

▪ Recognizing Equilibrium

Formulas & Theorems Covered Today:

- ★ Defining Equilibrium
- ★ Conditions for Equilibrium
- ★

Homework:



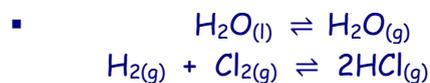
Notes:

Recognizing Equilibrium

- You have learned that the rate of any reaction depends on the concentration of the reacting chemicals
- However, as a reaction proceeds, the concentration of the products increases and the concentration of the reactants decreases
- As such concentrations change, so too does the rate of the reactions
- Because reactions can be viewed from either direction and the rate of the reaction depends on the concentrations of the reacting molecules, then it can be said that the rate of the forward reaction decreases as the rate of the reverse reaction decreases
- Equilibrium occurs when the rate of the forward reaction is equal to the rate of the reverse reaction
- The fundamental requirement for any equilibrium therefore is that opposing changes must occur at the same rate
 - Ex1. Sugar Dissolving in Water
 - If you add only a small amount of sugar into a large amount of water, it will completely dissolve
 - However, if you keep adding sugar, at some point or another it will reach a point where the number of sugar particles dissolving and the number of molecules precipitating will be equal (saturated solutions)
 - Ex2. Water in a close Container
 - The amount of water in a closed container is fixed
 - If the container is left sealed and the temperature of the water fluctuates, the amount of water in the vapour and liquid form changes
 - Ex3. A reaction with Reactants and Products in the same Phase
 - These particles will reach a homogeneous equilibrium
 - A reaction between 2 gasses to produce some other type of gaseous product
 - Ex4. A reaction with Reactants and Products in Different Phases
 - These particles will reach a heterogeneous equilibrium
 - A reaction between 2 aqueous solutions to produce a solid precipitate

4 Conditions that Apply to all Equilibrium Systems

1. Equilibrium is achieved in a reversible process where opposing changes are equal



2. The observable properties do not change and must remain constant
 - Colour, Pressure, concentration, pH etc.
3. Equilibrium must occur in a closed system
 - That is one that does not allow any input or escape of any component of that system
 - Constant pressure, temperature, number of molecules etc.
4. Equilibrium can be approached from either direction
 - The proportions of water vapour and liquid water are the same at equilibrium regardless of whether you started with the water vapor or the liquid water

Equilibrium Constant

Formulas & Theorems Covered Today:

- ★ Equilibrium Constant
- ★ Calculating K_{eq}
- ★

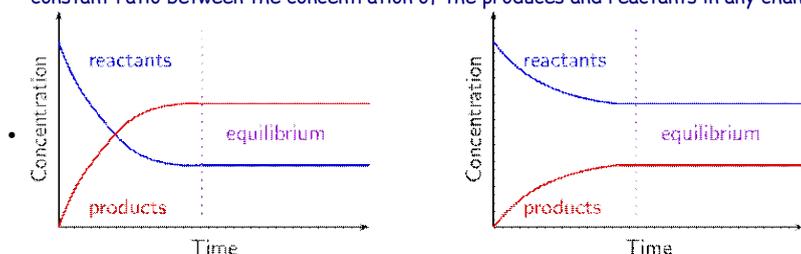
Homework:



Notes:

The Equilibrium Constant

- Chemists use thermodynamics and rates of reactions to study chemical reactions
- In 1864, two Norwegian chemists, Cato Maximilian Guldberg and Peter Waage, came up with the Law of Chemical Equilibrium which was built upon the work of Claude Louis Berthollet who had ideas of reversible chemical reactions
- This law is also known as the law of mass action and states that at equilibrium, there is a constant ratio between the concentration of the products and reactants in any change



- If we let the above graphs represent a chemical reaction like the decomposition of dinitrogen tetroxide into two nitrogen dioxide gas molecules then at some point or another, the rate at which reactants convert to products and products convert to reactants will be equal
- That means that at equilibrium $\text{Rate forward} = \text{Rate reverse}$
- This also means that there are no changes in the relative amounts of the dinitrogen tetroxide and the nitrogen dioxide
- We use this information on the rates of the reactions being simple to derive the generic equation for the equilibrium constant
- We know that the equation for the above reaction is:



Forward Rate = Reverse Rate

$$k_f[N_2O_4] = k_r[NO_2]^2$$

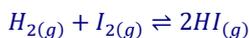
- By simply rearranging the formula we get:

$$\frac{k_f}{k_r} = k_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

- In another example, let's suppose that we have chemicals P and Q and they react to form chemicals R and S. They react in the proportions a, b, c, and d respectively to form the following equation

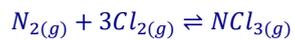
$$k_{eq} = \frac{[R]^c[S]^d}{[P]^a[Q]^b}$$

- The equilibrium expression depends on the stoichiometry of the reaction
 - Ex1. Determine the mass action expression (equilibrium constant expression) for the following reaction



Calculating the Equilibrium Constant

- Changing the temperature under which a reaction takes place changes the rate of the forward and reverse reactions by different amounts
- A reaction at a specific temperature has an equilibrium constant that is different to that of the same reaction at a different temperature
 - Ex2. A mixture of nitrogen and chlorine gas is kept at a certain temperature in a 5L flask where the following reaction takes place:



When the reaction reaches equilibrium, the flask was found to contain 0.0070mol of $N_{2(g)}$, 0.0022mol of $Cl_{2(g)}$, and 0.95mol of $NCl_{3(g)}$. What is the value of the equilibrium constant?

Measuring Equilibrium Concentrations

Formulas & Theorems Covered Today:

- ★ ICE Tables
- ★ Equilibrium Concentrations
- ★ Quadratic Equation

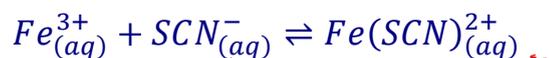
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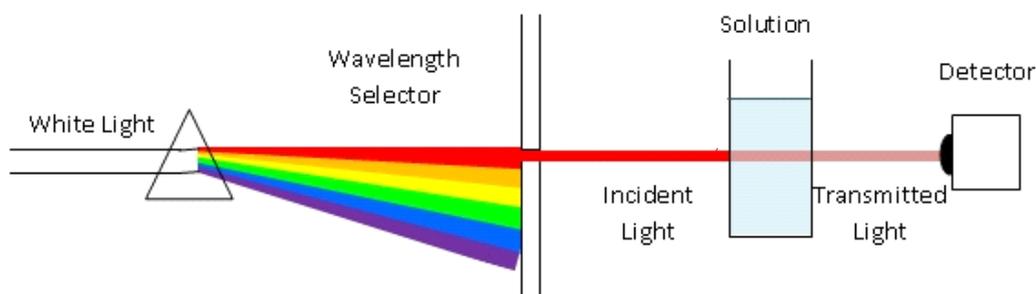
Notes:

Measuring Equilibrium Concentrations

- Unfortunately, unlike last less, we are not always given the concentrations of the chemicals in a reaction when equilibrium has been reached.
- Without these, we cannot calculate the equilibrium constant which means that we will not know where our equilibrium will lie, either towards the reactants or the products (left or right)
- We can however, calculate the equilibrium concentrations given the initial concentrations of the reactants
- Take the following example equation



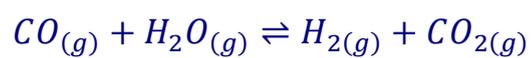
- Because this reaction involves a change in colour, we can measure the concentrations of the products at equilibrium using a method known as spectrophotometry



The difference between the incident and transmitted light indicates the absorbance

- Ex1. If the initial concentration of aqueous iron ion was found to be 0.0064 M, and the initial concentration of the aqueous thiocyanate ion was 0.0010 M and the equilibrium concentration of the Iron (III) thiocyanate ion was found to be (by spectrophotometry) 4.5×10^{-4} M. What are the concentrations of the reactants at equilibrium?

- Ex2 The below reaction happens at 700oC and has an equilibrium constant of 0.83. Suppose that you start with 1mol of carbon monoxide gas and 1mol of water vapour in a 5L container. What amount of each substance would be present at equilibrium?



Predicting the Direction of a Reaction

Formulas & Theorems Covered Today:



Homework:



Notes:

Predicting the direction of a Reaction

- We have discussed thus far that if a reaction is at equilibrium, then the concentration of the products and reactants is constant
- We have also looked at what happens when a mixture starts off and proceeds towards equilibrium from either direction (either starting with products or starting with reactants)
- What we have yet to look at is what happens when a reaction is in between initial conditions and equilibrium
- More importantly, how we can predict how a reaction will proceed if it is in between those conditions
- The directionality of a mixture of chemicals is dependent on the equilibrium constant, which if you recall is a ratio of products to reactants, and another value called the reaction quotient
- The reaction quotient is an expression of the current ratio between products and reactants and is calculated by placing the current values of concentration of reactants and products into an equation of the same form as the equilibrium expression
- The following reaction is given and the equation for the reaction quotient is given below



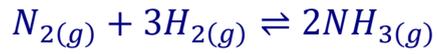
$$Q_c = \frac{[R]^c[S]^d}{[P]^a[Q]^b}$$

- If the value of $Q_c = K_c$, then the reaction is at equilibrium
- If the value of $Q_c > K_c$, then the reaction will push to the left (reactant form)
- If the value of $Q_c < K_c$, then the reaction will push to the right (products form)

Ex1. Sample Problem

The Haber process takes atmospheric nitrogen gas and reacts it with hydrogen gas to produce

ammonia in the following reaction. At 500°C the value for K is 0.40. The following concentration of gases are currently present in the reaction vessel



$$[N_2] = 0.1 \text{ M}$$

$$[H_2] = 0.3 \text{ M}$$

$$[NH_3] = 0.2 \text{ M}$$

Is the reaction, under the current conditions at equilibrium and if not, in which direction will the reaction proceed?

Le Châtelier's Principle

Formulas & Theorems Covered Today:

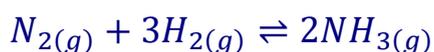


Homework:



Le Châtelier's Principle

- Up until this point, we have looked at equilibrium solely from a quantitative perspective
- We can however look at it from a qualitative perspective using Le Châtelier's Principle
- In order to facilitate this, we can ask ourselves, "what happens to a system at equilibrium, if one of the chemicals changes, or some of the conditions under which the reaction takes place change?"
- Much of industry relies on Le Châtelier's Principle to help create products for consumers
- In order to facilitate this, the industry may add more reactants, or take away products, or add heat, or change pressure (many things can be done)
- When this is done continually, it will produce the wanted outcome
- Yesterday, we looked at the Haber process in which atmospheric nitrogen reacts with hydrogen to produce ammonia gas in the following balanced equation



- When we performed our calculations, we discovered that under the conditions set out by the question and the calculated reaction quotient, that the reaction would push towards the left (produce reactants)
 - Using the theory behind the mass action expression, if we were to remove product (NH_3) then what would happen to the mass action expression would be that the numerator would shrink, and if we continued to remove product until $Q_c < K_c$ then the reaction will shift from left moving to right moving
 - The idea behind this, and ultimately Le Châtelier's Principle, is that everything in a system will change until equilibrium is re-established
 - We use the term Dynamic to describe any equilibrium system (always changing based on conditions)
 - The actual definition of Le Châtelier's Principle is below
 - Le Châtelier's Principle states "a dynamic equilibrium tends to respond so as to relieve the effect of any change in a condition that affects the equilibrium"
 - Le Châtelier's Principle qualitatively predicts what we have done quantitatively with the reaction quotient
 - It can also help us predict changes to a system that do not directly impact the quantities of a chemical, things like temperature, and pressure

Common Ion Effect

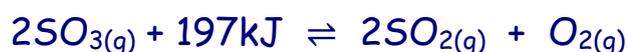
- The common ion effect is an effect on equilibrium based on the concentration of like ions in solution
- As the name suggests, its effect occurs when an ion is added to a solution with the same ion already present in solution
- As Le Châtelier's Principle states, the system will always move to oppose a force change and thus shift the equilibrium away from the added ion
- For now, this is going to be done qualitatively

Temperature and Equilibrium

- The value of the equilibrium constant changes with temperature because the rates of the forward and reverse reactions change and if you recall, the equilibrium constant, is a ratio between the forward rate constant and the reverse rate constant
- Le Châtelier's Principle can be used to predict what an increase or decrease in temperature will do to our equilibrium
- Take the following thermochemical equation for instance



- This reaction can be re-written with the energy portion embedded in the equation as follows



- If we treat the heat of a reaction as a product or as a reactant, then Le Châtelier's Principle will shift the equilibrium accordingly
- If I were to add heat to my reaction, heat is a reactant, and therefore my equilibrium will shift towards the products
- If we were remove heat, it would be the same as removing a reactant, and the equilibrium will shift towards the reactants
- The opposite is true for exothermic reactions

