

UNIT D

CHEMICAL EQUILIBRIUM ACID-BASE SYSTEMS

In Chemistry 20, we expanded our knowledge of what is an acid and what is a base from Arrhenius theory to Modified Arrhenius theory.

Arrhenius Acid base Theory

- An acid is a substance that forms an acidic solution (i.e. turns blue litmus paper red) that ionizes to form a hydrogen ion and a balancing species
 - e.g. $\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- An base is a substance that forms a basic solution (i.e. turns red litmus paper blue) that dissociates to form a hydroxide ion and a balancing species
 - e.g. $\text{Ba(OH)}_2(\text{s}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$
- This theory is very restricted and it was found that many substances were acidic or basic that could not be predicted based on the limitations of Arrhenius theory.
- Clearly this theory was inadequate and another theory was needed.

Modified Arrhenius Theory

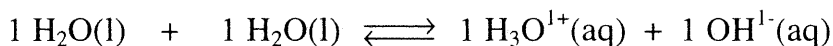
- An acid is a substance that forms an acidic solution (i.e. turns blue litmus paper red) as it reacts with water to form a hydronium ion and a balancing species
 - E.g. $\text{NaH}_2\text{PO}_4(\text{s})$
 1. $\text{NaH}_2\text{PO}_4(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{H}_2\text{PO}_4^{1-}(\text{aq})$
 2. $\text{H}_2\text{PO}_4^{1-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- An base is a substance that forms a basic solution (i.e. turns red litmus paper blue) that when reacting with water forms a hydroxide ion and a balancing species
 - E.g. $\text{NaCH}_3\text{COO}(\text{s})$
 1. $\text{NaCH}_3\text{COO}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
 2. $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$

The definitions of acids and bases will extend further in this chapter as new hypothesis and evidence is provided to you that will give you a more comprehensive understanding of the activity of acids and bases in a reaction

The Water Ionization Constant, Kw

It has been found that water is:

- very slightly conductive if measured with very sensitive instruments
- this is a result of a small amount of ionization or dissociation according to Arrhenius



$$K_w = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(l)]^2}$$

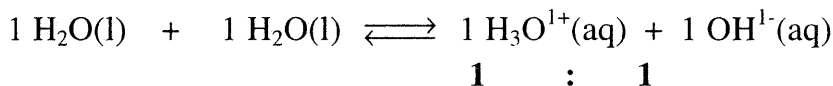
$\text{H}_2\text{O}(l)$ is essentially unchanged therefore

the value of K_w incorporates the

constant $[\text{H}_2\text{O}(l)]$ as part of its value.

Therefore:

$$\boxed{K_w = [\text{H}_3\text{O}^+(\text{aq})] \times [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2/\text{L}^2} \quad \text{water ionization constant}$$



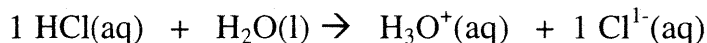
Note: the molar ratio of $\text{H}_3\text{O}^+(\text{aq})$ to $\text{OH}^-(\text{aq})$ is 1:1 therefore, we have equal amounts of both – therefore equal amounts of each will also react or be produced

Therefore, in a beaker of water since the $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ are in a 1:1 ratio the water is considered to be a neutral solution.

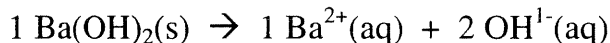
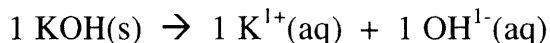
Therefore in a neutral solution $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ mol/L}$

Recall according to Modified Arrhenius:

- **acids** react with in water to increase the $[\text{H}_3\text{O}^+(\text{aq})]$



- **bases** dissolve in water to increase the $\text{OH}^-(\text{aq})$



Therefore in: $2 \text{ H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \uparrow \text{OH}^-(\text{aq})$

- **add a base** $1 \text{ NaOH}(\text{s}) \rightarrow 1 \text{ Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$

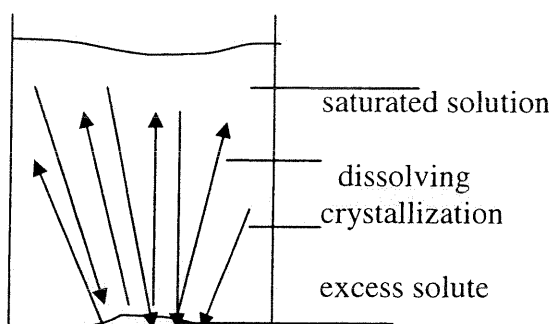
- solution $[\text{OH}^-(\text{aq})]$ increases immediately – solution becomes basic
- therefore according to Le Chatelier's Principle a slight equilibrium shift towards the reactants occurs as the system tries to reduce the added $\text{OH}^-(\text{aq})$

Equilibrium – Acid-Base Systems

Definition from Chemistry:

equilibrium: a state of a closed system in which all measurable properties are constant

e.g. Most substances dissolve in water to a certain extent, and then the dissolving process appears to have stopped. Even though macroscopic properties (temperature, pressure colour etc.) seem constant; if an observation could be made at a microscopic level, we would see that there is still a lot of activity.



While dissolving appears to have stopped, it is actually continuing. However the rate of crystallization is occurring at the same rate as dissolving, therefore it appears as if nothing is changing. This would be called a **solubility equilibrium**

Dynamic Equilibrium – the balance that exists when two opposing processes occur at the same rate is known as dynamic equilibrium.

Many chemical reactions can run in both directions and the consequences of this behavior has become known as equilibrium. In a chemical system that can come to equilibrium, both the forward reaction direction and the reverse reaction direction will run all the time.

Equilibrium in Chemical Systems

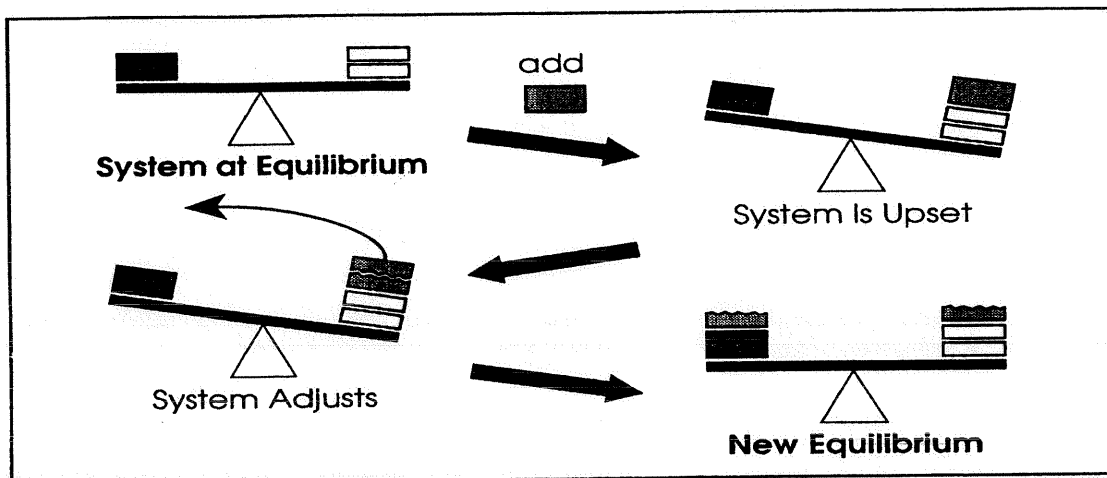
Chemical system: a group of chemicals (reactants) being studied, separated from the surroundings by a boundary. Can only be properly studied in a closed system.

Closed system: one which allows the transfer of energy in and out, but it does not allow the transfer of matter. ie. no substance can enter or leave.

