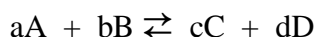




A reversible reaction is the type of reaction where a certain chemical process is able to proceed in a forward or reverse direction depending on experimental conditions. The chemical equation, which represents this, is written with double arrows as follows:



In an equation as above, the chemical symbols (capitol letters) represent not only moles of the substances involved in the process but also moles per liter of the substances. The lower case letters are the stoichiometric coefficients. At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. The equilibrium constant is expressed as the concentrations of the products over the concentrations of the reactants.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

In a reversible system, the species involved (on both sides of the double arrows) will be at a dynamic equilibrium with each other, so that a small disturbance of this balance affecting either side of the equation will involve all the species. The formal way of stating this is called *Le Chatlier's Principle* - If stress is placed on a system at equilibrium, the equilibrium will shift in a direction in order to overcome the stress.

The stress could be a change of concentration of one or more of the chemical species, change of pressure, change of temperature and etc. Shift means the direction of change of the concentration of certain species opposing the stress.

Examples of reversible systems at equilibrium are the following:

1. Weak acids or bases
2. Saturated solutions of salts
3. Sparingly soluble salts and hydroxides
4. Complex ion equilibria
5. Gas and heterogeneous equilibria

Strong acids and bases such as hydrochloric acid, nitric acid and sulfuric acids and sodium hydroxide are strong electrolytes (are 100% ionized) and therefore have no equilibrium. On the other hand acetic acid and aqueous ammonia solutions are weak electrolytes and therefore there is equilibrium between the concentration of their ions and the concentration of the original parent molecules.

Water dissociates into ions in the order of  $1 \times 10^{-7} \text{ M } [\text{H}^+]$  and  $1 \times 10^{-7} \text{ M } [\text{OH}^-]$ . The equilibrium equation for water is:



And the equilibrium expression for the *auto-ionization* for water is:

$$K_w = [\text{H}^+][\text{OH}^-] = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

### **Part 1 – Chemical Equilibriumm (Day 1)**

This experiment involves the qualitative description of some of the equilibrium systems before and after the stress is placed on the system. Apply Le Chatelier's Principle when describing your observations.

### **EQUIPMENT**

Test tubes, test tube rack, test tube clamp, beakers, plastic wash bottle, stirring rod, graduated cylinders, droppers, watch glass.

### **PROCEDURE**

#### **WEAR YOUR SAFETY GLASSES**

You must write down your observations and then discuss your results. Note the physical properties before and after additions. In some reactions, a precipitate may form and in others there may be a color change.

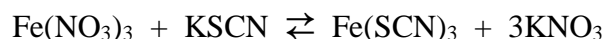
#### **1. Ion Equilibrium**

Test 1a – Chromate – Dichromate Equilibrium. Add 10 drops of potassium chromate in a small test tube and then add several drops of the following reagents to the same test tube one at a time. Discuss your results after each addition.



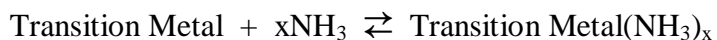
- (a) 6M HCl
- (b) 6M NaOH
- (c) 6M HCl

Test 1b – Ferric Thiocyanate Equilibrium. Add 5 drops each of ferric nitrate and potassium thiocyanate (KSCN) in a small beaker. Add about 50ml of water. Add more water to this if the solution looks too dark. Place small but equal quantities of this solution in each of five test tubes, then add the following:



- I. Test tube 1: 3ml of water
- II. Test tube 2: a few drops of KSCN
- III. Test tube 3: a few drops of ferric nitrate
- IV. Test tube 4: a few drops of 6M NaOH
- V. Test tube 5: a few drops of 6M HCl

Test 1c - Complex Ions with Ammonia.



- Add a drop of 6 M ammonia to a cupric nitrate,  $\text{Cu}(\text{NO}_3)_2$ , solution in a test tube. Mix and observe. Then add more ammonia drop by drop. Record observations.
- Carry out the same procedure on a zinc nitrate solution.
- Place several drops of silver nitrate solution in a test tube and then add one or two drops of dilute HCl. You will observe a white precipitate,  $\text{AgCl}_{(s)}$ . Now add 6M ammonia solution to this precipitate drop by drop with mixing and observe.