Pressure Change and Equilibrium

- You will recall from previous courses or from your own experience that as you decrease the volume of a system, the pressure will go up, and if you increase the volume of a system the pressure will go down
- Le Châtelier's Principle states that it will try and counteract whatever the change in pressure is and shift the equilibrium accordingly
- We know that pressure is a function of how many particles hit the walls of a container and with what force
- Using the same reaction as above, consider the following



- If we were to increase the pressure of the system by making the volume smaller, then the equilibrium in this case will shift left
- The reasoning behind this is if you were to look at the number of molecules on either side of the equation, there are 3 on the right and only 2 on the left
- If pressure is a function of how many particles strike the walls of the container, and Le Châtelier's Principle states that it will change the equilibrium so that it minimizes the change, then the equilibrium will move to the side of the equation that has fewer molecules (to decrease the number striking the walls of the container and to ultimately decrease pressure)
- Pressure can also change if a gas is added or taken out of a container but in order to have a change, it must be a gas that reacts in the equation
- Adding an inert gas, like helium or argon to a reaction mixture will increase the overall pressure of the vessel, but will have no effect on the equilibrium as it does not affect the partial pressures of the reacting or produced species

K_p and Equilibrium

Formulas & Theorems Covered Today:



Homework:



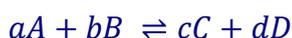
Notes:

Equilibrium Constants and Pressures

- It is convenient to express K_{eq} for a homogeneous chemical system composed only of gases using partial pressures of the gases rather than their molar concentrations
- This is because the partial pressures are more easily and accurately measured
- Recall from last year the ideal gas law, PV = nRT
- As long as each gas behaves as an ideal gas, you can use it to derive the equilibrium constant using partial pressures
- If we rearrange the ideal gas law we get the following

$$\frac{P}{RT} = \frac{n}{V}$$

- If you recall, the K_c value is based on concentrations and the second term above is the same
- With some simple mathematical calculations, we are able to derive the following from the generic equations



$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

- You can use this equation now to solve related equilibrium problems with regards to partial pressures
- Sometimes, you will be required to convert between K_p and K_c
- To do so, you will use the following equation

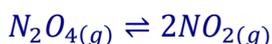
$$K_p = K_c (RT)^{\Delta n}$$

- To calculate Δn, use the following equation

$$\Delta n = \sum \text{coefficient}_{\text{products}} - \sum \text{coefficient}_{\text{reactants}}$$

Ex1. Sample Problem

Consider the following reaction



A reaction flask is charged with 3.00 atm of dinitrogen tetroxide gas and 2.00 atm of nitrogen dioxide gas. At 25°C, the gases are allowed to reach equilibrium. The pressure of the nitrogen dioxide was found to have decreased by 0.952 atm. Estimate the value of K_p for this system and

Then convert this K_p into a K_c .

Solubility Equilibria

Formulas & Theorems Covered Today:



Homework:



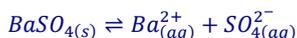
Notes:

Solubility Equilibria

- We learned in chapter 7 that a saturated solution with undissolved solute is an example of a heterogeneous equilibrium
- You also learned last year that solubility is the amount of a solute that can dissolve in a given amount of solvent at a particular temperature
- This solubility can be expressed using many units but for this course, we will express them as molar solubility

Heterogeneous Equilibria

- Consider the salt solution made of barium sulfate, $BaSO_4$
- When the salt crystals dissolve in water, the concentration of the dissolved ions is low and therefore the forward reaction is favoured



- However, as more and more of the solute dissolves, the rate of the forward reaction slows and the rate of the reverse reaction increases, or in other words the rate of dissolution slows and the rate of re-crystallization increases
- Eventually, the rates of the forward and reverse reactions will be the same, and equilibrium will be reached
- Because the products and reactants are in different phases, we call this type of equilibrium heterogeneous

Solubility Product

- When excess solid is present in a saturated solution, the equilibrium expression is as follows

$$k_{eq} = \frac{[Ba_{(aq)}^{2+}][SO_{4(aq)}^{2-}]}{BaSO_{4(s)}}$$

- The solids' concentration however is a constant and therefore the equilibrium constant can combine with the concentration of the solid to give us the solubility product as shown below

$$k_{eq} [BaSO_{4(s)}] = [Ba_{(aq)}^{2+}][SO_{4(aq)}^{2-}] = k_{sp}$$

- For the solubility product expression, remember that the terms of the concentration of the dissolved ions must be raised to the power of the co-efficients from the balanced chemical equations

Sample Problem 1

Calculate the solubility product if the solubility of silver carbonate is $1.3 \times 10^{-4} M$

Sample Problem 2

At 25°C, the solubility product of lead (II) iodide is found to be 9.8×10^{-9} . What is the molar solubility of lead iodide in water? What is the solubility in g/L? in PPM?

The Common Ion Effect and Predicting the Formation of a Precipitate

Formulas & Theorems Covered Today:



Homework:



Notes:

The Common Ion Effect

- Recall the common ion effect from when we discussed it during Le Châtelier's Principle
- If you add to a solution an ion that is already present in that solution, Le Châtelier's Principle states that the equilibrium will push away from that ion
- Take for example the equilibrium that exists for the solubility of lead (II) chromate

- If we add into the solution, or add lead (II) chromate to a solution of sodium chromate (as an example) then the equilibrium will shift and move left because of the presence of the chromate ion from the sodium chromate

- The K_{sp} however does not change because it is a constant at that particular temperature
- That being said, the only way for the K_{sp} to remain the same is to reduce the amount of the other (uncommon) ion which means that the solubility will decrease

Sample problem 1

The solubility of pure lead(II)chromate in water is $4.3 \times 10^{-7} M$

- Qualitatively predict how the solubility will change when it is placed in a 0.1M solution of sodium chromate
- What is the new solubility if the K_{sp} is 2.3×10^{-13}

Predicting when a Precipitation Occurs

- To determine if a precipitate will form when solutions are mixed together, you must compare the K_{sp} to the ion product quotient, Q
- Comparing the quotient to the K_{sp} , will produce one of three results
 - $Q > K_{sp}$ then a precipitate will form

- To determine if a precipitate will form when solutions are mixed together, you must compare the K_{sp} to the ion product quotient, Q
- Comparing the quotient to the K_{sp} , will produce one of three results
 - $Q > K_{sp}$ then a precipitate will form
 - $Q = K_{sp}$ then the solution is saturated
 - $Q < K_{sp}$ then a precipitate will not form

Sample Problem 2

Will a precipitate form if 100mL of a $1 \times 10^{-3}M$ $Pb(NO_3)_2$ solution is added to 100mL of a $2 \times 10^{-3}M$ solution of $MgSO_4$? $K_{sp} PbSO_4 = 6.3 \times 10^{-7}$

For the equilibrium $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + 2D_{(g)}$, 2.0 mol of A, 3.0 mol of B, 8.0 mol of C, and 7 mol of D were placed into a 10.0L vessel and allowed to come to equilibrium.

