EXPERIMENT 5

"VIOLENT FIRES SOON BURN OUT THEMSELVES

SMALL SHOW'RS LAST LONG,

BUT SUDDEN STORMS ARE SHORT"

EQUILIBRIA

Techniques

- Successive reactions
- buffer preparation
- use of indicators
- pH estimation

Principles

- equilibria
- pH
- buffer systems
- common-ion effect
- temperature effect

MSDS available for

- copper sulfate, $CuSO_4$ (aq)
- ammonia, NH_3 (aq)
- hydrochloric acid, HCl (aq)
- nitric acid, HNO_3 (aq)
- potassium iodide, KI (aq)
- sodium sulfide, Na_2S (aq)
- acetic acid, CH_3COOH (aq)

- silver nitrate, $AgNO_3$ (aq)
- sodium carbonate, Na_2CO_3 (aq)
- sodium acetate, $NaCH_3COO$ (aq)
- sodium hydroxide, NaOH (aq)
- cobalt chloride, $CoCl_2$ (aq)
- copper bromide, $CuBr_2$ (aq)
- universal indicator

Recommended Advanced Reading

- **Chapter 15 Silberberg, Lavieri and Venkateswaran, 1st CE, McGraw-Hill, 2013**

INTRODUCTION

The beginning

This lab will give you a chance to work on some qualitative assessments of pH, a scale used to measure acidity. In addition, you will be able to see the effect of different reactants and external stimuli on reaction equilibria. In today's session you will work with your partner to:

- observe shifts in equilibria
- observe multiple equilibria using the silver ion
- prepare a buffer system
- observe the effect of strong acids and bases on a buffer system
- observe the common-ion effect on equilibria
- observe how temperature affects equilibria

This is a general overview of what you will be accomplishing in this experiment.

EXPERIMENT 5: *Equilibria*

Introduction

> *"The normal pH of rain is 5.6...the lowest pH of rain recorded in the UK is 2.4, which is over one thousand times more acidic!"*

Equilibrium

Normally, when writing chemical reactions, we use a single arrow after the reactants and before the products to indicate that reactants are converted to products. The single arrow implies that all the reactants are converted to products, unless there is the presence of a limiting reagent, in which case it reacts to completion. In reality, however, very few reactions go all the way to completion. Before they can do so, a stage in the reaction is reached when the rate of reaction of reactants to form products is equalled by the rate of reaction of products to form reactants. This does not mean that the reaction stops! Instead, it signifies that any additional product formed is not guaranteed to remain in the form of the product and may well be converted back to reactants. This state is referred to as ***equilibrium***, and is a dynamic state.

For some reactions, equilibrium favours the products...that is to say, most of the reactants will be converted into the product. However, there are many reactions that do not favour the formation of products. If the reaction is of no concern to us, we don't mind whether all the reactants react or not. However, very often, the reaction is extremely important industrially. In such cases, it is not economically advantageous to have a reaction that does not go to completion or as far to completion as possible. It is thus important to know how to influence or affect the outcome of a reaction. In order to know this, it is important to be able to determine when a reaction will reach equilibrium.

Equilibrium Constant

For any aqueous reaction

$$aA + bB \leftrightharpoons cC + dD + \text{heat} \qquad [1]$$

we can write an expression for the ***equilibrium constant***, K, as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad [2]$$

From this expression, we can see that when the reaction is product favoured (ie. the concentration of the products is high), the equilibrium constant is large. Similarly, a small equilibrium constant indicates a reactant-favoured reaction.

LeChatelier's Principle

When a reaction is at equilibrium, we can use the equilibrium constant to calculate the concentrations of the reactants and/or products. What happens if, at equilibrium, we add a reactant or product? ***LeChatelier's Principle*** states that a reaction will always move in the direction that minimizes the effect of any change imposed on a system at equilibrium. Thus, in Equation [1], if more B is added, the reaction would shift to the right to use up the excess B. Does temperature have any effect on a reaction at equilibrium? In an exothermic reaction (as is the case for Equation [1]), the addition of heat would cause the reaction to shift in the direction that would consume the added heat. Thus, the reaction would shift to the left.

