An Investigation into the variation with temperature of the normal electrode Potential of zinc and of the activity coefficients of zinc sulphate solutions.
INTRODUCTION.

When two metals each dipping into a solution of one of its salts are joined together in the form of a circuit, a current flows between them. This fact although noted by Volta has so far resisted all attempts to interpret it convincingly.

Volta explained the source of this electric current on the theory of contact potential difference.

Faraday on the other hand put forward the theory that the current was merely the electrical energy produced by the chemical changes taking place in the cell.

Later experimentors have formulated theories embracing both of these points of view but still unanimity has not been reached. Probably the most outstanding of the determinations made was that due to Nernst. It is now well known how the gas laws were applied to liquids and solutions through the discovery of the Osmotic Pressure of liquids. The Nernst equation which gave a theoretical value to the E.M.F of a cell was first formulated as,

\[ E = \frac{RT}{nF} \log \frac{II}{II} \]

where \( R \) is the Gas constant, \( T \) the absolute Temperature, \( F \) a Faraday, \( n \), the valency of the metal ion.

\( II \) the solution Pressure of the metal (Nernst Zeit. Physical Chem. 2. p.613. 1889.)

\( II \) the osmotic pressure of the salt ions in solution.

The work of Lehfeldt (Phil. Mag. V. 48 p. 430 1899) showed that the excessive values that had to be assigned to the solution pressure
of the metal in many cases tended to throw doubt on the Nernst
equation. Moreover the solution pressures evaluated for the
metals showed a great disparity, e.g. Zinc = $9.9 \times 10^{18}$ while
Palladium = $1.5 \times 10^{-36}$. This solution pressure of the metal
was stated by Nernst to be due to a tendency on the part of the
metal to throw off positive ions into solution. The ions already
in solution would tend to resist this and an equilibrium would be
obtained depending on the Solution Pressure of the metal and the
concentration of its ions in solution.

Hamed, Bronsted Richards etc., were quick to see that where
the Nernst equation did not hold accurately enough it could be
made to hold by the introduction of the activity idea to solutions.
Thus the Nernst equation became:

$$E = \frac{RT}{nF} \log \frac{C}{c}$$

where $C$ = Solution Pressure of metal electrode,
c is concentration of solution used and $\gamma$ its activity coefficient.

On expansion this equation becomes;

$$E = \frac{RT}{nF} \log C - \frac{RT}{nF} \log \gamma c$$

When the concentration is molecular i.e. $\gamma = 1$ this equation
reduces to

$$E = \frac{RT}{nF} \log C$$

This is generally known as the electrode Potential of the metal
and is the Potential set up between the metal and an ionic normal
(theoretical) solution of one of its salts.

We thus obtain the following equation for the potential
difference between a metal and a solution of one of its salts at
concentration $c_x$.

$$E = E_P - \frac{RT}{nF} \log \frac{c_X}{c}$$

A knowledge of $E_P$ for the different metals therefore appears to be the key to the chemistry of aqueous solutions.

As doubt has been expressed as to the validity of the Nerst equation the work of other experimenters on electrode potential determinations will now be discussed.

C.H. Lewis and M. Randall have attacked the question of electrode potential from thermodynamic principles. (Thermodynamics, McGraw Hill) They find that

$$F = RT \log \left( \frac{c}{c_0} \right) = -NFE$$

$$E = \frac{RT}{nF} \log \frac{c}{c_0}$$

where $F$ is the change in free energy. This equation leads to

$$E = E^{o} - \frac{RT}{nF} \log a_{X}c_{X}$$

on expansion, which is similar in form to the Nerst equation. Lewis and Randall arrived at these conclusions by a method like that of Nerst.

That is, they dealt first with vapour pressures and obtained the function fugacity and then applied this to solutions and derived the function activity.

C.H. Lewis summarises the work by saying that it appears that the equation of Nerst errs only in accuracy of interpretation. (C.H. Lewis J.A.C.S. 1912, 34, p.1631)

Earliest workers had derived an equation similar to Lewis'
but had translated $A$ as the degree of ionization (see Bates J.A.C.S. 37, p. 1421, 1915). This term had given satisfactory results with certain typical electrolytes but had broken down with others and had proved useless in attempting to evaluate results of concentrated solutions.


deals with Electrode Potential from the Kinetic point of view.

He derives the equation,

$$E_{ob} = \frac{U}{nF} + \frac{RT}{nF} \log e \frac{AN_0}{1000 A'M'}, \quad \frac{RT}{nF} \log e C$$

$U$ - Heat absorbed during passage of one gram- ion of metal into solution.

$A = R/2M$. \quad $N_0$ = Avagadro Number.

This, in combination with the previous equations gives

$$E_{P} = \frac{U}{nF} + \frac{RT}{nF} \log e \frac{AN_0}{1000 A'M'},$$

which is equivalent to $-\frac{RT}{nF} \log e C$ of the Nernst formula, where $U$ - heat absorbed in the passage of 1 gram ion of metal into solution.

$A$ is a constant = $R/W$

$N_1$ is the number of ions per unit area of metal surface.

Butler concludes that the Nernst conception has given an adequate and physically acceptable explanation on the facts.


working from thermodynamical principles and applying Van der Waals equation for gas law obtains the equation
\[ E = \frac{1}{nF} \left( b \frac{P - p}{p} - RT \log \frac{P}{p} \right) \]

\( P \) = solution pressure of metal.
\( p \) = osmotic pressure of its ions in solution.

"This", he says "gives much more moderate values for \( P \), the solution pressure of the metal. Again an equation similar in form to that of Nernst is obtained.

A. Smith (Theory of Allotropy 1922.)

derives the equation

\[ E = -\frac{RT}{nF} \log \frac{K_{m} M_{s}}{M_{v}} \]

\[ = \frac{RT}{F} \log \frac{K(0_{e})}{(0_{1})} \]

where \( K_{m} \) = the saturation concentration of metallic ions.
\( M_{v} \) = the metallic ions in the electrolyte.
\( M_{s} \) = the metallic ions in the metal.

This equation he states is in agreement with Nernst's formula, and was first derived by Van Laar (Versl Kon Akad v. Wet Feb. 1903) in a somewhat different way. The latter considered the atoms only in the metal and applied the resolved molecular thermodynamic potential exclusively to the ions in the electrolyte.

This equation gives a space lattice system to metals and ascribes the properties possessed by metals as due to such a system.

Milner, Debye and Huckel (W.C.Lewis, A system of Physical Chem.
Vol.11 page 264)

have dealt with the question from kinetic and electrostatic laws
and have devised the recent interionic attraction theory of ionised salts. They find

$$F = RT \log \frac{C}{C_0} - \frac{A\nu^2}{k_{1.5}T^{0.5}} (c\nu^2)$$

\(\nu = \text{valence of ion}\)

where \(K\) = Dielectric constant for medium.

and as

$$F = -N E F$$

$$E = -\frac{RT}{nF} \log \frac{C}{C_0} - \frac{A\nu^2}{nF k_{1.5} T^{0.5}} (c\nu^2)$$

This again is similar to the Nernst equation as the last quantity is comparatively small.

**Summary.**

It appears therefore that the Nernst equation does give a satisfactory idea of the general principles underlying the production of electrical energy in these cells. The remarkable similarity shown by the equations derived from different sources tends to show that the correct explanation will be given by some form of the Nernst equation.

Lewis' statement that "the Nernst equation errs only in its interpretation", seems to sum up the position most clearly at the present day. From a study of the equation there are two unknown quantities to be found, \(E.P.\) the electrode Potential of the metal and \(A\), a factor expressing the state of the metal salt in a concentration \(C_x\) of the solution.

Hence if \(E.P.\) is to be determined from the equation values of \(A\) must be known correctly for different concentrations of salt.
solution. It would be as well to discuss here the knowledge of the activity coefficient.

Discussion of activity coefficients.

Some years ago owing to the inability to obtain an agreement between the observed and the calculated values of E.P. it was thought that the Nernst equation did not hold for strong electrolytes. S.J. Bates (J.A.C.S. 37 p. 1421 1915) showed that the Vant Hoff law \[ V = RT \] did not hold for strong electrolytes and hence doubted the applicability of the Nernst equation to them.

G.N. Lewis (J.A.C.S. 34, p. 1631, 1912)

Noyes and MacInnes (J.A.C.S. 48, p. 239, 1920)

Lewis and Lacey (J.A.C.S. 36, p. 804, 1914)

and others have shown that by the introduction of the term \( C \) as "the activity of the effective ions in solution" and not as "the actual ion concentration" as given by the degree of ionization concordant results could be obtained.

At high dilutions the activity coefficient and the degree of ionization are much the same and it was at these concentrations that good results were found. In more concentrated solutions the Nernst equation appeared to break down but on looking into recent tables of activity coefficients the reason is apparent.

These tables show

(1) That the activity coefficient decreases with increasing concentration much more rapidly than does the value of the degree of ionization.
(2) That for the majority of substances the activity coefficient goes through a minimum in the neighbourhood of 0.5M, while the degree of ionization varies in a perfectly regular manner. The lack of agreement between the observed and the calculated values of E.P. in their opinion was not due to a breaking down of the Hernst equation but to the use of the values of the degree of ionization. If correct values can be obtained for the activity coefficient the problem of E.P. becomes a simple one. Various methods have been used to determine activity coefficients of salts in solution.

