

## EXPERIMENT 4

### THERMODYNAMIC FUNCTIONS of a GALVANIC CELL

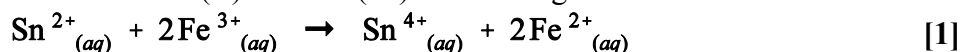
#### **Introduction**

##### *Chemical Reactions Involving the Transfer of Electrons*

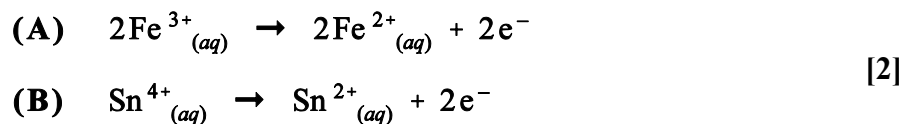
Numerous chemical reactions have been studied which involve the transfer of electrons from one species to another. The chemical species which has donated electrons is defined as the **reducing agent** and is said to have undergone the process of **oxidation** over the course of the reaction. The chemical species which receives the electrons is defined as the **oxidizing agent** and is said to have undergone the process of **reduction** over the course of the reaction. A **redox** (reduction/oxidization) **reaction** is the term applied to a reaction in which electrons are transferred from one chemical species to another.

##### *Half-Reactions*

Although the processes of oxidation and reduction occur simultaneously, the technique most widely used for understanding redox reactions involves separating them into half-reactions. This separation can be done in more than one equivalent fashion, with one way being outlined below. Consider the redox reaction where tin(II) and iron(III) are the reagents:



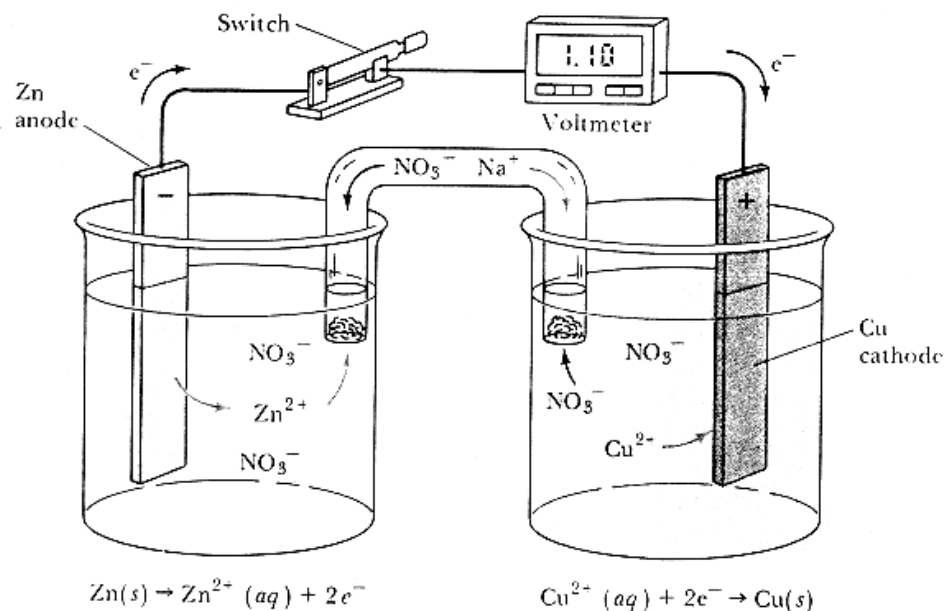
Above is the net ionic equation describing this redox reaction in aqueous media; below, the same redox reaction is expressed as two reduction half-reactions:



By taking the difference between the two half-reactions in [2], one can arrive at [1].

