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THE SOLUBILITY PRODUCT

OF MERCURIC CHLORIDE

AND DERIVED THERMODYNAMIC FUNCTIONS
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SUMMARY

1. The solubility product of mercurous chloride has been determined at the temperatures 15°C, 20°C, 25°C, 30°C, 35°C, 40°C and 45°C by means of an Owe cell.

2. The applicability of the Owe extrapolation procedures to 2:1 electrolyte has been further tested.

3. Thermodynamic functions for the solution process
   \[ \text{Hg}_2\text{Cl}_2 (s) \rightarrow \text{Hg}^{++} (\text{soln}) + 2\text{Cl}^- (\text{soln}) \]
   have been calculated.

4. Values of the thermodynamic functions have been derived for the reaction
   \[ \text{Hg}^{++} (\text{soln}) + \text{F}_2 (s) \rightarrow 2\text{F}^- (1) + 2\text{H}^+ (\text{soln}) \]

5. The relative partial molar entropy of the mercurous ion has been calculated and compared with the values obtained by previous workers.

6. A value for the entropy change for the dimerisation reaction
   \[ 2\text{Hg}^+ (\text{soln}) \rightarrow \text{Hg}_2^{++} (\text{soln}) \]
   has been estimated.

7. Activity coefficients of mercurous chloride over the ionic strength range .005m to .05m have been tabulated.

8. The standard potential of mercury and the equilibrium constant for the reaction
   \[ \text{Hg}^{++} (\text{soln}) + \text{F}_2 (1) \rightarrow \text{Hg}_2^{++} (\text{soln}) \]
   have been calculated.
INTRODUCTION

There are two types of liquid junctions encountered in electrochemical studies: homoionic junctions involving solutions differing only in ionic concentrations and heterionic junctions involving differences in ionic species. The potentials at heterionic junctions are not subject to simple thermodynamic definition which accounts for the necessity of their elimination when such junctions occur in cells used for thermodynamic purposes.

Owen and co-workers 1,2,3,4 introduced extrapolation procedures for the elimination of these junction potentials thus providing a means whereby direct and precise measurement of the solubility products of electrolytes of low solubility can be carried out. The criteria for the extrapolations to be linear have been well tested in the case of 1:1 electrolytes and found to be adequate.

Law 5 and Read 6 have extended the use of these extrapolation procedures to unsymmetrical electrolytes with determinations of the solubility product of mercurous chloride and mercurous bromide respectively. Both Law and Read used cells which did not obey the second criterion of Owen that constant ionic strength be maintained in the cells throughout an extrapolation, but Read was able to show that in his case this did not affect the extrapolation.

By combining the solubility product of mercurous bromide with the standard electrode potential of the
mercury/mercurous bromide electrode, Read was able to obtain a value of the standard potential of mercury. The value so obtained differed considerably from values obtained directly or indirectly by Linhart 7, Lewis and Randall, Law and Christensen 5. However good agreement was obtained with the value obtained by Bonner and Unietis 10 who measured the standard potential of mercury directly using a glass electrode. Read recalculated data obtained by Stetanen and Sillen 11 and showed that the value so obtained agreed with the value of Bonner and Unietis and with Read's own value.

However the standard potential of the mercurous bromide electrode is not known as accurately as the standard potential of the calomel electrode which has been accurately measured by Hils and Ives 12, Orzybowsk 13, Pouradier and Chateau 14, and by Mueller and Reutner 15. The values obtained are in good agreement with each other and seem beyond reproach.

In the present work, the solubility product of mercurous chloride is investigated with the view of combining this with the more accurately known standard potential of the calomel electrode at various temperatures to obtain a value of the standard potential of mercury and other thermodynamic functions. Furthermore a cell is used which obeys both the criteria postulated by Owen and provides a more exact test of the applicability of the Owen extrapolation methods to 2:1 electrolytes.
The electromotive force of a cell without liquid junction can be written in the form

\[ E = E^0 - \frac{RT}{nF} \sum \ln a \]

and writing the activity \( a \) in terms of the molality \( m \) and activity coefficient \( \gamma \), and putting \( k = 2.30259 \frac{RT}{F} \),

\[ E + \frac{k}{n} \sum \log m = E^0 - \frac{k}{n} \sum \log \gamma \]

Thus the evaluation of the standard potential \( E^0 \) depends on the evaluation of the term \( \log \gamma \).

The basis of the evaluation of \( \log \gamma \) is the Debye Huckel theory \(^{16}\) which relates \( \log \gamma \) to the ionic strength \( I \) of the solution.

\[ -\log \gamma = Az^2 \sqrt{I} \quad \text{where} \quad I = \frac{1}{2} \sum m_i z_i^2 \]

The formula for the activity coefficient has been proposed in a variety of different forms by Hitchcock \(^{17}\), Brown and MacInnes \(^{18}\), Cronwall, La Mer and Sanved \(^{19}\), Guntelberg \(^{20}\), Guggenheim \(^{21}\) and Davies \(^{22}\) but all the variations are based on the Debye Huckel theory.

Hales, Bower, Ganham and Prue \(^{23}\) have shown that the form of the activity coefficient expression can be a limiting factor in the interpretation of data. They studied the cell

\[ \text{Pt; } \text{H}_2(\text{g}) | Ca(OH)_2(m_1), | \text{KCl or CaCl}_2(m_2) | \text{AgCl; Ag} \]

with the view of obtaining a dissociation constant of \( \text{CaOH}^+ \) over a range of temperature.

They showed that for KCl in the centre compartment
\[ \log K_2 = \log K_w - \log (\gamma_{\text{Cl}} \gamma_{\text{OH}}^{m_{\text{Cl}}}) + \log \frac{m_{\text{OH}} - m_{1}}{2m_{1} - m_{\text{OH}}} + \log \frac{Y_{\text{Ca}} Y_{\text{Cl}}}{Y_{\text{CaOH}}} \]

where \( K_2 \) is the dissociation constant of \( \text{CaOH}^+ \).

\( K_w \) is the ionic product of water.

Calcium hydroxide is a fairly strong base, so that the concentration of \( \text{CaOH}^+ \) is much smaller than that of \( \text{Ca}^{++} \) i.e. the ratio \( \frac{m_{\text{OH}} - m_{1}}{2m_{1} - m_{\text{OH}}} \) is large.

Now \( \log m_{\text{OH}} = \log K_w - \log (\gamma_{\text{Cl}} \gamma_{\text{OH}}^{m_{\text{Cl}}}) + \log (\gamma_{\text{Cl}}/\gamma_{\text{OH}}) \)

The sensitivity of \( \log K_2 \) to the estimated \( m_{\text{OH}} \) is too great to permit the a priori assumption that \( \gamma_{\text{Cl}} \) and \( \gamma_{\text{OH}} \) are equal in all of the buffer solutions studied.

Thus to achieve greater generality:

\[ \log (\gamma_{\text{Cl}}/\gamma_{\text{OH}}) = kI \]

where \( k \) is an arbitrary constant.

It was found that the value of \( \log K_2 \) depended on the value of \( k \) used. For a given value of \( k \) it was found that the value of \( \log K_2 \) at \( I = 0 \) did not appear to depend on the form of the activity coefficient expression used for the term \( \gamma_{\text{Cl}} \gamma_{\text{OH}}^{m_{\text{Cl}}} \). However the slopes of the plots \( \gamma_{\text{Cl}} \) against \( I \) did depend on the form of the activity coefficient expression used. True and co-workers were unable to obtain an unambiguous value of the dissociation constant of \( \text{CaOH}^+ \) because of these uncertainties.

Thus there is some uncertainty as to the form of the activity coefficient expression. Reid has used a modified Davies equation (similar to the expression proposed by Schonheimer) which has the advantage of enabling direct
extrapolation against ionic strength. From the work of
Freud and co-workers it would appear that this would make
little difference to the value of the standard potential
obtained.

For cells with liquid junctions a further difficulty
arises. This is the heterionic liquid junction potential
which cannot be treated by thermodynamic means, and thus
must be eliminated if the cells are to be used for thermo-
dynamic purposes.

Owen and co-workers \(^1,2,3,4\) have introduced extra-
polation procedures for the elimination of liquid junction
potentials. The criteria postulated by Owen for the
extrapolations to be linear are:

I. The composition of the liquid systems in contact
are so chosen that, in a series of measurements, these
systems can be made to approach by extrapolation either
absolute identity or some condition which may be treated
by present thermodynamic methods.

II. The ionic strengths of the liquid systems in contact
are the same and the extrapolation is performed at constant
ionic strength.

These criteria for the extrapolations to be linear
have been well tested in the case of 1:1 electrolytes and
found to be adequate. Results obtained by Read indicate
that these criteria will also hold for 2:1 electrolytes.
Thus by making use of Owen's criteria for the elimination
of liquid junction potentials and using an appropriate
expression for the activity coefficients, standard potentials
can be evaluated.
THE SOLUBILITY PRODUCT OF MERCURIC CHLORIDE

The earliest figure for the solubility product of mercuric chloride was obtained by Behrend 24 who used a volumetric method of determining the concentration of chloride ions, using a sensitive electrometer. This gave a value of $1.64 \times 10^{-17}$ at 18°C.

Sherrill 25 by indirect means obtained from complex formation a value of $4.0 \times 10^{-18}$ at 25.5°C.

Ley and Heimbucher 26 measured the electromotive forces of cells of 0.1M and 1M calomel electrodes with 0.1M solutions of mercurous perchlorate and obtained values of 0.420 and 0.472 int. volts respectively. By sugar inversion they found that 3.4% of mercurous perchlorate contained in a 0.1M solution of that salt is hydrolysed and they assume that the dissociation of mercurous perchlorate was the same as that of barium perchlorate, which had been determined by conductivity measurements. This led to a solubility product of $2.0 \times 10^{-18}$ at 20°C.

Kohlrausch 27 measured the conductivity of a saturated solution of mercurous chloride in water. He obtained a value for the mercurous ion by conductance measurements on a solution of mercurous nitrate. However no allowance was made for activity coefficients or hydrolysis. At 24.6°C he obtained a value of $8.4 \times 10^{-16}$ for the solubility product.

Eversole and Aclachlan 28 determined the solubility of mercurous chloride in a solution of perchloric acid
and also in nitric acid by photometric means. By gradually increasing the amounts of the two reactants, turbidity was caused in the more concentrated of a series of solutions. The solubility was then taken between the highest concentration which failed to cause turbidity and the lowest concentration at which turbidity could be observed. At 25°C this led to a solubility product of $3.5 \times 10^{-16}$.

Erodink$^{28,30}$ has measured the emfs of a series of cells of the type

$$\text{H}_2 \mid \text{H}_2\text{SO}_4 \text{O}_3 \text{ Co} \mid \text{M}_2\text{O}_3 \text{ saturated} \mid \text{KCl} \text{ (c)} \mid \text{H}_2\text{Cl}_2 \mid \text{H}_2$$

He obtained the activity coefficients of the mercurous ion in aqueous solution from mercurous nitrate solutions of various concentrations. He obtained the following values for the solubility product of mercurous chloride:

- $2 \times 10^{-19}$ at 11°C
- $3.4 \times 10^{-19}$ at 15°C
- $5.3 \times 10^{-19}$ at 19°C
- $11.3 \times 10^{-19}$ at 25°C
- $12.2 \times 10^{-19}$ at 26.5°C

Dry and Gleamin$^{31}$ calculated a value of $1.33 \pm 0.01 \times 10^{-18}$ on the molality scale at 25°C for the solubility product of calomel from accurate measurements of the standard potential of the calomel electrode by Hills and Ives$^{12}$, and that of the mercury/mercurous ion couple by Bonnier and Uniecki$^{10}$.

THE STANDARD POTENTIAL OF THE CALOMEL ELECTRODE

The calomel electrode, introduced by Ostwald in 1890, was widely accepted as a reference electrode until 1920.
by which time its limitations had been discovered and the electrode had fallen into disrepute as an instrument of precision. All the early work was carried out in solutions containing dissolved air; although the reaction
\[ 2Hg + 2HCl + \frac{1}{2}O_2 = Hg_2Cl_2 + H_2O \]
was known to occur, it was thought to be significant only at low concentrations.

In 1922 Gerke\textsuperscript{32} carried out the first reliable measurements with the calomel electrode, using the cells of the type \( Ag, AgCl \); HCl or KCl (m); \( Hg_2Cl_2, Hg \) containing solutions which had been thoroughly deoxygenated. The value of the electromotive force of the cell should be independent of the chloride ion concentration at each temperature and should equal the difference between the standard potentials of the \( Hg \mid Hg_2Cl_2 \) and \( Ag \mid AgCl \) electrodes.

