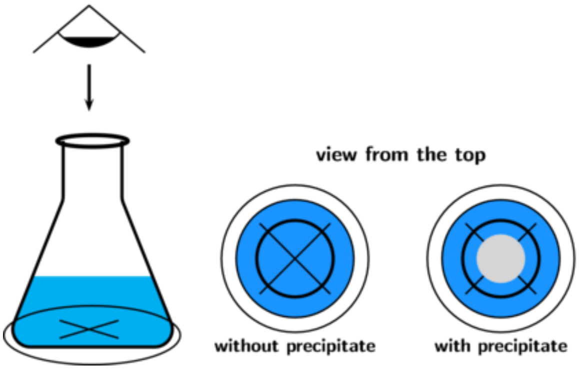
CEAC 104
GENERAL CHEMISTRY

Experiment 4

Effect of Concentration and Temperature on Rate of Reaction (Dissappearing Cross)



Purpose: To observe the effect of concentration and temperature upon the rate of the reaction of sodium thiosulfate with hydrochloric acid.

APPARATUS AND CHEMICALS:

Sodium thiosulfate solution	Thermometer	Bunsen burner
Hydrochloric acid	Measuring cylinder	Piece of paper
Distilled water	Conical flask	Wire gauze

THEORY:

On the basis of experiments you've performed, you probably have already noticed that reactions occur at varying speeds. There is an entire spectrum of reaction speeds, ranging from very slow to extremely fast. For example, the rusting of iron is reasonably slow, whereas the decomposition of TNT is extremely fast. The branch of chemistry that is concerned with the rates of reactions is called **chemical kinetics.**

Experiments show that rates of reactions in solution depend upon:

1. The nature of the reactants
2. The concentration of the reactants

3. The temperature
4. Catalysis.

Before a reaction can occur, the reactants must come into direct contact via collisions of the reacting particles. However, even then, the reacting particles (ions or molecules) must collide with sufficient energy to result in a reaction; if they do not, their collisions are ineffective and analogous to collisions of billiard balls. With these considerations in mind, we can quantitatively explain how the various factors influence the rates of reactions.

Concentration:

Changing the concentration of a solute in solution alters the number of particles per unit volume. The more particles present in a given volume, the greater the probability of them colliding. Hence, increasing the concentration of a solute in solution increases the number of collisions per unit time and therefore, increases the rate of reaction.

Temperature:

Since temperature is a measure of the average kinetic energy of a substance, an increase in temperature increases the kinetic energy of the reactant particles. The results in an increase in the velocity of the particles and therefore, increases the number of collisions between them in a given period of time. Thus, the rate of reaction increases. Also, an increase in kinetic energy results in a greater proportion of the collisions having the required energy for reaction.

Catalyst:

Catalysts, in some cases, are believed to increase reaction rates by bringing particles into close just a position in the correct geometrical arrangement for reaction to occur. In other instances, catalysts offer an alternative route to the reaction, one that requires less energetic collisions between reactant particles. If less energy is required for a successful collision, a larger percentage of the collisions will have the required energy, and the reaction will occur faster. Actually, the catalyst may take an active part in the reaction, but at the end of the reaction, the catalyst can be recovered chemically unchanged.

Let’s examine now precisely what is meant by the expression rate of reaction.

Order of Reaction Defined

Consider the hypothetical reaction:

$$A + B \rightarrow C + D \qquad [1]$$

The rate of reaction is measured by observing the rate of disappearance of the reactants A or B, or the rate of appearance of the products C or D. The species observed is a matter of convenience. For example if A, B, and D are colorless and C is colored, you could conveniently measure the rate of appearance of C by observing an increase in the intensity of the color of the solution as a function of time. Mathematically, the rate of reaction may be expressed as follows:

$$\text{Rate of disappearance of A} = \frac{-\text{change in the concentration of A}}{\text{time required for change}} = \frac{-\Delta[\text{A}]}{\Delta \text{t}}$$

$$\text{Rate of appearance of C} = \frac{\text{change in the concentration of C}}{\text{time required for change}} = \frac{\Delta[\text{C}]}{\Delta \text{t}}$$

In general, the rate of the reaction depends upon the concentration of one or more of the reactants. Thus, the rate of the reaction above is expressed as

$$\text{Rate} = k[A]^x\,[B]^y \qquad [2]$$

where [A] and [B] are the molar concentrations of A and B, x and y are the powers to which the respective concentrations must be raised, and k is the **rate constant.** The values of x and y must be determined experimentally. For example, if x = 2 and y = 1, then the rate law is:

$$\text{Rate} = k[A]^2\,[B] \qquad [3]$$

This reaction is first order in B, meaning that doubling the concentration of B while keeping A constant causes the reaction rate to double. Simultaneously, this reaction is second order in A, meaning that doubling the concentration of A while keeping B constant causes the rate to increase by a factor of four, since the rate of the reaction is proportional to the square of the concentration of A. The **overall order** of the reaction is the sum of the exponents: or third order in this case. The orders are determined experimentally by noting the effects of changing reagent concentrations on the rate of the reaction. The rate constant, k, is independent of the concentration. The rate constant is characteristic for a given reaction and varies only with temperature. Once the rate is known for a given set of concentrations, the value of k can be calculated.