##### *The Electrochemical Cell*

The separation of redox reactions into half-reactions is convenient, and it reminds one of the **electrochemical cell**, a common physical construct used when studying this type of reaction. Each physical half-cell is composed of a single **electrode**, which is placed in contact with an electrolyte of some sort. A *typical* half-cell will have a strip of metal, M, (the electrode) which is in contact with an aqueous solution that contains ions of this metal (the electrolyte),  $\text{M}^{n+}$ , where  $n$  is the charge number associated with a particular oxidation state of the metal. A low resistance wire will allow the passage of electrons from one electrode to the other. Note that there are many variations to this scheme, one of which will be utilized in this experiment. The fashion in which the cell circuit is completed also varies, but one regularly used method involves a **salt bridge**, and it is the method that will be used for this experiment. A salt bridge is often made by adding agar to an electrolytic solution followed by heating. Upon cooling, the solution will turn into a gel. A connected set of two half-cells is called an electrochemical cell; a general schematic of which is provided below:



**Figure 4.1**

Once connected, a redox reaction may begin to occur spontaneously, accompanied with the production of electricity. In cases of this sort, the electrochemical cell is referred to as a **galvanic cell**. If electricity is required to drive the chemical reaction, the redox reaction being considered is non-spontaneous and the electrochemical cell is known as an **electrolytic cell**. Regardless of the type of electrochemical cell, the flow of electrons is from the **anode** (this is the electrode at which the process of oxidation occurs) to the **cathode** (the electrode at which reduction occurs).

#### *Gibbs Energy Change and The Cell Potential*

In galvanic cells, as with any spontaneous process, the redox reaction occurs spontaneously due to the fact that the chemical potential,  $\mu$ , of the system decreases. If the system is under constant temperature and pressure conditions, the chemical potential change of the system can be related in a straightforward fashion to the Gibbs energy change,  $\Delta_r G$ . Additionally, as long as the process is reversible,  $\Delta_r G$  can be related to the **cell potential**,  $E_{\text{cell}}$ , (or the **electromotive force**, (emf)) which is defined as being the electrical potential difference between the anode and cathode and is related to the maximum amount of electrical work,  $w_{e,\text{max}}$ , that can be done by the system. The above statements are represented algebraically:

$$\mu_B - \mu_A = \Delta_r G = w_{e,\text{max}} = -\nu \mathcal{F} E_{\text{cell}} \quad [3]$$

Where B is some final state, A is some initial state,  $E_{\text{cell}}$  is in units of  $\text{V mol}^{-1}$ ,  $\nu$  is the number of electrons transferred (units of mol), and  $\mathcal{F}$  is the **Faraday constant** ( $96\,485 \text{ C mol}^{-1}$ ).

### *E<sub>cell</sub> as a function of Cell Composition*

The relationship between the reaction quotient,  $Q$ , and the Gibbs energy of reaction takes on the form below:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \quad [4]$$

Where  $\Delta_r G^\circ$  is the change in Gibbs energy when the system is under standard conditions. The above equation can be re-expressed using [3]:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{v\mathcal{F}} \ln Q \quad [5]$$

The form above is known as the *Nernst equation* and  $E_{\text{cell}}^\circ$  is defined as the *standard emf*.

### *Other Thermodynamic Functions*

It has been established that the emf is related directly to the Gibbs energy of reaction, but the fashion in which the emf varies with respect to temperature can allow one to determine the change in another thermodynamic function of state. By taking the derivative of the isolated  $E_{\text{cell}}$  value with respect to temperature, the entropy of reaction,  $\Delta_r S$ , can be determined:

$$\frac{dE_{\text{cell}}}{dT} = \frac{\Delta_r S}{v\mathcal{F}} \quad [6]$$

Once the values for  $\Delta_r S$  and  $\Delta_r G$  are known, the enthalpy of reaction,  $\Delta_r H$ , for the particular redox reaction may be determined.

### **Materials**

<ul style="list-style-type: none"><li>• 2 – 50 mL volumetric flasks</li><li>• 2 – scoopula</li><li>• 1 – 50 mL graduated cylinder</li><li>• 1 – hot plate/stirrer combo w/ temperature probe</li><li>• 1 – glass stir rod</li><li>• plastic tubing</li><li>• 4 – 100 mL beakers</li><li>• 2 – 100 mL beaker lids</li><li>• 1 – magnetic stir bar</li><li>• 1 – Pasteur pipette</li><li>• 1 – water bath</li></ul>	<ul style="list-style-type: none"><li>• 1 – 10.0 mL pipette</li><li>• 1 – 1 M<math>\Omega</math> resistor</li><li>• 1 – voltmeter</li><li>• 1 – platinum electrode</li><li>• 1 – zinc electrode</li><li>• potassium ferrocyanide (K<sub>4</sub>Fe(CN)<sub>6</sub>•3H<sub>2</sub>O)</li><li>• potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>)</li><li>• zinc chloride (ZnCl<sub>2</sub>)</li><li>• pH 4 buffer</li><li>• potassium nitrate (KNO<sub>3</sub>)</li><li>• agar</li></ul>
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### **Procedure**