- a) At equilibrium, the vessel was found to contain 5.0 mol of A, calculate the value of K_c (4 Marks) [T]

b) The volume of the vessel was changed to 5.0L and more of D was added. When equilibrium was once again established, there was found to be 7.0 mol of B. How many moles of D was added to the vessel? (4 Marks) [T]

Introduction to Acids and Base Theories

Formulas & Theorems Covered Today:



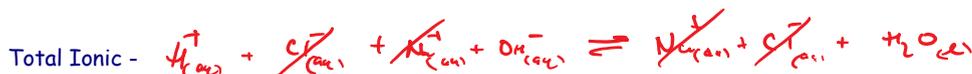
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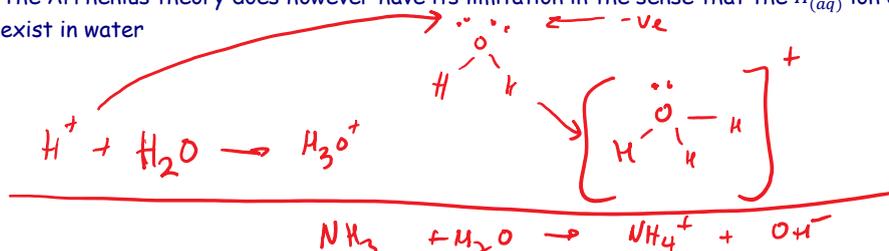
Notes:

Acid/Base Properties

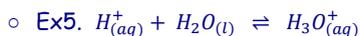
- According to the Arrhenius theory of acids and bases, acids are substances that dissociate in water to form hydrogen ions ($H^+_{(aq)}$)
 - Ex1. $HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$
 - Ex2. $H_2SO_4 \rightleftharpoons 2H^+_{(aq)} + SO_4^{2-}_{(aq)}$
- According to the same theory, a base is one in which the substances completely dissociate to form hydroxide ($OH^-_{(aq)}$) ions in solution
 - Ex3. $NaOH \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$
 - Ex4. $KOH \rightleftharpoons K^+_{(aq)} + OH^-_{(aq)}$
- Using the Arrhenius theory we have been able to understand some pretty simple interactions between acids and bases, such as the neutralization of a strong acids with a strong base



- Different combinations of strong and weak acids and bases will neutralize one another with the same exothermic result (no matter the acid or base)
- The Arrhenius theory does however have its limitation in the sense that the $H^+_{(aq)}$ ion does not exist in water



- The combination of the hydrated proton will produce a hydronium ion ($H_3O^+_{(aq)}$) in solution because the proton can't exist by itself and is attracted to the negative region of the water molecules' lone pairs forming a co-ordinate covalent compound

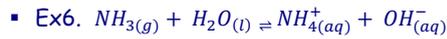


- The other limitations that the Arrhenius theory is that it has difficulty explaining the formation of certain alkaline solutions from chemicals that do not have a hydroxide ion present for dissociation

Bronsted-Lowry Theory of Acids and Bases

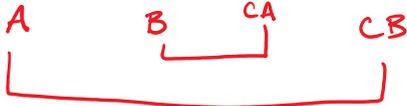
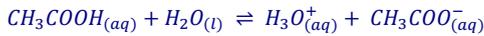
- Johannes Bronsted and Thomas Lowry were two chemists that came up with the general theory of acids and bases to help overcome the limitations of the Arrhenius Theory
- According to the Bronsted-Lowry theory, an acid is a substance that donates a proton and a base according to the theory is a substance that accepts a proton
- There are two advantages to this theory over the Arrhenius
 - This theory is able to explain acid base reactions that do not take place in aqueous solutions

- It is also able to explain the dissociation of acids and bases into water and more importantly explain how this happens in cases that are not so straight forward



Conjugate Acid Base Pairs

- The dissociation of acetic acid reaches an equilibrium and it has only a small percentage of the hydrogen dissociated
- This is due to the fact that the acetic acid is a weak acid and you should recall from last year that weak acids are those that only dissociate a small amount
- The equilibrium can be said to fall far to the left and that the reverse reaction is favoured

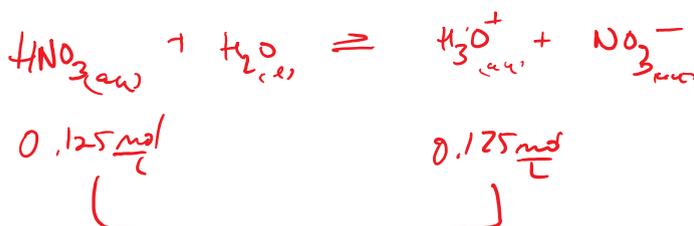
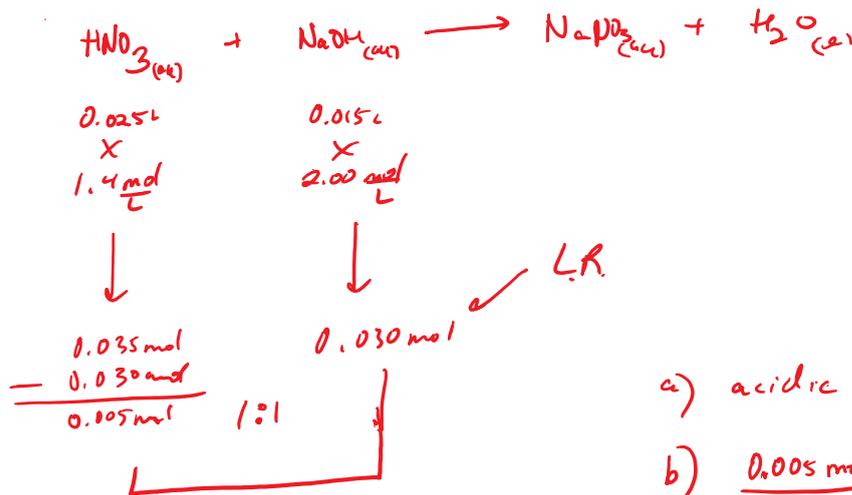


