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The Effect Of Temperature On the Standard Oxidation-Reduction Potential Of The Ferricyanide-Ferrocyanide System

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THE EFFECT OF TEMPERATURE
ON THE STANDARD
OXIDATION-REDUCTION POTENTIAL
OF THE
FERRICYANIDE-FERROCYANIDE SYSTEM

by

MICHAEL C. SCHNELLER

A Thesis Submitted To
The Department of Chemistry of Carroll College
In Partial Fulfillment of the Requirements for
Academic Honors with the B. A. Degree in Chemistry

Helena, Montana
May, 1966

Approved by

[Signature]
Date May 7, 1966
TO MY PARENTS, BROTHERS, AND SISTER
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I. INTRODUCTION

A) Previous investigation

In 1935 Kolthoff and Tomsicek determined the standard oxidation-reduction potential of the ferricyanide-ferrocyanide half-cell at 25°C (8). This cell is characterized as an open thermodynamic system of two soluble complexes in equilibrium at an inert Pt electrode; \( \overline{\text{Fe(ON}_6^{3-}, \text{Fe(ON}_6^{4-}; \text{Pt} \). The reduction half-cell reaction is expressed by

\[
\text{Fe(ON}_6^{3-} + e = \text{Fe(ON}_6^{4-}
\]

in which the iron (III) of ferricyanide is reduced to iron (II) of ferrocyanide. By convention the cell is completed by a standard hydrogen electrode (SHE), whose half-cell reaction is expressed by

\[
\text{H}^+ + e = \frac{1}{2} \text{H}_2
\]

and whose standard reduction potential is arbitrarily assigned a value of zero at all temperatures, when the hydrogen ion activity is unity and the hydrogen gas pressure is one atmosphere. In this study all reactions will be expressed in terms of reduction potentials. Therefore, those agents with positive standard potentials will be weaker reducing agents than the hydrogen ion.
The Nernst expression for the two half-cells under consideration is given as follows:

\[ E_{1/2} = E^0 + \frac{0.000199 T}{n} \log \frac{a_{Fe(CN)_6^{3-}}}{a_{Fe(CN)_6^{4-}}} \] (1)

\[ E_{1/2} = 0 + \frac{0.000199 T}{n} \log \frac{a_{H^+}}{P_{H_2}} \] (2)

\[ = 0 + \frac{0.000199 T}{n} \log 1 \]

\[ = 0 \]

where \( T \) is the absolute temperature, \( n \) the number of electrons involved in the transfer process, \( a \) the ionic activity, and \( P \) the pressure in atmospheres (4). The total cell reaction is

\[ Fe(CN)_6^{3-} + \frac{1}{2} H_2 = Fe(CN)_6^{4-} + H^+ \]

It can be readily seen in equation (1) that if the activity of the two species is the same, the half-cell potential will equal the standard electrode potential \( E^0 \), at that temperature. Since \( T \) is a variable in equation (1), \( E^0 \) will be temperature dependent.

B) Statement of the Problem

It is the purpose of this investigation to determine the temperature dependence of \( E^0 \), that is, \( E^0 \) as a function of the variable \( T \). From this data an entropy difference can be obtained for the total cell reaction (2). The entropy
data of this investigation will then be compared with the recent work done by R. H. Busey on absolute ion entropies in aqueous solution of the ferricyanide-ferrocyanide couple (3). Also, Debye - Hückel expressions for activity of salts in aqueous solutions will be computed in terms of ionic strength. The effect of activity on $E^0$ will be discussed on this basis (8).

Finally a brief treatment of reaction mechanism will be discussed with the hope of obtaining a picture of influencing factors directing the reaction process of the ferricyanide-ferrocyanide couple.
II. EXPERIMENTAL

A) Materials used

\[ K_4\text{Fe} (\text{CN})_6 \cdot 3\text{H}_2\text{O} \]. Reagent grade potassium ferrocyanide was used without further purification.

\[ K_3\text{Fe} (\text{CN})_6 \]. Also reagent grade potassium ferricyanide was used without further purification. With each reagent standard 10^{-2}M aqueous solutions were prepared in liter quantities.

A phosphate buffer (\( \text{Na}_2\text{HPO}_4 \) and \( \text{NaH}_2\text{PO}_4 \)) was prepared at \( \text{pH} = 7.00 \) (5). Ordinary distilled water was used throughout the procedure.