#### **A. Preparation of the Salt Bridge** (*another group member should start on part B*)

1. Using the 50 mL graduated cylinder, measure out 50 mL of de-ionized water and transfer this to a clean 100 mL beaker.
2. To this beaker, first add enough KNO<sub>3</sub> to make a 0.1 M solution, then add 2 grams of agar.

- Heat this solution with stirring to around 85 °C. To do this, turn the heating function of the hot plate on, and set the dial to around 150 °C. On the temperature probe display, set the temperature to 95 °C (*note that this is about 10 °C above the target temperature*). The probe is designed such that the solution may be heated by the hot plate to a range of desired temperatures. Wait until the solution is clear and bubbles have started to form.
- Remove the beaker from the heat, then using a Pasteur pipette attached to one end of the tubing, withdraw a portion of the hot solution into the tubing. Once this cools (let sit about 30 – 40 min), it will form a gel and may be used as the salt bridge.

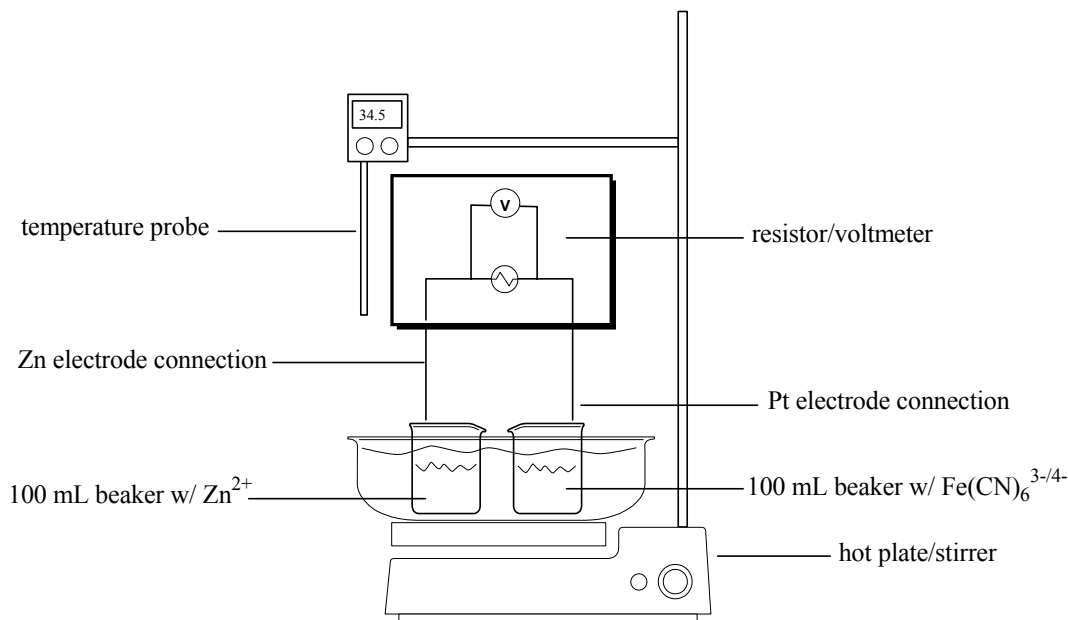
### B. Preparation of Required Solutions

Prepare the following solutions using de-ionized water (**note: do not use tap water**):

- 50 mL of a solution that is 0.10 M in BOTH potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ) and potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ).
- 50 mL of ca. 0.10 – 0.20 M zinc chloride ( $\text{ZnCl}_2$ ). ***Make sure to add 10.0 mL of pH 4 buffer before topping up with the de-ionized water.***

### C. Effect of Temperature on $E_{\text{cell}}$

- Create an ice slurry using the water bath as a container and then assemble the electrochemical cell as shown in Figure 4.2. Add a stir bar to the bath as well.



