Thesis Approved

C.L. Kenny  Major Advisor

Dean
PRACTICAL ELECTRODE POTENTIALS OF MERCURIC-MERCURIOUS SYSTEMS IN THE PRESENCE OF CHLORIDE IONS

BY

JAMES E. KOLLER

A THESIS

Submitted to the Faculty of The Creighton University in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Chemistry

OMAHA, 1944
DEDICATION

To Doctor Christopher L. Kenny whose wisdom, inspirational guidance and timely assistance made possible the successful completion of this investigation, the author gratefully dedicates this thesis.
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I. Introduction

In the Zimmerman-Reinhardt method for the determination of iron, .25 molar mercuric chloride (saturated) is used to oxidize excess stannous ion in a solution of hydrochloric acid leaving the iron in the ferrous state.¹ Rieman, Neuss and Naiman report that after the reaction has proceeded to completion, the oxidation-reduction potential of the solution is -.430 volts² and this value appears to be far out of proportion with the accepted value for the standard electrode potential for mercuric-mercurous systems determined by Popoff and his associates³ to be-.9050 volts. The potential for this system as roughly calculated from the approximate mercuric and mercurous ion concentrations in analytical solutions would appear to be approximately -1.3 volts. This certainly cannot be the true value for under such conditions ferrous iron would be oxidized to the ferric state

¹. Wm. Rieman, Jacob D. Neuss and Barnet Naiman, Quantitative Analysis, 183.
². Ibid., 199.
as evidenced by the standard electrode potential of 
-.783 volts for the ferrous-ferric system. The 
purpose of this thesis then, is to determine the 
practical electrode potentials of mercuric-mercurous 
systems in the presence of chloride ions and acids 
and to explain the behavior of these systems. The 
writer will endeavor to accomplish this by determin­
ing the electrode potentials of mercuric chloride 
solutions of varying concentrations with excess 
mercurous chloride present, and by investigating 
the potential values for solutions containing meas­
ured quantities of potassium chloride and of hydro­
gen chloride in addition to the calomel and mercuric 
chloride. This should show the separate effect of 
both the excess chloride and the acidity of the Zim­
merman-Reinhardt solutions.

1. W. C. Schumb and S. B. Sweetzer, ibid, 
57, 871 (1935).
II. Theoretical Discussion

A. "Oxidation-Reduction" Electrode Potentials

"Oxidation-Reduction" electrode potentials may be described as the potential impressed on an inert electrode by two soluble components in contact with it. An example of such an electrode is

\[(\text{Au}); \text{Hg}_2\text{Cl}_2, \text{HgCl}_2\].

Mercuric and mercurous ions are related by the reaction \(2 \text{Hg}^{++} + 2\text{e}^- = \text{Hg}_2^{++}\). A gold electrode inserted into a mercuric-mercurous solution might serve as a source of electrons for the reduction of mercuric ions and thus acquiring a positive charge, or it might serve as an acceptor of electrons for the oxidation of mercurous ions and as a result acquire a negative charge. Actually both processes must occur simultaneously and when equilibrium is reached, electrons are being deposited on and removed from the electrode at the same rate and the potential of the electrode as determined by comparison with a reference electrode indicates the relative strength of the oxidizing and reducing agents in the solution. At equilibrium, no changes in the concentrations of the ions occur since each is under-
going reaction at the same rate as that at which it is being formed.

Any change in the mercuric-mercurous solution which would effect the rate at which electrons are deposited or removed would interfere with the equilibrium and change the potential of the electrode. Where the two ions are at unit activity in the solution, the potential of the electrode is said to be the standard potential. (cf. later.) If the activity or effective concentration of the mercuric ion increases, the positive potential increases, and if the mercuric activity decreases, the potential will likewise decrease. The exact opposite will be true for changes in the activity of the mercurous ions.

In the presence of chloride ions, the dominating factor in determining the activity of mercurous ion in solution will be the low concentration due to the insolubility of mercurous ion. Mercuric ion activities will be much larger and will be affected by changes in mercuric chloride concentration, changes in activity due to formation of complex ions, possible hydrolysis or other effects brought about by variation of hydrogen ion concentration and, of course, variations in the ionic strength.
B. Practical Potential of Mercuric Chloride in Solution.