Weak Acids and Bases

When the equilibrium in an equation such as [1] lies overwhelmingly to one side (usually we write the equation so that the equilibrium favours the right side), the species which dissociates completely is termed as **strong**. In the case of a reaction between HCl and NaOH, the HCl dissociates completely and hence it is known as a **strong acid**, just as NaOH, which also dissociates completely, is known as a **strong base**. On the other hand, a **weak** acid or base is one that does not dissociate completely when placed in water. Acetic acid, CH_3COOH, and ammonia, NH_3, are examples of a weak acid and a weak base respectively. In these cases, the equilibrium expression strongly favours the left side of the equation (unless the solution is very dilute). Thus in the case of acetic acid,

$$\underset{\text{acid}}{CH_3COOH\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conj. acid}}{H_3O^+\,(aq)} + \underset{\text{conj. base}}{CH_3COO^-\,(aq)} \quad [2]$$

the equilibrium lies to the left, indicating that H_3O^+ is a stronger acid than CH_3COOH and that CH_3COO^- is a stronger base than H_2O.

Acid Dissociation Constant

How do you know, just by looking at an acid or base, whether it is strong or weak? Since all four of the species in the equation affect the equilibrium, we can define an equilibrium constant for the acid, also called an acid dissociation constant, K_a,

$$K_a = \frac{[CH_3COO^- (aq)]\,[H_3O^+ (aq)]}{[CH_3COOH\,(aq)]} = 1.8 \times 10^{-5} \qquad [3]$$

that is decided by the three aqueous terms in equation [2]. The terms in the square brackets represent the concentrations of the species in the brackets, where the concentration denotes the amount of the species in a given volume of solution. For all the aqueous species, the concentration is substituted as a reasonable approximation for the ***activity*** of the species (which is the correct variable to use in an equilibrium expression). However, the activity of water is 1, as water is a pure substance, and hence, we see that the liquid water does not appear in the expression for K_a.

For a solution of ammonium ion, NH_4^+ (aq), in water, the acid strength of the ammonium ion in the equilibrium

$$NH_4^+ (aq) + H_2O\,(l) \leftrightharpoons H_3O^+ (aq) + NH_3\,(aq) \qquad [4]$$

can be expressed as

$$K_a = = \frac{[NH_3(aq)]\,[H_3O^+ (aq)]}{[NH_4^+ (aq)]} = 5.5 \times 10^{-10} \qquad [5]$$

Water has the capacity to act both as an acid and as a base as shown below,

$$H_2O\,(l) + H_2O\,(l) \leftrightharpoons H_3O^+ (aq) + OH^- (aq) \qquad [6]$$

and this process, where one water molecule donates a proton to another, is called ***autoprotolysis***. From equation [6], we can derive an expression for the equilibrium constant of water,

$$K_W = K' [H_2O\ (l)]^2 = [H_3O^+\ (aq)]\ [OH^-\ (aq)] = 1 \times 10^{-14} \qquad [7]$$

Species that are capable of behaving both as an acid and a base are called ***amphoteric***. Some other amphoteric ions are HCO_3^- (aq), HSO_4^- (aq) and $H_2PO_4^-$ (aq).

If we look at the equilibrium between a weak base, such as ammonia, NH_3 (aq), and water,

$$\underset{\text{base}}{NH_3\ (aq)} + \underset{\text{acid}}{H_2O\ (l)} \rightleftharpoons \underset{\text{conj. acid}}{NH_4^+\ (aq)} + \underset{\text{conj. base}}{OH^-\ (aq)} \qquad [8]$$

we can define the base dissociation constant, K_b, as

$$K_b = \frac{[NH_4^+(aq)]\ [OH^-\ (aq)]}{[NH_3\ (aq)]} \qquad [9]$$

Note again, that we do not include H_2O (l) as it has an activity of 1. If we look at equations [5], [7], and [9], we find that there exists a relation between the terms K_a, K_b and K_W, which can be expressed as

$$K_W = K_a \times K_b = [H^+\ (aq)]\ [OH^-\ (aq)] = 1 \times 10^{-14} \qquad [10]$$

where H^+ (aq) is a simplified form for H_3O^+ (aq). This relation holds true for any acid and its conjugate base.