Randall and Young\textsuperscript{33} obtained the same average value of 0.0455 int. volts for the electromotive force at 25\(^\circ\)C as did Gerke. Combining this value with the accepted value of 0.2224 abs. volts\textsuperscript{34} for the \( Ag \mid AgCl \) gives a standard potential of 0.2679 abs. volts for the calomel electrode, compared with the value of 0.2680 abs. volts accepted today. However the reliability of the value of Gerke and Randall and Young was not high on account of comparatively large variations of the electromotive forces between the cells.

Mueller and Reuther\textsuperscript{15,35} measured the electromotive force of the cell
\[ Pt \mid H_2 \mid HCl (m) \mid Hg_2Cl_2 \mid Hg \]
They determined the standard potential from the relation
\[ E = E^0 - \frac{2RT}{F} \ln a_{\text{HCl}} \]

Using the experimental values of the mean activity coefficients of HCl found by Harned and Sherrill. They found that the standard potential of the calomel electrode is given by the equation

\[ E = 0.2680 - 3.12 \times 10^{-4}(t - 25) - 3.38 \times 10^{-6}(t - 25)^2 + 7.11 \times 10^{-9}(t - 35)^3 \text{ in abs. volts.} \]

The authors claimed a reproducibility of 0.10 mV and used a careful technique involving the complete exclusion of oxygen.

Hills and Ives made a series of studies on the reproducibility of the calomel electrode and recommended a series of precautions to ensure reproducibility.

Using a cell similar to that used by Mueller and Reuther, they obtained a value of \( E^0 = 0.26796 \) abs. volts at 25°C for the standard potential of the calomel electrode.

On the basis of measurements on the cell

\[ \text{Ag} : \text{AgCl} \mid \text{KCl(m)} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg} \]

and using an equation for \( E^0 \text{AgCl} \) as a function of temperature, Pouradier and Chateau determined the variation of the calomel electrode as a function of temperature up to 70°C. They found that

\[ E^0 = 0.26804 - 3.057 \times 10^{-4}(t - 25) - 3.28 \times 10^{-6}(t - 25)^2 - 3.0 \times 10^{-9}(t - 25)^3 \text{ in abs volts.} \]

This equation agrees well with that of Mueller and Reuther.

The most recent determination of the standard potential of the calomel electrode was by Grzybowski. The cell used was of the type \( \text{Pt} : \text{H}_2 \mid \text{HCl(m)} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg} \)
and activity coefficients were evaluated by means of the Debye Hückel equation, and the standard potential was evaluated by a series of approximations. The standard potential up to 60°C is given by the equation

$$\mu^0 = 0.266469 - 3.46466 \times 10^{-4}(t - 30) - 2.86428 \times 10^{-5}(t - 30)^2$$

$$+ 8.5384 \times 10^{-9}(t - 30)^3$$ in abs. volts.

Satisfactory agreement was found between thermodynamic quantities calculated from this equation and those quoted by the National Bureau of Standards. 33

The standard potential of the calomel electrode has been recalculated from the data obtained by Grzybowski using a modified Davies equation for the activity coefficients instead of the Debye Hückel equation used by Grzybowski. Now

$$E = E^0 - \frac{2RT}{F} \ln a_{\text{HCl}} \quad \text{ ... (1)}$$

Using the modified Davies equation

$$- \log Y = A \alpha^2 \frac{J_T}{1 + J_T} + bI$$

for the activity coefficients and substituting in equation (1) we obtain

$$E = E^0 - 2k \log m \cdot \frac{2kA J_T}{1 + J_T} - 2kbI$$

where $k = 2.30259 \frac{RT}{F}$

$$\therefore E + 2k \log m \cdot \frac{2kA J_T}{1 + J_T} = E^0 - 2kbI$$

Therefore a plot of $E + 2k \log m \cdot \frac{2kA J_T}{1 + J_T}$ vs I should be linear with an intercept $E^0$. The values of the Debye Hückel constant $A$ used are those of Manov, Bates, Hamer and Acree 35 and are the same ($\pm 0.0001$) as those used by Grzybowski.

The relevant data in abs. volts is given in Table I and plotted in Graph I.
Table I.

\( m = \) molality of HCl  
EMFs in abs. volts

<table>
<thead>
<tr>
<th>( m )</th>
<th>0.0050550</th>
<th>0.0059415</th>
<th>0.0072655</th>
<th>0.0082532</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>0.53706</td>
<td>0.52942</td>
<td>0.51978</td>
<td>0.51374</td>
</tr>
<tr>
<td>20°C</td>
<td>0.54033</td>
<td>0.53253</td>
<td>0.52276</td>
<td>0.51661</td>
</tr>
<tr>
<td>25°C</td>
<td>0.54349</td>
<td>0.53560</td>
<td>0.52564</td>
<td>0.51933</td>
</tr>
<tr>
<td>30°C</td>
<td>0.54656</td>
<td>0.53845</td>
<td>0.52835</td>
<td>0.52189</td>
</tr>
<tr>
<td>35°C</td>
<td>0.54944</td>
<td>0.54118</td>
<td>0.53089</td>
<td>0.52435</td>
</tr>
<tr>
<td>40°C</td>
<td>0.55219</td>
<td>0.54377</td>
<td>0.53328</td>
<td>0.52664</td>
</tr>
<tr>
<td>45°C</td>
<td>0.55432</td>
<td>0.54626</td>
<td>0.53556</td>
<td>0.52883</td>
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</table>

<table>
<thead>
<tr>
<th>( m )</th>
<th>0.0093286</th>
<th>0.0117000</th>
<th>0.0162626</th>
<th>0.0175946</th>
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<tr>
<td>15°C</td>
<td>0.50730</td>
<td>0.49705</td>
<td>0.48147</td>
<td>0.47779</td>
</tr>
<tr>
<td>20°C</td>
<td>0.51059</td>
<td>0.49967</td>
<td>0.48382</td>
<td>0.48009</td>
</tr>
<tr>
<td>25°C</td>
<td>0.51323</td>
<td>0.50214</td>
<td>0.48600</td>
<td>0.48221</td>
</tr>
<tr>
<td>30°C</td>
<td>0.51571</td>
<td>0.50445</td>
<td>0.48810</td>
<td>0.48421</td>
</tr>
<tr>
<td>35°C</td>
<td>0.51803</td>
<td>0.50683</td>
<td>0.49001</td>
<td>0.48607</td>
</tr>
<tr>
<td>40°C</td>
<td>0.52028</td>
<td>0.50864</td>
<td>0.49177</td>
<td>0.48775</td>
</tr>
<tr>
<td>45°C</td>
<td>0.52238</td>
<td>0.51095</td>
<td>0.49343</td>
<td>0.48939</td>
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</table>

The values of the intercepts are compared with the data of Pouradier and Chateau, Mueller and Reuther, Hills and Ives and the original data of Grzybowski in Table II.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gryzowski Original</th>
<th>Recalculated</th>
<th>Pouradier and Chateau</th>
<th>Mueller and Reuther</th>
<th>Hills and Ives</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>2710.5</td>
<td>2708.5</td>
<td>2707.7</td>
<td>2707.7</td>
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<tr>
<td>20°C</td>
<td>2696.8</td>
<td>2694.2</td>
<td>2684.9</td>
<td>2684.6</td>
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<tr>
<td>25°C</td>
<td>2681.3</td>
<td>2680.3</td>
<td>2670.4</td>
<td>2679.9</td>
<td>2679.6</td>
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<td>30°C</td>
<td>2664.7</td>
<td>2664.4</td>
<td>2664.3</td>
<td>2663.5</td>
<td></td>
</tr>
<tr>
<td>35°C</td>
<td>2646.7</td>
<td>2645.5</td>
<td>2646.5</td>
<td>2645.4</td>
<td></td>
</tr>
<tr>
<td>40°C</td>
<td>2627.3</td>
<td>2626.7</td>
<td>2627.1</td>
<td>2625.7</td>
<td></td>
</tr>
<tr>
<td>45°C</td>
<td>2606.6</td>
<td>2605.4</td>
<td>2605.9</td>
<td>2604.5</td>
<td></td>
</tr>
</tbody>
</table>

Thus the most probable values for the standard potential of calomel are as follows:

\[ T°C \quad 15 \quad 20 \quad 25 \quad 30 \quad 35 \quad 40 \quad 45 \]

\[ E^0 \quad 2708 \quad 2695 \quad 2680 \quad 2664 \quad 2646 \quad 2627 \quad 2605 \]

It will be noted that with the exception of the value at 15°C which is 0.05 mv lower, the most probable values taken from the work of Gryzowski (recalculations), Pouradier and Chateau, and Mueller and Reuther are identical with the recalculated value of Gryzowski.

The standard potential of the calomel electrode as a function of temperature between 15°C and 45°C is

\[ E = 0.2664 - 3.382 \times 10^{-4}(t - 30) - 3.28 \times 10^{-6}(t - 30)^2 + 2.22 \times 10^{-8}(t - 30)^3 \]

\[ t \text{ in °C} \]

\[ E = 0.8861 - 4.725 \times 10^{-3}T + 1.5323 \times 10^{-6}T^2 - 2.222 \times 10^{-9}T^3 \]

\[ T \text{ in °C} \]
Read has discussed the above topics and has recalculated several sets of data, a summary of which is given below in Table III. In this table \( e_{10}^0 \) and \( e_{21}^0 \) are the standard potentials of the mercury/mercurous electrode and the mercuric/mercurous electrode respectively. \( k_0 \) is the mercuric mercurous equilibrium constant. The values listed in column b are those recalculated by Read using extrapolation procedures, similar to those used in this work, for the determination of activity coefficients and, where the data allowed, junction potentials.
### TABLE III

<table>
<thead>
<tr>
<th>YEAR</th>
<th>WORKER</th>
<th>$E_{10}$</th>
<th>$E_{20}$</th>
<th>$k_0$</th>
<th>REF.</th>
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<tr>
<td></td>
<td></td>
<td>$a$</td>
<td>$b$</td>
<td>$a$</td>
<td>$b$</td>
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<td>1916</td>
<td>Linhart</td>
<td>.7923</td>
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<td></td>
<td>Recalc. by</td>
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<td></td>
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<tr>
<td></td>
<td>Lewis &amp; Randall</td>
<td>.7986</td>
<td></td>
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<tr>
<td></td>
<td>Recalc. by</td>
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<td>Tray &amp; Hershey</td>
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<td>1926</td>
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<td>Carter &amp; Robinson</td>
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<td>Popoff et al</td>
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<td>Bonner &amp; Unietis</td>
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<td>Schwarzenbach &amp; Anderson</td>
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<td>Gillen &amp; Pietanen</td>
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REF. Reference.
The solubility product of mercurous chloride has been investigated by means of the cell

\[
\text{Hg}_2^{2+} \mid \text{Hg}_2\text{Cl}_2 \mid \text{BaCl}_2 \left( \frac{x m}{3} \right) \mid \text{Ba(ClO}_4 \text{)}_2 \left( \frac{x m}{3} \right) \mid \text{Hg}_2(\text{ClO}_4 \text{)}_2 \left( \frac{x m}{3} \right) \mid \text{c} \mid \text{Hg}_2(\text{ClO}_4 \text{)}_2 \left( \frac{x m}{3} \right) \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}_2
\]

This cell is of the Owen type and differs from that used by Read and Law in that the centre compartment also contains a 2:1 electrolyte. Also the ionic strength equals m and is thus independent of the value of x.

The emf of the cell is given by

\[
E = \frac{k}{2} \log \frac{a'' \text{Hg}_2^{2+}}{a' \text{Hg}_2} + E_J
\]

where \(a''\) and \(a'\) refer to the activities of the mercurous ions in the right and left hand compartments respectively, \(E_J\) is the junction potential and \(k = 2.30259 \frac{RT}{F}\). The thermodynamic solubility product \(K = a'' \text{Hg}_2^{2+} a' \text{Cl}^-\) is used to substitute for \(a'' \text{Hg}_2^{2+}\) and writing \(a' = Y_m\) the emf expression becomes

\[
E = \frac{3k}{2} \log \frac{X_m}{3} + k \log 2 + \frac{k}{2} \log Y_{\text{Hg}_2^{2+}} + \frac{k}{2} \log Y_{\text{Cl}^-} - \frac{k}{2} \log K + E_J
\]

If the left hand side of this equation is plotted against \(x\) and extrapolated to \(x = 0\), junction potentials are eliminated. Substitution of the activity coefficient
expression \( \log y_1 = \frac{A z_i^2}{1 + \sqrt{1}} + b I \) gives

\[
(E - \frac{3k}{2} \log \frac{x_m}{3} - k \log 2)_{\lambda = 0} + \frac{3kA}{1 + \sqrt{1}} = - \frac{k}{2} \log K - \frac{k}{2}(b' + 2b'')I
\]

where \(b'\) and \(b''\) refer to the mercurous and chloride ions respectively. A plot of the left hand side of this expression against \(I - m\) should be linear with slope \(-\frac{k}{2}(b' + 2b'')\) and intercept \(-\frac{k}{2} \log K\) where \(K\) is the thermodynamic solubility product of mercurous chloride.