Chemical Systems at Equilibrium

- visually it seems that nothing is happening – the reaction is completed, properties appear constant
 - color
 - pressure
 - taste
 - temperature

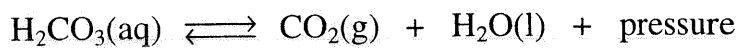
- disturbing the equilibrium of a chemical system
 - results in system adjustments to counter the disturbance
 - resulting in a new equilibrium being established



e.g. soft drink in a closed bottle

- when closed:
 - nothing happening
- when opened:
 - a reduction or decrease in pressure occurs
 - system equilibrium altered
 - $\text{CO}_2(\text{g})$ gas is lost, the soft drink becomes flat
 - new equilibrium is established

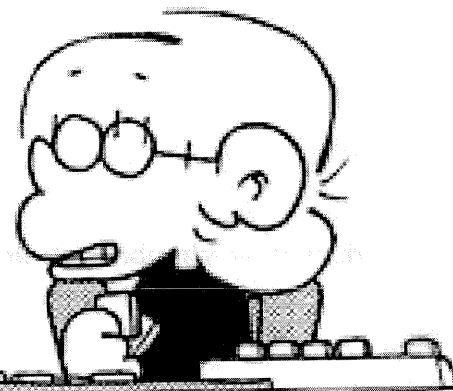
i.e. decomposition of carbonic acid



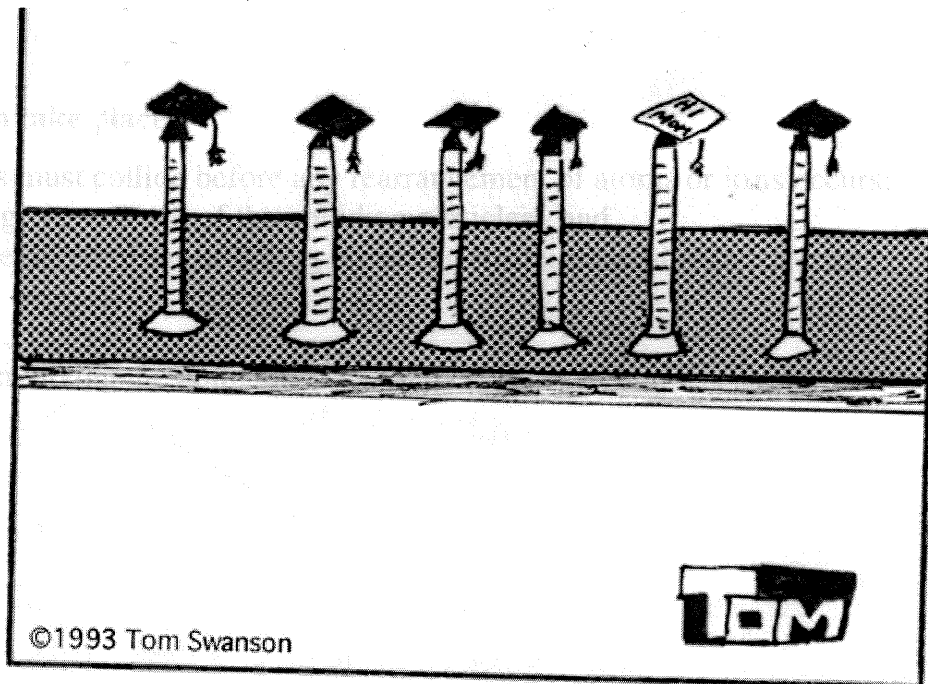
- can force carbonation by adding pressurized carbon dioxide gas

"H-O-H"?! WHAT'S THAT SPELL?!

WATER?



SCRAMBLE



Graduated Cylinders

- some reactions are not fast and may take years to complete
- reactions are not always quantitative
 - As a reaction begins in the reaction of reactants in the forward reaction, products of the reaction immediately begin to react to form a reverse reaction
 - An equilibrium is reached when the rate of the forward reaction is equal to the rate of the reverse reaction

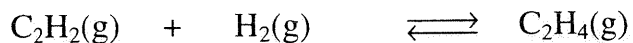
A percent reaction or a percent yield is defined as the yield of product measured at equilibrium compared with the maximum possible yield of product. Percent reaction is one way of communicating the position of an equilibrium.

$$\% \text{ reaction} = \frac{\text{actual amount obtained}}{\text{maximum possible}} \times 100$$

The maximum possible yield of product is calculated using the method of stoichiometry, assuming a quantitative (100%) forward reaction with no reverse reaction.

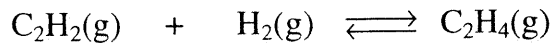
A percent reaction is a single value that can be used to describe and compare chemical reaction equilibria.

eg. #1. Calcium carbonate can be decomposed by heating:



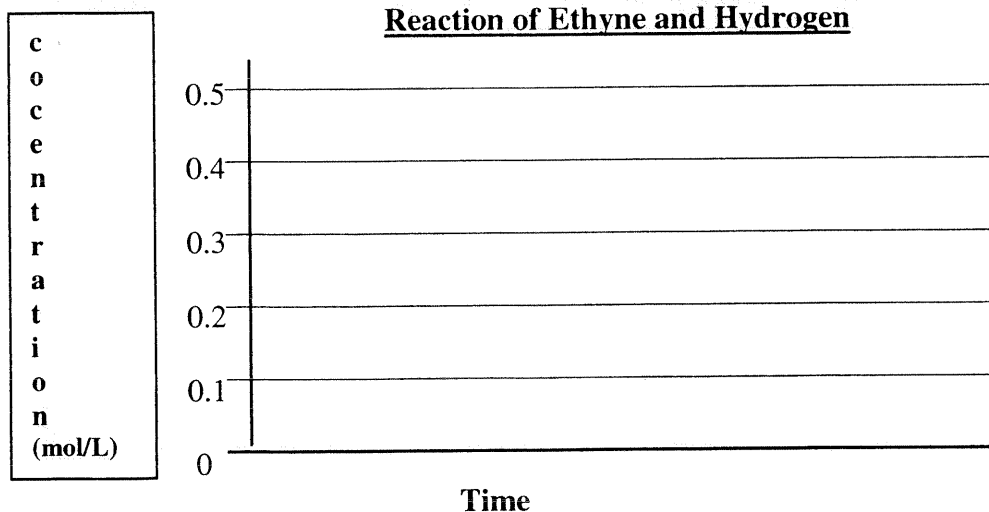
a. What is the maximum possible yield of this reaction if 10.4 g of C_2H_2 along with 1.01 g of hydrogen gas are heated in a 1.00 L container to give 7.02 g of $\text{C}_2\text{H}_4(\text{g})$ at equilibrium?

b. Draw an ICE table for this reaction



initial			
change			
EQ			

c. Sketch a graph showing how the concentration changes as the reaction reaches equilibrium.



To communicate that an equilibrium exists, equilibrium arrows (\rightleftharpoons) or (\longleftrightarrow) are used.

To communicate the extent (or completion) of a reaction, the percent (%) reaction is written above the equilibrium arrows in a chemical equation.

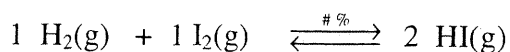


Table 3 – Classes of Chemical Reaction Equilibria:

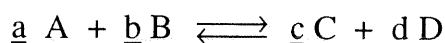
Percent Reaction	Equilibrium	Position of Equilibrium
Negligible < 1%	Non-spontaneous (no apparent reaction)	
< 50%	reactants favored	
> 50%	products favored	
> 99%	quantitative	

The Equilibrium Constant, K_c

A mathematical relationship provides a constant value for a chemical system over a range of concentrations. It is not limited to one set of initial conditions like percent reaction.

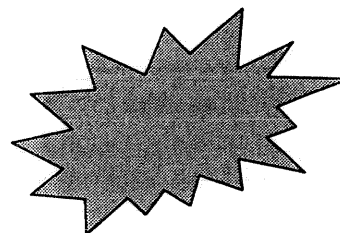
This constant value is called the **equilibrium constant, K_c** , for the reaction system.

Equilibrium Law:



the equilibrium law is

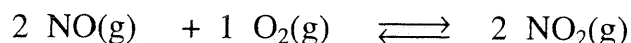
$$K_c = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b}$$



In this mathematical expression, A, B, C, and D represent chemical entities or species and a, b, c, and d represent their coefficients in the balanced chemical equation.

Example:

Write the equilibrium law (equilibrium law expression) for the reaction of nitrogen monoxide gas with oxygen gas to form nitrogen dioxide gas.



A balanced chemical equation with whole number coefficients is used to write the mathematical expression of the equilibrium law, as the coefficients of the balanced equation become the exponents of the concentrations.

The higher the numerical value of the equilibrium constant, the greater the tendency of the system or reaction to favor the forward direction. That is, the greater the equilibrium constant, the greater the percent reaction and the more the products are favored at equilibrium.

Both methods of expressing the position (or extent) of an equilibrium – the equilibrium constant and the percent reaction – have restricted applications.

The value of the equilibrium constant is found by experiments to depend on

- temperature, and
- the value is also affected by large changes in the equilibrium concentration of a reactant or a product.

The equilibrium constant provides only a measure of the equilibrium position of the reaction,

reactants favored	less than a 50 % reaction	$K_c < 1$
balanced reaction	reaction is near 50 %	K_c near 1
products favored	greater than a 50 % reaction	$K_c > 1$
quantitative	greater than a 99 % reaction (100 %)	$K_c > 10^{10}$
	regarded as not taking place at all	$K_c < 10^{-10}$

Note: K_c does not provide any information on the rate (speed) of the reaction.