Discussion "A" has shown that the positive electrode potential of a mixed mercuric-mercurous system must increase with an increase in mercuric ion activity but decrease with an increase in mercurous ion activity. This is shown by the classical equation for the electrical potential of a system in terms of the standard electrode potential, $E^0$, of the system and the activities of the components.¹

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_k \cdot a_l}{a_A \cdot a_B}$$

for the system:

$$aA + bB \rightarrow kK + lL$$

in which

$$E^0 = \frac{RT}{nF} \ln K$$

But an oxidation-reduction reaction must involve at least two partial reactions, e.g.

1. $aA + ne^- \rightarrow kK$

and 2. $bB - ne^- \rightarrow lL$

¹ D. A. MacInnes, The Principles of Electrochemistry, 280
and \[ E^0 = E_1^0 + E_2^0 \]

Addition of the liquid junction potential, \( E_L \), when the total potential is being determined gives

\[
E = E_1^0 + E_2^0 + E_L - \frac{RT}{nF} \ln \frac{a_L^{b_k} a_k^{l_a}}{a_A^{b} a_B^{l}}
\]

If for a cell

\[ \text{Hg; } \text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl (Sat)} \parallel \text{HgCl}_2(\text{C}_1), \]

\[ \text{Hg}_2\text{Cl}_2(\text{Sat}); (\text{Au}) \]

or

\[ \text{Hg; } \text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl (Sat)} \parallel \text{HgCl}_2(\text{C}_1), \]

\[ \text{Hg}_2\text{Cl}_2(\text{Sat}); (\text{Pt}) \]

the oxidation is considered to occur at the left electrode, then

\[
E_2^0 = \frac{RT}{nF} \ln \frac{a_L}{a_B} = E_{\text{Sat. Calomel}} = -0.2458 \text{ V}
\]

If a salt bridge is used and concentrations in the solutions are much lower than that of the KCl, then the liquid junction potential is approximately constant and probably negligible giving:

---


2. Samuel Glasstone, *An Introduction to Electrochemistry*, 218
\[ E = -0.2458 + E_0^{\text{Hg}^{2+}-\text{Hg}^2^+} - \frac{RT}{nF} \ln \frac{a_{\text{Hg}^{2+}}}{a_{\text{Hg}^2^+}} \]

In a solution containing mercuric and chloride ions a complex ion, \( \text{HgCl}^2^- \), is formed and for this complex the instability constant \( 1.1 \times 10^{-16} \) is given. From this it can be calculated that in any mercuric chloride solution the chloride ion concentration is approximately constant at about \( 10^{-4} \) gram-ionic-weights per liter of solution since the compound provides an excess of mercuric ions for complex formation. Thus, if the solution is saturated with mercurous chloride, for which the solubility product constant is given as \( 1.1 \times 10^{-18} \), the mercurous ion activity will change only slightly and may be considered as a constant. If a constant, \( E'_2 \text{Hg}^{2+}-\text{Hg}^{2+} \) is defined:

\[ E' = E_0^{\text{Hg}^{2+}-\text{Hg}^2^+} + \frac{RT}{nF} \ln \frac{a_{\text{Hg}^{2+}}}{a_{\text{Hg}^2^+}} \]

then \( E_{\text{obs}} + 0.2458 = E' + \frac{RT}{nF} \ln \frac{a_{\text{Hg}^{2+}}}{a_{\text{Hg}^2^+}} \)

1. L. P. Hammett, Solutions of Electrolytes, 126

or  \[ E_{\text{Hg}^{++} | \text{Hg}_2^2} = E' + \frac{RT}{nF} \ln a_{\text{Hg}^{++}} \]

and at 25° C.,

\[ E = E' + 0.0295 \log a_{\text{Hg}^{++}} \]

It is to be noted that this is a reduction potential and that the sign (plus) will be opposite that of the standard potential as normally recorded.

This shows that within the approximations made in the development, the cells to be studied have a potential varying only with the mercuric ion activity.