I. Vapour Pressure determinations.

By this method the vapour pressures of different concentrations of salt solutions have been measured and from these fugacities have been obtained. The fugacity value is then used to give a measure of activity, that is from the value of the fugacity of the vapour is obtained the activity of the solute.

II. The distribution of a solute between two solvents.

The distribution of a solute between two immiscible solvents is studied, so that if its activity at different concentrations in one solvent is known it may be calculated in the other.

III. Electro Motive force measurements.

Here the activities are found by using amalgams of the metal at different concentrations. From a cell so formed the E M F is measured and activities calculated from

\[ F = RT \log \frac{A_1}{A_2} = -N E F \]
IV. Freezing Point Determinations.

As the result of the work of a large number of experimenters' activities from freezing point data are in general extremely accurate. The method is somewhat complicated and is based on an empirical law for the lowering of the freezing point by electrolytes in solution. (Lewis and Randall's Thermodynamics.)

V. Graphical Methods.

These are somewhat varied and consist of the graphing of log with other variables, concentration and pressure.

Results obtained from these methods approximate fairly closely to each other and reference will be made to them later on.

Discussion of Activity Coefficients of Zinc Sulphate Solutions.

Metals of similar types (e.g. Na and K,) have been found to have corresponding activity coefficients in solutions of similar salts of the same strength. This fact is illustrated by reference to any comparative series of tables on activity coefficients.

Too great a reliance however cannot be placed on this fact as trouble arises if attempts are made to use the activities of one salt in place of activities of another. Again the activity of the cation varies with different anions; e.g. activity of Barium varies in Barium sulphate and Barium chloride. Then similar salts have been found in some cases to have similar coefficients e.g. NaCl, KCl, HCl. Here again too much reliance cannot be placed. The activity coefficients of zinc, cadmium, magnesium and copper sulphate show a very close similarity and the activity coefficients of any one salt may be used in place of those of another with a
a fair degree of accuracy.

The Recent Hypothesis that strong electrolytes are completely dissociate
or ionised in all concentrations which may be regarded as dilute has
tended to throw some doubt upon the question of activity. (c.f., Milner
(Phil. Mag. 35, 214, 315, 1918) Ghosh (Trans. Chem. Soc. 113, 449, 627
1918) Bjerrum (Zeit. Elektro. Chem. 24, 321, 1918) Debye and Huckel
Physikal Zeitsch 24, 185, 1923).

A.A. Noyes (J. Amer. Chem. Soc. 46, 1036, 1924) states that this view of
complete ionization will be confirmed if the deviations of the behaviour
of ions from that of a perfect solute are accounted for by the treat-
ment of Milner, Debye and Huckel, whose fundamental idea is that owing
to the electrical attraction between positive and negative ions, there
are on the average in the neighbourhood of any ion, more ions of unlike
than of like sign; and hence that when the solution is diluted the
separation of the ions involves doing work against the electrical
attraction and corresponding increase in the energy content of the
solution.

W.G. McLeish (Physical Chem. Vol.2) states that this assumption cannot
be true of course for the more concentrated solutions in which the
vapour pressure of the undissociated molecules of the electrolyte is
measurable.

Reviewing the state of knowledge by 1920, in regard to this point
Noyes and MacInnes (J. Amer. Chem. Soc. 42, 239, 1920) conclude that,
"It seems advisable to adopt for the present the hypothesis that
strong electrolytes are completely ionised and to attribute the
decrease in the conductivity ratio wholly to a decrease of ionic
mobility and the change in the activity coefficient to some unknown
effect of physical nature."

Recent work has attempted to explain these unknown effects as due to

(1) Hydration of the ions in solution,
(2) Complex formation in solution,
(3) Colloid formation.

Either one or more of these influences may be working at the one time.

N.C. Bray (J. Amer. Chem. Soc. 49, 2372, 1927)

compared the activity coefficients of zinc sulphate as derived from the Interionic Attraction theory of Debye and Hückel with those obtained from Electro Motive Force work. He worked at 25° c., with a lead/lead sulphate reference electrode and found that at extremely dilute solutions the results showed good agreement but at concentrations greater than .01 the error was greater than experimental (i.e. 45% difference).

Another important fact which emerges on comparing tables of activity coefficients and the corresponding degree of ionization is that A the activity coefficient passes through a minimum while y the degree of ionization varies in a perfectly regular manner. "This itself", states W. C. Lewis (Physical Chem. Vol. 2, page ) "indicates that the activity coefficient is something fundamentally different from the so-called degree of ionization."

"It has been pointed out that the activity of an ion over a
wide range of concentrations is less numerically than its concentra-
tion as determined from conductivity methods. Only at high con-
centrations of the electrolyte does the activity of the ions become
greater than their apparent concentration. At extremely high con-
centrations the activities appear to increase enormously being of
the order of $10^n$ where $n$ rises from 1 to 8. (c.f. Noyes and MacInnes
J. Amer. C.S. 42, 239, (1920) gives $L\text{Cl}$ as 1.64 at 3M, H.S. Harned,
Taylors Phys. Chem. Vol. 11 p. 759 gives value of 16 molar HCl as
43.2. Parton in thesis for this degree 1928 found values for zinc
chloride such as 2.2 x 10 at 10.31 molar.)

SUMMARY.

The interionic theory has so far brought us no nearer obtaining
a definite value of activity coefficients in moderately dilute solu-
tions and as it is at these dilutions only that accurate determina-
tions can be made in E.M.F. work the activities given by other
methods must be used.

A.A. Noyes (J. Amer. Chem. Soc. 46, page 1098, 1924) and W.C. Bray
(loc. cit) have shown that at very dilute solutions activities from
the interionic determinations and E.M.F. work agree very closely.

The position of activities may be summarised by saying that
those determined from E.M.F. data give reliable results and give some
idea of the unknown effects of physical nature. Thus some reliance
can be placed on the values of E.P. obtained by substitution of
these values of the activity coefficient in the Nernst equation.

It follows that if values of "the activity coefficient of
zinc sulphate, or of any similar salt, were known at different
temperatures then the electrode potential of the metal at those temperatures could be calculated by substitution in the Nernst Equation.

This possible method of attack depends upon the knowledge of the change with temperature of the activity coefficients of zinc sulphate solutions or solutions of allied salts.

**The Variation with Temperature of the Activity Coefficient.**

On this question very little work has been done both from the theoretical and the practical sides. As far as could be ascertained the work so far has aimed at determining the general change with temperature rather than the actual values of \( \gamma \) at different temperatures.

Lewis and Randall (loc. cit page 350) obtained the change of activity with temperature from freezing point and heat of dilution data. For Sodium Chloride at concentration 5.2M they give the activity coefficient at \(-21.12^\circ C\) as 0.692 and at \(25^\circ C\) as 0.874. They also show that in dealing with activity neglect of thermal effects introduces an error of 3% at 1M concentration and an error of 20% at 5.2M at any one temperature. (in this case \(25^\circ C\)) It is evident that these thermal effects must be known in order that the activity coefficient may be found at different temperatures. It is evident therefore that this avenue of approach is closed owing to lack of knowledge of the variation with temperature of the activity coefficient.
The Electrode Potential of Zinc in Zinc Salts.

Wilsomere (Zeit. Physch. Chem, 35, 291, 1900)
gave the value of $E_{Pzn}$ as 0.770 volts at 25°C. He made his measurements with a zinc rod dipping in zinc sulphate solutions and with an $\text{Hg/Hg}_2\text{SO}_4$ standard half element. His results lack accuracy due to

1. the use of $V$ the degree of ionisation instead of $A$ the activity coefficient, in the Nernst equation. The preceding work shows the source of error hereby introduced. (He used values of given by Freezing Pt. work).

2. the use of $\text{Hg/Hg}_2\text{SO}_4$ standard half element is made doubtful owing to the solubility of the mercurous sulphate (c.f. Horsch J. Amer. Chem. Soc. 41, 1787, 1919.)

Aberk, Auerbach and Lutner (Messungen elektromotorische Kräfte galvansicher Ketten "Abhandlungen der deutschen Bursengesellschaft No. 5. Halle 1911) obtained the value of $E_{Pzn}$ as 0.760 volts at 25°C. They obtained their value by measuring the P.D. between zinc and zinc sulphate solutions of known concentrations against the normal calomel electrode. Their general method of attack was similar to that of Wilsomere but greater accuracy was gained due to a better knowledge of and a more definite value of the reference electrode. They gave the accuracy as $0.01$ volt. The result however is still doubtful owing to the use of degree of ionization values.

Horsch (loc. cit)
attempted to obtain the value of $E_{P}$ by a more direct though some-
what similar method.

It is a well known fact that the activity coefficient $A_x$ increases slowly with decreasing concentration and at infinite dilution equals unity. Horsch's method was to take readings with extremely dilute solutions of zinc chloride and extrapolate the graph so obtained to infinite dilution. He took readings at first with the cell

$$\text{Zn/ZnCl}_2 \parallel \text{Hg}_2\text{SO}_4/\text{Hg}$$

but could not evaluate the P.D. Zn/ZnCl$_2$ at low concentrations owing to the uncertain effect of the solubility of mercurous sulphate. He made his later readings with an Ag/AgCl$^+$ reference electrode and also obtained a value of E.P. zn by using the Nernst equation and substituting values of $A_x$ as given by barium chloride i.e. making use of the fact stated previously that similar salts have the same activity coefficient in solutions of the same strength.