**Figure 4.2**

- Cut the ends of the salt bridge so that the gel runs the full length of the tubing. When ready, turn the heating/stirring functions on and set the temperature dial to around 175 °C. On the temperature probe display, set the temperature to 20 °C.
- As the temperature gets close to the desired value ( $\sim 1$  °C away), add the salt bridge.
- Proceed to take a measurement of the cell potential at 10 °C and record this value in your data sheet. ***Note: the voltmeter should be set to read direct current,  $\overline{\overline{V}}$ .***

- Once the reading has been made, remove the salt bridge and heat the system to 15 °C.
- Continue taking measurements and heating the system until the data sheet is completed.

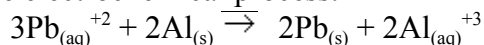
### Calculations

- Write out the chemical equation for the redox reaction that was under study in this lab and use it to calculate  $Q$ . **Note:** *you do not have to worry about activities*. Then, using  $Q$  and **[5]**, find the value of  $E_{\text{cell}}^{\circ}$  at each temperature point.
- Create a plot of  $E_{\text{cell}}^{\circ}$  versus temperature.
- Using the line of best fit, interpolate what the value of  $E_{\text{cell}}^{\circ}$  should be at  $T = 298$  K. This will be known as  $E_{298}^{\circ}$ . Compare your value with the literature.
- Using the value isolated for  $E_{298}^{\circ}$ , calculate  $\Delta_r G^{\circ}$ .
- Using the plot composed in step C2, determine  $\Delta_r S^{\circ}$  for this reaction. Then, using the value of  $\Delta_r G^{\circ}$  calculated earlier, find  $\Delta_r H^{\circ}$ .

### Lab Questions

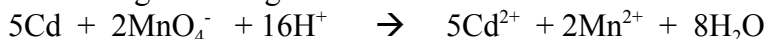
- The pH 4 buffer was used to maintain the cell potential over the course of the reaction. What possible side reaction does the use of this buffered solution prevent and why would this cause a change in the cell potential? (*see references*)
- Distinguish cell potential and electromotive force.
- Using the value  $\Delta_r G^{\circ}(\text{Al}_{(\text{aq})}^{+3}) = -481.2$  kJ/mole, calculate  $\Delta_r G^{\circ}$  in kJ mol<sup>-1</sup> for  $\text{Ba}_{(\text{aq})}^{+2}$  using the following Galvanic cell:  $\text{Al}|\text{Al}(\text{NO}_3)_3||\text{Ba}(\text{NO}_3)_2|\text{Ba}$

- Based on the electrochemical process:



Calculate the cell voltage at 25 °C given starting concentrations:  $[\text{Al}_{(\text{aq})}^{+3}]_0 = 0.00300$  M and  $[\text{Pb}_{(\text{aq})}^{+2}]_0 = 2.45$  M.

- Show a schematic diagram of a galvanic cell whose cell reaction is



### References

- Atkins, Peter and Julio de Paula. Physical Chemistry. 7<sup>th</sup> ed. New York: W. H. Freeman, 2002. 262-281.
- Brown, Theodore L., LeMay, H. E., and Bruce E. Bursten. Chemistry: The Central Science. 6<sup>th</sup> ed. Englewood Cliffs: Prentice Hall, 1994. 720-743.
- McSwiney, Harry D. *Journal of Chemical Education*. **1982**, 59, 165.
- Probst, Donald A., and Giles Henderson. *Journal of Chemical Education*. **1996**, 73, 962-964.

**Data Sheet**

**B.**

Actual concentration of  $\text{ZnCl}_2$  solution: \_\_\_\_\_  $\text{mol L}^{-1}$

**C.**

Temperature ( $^{\circ}\text{C}$ )	$E_{\text{cell}}$ ( $\text{V mol}^{-1}$ )
10	
15	
20	
25	
30	
35	
40	
45	
50	