pH

From equation [7], we can determine that in pure water, the concentrations of the hydrogen (or hydronium) and hydroxyl ions must be equal and have a value of 1×10^{-7} mol L^{-1}. If the solution has a greater concentration of hydronium ions, it will be ***acidic***, and $[H^+\ (aq)] > 1 \times 10^{-7}$ mol/L. If the solution has a greater concentration of hydroxyl ions, it will be ***basic***, and we would find $[H^+\ (aq)] < 1 \times 10^{-7}$ mol/L. However, the product of the two concentrations must **always** equal 1×10^{-14}. From these facts, it can be seen that the concentrations of [H^+(aq)] and [OH^-(aq)] vary over a large range, spanning orders of magnitude. It thus becomes useful to express their concentrations on a logarithmic scale, called the ***pH scale***, which is defined as

$$pH = -\log [H^+ (aq)] \qquad [11]$$

where the log scale mentioned is base ten. A similar scale can be applied to the species OH^-, and to K_a or K_b. In general, for any term X,

$$pX = -\log X \qquad [12]$$

Indicators

How then do we determine the pH of a solution? We can use pH meters, but an even simpler method is to use an ***indicator.*** Indicators are complex organic compounds. An indicator is usually a weak acid that dissociates to different extents in a solution depending on the acidity of the solution. If we designate the indicator as HIn, we can write

$$HIn\,(aq) \leftrightharpoons H^+\,(aq) + In^-\,(aq) \qquad [13]$$

and the equilibrium constant for dissociation of the indicator is

$$K_{In} = \frac{[H^+\,(aq)]\,[In^-\,(aq)]}{[HIn]} \qquad [14]$$

The important quality of an indicator is that it is **coloured**. Generally the undissociated and the dissociated species of the indicator have different colours. More than one colour is possible if the indicator is capable of establishing different equilibria in solution.

Concept of the Experiment

In this experiment, there are five main parts. First, you will observe the effect of adding and consuming reactants on a system at equilibrium. Second, you will establish multiple equilibria using the silver ion. Third, you will prepare a buffer solution and test the effect of adding a strong acid and a strong base to the buffer. Fourth, you will observe the effect of the addition of a common ion. Finally, you will determine the effect of temperature on a system at equilibrium.

The reactions that you will be studying are provided in a table at the end of the experiment.

(TTD) Things to Do

- Complete the prelab exercises before coming to the laboratory.
- Observe the effect of adding and removing a reagent on equilibrium.
- Observe multiple equilibria with the silver ion.
- Prepare a buffer system.
- Compare the effects of adding strong acid/base to water and to a buffer.
- Observe the common-ion effect.
- Observe the effect of temperature.
- Use safe laboratory procedures at all times.

Safety Precautions

1. **Wear approved eye protection at all times**.
2. Acids and bases, even in dilute solutions, are **corrosive**. Ensure that if you spill any acid or base, you clean up immediately (it is easy to mistake these solutions for water). If any is spilt on skin or clothing, rinse thoroughly with water for at least 15 minutes.
3. Silver nitrate stains. Sodium sulfide and ammonia STINK!

PROCEDURE

Equipment and chemicals needed

Chemicals	*Equipment*
0.1 M and 1 M HCl	test tubes
0.1 M $CuSO_4$	transfer pipets
0.1 M CH_3COOH	spatula
0.01M $AgNO_3$	well plate
0.1 M Na_2CO_3	toothpicks
0.1 M $NaCH_3COO$	hotplate
1 M $CoCl_2$2	test tube racks
0.1 M KI	250 mL beaker
solid $CuBr_2$, KBr	
6M HNO_3, conc NH_3	
0.1 M Na_2S	
0.1 M NaOH	

Equilibria

NOTE: This is a qualitative experiment. Make as many observations as possible!

Starting the experiment

Equilibrium Shift

1. Add approximately 1 mL (~20 drops) of 0.1 mol/L $CuSO_4$ to a clean test tube(a).

2. Dropwise, add concentrated NH_3 solution (NOTE: Ammonia has a VERY strong smell…do not breathe directly!!!) until you observe a change(b).