The average of a series of values obtained gave the value of E.P. zn as 0.7551 volts. His results vary within 72 millivolts but as they show no definite trend the average reading can be relied upon and the individual fluctuations ascribed to some variation in the zinc electrodes.

He however, states that the value has a possible error of 0.01 volt. His work was done at 25°C.

Summary.

These results show that the advances in E.M.F. work have enabled the E.P. to be measured with much greater accuracy.
Thus Horsch's value at 25°C for the Electrode Potential of zinc can be taken as definite and accurate. Both the methods so far used display certain difficulties first in regard to values of the activity coefficient and secondly in regard to extrapolation since the graph obtained is a curve and not a straight line.

The Electrode Potential of Zinc as a function of the Temperature.

The previous paragraph detailed the various methods used to obtain the electrode potential of zinc. It will be noticed that all of these methods were carried out at 25°C.

Spencer (Physical Chemistry, Vol 2 (1926)) gives his value at 18°C, as 0.493 measured against the normal calomel electrode. He also gives the Hydrogen electrode against the calomel electrode as -0.277. Thus $E_{\text{H}^+ | \text{zn}} (E = 0) = 0.7700$ volt. Unfortunately the source from which this value was derived could not be traced so that no criticism can be offered of the method employed in attaining this value. The value however, is useful from a comparative point of view. It seems that the Electrode Potential decreases with temperature although the change is very small and in the light of Horsch's work, well within the limits of experimental error.

As far as could be found the Electrode Potential of zinc has not been evaluated at any other temperature. Nor indeed could the effect of temperature on the electrode potential of any metal be traced.
Lewis and Randall (J. Amer. Chem. Soc. 36, 1912, 1914) accurately measured the E.M.F. of the cell

\[ \text{H}_2/\text{HCl} \ (0.1\text{M})// \text{HgCl}/ \text{Hg} \]

at different temperatures and obtained values which, when plotted against temperature, gave a smooth curve graph which was far from a straight line. Lewis however states that this is the "only" example which exhibits such a curve and that it is probably due to a change in the temperature coefficient of the partial molar heat capacity of the electrode reaction.

**The Gibbs Helmholtz Equation.**

The question of Electrode Potentials at any temperature is dealt with by the Gibbs Helmholtz equation. This equation is built up from thermodynamic principles and is most simply stated as

\[ E \cdot \frac{\Delta H}{\Delta F} = T \cdot \frac{\Delta F}{\Delta T} \]

where \( E \) is the E.M.F. of the cell at 25\(^\circ\)C.

\( H \) is the increment of heat capacity

\[ \frac{\Delta F}{\Delta T} \] is the temperature coefficient of the cell.

\( N, F, \) and \( T \) are as before.

Hence if \( H \) is known for any cell of which \( E \) is measurable at one temperature then \( \frac{\Delta F}{\Delta T} \) can be calculated and so \( E \) determined at any desired temperature.

When the cell is broken up into its parts

\( E \) becomes the single electrode Potential

\( \frac{\Delta F}{\Delta T} \) becomes its temperature coefficient

\( H \) becomes the heat of single electrode reaction.
This gives a method of determining the variation of the electrode potential with temperature when \( H \) for the metal concerned is known. Unfortunately the work on \( H \) is as yet not very extensive. It seems from what is known already that \( H \) is, for the majority of cases, a linear function of temperature.

**AIM OF THE WORK.**

It was decided to attack the question of the change with temperature of the Electrode Potential of zinc by first finding the temperature variation of the Electro-motive Force of cells consisting of Zinc/Sulphate solutions of different concentrations. If the temperature variation of such cells were graphed then this graph might give some idea of the temperature variation of the Electrode Potential of zinc.

From a knowledge of the latter the change with temperature of the activity coefficients of zinc sulphate solutions could be evaluated from the Nernst Equation.

**METHOD.**

In the Nernst equation,

\[
E_{\text{obs}} = E_{\text{P.zinc}} - \frac{RT}{nF} \log C.
\]

it is seen than when \( C = 1 \) then

\[
E_{\text{obs}} = E_{\text{P.zinc}}
\]

Since the Electrode Potential of zinc is the potential difference between a zinc rod and a normal ionic (theoretical) solution it should be a function of the temperature of the same type as \( E_{\text{obs}} \).
Thus if the temperature variation of $E_{\text{obs}}$ is obtained for cells made with different concentrations of zinc sulphate, it might be possible, by examination of the curves formed to determine the temperature variation of the Electrode Potential of zinc.

If such a temperature variation could be found, by accepting Morsch's value of the Electrode Potential of zinc at 25°C as the standard, the values of the Electrode Potential of zinc at any other temperature could be evaluated.

Different solutions of zinc sulphate were consequently prepared and the potential difference between them and a mercury amalgamated zinc rod measured at temperatures between 15°C and 50°C.

This was obtained by measuring the E.M.F. of the cell

$$\text{Zn/ ZnSO}_4 \quad \text{Fixed concentrations} \quad // \quad \text{Saturated/Saturated KCl} \quad \text{calomel} \quad / \quad \text{Hg}$$

By subtracting from this measured E.M.F. the value of the saturated calomel half element, which was known at various temperatures, the Potential Difference between the zinc rod and the various concentrations of zinc sulphate was found. From the potential difference recorded by the various solutions at different temperatures, the temperature coefficient of the zinc/zinc sulphate half elements composed of different strengths of zinc sulphate was obtained.

APPARATUS.

1. GENERAL

The E.M.F. of the cells described above was measured by means
of the Peggendorf Potentiometer method.

In order to eliminate thermal liquid contact P.Ds., as much as possible the whole of the cell was immersed in the thermostat (T). The potential vessel containing the experimental electrode and the solution of zinc sulphate is shown at E in contact with the middle vessel of saturated potassium chloride (M). Also making contact with the middle vessel was the saturated calomel electrode (C) of known temperature coefficient.

The E.M.F. of the cell was compared with that of a standard Weston cadmium cell (S) whose E.M.F. was 1.0189 volts at 18°C. The bridge wire used was a 100 cms. bridge wire a b with a sliding contact. The point of balance was determined by a sensitive moving coil galvanometer.

A two volt accumulator was used to give a constant potential gradient along ab. The temperature of the thermostat was kept by a thermometer accurate to within 0.05°C. The required temperature was maintained in the thermostat by means of a toluene-mercury gas regulator.

The circuit was connected up with double insulated wire which was encased in rubber tubing at any metal contact. The toluene regulator used was made specially with a mercury side tube so that mercury could be drawn off or added according as the temperature was to be raised or lowered.

The regulator enabled the temperature of the thermostat to be changed rapidly without disconnecting any apparatus and thus without
interfering with its accuracy.

MEASURING VESSELS.

All measuring vessels were first calibrated.

11. DETAIL.

SATURATED POTASSIUM CHLORIDE CALOMEL ELECTRODE.

Wilsmore (loc. cit) used as the standard half cell an Hg/Hg\textsubscript{2}SO\textsubscript{4} electrode. But Horsch (loc. cit) made some preliminary measurements with the cell Zn/Zn\textsubscript{SO\textsubscript{4}}// Hg\textsubscript{2}SO\textsubscript{4}/Hg and showed that the results could not be used as the solubility of mercurous sulphate varied with the dilution of zinc sulphate.

Horsch made his later readings with a Ag/AgCl reference electrode.

No work however could be traced referring to the applicability of this half cell to variations of temperature or to its stability on lengthy use.

It was finally decided to use a calomel electrode which numerous experimentors had shown to be suitable for such readings as were to be taken. The next point to decide was the type of calomel to use i.e. /H\textsubscript{2}O,18 or Saturate. As readings had to be taken from 15\textdegree{}C to 50\textdegree{}C and back to 15\textdegree{}C again over a period of time it was essential that the reference electrode should be either constant in its action or of known variation. Clark (The Determination of Hydrogen Ions 1928 Edition) states that as a working standard the saturated calomel half-cell is undoubtedly the best as pointed out by Michaelis and Davidoff (1912). It does not require careful protection from the saturated KCl solution usually
employed as a liquid junction and it has a high conductivity permitting full use of the sensitivity of a low resistance galvanometer.

Fales and Hidge (J.Amer.Chem.Soc. 42, 2434, 1920) made a lengthy study of the 1N, 0.1N and saturated KCl calomel electrodes over a wide range of temperatures 5°C - 60°C. Their work was the result of suggestions made by Loomis and Acrée (Amer. Chem. Journal 46, p.621, 1911) and Michaelis (Monograph Die Wass Konzeat Julius Springer Berlin 1914 p.151) that the saturated KCl calomel in conjunction with a saturated KCl salt bridge would eliminate liquid contact potentials and should show great stability over a wide range of temperatures. Their results are briefly these:

(1) 0.1N and 1N calomels show diffusion when used with saturated KCl salt bridge, which reduces E.M.F.

(2) Over a wide range of temperatures these two electrodes are unstable and cannot be used above a few days.