In a mercuric chloride solution, however, divalent mercury is present in at least two forms -- the free ions and the chloride complex ions, \( \text{HgCl}_4^{2-} \). In addition, the presence of intermediate chloride complex ions and hydration and hydrolysis products is possible and it is to be seen that no simple method can be used for calculating the mercuric ion activity. The potential effect of the mercuric ion has the value described by the standard potential while that of the complex ions will be different and most likely lower. But when all solute ions (except for the minute concentrations of ions from the mercurous chloride present) enter
the solution from mercuric chloride, then the mercuric ion concentration as well as those of all of the possible mercuric-chloride complex ions will vary directly with the original mercuric chloride concentration. Thus the developed equation should still correctly describe variation of the potential of mercuric chloride solutions if it is remembered that the activity is that of the mercuric ion constituent and not of the so-called free ion. This activity may be approximated from the concentrations of solutions tested or it may be estimated by use of the simplified Debye-Hückel equation,\(^1\)

\[ -\log \gamma = 0.509 \frac{z_1 z_2}{\sqrt{\mu}} \]

where \(\gamma\) is the mean activity coefficient, \(z_1\) and \(z_2\) are charges on the ions of the solute and \(\mu\) is the ionic strength of solutions. But this equation is only moderately accurate where \(\mu\) has a value greater than .01 and does not account for the complex ion formation. Thus, \(E_1\) values calculated from activities determined in this manner will be of less significance than the slope of the curve.

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\(^1\) Calculated for a single solute in water at 25° C. from P. Debye and E. Hückel, *Physik. Z.*, 24, 185 (1923).
when $E$ is plotted as the ordinate against $\log a$. Actually, when the activity coefficient of mercuric chloride in solution is determined by the freezing point method values obtained are much smaller than those calculated from the Debye-Hückel equation, this being due in part to the decrease in the number of ions because of complex formation and in part to the large size of the $\text{HgCl}_4^-$ ions present.

C. Variation of Mercuric-Mercurous Potential with Chloride Ion Concentration

If the mercuric-mercurous potential of the test solution is measured with varying concentrations of potassium chloride also present, then the effect of chloride ion can be determined. Study of this effect probably should be separated into two steps: first, when the chloride ion concentration is less than double that of the mercuric chloride and second, when the excess chloride-mercuric ratio is greater than two to one. This dividing point is anticipated because here the total number

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1. Author, Unpublished Notes, this laboratory.
of chloride ions is four times as great as that of mercuric ions, the ratio necessary to convert nearly all mercuric ions present to the complex form. Table "A" on the following page shows how the chloride, mercuric and complex ion concentrations vary with solution concentrations (all in gram formula weights per liter) as calculated from the instability constant for the complex ion.

In the first step the mercuric ion concentration is gradually being decreased by the excess chloride ion and the ionic strength of the solution is being increased slowly due to complex ion formation while the mercurous ion concentration is decreased slightly. If, as has been assumed, the oxidizing properties of the mercuric chloride complex ion are less strong than those of mercuric ion, then it is to be expected that a rather slow and regular decrease in the positive electrode potential of the system will be observed as the concentration of potassium chloride is increased until its concentration is twice that of the mercuric chloride.

In the second step the mercuric ion concentration decreases very sharply, as is indicated by
## Table A

Approximate Ion Concentrations in KCl Solutions in .050 Molar HgCl₂ Saturated with Hg₂Cl₂

<table>
<thead>
<tr>
<th>Conc. KCl m/l</th>
<th>Ionie Strength</th>
<th>Calculated Approximate Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cl⁻</td>
</tr>
<tr>
<td>.000</td>
<td>.100</td>
<td>.0001</td>
</tr>
<tr>
<td>.050</td>
<td>.125</td>
<td>.00013</td>
</tr>
<tr>
<td>.100</td>
<td>.157</td>
<td>.0014</td>
</tr>
<tr>
<td>.150</td>
<td>.200</td>
<td>.050</td>
</tr>
<tr>
<td>.200</td>
<td>.250</td>
<td>.100</td>
</tr>
<tr>
<td>1.000</td>
<td>.900</td>
<td>.900</td>
</tr>
</tbody>
</table>
the calculations in Table "A", and then gradually becomes approximately constant at an extremely low value. Again assuming that the potential of the complex ion is less than that of the simple mercuric ion, it is seen that in this region a sharp drop in the positive electrode potential should be observed. It is to be noted that in this region the mercurous ion concentration is also being decreased by an increasing excess of chloride ion. However, this change is much smaller than that in the mercuric ion concentration and this, coupled with the fact that the potential variation is with the square of the mercuric ion concentration and only with the first power of the mercurous concentration, would still indicate that a sharp decrease in the potential should be expected as the excess of chloride ion increases. Finally, as the chloride excess becomes large and the mercuric-mercurous concentration ratio approaches a constant value the potential readings should again decrease only slightly with added KCl.