- Using the Bronsted-Lowry definition, the acid donates its proton to the base
- The base, on the left side of the equation becomes what we call a conjugate acid because in the reverse equation, it is considered the acid
- The same is true for the acid on the left hand side of the equation, it becomes a conjugate base on the right side
- This rule also helps explain why an ammonia solution produces a basic reading without the presence of a hydroxide ion



Sample Problems

During an experiment, a student pours 25.0 mL of 1.40 mol/L nitric acid into a beaker that contains 15.0 mL of 2.00 mol/L sodium hydroxide solution. Is the resulting solution acidic or basic? What is the concentration of the ion that causes the solution to be acidic or basic



$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(0.125) \\ &= 0.9 \end{aligned}$$

The Equilibrium of Weak Acids and Bases

Formulas & Theorems Covered Today:



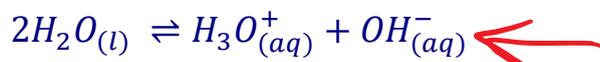
Homework:



Notes:

The Equilibrium of Weak Acids and Bases (Intro)

- When an acid and a base dissociates in water, the ions interact with the water
- The pH of the solution can be determined by the position of the equilibrium in reactions between the ions in solution and the water molecules
- Pure water however contains ions from the dissociation of water molecules themselves as shown below



- The dissociation (autoprotonation) is very low, approximately 1 in 500,000,000 water molecules at 25°C
- This is why water (pure not tap) is a poor conductor of electricity
- In a neutral sample of water, the concentrations of the hydronium and hydroxide ion concentration are both $1 \times 10^{-7} M$

Ion Product of Water

- K_c for water is given as the following

$$K_c \equiv \frac{[H_3O^+_{(aq)}][OH^-_{(aq)}]}{[H_2O_{(l)}]^2}$$

- Because so few ions of the water dissociate, the concentration of the water remains constant
- If you recall from K_{sp} , the solids concentration was solid and we were able to remove that part of the equilibrium
- The ion product of water is produced as follows

$$K_c [H_2O_{(l)}]^2 = [H_3O^+_{(aq)}][OH^-_{(aq)}] = K_w$$

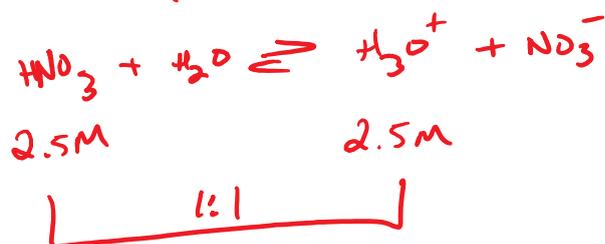
$$K_w = 1 \times 10^{-14} \quad \left(\downarrow \begin{matrix} (1 \times 10^{-7} M) \\ (1 \times 10^{-7} M) \end{matrix} \right) =$$

- This number represents the product of hydronium and hydroxide concentrations and has an inversely proportional relationship

Sample Problems:

Determine the concentration of hydronium and hydroxide ions in each solution

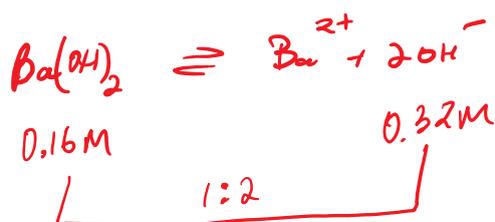
- 2.5M HNO₃
- 0.16M Ba(OH)₂



$$K_w = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$1 \times 10^{-14} = (2.5\text{M})[\text{OH}^-]$$

$$4 \times 10^{-15} \text{ M} = [\text{OH}^-]$$



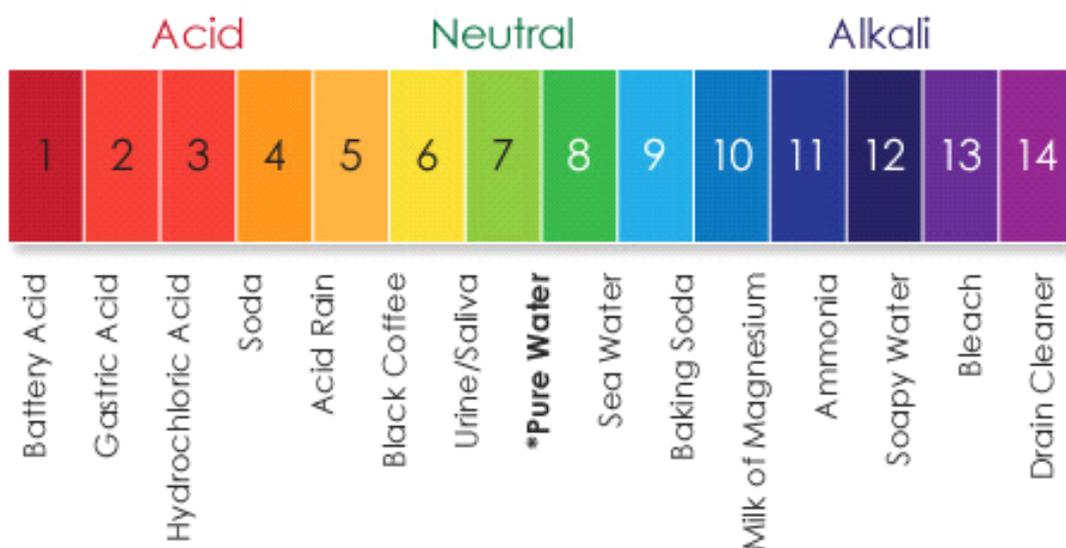
$$K_w = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$1 \times 10^{-14} = [\text{H}_3\text{O}^+](0.32)$$

$$3.125 \times 10^{-14} = [\text{H}_3\text{O}^+]$$

pH and pOH

- You can describe the acidity and alkalinity of a solution by determining the concentration of hydronium or hydroxide ions
- This is done using the pH/pOH scale which is a logarithmic scale
- A logarithmic scale is one in which each whole number increase or decrease is a 10x fold difference with the number changed from



- To calculate pH, pOH, or concentrations of acids and bases from given data, we have the following equations that we can use

$$\text{pH} = -\log [\text{H}_3\text{O}^+_{(aq)}]$$

$$\text{pOH} = -\log [\text{OH}^-_{(aq)}]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14$$

The Acid Dissociation Constant

Formulas & Theorems Covered Today:

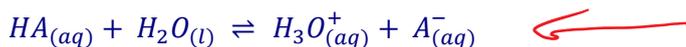


Homework:



Notes:

- Many acids that we come into contact with on a daily basis are weak acids
- Recall that over the last few classes, we learned that weak acids and bases dissociate into the hydronium or hydroxide ions and ultimately conjugate into an acid or a base
- For acids that are classified as monoprotic, their generic formula is as follows

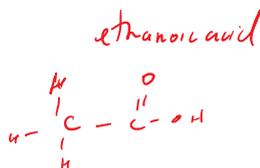
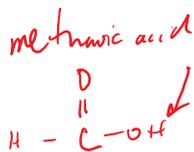


- The equilibrium expression for the above generic monoprotic acid is as follows

$$k_c = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}][H_2O_{(l)}]} \quad \leftarrow$$

- For similar reasons to the ion product of water, the concentration of water is considered a constant and can be combined with the equilibrium constant as shown below
- The resulting expression is called the acid dissociation constant

$$k_c[H_2O_{(l)}] = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} = k_a \quad \text{acid dissociation constant}$$



Sample Problem 1

Formic acid has a concentration of 0.025M. What is the pH of the resulting solution

	HA	+ H ₂ O	⇌	H ₃ O ⁺	+ A ⁻
I	0.025M	—		0	0
C	-x	—		+x	+x
E	0.025-x	—		x	x

$$k_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\frac{0.025}{1.8 \times 10^{-4}} = 138 \quad \text{not negligible}$$

$$x = 2.033 \times 10^{-3}$$

tabulated →

$$1.8 \times 10^{-4} = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.025-x)}$$

$$4.5 \times 10^{-6} - 1.8 \times 10^{-4}x - x^2 = 0$$

$$x = 2.033 \times 10^{-3}$$

$$pH = -\log [H_3O^+] = -\log(2.033 \times 10^{-3})$$

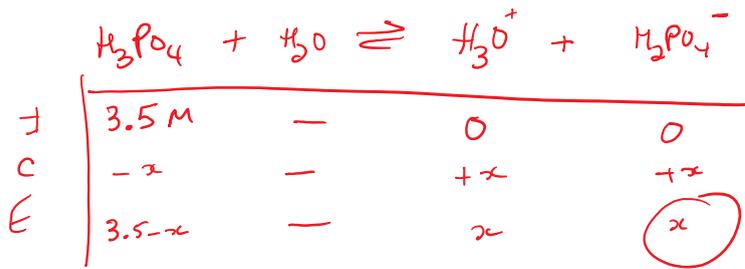
pH = 2.69

Polyprotic Acid Calculations

- Polyprotic acids have more than one hydrogen associated with the acid and therefore the dissociation happens more than once
- These problems, which are solved similarly to the problem above can be divided into different steps corresponding to the number of hydrogens present for the dissociation

Sample Problem 2

Phosphoric acid is used to make fertilizers, calculate the pH, $[HPO_4^{2-}]$ of a 3.5M solution of the phosphoric acid



$$\frac{3.5}{7 \times 10^{-3}} = 500$$

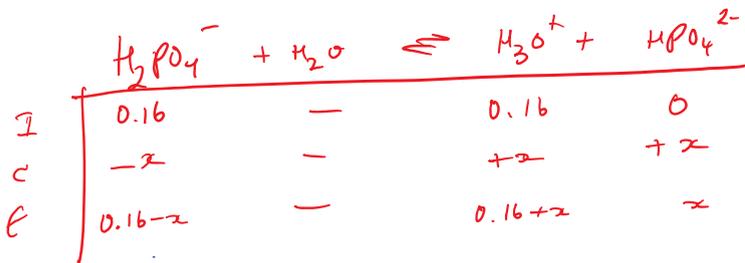
x is negligible

$$K_a = \frac{x^2}{3.5-x}$$

$$7 \times 10^{-3} = \frac{x^2}{3.5}$$

$$\sqrt{(7 \times 10^{-3})3.5} = x$$

$$0.16 = x$$



$$\frac{0.16}{6.3 \times 10^{-8}} > 500$$

x is neg

$$K_{a2} = 6.3 \times 10^{-8} = \frac{(0.16+x)(x)}{(0.16-x)}$$

$$= \frac{(0.16)(x)}{(0.16)}$$

$$6.3 \times 10^{-8} = x = K_a$$

$$pH = -\log [H_3O^+] = -\log(0.16 + 6.3 \times 10^{-8})$$

1 _____

$$pH = -\log(0.16 + 6.3 \times 10^{-8})$$

$$= 0.796$$

$$[HPO_4^{2-}] = 6.3 \times 10^{-8} M$$

- All polyprotic acids are weak except sulfuric acid
- Their second dissociation is much weaker than the first
- When calculating the hydronium ion concentration or the pH of a solution, it is only the first dissociation that needs to be considered
- The concentrations of the anions formed in the second dissociation are equal to K_{a2}

Percentage Dissociation

Formulas & Theorems Covered Today:



Homework:



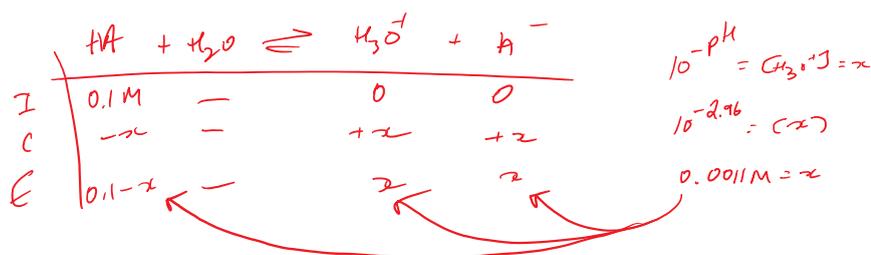
Notes:

Percent Dissociation

- When a weak acid dissociate, the extent to which it does depends on a number of factors
- Because these solutions are not all the same, they have a unique percentage dissociation (they all dissociate a different amount)
- Some can dissociate up to 8% while others only dissociate 0.1%
- By knowing the percent dissociation, we are able to identify stronger acids from weaker ones

Sample Problem 1

Propanoic acid is prepared at 0.1M with a pH of 2.96. What is the acid dissociation constant and what percent of the molecules has dissociated?