B) Apparatus

Figure (1) is a schematic diagram of the experimental apparatus. The ferricyanide-ferrocyanide system was kept in a 100 ml capacity water-jacketed cell. The reference half-cell employed was the saturated calomel electrode (SCE) immersed in a saturated solution of KCl. Electrical contact between the two half-cells was made by a KCl-agar salt bridge. The temperature control consisted of a thermally regulated heating element in an insulated water bath.
Fig. (1) SCHEMATIC DIAGRAM FOR CELL MEASURING APPARATUS
To insure uniform temperature, the bath was kept in constant agitation by a motor driven stirrer. The temperature control operated within ±0.05°C. A water pump was situated in the bath in order to circulate water around the reaction cell. To obtain potential measurements, a Leeds - Northrup student potentiometer was employed. Readings were taken to within ±.5 millivolt with a Pt single wire electrode.

0) Experimental procedure

E°'s were determined at 5°C increments in the temperature range 25°C to 75°C. Quantitative dilutions were performed to yield $10^{-3}$ M solutions of Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$.

A 25 ml. aliquot of one solution was buffered at pH = 7.00 with a 25 ml. aliquot of the phosphate buffer solution. Then portions of the other solution were quantitatively added with a 50 ml. buret to the reaction cell. The cell potentials were recorded at three different compositions in this manner. The addition process of the cyanide solutions was reversed at each temperature, thereby yielding a total of six cell compositions that were measured. Before a final reading was recorded, a period of time was allowed to elapse before thermal equilibrium could be attained. At this point no drift in the galvanometer null position could be detected. A magnetic stirrer insured the homogeneity of the reaction mixture.
To calibrate the potential of the reference calomel electrode, a saturated quinhydrone half-cell was used. This cell is an equilibrium system of equimolar mixtures of quinone and hydroquinone (6).

\[
\text{Quinone} + 2\text{H}^+ + 2e^- = \text{Hydroquinone}
\]

The Pt wire potential at a room temperature of 23°C measured against the SHE is

\[
E_{\text{qh}} = .701 + .0591 \text{ pH (3)}
\]

The total cell potential becomes

\[
E_{\text{cell}} = .701 + .0591 \text{ pH} - E_{\text{SCE}} \quad (4)
\]

\[
E_{\text{SCE}} = -.701 + .0591 \text{ pH} - E_{\text{cell}} \quad (5)
\]

The pH of the quinhydrone solution was measured to an accuracy of ± .01 pH unit on a Beckman Zeromatic pH meter. \(E_{\text{cell}}\) was measured with a Leeds - Northrup student potentiometer. Within the course of a week, three check calibrations were made on the calomel electrode.
TABLE 1

<table>
<thead>
<tr>
<th>Date</th>
<th>ESCB</th>
<th>Arithmetic Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/17/66</td>
<td>.238 volt</td>
<td>.238 volt</td>
</tr>
<tr>
<td>3/21/66</td>
<td>.235 volt</td>
<td></td>
</tr>
<tr>
<td>3/23/66</td>
<td>.242 volt</td>
<td></td>
</tr>
</tbody>
</table>

The value .238 volt differs from the standard value of .246 volt by 8 millivolts. This electrode was kept at a constant room temperature of 23°C.

In equation (1) the value of n represents the electron transfer. It can be determined from a preliminary examination of data. The observed cell potential (E\text{OBS}) should be a linear plot of \( \log \frac{(\text{OX.})}{(\text{RED.})} \).

![Fig. (2) LINEAR PLOT OF E\text{OBS.} VS. LOG (OX.) (RED.)](image-url)
where (OX.) is the concentration of the oxidized species Fe(CN)$_6^{3-}$, and (RED.) the concentration of the reduced species Fe(CN)$_6^{4-}$. The slope of the graph in figure (2) becomes

\[ \text{slope} = \frac{2.303 \, R \, T}{n \, F} \]  (6)

Solving for $n$

\[ n = \frac{2.303 \, R \, T}{(\text{slope}) \, F} \]  (7)