Do Not Include as Part of the K_c Expression:

- Solid reactants or products
- $H_2O(l)$ if the reaction is done in an aqueous environment

Quantitative Aspects of Equilibrium:

1. Interpret the K_c value:

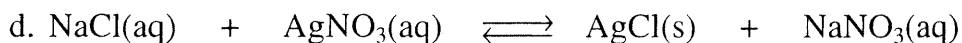
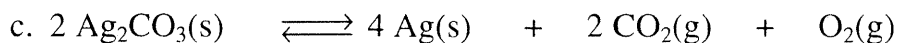
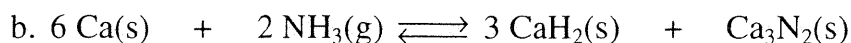
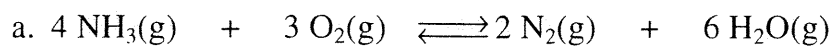
$K_c = 2.00$ reaction favours _____

$K_c = 0.0020$ reaction favours _____

$K_c = 13.69$ reaction favours _____

$K_c = 2.34 \times 10^{-11}$ reaction favours _____

2. Write equilibrium constant expressions for each of the following reactions:



a.

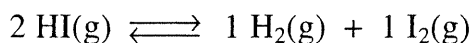
c.

b.

d.

3. Calculate the equilibrium constant (K_c) value for any reaction at equilibrium.

Eg.#1 This reaction involving hydrogen iodide, hydrogen, and iodine reaches equilibrium at 425 °C.



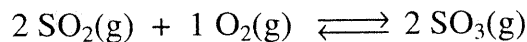
The equilibrium concentrations of the three gases are these: $[\text{HI}(\text{g})] = 0.0175 \text{ mol/L}$; $[\text{H}_2(\text{g})] = 0.00450 \text{ mol/L}$; $[\text{I}_2(\text{g})] = 0.00125 \text{ mol/L}$.

a. What is the value of the equilibrium constant for this reaction? (ans: $K_c = 1.84 \times 10^{-2}$)

b. Determine the K_c for the reverse reaction ?

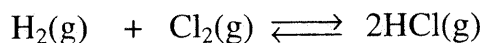
4. Calculate an equilibrium concentration for one of the reactants or products.

What is the equilibrium concentration of $\text{SO}_3(\text{g})$ in the following reaction if the equilibrium concentration of $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ are each 0.0500 mol/L and $K_c = 85.0$?
(ans: $[\text{SO}_3] = 0.103 \text{ mol/L}$)



5. Determining the equilibrium concentration when only the initial conditions are known along with the equilibrium concentration of only one of the species involved. Producing an ICE table.

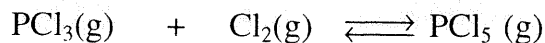
The following equilibrium is in a sealed 3.00 L container at a constant temperature.



Initially 0.0600 mol of $\text{H}_2(\text{g})$ and 0.0720 mol of $\text{Cl}_2(\text{g})$ were introduced into the container. When equilibrium was reached, it was found that the equilibrium concentration of $\text{HCl}(\text{g})$ was 0.0300 mol/L .

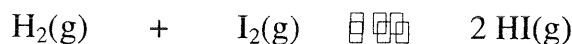
a. Calculate the value of K_c for this expression. (ans: 20.0)

6. In an experiment, 0.20 mol of $\text{PCl}_3(\text{g})$ and 0.10 mol of $\text{Cl}_2(\text{g})$ were placed in a 1.0 L flask at 250°C . The reaction



was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of $\text{PCl}_3(\text{g})$. What is the equilibrium constant and percent yield for this reaction? (ans: $K_{\text{eq}} = 33$, 80%)

7. To a heated reaction vessel with a volume of 1.00L, a lab technician adds 6.23 mmol $\text{H}_2(\text{g})$, 4.14 mmol of $\text{I}_2(\text{g})$, and 22.40 mmol of $\text{HI}(\text{g})$. At equilibrium, a spectrometer is used to determine that the concentration of iodine vapour is 2.58 mmol/L. Construct an ICE table and find K_c for the reaction system. (ans: 54.1)



Concentration			
I			
C			
E			

Qualitative Changes in Equilibrium Systems

- whenever equilibrium state of a system is dealt with, one must comment on the **temperature, composition, and concentration** of all entities involved.
- equilibrium state may be altered if any of the system properties are changed
 - ie.
 - temperature
 - pressure
 - concentration etc.

How is equilibrium altered? Can the equilibrium shift be predicted?

LeChatelier's Principle

- If a reaction or system is at equilibrium and a disturbance or stress occurs by a change in a system property, the equilibrium will shift to try and oppose (get rid of) the disturbance or stress until a new equilibrium is established.

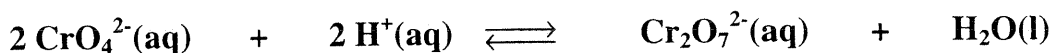
eg. of disturbances

- temperature change (by adding or removing heat energy)
- pressure change (by changing the volume of the reaction container or by adding an inert gas to increase system pressure)
- concentration change (removal or addition of a product or reactant)

Important discovery since this allowed chemical engineers to make some industrial processes

- more economical
- more reliable
- more simple

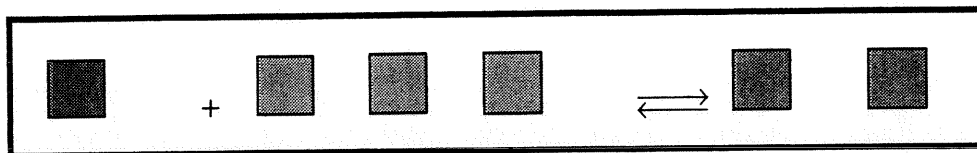
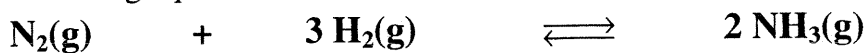
1. Consider the equilibrium equation:



a. What would happen if you added $\text{HCl}(\text{aq})$ to the above reaction?

b. What would happen if you added $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ to the above reaction?

In an equilibrium system involving gases, the total pressure in the system can be changed by increasing or decreasing the volume of the system. The formation of ammonia is represented by the following equation:



4 volumes \rightleftharpoons 2 volumes

If the pressure on the reaction vessel is increased, (ie by reducing the size of the reaction vessel) the system will try to reduce the pressure by shifting to the size of fewest gas volumes. This means a shift to the right.

1. Fill in the blanks:

Pressure and volume are inversely proportional: therefore to increase the pressure of a system, you must _____ the volume of the container and to decrease the pressure, you _____ the volume.

By Le Chatelier's principle, if the volume of a system is decreased, the equilibrium will shift to _____ the pressure by _____ the total number of gas particles.

If the volume is increased, the equilibrium will shift to _____ pressure by shifting to the side of the _____ number of gas particles

This shift is only productive if the total number of gas molecules on the reactant side of the equation is _____ than the total number of molecules on the product side.

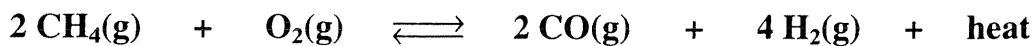
A decrease in volume shifts the equilibrium to the side with the _____ number of molecules.

2. How does a change in pressure affect a system with the same number of molecules on both sides of the equation?

3. a. How does the addition of a catalyst affect a system already at equilibrium?

b. How does the addition of a catalyst affect a system not yet at equilibrium?

4. Methane, CH_4 , reacts with limited oxygen and releases heat according to the equation:



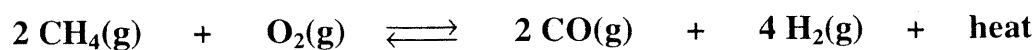
Predict the direction of the equilibrium shift for each of the following. Is K_c affected? If so, how is it affected

a. CH_4 is added

b. CO is added

c. O_2 is removed

d. H_2 is removed



- e. Temperature increases
- f. Pressure decreases
- g. Volume decreases

Note: As demonstrated by the above examples, a change temperature will affect the equilibrium constant (K_c) of a reaction if there is an equilibrium shift. All other stresses will **NOT** affect the equilibrium constant.