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{(0.0011)(0.0011)}{0.1 - 0.0011}$$

$$K_a = 1.2 \times 10^{-5}$$

$$\% \text{ dissociation} = \frac{[H_3O^+]}{[HA]} \times 100\%$$

$$= \frac{0.0011}{0.1} \times 100\%$$

$$= 1.1\%$$

Sample Problem 2

Calculate the concentration in mol/L of an acetic acid solution which is 2.0% ionized. What is the corresponding pH

$$K_a = 1.8 \times 10^{-5}$$

Let x represent [HA]



$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][A^-]}{x}$$

$$1.8 \times 10^{-5} = \frac{(0.02x)(0.02x)}{x}$$

$$1.8 \times 10^{-5} = \frac{0.0004x^2}{x}$$

$$1.8 \times 10^{-5} = 0.0004x$$

$$4.5 \times 10^{-2} = x$$

$$(0.02)(4.5 \times 10^{-2}) = [H_3O^+]$$

$$9 \times 10^{-4} = [H_3O^+]$$

$$pH = -\log(9 \times 10^{-4})$$

$$pH = 3.05$$

Bases and Buffers

Formulas & Theorems Covered Today:



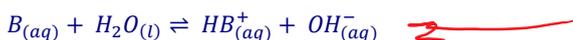
Homework:



Notes:

Equilibrium Forming Basic Solutions

- Many compounds in everyday life are weak bases
- They interact with water as per the following generic equation



- The equilibrium from that reaction is shown just below

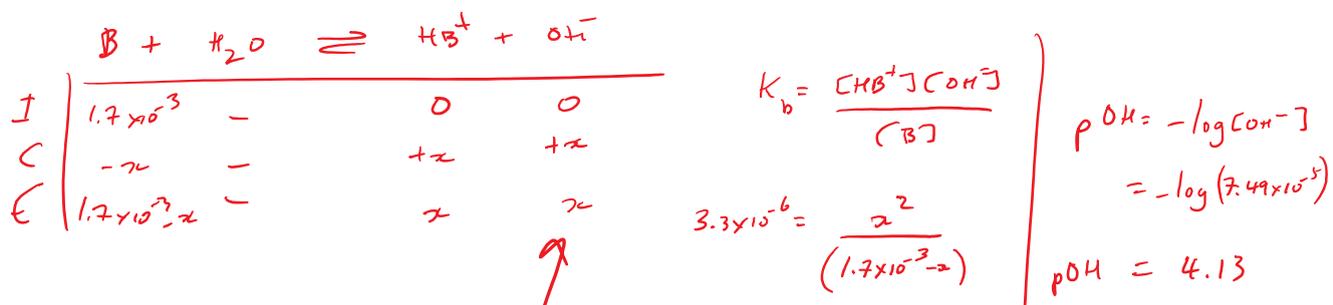
$$K_c = \frac{[HB^+_{(aq)}][OH^-_{(aq)}]}{[B_{(aq)}][H_2O_{(l)}]}$$

- If you recall from the lesson on the dissociation of an acid, the acid dissociation constant was derived from an equation similar to the one above by removing the water concentration as it is kept constant
- In similar fashion, the base dissociation constant is as follows

$$K_c[H_2O_{(l)}] = \frac{[HB^+_{(aq)}][OH^-_{(aq)}]}{[B_{(aq)}]} = K_b$$

Sample Problem 1

Quinine has a base dissociation constant of 3.3×10^{-6} . Calculate the $[OH^-]$ and the pH a $1.7 \times 10^{-3} M$ solution of quinine.



$$\frac{1.7 \times 10^{-3}}{3.3 \times 10^{-6}} > 500$$

x is neg

$$5.3 \times 10^{-5} = \frac{x}{(1.7 \times 10^{-3} - x)}$$

$$3.3 \times 10^{-6} = \frac{x^2}{1.7 \times 10^{-3}}$$

$$\sqrt{(3.3 \times 10^{-6})(1.7 \times 10^{-3})} = x$$

$$7.49 \times 10^{-5} = x$$

$$pOH = 4.13$$

$$14 = pH + pOH$$

$$14 - pOH = pH$$

$$14 - 4.13 = pH$$

$$9.87 = pH$$

Sample Problem 2

Calculate the K_b in a C_5H_5N solution with a concentration of 0.125M and a pH of 9.1

$$B + H_2O \rightleftharpoons HB^+ + OH^-$$

I	0.125	-	0	0
C	-x	-	+x	+x
E	0.125-x	-	x	x

$$pOH = 14 - pH$$

$$= 14 - 9.1$$

$$pOH = 4.9$$

$$10^{-4.9} = [OH^-]$$

$$1.26 \times 10^{-5} = [OH^-] = x$$

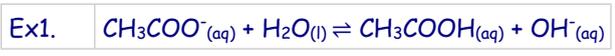
$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$= \frac{(1.26 \times 10^{-5})^2}{0.125 - 1.26 \times 10^{-5}}$$

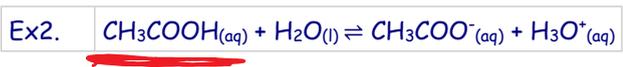
$$K_b = 1 \times 10^{-9}$$

Acids and their Conjugate Bases

- There is a relationship between the K_a of an acid and the resulting K_b of its conjugate base
- Take for example the two reactions below



$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$



$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

- If we take the product of the two equilibrium expressions above we are given the following

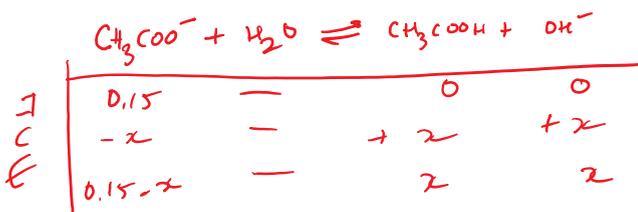
$$K_a K_b = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \cdot \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = [H_3O^+][OH^-] = K_w$$

$$\therefore K_a K_b = K_w$$

- The explanation as to why this equation is the case is that the stronger the acid, the weaker its conjugate base, and of course vice versa
- The dissociation constant tells us how far to the left or right our equilibrium lies

Sample Problem 3

A sodium acetate solution contains 12.5g of the salt in 1L of water. Calculate the base dissociation constant and the pH of the resulting solution (assume that only the acetate affects the pH)