Reaction of Sodium thiosulfate and Hydrochloric acid

In this experiment you will measure the rate of the reaction between a sodium thiosulfate solution and hydrochloric acid:

$$2HCl_{(aq)} + Na_2S_2O_{3(aq)} \rightarrow 2NaCl_{(aq)} + SO_{2(aq)} + S_{(s)}\downarrow + H_2O_{(l)}$$

The precipitate of sulfur formed gradually and makes the solution cloudy. The formation of cloudy mask a cross marked on paper. The rate of reaction, and consequently the time taken to obscure the cross, depends on a number of variables such as temperature, concentration and volume. The rate of reaction can be measured by timing how long it takes for the solution to become cloudy and the precipitation of sulfur. In other words the time taken for a certain quantity of sulphur to form and cause the ‘X’ mark to disappear is used to determine the rate of reaction. The rate of this reaction directly proportional with the inverse of the time taken for a formation of precipitation of sulfur.

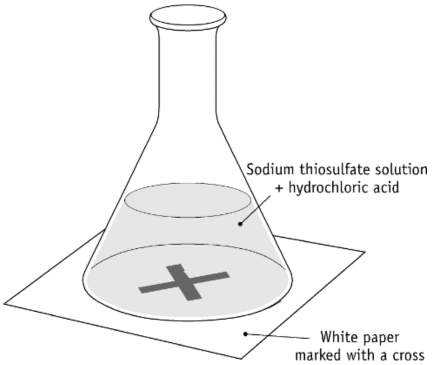
SAFETY PRECAUTIONS

- Wear your eye protection.
- Do not inhale any fumes.
- Sulfur dioxide is toxic and corrosive. Dispose of the solution immediately after the experiment following your teacher's instructions.
- Wash your hands when finished.

PROCEDURE:

A.Effect of concentration

1. Using a pencil, draw a cross in the middle of the filter paper.
2. Place 20 mL of the 0,1 M sodium thiosulfate solution into a conical flask.
3. Add 20 mL of 1 M hydrochloric acid to the flask, while starting the stop clock at the same time.
4. Swirl the flask and place it on a paper marked with a cross.



5. Record the time taken for the cross to disappear.
6. Repeat the experiment using 10,12, 14, 16 and 18 mL of sodium thiosulfate solution respectively. In each case, add water to make the volume up to 20 mL and mix before adding HCl.
7. Record the results in data sheet.

B.Effect of temperature

1 . Place 20 mL of 0.05 M sodium thiosulfate solution into a conical flask.

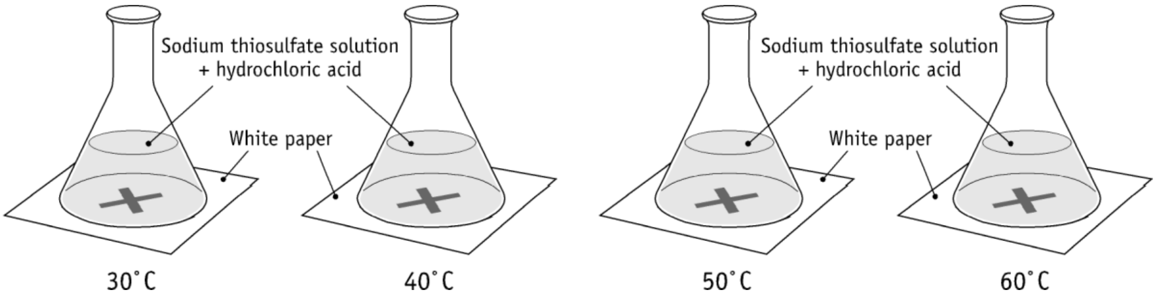
2. Warm or cool the flask gently until the temperature is about 20 ^{0}C.

3. Add 20 mL of 1 M HCl, starting a stop clock at the same time, before proceeding.

4. Without delay, swirl the flask, place it on a paper marked with a cross, and record the exact temperature of the contents of the flask.

5. Record the time taken for the cross to disappear.

6. Repeat the experiment, heating or cooling the thiosulfate solution to temperatures of approximately 10 ^{0}C, 30 ^{0}C, 40 ^{0}C, 50 ^{0}C and 60 ^{0}C respectively (before adding the HCl).



7. Record the results in data sheet.

QUESTIONS

1. What is the meaning of directly proportionality of two quantities ?

2. What is the effect of increasing the concentration on the reaction time and reaction rate?
3. What is the effect of raising the temperature on the reaction time?
4. What is the effect of raising the temperature on the reaction rate? Suggest two factors responsible for the result observed.
5. Suggest a reason why it is not recommended to carry out the experiment at temperatures higher than about 60 ^{0}C.
6. Which is the limiting reactant in the temperature experiment.