3. Dropwise, add 1 mol/L HCl until you observe a change(c).

4. What happens if you try to repeat Steps 2-3?

Moving on

Multiple Equilibria

5. Place 0.5 mL of 0.1 mol/L Na_2CO_3 solution in a test tube(d).

6. Add 0.5 mL of 0.01 mol/L $AgNO_3$ solution to the test tube(e).

7. Dropwise, add 6 mol/L HNO_3 (NOTE: This acid is VERY concentrated and thus CORROSIVE!!) until you see a change(f).

8. When the solution is clear, add 0.1 mol/L HCl dropwise until you see a change(g).

9. Dropwise, add concentrated NH_3 until you see a change(h).

10. What happens if you repeat Step 7 and then Step 9?

11. Add 0.1 mol/L KI dropwise until you see a change(i).

12. Dropwise, add 0.1 mol/L Na_2S until you see a change(j).

Preparation and Testing of a Buffer Solution

13. Obtain a well plate.

14. Using a plastic transfer pipet, add 10 drops of 0.1 mol/L CH_3COOH to two wells.

15. Add 3 drops of universal indicator to each well(k).

16. Use a strip of pH paper to note the pH of the acid in the wells(l).

17. Using another clean transfer pipet, add 10 drops of 0.1 mol/L $NaCH_3COO$ to each of the wells containing the acid(m). Measure the pH using a strip of the pH paper(n). These two wells now contain a buffer system.

18. In each of two different wells, use a clean transfer pipet to add 20 drops of distilled water. Add 3 drops of universal indicator. Check the pH with pH paper(o).

19. Use a clean transfer pipet to add 5 drops of 0.1 mol/L HCl to ONE well containing the buffer and 5 drops of 0.1 mol/L HCl to ONE well containing water(p). Measure the pH of both wells using two strips of pH paper(q).

20. Use a clean transfer pipet to add 5 drops of 0.1 mol/L NaOH to THE OTHER well containing the buffer and 5 drops of 0.1 mol/L NaOH to THE OTHER well containing water(r). Measure the pH of both wells using two strips of pH paper(s).

Almost there!

Common-Ion Effect

21. Use a clean transfer pipet to place 5 drops of 1 mol/L $CoCl_2$ in an empty well of the wellplate(t).

22. Dropwise, add concentrated (12 M) HCl (NOTE: VERY CORROSIVE!!!) to the $CoCl_2$ until you see a change(u).

23. Dropwise, add distilled water to the above mixture until and swirl until you see a change(v).

24. Use a spatula to place a “pinch” of solid $CuBr_2$ in an empty well(w).

25. Using a clean transfer pipet, add 5 drops of distilled water(x) to the $CuBr_2$ and then add another 10 drops(y). Continue adding water until the total volume is close to 2 mL(z).

26. Put a few crystals of KBr in another empty well. Add enough distilled water to dissolve the crystals(aa).

27. Use a clean transfer pipet to place approximately 0.5 mL of the solution in Step 25 to a test tube. Add a “pinch” of KBr and shake gently[(bb)]. Save this solution for the next step.

Finishing the Experiment

Temperature Effect

28. Place the test tube from Step 27 in a boiling water bath[(cc)]. If no colour change is seen, add 1 mL more of H_2O.

29. Place approximately 1 mL of 1 mol/L $CoCl_2$ solution in a clean test tube. Put the test tube in the boiling water bath[(dd)].

Cleaning Up!

30. Rinse the well plate and other glassware thoroughly with distilled water and return them to the demonstrator.

31. Empty all the transfer pipets and rinse well with warm water (draw in water, shake well, and squeeze the water out several times).

32. All solutions may be poured down the drain with plenty of water, EXCEPT for the silver solutions, which should be disposed in the container marked "SILVER WASTES".

33. Clean your bench thoroughly and throw away all paper towels.

Observations

Part 1. Equilibrium Shift

(a) What colour do you observe?

(b) What changes do you observe? Why do they occur?

(c) What changes do you observe? Why do they occur?