5. Traces of formaldehyde in smog are responsible for an eye burning sensation. Formaldehyde, CH_2O , results from the reaction of ozone and the hydrocarbon pollutant ethene, C_2H_4 , as follows:



Predict the direction of the equilibrium shift for each of the following stresses:

- a. C_2H_4 is added
- b. O_3 is added
- c. O_2 is removed
- d. Temperature increases
- e. Volume decreases
- f. Catalyst is added before equilibrium is reached

Catalyst

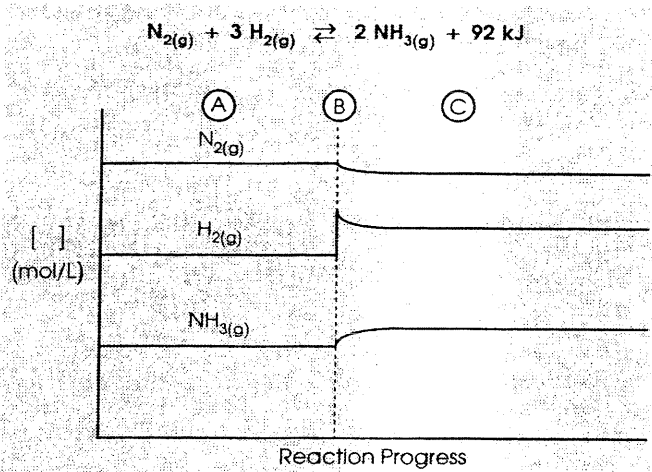
A catalyst is a chemical substance that will increase the rate(speed) of a chemical reaction without being altered or consumed during the chemical reaction.

A catalyst does not affect the position of the equilibrium, since it increases both the forward and reverse reactions to the same degree. Hence, it will not increase the yield of the desired products, but it will decrease the time required for the equilibrium to be established.

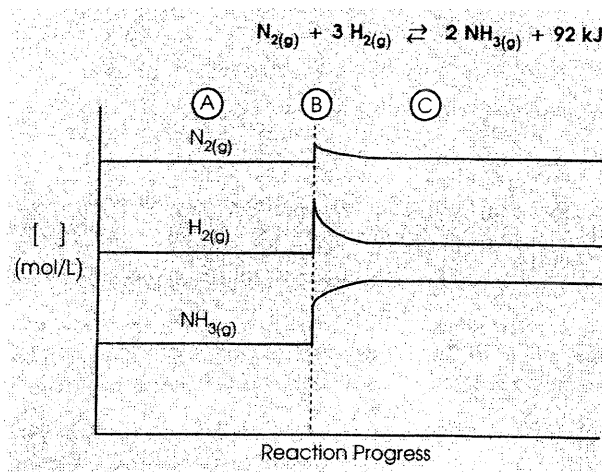
Equilibrium changes can be shown on a graph when concentration of reactants and products are plotted along with time. The effect of adding a stress can be more easily seen.

In the following examples determine the stress(s) that occurred on the reaction. Explain how the reaction reacted to overcome the stress. Also state if this stress affected K_c .

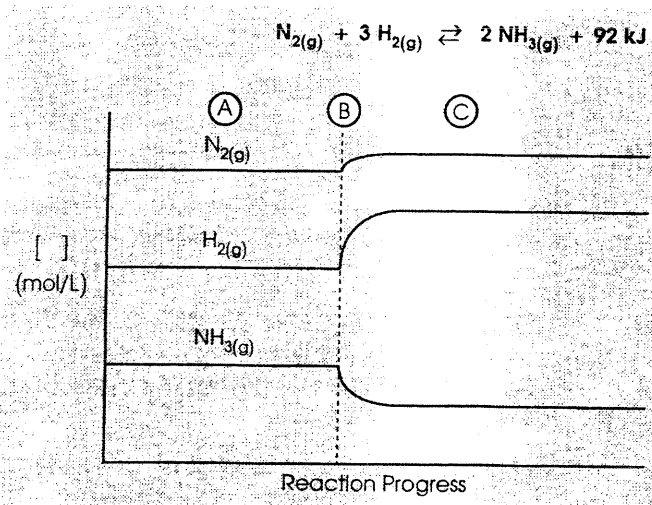
1.



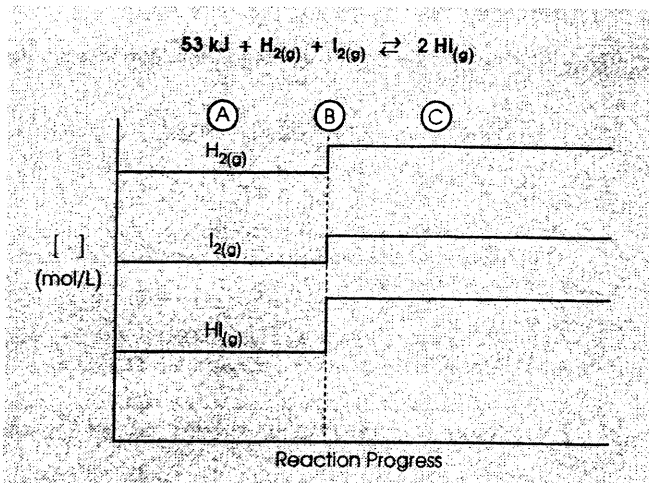
3.



2.



4.



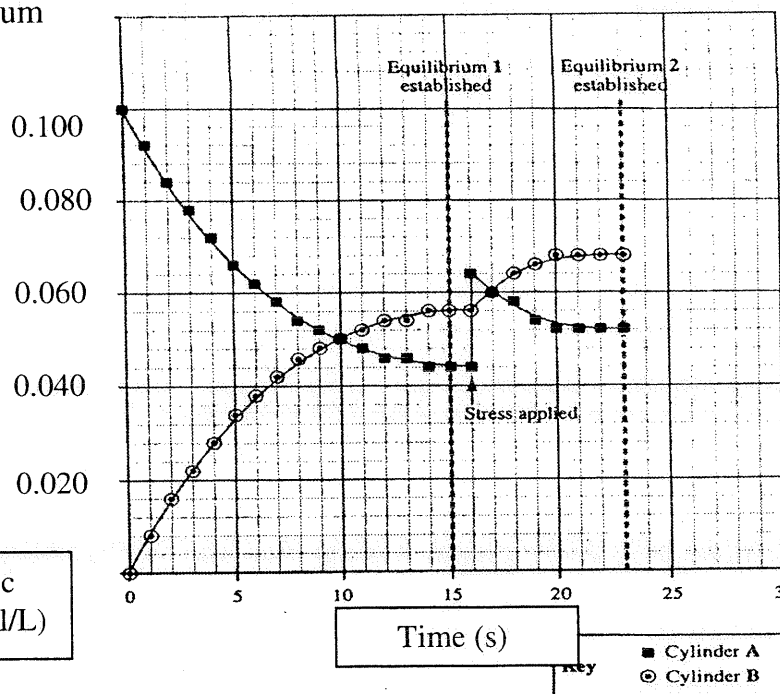
5. In the following equilibrium graph, the following reaction is demonstrated



a. At what time was the first equilibrium established? Calculate the K_c .

b. What was the stress applied?

c. How did the system react to the stress applied?



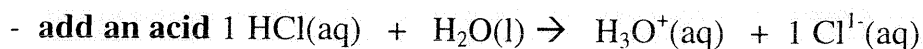
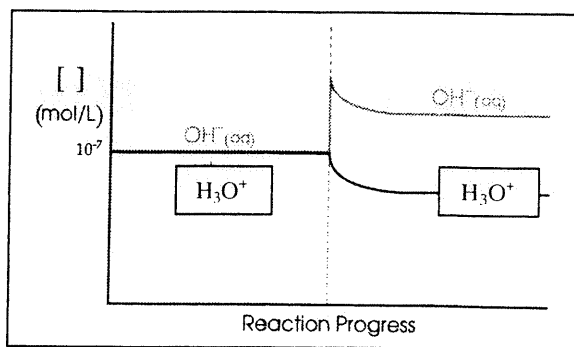
d. Determine K_c at the second equilibrium. How does it compare to the first? Explain.