Guggenheim \(^{45}\) has found that with cells of the type

\[
\text{H}_2 : \text{Hg}_2\text{Cl}_2 \mid \text{0.1N KCl} \mid \text{c KCl} \mid \text{0.1N KCl} \mid \text{Hg}_2\text{Cl}_2 ; \text{H}_2
\]

the emf produced was independent of the concentration \(c\) of the bridge potassium chloride solution. This was tested further using cells of the type

\[
\text{H}_2 : \text{Hg}_2\text{Cl}_2 \mid \text{BaCl}_2(\frac{x_m}{3}) \mid \text{X} \mid \text{Hg}_2\text{(ClO}_4)_2(\frac{x_m}{3}) \mid \text{Hg}_2\text{Cl}_2 ; \text{H}_2
\]

where \(X\) was a variety of solutions. The emfs of the cell are contained in Table VIII.

Using the cell

\[
\text{H}_2 : \text{Hg}_2\text{Cl}_2 \mid \text{BaCl}_2 \cdot 004 \mid \text{Ba(ClO}_4)_2 \cdot 004 \mid \text{Hg}_2\text{(ClO}_4)_2 \cdot 004 \mid \text{Hg}_2\text{Cl}_2 ; \text{H}_2
\]

where \(c\) was \(\text{Hg}_2\text{Cl}_2 \cdot 004\). The emfs of the cell are contained in Table IX.

the perchloric acid concentration \(y\) was decreased and an attempt was made to obtain an approximate value of the hydrolysis constant for the mercurous ion. Measurements were taken with an acid concentration of 0.005, 0.006, 0.002, 0.001, 0.0001 molar. The emfs of the cell are contained in Table IX.
PERCHLORIC ACID

Perchloric Acid [Analal, Hopkin and Williams] was used without further purification.

HYDROCHLORIC ACID

Hydrochloric Acid [Analal, Hopkin and Williams] was used without further purification.

HAFNOCIOUS PERCHLORATE

Mercuric perchlorate, prepared by dissolving red mercuric oxide in perchloric acid, was reduced to the mercurous state by shaking with mercury. This method is due to Chikashige\textsuperscript{46}, later modified by Popoff, Riddick, Wirth and Cush\textsuperscript{43}.

Red mercuric oxide (Ray and Paker) was used without further purification.

About 100 gms of red mercuric oxide was dissolved in perchloric acid until a slight turbidity remained. The solution was then filtered through a scintillated glass disc; concentrated over sulphuric acid in a vacuum desiccator at 50°C and crystallised.

The mercuric perchlorate was then recrystallised from perchloric acid twice; the crystals were then dissolved in perchloric acid and the solution was shaken violently with mercury under an atmosphere of carbon dioxide for 60 hours. Chikashige stated that only a few minutes were required to reduce the mercury to the mercurous state but Popoff found that shaking at 50°C for 48 hours was required. This time factor probably accounts for the inability of
Carter and Robinson to prepare mercurous perchlorate by this method.

Popoff et al. drained their mercuric perchlorate crystals in a centrifuge at 800 - 900 r.p.m. for 20 minutes.

Thaw dried mercurous perchlorate crystals by centri- fuging the crystal over cotton wool for 15 minutes at 600 r.p.m. This method is likely to allow oxidation and/or hydrolysis of the mercurous perchlorate crystals.

**MERCURIC CHLORIDE**

Mercuric chloride was prepared by the method of Hills and Ives.

A solution of 25 hydrochloric acid was electrolysed under a potential difference of 2 volts using a platinum gauze cathode and a pool of mercury as the anode. Both acid and mercury were kept well stirred by a mechanical stirrer - the stirrer just skimming the top of the mercury anode.

After two hours the electrolysis was stopped, the electrodes removed and stirring continued for a further 6 hours.

The precipitate was allowed to settle, the electrolyte was decanted off and replaced by fresh hydrochloric acid and the stirring was then continued for a further 6 hours.

This was repeated and the calomel was then washed, first with 25 hydrochloric acid and then with distilled water.

The calomel was filtered at the pump and washed with distilled water until the washings gave no test for chloride.

The product was then dried and kept in a blackened desiccator over P₂O₅.
BARIUM CHLORIDE

Barium Chloride [Hopkin and Williams Analar] was used without further purification.

MERCURY

All mercury used was passed through a column containing a solution of 3% mercurous nitrate in 5% nitric acid at least fifteen times before being vacuum distilled twice. Tests for lead, silver, zinc and cadmium, as described by Vogel, were negative.

NITROGEN

Nitrogen from a cylinder was purified by passing it through concentrated sulphuric acid, over copper clips, at 750°C in an electric furnace, through a saturator, a chromous sulphate solution, and an oxygen indicator solution, a copper sulphate solution to remove any sulphur from rubber bungs, and a series of three saturators, the last two of which were in the thermostat bath before it was passed through the cell solutions.

The copper clips were packed into a silica tube in sections separated by copper gauze to prevent channeling.

The chromous sulphate solution was prepared by reducing an acidified 0.4M solution of chrome alum with zinc amalgam in a Jones reductor column. Following recommendations of Stone and Deason, a freshly-prepared chrome alum solution, violet in colour, acidified with sulphuric acid was used as this is more readily reduced than the corresponding green solution. Sulphuric acid was used in preference to hydrochloric acid, as the chronic
sulphate solution is more stable under these circumstances. The light blue chromous solution was run directly from the Jones reductor column into the gas line which had been previously flushed with nitrogen.

The indicator was an aqueous solution containing indigo carmine, glucose and potassium carbonate—an indicator that has been used for spectrophotometric determination of oxygen\(^{45}\). When reduced the indicator is a khaki colour which changes to a blue colour on oxidation. The reagent is very sensitive to oxygen and the fact that it remained a yellow-khaki colour at all times indicated that little, if any, oxygen remained in the nitrogen.

**SOLUTIONS**

The weights were intercalibrated and vacuum corrections were employed in all weighings. Weights of less than 40 mg were weighed to 0.05 mg on a kettler balance while larger weights were weighed to 0.01 mg.

A stock solution of approximately 0.5 M perchloric acid was standardised against borax using methyl red as indicator and employing a colour standard. Borax was recrystallised twice from distilled water and kept in a dessicator over a solution saturated with sucrose and sodium chloride as described by Vogel\(^{50}\). From the approximately 0.5 M perchloric acid solution, a 0.1000 M (± 0.05%) perchloric acid solution was prepared and used in the preparation of cell solutions.

All solutions of mercurous perchlorate were kept in contact with mercury and shaken regularly to ensure that
equilibrium was maintained. To prevent atmospheric oxidation, all mercurous perchlorate solutions were kept under carbon dioxide, a procedure initiated by Popoff. This procedure was extended to include also the period of preparation of mercurous perchlorate cell solutions. All distilled water used in the preparation of solutions had previously been deoxygenated with nitrogen from the gas line.

Potassium Iodate [Analar, Hopkin and Williams, Analab] was used without further purification.

The mercurous perchlorate stock solution was analysed for mercury (I) using a potassium iodate titration as described by Vökel. This titration is also known as Andrews' method and is discussed as such by Jesper. A blank titration was done using freshly-prepared mercurous chloride. The mercurous chloride was precipitated from mercurous nitrate [Analar, Hopkin and Williams] using hydrochloric acid. The precipitate was then filtered at the pump, washed thoroughly with dilute hydrochloric acid, dried and placed in a darkened desiccator over phosphorus pentoxide. Approximately 0.4 gms of HgCl₂ was weighed out and on analysis by potassium iodate gave a yield of 101.99% of Hg₂Cl₂. The appropriate correction factor was applied.

For the analysis of the stock solution, about 2 gms of solution containing about 0.5 gms of mercury was used.

The perchloric acid in the stock solution was obtained from the total perchlorate concentration determined by an ion exchange method. The resin used was a sulphonated polystyrene type of cation exchanger called Seokarte 225.
(Hopkin and Williams). The sodium form was converted in the usual way to the hydrogen form. On passing a solution of mercuric perchlorate through the column, mercurous ions were exchanged for hydrogen ions in the resin. The column was then washed thoroughly with several bed volumes of distilled water until the liquid issuing from the bottom was not acid to universal test paper. Tests for mercurous ions in the effluent solution were negative. The resulting perchloric acid solution was titrated against standard boric solution using methyl red indicator.

The barium perchlorate stock solution was prepared by dissolving barium hydroxide [Hopkin and Williams, AnalaR] in a perchloric acid solution. The perchloric acid concentration was obtained by titration of a sample of the stock solution with boric using methyl red indicator. By dissolving barium chloride [Hopkin and Williams, AnalaR] in perchloric acid of known strength, it was shown that barium ions did not affect the boric titration. The barium perchlorate concentration was found by difference from the total perchlorate concentration, which was determined by means of the ion exchange method.

The barium chloride stock solution was prepared by dissolving barium chloride [Hopkin and Williams, AnalaR] in perchloric acid of known strength.

An approximately 0.5 M sodium hydroxide solution was prepared by dissolving sodium hydroxide [Hopkin and Williams, AnalaR] in water. This solution was analysed by titration with standard perchloric acid using methyl red indicator.
ELECTRODES

These were prepared by the method of Hills and Ives\textsuperscript{12}.

Dry mercurous chloride was shaken with pure mercury when a skin of the admixture was formed. When a little of this was introduced on to pure mercury, a characteristic spreading of the mercurous chloride – mercury admixture over the mercury surface was noticed under certain conditions. This characteristic spreading was regarded by Hills and Ives as an "Essential prerequisite for the formation of a completely depolarised calomel electrode" and was only formed if the interaction of the mercury with the mercurous chloride was not too brief and providing there was no moisture present.

THE CELL

The cells used were similar to those used by Owen\textsuperscript{1,2,3,4} and the same as those used by Read\textsuperscript{9}. The three compartments were joined by three-way taps A and E, and all taps were lightly greased with Dow Corning\textsuperscript{2} Silicone grease. D and E are the external mercury contacts through the Pt insulants J and C.

To ensure that the levels of liquid in the two outer compartments were the same, the cells were placed in their stands in the thermostat bath, with the cell taps open. The cells were filled; the taps were then closed and liquid levels were marked on the outer compartments. Subsequently the cells were always filled to these marks. Following the method of Hills and Ives\textsuperscript{12}, the glass walls of the outer compartments were rendered hydrophobic by the use of a
silicone fluid under conditions which ensured bonding between the silicone and the glass. This eliminated any similar film which may have been formed by capillary action of the bulk solution between the mercury and the glass surfaces. Had any such action occurred, this part of the cell solution might be expected not to be in equilibrium with the bulk solution.

Hicks and Ives suggest furthermore that this siliconing of the glass may also have virtue in reducing ion exchange between dilute acid solution and glass.

The cells were rinsed with a 3% solution of silicone Fluid No. 200 in carbon tetrachloride and then baked at 350°C in an oven overnight. Any unbonded silicone was removed by washing with carbon tetrachloride. It is claimed that this silicone treatment is not affected by subsequent washing of the cells.

The cells were cleaned between measurements in the following manner - they were scrubbed with hot water and detergent, and rinsed successively with hot water, distilled water and methanol, and after draining, were dried in an oven for two hours.

In filling, the cells about 1.5 ml of pure mercury was introduced into the side compartments followed by calomel, as described previously. The centre compartment was filled to above tap C by means of an all-glass syringe fitted with a piece of fine-bore polythene tubing. Rubber plugs were placed over the outlets II and I and the outer compartments plus the covered outlets III and I were filled using the all-glass syringe and polyethylene tubing.

The solutions in the outer compartments were deoxygenated
using purified nitrogen, but, following the generally accepted practice, the centre compartment was not deoxygenated. Trial experiments showed that bubbling nitrogen for 2 hours after filling the cells and a further hour after leaving the cells overnight was required to deoxygenate the cell solutions. The different bubbling times quoted by Read are probably owing to a difference in bubbling rates.

The gas line was arranged so that the main inlet was connected to all the bubbler tubes in the outer compartments, and the outlets from these compartments were then connected to a common exit tube, which was a capillary tube to prevent back diffusion. This ensures that the gas pressure above the cell solutions was the same in all cases and hence there could be no solution flow owing to differences in gas pressure above the cell solutions, when the taps A and B were opened during measurements.

The overall effect of the removal of oxygen was to raise the measured potentials by 0.2 - 0.5 mV.

Before measurements at each temperature, tap C of each cell was opened to allow pressure adjustment in the centre compartment.

The cells were measured at seven temperatures taken at 5°C intervals from 15°C to 45°C. It was found that equilibrium was established in 3 hour after the temperature had been raised 5°C except in the case of the m = 0.005 cell when the time required was nearer to one hour.