(3) Over a wide range of temperatures the saturated KCl calomel electrode is very stable (can be relied upon for 16 months), has a very small temperature coefficient, is easily reproducible and can be relied upon for its constancy of value from 5°C -60°C over long periods of time. (One cell was used for 147 days through the cycle 25°C - 60°C, showing no change; it was then used through the cycle again and still showed no variation. It was thus decided to use the saturated KCl calomel electrode. The objections to keeping the electrode in a separate vessel kept at a known temperature (say 25°C) were:
(1) Temperature difference between it and the salt bridge would cause a thermal P.D.

(2) Diffusion and

(3) Contamination of solutions.

It may be mentioned here that Bray (loc. cit) made his investigations of zinc sulphate activity at 25° C. using as a reference electrode Pb/PbSO₄. This overcame the difficulty introduced by mercurous sulphate but as its temperature coefficient was not known it could not be used in this work.

The saturated pot. chloride calomel electrode was prepared as described by Fales and Midge (loc. cit). The materials used in its construction were:

(3) Pure distilled water.
(4) Mercury prepared as follows.

It was first dropped through concentrated sulphuric acid, washed several times with dilute nitric acid as described by Hildebrand (J. Amer. Chem. Soc. 31, (1909) p.933) and filtered through clean fine filter papers.

Excess of Pot. Chloride crystals were added to the electrode vessel to ensure saturation at 50° C. A thin layer of KCl solution was formed round the stopcock by turning the latter when the electrode was filled. The stopcock was kept closed all the time as a quite sensitive result was so obtained. Also diffusion was prevented and
and hence contamination avoided.

The type of electrode vessel used enabled the electrode to be kept well under water, thus making sure that the whole electrode vessel was at the same temperature as that of the thermostat. Also the long connecting tube of the vessel minimised diffusion. All stoppered parts were liberally greased on the outside to keep the electrode free from air and to stop water creep from the thermostat.

Two saturated calomels were prepared and gave identical readings. A normal calomel and a tenth normal electrode were also made and gave the same difference of potential when measured against the saturated calomels as was given by Fales and Midge. The saturated calomel electrodes were finally read against two other similar electrodes in use in the Laboratory and again identical results obtained.

The value of the cell was given by Fales and Midge as 0.5266 at 25°C when the normal calomel at 25°C was 0.5643. It was shown to have a temperature coefficient of 0.00020 volt per degree rise in temperature for temperatures between 5°C - 60°C. Clark (loc cit) dealing with standardization of electrode values favours the use of the normal hydrogen electrode as zero. He states that "We have no concern for the temperature coefficient of the absolute potential difference of the calomel electrode. By agreement the potential assigned is that of the cell

\[ \text{Hg/HgCl,KCl// } \text{H}_2\text{ a = 1 } / \text{Pt } \text{H}_2 \text{ (1 atm)} \]

when the potential difference at the normal hydrogen electrode is
assumed to be zero at all temperatures. Thus it comes about that the absolute temperature coefficient for the saturated calomel half-cell (as measured directly in absence of the thermal equilibrium is low and positive while by the standard of reference it is high and negative. The following values of the saturated calomel have been collected from Clark.

<table>
<thead>
<tr>
<th>Temperature Degrees (Centigrade)</th>
<th>Michaelis 1914</th>
<th>Clark's value from considerations of all others</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.2503</td>
<td>0.2510</td>
</tr>
<tr>
<td>20</td>
<td>0.2488</td>
<td>0.2503</td>
</tr>
<tr>
<td>25</td>
<td>0.2458</td>
<td>0.2458</td>
</tr>
<tr>
<td>30</td>
<td>0.2418</td>
<td>0.2420</td>
</tr>
<tr>
<td>35</td>
<td>0.2378</td>
<td>0.2380</td>
</tr>
<tr>
<td>38</td>
<td>0.2350</td>
<td>0.2360</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.2340</td>
</tr>
</tbody>
</table>

The temperature coefficient of the saturated calomel is thus - 0.0008 volt per degree rise in temperature. It was decided that Clark's values of the saturated Calomel against the normal Hydrogen would be used taking the above value to be the temperature coefficient. It was also decided to give the values on the absolute scale taking 0.5228 volt to be the value of the saturated calomel at 25°C and 0.0002 volt per degree rise in temperature to be its temperature coefficient as shown by Fales and Mudge (loc. cit.)

**Saturated Pot. Chloride Bridge.**

G. L. Levin (Loc. Cit page 599) states that "the problem of liquid/liquid potentials is a difficult one". Instead of calcu-
lating liquid potentials," he continues "numerous investigators have
sought to eliminate them by interposing between the two electrolytes
a concentrated solution of some salt such as ammonium nitrate or
potassium chloride. It is now certain that the first of these salts
by no means eliminates and in some cases may even increase the
liquid potential. The use of saturated potassium chloride doubtless
serves in many cases to reduce a large liquid potential to the order
of a few millivolts but the elimination has certainly never been
complete."

Michaelis (Hydrogen Ion Concentration) and
Abegg and Cuming (Zeit Elektro 1907, 13, 17)
also show the suitability of saturated KCl for eliminating liquid
potentials.

Rideal (An Introduction to Surface Chemistry"page 249, 1926)
in discussing Electrification at liquid-liquid interfaces derives a
very simple method for deriving diffusion potentials. He shows KCl
to have a value of -0.4 millivolts.

determined the effect of temperature upon Diffusion Potentials. He
showed NaCl to have a temperature coefficient of -0.05 millivolts
which with experimental error gave a value of -0. millivolts.

CONTACT POTENTIALS IN CELLS

Since one half-element was the saturated calomel electrode there
would be no liquid potential forced with a saturated KCl middle vessel

Consequently a middle vessel solution was made with saturated
POTENTIAL VESSELS.

Many types of potential vessels were first tried and the type found most suitable was the type. It was about three inches in length and about half-an-inch wide. It was fitted with a tube which made the connection with the middle vessel. The zinc electrode was held in the vessel by means of a rubber cork.

The type of vessel enabled it to be easily cleaned and dried and avoided contamination with previous solutions of zinc sulphate.

ZINC ELECTRODES.

It was found that pure zinc rods used alone as electrodes gave unreliable readings. This was evidently due to two causes.

(i) Uneven surface of zinc gave variation in solution pressure.
(ii) Oxidation of the zinc rod tended to take place in solution.

Thus some prepared type of electrode had to be tested and used.

The first were made up according to Warton and Shutt (Trans. Farad. Soc. 22, p. 480, 1927). Pure zinc rods were turned on a lathe to give a bright surface and plated in an ammonical solution of zinc sulphate. These however gave no more reproducible results than amalgam electrodes, which were prepared according to Spencer (Physical Chem., Vol. 2, p. 127).

The latter were simpler to make and keep clean. Four were prepared by amalgamating and tested against each other. Two were obtained which gave identical results and were used right throughout the series of readings giving concordant results. Whenever the results were not in agreement both electrodes were cleaned washed and reamalgamated and then used in the same strength solution. In

- 27 -
all cases such as this corroborative results were obtained.
Richardson and Dunham (J. Amer. Chem. Soc. 1923, 45 page 673)
show that since zinc forms no solid amalgam the potential of
pure zinc should be that of the saturated liquid amalgam.
The actual method of preparation of the amalgam electrodes
was as follows:

Rods of Merck's Zinc Puriss pro Analysi were turned on a lathe
and smoothed off with emery paper. They were then washed in
dilute sulphuric acid and distilled water and finally dipped into
a vessel of pure mercury. This was repeated and the electrodes
rubbed lightly with cotton wool as described in Findlay (Practical
Phys. Chem. page 252). They were sealed into glass rods and when
not in use were kept in T est tubes containing distilled water
acidulated with a drop of dilute sulphuric acid. The reason for
the addition of the latter was due to the fact that when the
electrodes were kept in distilled water alone they became covered
with what appeared to be hydroxide. On the addition of the acid
this disappeared. Before commencing each new series of readings
the electrodes were always reamalgamated and also in cases such as
cited above.

STANDARD CADMIUM CELL.

This cell was prepared as described in Spencer (Vol. II page 106,
using pure materials. It was allowed to stand for some weeks
readings being taken meanwhile against the Laboratory Standard
(Eppley Laboratory Newport U.S.A. No. 16723). The reading at
18°C, was found to be 1.0189 volts.

**ZINC SULPHATE SOLUTIONS.**

The sample of zinc sulphate used was B.D.H. Anal. Reagent. A qualitative analysis showed that there were no impurities present. A quantitative analysis was next carried out and the sample proved to have the composition ZnSO₄ 7H₂O.

Gravimetrically prepared solutions of zinc sulphate of the following concentrations were then prepared,

1M; 0.5M; 0.2M; 0.1M; 0.02M; 0.01M; 0.001M.

These solutions were kept in stoppered glass bottles away from light.

The solutions were next standardised by the internal indicator method of Conant and Cady, described below. The agreement given by these two methods ensured the accuracy of the concentrations of zinc sulphate.