DATA SHEET
The Effect of Concentration and Temperature on Rate of Reaction
(Dissappearing Cross)

Student’s Name : Date:

Laboratory Section/Group No :

Assistant’s Name and Signature :

A. Effect of Concentration

1.Record your results.

	Volume of 1 M HCl (mL)	Volume of 0.1 M sodium thiosulfate solution (mL)	Volume of water (mL)	Concentration of thiosulfate solution (M)	Reaction time (s)	1/time (s^{-1})
1						
2						
3						
4						
5						
6						

2. Draw a graph of 1/time against concentration of thiosulfate solution and reaction time and concentration of thiosulfate solution using excel. Write your comments about the graph. (**Hint:** 1/time for this reaction is the measure of reaction rate.)

B. Effect of Temperature

1. Record your results.

	Volume of 1 M HCl (mL)	Volume of 0.05 M sodium thiosulfate solution (mL)	T (˚C)	Reaction time (s)	1/time (s^{-1})
1					
2					
3					
4					
5					
6					

2. Draw a graph of 1/time against temperature and reaction time against temperature using excel and write your comments about the graph. (**Hint:** 1/time for this reaction is the measure of reaction rate.)

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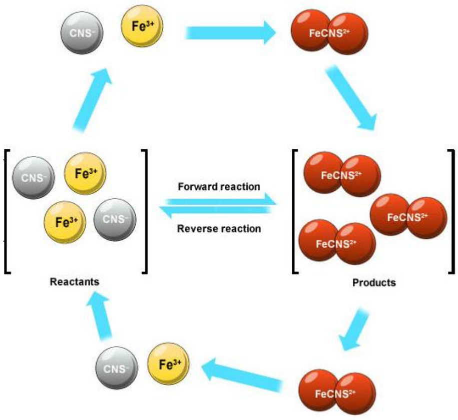
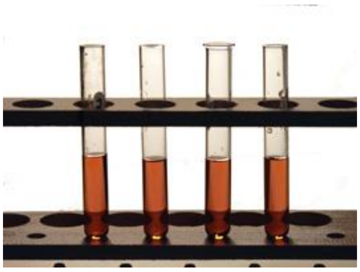
Experiment 5

Chemical Equilibrium



Fe^{3+} (aq) + SCN^- (aq) $\rightleftharpoons$ $FeSCN^{2+}$ (aq)

(yellow) (clear) (red/brown)



Purpose: Given the equation for a chemical equilibrium, predict and explain, the direction of a shift in the position of an equilibrium caused by a change in the concentration of the species on the basis of LeChatelier’s principle and finally to find the value of an equilibrium constant, K_{eq}, experimentally.

APPARATUS AND CHEMICALS:

distilled water	test tubes
sodium thiocyanate (NaSCN)	graduated cylinder
ferric nitrate ($Fe(NO_3)_3$)	white paper
ruler	250-mL beaker

THEORY:

Most of the chemical reactions occur so as they approach a state of chemical equilibrium. The equilibbrium state can be characterized by specifying its equilibrium constant, i.e., by indicating the numerical value of the mass-action expression. In this experiment you will determine the value of the equilibrium constant fort he reaction between ferric ion Fe^{3+} and isothiocyanate ion SCN^{-},

$$Fe^{3+} + SCN^{-} \leftrightarrow FeSCN^{2+}$$

for which the equilibrium condition is

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$$

To find the value of K, it is necessary to determine the concentration of each of the species Fe^{3+} , SCN^{-}, and $FeSCN^{2+}$ in the system at equilibrium. This will be done calorimetrically, taking advantage of the fact that $FeSCN^{2+}$ is the only highly colored species in the solution. The color intensitty of a solution depends on the concentration of the colored species and on the depth of solution viewed. Thus, 2 cm of a solution of a 0.1 M colored species appears to have the same color intensity as a 1 cm of a 0.2 M solution. Consequently, if the depths of two solutions of unequal concentrations are chosen so that the solutions appear to be equally colored, then the ratio of concentrations is simply the inverse of the ratio of the two depths. it should be noted that this procedure permits only a comparison between concentrations. it does not give an absolute value of either one of the concentrations. To know the absolute values, it is necessary to compare unknown solutions with a standard of known concentration.

For color determination of $FeSCN^{2+}$ concentration, you must have astandard solution in which the concentration of $FeSCN^{2+}$ is known. Such a solution can beprepared by starting with a small known concentration of SCN^{-} and adding such a large excess of Fe^{3+} that essentially all the SCN^{-} is converted to $FeSCN^{2+}$ Under these conditions, you can assume that the final concentration of $FeSCN^{2+}$ is equal to the initial concentration of SCN^{-}.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the fol1owing questions:

1. How could temperature changes affect the equilibrium?
2. What is the unit of the equilibrium constant?
3. Which factors affect the equilibrium constant?