In general, cell readings agreed to within ± 0.1 mV and repeated measurements were within the same limits of
error. However, at 45°C readings were only reproducible to ± 0.2 mV indicating higher errors in potentials measured at this temperature. Also, results for n = 0.005 are reproducible to ± 0.2 mV owing to the much higher cell resistances when working at these ionic strengths.

**OTHER APPARATUS**

The thermostatic bath was electrically heated and maintained at any particular temperature to within 0.02°C by a mercury toluene regulator. A refrigerating unit was attached to the bath and was used as required. Changes in temperature were effected by means of an immersion heater, a 5°C change taking about 15 minutes. A thermometer readable to ± 0.02°C, which was calibrated against a N.P.L. tested standard, was used to indicate bath temperatures. A mechanical stirrer was used but this was turned off during measurements to reduce diffusion effects and to eliminate possible electrical interference from this source.

The potentiometer was made by the Cambridge Instrument Company, having a range 0 to 1.8 volts and being readable to 0.05 mV.

The Weston Cadmium standard cell of the saturated type, which was used to calibrate the potentiometer before and after each measurement, was calibrated in the Electrical Standards Laboratory of the National School of Engineering and found to have an emf of 1.01861 absolute volts. The voltmeter was of the M'arsenval type made by the Leeds and Northrup Company, having an internal resistance of 11,000 ohms for critical damping and having a sensitivity of 2,500 ma per A with the scale at one metre.
Following the recommendations of White\textsuperscript{53}, the measuring apparatus was placed on a metal sheet which served as an equipotential surface to guard against DC potentials developed by DC leakage currents.
In Table IV are recorded the e.f.s of the cell

\[
\text{Hg} \quad \text{Hg}_2\text{Cl}_2 \quad \text{BaCl}_2 \quad \text{Hg}_2\text{Cl}_2 \quad \text{Hg}_2\text{Cl}_2 \quad \text{Hg}_2\text{Cl}_2 \quad \text{Hg}_2\text{Cl}_2 \quad \text{Hg}_2\text{Cl}_2 \quad \text{Hg}_2\text{Cl}_2
\]

\[
\text{HCl}_4 \quad (1-x) \quad \text{HCl}_4 \quad (1-x) \quad \text{HCl}_4 \quad (1-x) \quad \text{HCl}_4 \quad (1-x) \quad \text{HCl}_4
\]

where \( C = \frac{\text{Hg}_2\text{Cl}_2}{\text{Hg}} \)

at the seven different temperatures 15\(^\circ\)C, 20\(^\circ\)C, 25\(^\circ\)C, 30\(^\circ\)C, 35\(^\circ\)C, 40\(^\circ\)C, and 45\(^\circ\)C.

The corresponding values of the expression

\[ E = -\frac{3k}{2} \log \frac{x_m}{3} - k \log 2 \]

are given in Table V. A correction factor of 0.1 mV has been added to the values in this table. This factor allows for the change in equilibrium constant \( K_0 \) of the mercuric/mercurous equilibrium between the bulk solution which was analysed and where the ionic strength \( I = 2.5 \), and the cell solutions where \( I = 0.05 \) to 0.005. Data on the variation of \( K_0 \) with ionic strength obtained by Schwarzenbach and Anderson was used in the calculation.

The values of the expression (1) above are plotted against \( x \) in Graph II for all values of \( m \) at the temperatures 15\(^\circ\)C, 20\(^\circ\)C, 25\(^\circ\)C, 30\(^\circ\)C, and 45\(^\circ\)C, and the intercepts

\[ E = -\frac{3k}{2} \log \frac{x_m}{3} - k \log 2 \]

were listed in Table VI.

Using these intercepts, values of the expression

\[ E = -\frac{3k}{2} \log \frac{x_m}{3} - k \log 2 + \frac{3kA}{1.51} \]

were plotted against \( I \) (\( \text{m} \)) for all temperatures in Graph III and the intercepts \( -\frac{3}{2} \log \gamma \) are listed in Table VII.
### TABLE IV

**OBSERVED ELECTROLYTIC FORCES**

<table>
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<tr>
<th>Temp.</th>
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<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
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</table>

TABLE V

Corresponding values of $E = \frac{3x}{2} \log_{10} \frac{A_m}{3} - x \log_{10} 2$.

<table>
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<tr>
<th>Temp.</th>
<th>15°C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
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### Table VI

VALUES OF THE INTERCEPTS \( \left( x - \frac{3}{2} \log \frac{x}{3} - k \log 2 \right)_{x=0} \)

<table>
<thead>
<tr>
<th>Temp</th>
<th>15°C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
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### Table VII

CORRESPONDING VALUES OF
\[
\left( x - \frac{3}{2} \log \frac{x}{3} - k \log 2 \right)_{x=0} + \frac{3kA}{1+\sqrt{1}}
\]

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<tr>
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<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
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<td>5.293</td>
<td>5.298</td>
<td>5.305</td>
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<td>0.02</td>
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<td>5.265</td>
<td>5.267</td>
<td>5.272</td>
<td>5.276</td>
<td>5.280</td>
</tr>
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</table>
TABLE VIII

VARIATION OF M.F. WITH CENTRAL COMPARTMENT

Temperature = 25°C  Cell  m = 0.02  x = 0.6

Centre compartment

\[
\begin{array}{ccc}
\text{Ba(\text{ClO}_4)}_2 \times \frac{x}{3} & \text{HClO}_4 (1-x)m & m = 0.02 \quad x = 0.6 \\
\text{Ba(\text{ClO}_4)}_2 \times \frac{x}{3} & \text{HClO}_4 (1-x)m & m = 0.05 \quad x = 0.4 \\
\text{Ba(\text{ClO}_4)}_2 \times \frac{x}{3} & \text{HClO}_4 (1-x)m & m = 0.03 \quad x = 0.2 \\
\text{Ba(\text{ClO}_4)}_2 \times \frac{x}{3} & \text{HClO}_4 (1-x)m & m = 0.01 \quad x = 0.1 \\
\text{HClO}_4 & 0.1000 \text{ molar} &
\end{array}
\]

TABLE IX

HYDROLYSIS

Temperature = 25°C

\[
\begin{array}{ccc}
\text{HClO}_4 \text{ concentration} & X & \text{F} \\
(\text{molar}) & & \\
0.003 & 0.3218 & \\
0.006 & 0.3218 & \\
0.002 & 0.3212 & \\
0.001 & 0.3200 & \\
0.0001 & 0.3153 & \\
\end{array}
\]

The values of all relevant constants are given in Appendix I.

By the method of least squares the intercepts \[-\frac{k}{2} \log_{10} K\] have been fitted to the cubic equation

\[
\frac{k}{2} \log_{10} K = 0.5275 + 6.462 \times 10^{-5}(t-30) + 2.52 \times 10^{-6}(t-30)^2
\]

\[
-2.22 \times 10^{-8}(t-30)^3
\]

\[
= 1.3587 - 7.5398 \times 10^{-3} T + 2.273 \times 10^{-5}T^2 - 2.222 \times 10^{-7}T^3 - (2)
\]
The values of \( -\frac{\Delta H}{2} \log \gamma \) obtained from this equation are compared with the experimental values in Table V. The corresponding values of \( \log \gamma \), and \( \Delta H \) are also tabulated.

<table>
<thead>
<tr>
<th>Temp. C</th>
<th>( \frac{\Delta H}{2} \log \gamma )</th>
<th>( \log \gamma )</th>
<th>( \Delta H \times 10^{-18} )</th>
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<tbody>
<tr>
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<td>.5273</td>
<td>18.445</td>
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<td>.5272</td>
<td>18.127</td>
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<td>.5273</td>
<td>.5273</td>
<td>17.827</td>
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<tr>
<td>30</td>
<td>.5277</td>
<td>.5276</td>
<td>17.543</td>
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<tr>
<td>35</td>
<td>.5280</td>
<td>.5280</td>
<td>17.272</td>
</tr>
<tr>
<td>40</td>
<td>.5284</td>
<td>.5285</td>
<td>17.012</td>
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<tr>
<td>45</td>
<td>.5291</td>
<td>.5291</td>
<td>16.733</td>
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</table>

The standard free energy change for the reaction

\[ \text{Hg}_2 \text{Cl}_2 (s) \rightarrow \text{Hg}^{++} (\text{soln}) + 2\text{Cl}^- (\text{soln}) \]

is given by the expression:

\[ \Delta G^0 = 2.303 \log \gamma \]

The expression for the variation of \( \Delta G^0 \) with temperature obtained from equation (2) is

\[ \Delta G^0 = \Delta G^0 + \Delta H^0 \frac{T}{RT \log \gamma} \]

The negative temperature coefficient of the standard free energy is equal to the standard entropy change and this is given by

\[ \Delta S^0 = 349.35 - 2.899 T + 0.003072 T^2 \text{ e.u.} \]

Then the heat of solution \( \Delta H^0 = \Delta G^0 + T \Delta S^0 \) is given by

\[ \Delta H^0 = 62.554 - 1.0475 T + 0.002048 T^2 \text{ cal/mole.} \]
The accuracy of this work is not sufficient to justify further differentiation to obtain $\Delta S^0$.
The values of $\Delta H^0$, $\Delta S^0$, and $\Delta H^0$ calculated from these equations are listed in Table VI.

**Table VI**

Thermodynamic quantities for the reaction

$$ \text{Na}_2\text{Cl}_2(s) \rightarrow \text{Na}_2^+ \text{ (soln)} + 2\text{Cl}^- \text{ (soln)} $$

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\Delta H^0$ (cal.)</th>
<th>$\Delta S^0$ (e.u.)</th>
<th>$\Delta G^0$ (cal.)</th>
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DISCUSSION

MENTED

In cells that contain liquid junctions, some extra thermodynamic assumptions must be made in order to eliminate any potentials set up at these junctions. Owen, 1, 2, 3, 4 evolved a simple method for dealing with this situation wherein measurements were made on a series of cells in which the concentration of the heterolious causin., these liquid junction potentials was varied, but constant ionic strength was maintained through any such set of cells. Under these conditions a plot of emf against concentration should be linear and this was found to be the case.

Law, 5 and Read, 2 measured cells in which, in any given cell, the ionic strength was constant throughout, but the ionic strength was not constant during the extrapolation. This variation in activity coefficients will cause the plots against x to be slightly curved and assuming linear extrapolations will cause errors in the intercepts at x = 0. Read was able to show that these errors would be small over the concentration range used and that, as a first approximation, they would extrapolate out in the final plots against ionic strength.

Thus the work of Law and Read, and the present work, seems to indicate that application of the Owen extrapolation procedure to 2:1 electrolytes leads to linear plots and thus extrapolates out quantities such as liquid junction potentials.
(b) $\text{H}_2\text{OCl}_2$ (aq) + 2$\text{Cl}^-$ (solv) $\Rightarrow$ $\text{H}_2$ (aq) + $\text{H}_2\text{OCl}_2^4$ (solv)

The equilibrium constants for these reactions are

$\text{k}_a = 1.2 \times 10^{-5}$  
$\text{k}_b = 1.2 \times 10^{-4}$

It has been assumed that all data in Table II is applicable at ionic strengths 0.05 - 0.005. Complexions such as this will reduce the effective chloride ion concentration of the barium chloride but it can be shown that the effects of chloride complexing can be neglected. Also the extrapolations against $x$ to $x=0$ should eliminate any effects owing to chloride complexes because at $x=0$ the chloride ion concentration is zero. Chloride complexing can be regarded also as contributing to the activity coefficients and will be extrapolated out at zero ionic strength.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log k_i$</th>
<th>$\log \pi_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{H}_2\text{OCl}_2$ (aq) = $\text{H}_2$ + 2$\text{Cl}^-$</td>
<td>$17.12 \pm 0.01$</td>
<td>$18.123$</td>
</tr>
<tr>
<td>2. $\text{Ba}^{++}$ + $\text{H}_2$ (aq) = $\text{Hg}_2^{++}$</td>
<td>$2.114 \pm 0.032$</td>
<td>$2.114 \pm 0.032$</td>
</tr>
<tr>
<td>3. $\text{Ba}^{++}$ + $\text{H}_2$0 = $\text{Hg}_2\text{OH}^+$ + $\text{H}^+$</td>
<td>$4.30 \pm 0.07$</td>
<td>$4.31 \pm 0.20$</td>
</tr>
<tr>
<td>4. $\text{Ba}^{++}$ + 2$\text{H}_2$0 = $\text{Hg}_2\text{(OH)}_2$ + 2$\text{H}^+$</td>
<td>$7.70 \pm 0.05$</td>
<td>$7.35 \pm 0.12$</td>
</tr>
<tr>
<td>5. $\text{Hg}_2^{++}$ + $\text{H}_2$0 = $\text{Hg}_2\text{OH}^+$ + $\text{H}^+$</td>
<td>$5.0 \pm 0.3$</td>
<td>$5.6 \pm 0.4$</td>
</tr>
<tr>
<td>6. $\text{Hg}^{++}$ + $\text{Cl}^-$ = $\text{HgCl}$</td>
<td>$6.74 \pm 0.02$</td>
<td>$7.34 \pm 0.27$</td>
</tr>
<tr>
<td>7. $\text{Hg}^{++}$ + 2$\text{Cl}^-$ = $\text{HgCl}_2$</td>
<td>$13.22 \pm 0.02$</td>
<td>$14.26 \pm 0.09$</td>
</tr>
<tr>
<td>8. $\text{Hg}^{++}$ + 3$\text{Cl}^-$ = $\text{HgCl}_3$</td>
<td>$14.07 \pm 0.15$</td>
<td></td>
</tr>
<tr>
<td>9. $\text{Hg}^{++}$ + 4$\text{Cl}^-$ = $\text{HgCl}_4^{2-}$</td>
<td>$15.67 \pm 0.06$</td>
<td></td>
</tr>
</tbody>
</table>

$\log k_i$ refers to data of Sillen and co-workers  
$\log \pi_i$ refers to data of Dry and Gledhill
LIQUID JUNCTION POTENTIAL

If two solutions of electrolytes are brought into contact, there will be a region in which the composition varies from that of one of the two solutions to that of the other. The constitution of this region will depend on such factors as diffusion, convection and mixing. Owing to differences in the transfer of electricity by the ions, a potential is set up across the boundary.