ACID-BASE CHEMISTRY

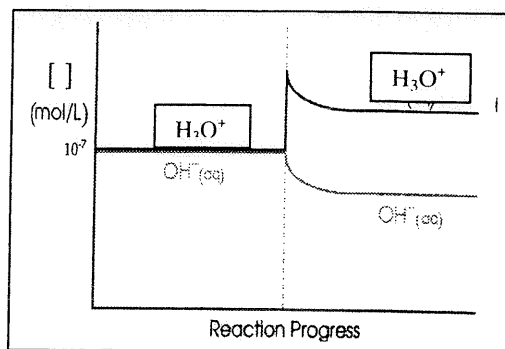
Chemical compounds can be classified as acidic, basic, neutral ionic or neutral molecular

ACIDS	BASES	NEUTRAL IONIC	NEUTRAL MOLECULAR
form conducting solutions	form conducting solutions	form conducting solutions	do not dissociate into ions, solutions do not conduct
turns blue litmus paper red	turns red litmus paper blue	no effect on litmus	no effect on litmus
tastes sour	tastes bitter	all exist as solids	exists as solid, liquids and gases
react with active metals like Ca and Mg to form $H_2(g)$	feels slippery to touch	forms colorless and colored solutions	form colourless solutions
neutralizes bases	neutralizes acids		

- $[\text{OH}^-(\text{aq})] > 1.0 \times 10^{-7} \text{ mol/L}$
- $[\text{H}_3\text{O}^+(\text{aq})] < 1.0 \times 10^{-7} \text{ mol/L}$



- solution $[\text{H}_3\text{O}^+(\text{aq})]$ increases – solution becomes acidic
- therefore according to Le Chatelier's Principle a slight equilibrium shift towards the reactants occurs as the system tries to reduce the added $\text{H}_3\text{O}^+(\text{aq})$



- $[\text{H}_3\text{O}^+(\text{aq})] > 1.0 \times 10^{-7} \text{ mol/L}$
- $[\text{OH}^-(\text{aq})] < 1.0 \times 10^{-7} \text{ mol/L}$

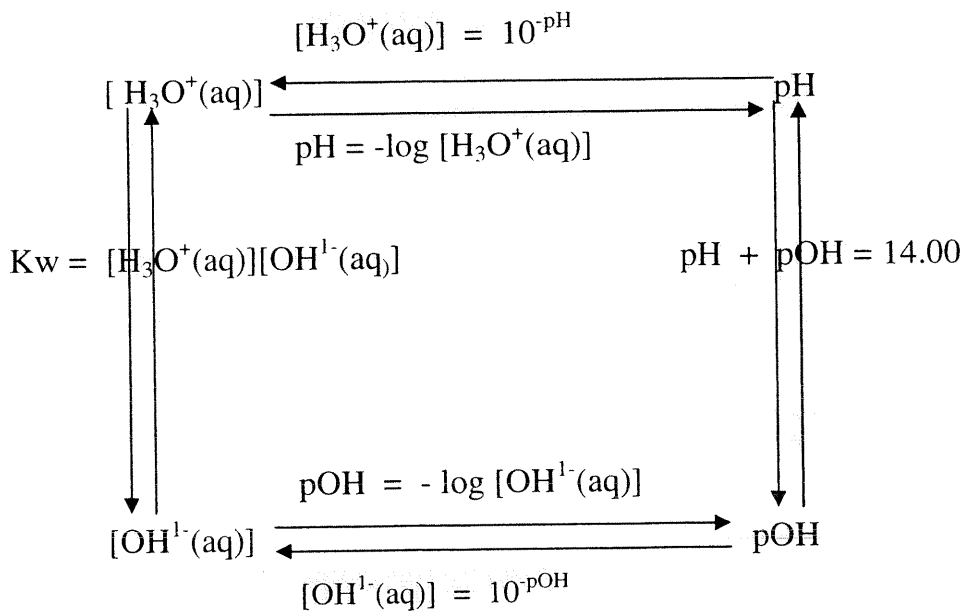
Aqueous Solutions

	<i>Acidic</i>	<i>Neutral</i>	<i>Basic</i>
$[\text{H}_3\text{O}^+(\text{aq})]$ value	$> 1.0 \times 10^{-7} \text{ mol/L}$	$= 1.0 \times 10^{-7} \text{ mol/L}$	$< 1.0 \times 10^{-7} \text{ mol/L}$
$[\text{OH}^-(\text{aq})]$ value	$< 1.0 \times 10^{-7} \text{ mol/L}$	$= 1.0 \times 10^{-7} \text{ mol/L}$	$> 1.0 \times 10^{-7} \text{ mol/L}$

eg. #1. Calculate the $[\text{H}_3\text{O}^+(\text{aq})]$ in an aqueous solution with an $[\text{OH}^-]$ of $2.42 \times 10^{-3} \text{ mol/L}$
Is this solution acidic or basic (ans: $4.1 \times 10^{-12} \text{ mol/L}$)

eg.#2. Determine the $[\text{OH}^-]$ if the $[\text{H}_3\text{O}^+(\text{aq})]$ is $2.41 \times 10^{-6} \text{ mol/L}$.(ans: $4.1 \times 10^{-9} \text{ mol/L}$)

Flow Diagram Connecting All of the Formulas



Solve the following

1. Determine the pH of a solution with $[H_3O^+(aq)] = 2.0 \times 10^{-3}$ mol/L. (ans: 2.70)
2. Calculate the pH of a solution with an $[OH^-(aq)] = 5.0 \times 10^{-6}$ mol/L. (ans: 8.70)
3. Determine the pOH of a 2.50 mol/L solution of HBr. (ans: 14.398)
4. A solution contains 50.0 g of $Ba(OH)_2$ in 500 mL of solution. Determine the pH. (ans: 14.067)
5. Calculate the $H_3O^+(aq)$ of a solution with a pOH of 10.32. (ans 2.1×10^{-4} mol/L)

6. A solution has a pH of 3.50, determine the $[\text{OH}^-(\text{aq})]$ (ans: $3.2 \times 10^{-11} \text{ mol/L}$)

7. Fill in the blanks

pH	$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pOH	acidic/basic
	2.0 mol/L			
		$2.53 \times 10^{-2} \text{ mol/L}$		
4.83				
			1.88	
	$3.56 \times 10^{-2} \text{ mol/L}$			
		$5.90 \times 10^{-8} \text{ mol/L}$		
				neutral

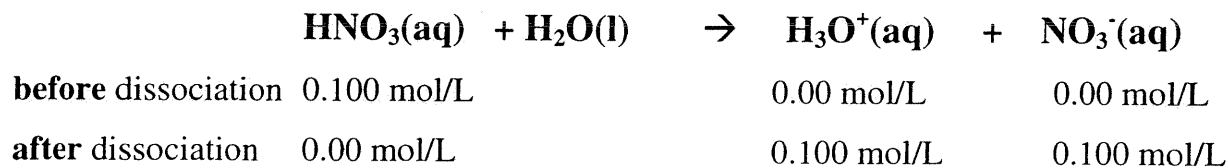
8. Calculate the hydronium ion concentration and pOH in a saturated solution of calcium hydroxide (limewater) that has a solubility of 0.0069 mol/L. (ans: pOH = 1.86)

WEAK ACIDS AND BASES

Strong acids and strong bases completely dissociate like the acids and bases we have been dealing with in the previous pages. We say they **dissociate or ionize 100 %**.

Example:

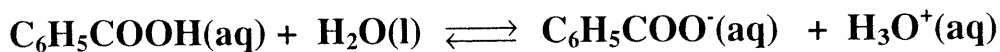
Nitric acid is a strong acid. In a solution that is 0.100 mol/L, the concentration of the species before dissociation would be



Weak acids and bases do not dissociate 100%. Only a few molecules at any given time separate into ions. There are always some molecules present that have not come apart.

Example:

A 0.100 mol/L solution of **benzoic acid** dissociates only 2.6%. This means that after the acid is mixed with water, the resulting species are present in the following concentrations:



before dissociation	0.100 mol/L	0.00 mol/L	0.00 mol/L
after dissociation	0.0974 mol/L	0.0026 mol/L	0.0026 mol/L

97.4% $0.974 \times 0.100 \text{ mol/L}$ $= 0.0974 \text{ mol/L}$

2.6% $0.026 \times 0.100 \text{ mol/L}$ $= 0.0026 \text{ mol/L}$
--

2.6% $0.026 \times 0.100 \text{ mol/L}$ $= 0.0026 \text{ mol/L}$
--

When an acid or base dissociates 100% it is described as **STRONG**.

Consider the following strong acid: 1.00 mol of **hydrogen chloride** gas is added to 1.00 L of water.

	HCl(g)	+	H₂O(l)	→	H₃O⁺(aq)	+	Cl⁻(aq)
before HCl dissolves	1.0 mol/L				0.00 mol/L		0.00 mol/L
after the HCl dissolves	0.00 mol/L				1.00 mol/L		1.00 mol/L

A strong acid is strong because it has a weak conjugate base (ie in this example Cl⁻(aq) is much weaker than H₂O(l) and cannot retain the H⁺(aq). Strong acids have very weak conjugate bases.

A single arrow to the right means that the reaction is not reversible. (→ means the reaction is quantitative or 99% or higher to the right)

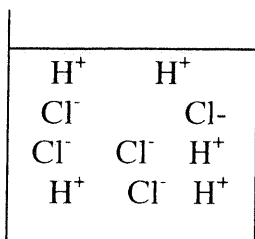
A **weak acid** or base only partially reacts with water or dissociates: (⇌ means the reaction is not quantitative – it reaches equilibrium)

Consider the following weak acid: 1.00 mol of **hydrogen fluoride** gas is added to 1.00 L of water. (7.8 % dissociation)

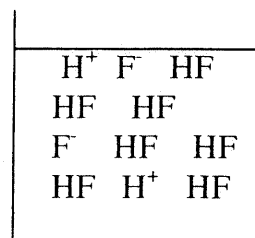
	HF(g)	+	H₂O(l)	⇌	H₃O⁺(aq)	+	F⁻(aq)
before HF dissolves:	1.00 mol/L				0.00 mol/L		0.00 mol/L
after the HF dissolves:	$0.922 \times 1.00 \text{ mol/L}$ $= 0.922 \text{ mol/L}$				$0.078 \times 1.0 \text{ mol/L}$ $= 0.078 \text{ mol/L}$		$0.078 \times 1.0 \text{ mol/L}$ $= 0.078 \text{ mol/L}$

A weak acid has a relatively strong conjugate base which is reluctant to give up the H⁺(aq) to the weaker base H₂O(l). A weak acid has a relatively strong conjugate base.