$n$ was computed at 25, 45, 50, and 70°C, and was found to be equal to one ($n = 1$). Therefore, it was assumed that $n$ took on a value of one at all intermediate temperatures. Equation (1) now becomes

\[ E_{\text{GC}} = E^0 + 0.00199T \log \frac{a_{\text{Fe(CN)}_6^{3-}}}{a_{\text{Fe(CN)}_6^{4-}}} \]  (8)
III. EXPERIMENTAL RESULTS

At zero ionic strength, or unit activity, \( E^0 \) has been extrapolated to a value of .3560 volt \((8)\). \( E^0 \) depends directly upon the ionic strength of the solution and varies from .3560 to .4762 volt \((8)\). In this investigation, the buffering agent is the only contributing factor to ionic strength. Utilizing Debye - Hückel theory, the mean ionic activity \( f \) can be expressed in terms of the ionic strength \( I \) by

\[
\log f = -0.509 \ Z \ I^{1/2}
\]  

\((9)\)

where

\[
I = M_1 Z_1^2 + M_2 Z_2^2 + M_3 Z_3^2 + \cdots + M_n Z_n^2
\]

\((10)\)

and \( Z \) denotes the charge on an ionic species with concentration \( M \). Therefore, all \( E^0 \)'s reported in this investigation were measured at the computed ionic strength of .148 according to equation \((10)\).

Since ferricyanide has a charge \((-3)\) and ferrocyanide \((-4)\), the Debye - Hückel expression of equation \((9)\) can be substituted into equation \((1)\) at unit concentration to yield

\[
E_{3C} = E^0 + 0.00199T \log \frac{f_3}{f_4}
\]

\((11)\)
where $f_3$ and $f_4$ are the activity coefficients of the ferricyanide and ferrocyanide anions respectively.

Further manipulation results in

$$E^\circ_{34} = E^\circ + .000199T (3.5 \text{ I}^\circ)$$  \hspace{2cm} (12)

However the last term of the preceding equation (12) will be neglected in reporting $E^\circ$'s.

Measurement against the SHE yields

$$E_{\text{cell}} = E^\circ_{34} - E_{\text{SCE}} = E^\circ + .000199T \log \frac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe(CN)}_6^{4-}]} - E_{\text{SCE}}$$  \hspace{2cm} (13)

Solving for $E^\circ$

$$E^\circ = E_{\text{cell}} - .000199T \log \frac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe(CN)}_6^{4-}]} + .238$$  \hspace{2cm} (14)

The following calculated values in table (2) are at the temperatures listed. Each determination was at an ionic strength (I) of .148.
A plot of $E^0$ as a function of temperature $T$ yields a set of points as shown in figure (3).

It is immediately noticeable that this set of points produces two linear plots instead of the expected one. Such anomaly is unpredicted and might possibly indicate a certain transition taking place between $45^\circ C$ and $50^\circ C$. Thus there are two slopes in this temperature range. They have been computed on the basis of figure (3) and are designated by

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$E^0$</th>
<th>Number of Determinations</th>
<th>Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>25$^\circ$C</td>
<td>.404 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>30$^\circ$C</td>
<td>.391 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>35$^\circ$C</td>
<td>.384 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>40$^\circ$C</td>
<td>.376 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>45$^\circ$C</td>
<td>.368 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>50$^\circ$C</td>
<td>.367 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>55$^\circ$C</td>
<td>.354 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>60$^\circ$C</td>
<td>.344 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>65$^\circ$C</td>
<td>.334 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>70$^\circ$C</td>
<td>.323 volt</td>
<td>6</td>
<td>.148</td>
</tr>
<tr>
<td>75$^\circ$C</td>
<td>.312 volt</td>
<td>6</td>
<td>.148</td>
</tr>
</tbody>
</table>
Fig. (3) $E^0$ VS. $T$

$\text{SLOPE} = \left(\frac{2E^0}{2T}\right)_p$

$pH = 7.00$
\[ 25^\circ \leq T \leq 45^\circ \quad \left( \frac{\partial E^o}{\partial T} \right)_P = -0.00161 \text{ volts-degrees}^{-1} \quad (15) \]

\[ 50^\circ \leq T \leq 75^\circ \quad \left( \frac{\partial E^o}{\partial T} \right)_P = -0.00220 \text{ volts-degrees}^{-1} \quad (16) \]

where \( P \) is the prevailing atmospheric pressure and is constant. All subsequent operations involving