It has already been pointed out that the logarithm of the activity coefficient of a solute varies with the square root of the ionic strength
of the solution according to the theory of Debye and Huckel. The validity of this theory as applied to the potential of concentration cells has been established and discussed by MacInnes and a number of his associates.\(^1\) \(^2\) \(^3\) Therefore, it is to be concluded that in the mercuric-mercurous systems a decrease in the potential effect of the mercuric-chloride complex ion should be noted in solutions where this concentration remains approximately constant while the ionic strength of the solution is being increased such as is the case in the second step of this section of the study. This would add to the effect anticipated as a result of the discussion in the preceding paragraph and a gradual decrease in potential should be observed, even when the concentration of other salts in solution are being increased from an already high level.


\(^3\) D. A. MacInnes and A. S. Brown, *Chem. Rev.*, 18, 335 (1936).
D. Variation of Potential with Increased Acidity

Since the oxidation of stannous tin with mercuric chloride in the Zimmerman-Reinhardt method is carried out in a solution which is strongly acidic (.5 to 5 molar with respect to HCl) an investigation of the oxidizing properties of the mercuric chloride must include potential determinations in the presence of hydrochloric acid. The differences between the potentials of such solutions and similar ones containing potassium chloride can be attributed to the presence of hydrogen ions. Variation of more than a few millivolts is not to be expected. In the classic experiment of Popoff and his associates, a property $E''$ defined as:

$$E'' = E^0 - \frac{RT}{2F} \ln \frac{\gamma_{Hg^{2+}}}{\gamma_{Hg^{2+}_2}}$$

for the cell:

$$(Pt)H_2; Hg(ClO_4)_2 (m_1), Hg_2(ClO_4)_2 (m_2), HClO_4 (m_2); HClO_4 (m_2); H_2(Pt)$$

1. Calculated from the procedure of Rieman, Neuss and Naiman, op. cit., 183

2. S. Popoff, J. A. Riddick, V. I. Worth and L. D. Cugh, op. cit., 1195
was found to be constant for a given value of \( m_2 \)
and to vary only slightly with variation in \( m_2 \).
The value of \( E_0'' \) dropped from -.9072 volts at \( m_2=1.0 \)
molal to -.9008 at \( m_2=0.2 \) and then rose to an extra-
polated value of .9050 at \( m_2=0 \). Compared with vari-
tion in potential anticipated as a result of changes
in chloride ion concentration, it can be seen that
the effect of acidity on the potential of mercuric-
mercurous systems being measured should be of minor
importance.

Oxidation-reduction potentials in the pre-
sence of acids are of importance for analytical ap-
lication and have been treated in different ways
by different writers. Rieman, Neuss and Naiman de-
fine a useful term, the formal redox potential,
\( E'_0 \) as\(^1\)

\[
E'_0 = E_0 + \frac{RT}{nF} \ln \frac{J_2}{J_1} + \frac{RT}{nF} \ln \frac{f_2}{f_1}
\]

where \( J_1 \) and \( J_2 \) represent fractions of reduced and
oxidized forms present as free ions in a solution
that is more concentrated with respect to an acid,
and \( f_1 \) and \( f_2 \) are their activity coefficients.