PROCEDURE:

1. Clean six 15-cm test tubes with distilled water and let them drain.
2. To each of these test tubes add 5 mL of 0.0020 M NaSCN.
3. To the first test tubes add 5 mL of 0.20 M $Fe(NO_3)_3$. This tube will serve as the standard.
4. For the other test tubes proceed as follows:

   Add 10 mL of 0.20 M $Fe(NO_3)_3$ to a graduated cylinder. Add 15 mL distilled water so that you have a 25 mL of diluted solution. Stir thoroughly to mix. Take 5 mL from this solution and pour it into the second test tube.

5. Discard 10 mL of the diluted solution in the graduated cylinder and add 15 mL of distilled water and again you complete it to 25 mL. Stir thoroughly. Take 5 mL from this solution and pour it into the third test tube.

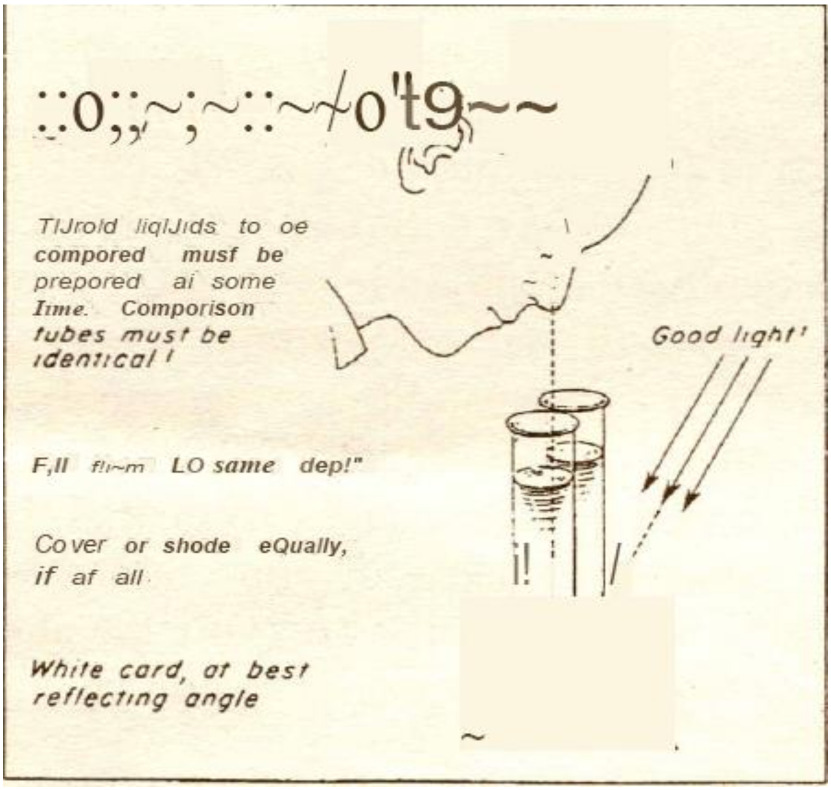


Figure 5.1 How to make a comparison of color.

6. Again discard 10 mL of the solution in the graduated cylinder and add 15 mL distilled water. Continue this procedure until you prepare six of the test tubes.
7. Now the problem is to determine the concentration of $FeSCN^{2+}$ in each test tube relative to the standard in test tube 1. Compare the color intensity in test tube 1 with that in each of the other test tubes (see Figure 5.1). To do it, take two tubes to be compared,

hold them side-by-side and wrap a strip of white paper around both. Look down through the solutions as shown in Figure. If color intensities appear identical, measure the heights of the solutions in the two tubes being compared. If not, take test tube 1 and pour out some of the standard into a clean beaker (you may need to pour some back) until the color intensities appear identical. Do this comparison for all five tubes.

CALCULATIONS:

In calculating initial concentrations, assume that each of $Fe(NO_3)_3$ and NaSCN are completely dissociated. Remember also that mixing two solutions dilutes both of them. In calculating equilibrium concentrations, assume that all the initial SCN^- has been converted to $FeSCN^{2+}$ in test tube 1, for the other test tubes; calculate $FeSCN^{2+}$ from the ratio of heights in the color comparison. Equilibrium concentrations of Fe^{3+} and SCN^- are obtained by subtracting $FeSCN^{2+}$ formed from initial Fe^{3+} and SCN^-. For each of test tube 2 to 6 calculate the value of K. Decide which of these values is most reliable.

QUESTIONS:

1. In this experiment you examine the equilibrium

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+}$$

The following equilibria are somewhat competing with the above equilibrium

$$Fe^{3+} + SCN^- \leftrightarrow Fe(SCN)^{2+} \text{ and } Fe(SCN)^{2+} + 2SCN^- \leftrightarrow Fe(SCN)_3$$

a. To allow you to ignore these equilibria, how must their equilibrium constants be in comparison with that of the equilibrium being studied ?

b. Given that all ions are colorless except for $FeSCN^{2+}$, what effect should competing equilibria have on the value of K determined in this experiment? Explain.