It can be shown that

$$dE_j = \frac{RT}{F} \sum t_{i-1} a_i \ln a_i$$

where $E_j$ is the liquid junction potential, $t_i$, $z_i$, $a_i$ are the transport number, valency and activity respectively of each ion.

With the exception of the case of a boundary between two solutions of the same salt, it is necessary when integrating equation (1) to assume the relations of the concentrations of the ions with each other, and also to make an assumption concerning the activities $a_i$. A simple assumption as to the nature of the boundary which leads to easy integration of equation (1) is that the junction consists of a continuous series of solutions produced by mixing the two solutions initially brought into contact. If $x$, the mixing fraction, is the proportion of solution I at a given point then the proportion of II will be $(1-x)$. On this basis it can be shown that
\[ \eta_j = \frac{e \mathcal{F}}{v} \left( \frac{\sum C_i z_i (c_i'' - c_i')}{\sum C_i (c_i'' - c_i')} \right) \ln \left( \frac{\sum C_i' G_i'}{\sum C_i' G_i} \right) \]

where \( C_i \) and \( C_i' \) are the mobility and concentration of each ion. This equation is due to Henderson. The derivation requires no particular spatial arrangement of the layers of solution in the boundary; the only requirement being that solutions composing the boundary should be a series of mixtures of the end solutions I and II.

A second type of junction is called the constrained diffusion junction and may be described as follows: 56

"the composition of the liquid is artificially maintained constant and the same as that in solution I at all points to the left of a certain fixed plane \( A \), similarly with solution II to the right of a parallel plane \( B \); subject to these restraints the ions diffuse freely between \( A \) and \( B \) until a steady state is reached, after which the junction potential should remain constant."

Using these conditions, it can be shown that the difference in potential \( \psi \) between \( A \) and \( B \) is independent of the distance \( x \) and is determined by the equation

\[
\ln \left( \frac{\sum C_i z_i}{\sum C_i x} \right) = \frac{\sum C_i e \psi/RT}{\sum C_i x e \psi/RT} \ln \left( \frac{\sum C_i}{\sum C_i^x} \right) + \frac{\sum C_i e \psi/RT}{\sum C_i x e \psi/RT} \times \frac{\sum C_i x e \psi/RT}{\sum C_i x e \psi/RT}
\]
\[ \Sigma_+ \Sigma_- \Sigma_0 \]
denote summation over all ions, cations, and anions respectively. \( -\varepsilon \) is the change in an electron. This formula was derived for ions of the same numerical valency by Planck \(^52,53\) and a more general expression for ions of different valencies was derived by Pleisch \(^54\).

The solution is in general different to that of the Anderson equation because under the conditions of constrained diffusion, a steady state is reached in which the solution at each point cannot be regarded as a mixture of the two end solutions.

A third type may be described as the free diffusion junction, the conditions being that the transition layer should be initially short compared with the distance between the electrodes, an absolutely sharp boundary being of course impossible, and that unconstrained diffusion should be allowed to take place. Under these conditions, the length of the transition is always increasing, but if there is cylindrical symmetry it appears that the potential difference is independent of time. This type of junction is discussed by Taylor \(^56\). A number of approximations must be made to obtain solutions to the equations obtained, and Sugheim \(^58\) points out that these may account for the discrepancies between this method of treating the problem and the method of continuous mixture.

Sugheim points out that the most interesting quantitative result of measurements done is that, as long as there is cylindrical symmetry, the free diffusion junction model gives values for the junction potential differing only by a few tenths of a millivolt from those given by assuming.
a continuous mixture layer. Hence in computations of the
liquid junction potentials, it may be allowable to use the
formula corresponding to a continuous mixture layer even
if the actual junction is of the free diffusion type.

Guggenheim has found that in cells of the type

\[ \text{He} : \text{He}_2\text{Cl}_2 \rightarrow 0.1\text{M HCl} \rightarrow \text{KCl} \rightarrow 0.1\text{M KCl} \rightarrow \text{He}_2\text{Cl}_2 : \text{Fe} \]

the emf produced was independent of the concentration of
the centre compartment. This was further tested in the
present work and was found to be the case (see Table VIII).
The variations observed were within experimental error. Thus
it appears that the composition and concentration of the
centre compartment has, within experimental error, no
effect on the emf of the cell of which it is part. Thus it
would appear that the composition and concentration of the
two outer compartments only will contribute to the measured
emf of the cell.

On the basis of the Henderson equation, it is not
surprising that Guggenheim found that, for the cell he
measured, the emf produced did not depend on the
concentration of the centre compartment. Substitution in
the Henderson equation gives a value for the junction
potential which is independent of the concentration of the
potassium chloride in the centre compartment. This should
hold, according to the Henderson equation for any cell of
the type

\[ \text{Electrode} \rightarrow \text{Ag} (\text{C}_1) \rightarrow \text{Ag} (\text{C}_2) \rightarrow \text{Ag} (\text{C}_3) \rightarrow \text{Electrode} \]

It was found during the present work that the plots
against \( x \) (Graph II) were horizontal. This means that, in all cells, the junction potential was less than experimental error. Applying the Henderson equation to the cell

\[
\begin{array}{c|c|c|c}
E_0 & \text{BaCl}_2 \frac{2}{3} & \text{Ba(ClO}_4)_2 \frac{2}{3} & \text{Hg}_2(\text{ClO}_4)_2 \frac{2}{3} \\
\text{HClO}_4 (1-x) & \text{HClO}_4 (1-x) & \text{HClO}_4 (1-x) & \right.
\end{array}
\]

where \( c = \frac{\text{BaCl}_2}{\text{Hg}_2(\text{ClO}_4)_2} \); \( E_g \)

and using the values of the mobility of the ions concerned given in Robinson and Stokes \( ^{63} \), and assuming \( \nu_{Hg} \approx 55 \) it can be shown that

\[
E_j = k \log \left( \frac{(1 - 0.844x)^3}{(1 - 0.848x)(1 - 0.827x)} \right)
\]

At 25°C for \( x = 0.6 \) \( E_j = -0.04 \) mV

for \( x = 0.1 \) \( E_j = 0.03 \) mV

Thus the Henderson equation predicts that the junction potential will be less than experimental error, as was observed.

The hydrogen ion has a high mobility and thus the concentration of hydrogen ions will be an important factor in the determination of the junction potential. If the hydrogen ion concentration is equal on both sides of the junction and approximately equal to or greater than the concentration of other ions present in the solutions, then the junction potential will probably be small.

There are several other methods of eliminating or reducing junction potentials. Kern \( ^{64} \) has suggested the device of adding an indifferent electrolyte (e.g., KCl, KNO_3)
at the same concentration to both sides of the cell; if the concentration of this added substance is much greater than that of any other electrolyte present, the former will carry almost all of the current. Since its concentration is the same on both sides or the boundary, it will produce no potential difference at the junction. This method is of limited application chiefly because the addition of an excess of electrolyte will have a marked effect on the activities of the ions.

Another method is to use a salt bridge usually made of potassium chloride or ammonium nitrate. Fales and Vosburgh\(^55\) consider that there is no contact potential between 4.1 N potassium chloride solution and 0.1 to 0.01 N hydrochloric acid, hence the concentrated salt solution is able to eliminate the high potential to be expected from the mobile hydrogen ions. However, Scatchard\(^56\) has cast doubts as to whether the salt bridge is this effective in reducing junction potentials. The work of Buggenheim\(^58\) and the author has shown that the centre compartment has no influence on the potential of the cell. Thus it would be even unlikely that a salt bridge would reduce or eliminate liquid junction potentials.

**HYDROLYSIS OF THE MERCURIC ION**

The emf of the cell

\[
\begin{array}{c|c|c|c}
\text{Hg} & \text{Hg}_2\text{Cl}_2 & \text{BaCl}_2 \ 0.004 \text{m} & \text{Ba(}\text{ClO}_4\text{)}_2 \ 0.004 \text{m} \\
\text{HClO}_4 & \text{y} & \text{HClO}_4 & \text{y} & \text{C} \\
\end{array}
\]

where \(C = \frac{\text{Hg}_2(\text{ClO}_4)_2 \ 0.004 \text{m}}{\text{HClO}_4 \ y} \quad \text{Hg}_2\text{Cl}_2 ; \text{Hg} \)
was measured over a range of acid concentration.

The perchloric acid concentration was varied from 0.0001 m to 0.0001 m. The following equilibria were then considered:

\[
\begin{align*}
\text{H}_2\text{O}^2^+ & + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ & + \text{H}^+ \\
\text{H}_2\text{O}^2^+ & + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ & + \text{H}^+ \\
\text{H}_2\text{O}^2^+ & + 2\text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ & + 2\text{H}^+ \\
\text{H}_2\text{O}^2^+ & + \text{H}_2\text{O} &\rightleftharpoons \text{H}_2\text{O}_2 & \rightleftharpoons \text{H}_2^+ & + \text{O}_2 \\
\end{align*}
\]

The values of \( I \) and \( \mu \) used were those corrected, to an ionic strength of \( 10^{-5} \), from data of Millen\textsuperscript{54,55,56} by Fry and Gledhill\textsuperscript{31}.

As is to be expected there is a considerable increase in the hydrogen ion concentration caused by the hydrolysis of the mercurous and mercuric ions. This increase in hydrogen ion concentration in the one compartment only would be expected to give rise to junction potentials. Estimations of these by means of the Henderson equation showed them to be of the same order as the difference in emf between the emf of the cell at a perchloric acid concentration of 0.0001 m and at the perchloric acid concentration under consideration. Furthermore the junction potential was assisting the hydrolysis of the mercurous ion to change the emf of the cell. This means that any value of the hydrolysis constant of the mercurous ion obtained from this data will be very inaccurate and it appears that this method is not suitable for estimating the hydrolysis constant of the mercurous ion. It was, however, noticed that hydrolysis became significant between perchloric acid concentrations of \( 6 \times 10^{-5} \) and \( 2 \times 10^{-5} \).
This is confirmed by the fact that the \( n = 0.005 \) points were lower than those expected if no hydrolysis had taken place.

**ACTIVITY COEFFICIENT EXPRESSION**

The most general form of activity coefficient expression is

\[
- \log \gamma = \frac{A^2}{1 + E_{a}} \left[ \frac{1}{\sqrt{1 + 1}} \right] + bI \quad \ldots \ldots \ldots \ldots (1)
\]

This expression contains two variables \( a_{o} \) and \( b \).

In the present work equation (1) has been used with \( a_{o} = \frac{1}{I} \), i.e. \( E_{a} = 1 \). This yields a modified Davies equation

\[
- \log \gamma = \frac{A^2}{1 + bI} \quad \ldots \ldots \ldots \ldots (2)
\]

which reduces to the Davies equation if \( b = -0.4 \).

Another special case of equation (1) is when \( b = 0 \) which yields the Debye-Hückel equation

\[
- \log \gamma = \frac{A^2}{1 + E_{a}} \quad \ldots \ldots \ldots \ldots (3)
\]

Normally \( a_{o} \) is interpreted as the distance of closest approach of the ions concerned, but in the present work the value of \( a_{o} \) has no physical significance whatsoever, as the two ions concerned (\( Na^{+} \) and \( Cl^{-} \)) are in different compartments in the cell.

Prue and co-workers\(^2\) have found that the dissociation constant of \( CaOH^{+} \) depended on the form of the activity coefficient expression used in the interpretation of their
data. The effect of different forms of the activity coefficient expression on the solubility product of mercuric chloride obtained has been calculated from experimental data obtained for 25° C in the present work.