---

\(^1\) Rieman, Neuss and Naiman, op.cit., 194.
These values are considered to be constant in the presence of the excess of acid and the formula for the potential of any solution reduces to

\[ E = E'_0 + \frac{RT}{nF} \ln \frac{(X_0)}{(X_r)} \]

where \((X_0)\) and \((X_r)\) are ion constituent concentrations. For the system being studied, the term \(\frac{RT}{nF} \ln (\text{Hg}^{++})\) might also be considered constant and at 25°:

\[ E'_0 = E'_0 - \frac{RT}{nF} \ln (\text{Hg}^{++}) = E - 0.0295 \log (\text{Hg}^{++})^2. \]

The value of \(E'_0\) will not be absolutely constant but may be calculated at different hydrochloric acid concentrations from data to be obtained in this study. Formal redox values for mercuric-mercurous systems have not been published.
III. Experimental Procedure

A. Saturated Calomel Reference Electrode

The electrode potentials for the cells:

1. $\text{Hg; } \text{Hg}_2\text{Cl}_2 (s), \text{KCl (sat)} \parallel \text{HgCl}_2 (c), \text{Hg}_2\text{Cl}_2 (s);$ (Pt)

2. $\text{Hg; } \text{Hg}_2\text{Cl}_2 (s), \text{KCl (sat)} \parallel \text{HgCl}_2 (c), \text{Hg}_2\text{Cl}_2 (s);$ (Au)

3. $\text{Hg; } \text{Hg}_2\text{Cl}_2 (s), \text{KCl (sat)} \parallel \text{HgCl}_2 (c_1), \text{KCl (c}_2), \text{Hg}_2\text{Cl}_2 (s);$ (Au)

4. $\text{Hg; } \text{Hg}_2\text{Cl}_2 (s), \text{KCl (sat)} \parallel \text{HgCl}_2 (c_1), \text{HCl (c}_2), \text{Hg}_2\text{Cl}_2 (s);$ (Au)

were determined where $c_1$ was .05 molar and $c$ and $c_2$ values were varied.

The electrode vessel (see diagram on following page) was a 25 x 150 mm. pyrex test tube with a platinum wire leading through the bottom of the tube into a mercury filled pyrex tube. A pyrex tube leading to a three-way stopcock was sealed into the side of the cell vessel. The other two tubes connected from the stop cock led respectively to a funnel used as a reservoir for the cell liquid and as a salt bridge to the beaker containing the solution being measured. A constriction about 1 mm. in inside
Sat. Soln., KCl-Hg_2Cl_2
Mixture, Hg-Hg_2Cl_2
Hg
Test Solution
N_2
Au or Pt

DIAGRAM OF APPARATUS
diameter was formed about 1 cm. from the end of the salt bridge and tip of the tube was bent upward. This permitted submerging the bridge in the solution without the potassium chloride solution contaminating the solution being tested. It is to be noted that the entire reference arrangement permitted easy flushing from the salt bridge of contaminated KCl solution. As a matter of practice, this bridge solution was replaced after each determination.

For preparing the reference electrode, Mallinckrodt Analytical Reagent grade mercury was passed in a fine stream through two successive columns of 10% nitric acid. Baker and Adamson Reagent grade potassium chloride was twice recrystallized from distilled water and the resulting crystals were suction-filtered, air dried and then dissolved in distilled water at 30° C. leaving a slight excess of solid KCl present. Mallinckrodt Analytical Reagent grade mercurous chloride was washed five times in distilled water and three times in saturated KCl solution, all at 30-35° C., and finally shaken with a small amount of the purified mercury in saturated KCl solution. Purified mercury was poured into the cell vessel to a depth of about 2 cm., com-
pletely covering the platinum connecting wire, and the mercury was covered with the Hg-Hg$_2$Cl$_2$-KCl mixture. After the calomel had settled, the cell vessel was filled with saturated KCl solution to within 3 cm. of the top and tightly stoppered.

B. Cell Vessel and Electrodes

Electrodes for use were prepared from thin sheets of platinum sealed into glass tubes. The area of the electrodes found most suitable was about .5 cm$^2$. Each electrode tube as well as the connecting tube for the calomel vessel was filled with mercury and a copper wire was inserted and sealed in with sealing wax. All electrodes were washed in concentrated nitric acid or chromate cleaning solution to remove any iron or other impurities present, then in dilute acid and finally in distilled water. Gold electrodes were prepared by plating on platinum from AuCl$_3$-NaCN solution for about seven minutes with a current of .01 ampere. Electrodes being plated were slowly rotated to assure uniform gold plating.