2. How reasonable was your assumption that all the SCN^- in test tube 1 was converted to $FeSCN^{2+}$? (Calculate the percent of SCN^- converted to $FeSCN^{2+}$ using your best K value.)

3. Why are the values of K determined for test tubes 3, 4 and 5 probably more reliable than those determined for tubes 2 or 6?

4. In your own words, give the rational behind the procedure and methodology in this experiment.

DATA SHEET

Chemical Equilibrium

Student's Name : Date:

Laboratory Section/Group No :

Assistan's Name and Signiture :

Test tube	Height of liquid in cm	Comparison of height in cm of standard
1	………………………..	………………………………..
2	………………………..	………………………………..
3	………………………..	………………………………..
4	………………………..	………………………………..
5	………………………..	………………………………..
6	………………………..	………………………………..

RESULTS:

Test tube	**Initial Concentrations**			**Equilibrium Concentrations**			
	$[Fe^{3+}]$	**$[SCN^{-}]$**	**$[FeSCN^{2+}]$**	**$[Fe^{3+}]$**	**$[SCN^{-}]$**	**$[FeSCN^{-2}]$**	**Keq**
1							
2							
3							
4							
5							
6							

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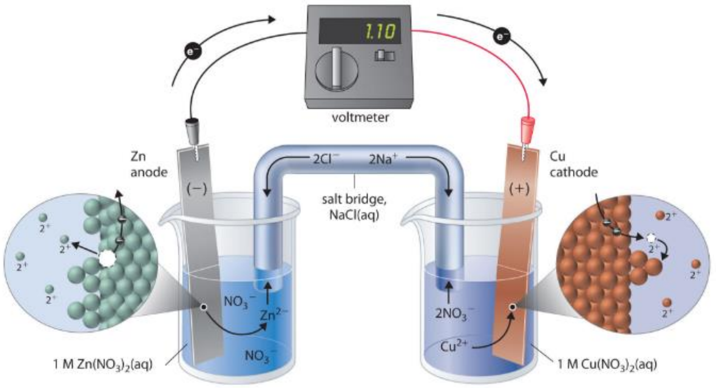
Experiment 6

Electrochemical Cells and Thermodynamics



Purpose: To examine the correlation between the reactions of metals and their ions (half cells), and to measure the voltages produced at various concentrations when two half cells are combined to form electrochemical (voltaic) cells. The voltage of the redox reactions will be calculated theoretically via Nernst equation.

Apparatus and Chemicals:

Copper strips or wire	Cotton	Ring stand, iron ring and wire
KNO_3	Agar-agar	Zinc strips or wire
$ZnSO_4$ solution	Wires	$CuSO_4$ solution
DC voltmeter or potentiometer	250-mL beaker	HCl solution
Glass U-tubes	Emery cloth	2 sets clips
Thermometer	Clamps	

THEORY:

Electrochemistry is that area of chemistry that deals with the relations between chemical changes and electrical energy. It is primarily concerned with oxidation-reduction phenomena. Chemical reactions can be used to produce electrical energy in cells that are referred to as ***voltaic***, or galvanic, cells. Electrical energy, on teh other hand, can be used to bring about chemical changes in what are termed ***electrolytic*** cells. In this experiment you will investigate some of the properties of voltaic cells.

Oxidation-reduction reactions are those that involve the transfer of electrons from one substance to another. The substance that loses electrons is said to be oxidized, while the one gaining electrons is reduced. Thus if a piece of zinc metal were immersed into a solution containing copper (II) ions, zinc would be oxidized by copper (II) ions. Zinc loses electrons and is oxidized, and the copper (II) ions gain electrons anda re reduced. We can conveniently Express these processes by the following two half-reactions, which add to give the overall reaction:

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

[1]

Net reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In principle, any spontaneous redox reaction can be used to produce electrical energy- that is, the reaction can be used as the basis of a voltaic cell. The trick is to seperate the two half reactions so that electrons will flow through an external circuit. A voltaic cell that is based upon the reaction in Equation [1] and that uses a salt bridge is shown in Figure 6.1.

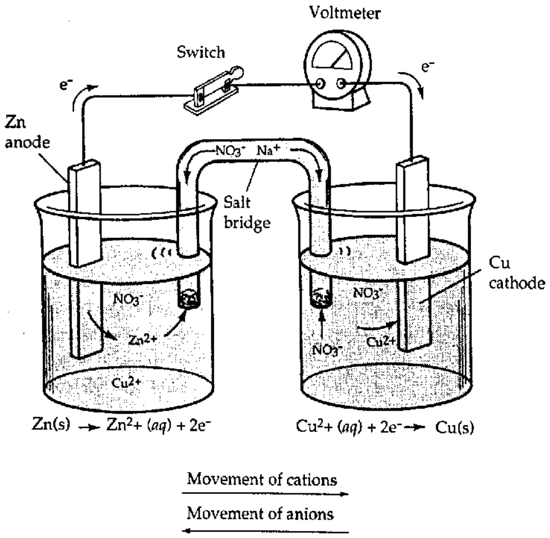


Figure 6.1 Complete and functioning voltaic cell using a salt bridge to complete the electrical circuit.