**STANDARDIZATION OF ZINC SULPHATE SOLUTIONS.**

1. This was done gravimetrically since the analysis of the sample of zinc sulphate had given satisfactory results.

2. The solutions prepared were tested volumetrically by titrations against Standard Potassium Ferrocyanide solution (Treadwell and Hall Analytical Chemistry Vol.11 page 620 Sixth Edition). Conant and Cady (J. Amer. Chem. Soc. 49, 356, 1927) have shown that the usual external indicator uranin nitrate may be replaced by a solution containing one grain of diphenylbenzidine in 100 c.c. of concentrated sulphuric acid used as an internal indicator and that the results obtained are more accurate. Standard Potassium ferrocyanide was prepared by dissolving
22 gms of pure Pot. Ferrocyanide and 0.3 gms of Potassium ferri-
cyanide in a litre of distilled water. This was standardised by
the following method of titration against weighed quantities of
Merek's Zinc Puriss dissolved in sufficient sulphuric acid (about
15 c.c.s.).

METHOD OF TITRATION.

The quantity of solution taken was such as to contain about
0.1 gms. of zinc. To this was added 10 c.c. of 30% sulphuric acid,
the whole diluted to about 100 c.c.s. with distilled water and about
10 gms of ammonium chloride added. The solution was then titrated
cold as the indicator decomposes on heating. Three or four drops
of the indicator were added and also a few c.c.s of the standardised
Potassium ferrocyanide run in from the burette. The whole was then
shaken vigorously until a deep blue colour was obtained. This
faded slowly as the titration proceeded with the running in of the
potassium ferrocyanide in two to three c.c. quantities, until on
nearing the end point a deep purple colour was obtained. (This
colour was not obtained if the titration was carried out too
rapidly or if the solution had insufficient shaking.) At the end
point this purple colour faded sharply to a pale green within one
drop of potassium ferrocyanide. (The indicator does not keep
for longer than a month. Hence at the end of the experimental
work when the solutions were again standardised, fresh indicator
was used and the concentrations found to be unaltered.) The
titrations first carried out agreed with the gravimetric values
in all cases. The hundredth and thousandth normal solutions could not be so titrated owing to the low zinc content. The zinc sulphate concentrations are expressed throughout in molecular normality.

**METHOD OF TAKING MEASUREMENTS OF THE E.M.F. OF CELLS.**

Cells of the type

\[
\text{Zn/ xZn SO}_4 \ || \ \text{Sat KCl} \ || \ \text{Sat KCl/ Calomel/ Hg}
\]

were made up and measured at the required temperatures 15°- 50° C in the following manner.

The thermostat was first taken two or three degrees above the desired temperature in order to ensure the saturation of the calomel electrode. It was then made constant at the temperature and kept so by the toluene regulator. The potential vessel was then filled with zinc sulphate of a known concentration, a rubber stopper was placed over the tube end and the vessel hung over the middle vessel in the thermostat and left for some minutes until the solution had taken on the temperature of the bath. The rubber was removed and the electrode inserted and the value of the composite cell against the accumulator found.

The Standard Cadmium cell was then thrown into circuit against the accumulator and its point of balance obtained on the metric bridge.

Thus by simple ratio the value of the E.M.F. of the composite cell was found from the known value of the standard Cadmium Cell. Two zinc electrodes that had been found to give concordant results were always used with each concentration of zinc sulphate and the two potential vessels thrown into circuit with the calomel electrode
in succession to give readings. The mean value of these two readings was taken as the required reading.

**FIRST MEASUREMENTS.**

The object of these was to take readings of zinc sulphate cells at 25°C and to evaluate the activity coefficients for them by substitution in the Nernst equation by use of Horsch's value of Electrode Potential of zinc at 25°C. If these values of compared well with those already determined then it could be concluded that the method used was satisfactory and readings could be taken at other temperatures.

The standard cell was first read and then the composite cell. Since the E.M.F. of these cells are proportional to the readings on the sliding bridge, and the value of the standard cell was known at the atmospheric temperature holding during the experiment, that of the composite cell was easily calculated.

Again representing the composite cell diagramatically we have

\[
\text{Zn/ ZnSO}_4//\text{Saturated Pot. Chloride // Saturated KCl Calomel Electrode.}
\]

Since the value of the saturated calomel at 25°C is known (Clark 1928 Edition gives value .2458) the value of the half cell Zn/ZnSO_4 can be found. For example, with the 1M ZnSO_4 solution at 25°C

- **Composite cell** = 1.0300 volts,
- **Sat. KCl calomel** = 0.2458 volts
- **Zn/ZnSO_4 half element** = 0.7842 volts.

In this way the values of all the half elements formed with the seven concentrations of zinc sulphate were obtained. The first
results are given in the table below.

EXAMINATION OF PRELIMINARY RESULTS.

From the Nernst equation the relationship is obtained that

\[ E_{\text{obs}} = E_{\text{Pzn}} - \frac{RT}{F} \log C \]

where

- \( E_{\text{obs}} \) = the observed Pot. Difference between Zn/Zn\textsuperscript{2+}
- \( E_{\text{Pzn}} \) = the electrode Potential of Zinc (Horsch's value at 25\(^\circ\)C = 0.7581
- \( R \) = Gas Constant.
- \( T \) = Temperature on Absolute Scale.
- \( F \) = 1 Faraday 96,540 coulombs.
- \( n \) = valency of zinc ions.
- \( \gamma \) = activity coefficient of concentration of Zn\textsuperscript{2+} concerned.
- \( C \) = molecular concentration of zinc sulphate used.

In the above equation everything is known with the exception of the activity coefficient. By substituting and equating the values of \( \frac{1}{\gamma} \) were obtained for the various solutions used. In the table below the values obtained for \( \frac{1}{\gamma} \) are given in the 3rd last column. The values found by Bray and Lewis are given in the last two columns respectively.

**TABLE 1.**

<table>
<thead>
<tr>
<th>Temp,(^\circ)C</th>
<th>Zn\textsuperscript{2+}</th>
<th>E.M.F. of Zn\textsuperscript{2+}</th>
<th>P.D. of Zn\textsuperscript{2+}</th>
<th>Activity Bray's</th>
<th>Activity Lewis'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soln. comp.</td>
<td>site cell</td>
<td>calc.</td>
<td>coeff.</td>
<td>coeff.</td>
</tr>
<tr>
<td></td>
<td>Zn\textsuperscript{2+}</td>
<td>Sat.</td>
<td>at 25(^\circ)C</td>
<td>at 25(^\circ)C</td>
<td>Act.</td>
</tr>
<tr>
<td>25</td>
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<td>-0.7842</td>
<td>0.1309</td>
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<tr>
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<td>0.5M</td>
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<td>-</td>
<td>-0.7946</td>
<td>0.1106</td>
</tr>
<tr>
<td></td>
<td>0.2M</td>
<td>1.0503</td>
<td>-</td>
<td>-0.8045</td>
<td>0.1545</td>
</tr>
</tbody>
</table>

-
TABLE 1 (Cont.)

<table>
<thead>
<tr>
<th>Temp.,°C</th>
<th>ZnSO₄ Solution</th>
<th>0°Cent.</th>
<th>P.D. of</th>
<th>Activity</th>
<th>Bray's</th>
<th>Lewis'</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>.1M 1.0568</td>
<td>0.2459</td>
<td>- .8110</td>
<td>.1628</td>
<td>.161</td>
<td>.166</td>
</tr>
<tr>
<td></td>
<td>.02M 1.0590</td>
<td>-</td>
<td>- .8232</td>
<td>.3148</td>
<td>.324</td>
<td>.321</td>
</tr>
<tr>
<td></td>
<td>.01M 1.0742</td>
<td>-</td>
<td>- .8284</td>
<td>.4188</td>
<td>.421</td>
<td>.400</td>
</tr>
<tr>
<td></td>
<td>.001M 1.0970</td>
<td>-</td>
<td>- .8512</td>
<td>.7090</td>
<td>.734</td>
<td>.690</td>
</tr>
</tbody>
</table>

DISCUSSION.

Lewis' values are given for the group of sulphates of Magnesium, Cadmium, copper and zinc, and are derived from the activity coefficients given by different methods. That the limits of these values are fairly large can be seen from the following excerpt from Lewis and Randall's "Thermodynamics". "Finally in considering the sulphates of Mg, Cd, Cu and Zn, which we have grouped together as MgSO₄ we have altered the values given by Lewis and Linhart (e.g. at 0.01M = .33). These values rested chiefly upon measurements made by Hauersrath in 1902. These were undoubtedly the most accurate freezing-point date ever obtained up to that time. But in the meantime, important improvements in thermometry have been made and Hauersrath's values in dilute solutions may be regarded as uncertain. By a method which we cannot give here in full and which involves the use of Horsch's measurements (J. Amer. Chem. Soc. 41, 1787, 1919) on cells with zinc electrodes in ZnSO₄ and ZnCl₂ we have obtained new
values for the activity coefficients of ZnSO₄. By this method at 0.01M = 0.47. Giving equal weight to the two independent determinations we obtain as an average at 0.01M = 0.40".