The solution being measured was placed in a 100 ml. pyrex beaker covered with a rubber stopper with four holes from which any loose particles of
rubber had previously been removed. Gold and platinum electrodes were introduced through two of these holes, the third was for the salt bridge and the fourth permitted insertion of a capillary tube through which nitrogen could be admitted to agitate the solution gently and to expel oxygen when readings were being taken.

C. Solutions for Measurement

In general, solutions of known molarity with respect to mercuric chloride and potassium chloride or hydrochloric acid were mixed, suspended mercurous chloride in excess was added and the entire mixture was diluted in volumetric flasks in order to obtain solutions for measurement. Sixty milliliter portions of these mixtures were always used.

One liter of .200 molar mercuric chloride solution was prepared by diluting Mallinckrodt Analytic Reagent grade HgCl₂ which had been previously dried four days over calcium chloride. Baker and Adamson Reagent grade KCl was dried at 110°C twenty-four hours and then weighed and diluted volumetrically. Approximately 3 molar hydrochloric acid was prepared from Mallinckrodt Analytical Reagent grade HCl and then standardized with silver nitrate. The
exact concentration was found to be 2.780 molar and this solution was diluted volumetrically to give a 1.000 molar solution. Concentrations were stated in gram-formula-weights per liter rather than by molarity in order to make possible preparation of solutions containing more than one solute and at varying concentrations by dilution.

D. Measurement of Electrode Potentials

Measurements of the potential difference between the gold and platinum electrodes submerged in solutions and the reference electrodes were made with a Leeds and Northrup type K potentiometer using a Leeds and Northrup type R high sensitivity galvanometer. The working cell was made up of two 1/2 volt dry cells in series referred to an Eppley Standard Cell. The EMF of the latter was checked against that of a Weston Standard Cell in order to verify its condition.

It was found that periods of three to ten days were required for constant readings to be obtained, the shorter times being required where a solute other than HgCl₂ was present. Equilibrium was reached more rapidly at elevated temperatures, more rapidly when nitrogen was being used to agitate the solution and
more rapidly for gold than platinum electrodes. Final readings were recorded when variation over a period of three to five hours at constant temperature (25.0 ± 0.1 °C.) did not exceed two tenths of a millivolt. After equilibrium had been reached and with nitrogen bubbling slowly through the solution the voltage rose very slowly if the nitrogen flow was stopped except in the case of the acid solutions where the rise occurred more rapidly. Total rise on exposure to air was usually about two or three millivolts. Nitrogen for this purpose was obtained by passing air slowly over red hot copper screen in a porcelain tube, a method found suitable for removing atmospheric oxygen by Harcourt and Lupton.¹

### Table I

**Observed Electrode Potentials**

\[ \text{Hg: Hg}_2\text{Cl}_2 (s), \text{KCl (sat)} || \text{HgCl}_2 (c), \text{Hg}_2\text{Cl}_2 (\text{sat}); (\text{Me}) \]

<table>
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<th>Solution Designation</th>
<th>c, m/l</th>
<th>E\text{Observed Me = Au}</th>
<th>E\text{Observed Me = Pt}</th>
<th>E = E\text{Obs - .246}</th>
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<td>.275</td>
<td>.521</td>
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### Table II

**Observed Electrode Potentials**

\[ \text{Hg; } \text{Hg}_2\text{Cl}_2 \text{ (s), KCl (sat) }| \text{HgCl}_2 \text{ (0.050), Solute (c), Hg}_2\text{Cl}_2 \text{ (sat); (Me)} \]

<table>
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<tr>
<th>Solution Designation</th>
<th>Solute</th>
<th>(c, \text{ m/l} )</th>
<th>(E_{\text{Observed}})</th>
<th>(E = E_{\text{Observed}} - 0.246)</th>
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<td>.233</td>
<td>.234</td>
</tr>
<tr>
<td>24</td>
<td>HCl</td>
<td>0.400</td>
<td>.229</td>
<td></td>
</tr>
</tbody>
</table>
### Table III