Strong acid:



Weak acid:



More ions
Few molecules

Few ions
More molecules

A weak acid or base in water reaches equilibrium and only a small percentage of molecules are separated into ions at any given time. In a solution of a **weak acid**, there are **more molecules than ions** in solution

To calculate the hydronium ion concentration the following formulas can be used:.

$$[\text{H}_3\text{O}^+(\text{aq})] = \frac{P \times [\text{Acid}]}{100}$$

$$P = \frac{[\text{H}_3\text{O}^+(\text{aq})] \times 100}{[\text{Acid}]}$$

1. Calculate the $[\text{H}_3\text{O}^+]$ in a 0.100 mol/L solution of nitrous acid with a 8.2 % dissociation.
(ans: 8.2×10^{-3} mol/L)
2. Determine the percent reaction of a 0.100 mol/L acid that has a $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-4}$ mol/L. (ans: 0.100%)
3. Determine the percent dissociation of a 0.500 mol/L of an acid with a pH of 4.40.
(ans: 8.0×10^{-3} %)
4. A 0.100 mol/L solution of acid A has a pH of 3.50 while a 0.500 mol/L solution of acid B has a pH of 1.50. Which acid is the strongest? Show calculations.

5. Consider a 0.100 mol/L solution of a strong acid HA(aq). Calculate:

a. $[H_3O^+]$ _____

b. $[HA]$ _____

c. $[A^-]$ _____

d. $[OH^-]$ _____

6. Consider a 0.100 mol/L solution of a weak acid, HX(aq), which is 40 % dissociated at equilibrium. Calculate the following at equilibrium:

a. $[H_3O^+]$ _____

b. $[OH^-]$ _____

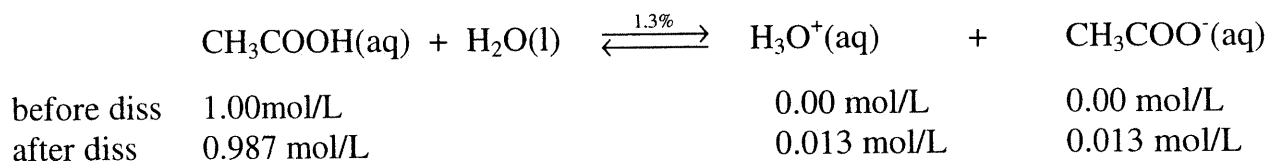
c. $[X^-]$ _____

d. $[HX]$ _____

7. What two diagnostic tests can distinguish a weak acid from a strong acid?

INFLUENCE OF ACID BASE STRENGTH ON QUANTITY OF PRODUCT IN A REACTION

Weak acids are different from strong acids in water because weak acids do not dissociate 100% like strong acids do.



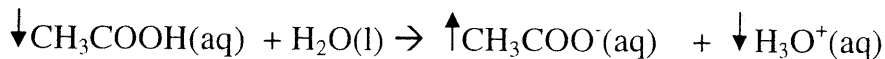
However, weak acids behave in a similar manner to strong acids when they are reacting with other things like active metals or strong bases.

The metals force the weak acids to come apart and thus they behave more like strong acids.

Therefore, in a chemical reaction, we do not have to consider the % dissociation of the weak acid.

	$\text{CH}_3\text{COOH}(\text{aq})$	+	$\text{OH}^-(\text{aq})$	\rightarrow	$\text{CH}_3\text{COO}^-(\text{aq})$	+	$\text{HOH}(\text{l})$
before rxn	1.0 mol/L		1.0 mol/L		0		0
after rxn	0		0		1.0 mol/L		1.0 mol/L

Le Chatelier's Principle explains this:



By the addition of of a base, hydronium ions are reacted and thus more molecules dissociate forcing the reaction to shift to the right.

There is one difference between weak acids and strong acids in a chemical reaction: The RATE of the reaction is SLOWER when a weak acid is reacting. Like weak acids, weak bases in reactions also dissociate completely.

Assorted Problems

- Which solution would react with more zinc, 50 mL of a 0.300 mol/L HCl(aq) or 50 mL of 0.300 mol/L CH₃COOH(aq)?

Use the following to answer the next question:

- A solution of 1.0 mol/L HA(aq) whose $[\text{H}_3\text{O}^+(\text{aq})] = 1.0 \times 10^{-2}$ mol/L
 - A solution of 1.0 mol/L HX(aq) whose $[\text{X}^-(\text{aq})] = 1.0 \times 10^{-4}$ mol/L
 - A solution of 1.0 mol/L HB(aq) whose $[\text{OH}^-(\text{aq})] = 1.0 \times 10^{-4}$ mol/L
 - A solution of 1.0 mol/L HW(aq) whose percent reaction is 2 %.
- The acids above listed from strongest to weakest are: (ans: 4, 1, 2, 3)
 - If the pH of a solution increased by 2, the resulting change in:
 - $[\text{H}_3\text{O}^+(\text{aq})]$ is increased / decreased by a factor of _____
 - $[\text{OH}^-(\text{aq})]$ is increased / decreased by a factor of _____

Previous Diploma Exam Questions:

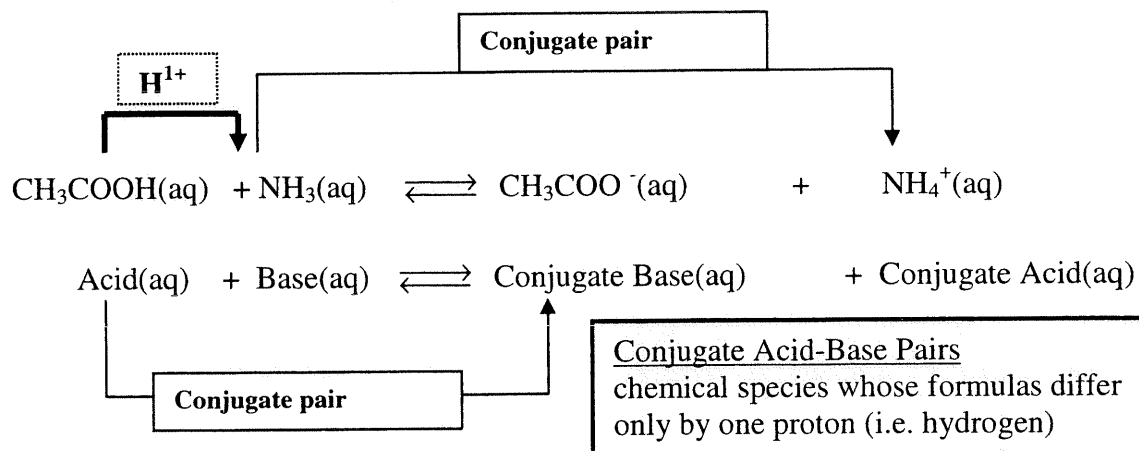
- A 0.40 mol/L acid that is 10 % dissociated will have a pH of
 - 1.40
 - 0.60
 - 0.40
 - 0.040
- A 10.0 mol/L solution of $\text{CH}_3\text{COOH}(\text{aq})$ is best described as a
 - dilute weak acid
 - dilute strong acid
 - concentrated weak acid
 - concentrated strong acid
- During an experiment to determine the relative strengths of acids, 8.0 g of HF dissolved in 2.0 L of water, yielding a pH of 2.08. Using these data, the per cent ionization of this acid is
 - 20 %
 - 9.0 %
 - 5.9 %
 - 4.2 %
- A student considers the ionization of an acid $\text{HA}(\text{aq})$ represented as
$$\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^{1+}(\text{aq}) + \text{A}^{1-}(\text{aq})$$
The observed pH of a 0.040 mol/L solution of $\text{HA}(\text{aq})$ is 2.00. The student should predict that the per cent dissociation of $\text{HA}(\text{aq})$ would be
 - 4.0 %
 - 10 %
 - 25 %
 - 40 %