\( \left( \frac{\partial E^o}{\partial T} \right)_P \)

will therefore necessarily involve two operations, one with equation (15), and the other with equation (16).
IV. DISCUSSION OF EXPERIMENTAL RESULTS IN TERMS OF THERMODYNAMIC PROPERTIES AND DEBYE-HÜCKEL THEORY

A) Gibbs-Helmholtz equation

Chemical thermodynamics is concerned with the changes in the state of a system that occur in a variety of processes. State functions are used to describe the state of the equilibrium system, and they have the property of being path independent. That is, only initial and final states are necessary to describe the system. However, these state functions are defined in terms of variables that dictate which path is taken. Therefore, a close examination of those variables that affect a chemical reaction is necessary (10).

A criterion of chemical spontaneity can be expressed in terms of the Gibbs free energy $G$, which is a function of the state of a system and has the units of energy

$$G = H - TS$$

(17)

where $H$ is the enthalpy, $T$ the temperature, and $S$ the entropy of the system. For an infinitesimal change

$$dG = dH - TdS - SdT$$

(18)

$$dG = dH - TdS \quad \text{(constant $T$)}$$
and for a reversible process

\[ \int_{1}^{2} dG = \Delta G = \Delta H - T \Delta S \]  

(19)

For an isothermal process, equation (19) relates the free energy change to the simultaneous changes in enthalpy and entropy. It can be shown from the first and second laws of thermodynamics that for an irreversible spontaneous process

\[ \Delta G < 0 \]  

(20)

Thus Gibbs free energy is a minimum at equilibrium for a constant temperature and pressure process. For equation (19) to satisfy equation (20) then, it holds that the more negative \( \Delta H \) is, the more negative \( \Delta G \) becomes. Furthermore, the more positive \( \Delta S \) is, \( \Delta G \) becomes more negative.

Therefore, there are two driving forces governing the behavior of thermodynamic systems: a tendency toward minimum enthalpy and a tendency toward maximum entropy (10). At all times, however, it must be acknowledged that thermodynamic relations do not prescribe the reaction rate or mechanism.

From equation (17) the following expressions can be derived:

\[ dG = - SdT + VdP \]  

(21)

\[ \left( \frac{\partial \Delta G}{\partial T} \right)_P = - \Delta S \]  

(22)
Thus equation (22) is a method for determining entropy differences. The change in the Gibbs free energy difference with respect to temperature is equal to the decrease in entropy (9).

An electrochemical half-cell can be considered as a thermodynamic system capable of performing reversible work ($W_{\text{elec}}$) by transferring electrical charge through an external circuit. For the cell to proceed spontaneously toward an equilibrium position

$$
\Delta G = -W_{\text{elec}}
$$

(23)

The nature of this infinitesimal electrical work is defined as the product of a potential difference (intensity factor) and a quantity of charge (capacity factor), and this work can be related to the Gibbs free energy change (10)

$$
\Delta G = -n \frac{F}{z} \Delta E
$$

(24)

where $n$ is the number of electrons transferred, and $\frac{F}{z}$ is the Faraday constant (96,500 coulombs). If reactants in their standard states are converted to products in their standard states, the standard free energy change may be written

$$
\Delta G^0 = -n \frac{F}{z} \Delta E^0
$$

(25)

If $E^0$ is measured against the SHE, equation (25) becomes
\[ \Delta G^0 = -n F E^0 \]  (26)

According to equation (22), the entropy difference can be derived on the basis of equation (26)

\[ \left( \frac{\partial \Delta S^0}{\partial T} \right)_P = -n F \left( \frac{\partial E^0}{\partial T} \right)_P \]  (27)

and

\[ \Delta S^0 = -n F \left( \frac{\partial E^0}{\partial T} \right)_P \]  (28)

Substitution into equation (19) yields the Gibbs–Helmholtz equation (9)

\[ \Delta H^0 = -n F E^0 + n F T \left( \frac{\partial E^0}{\partial T} \right)_P \]  (29)

On the basis of equation (28), the standard entropy difference of the ferricyanide-ferrocyanide couple versus the standard hydrogen electrode can be computed with the experimental data obtained.