It can be shown that for the cell used in the present work, extrapolations to $x = 0$ for elimination of liquid junction potentials give intercepts which are represented by the expression

$$\frac{k}{2} \log \frac{x}{3} - k \log 2 \ln k_o = - \frac{k}{2} \log k + \frac{k}{2} \log Y_{\text{HgCl}_2} + Y^2$$

(4)

Using the activity coefficient expression given in equation (3)

$$\frac{k}{2} \log \frac{x}{3} - k \log 2 \ln k_o = - \frac{k}{2} \log k + \frac{k}{2} \log k_o, x = - \frac{3kA \sqrt{1}}{1 + E_k \sqrt{1}}$$

Using the value of $k$ determined by using the expression given in equation (2) for the activity coefficients, the left hand side of equation (4) was plotted against $\sqrt{1}$ for $1 + E_k \sqrt{1}$ the following values of $k_o : 0, 2, \frac{1}{2} = 3.037, 4, 5, 6, 8$ and 10 Angstroms. The relevant data is given in Table XIII and plotted in Graph IV.

Substituting the activity coefficient expression given by equation (1) in equation (4) gives

$$(x = \frac{3k}{2} \log \frac{x}{3} - k \log 2), x = 0 + \frac{k}{2} \log k + \frac{3kA \sqrt{1}}{1 + E_k \sqrt{1}} = - \frac{k}{2} (b' + 2b'') I$$
where \( b', b'' \) are the values of \( b \) for the mercurous and chloride ions respectively. The left hand side of this equation was plotted against \( I \) for the above values of \( a_0 \). The relevant data is given in Table XIII and plotted in Graph IV.

In Graph IV, it will be noticed that only data for \( a_0 = 5 \) Angstroms leads to a linear extrapolation through the origin. The plots for \( a_0 \) equal to six and eight Angstroms appear linear but the could be slightly curved, which would account for the extrapolations, which have been assumed linear, not passing through the origin. The plots for all other values of \( a_0 \) are curved, as the value chosen for \( a_0 \) is inadequate to compensate for the neglect of the linear term in \( I \), and therefore do not lend themselves to accurate extrapolation.

In Graph V, all the extrapolations are linear although the points for \( I = 0.05 \) and \( a_0 \gg 4 \) lie off the straight line through the points for \( I = 0.01, 0.02 \) and 0.03. The extrapolation for \( a_0 = 5 \) is horizontal, corresponding to a zero coefficient of the linear term in \( I \), and passes through the origin. The extrapolation \( a_0 = \frac{1}{b} \) has been used to define the origin and all extrapolations corresponding to values of \( a_0 \) between this value and 5 Angstroms pass through the origin.

The general expression for the activity coefficients, which contains two adjustable parameters, thus leads to a series of linear extrapolations, the intercepts of which vary from \(-0.40 \text{ mV}\) to \(+0.20 \text{ mV}\) as one parameter is adjusted from \( a_0 = 0 \) to \( a_0 = 10 \) Angstroms. However, the
results of extrapolation using a one parameter equation, obtained either by putting \( \text{Pa}_0 = 1 \) or by equating the coefficient of the linear term to zero, are identical.

**Table XIII**

| Values of \( \left( 1 - \frac{3k}{2} \log \frac{x_m}{3} - k \log 2 \right) \) at 25°C |
|---|---|---|---|---|
| \( m \) | 0.01 | 0.02 | 0.03 | 0.04 |
| \( 0.5135 \) | \( 0.5162 \) | \( 0.5151 \) | \( 0.5127 \) |

**Values of \( \left( 1 - \frac{3k}{2} \log \frac{x_m}{3} - k \log 2 \right) + \frac{k}{2} \log \varpi \) at 25°C**

<table>
<thead>
<tr>
<th>( m )</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -0.0073 )</td>
<td>( -0.0104 )</td>
<td>( -0.0122 )</td>
<td>( -0.0146 )</td>
<td></td>
</tr>
</tbody>
</table>

**Values of \( \sqrt{\frac{1}{1 + \text{Pa}_0 \varpi}} \) \( (1 \leq m) \)**

<table>
<thead>
<tr>
<th>( \text{Pa}_0 )</th>
<th>( m = 0.01 )</th>
<th>( 0.02 )</th>
<th>( 0.03 )</th>
<th>( 0.04 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>1.1414</td>
<td>1.1732</td>
<td>1.2236</td>
</tr>
<tr>
<td>2</td>
<td>0.9388</td>
<td>1.1294</td>
<td>1.1555</td>
<td>1.1848</td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>0.909</td>
<td>1.1239</td>
<td>1.1475</td>
<td>1.1723</td>
</tr>
<tr>
<td>4</td>
<td>0.8384</td>
<td>1.1182</td>
<td>1.1411</td>
<td>1.1728</td>
</tr>
<tr>
<td>5</td>
<td>0.8589</td>
<td>1.1147</td>
<td>1.1348</td>
<td>1.1613</td>
</tr>
<tr>
<td>6</td>
<td>0.835</td>
<td>1.1166</td>
<td>1.1281</td>
<td>1.1551</td>
</tr>
<tr>
<td>8</td>
<td>0.792</td>
<td>1.1031</td>
<td>1.1150</td>
<td>1.1408</td>
</tr>
<tr>
<td>10</td>
<td>0.752</td>
<td>0.9955</td>
<td>1.103</td>
<td>1.1288</td>
</tr>
</tbody>
</table>
VALUES OF

\[
(3 - \frac{3r}{2} \log \frac{E}{2} - k \log 2)_{x=0} + \frac{r}{2} \log K + \frac{3r}{2} \sqrt{1}
\]

<table>
<thead>
<tr>
<th>r</th>
<th>m =</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.0013</td>
<td>.0024</td>
<td>.0035</td>
<td>.0057</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>.0007</td>
<td>.0013</td>
<td>.0019</td>
<td>.0031</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>.0004</td>
<td>.0008</td>
<td>.0012</td>
<td>.0020</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>.0002</td>
<td>.0004</td>
<td>.0006</td>
<td>.0011</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.0000</td>
<td>.0000</td>
<td>.0000</td>
<td>.0002</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>- .0002</td>
<td>- .0004</td>
<td>- .0005</td>
<td>- .0005</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>- .0006</td>
<td>- .0010</td>
<td>- .0014</td>
<td>- .0018</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>- .0010</td>
<td>- .0016</td>
<td>- .0022</td>
<td>- .0029</td>
<td></td>
</tr>
</tbody>
</table>
SYMBOLS
+ a_1 = 0
○ a_2 = 2
Δ a_3 = 7/6 = 1.167
X a_4 = 3.057
a_6 = 4
a_7 = 5
a_8 = 6
a_9 = 7
a_10 = 8
a_11 = 9
a_12 = 10

a_0 in Angstroms.
THE STANDARD POTENTIAL OF MERCURY.

By combining the solubility product of mercurous chloride with the standard potential of the calomel electrode, a value for the standard potential of mercury may be obtained according to the equation

\[ E^0_{\text{Hg}} = E^0_{\text{Hg}_2\text{Cl}_2} - \frac{k}{2} \log K \]

The results of this calculation for the range 15°C to 45°C are given in Table XIV. A comparison is also given with the values obtained by Read.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>(E^0_{\text{Hg}_2\text{Cl}_2})</th>
<th>(\frac{k}{2} \log K)</th>
<th>(E^0_{\text{Hg}})</th>
<th>(E^0_{\text{Hg}}) (Read)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>.2708</td>
<td>.5273</td>
<td>.7981</td>
<td>.7986</td>
</tr>
<tr>
<td>20°C</td>
<td>.2695</td>
<td>.5272</td>
<td>.7987</td>
<td>.7971</td>
</tr>
<tr>
<td>25°C</td>
<td>.2680</td>
<td>.5273</td>
<td>.7953</td>
<td>.7956</td>
</tr>
<tr>
<td>30°C</td>
<td>.2654</td>
<td>.5278</td>
<td>.7940</td>
<td>.7943</td>
</tr>
<tr>
<td>35°C</td>
<td>.2646</td>
<td>.5280</td>
<td>.7926</td>
<td>.7926</td>
</tr>
<tr>
<td>40°C</td>
<td>.2627</td>
<td>.5285</td>
<td>.7912</td>
<td>.7909</td>
</tr>
<tr>
<td>45°C</td>
<td>.2605</td>
<td>.5291</td>
<td>.7896</td>
<td>.7892</td>
</tr>
</tbody>
</table>

The standard potential of mercury (+ 0.0001 mV) is given by

\[ E^0_{\text{Hg}} = 2.0448 - 12.062 \times 10^{-3} T + 3.9653 \times 10^{-5} T^2 - 4.444 \times 10^{-8} T^3 \]

at 25°C the standard potential of the calomel electrode is taken as 0.2620 ± 0.0001 abs. V. This gives
$E^0_{\text{Hg}} = 0.7953 \pm 0.0002$ abs. V. It will be noted that this value is 0.0003 abs. V. lower than that obtained by Read, but within experimental error. It is interesting to note that a value for $E^0_{\text{Hg}}$ of $0.7956 \pm 0.0004$ abs. V. covers the values obtained by Read, Villén (recalculated), Bonner and Unistis (recalculated), and the present work. Thus it appears that the values obtained by Lee and Christiansen are in error, as they lie well outside the above range of values.
THE MERCURIC/MERCURIOUS ELECTRODE POTENTIAL AND THE EQUILIBRIUM

\[ \text{Hg}^{2+} \text{(soln)} + \text{H}_2 \text{(l)} \rightleftharpoons \text{Hg}_2^{2+} \text{(soln)} \]

Recalculations of data of Popoff et al,\textsuperscript{43} and of Hietanen and Sillén,\textsuperscript{67} by Read\textsuperscript{6} showed that the most probable value of the mercuric/mercurous electrode potential was 0.9126 ± 0.0003 abs. V. at 25°C. Read pointed out that this value could be in error as a correction was required for the hydrolysis of the mercuric ion. The value Read used for this correction is that quoted by Dry and Gledhill,\textsuperscript{31} who calculated the thermodynamic value from a measure of the hydrolysis constant of the mercuric ion at an ionic strength of 0.5, made by Hietanen and Sillén.

Now \[ k \log K_0 = E_0^{E_{21}} - E_0^{E_{10}} \]

where \( E_0^{E_{21}} \) and \( E_0^{E_{10}} \) are the mercuric/mercurous and mercury/mercurous electrode potentials respectively, and \( K_0 \) is the equilibrium constant for the reaction

\[ \text{Hg}^{2+} \text{(soln)} + \text{H}_2 \text{(l)} \rightleftharpoons \text{Hg}_2^{2+} \text{(soln)} \]

\[ k \log K_0 = 0.9126 - 0.7953 = 0.1173 \pm 0.0005 \text{ abs. V.} \]

Hence \( K_0 = 96.1 \pm 2.0 \) at 25°C.

The value of \( K_0 \) is very sensitive to the difference \( E_0^{E_{21}} - E_0^{E_{10}} \) and a more accurate value could probably be obtained directly. However, this would probably necessitate prior measurement of the hydrolysis constants of the mercurous, and in particular, the mercuric ion.
THE SOLUTION PROCESS

\[
\text{Hg}_2\text{Cl}_2 \text{(s)} \rightarrow \text{Hg}_2^{++} \text{(soln)} + 2\text{Cl}^- \text{(soln)}
\]

The equation obtained in the present work which describes the temperature variation of the standard free energy change for this reaction is
\[
\Delta G^0 = 62,654 - 349.85 \, T + 1.0475 \, T^2 - 0.001024 \, T^3 \, \text{cal/mole. (1)}
\]
This may be compared with the equation
\[
\Delta G^0 = 17,755 + 11.1476 \, T + .04005 \, T^2
\]
derived from measurements of Broidy.\textsuperscript{29,30}

The solubility products and \( \Delta G^0 \) values obtained by Broidy and Law\textsuperscript{5} are compared with those of the present work in Graphs VI and VII. The solubility product obtained by Broidy compares fairly well with the value of \( 1.49 \times 10^{-18} \) obtained in the present work. It also agrees with the value of \( 1.33 \times 10^{-18} \) calculated indirectly by Dry and Gledhill.\textsuperscript{31} Law obtained a value of \( 5.35 \times 10^{-18} \) which is higher than all the above values.

