

TEMPERATURE DEPENDENCE OF EMF

(Last Revision: September 1, 2022)

- **ABSTRACT:**

The emf of a cell is measured at several temperatures. On the basis of these measurements, the enthalpy, entropy and free energy changes are found for the cell reaction.

- **TEXT REFERENCE:**

"Experiments in Physical Chemistry", Garland et al. Eighth Ed., McGraw-Hill, 2009, pp 245-248.

- **GENERAL DESCRIPTION AND THEORY:**

The emf produced by an electrochemical reaction will generally change with temperature. The free energy change can be found directly from the measured emf, while the entropy change can be found from the slope of the plot of the emf vs. the temperature. The enthalpy change can then be found from the free energy and entropy changes.

- **EQUIPMENT:**

H-cell or suitable cell vessel, calomel and Ag,AgCl electrodes, potentiometer, dry cells, thermostats.

- **CHEMICALS:**

Mercury, mercurous chloride, 0.1 M KCl, silver, 1 M HCl.

- **LABORATORY PROCEDURE:**

Use a piece of emery cloth to clean the silver electrode supplied. Then immerse the electrode in 1 M HCl and connect to the positive terminal of a dry cell. The negative terminal should be attached to a platinum electrode also immersed in the HCL solution. This should result in hydrogen evolution at the platinum electrode and a violet AgCl coating at the silver electrode. Make sure that everything is clean and keep your hands off of electrode surfaces. Set up the potentiometer and connect it to an external battery (three dry cells connected in series) and the cell. The internal standard on the potentiometer has a potential of 1.018 V. The cell should be placed in the appropriate thermostat and the emf measured at several different temperatures, at least three, preferably six. Randomize the order in which the temperatures are accessed. Measure the cell potential at a temperature until the readings appear to stabilize.

- CALCULATIONS:

The calculations are those described in the text. The slopes called for can be determined by using a spreadsheet.

- LITERATURE VALUES:

Harned and Owen, "Physical Chemistry of Electrolytic Solutions,"