### TABLE 3

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>( \left( \frac{\partial E^0}{\partial T} \right)_P )</th>
<th>( \Delta S^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25° ≤ T ≤ 45°</td>
<td>-.00161 volts-degrees^{-1}</td>
<td>-37.1 cal-degrees^{-1}</td>
</tr>
<tr>
<td>50° ≤ T ≤ 75°</td>
<td>-.00220 volts-degrees^{-1}</td>
<td>-50.6 cal-degrees^{-1}</td>
</tr>
</tbody>
</table>
B) Absolute ion entropies

The third law of thermodynamics states that the entropy of a perfect crystal approaches zero as the absolute temperature approaches zero. On this basis absolute entropies of systems can be calculated by \( S^0 = \int_0^T \frac{dQ}{T} \) and \( S = 0 \) \( (30) \)

\[
S^0 = \int_0^T C_p \frac{dT}{T} \tag{31}
\]

Once \( C_p \) is known as a function of temperature, then equation (31) will give an absolute entropy value. If entropies of aqueous ions are desired, then heats of solution must be measured. Heat capacity measurements have been run on potassium ferricyanide from 0°K to 273.15°K \( (3) \). The calorimetric work on this system has been done by Watt, Christensen, and Izatt \( (13) \). The calculation of an entropy change in aqueous solution involves changes in vibrational, translational, and rotational energy states \( (7) \). Even the gaseous electron of an ion has been assigned thermodynamic values \( (11) \).

On the basis of the preceding work, Busey has reassigned values for the entropies of \( \text{Fe(CN)}_6^{3-} \) (aq) and \( \text{Fe(CN)}_6^{4-} \) (aq) \( (3) \).

\[
\begin{align*}
\text{Fe(CN)}_6^{3-} \text{ (aq)} & \quad S^0 = 64.8 \text{ e.u.} \\
\text{Fe(CN)}_6^{4-} \text{ (aq)} & \quad S^0 = 24.0 \text{ e.u.}
\end{align*}
\]
Now the entropy change ($\Delta S^0$) for the total cell reaction may be computed.

$$\text{Fe(CN)}_6^{3-} + \frac{1}{2} \text{H}_2 = \text{Fe(CN)}_6^{4-} + \text{H}^+$$

$$\Delta S^0 = S^0_{\text{Fe(CN)}_6^{3-}} + S^0_{\text{H}^+} - S^0_{\text{Fe(CN)}_6^{4-}} - S^0_{\text{H}_2}$$  \hspace{1cm} (32)

By convention $S^0_{\text{H}^+} = 0$, and

$$\Delta S^0 = 24.0 + 0 - 64.3 - \frac{1}{2}(31.2)$$

$$\Delta S^0 = -56.4 \text{ e.u.}$$  \hspace{1cm} (33)

where $S^0_{\text{H}_2} = 31.2 \text{ e.u.}$

**TABLE 4**

<table>
<thead>
<tr>
<th>Method of Absolute Ion Entropies</th>
<th>$\Delta S^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometric Method</td>
<td>-56.4 cal-degree$^{-1}$</td>
</tr>
<tr>
<td>$\left(\frac{\partial S^0}{\partial T}\right)_P = -0.00161$</td>
<td>-37.1 cal-degree$^{-1}$</td>
</tr>
<tr>
<td>$\left(\frac{\partial S^0}{\partial T}\right)_P = -0.00220$</td>
<td>-50.6 cal-degree$^{-1}$</td>
</tr>
</tbody>
</table>

From table (4) it is noted that the value for $\Delta S^0$ calculated in the higher temperature region agrees more closely with the absolute entropy calculation. The reason for this is not clearly understood. Association factors due to the buffer cannot be overlooked. Thus there exist
two markedly distinct methods of obtaining $\Delta S^0$, and in this investigation a close degree of agreement has been found in the presence of a certain anomaly.