The cell voltage, or electromotive force (abbreviated emf), is indicated on the voltmeter in units of volts. The cell emf is also called the cell potential. The magnitude of teh emf is a quantitative measure of the driving force or thermodynamic tendency fort the reaction to occur. In general, the emf of a voltaic cell depends upon the substances that make up the cell as well as on their concentrations. Hence, it is common practice to compare ***Standard cell potentials,*** symbolized by E^0_{cell}. These potentials correspond to cell voltages under Standard state conditions-gases at 1 atm pressure, solutions at 1 M concentration and temperature at 25^0C.

Just as the overall cell reaction may be regarded as the sum of two half-reactions the overall cell emf can be thought of as the sum of two half-cell potentials, that is, the sum of the voltage of the oxidation half-reaction (E_{ox}) and the voltage of the reduction half-reaction (E_{red}):

$$E_{cell} = E_{ox} + E_{red}$$

Because it is impossible to measure directly the potential of an isolated half-cell, the Standard hydrogen half-reaction has been selected as a reference and has been assigned a standar reduction potential of exactly 0.000 V:

$$2H^+(1M) + 2e^- \rightarrow H_2(1atm) \qquad E^0_{red} = 0.000V$$

To demonstrate the consequence of this, let us consider a voltaic cell that utilizes the following reaction:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

The corresponding half-cell reactions are as follows:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^0_{ox} = 0.76\,V$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^0_{red} = 0.000\,V$$

The Standard cell emf of this cell is 0.76 V (that is, E^0_{cell} = 0.76 V). Because the Standard reduction potential of H^+ is 0.000 V, it is possible to calculate the Standard oxidation potential, E^0_{ox}, of Zn:

$$E^0_{cell} = E^0_{red} + E^0_{ox}$$

$$0.76\,V = 0.000 + E^0_{ox} \qquad [2]$$

Thus the Standard oxidation potential of 0.76 V can be assigned to Zn. By measuring other Standard-cell emf values, we can establish a series of Standard potentials for other half-reactions.

It is important to note that the half cell potential for any oxidation is equal in magnitude but opposite in sign to that of the reverse reduction. Hence,

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad E^0_{red} = -0.76\,V$$

It is customary today to tabulate half-cell potentials as Standard reduction potentials and also to refer to them as Standard electrode potentials.

EXAMPLE 1:

The cell in Figure 5.1 may be represented by the following notation:

$|Zn|Zn^{2+}||Cu^{2+}|Cu$

The double bar represents the salt bridge. Given that E^0_{cell} for this cell is 1.10 V and that E_{ox} is 0.76 V for zinc (see Equation [2]), find the Standard electrode potential, E^0_{red}, for the reduction of copper ($Cu^{2+} + 2e^- \rightarrow Cu$).

Solution :

$E^0_{cell} = E^0_{red} + E^0_{ox}$

$1.10\,V = 0.76\,V + E^0_{red}$

$E^0_{red} = 1.10\,V - 0.76\,V \qquad E^0_{red} = 0.34\,V$

The free-energy change, *Δ*G, associated with a chemical reaction is a measure of the driving force or spontaneity of the process. If the free-energy change of a process is negative, the reaction will ocur spontaneously in the direction indicated by the chemical equation.

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G = -nFE$$

In this equation, F; is Faraday's constant, the electrical charge on 1 mol of electrons:

$$1\mathrm{F} = 96.500\ \mathrm{C/mol\ e^-} = 96500\ \mathrm{J/V\ \ mol\ e^-}$$

and *n* represents the number of moles of electrons transferred in the reaction. For the case when both reactants and products are in their standard states, Equation [3] takes the following form:

$$\mathrm{w_{max}} = \Delta\mathrm{G} = -\mathrm{nFE^0} \qquad [4]$$

The maximum amount of work that can be obtained from a galvanic cell is equal to the free energy change, ΔG, for the process.

The standard free-energy change of a chemical reaction is also related to the equilibrium constant for the reaction as follows:

$$\Delta\mathrm{G}^\circ = -\mathrm{RT\ In\ K} \qquad [5]$$

where R is the gas-law constant (8.314 J/K mol) and T is the temperature in Kelvin. Consequently, E° is also related to the equilibrium constant. From Equations [4] and [5] it follows that

$$-\mathrm{nFE}^\circ = -\mathrm{RTlnK}$$

$$\mathrm{E}^\circ = \frac{\mathrm{RT}}{\mathrm{nF}}\ \mathrm{InK} \qquad [6]$$

When T = 298 K, In K is converted to log K, and the appropriate values of R and 9; are substituted, Equation [6] becomes

$$E^0 = \frac{0.0591}{n} logK \qquad [7]$$

We can see from this relation that the larger K is, the larger the standard-cell potential will be.