Ans: 1. A 2. C 3. D 4. C

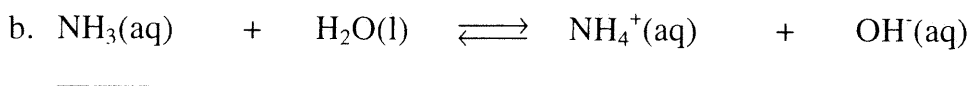
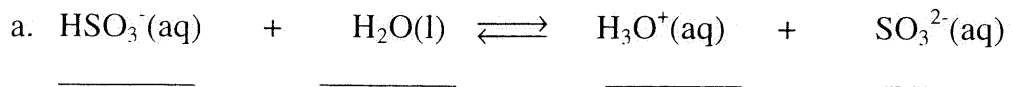
Bronsted – Lowry Equations

- The definition of a Bronsted-Lowry acid is:
- The Bronsted-Lowry definition of a base is :

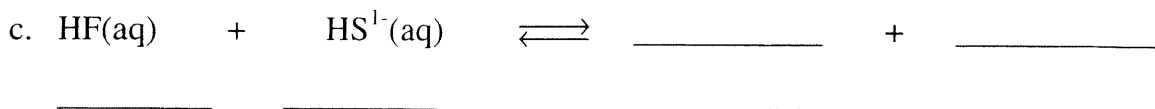
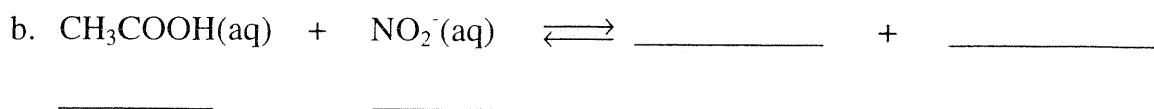
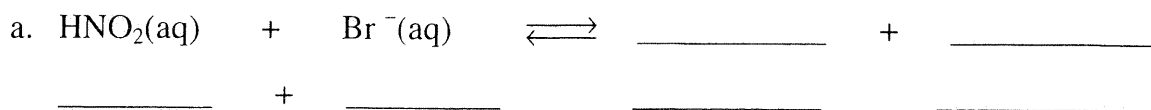
An acid-base reaction is a chemical reaction in which a proton (i.e. a hydrogen) is transferred (or exchanged) from an acid species to a base species to form a new acid and a new base. The new species may transfer the proton (hydrogen) back (through a reverse reaction) to reform the original species (thereby establishing an equilibrium between the reactants and products).



3. Label each species in the following equations as an Bronsted-Lowry acid or base:



4. Write in the products for each reaction that follows and label each species as an acid/base.



RULES FOR WRITING ACID-BASE REACTIONS

1. List all species mentioned

- All strong acids must be ionized as $\text{H}_3\text{O}^+(\text{aq})$ and its conjugate base
- Weak acids are left as the molecule or ion. e.g. $\text{H}_2\text{S}(\text{aq})$, $\text{H}_2\text{PO}_4^-(\text{aq})$
- All soluble ionic compounds must be dissociated
- Molecular compounds are left as the molecule. e.g. $\text{NH}_3(\text{aq})$

2. Starting at the bottom right hand side of the table and moving up find the strongest base.

3. Starting at the top left hand side of the table and moving down find the strongest acid.

4. Write a Bronsted-Lowry acid-base reaction with the SA & SB. (They form their conjugate partners as products)

5. Determine appropriate reaction arrows:

➤ When acid is above base on table $\xrightleftharpoons{>50\%}$ (product favoured)

➤ When acid is below base on table $\xrightleftharpoons{<50\%}$ (reactant favoured)

➤ Quantitative: one arrow \rightarrow or $\xrightleftharpoons{>99\%}$

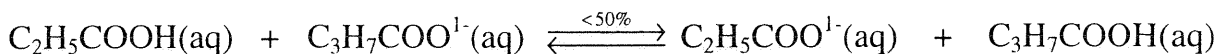
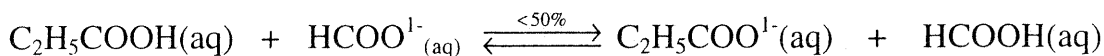
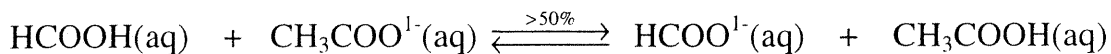
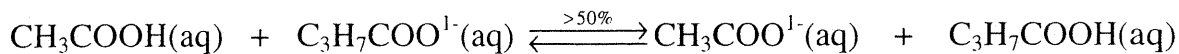
Write equations for the following reactions:

1. Solutions of sodium hydrogen carbonate and sulfurous acid are mixed
2. Perchloric acid is added to a solution of sodium sulfite in a quantitative reaction
3. Nitrous acid is combined with a solution of sodium hydrogen phosphate
4. Carbonic acid is used to neutralize an ammonia solution
5. Vinegar (ethanoic acid) is used to completely neutralize some spilled lye (NaOH).
6. Lithium cyanide is added to a solution of sodium hydrogen sulfite.
7. Methanoic acid is added to an aqueous solution of sodium hydrogen sulfide

Building An Acid – Base Table

What is the order of acid strength for the first four members of the carboxylic acid family?

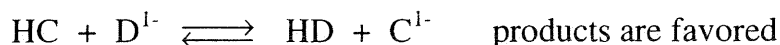
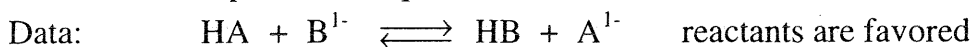
Evidence:



Analysis: Produce an acid-base table for the above.

Building Acid-Base Tables:

1. Assume all species are aqueous:



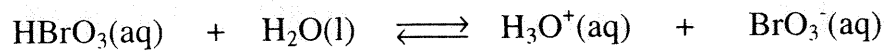
Key:

1	HA	5	A^{1-}
2	HB	6	B^{1-}
3	HC	7	C^{1-}
4	HD	8	D^{1-}

a) When these acids are arranged in order of decreasing strength, the order is _____ (Record all four digits.)

b) When these bases are arranged in order of decreasing strength, the order is _____ (Record all four digits.)

Eg.#1 Determine the K_a of HBrO_3 if 1.15 grams is dissolved into 5.24 L of water to give a pH of 4.15.



Amount concentration	$[\text{HBrO}_3(\text{aq})]$	$[\text{H}_3\text{O}^+(\text{aq})]$	$[\text{BrO}_3^-(\text{aq})]$
Initial			
Change			
equilibrium			

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{BrO}_3^-(\text{aq})]}{[\text{HBrO}_3(\text{aq})]}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{HBrO}_3(\text{aq})]$$

(ie. This is a 1:1 ratio)

Therefore the K_a equation can be simplified to look like

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{[\text{HBrO}_3(\text{aq})]}$$

From the example above we can see that to calculate K_a we can simplify the formula to

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{WA}] - [\text{H}_3\text{O}^+]}$$

where WA = weak acid

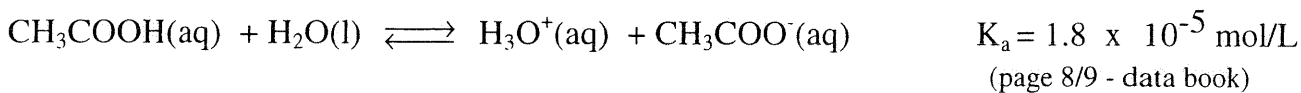
Using K_a to find the concentration or mass of acid required to make a solution with a specific pH.

eg. #2 Determine the concentration of sulfurous acid of water to get a pH of 2.19. Draw an ICE table.

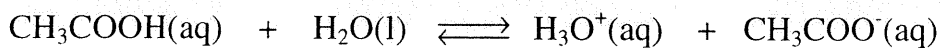
Amount concentration			
Initial			
Change			
equilibrium			

Using K_a to calculate $[H_3O^+(aq)]$ & pH

eg.#3 Calculate the $[H_3O^+(aq)]$ and pH of a 1.0 mol/L acetic acid solution. Draw an ICE table



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



Amount concentration	$[CH_3COOH(aq)]$	$[H_3O^+(aq)]$	$[CH_3COO^-(aq)]$
Initial	1.0	0	0
Change	- x	x	x
equilibrium	1.0 - x	x	x

Where $x = [H_3O^+(aq)]$ and $[H_3O^+] = [CH_3COO^-]$

Therefore the K_a expression can be simplified to look like

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]} \quad \text{substitution into this equation gives us}$$

$$1.8 \times 10^{-5} = \frac{x^2}{1.0 - x}$$

normally this would require a quadratic equation to solve for x

$$x^2 = 1.8 \times 10^{-5}(1-x)$$

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

$$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-5} \quad (\text{quadratic equation})$$

However the following short cut can be taken for the following reasons

- The amount of acid dissociated, 'x' or $H_3O^+(aq)$ is relative to the size of the K_a . If the K_a is small x is small.

