Thermodynamic Data from a Calomel-Silver/Silver Chloride Cell

In this laboratory exercise we will construct a Calomel-Silver/Silver Chloride electrochemical cell and measure its Standard Cell Potential ($\varepsilon^0$) at various temperatures. From this data we will determine $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ for the Cell's underlying chemical reaction.

Voltaic Cells, the modern descendants of the Pile of alternating Copper and Zinc plates, separated by saline soaked cardboard disks, constructed by Alessandro Volta, are referred to in the common parlance as Batteries. A Voltaic Cell is an electrochemical cell that is constructed such that its Cell Reaction proceeds spontaneously; with the concomitant possibility of producing work in the surroundings by shunting electrons up an electric Potential and through an external device.

The Potential ($\phi$) at each electrode of a Voltaic Cell can be determined by measuring the work required to bring a positive test charge ($q_o$) from infinity to the electrode. The Cell Potential ($\varepsilon$) or electromotive force is the potential difference between the two electrodes.

$$\varepsilon = \phi' - \phi$$
Since electrons, which are negatively charged, spontaneously move from the anode to the cathode of the Voltaic Cell we know that $\phi'$ is higher than $\phi$. In this case, the work done by the system (recall our sign convention for work) in moving $n$ moles of electrons, a total charge of $nF$ ($F$ is the Faraday Constant of 96485 C/mol), from the anode to the cathode, is given by:

$$W_{el} = -nFE$$  \hspace{1cm} (Eq. 1)

Since at constant $T$ and $P$, the change in the Gibbs Free Energy is the maximum non-hydrostatic (P-V) work available:

$$W_{el} \leq \Delta G$$  \hspace{1cm} (Eq. 2)

giving us:

$$-nFE \leq \Delta G$$  \hspace{1cm} (Eq. 3)

If the process is carried out reversibly, then:

$$\Delta G = -nFE$$  \hspace{1cm} (Eq. 4)

Finally, if all the species of the Cell Reaction are in their Standard States, then we have:

$$\Delta G^0 = -nFE^0$$  \hspace{1cm} (Eq. 5)

The temperature dependence of the Cell’s potential allows us to determine the entropy change:

$$\Delta S^0 = -\left(\frac{\partial \Delta G^0}{\partial T}\right)_P = nF \left(\frac{\partial E^0}{\partial T}\right)_P$$  \hspace{1cm} (Eq. 6)

This, finally, allows us to determine the enthalpy change:

$$\Delta H^0 = \Delta G^0 - T \Delta S^0 = -nFE^0 + nFT \left(\frac{\partial E^0}{\partial T}\right)_P$$  \hspace{1cm} (Eq. 7)

If the temperature dependence of $E^0$ shows significant curvature, then:

$$\Delta C_P^0 = \left(\frac{\partial \Delta H^0}{\partial T}\right)_P = nFT \left(\frac{\partial^2 E^0}{\partial T^2}\right)_P$$  \hspace{1cm} (Eq. 8)
It should be noted that the Cell is operating reversibly when it is configured such that it is in an Open Circuit configuration. Thus, for open circuit operation $Q_{\text{rev}}$ is:

$$Q_{\text{rev}} = T \Delta S$$  \hspace{1cm} (Eq. 9)

If the Cell is shorted, then the processes occur irreversibly and we have:

$$Q_{\text{irrev}} = \Delta H$$  \hspace{1cm} (Eq. 10)

As the Cell must conform to the constraints of the Second Law of thermodynamics, this data should be consistent with the Inequality of Clausius:

$$dS > \frac{\delta Q_{\text{irrev}}}{T}$$  \hspace{1cm} (Eq. 11)

In this exercise, we will extract the above thermodynamic data from a Calomel-Silver/Silver Chloride Cell.

$$\text{Ag(s)} \mid \text{AgCl(s)} \mid \text{KCl(aq)} \parallel \text{KCl(aq)} \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Hg(l)} \mid \text{Pt(s)}$$

The Cell Reaction for this Cell is:

$$2 \text{Ag(s)} + \text{Hg}_2\text{Cl}_2(s) \rightarrow 2 \text{AgCl(s)} + 2 \text{Hg(l)}$$  \hspace{1cm} (Eq. 12)

Note that as long as we are working reasonably close to $P^0 = 1$ barr, all the reaction species will be in their standard states and thus cell potential measurements will be determinations of $\varepsilon^0$.

A schematic of this Cell is as follows.
Chloride is plated-out onto a thin foil of Silver and acts as the anode. The cathode is a Platinum foil connected to the voltmeter via a Copper wire and is dipped into a pool of liquid Mercury onto which has been sprinkled Calomel.

Both the Calomel and Silver/Silver Chloride electrodes have a long history of use as reference electrodes in potentiometric analyses. The temperature coefficients for each of these electrodes are well known.

We will first construct this Cell and then measure $e^0$ at several temperatures. This will allow us to determine the thermodynamic parameters $\Delta G^0$, $\Delta H^0$, $\Delta S^0$ and $\Delta C_P^0$ for the cell reaction.
Procedure

Both Hg and Hg₂Cl₂ are toxic. Work over an enameled pan to avoid spilling either on the lab bench.

1. Obtain a piece of Silver foil and remove any old AgCl from it by scrubbing it in conc. Ammonia under a fume hood. Dry the foil and polish it with Steel Wool or emery paper. Clean the foil with 1 M HCl. Dip it into a small beaker of 1 M HCl. Connect it to the (+) electrode of a 1.5V D Cell. Connect the (-) electrode of the D Cell to a Pt wire and dip it into the beaker of HCl. Electrolyze the solution for 5 minutes. This will cause a deposit of AgCl to form on the Silver foil.

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2 \text{Ag(s) + 2HCl(aq)} \rightarrow 2 \text{AgCl(s) + H}_2\text{(g)}
\]

The Silver Chloride will appear as a Purple-White solid on the surface of the foil. Rinse the electrode with some DI Water. Do not allow it to dry out.

2. Obtain an H-Cell.
3. Fill the Cathode half-cell first. Add about 5 mL of Triple Distilled Mercury to the bottom of the cathodic arm of the H-Cell. Fill both compartments of the H-Cell with 0.1 M KCl. Add a spatula tip of Hg₂Cl₂ to the cathodic compartment such that it settles on top the Hg. Insert the Pt electrode such that the Pt foil is submerged entirely in the Hg.

4. Place the Silver/Silver Chloride electrode into the anodic compartment.

5. Place the entire system into a 0°C bath and allow it to come to equilibrium. Measure the cell potential ε₀ using a Digital Volt Meter. Make several measurements over time to ensure it is at equilibrium.

6. Make similar measurements at 25°C, 30°C and 35°C.

7. Repeat the measurements in reverse; 35°C, 30°C, 25°C and 0°C. This will allow you to determine the approximate error in each measurement.
Data Analysis

1. Tabulate your $\varepsilon^0$ vs. $T$ data. Plot this data and fit it to an appropriate function using a Least-Squares analysis. (Linear or Quadratic according to the curvature of the data.)

2. Using your graph, determine $\Delta G^0$, $\Delta S^0$, $\Delta H^0$ and $\Delta C_P^0$ at 25°C. You should estimate the error in each determination.

3. Determine $Q_{\text{irrev}}$ and $Q_{\text{rev}}$ and confirm your data is consistent with the Inequality of Clausius.

4. Compare your results with those of the literature.
References