Calculated Values, $E' = E - 0.0295 \log m^2 \gamma^2$

<table>
<thead>
<tr>
<th>Concentration of HgCl₂ (m/1)</th>
<th>Molality¹</th>
<th>$\gamma_a^2$</th>
<th>$m\gamma_a$</th>
<th>$\log m\gamma_a$</th>
<th>$E$</th>
<th>$E'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.200</td>
<td>.211</td>
<td>.163</td>
<td>.0343</td>
<td>-1.424</td>
<td>.560</td>
<td>.644</td>
</tr>
<tr>
<td>.100</td>
<td>.104</td>
<td>.277</td>
<td>.0288</td>
<td>-1.540</td>
<td>.572</td>
<td></td>
</tr>
<tr>
<td>.050</td>
<td>.051</td>
<td>.404</td>
<td>.0206</td>
<td>-1.697</td>
<td>.550</td>
<td>.650</td>
</tr>
<tr>
<td>.025</td>
<td>.025</td>
<td>.527</td>
<td>.0132</td>
<td>-1.881</td>
<td>.539</td>
<td>.651</td>
</tr>
<tr>
<td>.020</td>
<td>.020</td>
<td>.563</td>
<td>.0113</td>
<td>-1.948</td>
<td>.530</td>
<td>.648</td>
</tr>
<tr>
<td>.010</td>
<td>.010</td>
<td>.667</td>
<td>.0067</td>
<td>-2.176</td>
<td>.523</td>
<td>.651</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of HgCl₂ (m/1)</th>
<th>$\gamma_b^3$</th>
<th>$m\gamma_b$</th>
<th>$\log m\gamma_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.200</td>
<td>.052</td>
<td>.109</td>
<td>-1.965</td>
</tr>
<tr>
<td>.100</td>
<td>.123</td>
<td>.0128</td>
<td>-1.894</td>
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<tr>
<td>.050</td>
<td>.227</td>
<td>.0116</td>
<td>-1.936</td>
</tr>
<tr>
<td>.025</td>
<td>.350</td>
<td>.0088</td>
<td>-2.057</td>
</tr>
<tr>
<td>.020</td>
<td>.392</td>
<td>.0078</td>
<td>-2.106</td>
</tr>
<tr>
<td>.010</td>
<td>.515</td>
<td>.0052</td>
<td>-2.288</td>
</tr>
</tbody>
</table>

1. Calculated from the density of solutions
2. Calculated for HgCl₂ as a 1:2 salt
3. Calculated for the salt, Hg⁻⁻⁻⁻⁻⁻⁻⁻ HgCl₄⁻
Graph I

Variation of $E$ with $-\log a_{\text{HgCl}_2}$

---

Theoretical Slope,

$E = E' + 0.0296 \log a_{\text{Hg}^{2+}}$
Graph II

Variation of E with Added Chloride Ion

- Values, KCl as Solute
- Δ Values, HCl as Solute
V. Discussion of Results

Values of $E'$ were calculated from activity coefficients calculated for $\text{HgCl}_2$ as a $1:2$ salt and considering it as the salt, $\text{Hg}^{++} + \text{HgCl}_4^{-}$. The latter values for the coefficient coincided reasonably well with experimental determinations but $E'$ values were in much better coincidence when calculated by the former method. Between $\text{HgCl}_2$ concentrations of .01 and .05 moles per liter, values of $E'$ coincided within $\pm .0015$ volts, well within the range of experimental error for methods used.

The slope "X" of the curve $E' = E - X \log a_{\text{Hg}^{++}}$ is .058 compared with the calculated .0591, and a value $E' = .650$ V. may be given although a more accurate method of determining the activity of the solute might lead to minor revision of this value. The breakdown of the curve at higher concentrations is undoubtedly due to difficulties encountered in measuring equilibrium potentials for these solutions. Potentiometer readings were more constant and equilibrium was reached more rapidly at lower concentrations.