In the light of this, the agreement given by the last three columns is very good. The solutions from 0.2M to 0.001M show a marked similarity. It will be seen from the table that Lewis gives no values for solutions of a greater concentration than 0.1M and that Bray's results for such solutions continues to decrease. These solutions were carefully measured again but no irregularity was found. Actually the solutions were left in contact with the middle vessel for twenty-four hours and no change in value took place. The values of the activity coefficient calculated from the experimental results show a minimum in the neighbourhood of 0.5M. This agrees with the statement of W.C. Lewis (Physical Chem. Vol. 2) that the activity coefficients of strong electrolytes pass through a minimum in the neighbourhood of 0.5M. Since the calculated results showed a very good agreement with the already known values it was decided that the method and technique followed was suitable and readings at 20°C etc were proceeded with in order to obtain the temperature coefficient of the half elements.

SECOND MEASUREMENTS.

The thermostat was taken to the next temperature 30°C and readings taken with the Zinc Sulphate solutions as before. The solutions were always brought to the temperature required first and then the electrodes were put in and the readings taken. Temperatures of 18°C and 15°C were next worked at; 15°C - 50°C.
and finally $50^\circ C - 25^\circ C$. This gave duplication of every temperature and a very good agreement was obtained in almost all cases. The values given below are the average of the two readings.

The Potential Difference $Zn/ZnSO_4$ is given against the normal Hydrogen electrode and against the absolute scale.

In the following table column 3 gives the value of the saturated calomel on the hydrogen scale, and column 4 gives the value of the Zinc/Zinc Sulphate half element on the hydrogen scale. Thus the value of the whole cell is obtained by adding columns 3 and 4 together. Column 5 gives the value of the saturated calomel on the absolute scale and column 6 the value of the Zinc/Zinc Sulphate half elements on the absolute scale. As above the value of the whole cell is given by adding columns 5 and 6 together.
<table>
<thead>
<tr>
<th>Concentration of ZnSO₄ °Centi.</th>
<th>Temperature</th>
<th>Sat. Calomel EH = 0</th>
<th>P.D. Zn/ZnSO₄ EH = 0</th>
<th>Sat. Calomel absolute scale</th>
<th>P.D. Zn/ZnSO₄ absolute scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M</td>
<td>15°</td>
<td>0.2540</td>
<td>-0.7820</td>
<td>0.5208</td>
<td>-0.5152</td>
</tr>
<tr>
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<td>0.2516</td>
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<tr>
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<td>-0.7829</td>
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<td>-0.5111</td>
</tr>
<tr>
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<td>-0.5072</td>
</tr>
<tr>
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<tr>
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<td>-0.4991</td>
</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<td>-0.7917</td>
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<tr>
<td>Concentration of ZnSO₄ (M)</td>
<td>Temperature (°C)</td>
<td>Sat. Calomel (Eₜ = 0)</td>
<td>P.D. Zn/ZnSO₄ (Eₜ = 0)</td>
<td>Sat. Calomel absolute scale</td>
<td>P.D. Zn/ZnSO₄ absolute scale</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>------------------</td>
<td>------------------------</td>
<td>-------------------------</td>
<td>----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>0.2M</td>
<td>15°</td>
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<td>Temperature</td>
<td>Sat. Calomel $E_H = 0$</td>
<td>$P.D. \frac{Zn}{Zn^{86}}$ $E_H = 0$</td>
<td>Sat. Calomel Absolute</td>
<td>$P.D. \frac{Zn}{Zn^{86}}$ absolute scale</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------</td>
<td>------------------------</td>
<td>--------------------------------------</td>
<td>------------------------</td>
<td>--------------------------------------</td>
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<tr>
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<td>-0.5663</td>
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<tr>
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<td>0.5258</td>
<td>-0.5625</td>
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<td>-0.8558</td>
<td>0.5268</td>
<td>-0.5590</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.2260</td>
<td>-0.8577</td>
<td>0.5278</td>
<td>-0.5559</td>
</tr>
</tbody>
</table>
DISCUSSION OF RESULTS.

It is seen from the tables that there is a regular increase in the P.D.'s of Zn/ZnSO₄ as the dilution increases. (Temperature constant). This is in perfect agreement with Arrhenius' Theory and the Nernst Equation. Thus as the dilution increases more zinc ions tend to leave the zinc electrode therefore it is left more negative.

The results are graphed on Figs. V and VI, the former giving the values on the absolute scale.

Two things stand out from the graphs:

1. The observed P.D.'s at the various concentrations for any fixed temperature give straight line graphs.

2. These straight line graphs are parallel or nearly so.

From these results the conclusion is drawn that the temperature coefficient of the Potential difference between Zinc and a solution of Zinc sulphate is within the limits tested, the same for all concentrations of sulphate. Since the Electrode Potential of zinc is the Pot. Difference between a zinc rod and an ionic normal solution of a zinc salt, this Electrode Potential should possess the same temperature coefficient as may be deduced from Figs. I and II.

On taking the average slope of the graphs on Fig I, it is found that the temperature coefficient obtains the value of 0.0002 volt per degree rise in Temperature against the Hydrogen electrode.

From Fig. II, in the same way, the value for the temperature coefficient is -0.0008 volt per degree rise in temperature on the absolute scale.

Accepting Horsch's value for the Electrode Potential of zinc at 25°C as correct and applying the temperature coefficients found
above the values of the electrode potential of zinc are obtained at temperatures between 15°C and 50°C.

**TABLE III**

<table>
<thead>
<tr>
<th>Temperature Degrees Centigrade</th>
<th>Eₚ₋ₐₗₜ (H = 0)</th>
<th>Eₚ₋ₐₗₜ (Absoluate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°</td>
<td>-0.7561</td>
<td>-0.4891</td>
</tr>
<tr>
<td>18°</td>
<td>-0.7567</td>
<td>-0.4867</td>
</tr>
<tr>
<td>20</td>
<td>-0.7571</td>
<td>-0.4851</td>
</tr>
<tr>
<td>25</td>
<td>-0.7581</td>
<td>-0.4811</td>
</tr>
<tr>
<td>30</td>
<td>-0.7591</td>
<td>-0.4771</td>
</tr>
<tr>
<td>35</td>
<td>-0.7601</td>
<td>-0.4731</td>
</tr>
<tr>
<td>40</td>
<td>-0.7611</td>
<td>-0.4691</td>
</tr>
<tr>
<td>45</td>
<td>-0.7621</td>
<td>-0.4651</td>
</tr>
<tr>
<td>50</td>
<td>-0.7631</td>
<td>-0.4611</td>
</tr>
</tbody>
</table>

The only other temperature at which the electrode potential of zinc has been given is at 18°. At this temperature Spencer gave the value on the absolute scale as 0.493 volt. This value agrees very closely with the value given in column III.

*Bouty (C. v. 90, 217, 1880)*

determined the temperature coefficient of cells made up of zinc in different concentrations of zinc sulphate and found that it was independent of concentration. The value obtained for the temperature coefficient was -0.77 millivolt per degree rise in temperature on the absolute scale.
This value is in agreement with the one given by the graphs on Figs. 11.

As the above graphs and tables show the E.M.F.'s of the cells are varying in a fairly regular manner with the temperature. This variation may be caused by one or more factors. In the Nernst equation

\[ E_{obs} = \frac{RT}{nF} \log \frac{P_1}{P_2} \]

there are two factors which vary with temperature; \( P \) the Solution Pressure of the metal and the activity of the ions in the solutions. The factor \( P \) will be dealt with first and the other later. If the above values for the Electrode Potential of zinc at different temperatures are correct (that is if the assumption that the electrode potential varies in the same way as the potentials of the solution measured is allowable) then it is possible to evaluate the Solution Pressure at different temperatures by use of the above equation. The latter gives,

Electrode Potential = \( \frac{RT}{nF} \log P \).

Taking the above values of \( E_P \), zinc and solving for \( P \) the following results are obtained.

<table>
<thead>
<tr>
<th>Temp. ( ^\circ )C</th>
<th>15</th>
<th>18</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P ) (atmos)</td>
<td>1.862 x 10^{17}</td>
<td>1.61 x 10^{17}</td>
<td>6.71 x 10^{16}</td>
<td>2.57 x 10^{16}</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Temp. ( ^\circ )C</td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>( P ) (atmos)</td>
<td>1.02 x 10^{16}</td>
<td>4.17 x 10^{15}</td>
<td>1.75 x 10^{15}</td>
<td>7.76 x 10^{14}</td>
</tr>
</tbody>
</table>

The Solution Pressure of zinc is therefore decreasing with increase of temperature in a fairly regular manner. Just what this is due to is impossible to say with certainty owing to the
difficulty of giving a definite physical significance to \( P \). (see Lewis W.C. Phys. Chem. Vol.11 p. 151.)

**COMPARISON OF FOUND VALUES**

of E.P. Zn at various temperatures and those given for other substance show a marked similarity.

**SPENCER (loc.cit.) And Others Give The Value of The Decinormal Calomel electrode as .6130 \( .0003 (t - 18) \) volts; that is the decinormal calomel electrode has a linear temperature coefficient. The value of the normal calomel electrode is given as .5600 \( .0006 (t - 18) \) volts (Palmer). This electrode has a linear temperature coefficient.

**THE SATURATED CALOMEL ELECTRODE**

Has been shown by Fales and Nudge (loc.cit.) to have the following value:

\[ .5266 \quad .0002 (t - 25) \text{ volts}. \]

This electrode also has a linear temperature coefficient.