The \( \Delta G^0 \) values of Law and Broidy show similar trends to those obtained in the present work, although the author observed a slight minimum in the free energy at about 20\textdegree C. Read\textsuperscript{6} however found that there was a discrepancy between his work and that of Broidy for the reaction
\[
\text{Hg}_2\text{Ir}_2 \text{(s)} \rightarrow \text{Hg}_2^{++} \text{(soln)} + 2\text{Ir}^- \text{(soln)}
\]

From equation (1) above, the temperature for a minimum to occur in the plot of \( \Delta G^0 \) vs. \( T \) is given by
\[
\frac{\partial}{\partial T} (\Delta G^0) = 0. \text{ The value of } T \text{ corresponding to this
minimum is \( T = 294.14 \)°A. It was observed that - \( \log T \)
showed a minimum between 283.16°A and 298.15°A. At this
temperature (294.14°A), \( \Delta S \)° for the solution process is
zero, and the sum of the absolute entropies of the ions
in solution would equal the entropy of the crystal.

Lew obtained the following equations for \( \Delta G \)°, \( \Delta H \)°,
and \( \Delta S \)° as a function of temperature.

\[
\begin{align*}
\Delta G \text{°} &= 10,264.6 + 77.5048 \cdot T - 0.10966 \cdot T^2 \\
\Delta H \text{°} &= -77.5048 + 0.21533 \cdot T \\
\Delta S \text{°} &= 10,264.6 + 0.10966 \cdot T^2
\end{align*}
\]

The value of \( T \) when \( \frac{\partial}{\partial T} (\Delta S \text{°}) = 0 \) is 353.4°A.

A comparison of these results with those obtained
in the present work reveals large discrepancies. This is
not surprising considering that the values for the solubility
product of mercurous chloride and also the activity
coefficient of mercurous chloride obtained are completely
different.

Some thermodynamic values for the solution process
are compared in Table XV. The values of Kohlrausch were
calculated by Lew from data of the solubility product of
mercurous chloride obtained by Kohlrausch 27.
**TABLE XV**

**THERMODYNAMIC VALUES FOR THE PROCESS**

\[ \text{Hg}_2\text{Cl}_2 (s) \rightarrow \text{Hg}_2^{4+} \text{ (soln)} + 2\text{Cl}^- \text{ (soln)} \]

\[ \Delta G^0 \text{ (cals/mole.)} \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Kohlrausch</th>
<th>Brodsky</th>
<th>Law</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5°C</td>
<td>20,009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.0°C</td>
<td></td>
<td>23,937</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0°C</td>
<td></td>
<td>24,093</td>
<td>24,492</td>
<td>24,319</td>
</tr>
<tr>
<td>18.0°C</td>
<td>20,565</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.5°C</td>
<td></td>
<td>24,242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td></td>
<td></td>
<td>23,561</td>
<td>24,317</td>
</tr>
<tr>
<td>25°C</td>
<td>20,512</td>
<td></td>
<td>23,624</td>
<td>24,323</td>
</tr>
<tr>
<td>26.5°C</td>
<td></td>
<td>24,492</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td></td>
<td></td>
<td>23,682</td>
<td>24,334</td>
</tr>
<tr>
<td>35°C</td>
<td></td>
<td>23,734</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td>23,780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43°C</td>
<td>20,075</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45°C</td>
<td></td>
<td>23,822</td>
<td></td>
<td>24,401</td>
</tr>
</tbody>
</table>

\[ \Delta S^0 \text{ at 25°C} \]

- Kohlrausch: 10.0 e.u.
- Brodsky: -35.0 e.u.
- Law: -12.6 e.u.
- Latimer, Schutz and Hicks: -2.4 e.u. and -2.1 e.u.
- Present work: -1.70 e.u.

The value of $\Delta S^0$ obtained in the present work agrees with that of Latimer, Schutz and Hicks but is much smaller.
Graph VI

Symbols:
- LAW
- BRODSKY
+ PRESENT WORK.
in magnitude than the values obtained by Irodsky and law. The value of Latimer, Schatz and Hicks was calculated from a value of $\Delta H^0$ obtained by Kohlrausch and a value of $\Delta S^0$ calculated from specific heat data obtained by Pollitzer. The values of $\Delta S^0$ obtained by Kohlrausch show different trends to those obtained by law, Irodsky and the author. It is therefore likely that the values of $\Delta H^0$ will be in error. Using the value of $\Delta H^0$ obtained in the present work and the value of $\Delta G^0$ obtained by Pollitzer, the value $\Delta S^0 = -2.1$ e.u. is obtained. This shows good agreement with the value obtained in the present work.
THE RELATIVE PARTIAL IONIC FUNCTIONS
OF THE NERCIROUS ION

The free energy changes and the temperature coefficients of the reactions

\[ \text{Hg}_2\text{Cl}_2 (s) + \text{H}_2 (s) \rightarrow 2\text{Hg} (l) + 2\text{H}^+ (\text{soln}) + 2\text{Cl}^- (\text{soln}) \]  \hspace{1cm} (1)

\[ \text{Hg}_2\text{Cl}_2 (s) \rightarrow \text{Hg}_2^{++} (\text{soln}) + 2\text{Cl}^- (\text{soln}) \]  \hspace{1cm} (2)

have been combined to give values of the thermodynamic functions for the reaction

\[ \text{Hg}_2^{++} (\text{soln}) + \text{H}_2 (s) \rightarrow 2\text{Hg} (l) + 2\text{H}^+ (\text{soln}) \]  \hspace{1cm} (3)

The quantities \( \Delta G^0 \), \( \Delta S^0 \) and \( \Delta H^0 \), as a function of temperature, for reaction (3) are given below:

\[ \Delta G^0 = -94,283 + 555.34 \ T - 1.8281 \ T^2 + 2.049 \times 10^{-3} \ T^3 \ \text{cal/mole} \]

\[ \Delta S^0 = -555.34 + 3.6552 \ T - 6.147 \times 10^{-3} \ T^2 \ \text{e.u.} \]

\[ \Delta H^0 = -94,283 + 1.8281 \ T^2 - 4.098 \times 10^{-3} \ T^3 \ \text{cal/mole} \]

The values of these functions for the temperature range 15°C - 45°C are given in Table XVI and for comparison the values obtained by Read for the same reaction are given in Table XVIa.
DERIVED THERMODYNAMIC FUNCTIONS FOR THE REACTION

\[ \text{Hg}_2^{++} (\text{soln}) + \text{H}_2 (g) \rightarrow 2 \text{H}^+ (\text{soln}) + 2 \text{Hg} (l) \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$E^0$</th>
<th>$-\Delta G^0$</th>
<th>$-\Delta S^0$</th>
<th>$-\Delta H^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>0.793</td>
<td>36.88 K cal</td>
<td>12.69 e.u.</td>
<td>40.54 K cal</td>
</tr>
<tr>
<td>20°C</td>
<td>0.793</td>
<td>36.82 &quot;</td>
<td>12.28 &quot;</td>
<td>40.42 &quot;</td>
</tr>
<tr>
<td>25°C</td>
<td>0.793</td>
<td>36.78 &quot;</td>
<td>12.17 &quot;</td>
<td>40.39 &quot;</td>
</tr>
<tr>
<td>30°C</td>
<td>0.794</td>
<td>36.70 &quot;</td>
<td>12.38 &quot;</td>
<td>40.45 &quot;</td>
</tr>
<tr>
<td>35°C</td>
<td>0.792</td>
<td>36.56 &quot;</td>
<td>12.90 &quot;</td>
<td>40.61 &quot;</td>
</tr>
<tr>
<td>40°C</td>
<td>0.791</td>
<td>36.58 &quot;</td>
<td>13.69 &quot;</td>
<td>40.96 &quot;</td>
</tr>
<tr>
<td>45°C</td>
<td>0.789</td>
<td>36.50 &quot;</td>
<td>14.82 &quot;</td>
<td>41.21 &quot;</td>
</tr>
</tbody>
</table>

**Table XVIa**

DATA FOR ABOVE REACTION OBTAINED BY READ

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$E^0$</th>
<th>$-\Delta G^0$</th>
<th>$-\Delta S^0$</th>
<th>$-\Delta H^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>0.798</td>
<td>36.63 K cal</td>
<td>12.53 e.u.</td>
<td>40.53 K cal</td>
</tr>
<tr>
<td>20°C</td>
<td>0.797</td>
<td>36.78 &quot;</td>
<td>13.27 &quot;</td>
<td>40.69 &quot;</td>
</tr>
<tr>
<td>25°C</td>
<td>0.795</td>
<td>36.70 &quot;</td>
<td>13.91 &quot;</td>
<td>40.85 &quot;</td>
</tr>
<tr>
<td>30°C</td>
<td>0.793</td>
<td>36.53 &quot;</td>
<td>14.46 &quot;</td>
<td>41.01 &quot;</td>
</tr>
<tr>
<td>35°C</td>
<td>0.789</td>
<td>36.55 &quot;</td>
<td>15.00 &quot;</td>
<td>41.18 &quot;</td>
</tr>
<tr>
<td>40°C</td>
<td>0.789</td>
<td>36.48 &quot;</td>
<td>15.54 &quot;</td>
<td>41.34 &quot;</td>
</tr>
<tr>
<td>45°C</td>
<td>0.789</td>
<td>36.40 &quot;</td>
<td>16.08 &quot;</td>
<td>41.52 &quot;</td>
</tr>
</tbody>
</table>
It will be noted that values for $\Delta G^\circ$ follow similar trends in the two sets of data. However the data for $\Delta S^\circ$ and $\Delta H^\circ$ show some marked differences. The values obtained in the present work show a maximum at about 298°K whereas the values obtained by Read show no such maximum. Also the values for $\Delta G^\circ$ show a different dependence on temperature in the two sets of data.

One explanation of this difference could be that the temperature coefficient of the mercurous bromide electrode potential, from which Read's results were derived, is not known with any certainty, whereas the mercurous chloride electrode potential is known accurately over the range of temperature used.

Dakin and Twiner measured the emf of the cell

$$A_2 | A_2Br^- | Br^- | Hg_2Br_2 | Hg$$

during a range of temperature. The temperature coefficient of $E^\circ_{Hg_2Br_2}$ was obtained by combining the measured emfs with values for $E^\circ_{A_2Br^-}$ in the literature. Read considered three different determinations 71,72,73 of $E^\circ_{A_2Br^-}$ but they had different temperature coefficients.

Using $E^\circ_{H_2 (g)} = 31.21$ e.u. and $E^\circ_{H_2 (l)} = 18.5$ e.u. as listed by the National Bureau of Standards 74, a value of the relative partial molar ionic entropy of the mercurous ion may be calculated from the entropy change of equation (3) at 25°C. The value obtained in this way is $S^\circ_{Hg_2^{+}} = 17.56$ e.u.
A value for the partial molal entropy of the mercurous ion may also be calculated from a consideration of the solution process. For this reaction,
\[ \Delta S^\circ_{\text{soln}} = S^\circ_{\text{Hg}_2^{++}} + 2S^\circ_{\text{Cl}^-} - S^\circ_{\text{Hg}_2\text{Cl}_2}(s) \]

Using \( S^\circ_{\text{Cl}^-} = 13.17 \) e.u. and \( S^\circ_{\text{Hg}_2\text{Cl}_2}(s) = 46.80 \) as listed by the National Bureau of Standards, the value \( S^\circ_{\text{Hg}_2^{++}} = 18.8 \) e.u. is obtained.

The partial molal entropy of the mercurous ion obtained in the present work is compared with values obtained by other workers in Table XVII.

The value of 16.2 e.u. quoted by Latimer, Schatz and Hicks was derived from Kohlrausch's data for the temperature coefficient of the solution of mercurous chloride. Lew found that the value quoted by Latimer, Schatz and Hicks can only be obtained by considering the values of the solubility product at 0.5°C and 45°C, but this seems unjustified when the shape of the \( \Delta G^\circ \) vs \( T \) graph is considered. Recalculation of the Kohlrausch data by Lew gave 28.5 e.u. Latimer, Pitzer and Smith quoted the value of 17.7 e.u. using an entropy change of -11.9 e.u. for the reaction,
\[ \text{Hg}_2^{++} \text{ (solv)} + \text{H}_2(g) \rightarrow 2\text{Hg}(l) + 2\text{H}^+(\text{solv}) \]

The value of \( \Delta S^\circ \) used compares favourably with the value of -12.17 e.u. found in the present work.

Christensen obtained a value of -10.84 e.u. for the entropy change of the above reaction from which he derived \( S^\circ_{\text{Hg}_2^{++}} = 16.6 \) e.u.
Law obtained completely different values from both his data and that of Frodsky.

Thus there is satisfactory agreement between the values of $S^0_{\text{Hg}^2+}$ obtained by Read, Latimer, Pitzer and Smith, and the author.

The value of $S^0$ obtained for the mercurous ion is considerably larger than that of other divalent ions, which in general have partial molal entropies that are either small and positive, or negative. In view of the diatomic nature of the mercurous ion, it is not surprising that its partial molal entropy is somewhat different.