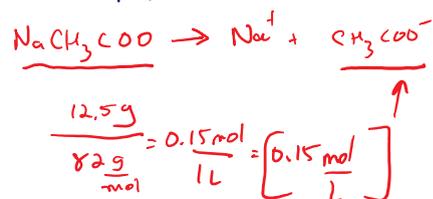


ICE

$$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

$$K_a K_b = K_w$$

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = K_b$$



$$K_b = \frac{x^2}{0.15-x}$$

$$\sqrt{(5.56 \times 10^{-10})(0.15)} = x$$

$$9.13 \times 10^{-6} = x = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log 9.13 \times 10^{-6}$$

$$= 5.04$$

$$\text{pH} = 14 - \text{pOH}$$

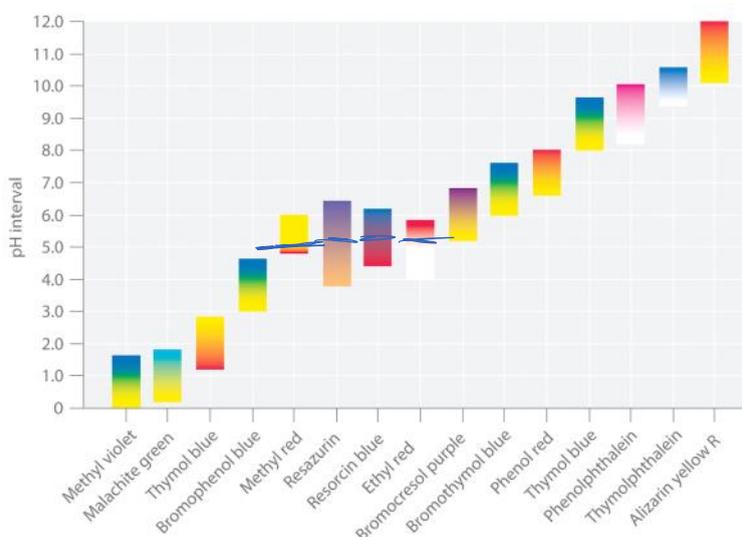
$$\boxed{\text{pH} = 8.96}$$

Buffers

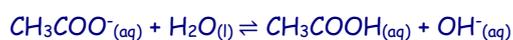
- These are solutions that contain a weak acid and the salt of that weak acid
- This solution restricts changes in pH when a moderate amount of acid or base is added
- If, for example, 10mL of a 1M solution of HCl were added to 1L of water, the pH would change from 7 to 3
- By adding the same amount of acid to a buffered solution, it may only change the pH by as little as 0.1
- This is all dependent on the ranges of pH that the buffer capacity works at

- Because all buffered systems work at different pH (as seen above) the correct indicator must be chosen in order to identify when we have reached the end point of our titration (buffering capacity)
- To do this, we can use the following chart to help us identify which buffer to chose

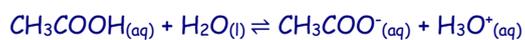
Indicator	pK _{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue



- To create these systems, as mentioned above, we have to add a weak acid/base and the salt of that weak acid or base (see below)



And



- When acids or bases are added to these buffered systems, the hydronium or hydroxide ions are removed by one component of the buffer because of a shift in the equilibrium of that system
- The buffer capacity is the amount of acid or base that can be added before a significant pH change occurs

Acid Base Properties of Salt Solutions

Formulas & Theorems Covered Today:



Homework:



Notes:

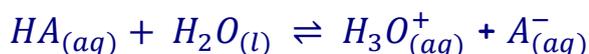
The Acid-Base Properties of Salt Solutions

- You learned that the reaction between an acid and a base is known as a neutralization reaction and that it always produces some salt and some water



- The acid and base properties of that salt solution depend on the interactions between the dissociated salt ions and the water in which they exist
- Some, as you would imagine, do not interact with the water and they ultimately produce neutral solutions whereas others will react with the water molecules producing equilibria that have the ability of producing hydronium or hydroxide ions
- How high or low the pH will get depends on the extent of the interaction

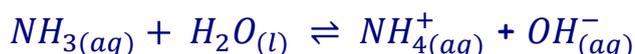
Salts that Form Neutral Solutions



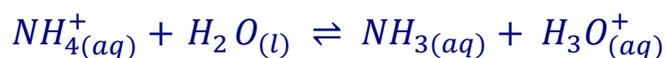
- Looking at the equation we see that the conjugate base to the strong acid has no tendency to combine with $H_3O^+_{(aq)}$
- This salt has no effect on the pH of a solution because it does not interact with the water
- Similarly to this, a strong base's conjugate acid tends to not interact with the water to produce $OH^-_{(aq)}$ ions
- The reason for this is that the conjugate acid or base from a strong base or acid is weak
- To understand this, convert the K_a to a K_b or vice versa
- If the left side of the equation boasts a large K then the reverse reaction will have a small K
- In either case, water is the stronger acid or base respectively
- If the salt of a strong acid and salt of a strong base are placed into the same vessel, the effective pH will be 7

Salts that Form Acidic Solutions

- A weak base, like ammonia, dissociates very little and therefore the equilibrium lies far towards the reactants



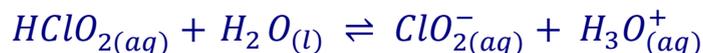
- The reverse reaction consists of an ammonium ion which is a relatively strong acid in comparison to the water and is therefore likely to react with the water in the following way



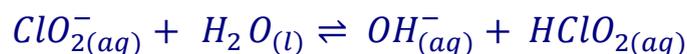
- "Salts of a weak base and a strong acid will dissolve in water to form acidic solutions"

Salts that Form Basic Solutions

- As a complete opposite to the above example, a weak acid will react with water to form a relatively strong conjugate base



- Chlorous acid is weak and produces the chlorite ion which is a stronger base than water and therefore will interact with the water to form a basic solution as shown below



- "Salts of a weak acid and a strong base will dissolve in water to form basic solutions"

Salts of Weak Acids and Weak Bases

- If a salt consist of the cation of a weak base and the anion of a weak acid, both of them will interact with the water
- To determine the relative strength of the two, you must compare the K_a with the K_b values
- If $K_a > K_b$ then the solution will be acidic (pH less than 7)
- If $K_a < K_b$ then the solution will be basic (pH greater than 7)

Sample Problems

Predict the acid base properties of the following aqueous solutions

- Ammonium nitrate
- Sodium phosphate
- Sodium chloride
- Ammonium cyanide

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Calculating pH at Equivalence Point

Formulas & Theorems Covered Today:



Homework:



Notes:

Calculating pH at Equivalence

- The equivalence point of an acid-base titration is when the perfect amount of an acid has been added to completely react all the base or vice versa
- By knowing how much of a base or acid has been added and the concentration of that compound, you can use the stoichiometry to then find the other ones concentration
- Being able to figure out the equivalence point will also help us chose the correct indicators to use for that titration

Sample Problem

20mL of a 0.2M NH_3 is titrated against 0.2M HCl. Calculate the pH at equivalence and recommend the correct indicator.