**LEWIS AND RANDALL (J.A.C.S. 36 1914 (1914))**
carefully measured the electromotive force of the cell

\[ \text{Hg}/\text{HCl} (0.1M) || \text{HgCl} / \text{Hg} \text{ at diff. temps.} \]

and found that when the E.M.F. was plotted against temperature a smooth curve which was far from being a straight line was obtained; thus showing that the temperature coefficient was itself diminishing rapidly with measure of temperature. Working from calorimetric data they found that the great change in \( d\,E/dT \) and in \( H, \) in such a case as this was due to the high negative partial molal heat capacity of the electrolyte.
Further they say that this is perhaps the only case in which they have any evidence as to the change in partial molar heat capacity with temperature and that it is interesting to note that the high negative value of \( C_p \) for HCl is apparently falling rapidly as the temperature increases.

FOXTON AND SHUTT (TRANS. FARAD. SOC. V 23 No.77 Page 480) determined the temperature coefficient of the cell 
\[ \text{Zn/ZnCl}_2/\text{Cl}_2 \text{ Pt between temps. 60° - 80°} \]
and found it to be \( 0.0007128 \) volt per degree rise in temperature.

In general it may therefore be stated that the temperature coefficients of all the half elements hitherto recorded agree closely with that found for the Zn/ZnSO\(_4\) half-element.

**DISCUSSION FROM THERMODYNAMIC VIEWPOINT.**

In the Introduction reference was made to the Gibbs Helmholtz equation i.e.
\[ E = \frac{\Delta H}{nF} = T \frac{dE}{dT} \]
Since \( E \) and \( F \) are constants with the substance taken and if \( E \) were known at one temperature than a knowledge of \( \Delta H \) would enable \( \frac{dE}{dT} \) to be determined.

This again would enable \( E \) to be determined at any temperature. However there is no direct means of obtaining \( \Delta H \). All that is known is that the sum of the two values of \( \Delta H \) (for each separate electrode reaction) is \(-3291\) cal.

A method had been devised to obtain \( \Delta H \) for any substance by arbitrarily fixing \( \Delta H \) for Hydrogen \((E_0 = 0\) for all temperatures).
Lewis and Randall (Loc. cit.)

summarise the present knowledge of \( H \) thus; "We had indeed contemplated the preparation of such a table, but the heats of reaction now available differ so greatly in accuracy (the probable error ranging from less than one calorie to more than ten thousand) that we have felt that such a table would be too misleading, unless we should go more fully than is desirable into the sources of error attending the several measurements. New determinations carried out both electrometrically and calorimetrically which would furnish us an adequate table of this character constitute one of the most important tasks of applied thermodynamics".

It has been generally accepted that for most substances \( H \) may be regarded as a linear function of temperature. Hence since \( E \), and \( F \) are constants \( \frac{dE}{dT} \) should be a linear function of temperature also.

Using this found temperature coefficient we can calculate the heat of reaction which takes place at the zinc electrode, viz.

\[
H = NF \left( T \frac{dE}{dT} - E \right)
\]

\[
H_{298} = 2 \times 23074 \left( 298.1 \times 0.023 \right)
\]

\[
= -33880 \text{ cal.}
\]

Thus by varying \( T \) in this equation \( H \) can be obtained at different temperatures.

DISCUSSION OF ACTIVITY COEFFICIENTS OF SOLUTIONS.

All experimenters are agreed that, at the present time, the Nernst equation gives the most suitable explanation of the chemistry of solutions. From this equation it is possible to obtain some idea
of the state of a solution from a knowledge of its E.N.F. The equation may be conveniently represented as

\[ E_{\text{obs}} = E.P. - \frac{RF}{nF} \log xC_x \]

where \( E_{\text{obs}} \) = the observed P.D. between Zinc and the solution of Zinc sulphate concerned.

\( E.P. \) = the Electrode Potential of the Zinc.

\( R \) = the Gas constant.

\( T \) = the temperature on Absolute Scale.

\( F \) = 1 Faraday 96500 coulombs.

\( n \) = valency of the zinc ion.

\( x \) = the activity coefficient of concentration of Zinc Sulphate used.

\( C_x \) = the molecular concentration of zinc sulphate used.

Since the values of \( E_{\text{obs}} \) and of \( E.P. \) are known from \( 15^\circ \)C to \( 50^\circ \)C, it is possible to evaluate \( x \) at different temperatures (15°C - 50°C) for the solutions used. Table IV gives the values obtained on substitution. Clark's values of \( \frac{RF}{nF} \) (Hydrogen Ion Concentration 1928) were used.
<table>
<thead>
<tr>
<th>Temp. Centigrade</th>
<th>1M</th>
<th>0.5M</th>
<th>0.2M</th>
<th>0.1M</th>
<th>0.02M</th>
<th>0.01M</th>
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<tbody>
<tr>
<td>15°</td>
<td>0.1240</td>
<td>0.1034</td>
<td>0.1278</td>
<td>0.1452</td>
<td>0.2691</td>
<td>0.3776</td>
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<tr>
<td>18°</td>
<td>0.1285</td>
<td>0.1168</td>
<td>0.1326</td>
<td>0.1541</td>
<td>0.2802</td>
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<td>20°</td>
<td>0.1295</td>
<td>0.1182</td>
<td>0.1358</td>
<td>0.1614</td>
<td>0.2838</td>
<td>0.4000</td>
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<td>0.1309</td>
<td>0.1189</td>
<td>0.1345</td>
<td>0.1628</td>
<td>0.3148</td>
<td>0.4188</td>
<td>0.7080</td>
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<tr>
<td>30°</td>
<td>0.1417</td>
<td>0.1297</td>
<td>0.1452</td>
<td>0.1803</td>
<td>0.3290</td>
<td>0.4680</td>
<td>0.7870</td>
</tr>
<tr>
<td>35°</td>
<td>0.1430</td>
<td>0.1357</td>
<td>0.1525</td>
<td>0.1866</td>
<td>0.3260</td>
<td>0.4955</td>
<td>0.9036</td>
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<tr>
<td>40°</td>
<td>0.1530</td>
<td>0.1435</td>
<td>0.1638</td>
<td>0.1959</td>
<td>0.3495</td>
<td>0.5205</td>
<td>0.9955</td>
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<tr>
<td>45°</td>
<td>0.1624</td>
<td>0.1446</td>
<td>0.1740</td>
<td>0.2073</td>
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<td>0.5715</td>
<td>1.0715</td>
</tr>
<tr>
<td>50°</td>
<td>0.1635</td>
<td>0.1536</td>
<td>0.1820</td>
<td>0.2249</td>
<td>0.4114</td>
<td>0.6000</td>
<td>1.1130</td>
</tr>
</tbody>
</table>

An examination of the method used to evaluate brings out its variation with temperature.

\[
E_{\text{obs}} 25^\circ C \quad (25^\circ - t^\circ) \quad \left( \frac{\text{d}E}{\text{d}T} \right) = E^p_{\text{obs}} 25^\circ C \quad (25^\circ - t^\circ) \quad \left( \frac{\text{d}E}{\text{d}T} \right) \quad \frac{RT}{nF} \log C
\]

Where \( E_{\text{obs}} 25^\circ \) = the observed E.M.F. of the Zinc/ZnSO₄ half element

\( \frac{\text{d}E}{\text{d}T} \) = its temperature coefficient as found.

\( E^p_{\text{obs}} 25^\circ \) = the electrode Potential of Zinc at 25° (Horsch's value)

\( \frac{RT}{nF} \log C = A \text{ constant}. \)

\( T = \frac{1}{\log c} \)

or

\( - \log c \cdot \frac{1}{1} \quad \text{and since C is constant} \)

\( - \log \frac{1}{1} \)
Graph of Activity Coefficients and Temperature

Activity
That is as $T$ increases $-\log K$ decreases numerically. Therefore decrease in $-\log K$ produces an increase in the value of $K$.

Thus increase of temperature produces increase in the value of the activity coefficient for zinc in zinc sulphate solution.

Figure VII illustrates this point. The activity coefficients for all the solutions observed show an increase with temperature.

Ewart and Randall (loc. cit. page 276)
deal with the temperature change of activity from thermodynamic principles and show the same result as the above.

$$\frac{d \log K}{dT} = -\frac{L}{RT}$$

where $L$ is the heat content which with small changes in $T$ is a linear function of $T$.

G.N. Lewis (Systematic Physical Chemistry, W.C. Lewis, page 277)

obtained an expression from the inter-ionic attraction theory for the activatrons of ions.

$$-\log K = \frac{A \nu^2}{R (\Theta T)^{1.5}} (c \nu^3)$$

The only variables here are $c$ and $\Theta$ and it is seen that increase in $T$ will mean decrease in $-\log K$ with the same change in as obtained above.

Certain points however, stand out from graphs III and IV which require some comment.

(1) What is the meaning of an activity coefficient for 0.001M solution of L.0715 and 1.1130 at 45°C and 50°C respectively.

(2) Why do the activity coefficients go through a minimum in the neighbourhood of 0.5M, Fig. IV.

Since, as Noyes and MacInnes have stated (p. ) "The change in
the activity coefficients of strong electrolytes is due to some unknown effect of physical nature; it is somewhat difficult to give a satisfactory explanation of the first point. This increase in activity with temperature is what would be expected from the theory of complete ionization of strong electrolytes; that is increase of temperature has increased the speed of the ions and thus work has been done against the electrical attraction and a corresponding increase in the energy content has taken place. The latter is shown by an increase in the activity of the solution.