**Table VII**

<table>
<thead>
<tr>
<th>Partial Molal Entropy of the Mercurous Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latimer, Schutz and Hicks</td>
</tr>
<tr>
<td>Kohlrausch data (Law)</td>
</tr>
<tr>
<td>Frodsky data</td>
</tr>
<tr>
<td>Law</td>
</tr>
<tr>
<td>Christensen</td>
</tr>
<tr>
<td>Latimer, Pitzer and Smith</td>
</tr>
<tr>
<td>Read</td>
</tr>
<tr>
<td>Present work</td>
</tr>
</tbody>
</table>

**Relative Partial Molal True Energy of the Mercuric Ion**

Combination of the standard potential of mercury at 25°C with the mercurous/mercuric electrode potential gives a value of the standard electrode potential of the mercuric/mercury couple.
\[ E_2^0 = \frac{1}{3}(E_{21}^0 + E_{10}^0) \]
\[ = \frac{1}{3}(0.8126 + 0.7552) \]
\[ = 0.3539 \text{ abs. v. at } 25^\circ C \]

This leads to a value of 39.38 \text{ cal} for the relative partial molal entropy of the mercuric ion at 25^\circ C. Red, using the same value of \( E_{21}^0 \), obtained a value of 39.39 \text{ cal}. The most likely source of error in this calculation is in \( E_{21}^0 \), which is not known accurately.
THE ENTROPY CHANGE FOR THE REACTION

\[ 2\text{Hg}^+ (\text{soln}) \rightarrow \text{Hg}_2^{2+} (\text{soln}) \]

This may be calculated from a consideration of the entropy changes for the solution of mercurous chloride, and for the reaction

\[ \text{Hg}_2\text{Cl}_2 (s) \rightarrow 2\text{Hg}^+ (\text{soln}) + 2\text{Cl}^- (\text{soln}) \]

The entropy change for this reaction has been calculated from \( S^0_{\text{Hg}_2\text{Cl}_2 (s)} = 46.80 \text{ e.u.} \) and \( S^0_{\text{Cl}^-} = 13.17 \text{ e.u.} \) from the National Bureau of Standards \(^\text{74}\). The value of \( S^0_{\text{Hg}^+} = -1.5 \text{ e.u.} \) was calculated by using the radius of Hg 1.41 Ångströms as interpolated by Cartledge \(^\text{76}\), and the Powell Latimer equation \(^\text{77}\) for relative ionic entropies.

The entropy of dimerisation calculated this way is compared with the values of Law, Christensen and Read in Table \(\text{VIII}\).

As Law pointed out, a large entropy change is to be expected from the increased ordering resulting from the formation of the diatomic ion, from the effect of this ion on its surrounding solvation sheath, and from the fact that each double ion introduced new entropy terms owing to vibration and rotation.

The value obtained in the present work is in reasonable agreement with those of Read and Christensen. These three values are probably more correct than that obtained by Law, as doubts have been cast on his work in recent investigations.
<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta S^0$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Law</td>
<td>-44.5 e.u.</td>
</tr>
<tr>
<td>Christensen</td>
<td>-27.8 e.u.</td>
</tr>
<tr>
<td>Lead</td>
<td>-20.7 e.u.</td>
</tr>
<tr>
<td>Present work</td>
<td>-25.1 e.u.</td>
</tr>
</tbody>
</table>
ACTIVITY COEFFICIENTS

A comparison of the intercepts (\( -\frac{k}{2} \log X \)) and
\( \left( -\frac{k}{2} \log \mathbf{Y} + \frac{k}{2} \log \mathbf{Y}^{++} + \mathbf{Y}_{\text{Cl}^-} \right) \) given in Graphs III
and II respectively, allows the determination of values for
the activity coefficient term at various values of \( m \).
This term may be written in the form \( \frac{3k}{2} \log \mathbf{Y}_f \) where \( \mathbf{Y}_f \)
is the mean ionic activity coefficient of mercurous chloride.

The results are plotted on Graph VIII and the plot
approaches, at highest dilutions, the theoretical slope
of the Debye-Hückel limiting law. As hydrolysis is not
negligible at \( m = 0.005 \), the point corresponding to this
molarity would be expected to be erroneous. The values
of \( -\log \mathbf{Y}_f \) and \( \mathbf{Y}_f \) for \( 25^\circ C \) are listed below in Table XIX.

For comparison, the values of \( \mathbf{Y}_f \) for mercurous bromide,
obtained by Read, are also listed.

TABLE XIX

<table>
<thead>
<tr>
<th>( m )</th>
<th>( 0.05 )</th>
<th>( 0.03 )</th>
<th>( 0.02 )</th>
<th>( 0.01 )</th>
<th>( 0.005 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\log \mathbf{Y}_f )</td>
<td>0.1645</td>
<td>0.1375</td>
<td>0.1172</td>
<td>0.0879</td>
<td>0.0755</td>
</tr>
<tr>
<td>( \mathbf{Y}_f (\text{Hg}_2\text{Cl}_2) )</td>
<td>0.635</td>
<td>0.729</td>
<td>0.763</td>
<td>0.817</td>
<td>0.840</td>
</tr>
<tr>
<td>( \mathbf{Y}_f (\text{Hg}_2\text{Br}_2) )</td>
<td>0.685</td>
<td>0.729</td>
<td>0.764</td>
<td>0.817</td>
<td>0.858</td>
</tr>
</tbody>
</table>

It will be noted that the values of \( \mathbf{Y}_f \) for mercurous
chloride, obtained in the present work, and for mercurous
bromide, obtained by Read, are identical except for the value
at \( m = 0.005 \) where hydrolysis is probably making a variable
contribution.

Law obtained mean ionic activity coefficients of mercurous
chloride which were greater than unity.

This resulted from lines of incorrect slope in his plot against ionic strength, which were caused by hydrolysis and oxidation of his mercurous perchlorate crystals, with consequent errors in mercurous perchlorate concentrations.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Author(s)</th>
<th>Journal or Title</th>
<th>Volume</th>
<th>Page</th>
<th>Year</th>
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<tbody>
<tr>
<td>1.</td>
<td>Owen</td>
<td>J.A.C.S.</td>
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<td>2.</td>
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<td>1938</td>
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<tr>
<td>3.</td>
<td>Owen and King</td>
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<td>63</td>
<td>1711</td>
<td>1941</td>
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<td>Owen and Brinkley</td>
<td>J.A.C.S.</td>
<td>64</td>
<td>2071</td>
<td>1942</td>
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<td>5.</td>
<td>Law</td>
<td>Thesis, Univ. of N.Z.</td>
<td></td>
<td></td>
<td>1946</td>
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<td>7.</td>
<td>Linhart</td>
<td>J.A.C.S.</td>
<td>38</td>
<td>2356</td>
<td>1916</td>
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<td>8.</td>
<td>Lewis and Kendall</td>
<td>&quot;Thermodynamics&quot;</td>
<td>9</td>
<td>419</td>
<td>1923</td>
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<tr>
<td>10.</td>
<td>Tommer and Unietis</td>
<td>J.A.C.S.</td>
<td>75</td>
<td>5111</td>
<td>1953</td>
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<td>12.</td>
<td>Hills and Ives</td>
<td>J.O.S.</td>
<td>154</td>
<td>311</td>
<td>1951</td>
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<td>16.</td>
<td>Debye and Hückel</td>
<td>Physik. Z.</td>
<td>24</td>
<td>185</td>
<td>1923</td>
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<td>17.</td>
<td>Hitchcock</td>
<td>J.A.C.S.</td>
<td>50</td>
<td>2076</td>
<td>1928</td>
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<td>18.</td>
<td>Brown and MacInnes</td>
<td>J.A.C.S.</td>
<td>57</td>
<td>1356</td>
<td>1935</td>
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<td>19.</td>
<td>Gronwall, Le Her and Sanved</td>
<td>Physik. Z.</td>
<td>29</td>
<td>358</td>
<td>1928</td>
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<tr>
<td>22.</td>
<td>Davies</td>
<td>J.C.S.</td>
<td>141</td>
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<td>1938</td>
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<td></td>
<td>and Prue</td>
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<tr>
<td>24.</td>
<td>Behrend</td>
<td>Z. Physik.</td>
<td>11</td>
<td>466</td>
<td>1893</td>
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</tbody>
</table>
|   | Author(s)                        | Journal                        | Volume | Page | Year  
|---|----------------------------------|--------------------------------|--------|------|-------
| 23 | Sherrill                         | Z. Physik.                     | 43     | 735  | 1903  
| 26 | Ley and Heimbucher              | Z. Electrochem.                 | 10     | 301  | 1904  
| 27 | Kovalrausch                      | Z. Physik.                     | 64     | 129  | 1908  
| 28 | Eversole and Maclachlan         | J.A.C.S.                       | 54     | 864  | 1932  
| 29 | Brodsky                          | Z. Electrochem.                 | 35     | 833  | 1929  
| 30 | Brodsky and Scherschewer         | Z. Electrochem.                 | 32     | 3    | 1926  
| 31 | Dry and Gledhill                 | Trans. Far. Soc.               | 51     | 1119 | 1955  
| 32 | Gerke                            | J.A.C.S.                       | 44     | 1684 | 1922  
| 33 | Randall and Young                | J.A.C.S.                       | 50     | 989  | 1928  
| 35 | Mueller and Reuther              | Z. Electrochem.                 | 48     | 220  | 1942  
| 36 | Earned and Ehlers                | J.A.C.S.                       | 55     | 1350 | 1932  
| 37 | Swinehart                        | J.A.C.S.                       | 74     | 1100 | 1952  
| 38 | "Values of Chem Thermodynamic data."  
| 39 | National Bureau of Standards, Series I |                      | (1947) |      |       
| 40 | | J.A.C.S.                       | 65     | 1767 | 1943  
| 41 | Pry and Hershey                  | J.A.C.S.                       | 56     | 1889 | 1934  
| 41 | Fenwick                          | Dissertation Univ. of Mich.    | 3      | 79   | 1922  
| 42 | Carter and Robinson              | J.C.S.                         | 130    | 267  | 1927  
| 43 | Popoff, Riddick, Birtch and Cough | J.A.C.S.                      | 53     | 1195 | 1931  
| 45 | Suggenheim                       | J.A.C.S.                       | 52     | 1315 | 1930  
| 46 | Chikashige                       | J.C.S.                         | 67     | 1013 | 1935  
| 47 | Vogel "Quantitative Inorganic Analysis" | Longmans |                 |       | 1953  
| 48 | Stone and Beeson                 | Ind. and Eng. Chem.            | 8      | 188  | 1935  

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CHRISTCHURCH, N.Z.
49. Loccis, Anal. Chem. 28, 1347 (1956)
50. Vogel, "Quantitative Inorganic Analysis" p. 232 (1953)
51. Vogel, "Quantitative Inorganic Analysis" p. 363 (1953)
52. Oesper, "Newer Methods of Vol. Analysis"

Van Nostrand, N.Y. (1938)

53. White, J.A.C.S. 36, 2011 (1914)
54. Dorsling, Hietanen and Sillén, Acta. Chem. Scand. 6, 901 (1952)
55. Hietanen and Sillén, Acta. Chem. Scand. 8, 741 (1952)
57. MacInnes, "Principles of Electrochemistry" p. 220 (1939)
58. Guggenheim, J.A.C.S. 52, 1315 (1930)
60. Planck, Wied. Ann. 40, 561 (1890)
61. Pleijel, Z. Phys. Chem. 72, 1 (1910)
62. Taylor, J. Phys. Chem. 31, 1478 (1927)
64. Glasstone, "The Electrochemistry of Solutions" p. 280 (1930)
65. Tait and Vosburgh, J.A.C.S. 40, 1291 (1918)
66. Scatchard, J.A.C.S. 47, 696 (1925)
68. Latimer, Schutz and Hicks, J. Chem. Phys. 2, 32 (1934)
69. Pollitzer, Z. Electrochem. 19, 513 (1913)
70. Dukin and Ewing, J.A.C.S. 62, 2280 (1940)
71. Harned, Keaton and Donelson, J.A.C.S. 58, 989 (1936)
72. Harned and Donelson, J.A.C.S. 58, 1280 (1937)
73. Owen and Poering, J.A.C.S. 58, 1575 (1936)
74. J.S. National Bureau of Standards (1948)
75. Latimer, Pitzer and Smith J.A.C.S. 60 1830 (1938)
76. Cartledge J.A.C.S. 63 911 (1941)
APPENDIX I

\[ R = 8.3144 \text{ abs. joules mole}^{-1} \]
\[ = 1.98713 \text{ cal mole}^{-1} \]
1 cal. = 4.1840 abs. joules
\[ T = 0.96490 \times 10^5 \text{ abs. coulombs} \]

<table>
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<th>T (°C)</th>
<th>( k = \frac{2.30259 \frac{RT}{F}}{\text{abs. } V} )</th>
<th>( \text{Molar values of } A )</th>
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<td>15</td>
<td>0.057474</td>
<td>0.5026</td>
</tr>
<tr>
<td>20</td>
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