not allow for the possibility of association between sodium and sulphate ions. Righellato & Davies\textsuperscript{53} determined $K$ for $\text{NaSO}_4^-$ at 18°C finding 0.20.
while more recently Jenkins & Monk\textsuperscript{59} obtained $K = 0.19$ at 25$^\circ$C. To avoid such complications the salt cerous sulphate was prepared for the present work.

However this does not explain the difference between the values of $K_{\text{CeSO}_4^+}$ obtained. The neglecting of the modification of concentrations by the formation of sodium sulphate ion-pairs would tend to lower not raise the results; the difference would thus become greater. The spectrophotometric method necessitates a sulphate concentration in excess of that of cerous ions. This means there is more chance of a higher complex being formed.

\[
\begin{align*}
\text{Ce}^{3+} + \text{SO}_4^{2-} & \rightleftharpoons \text{CeSO}_4^+ & K_1 \\
\text{CeSO}_4^+ + \text{SO}_4^{2-} & \rightleftharpoons \text{CeSO}_4^- & K_2
\end{align*}
\]

Newton & Arcand's results indicate such formation, and Austin\textsuperscript{60} more recently in investigating this system has data supporting this hypothesis. This means that the dissociation constant measured is not just a $K_{\text{CeSO}_4^+}$ but a combination of $K_1$ and $K_2$. Chloupek, Danes & Danesova used a similar system.

The difference in the values of the dissociation constants determined by different methods is quite large, but not uncommon in this work. A similar ion-pair to cerous sulphate, lanthanium sulphate LaSO$_4^+$, has been studied quite extensively.
Here the electromotive force value is considerably lower than that found by other methods. Jones & Monk also compare $K_{\text{MgSO}_4}$ determined by conductivity and electromotive measurements, $K_{\text{MgSO}_4}$ being respectively $5.4 \times 10^{-3}$ and $4.4 \times 10^{-3}$. A similar trend is noticeable $K_{\text{CeSO}_4}$ when the values obtained from these two methods are compared.

Stokes & Robinson demonstrate an interesting result by investigating the data of Davies, who measured the solubility of lanthanum iodate in potassium sulphate solutions. The solubility product of lanthanum iodate in water at $25^\circ C$ is $6.06 \times 10^{-12}$ if we calculate the activity coefficient by the Debye-Hückel Limiting Law equation (14). The solubility product in potassium sulphate solution is $11.64 \times 10^{-12}$ so that it seems that too much lanthanum iodate has dissolved. It is assumed that the true concentration of lanthanum ions is reduced due to the formation of $\text{LaSO}_4^+$ ions, and by successive approximations to get the total ionic strength at which the activity coefficient is to be calculated, the correct result is obtained if the concentration of $\text{LaSO}_4^+$ ions is $7.499 \times 10^{-4}$ moles/litre.

By the law of mass action $K_{\text{LaSO}_4} = 2.12 \times 10^{-4}$. If however instead of equation (14) for calculating activity coefficients we use Davies Equation (equation (17)) we find the solubility
product of lanthanum iodate is $6.60 \times 10^{-12}$ moles/litre, the concentration of $\text{LaSO}_4^{+}$ ions in the potassium sulphate solution is $7.753 \times 10^{-4}$ moles/litre and $K_{\text{LaSO}_4^{+}} = 2.15 \times 10^{-4}$ at $25^\circ\text{C}$.

This means the dissociation constant derived is almost independent of the assumption made about the equation for the activity coefficient. There is a very large difference in the two types of expressions used, their applicability and accuracy in predicting experimental behaviour, as explained in the introduction. This is a rigorous test, and it gives good agreement with the dissociation constants deduced by an entirely different argument from conductivity data by two independent investigations.

From this reasoning it would appear that values of dissociation constants determined from solubility or conductivity data would be correct rather than values obtained by other methods, e.g. electromotive force. For the cerous sulphate ion-pair there is however a wide discrepancy between the values of $K$ deduced by the above methods. Unfortunately no access is available to the original paper of Chloupek, Danes & Danesova\textsuperscript{56}, and the data published by Newton & Arcand is not complete, so it is not possible to assess the value of this result from solubility measurements. On the other hand Spedding & Jaffe\textsuperscript{21} have carried out a parallel determination of $K_{\text{LaSO}_4^{+}}$, the result being identical with that of Davies. On this scanty evidence it would seem reasonable to suggest the conductivity
value is more correct.

The examples quoted showing the difference explained above are restricted to sulphates. Table VI shows examples of dissociation constants of chlorides of cations at 25°C.

<table>
<thead>
<tr>
<th>Conductivity</th>
<th>E.m.f.</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{TlCl}}$</td>
<td>0.34 63</td>
<td>0.31 64</td>
</tr>
<tr>
<td>$K_{\text{PbCl}^+}$</td>
<td>2.6x10^-2 66</td>
<td>3.8x10^-2 67</td>
</tr>
<tr>
<td>$K_{\text{CaCl}^+}$</td>
<td>* 1x10^-3 69</td>
<td>1x10^-3 70</td>
</tr>
</tbody>
</table>

*18°C

This table shows none of the trends explained above.