In dilute solutions where there is a smaller concentration of ions of unlike charge around any single ion and where the ions are further apart the effect of temperature would be greater than in more concentrated solutions in which larger forces have to be overcome. The experimental results illustrate this point. For example the activity coefficient of the 0.001M Zine sulphate solution increases from 0.6252 at 15°C to 1.113 at 50°C while that of the 1M solution increases from 0.1240 at 15°C to 0.1635 at 50°C.

The second point is illustrated by the graphs on Fig.1V (all the lines have not been drawn in this figure owing to their proximity to each other. The two extreme temperatures have been graphed and the results of the other temperatures fall evenly between c.f. 18°C.) It is seen from these graphs that the active ion concentration decreases rapidly with increasing concentration, passes through a minimum in the neighbourhood of 0.5M and commences to increase with increasing concentration.

Further in dilute solutions the activity is apparently a linear
function of \( \log C \). The presence of the minimum points shows that two factors in are varying inversely with each other.

The general effect of the factors may be stated as follows. Starting at infinite dilution the first factor may decrease with increasing concentration (the second factor having little effect in such dilute solutions) and so the values move down to the minimum. As the solutions become more concentrated the second factor which tends to increase begins to function and at a certain point the two opposing effects equal each other (minimum point); beyond this concentration the second factor increases and the values commence to increase again.

It is possible only to surmise what these two factors are. The first factor may be due to the decrease in the mobility of the ions as concentration increases, owing to a change in the electrostatic attraction of the ions. Presuming complete ionization in dilute solutions it is reasonable to infer that the speed of the ions will decrease as the oppositely charged ions come closer together with increasing concentration. This would give a decrease in the mobility of the ions concerned and a decrease in their activity would result.

The second factor may be an increase in the mobility of the ions due to a change in the hydration of the ions. (Bjerrum's theory) Bjerrum's theory is that each ion is surrounded with layers of neutral water molecules owing to the charges they carry. In the cations the free charge is located at the atomic nucleus and hence the water molecules will be firmly firmly held. This will increase
the weight of the cation and decrease its mobility. Now as the concentration of the cations increases the number of water layers round each cation will decrease, thus the cation will become lighter and freer and its mobility will tend to increase again. These two opposing effects will equal each other at a certain concentration, the minimum point, while at a greater concentration the latter will predominate and the activity will appear to increase. The question of Hydration will be discussed again later.

Other influences however may be at work in the solutions which affect the concentration of the "active" ions. It is this concentration which C. J. Lewis shows the E.M.F. method to measure. This is the reason why activity coefficients given by the E.M.F. method always differ from those given by Freezing Point determinations etc. It must be borne in mind that the present view of activity is widely different from the old Arrhenius idea of degree of dissociation. In fact the activity measured by E.M.F. work does not merely give the concentrations of the "active ions" in solutions but the total effect of the number of the active ions in solution, the dielectric medium (environment) the speed of the ions (mobility) temperature, degree of hydration of ions, size of ions etc.

Whether this total effect should pass through a minimum and should become greater than unity will depend on the combination of factors mentioned above. The question is thus so complicated that it is almost impossible to predict the action of solutions. Some of these influences must hence be discussed.
1. COMPLEX FORMATION.

Much evidence has been obtained of the formation of complexes in solutions of zinc salts.

Kunschert (Zett. Anorg. Chem. 41, 337, 1904)

investigated solutions of zinc oxalate in ammonium oxalate and potassium oxalate and of zinc hydrate in sodium hydroxide. The complex anions \( \text{Zn(C}_2\text{O}_4\text{)}_3 \) and \( \text{Zn(C}_2\text{O}_4\text{)}_2 \) were found in the former case, while alkaline solutions of zinc hydroxide were shown to contain the zincate ion \( \text{ZnO}_2^- \).

Drucker (Zeit. Electrochem. 79, 236, 1912)

showed by conductivity, transport number and electromotive force measurements that even in concentrations less than 0.1M an aqueous solution of zinc chloride contains a complex cation, probably \( \text{ZnCl}^+ \), in considerable concentration.

Kimball (Ann. Phys. Chem. 1464, 655, 1898)

showed that zinc sulphate solutions probably contain a complex anion \( \text{Zn(SO}_4\text{)}^2^- \).

The suggestion that the abnormal behaviour of certain electrolytes might be accounted for by assuming the formation of complex ions was first put forward by Kittorf who in the course of his study of migration discovered that the migration ratio for the anion in solution of many double salts and certain single ones decreased rapidly with increase of concentration and at high concentration became greater than minus one.

The evidence which has been collected shows that zinc in
aqueous solutions of its salts has a tendency to form a complex ion.

Complex formation has been shown to be promoted by rise of temperature. If this did take place it would be evidenced by a decrease in zinc ion concentration which would give a decrease in activity. The experimentally found values of exhibit an increase with temperature which means that complex formation, if any does exist in Zinc sulphate solutions of the strength used, decreases with rise in temperature. This disagrees with the general effect of temperature on complex formation.

These results therefore tend to throw considerable doubt on the presence of complex formation in dilute aqueous solutions of zinc sulphate. Present work on complete ionization and ionic attraction has arrived at a similar conclusion.

**II HYDRATION OF THE IONS.**

A number of circumstances have led to the belief that many electrolytes are "hydrated" in solution. The latest idea is that each solute molecule is surrounded by sheaths of solvent water molecules which vary in number and proximity according to the nature of the electrolyte and the general condition of the solution concerned as regards concentration, temperature etc.

The formation of hydrates has been supported by the work of **Jones & Ota** (Amer. Chem. Jour. 22, 5, 1909) freezing point determinations, **Jones** (Zeit. Phys., Chem. 74, 325, 1910) resume of general results, **Riesenfeld & Reinhold** (Zeit. Phys., Chem. 65, 672, 1909) comparison of ionic volume and ionic mobility;
transport observations.

Remy (Trans. Farad. Soc., V23, 361, 1927) transference data. The work of Remy has extended the idea of hydration to the ions and has enabled the number of water sheaths of the various ions to be calculated (e.g. Li 13.6, Na 7.4, Mg 14.1, Ca 12.1).

Ejlersum (Z. Anorg. Chem., 109, 275, 1920) considers that E.M.F. measurements give the activities of nonhydrated ions and he has evaluated ionic hydration values on the assumption of complete dissociation.

In concentrated solutions owing to the large number of zinc ions and sulphate ions present the relative hydration of ions will decrease and hence the activities will appear to be greater than their concentration warrants; thus the presence of the minimum point in values of the activity coefficients of zinc sulphate, as has been stated above. The graphs on Fig. 1V show the various minimum points obtained at the various temperatures, which all appear to be in the neighbourhood of concentration 0.5M. This value differs from that of Bray (see Table 1) who obtains the minimum in the neighbourhood of 2.0M concentration for Zinc Sulphate.

MacInnes and Parker (J. Amer. Chem. Soc., 37, 1445, 1915)

Ellis (ib. 39, 737, 1916) and

Noyes (ib. 39, 2532, 1917)

MacInnes, Beattie and Chow (ib. 42, 482, 1920)
have shown that has a minimum at about 0.5M.
The effect of Temperature on the hydration of the zinc ions cannot be definitely stated but it is to be expected that it will favour the dissociation of the zinc hydrates which exist in solution e.g.

\[ \text{Zn(H}_2\text{O)}_n \text{Zn} \text{ nH}_2\text{O} \]

This dissociation from left to right will increase the concentration of the active zinc ions and give a greater activity coefficient for the Zinc sulphate.

The graphs on Fig. 111 show this to be the case.

From a comparison of these graphs it is seen that the variation with temperature of the activity coefficient of the more dilute solutions is greater than that of the more concentrated. This is to be expected when the relative number of zinc ions liberated in the above equation is considered for the various concentrations; that is, the relative number of zinc ions liberated on increase of Temperature will be greater in those solutions which contain a small concentration of zinc sulphate.

Randall, Mcbain, and White (J. Amer. Chem. Soc. Vol. 48, 2517, 1926) have determined the activity of soap solutions at temperatures of 0°C. and 90°C. Their results show that the activity increases with temperature.

Review of Hypothesis.

1. The variation of the activity coefficients with temperature does not support the theory of complex formation in aqueous solutions of zinc sulphate of concentrations below 1M.
2. The behaviour of zinc sulphate solutions with change of concentration and temperature is satisfactorily explained on the assumption of Hydration of the ions.

3. The experimental results agree with the theories of complete ionization and inter-ionic attraction.
SUMMARY OF WORK.

1. The Electrode Potential of zinc has been determined at temperatures between 15°C and 50°C.

2. From the knowledge of the Electrode Potential of zinc at temperatures between 15°C and 50°C, the values of the activity coefficients of zinc sulphate solutions at these temperatures have been calculated.

3. The variation with temperature in values of the activity coefficient appears to be best explained on the assumption of Hydration of the ions. A graph of the relation between and Temperature is given.

4. From the Temperature coefficient determined from the half cells used the heat of reaction at the zinc electrode has been determined at 25°C. Further heats of reaction at other temperatures can be evaluated by substitution if required.

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