2. Weak acid/base equilibria and the effect of a common ion on the equilibrium.



(Ammonia solution must be written as  $\text{NH}_{3(g)} + \text{H}_2\text{O}_{(l)}$ )

(a) You must use indicators for this part of the experiment. You should therefore test the color of each indicator using a strong acid (HCl) and a strong base (NaOH).

|                 | Color in Acid | Color in Base |
|-----------------|---------------|---------------|
| Phenolphthalein |               |               |
| Methyl Orange   |               |               |

(b) Add 10 drops of a 0.1M Ammonia solution in each of two different test tubes. Add one drop of phenolphthalein indicator to each of these tubes and then add the following:

- 10 drops of 6M HCl to test tube one
- 10 drops of 1M  $\text{NH}_4\text{Cl}$  to test tube two

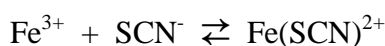
(c) Place 10 drops of 0.1M acetic acid solution in each of two different test tubes. Add one drop of methyl orange indicator to each test tube and then add the following:

- 10 drops of 6M NaOH to test tube one
- 10 drops of 1M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to test tube two

### 3. Complex ion equilibria

You may have to dilute your stock solutions. Use  $M_1 V_1 = M_2 V_2$

Ferric ion – thiocyanate ion equilibria



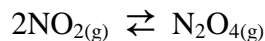
- Add 10 drops of 0.1M sodium thiocyanate to a 0.1M ferric thiocyanate solution. Record your observations.

### 4. Saturated solution equilibria.

- (a) Place 20 drops of clear saturated NaCl salt solution in a test tube and then add concentrated HCl (CAUTION) drop by drop and observe.
- (b) Place 10 drops of 0.1M barium chloride solution in a test tube. Add a few drops of potassium chromate. Observe. Now add a 6M HCl solution drop by drop and observe.

### 5. Effect of temperature on equilibria. (If available)

The stockroom will supply us with two sealed glass flasks containing nitrogen dioxide and dinitrogen tetroxide gases. These two gases are at equilibrium with each other and the relative concentration of each of these gases depends on the temperature.



The NO<sub>2</sub> is reddish-brown while the N<sub>2</sub>O<sub>4</sub> is colorless. One of the flasks will be kept at room temperature, while the second one will be covered with crushed ice. Examine the two flasks then discuss your observations.

**Part 2 -Ionization constants ( $K_a$  and  $K_b$ ) of weak acids and bases. (Day 2)**

The pH scale is a mathematical way of expressing the hydrogen ion concentration,  $[H^+]$ , of solutions (the acidity or the basicity is as defined by the Arrhenius theory for acids and bases). It is defined as:

$$pH = -\log [H^+] \text{ (the logarithm is to base 10)}$$

Therefore

$$[H^+] = \text{antilog} (-pH) \text{ or } [H^+] = 10^{-pH}$$

also, by definition

$$pOH = -\log [OH^-]$$

and

$$[OH^-] = \text{antilog} (-pOH) \quad \text{or} \quad [OH^-] = 10^{-pOH}$$

$$pH + pOH = 14 \quad \text{and} \quad K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$

For a weak acid of the type:



The mathematical expression for the equilibrium is written as:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

For a weak base of the type



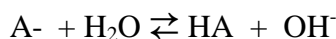
The mathematical expression for the equilibrium is written as:

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

The symbols in square parenthesis mean concentration (moles per Liter).

Experimentally measured pH values of solutions give us hydrogen ion concentrations at equilibrium. Other equilibrium concentrations are found from initial concentrations of some of the species and the stoichiometry of the process.

The soluble salts of the weak acids and bases when dissolved in water produce solutions that are basic or acidic. This process is called hydrolysis.



## Equipment

pH meter with glass electrodes, beakers, plastic wash bottle, stirring rod, graduated cylinders, buret, pipet, indicator, commercial vinegar.

## Procedure (Day 2)

1. Turn on the pH meter to standby and let it warm up for 15 minutes.
2. Connect the electrodes and dip them in the given buffer solution.
3. When the instrument is ready, switch it to the read mode and adjust the meter to read the pH value of the buffer using the “calibrate” dial.
4. The instrument is now ready to be used. You must switch the meter to standby before the electrodes are removed from the solution. The electrodes must be rinsed with DI water when changing solutions.
5. Do step #6 if the stockroom does not supply you with the diluted acid, otherwise go directly to step #7 below.
6. Dilute some acetic acid to about 0.1M (use  $V_1 M_1 = V_2 M_2$ ). Titrate this acid against the standard NaOH. The molarity of the acid determined is the *initial concentration* of the acid before dissociation.
7. Do this step if the stockroom supplies you with the acid. The molarity of the acid as written on the reagent bottle will be the *initial concentration* of the acid. Make sure you record this concentration value.
8. Measure and record the pH values of the following solutions and then calculate the  $K_a$  and  $pK_a$  of the weak acid for each of the solutions and discuss and compare it to the literature value.
9. Solution 1: a sample of the original dilute acid  
Solution 2: take 10ml of the dilute acid and dilute it to 100ml. Calculate the new initial concentration.  
Solution 3: 20ml to 30ml of the dilute acid mixed with an equal volume of the sodium salt of the weak acid. Calculate the new initial concentrations of the acid and the salt of this acid.  
Solution 4: Mix 5ml of the dilute acid with 25mL of the salt of this acid plus 20ml of water. Calculate the new initial concentrations of the acid and the salt of this acid.

