

Experiment # 4**Title of experiment:** Thermodynamics of a galvanic cell**Aim:**

Thermodynamics is an important branch of physical chemistry. Using thermodynamic it is possible to discuss how energy is transformed from one form into another,

Introduction:

The purpose of this experiment is to explore the thermodynamics of an electrochemical cell, and the relationships of energy, work and power associated with this spontaneous electron-transfer (oxidation reduction) redox reaction. In a galvanic cell the electrons transferred between reactants in an oxidation-reduction reaction can be used to do work. The work that is done in the environment (the surroundings) comes from the change in energy of the chemicals in the galvanic cell (the system) as the reaction proceeds. The free energy change for a reaction ($\Delta_r G$) represents the maximum work available from a reaction, if spontaneous, or the minimum energy required to drive the process, if non-spontaneous. A galvanic cell, of course, encapsulates a spontaneous reaction, so it provides energy for work. Maximum value of work corresponding to $\Delta_r G$ are only encountered in the specialized (and impossible) circumstances of thermodynamic reversibility. An electrochemical cell probably come closest to thermodynamic reversibility of any energy conversion device. Work is defined as the energy transfer that occurs as a mass is moved through a distance against an opposing force. In an electrochemical cell there is another type of work called electrical work defined as w_{elec} , equal to the energy transfer as a charge is moved through an electrical potential energy difference. This can be expressed as

$$w_{\text{elec}} = q \cdot E \quad \text{or} \quad w_{\text{elec}} = n \cdot F \cdot E \quad (1)$$

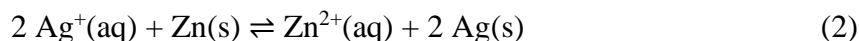
where q is the charge (in coulombs, C) and E is the electrical potential difference (in volts, V).

One joule of work is associated with moving a coulomb of charge across a potential energy difference of one volt, so $1 \text{ V} = 1 \text{ J/C}$. That will relate voltage and energy units.

In the wires of an electrical circuit, the charge is carried by moving electrons, but each electron carries only a very small charge, $1.602 \times 10^{-19} \text{ C}$. So, the charge is typically described in terms of the number (n) of moles of electrons exchanged in a reaction, where each mole contains Avogadro's number of electron charges. The latter quantity (symbolized F) is called the Faraday constant, and has the value of 96485 coulombs/mole e^- .

A galvanic cell provides the electrical potential energy difference (voltage) to drive the electrons through the circuit. The cell does work on a charge to move it from the low energy terminal to the high energy terminal. The energy of the cell that is transferred in the form of work comes from the chemical potential energy change that occurs as the chemical reaction of the battery proceeds.

The reaction for the galvanic cell $\text{Zn(s)}/\text{Zn(NO}_3)_2//\text{AgNO}_3/\text{Ag(s)}$ is:



For the reaction to be spontaneous reaction $\Delta_r G < 0$. Since $\Delta_r G$ represents the maximum non-PV work that can be obtained from the cell (and we will assume that all of it is electrical), we can relate $\Delta_r G$ to the voltage obtained from the cell.

$$\Delta_r G = -n \cdot F \cdot E \quad (3)$$

The negative sign appears because of the convention that E is positive for spontaneous cells.

$\Delta_r G$ is defined as

$$\Delta_r G = \Delta_r H - T\Delta_r S \quad (4)$$

$$\Delta_r S = -\frac{d(\Delta_r G)}{dT} \quad (4A)$$

where $\Delta_r H$ and $\Delta_r S$ are the enthalpy change and entropy change for a reaction, respectively.

We know that ΔG is strongly dependent on temperature, while $\Delta_r H$ and $\Delta_r S$ are constant over a small temperature range. In this experiment we will examine the change in voltage of a cell, $\frac{dE}{dT}$, over a small temperature range. Combining equations (3) and (4A), provides the following equations

$$-\frac{d(\Delta_r G)}{dT} = nF \left(\frac{dE}{dT} \right) = \Delta_r S \quad (5)$$

$$\Delta_r H = -nFE + nFT \left(\frac{dE}{dT} \right) \quad (6)$$

Measurement of E of a galvanic over a suitable temperature range will give a straight line when plotted as E vs. T . The slope of this straight line is called the *temperature coefficient* of the galvanic cell from which $\Delta_r S$ and $\Delta_r H$ can be calculated using equations 5 and 6.

Materials:

12x75 test tubes (3); thermometer with rubber stopper for test tube;

4" Ag and Zn wire electrodes;

salt bridges; water bath;

digital multimeter with alligator clip leads;

0.50 M AgNO_3 ; 0.25 M $\text{Zn(NO}_3)_2$

Procedure:

- 1) Prepare a salt bridge using saturated KNO_3 solution.
- 2) Cut silver electrodes (50 x 10 mm) from the silver sheet and clean them by a small piece of polishing paper until shiny. Then clean it rinse by distilled water and leave it to dry in air.
- 3) Cut zinc electrodes (50 x 10 mm) from the zinc sheet and clean them by small piece of polishing paper until shiny , rinse by distilled water and leave it to dry in air.
- 4) Take a rubber band and hold three small test tubes together, Label one with A for AgNO_3 solution and the other with Z for $\text{Zn(NO}_3)_2$ solution. Fill the two tubes with the corresponding solutions and the third test tube with distilled water.
- 5) Place a wet salt bridge in two test tubes with Ag and Zn solutions.
- 6) Place the three test tubes in the water bath and start recording the temperature.
- 7) Insert the two metals in the corresponding solutions and attach the positive wire of the multimeter to the Ag metal and the negative wire to Zn metal. A potential reading should be displayed on the multimeter. If not then check that, the metals are inserted in the solution.
- 8) Measure the temperature using the temperature probe and record a stable value of the potential in the given table below.

Results:

Using the given galvanic cell and recording its potential at a known temperature in table 1 given below, the thermodynamic quantities of the reaction can be calculated using equations 3, 5 and 6. Plot the average potential vs. absolute temperature and estimate the slope of the straight line and the correlation coefficient R^2 .

Table 1 Experimental data

Heating		
Temperature, °C	Temperature, K	Potential, V
25		
30		
35		
40		
45		
50		
55		

Report:

Use Table 2 to report the values obtained from the measurements and calculation.

Table 2

Slope	Intercept	R ²
Number of moles of e ⁻ in cell reaction		
E_{298K} , V		
Thermodynamic quantity	Value	Unit
$\Delta_r G$		
$\Delta_r S$		
$\Delta_r H$		
w_{elec}		