C) Debye - Hückel theory

Equation (12) is the Debye - Hückel expression for the standard potential dependence on ionic strength $I$. However, this equation gives $E^0$'s that are consistently high compared with observable data. There is evidence to believe that potassium ferrocyanide is an incompletely dissociated species (8).

$$\text{HFe(CN)}_6^{3-} = \text{H}^+ + \text{Fe(CN)}_6^{4-}$$

Ferrocyanic acid

Also other cations are believed to behave similarly ($\text{Cs}^{++}$, $\text{Rb}^{++}$, $\text{K}^+$, $\text{NH}_4^+$, $\text{Na}^+$, $\text{Li}^+$). The type of cation has been shown to have a pronounced effect upon the amount of dissociation (8). Divalent ions influence $E^0$ more than do univalent ions (8). More work is needed to settle this problem.
V. OXIDATION-REDUCTION MECHANISMS OF COMPLEX IONS

Both ferricyanide and ferrocyanide ions are inert, low-spin, octahedral complexes. The cyanide ligands have forced the unpaired electrons of the gaseous metal ions to pair off into low-spin states of $t_{2g}$ orbitals, with the cyanide ions occupying the higher energy $e_g$ orbitals (4).

Obstacles to a rapid electron transfer are due in part to ion accessibility and in part to high energies of activation.

**Fig. (4) ELECTRONIC STRUCTURE OF Fe(CN)$_6^{3-}$ AND Fe(CN)$_6^{4-}$**
Experiments have verified that redox reactions are generally rapid if the equilibrium structures do not change appreciably in the course of the reaction. Radioactive tracer methods are employed to determine reaction rates. A reducing agent may be prepared "hot" and added to the oxidizing species. After a time, an analysis of products indicates the rate of electron transfer (12). The rate of the redox reaction

\[ *\text{Fe(CN)}_6^{4-} + \text{Fe(CN)}_6^{3-} = *\text{Fe(CN)}_6^{3-} + \text{Fe(CN)}_6^{4-} \]

experimentally is very fast.

For redox reactions two basic paths appear plausible. In one, direct electron transfer provides a path for an electron jump from one species to another. This is also called an outer-sphere activated complex mechanism. In the other process the oxidant and reductant are attached to each other by a bridging molecule, atom, or ion through which the electron can pass. This is called the bridged activated complex mechanism (1).

Since the ferricyanide-ferrocyanide redox reaction is quite fast, the bridged activated complex can be eliminated in favor of direct electron transfer. The Franck-Condon principle stipulates that atomic arrangement must not be appreciable during the course of the reaction. The cyanide ligands approach the $\text{Fe}^{3+}$ ion
more closely than the Fe$^{+2}$ ion. During electron transfer from Fe(CN)$_6$$^{4-}$ to Fe(CN)$_6$$^{3-}$, none of the Fe, O, or N atoms move. As a result there is the formation of Fe(CN)$_6$$^{3-}$ in which Fe-O bonds are too long and Fe(CN)$_6$$^{4-}$ in which the Fe-O bonds are too short. Both of these products are of a higher energy state than the equilibrium position. However, this reaction cannot run uphill; there can be no net gain in energy. Therefore, before electron transfer will take place, the Fe-O bonds in Fe(CN)$_6$$^{4-}$ must become shorter, and the Fe-O bonds in Fe(CN)$_6$$^{3-}$ must become longer. For this to happen, the system requires energy. A compatible structure for reaction would be one in which the Fe(CN)$_6$$^{3-}$ and Fe(CN)$_6$$^{4-}$ ions have equivalent geometries. Then no net gain of energy would be produced. Since Fe(CN)$_6$$^{3-}$ and Fe(CN)$_6$$^{4-}$ are similar, a rather small amount of activation energy will make the ions alike; thus electron transfer can occur rapidly (1).
VI. CONCLUSION

The great strength of the field of chemical thermodynamics is the verification of theoretical concepts by a very large number of experiments. This experimental study has been one of just such a type. It has been shown that a single measurement of an entropy difference can be obtained by two distinctive methods, one a potentiometric method, and the other a method of heat capacity and calorimetry. The results obtained in this investigation of the entropy difference of the ferricyanide-ferrocy anide couple has been shown to agree favorably with the calorimetry study.

Still unexplained are the two slopes attained in calculating the temperature dependence of the half-cell. Association factors of this couple await further investigation. It is the field of reaction rates and reaction mechanisms, based on advances in bond theory of the transition metals, that will afford the best look at the properties of the ferricyanide-ferrocy anide system.
BIBLIOGRAPHY


(3) Busey, R. H.. The Entropy of K₃Fe(CN)₆ and Fe(CN)₆³⁻ (aq). Free Energy of Formation of Fe(CN)₆³⁻ (aq) and Fe(CN)₆⁴⁻ (aq), J. Phys. Chem., 24, 3179 (1965).