1. In Step 4, are you able to see the same changes or are they different?

Part 2. Multiple Equilibria

(d) What do you observe?

(e) What changes do you observe? Why do they occur?

(f) What changes do you observe? Why do they occur?

(g) What changes do you observe? Why do they occur?

(h) What changes do you observe? Why do they occur?

2. Can you observe the same changes if you repeat Steps 7 and 9?

(i) What changes do you observe? Why do they occur?

(j) What changes do you observe? Why do they occur?

Part 3. Buffers

(k) What colour do you observe with the universal indicator? With what pH does this correspond?

(l) What pH does the pH paper indicate? Do the two pHs correspond?

(m) What happens to the pH when you add the salt? What is the solution that results after you add the salt solution to the acid solution?

(n) Do the pHs determined by the indicator and the pH paper correspond?

(o) What colour is the universal indicator in distilled water? To what pH does this colour correspond?

(p) How does the addition of acid affect the pH of the water? How does it affect the pH of the buffer solution? What is the colour of the indicator in each solution?

(q) How does the pH compare using the indicator and the pH paper?

(r) How does the addition of base affect the pH of the water? How does it affect the pH of the buffer solution? What is the colour of the indicator in each solution?

(s) How does the pH compare using the indicator and the pH paper?

3. If we assume 5 drops to equal 0.25 mL, calculate the change in the pH of the buffer and the change in the pH of the water upon addition of 5 drops of 0.1 M HCl and 5 drops of 0.1 M NaOH.

Part 4. Common-Ion Effect

(t) What is the appearance of the solution at room temperature?

(u) What changes do you see? Why do they occur?

(v) How and why does the addition of water change the equilibrium?

(w) What is the appearance of the solid?

(x) What is the appearance of the solution?

(y) How does the further addition of water change the appearance of the solution? Why?

(z) What happens if more water is added? What equilibria are involved?

(aa) What is the appearance of the dissolved crystals? What does this tell you about the colour of each of the ions in the salt?

(bb) How does the addition of the solid change the appearance of the solution?

Part 5. Temperature Effect

(cc) What happens when heat is added to the solution?

(dd) What is the appearance of this solution? How does it compare to the appearance of the same solution at room temperature (Observation t)?

Wherever possible, use BALANCED chemical equations to describe what is occurring.

Points to Ponder

- Are there other ways to affect the equilibrium?

Lab Report

- *Refer to page iii in the FYI section and the lab report section in experiment 1.*

- You may choose to write your observations and discussion separately or to combine the two sections in your report. Remember to use CHEMISTRY to explain all your observations!

Table 1. Reactions Being Studied

$[Cu(H_2O)_4]^{2+}\ (aq) + 4\ NH_3\ (aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}\ (aq) + 4\ H_2O\ (l)$
$2AgNO_3\ (aq) + Na_2CO_3\ (aq) \rightleftharpoons Ag_2CO_3\ (s) + 2\ NaNO_3\ (aq)$
$2\ H^+\ (aq) + CO_3^{2-}\ (aq) \rightleftharpoons H_2CO_3\ (aq) \approx H_2O\ (l) + CO_2\ (g)$
$Ag^+\ (aq) + Cl^-\ (aq) \rightleftharpoons AgCl\ (s)$
$Ag^+\ (aq) + 2NH_3\ (aq) \rightleftharpoons [Ag(NH_3)_2]^+\ (aq)$
$H^+\ (aq) + NH_3\ (aq) \rightleftharpoons NH_4^+\ (aq)$
$Ag^+\ (aq) + I^-\ (aq) \rightleftharpoons AgI\ (s)$
$2Ag^+\ (aq) + S^{2-}\ (aq) \rightleftharpoons Ag_2S\ (s)$
$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$
$4Cl^-\ (aq) + [Co(H_2O)_6]^{2+}\ (aq) \rightleftharpoons [CoCl_4]^{2-}\ (aq) + 6\ H_2O\ (l)$
$4\ Br^-\ (aq) + [Cu(H_2O)_4]^{2+}\ (aq) \rightleftharpoons [CuBr_4]^{2-}\ (aq) + 4\ H_2O\ (l)$