In practice, most voltaic cells are not likely to be operating under standard-state conditions. It is possible, however, to calculate the cell emf, E, under non-standard-state conditions from a knowledge of E°, temperature, and concentrations of reactants and products:

$$\mathrm{E} = \mathrm{E^0} - \frac{0.0591}{\mathrm{n}}\mathrm{logQ} \qquad [8]$$

Q is called the reaction quotient; it has the form of an equilibrium-constant expression, but the concentrations used to calculate Q are not necessarily equilibrium concentrations. The relationship given in Equation [8] is referred to as the Nernst equation).

Let us consider the operation of the cell shown in Figure 1 in more detail. Earlier we saw that the reaction

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

is spontaneous. Consequently, it has a positive electrochemical potential (E° = 1.10 V) and a negative free energy ($\Delta G° = - nFE°$). As this reaction occurs, Cu^{2+} will be reduced and deposited as copper metal onto the copper electrode. The electrode at which reduction occurs is called the cathode. Simultaneously, zinc metal from the zinc electrode will be oxidized and go into solution as Zn^{2+}. The electrode at which oxidation occurs is called the anode. Effectively, then, electrons will flow in the external wire from the zinc electrode through the voltmeter to the copper electrode and be given up to copper ions in solution. These copper ions will be reduced to copper metal and plate out on the copper electrode. Concurrently, zinc metal will give up electrons to become Zn^{2+} ions in solution. These Zn^{2+} ions will diffuse through the salt bridge into the copper solution and replace the Cu^{2+} ions that are being removed.

EXAMPLE 2:

Calculate the cell potential for the following cell:

$Zn \mid Zn^{2+}$ (0.6 M) $\parallel$ Cu^{2+} (0.2 M) Cu

given the following:

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ E°=1.10V

(HINT: Recall that Q includes expressions for species in solution but not for pure solids.)

SOLUTION:

$$E = E^0 - \frac{0.059}{n} log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10\, V - \frac{0.059}{2} log \frac{[0.6]}{[0.2]}$$

$$= 1.10 - 0.014$$

$$= 1.086$$

$$= 1.09\, V$$

You can see that small changes in concentrations have small effects on the cell emf.

A list of the properties of electrochemical cells and some definitions of related terms are given in Table 6.1.

TABLE 6.1 Summary of Properties of Electrochemical Cells and Some Definitions

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Voltaic cells: $E > 0$, $\Delta G < 0$: reaction spontaneous, K large (greater than 1)

Electrolytic cells: $E < 0$, $\Delta G > 0$; reaction nonspontaneous, K small (less than 1)

Anode electrode at which oxidation occurs

Cathode electrode at which reduction occurs

Oxidizing agent-species accepting electrons to become reduced

Reducing agent-species donating electrons to become oxidized

Chemists have developed a shorthand notation for electrochemical cells, as seen in Example 1. The notation for the Cu-Zn cell that explicitly shows concentrations is as follows:

$Zn \mid Zn^{2+}(xM) \parallel Cu^{2+}(yM) \mid Cu$
Anode Cathode
(oxidation) (reduction)

In this notation, the anode (oxidation half-cell) is written on the left and the cathode (reduction half-cell) is written on the right.

Your objective in this experiment is to construct a set of three electrochemical cells and to measure their cell potentials. With a knowledge of two half-cell potentials and the cell potentials obtained from your measurements, you will calculate the other half-cell potentials and the equilibrium constants for the reactions. By measuring the cell potential as a function of temperature, you may also determine the thermodynamic constants, ΔG, ΔH, and ΔS, for the reactions. This can be done with the aid of Equation [9]:

$$\Delta G = \Delta H - T\Delta S \qquad [9]$$

ΔG may be obtained directly from measurements of the cell potential using the relationship

$$\Delta G = -nFE$$

A plot of ΔG versus temperature in degrees Kelvin will give -ΔS as the slope and AH as the intercept. A more accurate measure of ΔH can be obtained, however, by substituting ΔG and ΔS back into Equation [9] and calculating ΔH.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. Define the following: faraday, salt bridge, anode, cathode, voltaic cell, electrolytic cell.

2. Write a chemical equation for the reaction that occurs in the following cell:

$Ag\,|\,Ag^{+}\,||\,Cu^{2+}|\,Cu$.