The format for recording your data should be as follows

|                                                                          |  |
|--------------------------------------------------------------------------|--|
| Name of the acid sample                                                  |  |
| Concentration of weak acid [HA]<br>(from the titration)                  |  |
| Concentration of salt of weak acid [A <sup>-</sup> ]<br>(from the label) |  |

|          | Initial conc of the acid | Initial conc of the salt | pH |
|----------|--------------------------|--------------------------|----|
| Sample 1 |                          |                          |    |
| Sample 2 |                          |                          |    |
| Sample 3 |                          |                          |    |
| Sample 4 |                          |                          |    |

### Calculations

For each of the samples you should make a table resembling the following:



|   | HA | H <sup>+</sup> | A <sup>-</sup> |
|---|----|----------------|----------------|
| I |    |                |                |
| C |    |                |                |
| E |    |                |                |

For solutions 1 and 2, use an ICE box to calculate the equilibrium concentrations for each solution. Use the pH values to calculate [H<sup>+</sup>] which is equal to x. Calculate the K<sub>a</sub> values for solutions 1 and 2 from the equilibrium values.

For solutions 3 and 4, use the Henderson-Hasselbach equation to calculate pK<sub>a</sub> and K<sub>a</sub>.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Calculate the pK<sub>a</sub> and K<sub>a</sub> value of this acid for samples 3 and 4. Calculate the average pK<sub>a</sub> for the acid and then compare this with the theoretical value in your book.

Calculate the % error for the average pK<sub>a</sub> values.

### Discussion

Discuss and compare the experimentally determined pK<sub>a</sub> values to the known literature value. Also discuss possible sources of error, human error, and instrument error?

### Part 3 - Beer's Law and the Spectrophotometric Determination of K. (Day 3)

#### Complex Ion Equilibria

The purpose of this experiment is to determine the equilibrium constant for the following reversible system:



Where  $\text{FeSCN}^{2+}$  is a “complex ion” and its color is red (you saw this in the previous experiment): while the thiocyanate ion ( $\text{SCN}^{-}$ ) is colorless and the ferric ion is almost colorless in dilute solutions. The equilibrium constant can be written as

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

The equilibrium concentration of the  $\text{FeSCN}^{2+}$  is determined by using Beer's Law as described below.

#### Beer's Law

When electromagnetic radiation passes through a substance, some of the wavelengths of the radiation may be absorbed and some of it is transmitted. Which wavelength is absorbed and which is transmitted depends on the structure of the molecules and the medium (solvent) in which they are contained.

The percent ratio of the intensities of the transmitted light to that of the incident light is called percent transmittance (%T), that is

$$\%T = \frac{I}{I_0} \times 100$$

where

I = Intensity of incident radiation

$I_0$  = Intensity of transmitted radiation

By definition, absorbance (A)

$$A = -\log (\% T / 100)$$

That is

$$A = 2 - \log (\% T) \dots (\text{Eq \#1})$$

For dilute solutions, constant light path (b) and at a fixed wavelength, absorbance is directly proportional to the concentration (c) of the absorbing species in moles per liter, that is

$$A = \epsilon bc \dots (\text{Eq \#2})$$

where the constant ( $\epsilon$ ) is a proportionality constant called the molar absorptivity or molar extinction coefficient.



|            | % T | Absorbance |
|------------|-----|------------|
| Solution 1 |     |            |
| Solution 2 |     |            |
| Solution 3 |     |            |
| Solution 4 |     |            |

### Calculations

#### 1. The proportionality constant in Beer's Law

In solution 1 the concentration of the iron is so large that it is assumed the equilibrium has COMPLETELY SHIFTED TO THE RIGHT. Therefore, this means that the  $\text{SCN}^-$  concentration is zero and that the concentration of the complex is equal to the initial concentration of the  $\text{SCN}^-$ .

$$\text{Therefore } A = \epsilon b[\text{FeSCN}^{2+}] \quad ; \quad b = 1 \text{ cm}$$

$$\epsilon = A / (\text{FeSCN}^{2+})$$

(Theoretical value =  $3550\text{M}^{-1}\text{cm}^{-1}$ )

#### 2. Calculation of the equilibrium concentrations of $\text{FeSCN}^{2+}$

Using the Beer's Law constant from solution 1 and the absorbance readings for solutions 2, 3 and 4, calculate the equilibrium concentrations of the  $\text{FeSCN}^{2+}$  and record.

|             | $[\text{FeSCN}^{2+}] \text{ mol/L}$ |
|-------------|-------------------------------------|
| Solutions 2 |                                     |
| Solutions 3 |                                     |
| Solutions 4 |                                     |

#### 3. Use an ICE box to calculate the equilibrium concentrations of all species. Calculate the equilibrium constant K.

For solutions 2, 3, and 4 you should make a table resembling the following

|                     | Initial conc | Equilibrium conc |
|---------------------|--------------|------------------|
| $\text{FeSCN}^{2+}$ |              |                  |
| $\text{Fe}^{2+}$    |              |                  |
| $\text{SCN}^-$      |              |                  |

Calculate K of this complex for each of the samples, average the three values of the K, then report this value in your book.