As is shown by the graph of potentials for solutions containing $\text{KCl}$ and $\text{HCl}$, the effect
anticipated as a result of chloride ion excess was born out to a remarkably accurate degree. Not only did the potential values for the chloride ion variation follow a curve exactly as predicted but at the extremities it was found that the effect of HCl and KCl is almost identical. Further investigation with HCl is being carried out as this report is being written. The one questionable aspect of this part of the study is that the sharp drop in the potential would appear to occur at a concentration of chloride ion which is slightly too high since the value at (KCl) = .10 is in prolongation of the line for values observed at lower concentrations rather than at a point on the sharp decline of the curve. However, this could well be due to a very slight error in determining the concentration of either of the solutes present.

A number of suggestions for practical applications of the variation of the practical potentials of mercuric-mercurous systems in the presence of chloride ion can be advanced. First of all, the possibility of its use in a potentiometric method for the determination of mercuric ion cannot be overlooked. The observed potential drop of only .06
volts may be too small for practical determination but on the other hand, the required chloride-mercuric ion ratio of four to one would make the determination very accurate, even where the mercuric ion concentration is rather low.

Another general idea to be pursued is that of the determination of the solute activity of the mercuric-chloride complex solutions, a possibility advanced by Glasstone.\(^1\) Applied to this complex, the formula for calculation would be

\[
E = 0.650 + 0.0591 \log K_i + 0.0591 \log a_{\text{HgCl}_4^{2-}} - 0.0591 \log a_{\text{Cl}^-}
\]

where \(K_i\) is the instability constant for the complex ion. Approximating \(E\) as 0.500v in a solution of equal mercuric and chloride ion concentration, a value of 0.20 for the activity coefficient of the complex is obtained.

Still another possibility is that of using a cell of this type for determining the composition and instability constant for complex ions. This experiment verifies the composition of the mercuric-chloride complex ion but accurate values for the

\[1. \] Samuel Glasstone, op. cit., 261.
instability constant could be obtained only with additional development and experimentation.

Using the data obtained for solution 22 the formal redox potential of mercuric chloride in .40 molar hydrochloric acid is calculated as \( E_0^\prime = .603 \text{v} \). Under the same conditions the values given by Rieman, Neuss and Naiman include

\[
\begin{align*}
E_0^{\prime} & \text{Fe}^{3+} - \text{Fe}^{2+} = .715 \text{v} \\
E_0^{\prime} & \text{Sn}^{4+} - \text{Sn}^{2+} = .145 \text{v}
\end{align*}
\]

From this it is calculated that the concentration ratio \( \text{Fe}^{3+} : \text{Fe}^{2+} \) in a .05 molar mercuric chloride solution in .40 molar HCl is .00009 of oxidation of ferrous iron would occur to a degree of less than .01 percent of the total iron present. On the other hand, the ratio \( \text{Sn}^{4+} : \text{Sn}^{2+} \) is \( 1.6 \times 10^{11} \) so oxidation of stannous ion is complete. The observed potential of the solution concerned is .475 volts, substantially the same as the published value for the actual Zimmerman-Reinhardt mixture.

VI. Conclusions

1. A simple cell using a saturated calomel electrode for reference was designed and found satisfactory.

2. Electrode potentials for .01 - .10 molar solutions of mercuric chloride saturated with mercurous chloride were found to be $E = 0.650 + 0.0295 \log a \text{Hg}^2^+ +$.

3. Mercuric-mercurous systems in the presence of excess KCl and HCl were found to have electrode potentials predictable by concentration changes due to the formation of the mercuric-chloride complex ion.

4. The composition of the mercuric-chloride complex ion was verified.

5. The formal redox potential for .05 molar mercuric chloride in .40 molar hydrochloric acid was found to be .603 V, a value adequately explaining the action of this compound in the Zimmerman-Reinhardt iron determination.

6. Possibilities for additional research were discussed.


Randall, Merle and Young, Leona E., "The Calomel and Silver Electrodes in Acid and Neutral Solutions," *Journal of the American Chemical Society, 50* (1928) 989-1004


Shedlovsky, Theodore and MacInnes, Duncan A., "The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. III. Potassium Chloride. IV. Calcium Chloride," *Journal of the American Chemical Society, 59* (1937) 503-6