3. Given the following E°'s, calculate the standard-cell potential for the cell in question 2.

$Cu^{2+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu(s)}$ E° = +0.34 V

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ E° = +0.80 V

4. Calculate the voltage of the following cell:

$$Zn\,|\,Zn^{2+}\ (0.10\ M)\ ||\ Cu^{2+}\ (0.40\ M)\,|\,Cu$$

5. Calculate the cell potential, the equilibrium constant, and the free energy for the following cell:

$$Ba(s) + Mn^{2+}(aq)(1\ M) \rightarrow Ba^{2+}(aq)(1\ M) + Mn(s)$$

given the following E° values:

$Ba^{2+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{Ba(s)}$ E° = -2.90 V

$Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s)$ E° = -1.18 V

6. Would you normally expect ΔH^{0} to be positive or negative for a voltaic cell? Justify your answer.

7. Predict whether the following reactions are spontaneous or not.

$Pd^{2+} + H_2 \rightarrow Pd + 2H^{+}$ $Pd^{2+} + 2e^{-} \rightarrow Pd$ E° = 0.987 V

$Sn^{4+} + H_2 \rightarrow Sn^{2+} + 2H^{+}$ $Sn^{4+} + 2e^{-} \rightarrow Sn^{2+}$ E° = 0.154 V

$Ni^{2+} + H_2 \rightarrow Ni + 2H^{+}$ $Ni^{2+} + 2e^{-} \rightarrow Ni$ E° =-0.250 V

$Cd^{2+} + H_2 \rightarrow Cd + 2H^{+}$ $Cd^{2+} + 2e^{-} \rightarrow Cd$ E° = -0.403 V

From your answers decide which of the above metals could be reduced by hydrogen.

8. Identify the oxidizing agents and reducing agents in the reactions in question 7.

PROCEDURE:

Construct the apparatus shown in the Figure 6.1 with great care when installing the U-tube salt bridge.

A. **Cell Voltage**

1. Pour about 150 mL of 0.5 M $CuSO_4$ into a beaker. Bend a sand papered Cu strip and hang over the side of the beaker so that it is partly immersed in the solution.
2. Clean a Zn strip by briefly immersing it in about 75 mL diluted HC1 in a beaker. Do not let the strip remain for very long in the, HCl solution. Otherwise, it will react liberating H_2. (HCl cleans Zn by dissolving the surface layer exposing the fresh metal.) **Immediately rinse the Zn strip thoroughly** in distilled water.
3. Bend the Zn strip and hang it over the side of the beaker containing 150 mL of 0.5 M $ZnSO_4$.
4. Use the crocodile clips to connect the terminals of the multimeter to the metal electrodes.
5. Construct the salt bridge as described above and immediately read the initial cell voltage. Be certain that the clips make good contact with the metal strips. Record this voltage and the temperature of the cells on your data sheet. If your measured potential is negative, reverse the wire connection.

Record the voltage and temperature of each cell on your data sheet.

DO NOT MOVE any part of the cell, because the voltage will fluctuate if you do.

B. Concentration Effects on Cell Voltage

In order to observe the concentration effects on cell voltage, vary the concentration of the salt solution in one of the compartments by adding successive amounts of salt or by dilution of solutions. For example, double the concentration of $CuSO_4$ solution in the corresponding compartment or dilute $ZnSO_4$ solution by some factor. So the experiments that will reveal the effects varying solution concentrations will be designed.

The following points should be considered for the design of the experiment:

1. The effect may be investigated for only the cathode compartment solution instead of both solutions.
2. Vary the concentration of reactants from 0.5 M to 0.25 M and 0.05 M to determine the effects of concentration changes. Before coming to the laboratory,

make the necessary calculations for the design of the experiment in order to observe significant changes in the cell potential.

3. Try to determine if the cell voltage varies in some regular way with concentration. Is variation linear or exponential or whatever?

CALCULATIONS:

1. For each cell write the anode half reaction and the cathode half reaction.
2. For each cell measure the initial cell potential. Calculate the cell potential using the Nernst equation and compare it with the measured value. What is the percent error in your measurement?
3. Calculate the maximum work in Joule for the galvanic cell you constructed.

QUESTIONS:

1. Write the chemical equations that occur in the following cells;

$Pb \mid Pb(NO_3)_2 \parallel AgNO_3 \mid Ag$

$Zn \mid ZnCI_2 \mid Pb(NO_3)_2 \mid Pb$

$Pb \mid Pb(NO_3)_2 \parallel NiCl_2 \mid Ni$

2. Which of the following reactions should have the larger ernf under standard conditions? Why?

$CuSO_4(aq) + Pb(s) \rightarrow PbSO_4(s) + Cu(s)$

$Cu(NO_3)_2(aq) + Pb(s) \rightarrow Pb(NO_3)_2(aq) + Cu(s)$.

3. Calculate ΔG for the reaction in Example 2.
4. Voltages listed in textbooks and handbooks are given as *standard-cell potentials* (voltages). What does a standard cell mean? Were the cells constructed in this experiment standard cell? Why or why not?
5. As a standard voltaic cell runs, it "discharges" and the cell potential decreases with time. Explain.
6. Using standard potentials given in the appendices, calculate the equilibrium constants for the following reactions:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$$

DATA SHEET

Electrochemical cells and Thermodynamics

Student's Name : Date:

Laboratory Section/Group No :

Assistant's Name and Signature :

Calculations:

Cathode half reaction:

Anode half reaction:

T (°C):

Cu^{2+} (mol/L)	Zn^{2+} (mol/L)	E_{cell} (Nernst Eqn)	E_{cell} (exp)	% error	W_{max} (J)
0.50	0.50				