Let us examine the electromotive force method for determining dissociation constants. There is little difference in the way it is applied to different systems; the procedure, and the theory used to calculate the results is the same. The only source of variation would be in the constants used. They are, those in the activity coefficient expression, standard electrode potentials, and the case of sulphates the second dissociation of sulphuric acid. The first would be very similar for all investigations. Standard electrode potentials have been accurately determined and are not subject to an uncertainty of greater than 1%. However the amount of work done on the second dissociation constant of sulphuric acid is not very great as such systems used to investigate $K_{\text{HSO}_4^-}$ are not completely understood. A higher value would decrease the discrepancy previously illustrated.
An approximate calculation shows than an increase of 5% in $K_{\text{HSO}_4^-}$ increases the value of $K_{\text{CeSO}_4^+}$ by 14%. In other words at 25°C if $K_{\text{HSO}_4^-} = 1.03 \times 10^{-2}$ and not $1.03 \times 10^{-2}$ then $K_{\text{CeSO}_4^+} = 2.08 \times 10^{-4}$ not $1.80 \times 10^{-4}$, a very significant change.

In a very recent paper Nair & Nancollas determined more accurately $K_{\text{HSO}_4^-}$ at varying ionic strengths and temperature. They used the cell:

$$
\text{H}_2 - \text{Pt} \mid \text{H}_2\text{SO}_4, \text{HCl} \mid \text{AgCl} - \text{Ag}
$$

as did Davies, Jones & Monk but quote electromotive force readings correct to ± 15 μ-V, compared with ± 100 μ-V. Their value of $1.10 \times 10^{-2}$ at 25°C may at first sight seem quite different from the value used here. But Nair & Nancollas recalculated Davies, Jones & Monk's results using more accurate terms in the activity coefficient expression getting a value of $K = 1.09 \times 10^{-2}$ at 25°C.

Unfortunately this date was not available when the results of the present work were calculated. However this only partially explains the discrepancy between the dissociation constants obtained from different methods.

It has been assumed that in the solutions used the only tendency for ion-pair formation is between $\text{H}^+$ and $\text{SO}_4^{2-}$ ions, $\text{Ce}^{3+}$ and $\text{SO}_4^{2-}$ ions, but such an assumption is subject to much uncertainty. Interaction between $\text{Ce}^{3+}$ and $\text{HSO}_4^{2-}$ and between $\text{CeSO}_4^+$ and $\text{SO}_4^{2-}$ ions are both reasonable possibilities and worthy of independent investigation within.
themselves. While on general grounds these may not have much influence on the general result, they may account for the difference in the results from electromotive force measurements.

**Derived Thermodynamic Functions:**

Thermodynamic data can be derived from the results, but the values are not very accurate. This may be seen by magnitude of the mean square deviations of $K_{\text{CeSO}_4}$ at each temperature (Fig. III). This graph was drawn in such a way to place more weight on values of $K_{\text{CeSO}_4}$ at lower temperatures where the electrodes are generally considered more reliable. The uncertainty in the slope of this line is $\pm 1.9\%$, the error in the values of $K_{\text{CeSO}_4}$ is $\pm 3.5\%$, enabling $\Delta H^0$ to be quoted within $\pm 5.4\%$. The error in $\Delta G^0$ will be that in $K_{\text{CeSO}_4}$. The confidence which $\Delta S^0$ may be obtained is thus not great being $\pm 8.3\%$.

The values may be compared with those of Newton & Arcand.55

<table>
<thead>
<tr>
<th>$\Delta H^0$ (kcal.)</th>
<th>$\Delta G^0 _{25^\circ C}$ (kcal.)</th>
<th>$\Delta S^0 _{25^\circ C}$ (e.u.)</th>
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<tbody>
<tr>
<td>Newton &amp; Arcand</td>
<td>$-4.69 \pm 0.3$</td>
<td>$+4.61 \pm 0.02$</td>
</tr>
<tr>
<td>Present Work</td>
<td>$-2.3 \pm 0.2$</td>
<td>$+5.1 \pm 0.2$</td>
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Comparison shows that the spectrophotometric measurements yields values of thermodynamic functions in which there is less uncertainty than those derived from cell measurements. The temperature coefficients of $K_{\text{CeSO}_4}$ show a marked difference Newton & Arcand’s being twice as great.
SUMMARY

1. The salt cerous sulphate, in the form of its octahydrate was prepared by a method different from any previously reported.

2. A recently published method for depositing silver on platinum for preparing silver-silver chloride electrodes was employed and found satisfactory.

3. The dissociation constant of the ion-pair CeSO$_4^+$ was determined from cell measurements and compared with other values published in the literature.

4. Suggestions as to why values of dissociation constants for sulphate ion-pairs calculated from electromotive force measurements differed from values obtained from other types of measurements. Some supporting evidence is presented.

5. Derived thermodynamic functions of the ion-pair CeSO$_4^+$ have been calculated.
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