Rule of 1000s

- If the x value is small enough, which occurs when the K_a is at least **1000X** smaller than the acid concentration, it makes very little difference to the acid concentration when x is subtracted from it. ie. **1.0 mol/L - x \approx 1.0 mol/L** since x is so small. And K_a is only to 2 significant digits

$$\text{Approximation rule} = \frac{[\text{acid}]}{K_a} > 1000$$

$$\text{for acetic acid} = \frac{1.0}{1.8 \times 10^{-5}} = 55350 > 1000 \text{ (approx can be made)}$$

$$1.8 \times 10^{-5} = \frac{x^2}{1.0}$$

$$x = \sqrt{1.8 \times 10^{-5}} \quad (\text{notice the } 1.0 - x \text{ is now } 1.0)$$

$$= 4.2 \times 10^{-3} \text{ mol/L} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(4.2 \times 10^{-3} \text{ mol/L}) \\ = 2.37$$

Notice that the formula used is basically

$$[\text{H}_3\text{O}^+] = \sqrt{K_a [\text{WA}]}$$

The general guideline followed

- If the [acid] is at least 1000 X greater than the K_a , the $[\text{H}_3\text{O}^+(\text{aq})]$ can be solved as shown
- This process can be reversed to solve for K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{WA}] - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a [\text{WA}]}$$

Use to find $[\text{H}_3\text{O}^+(\text{aq})]$

Used to find K_a or [initial acid]

Note: For all acid calculations from now on:

1. All problems involving **weak acids must use the K_a** in the calculations
- For calculations involving the **six strong acids, the acid completely dissociates**, therefore the $[\text{H}_3\text{O}^+(\text{aq})]$ at equilibrium is equal to the original [strong acid].

3. 12.98 grams of ascorbic acid is dissolved into 450 mL of water. Find the pH.
(ans: pH = 2.41)
4. Calculate the concentration of hydrofluoric acid that must be prepared to get a pH of 1.94. (ans: 0.22mol/L)
5. Calculate the pH and pOH if 2.12 grams of hydrogen bromide is dissolved into 850 mL of water. (ans: pH = 1.51)
6. A 0.10 mol/L of lactic acid, a weak acid found in milk, has a measured pH of 2.43. The chemical name of this very common organic compound is 2-hydroxypropanoic acid.
a. Find the percent reaction of this lactic acid solution. (ans: 3.7%)

b. Calculate the K_a value for aqueous lactic acid. (ans: 1.4×10^{-4})

Base Strength and the Ionization Constant K_b

- **Strong bases are defined by Bronsted-Lowry contain hydroxide ions**
- We will consider that all bases with hydroxide ions i.e. $\text{Ca}(\text{OH})_2(\text{aq})$ and $\text{NaOH}(\text{aq})$ dissociate completely in water.
- Therefore we can find the hydroxide concentration directly from the dissociation equation.

e.g.#1. Determine the pH of a 0.044 mol/L strontium hydroxide solution.

2. Other species that act as bases are considered weak bases and therefore do not attract protons with the same strength.
3. Therefore these bases vary in strength just like acids and are ranked on the acid- base table on page 8/9 on the data book.
4. Almost all weak bases react less than 50% with water to produce hydroxide ions.
5. The extent of their reaction with water is represented by a base ionization constant K_b .

Weak Bases(WB) & K_b

- bases which do not contain an $\text{OH}^-(\text{aq})$ ion
- however a weak base uses the idea that a weak base reacts with water to form an equilibrium that includes aqueous hydroxide ions. (Modified Arrhenius)

ie. weak base + $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq})$ + balancing entity

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{balancing entity}]}{[\text{WB}]}$$

K_b - base ionization constant

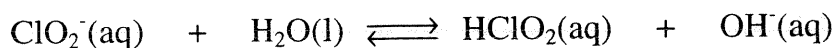
- also $[\text{OH}^-(\text{aq})] = [\text{balancing entity}]$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{WB}] - [\text{OH}^-]}$$

therefore Used to find K_b or [initial WB]

- notice the parallels with the calculation of K_a

e.g.#2. Calculate the K_b for a 0.230 mol/L sodium chlorite solution that has a measured pH of 11.10. Include an ICE table.



Amount concentration	$[\text{ClO}_2^-(\text{aq})]$	$[\text{OH}^-(\text{aq})]$	$[\text{HClO}_2(\text{aq})]$
Initial			
Change			
equilibrium			

Relationship between K_a and K_b for Conjugate Acid-Base Pairs

$K_w = K_b K_a$ - since K_w is 1.0×10^{-14} and K_a can be found in the data book, K_b can be calculated using the following formula

$$K_b = \frac{K_w}{K_a}$$

Find the K_b for $\text{NH}_3(\text{aq})$

- in the data book the $K_a = 5.8 \times 10^{-10}$ for $\text{NH}_4^+(\text{aq})$ (conjugate acid of $\text{NH}_3(\text{aq})$)
- therefore

$$K_b = \frac{1.00 \times 10^{-14}}{5.8 \times 10^{-10} \text{ mol/L}} = 1.8 \times 10^{-5} \text{ mol/L}$$

e.g. #3. Calculate the K_b for potassium hydrogen sulfite.

Finding pH or pOH of a base when the [WB] or mass and volume of a base is given.

The same rationalization used to find the pH of a weak acid can also be applied to a weak base.

$$K_b = \frac{[\text{OH}^-]^2}{[\text{WB}] - [\text{OH}^-]}$$

Recall

This formula can only be solve for $[\text{OH}^-]$ using a quadratic equation.

However as in acids, if the

$\frac{[\text{WB}]}{K_b} > 1000$ an approximation can be made that $[\text{WB}] - [\text{OH}^-] \approx [\text{WB}]$

And the formula can be simplified to $K_b = \frac{[\text{OH}^-]^2}{[\text{WB}]}$ which is reduced to

$$[\text{OH}^-] = \sqrt{K_b [\text{WB}]}$$

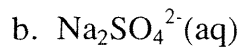
e.g.#4 Calculate the percent ionization pH and pOH of a 1.50 mol/L solution of sodium acetate. Include an ICE table.

Amount concentration	$[\text{CH}_3\text{COO}^-(\text{aq})]$	$[\text{OH}^-(\text{aq})]$	$[\text{CH}_3\text{COOH}(\text{aq})]$
Initial			
Change			
equilibrium			

eg. #5 Determine the pH if 10.0 grams of NH_3 is dissolved into 450 mL of water.

Questions on Bases

- For each of the following weak bases write the equilibrium reaction and the equilibrium expression for K_b
 - $\text{NaCN}(\text{aq})$

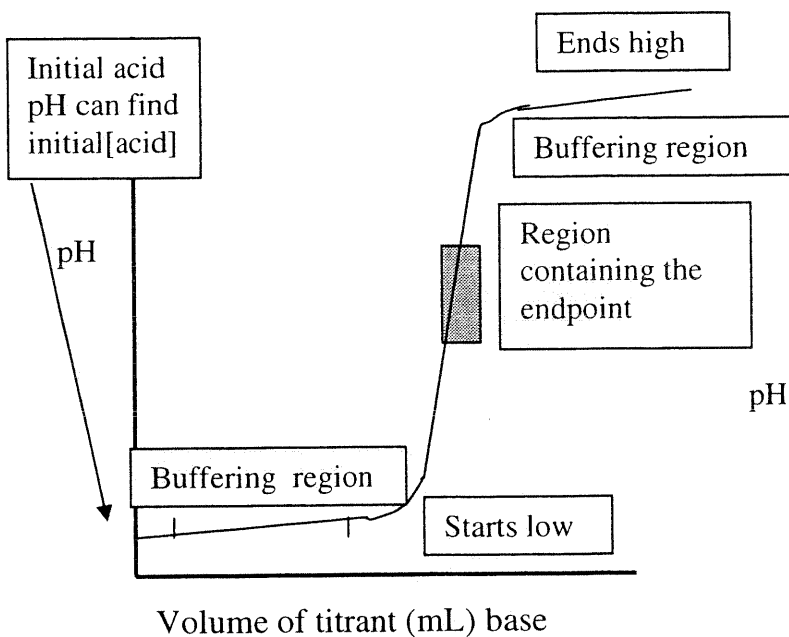


- In a 0.157 mol/L solution of sodium propanoate $\text{NaC}_2\text{H}_5\text{COO}(\text{aq})$, the hydroxide ion concentration is found to be 1.1×10^{-5} mol/L. Calculate the base ionization constant (K_b) for the propanoate ion. (ans: $K_b = 7.7 \times 10^{-10}$)
- Aniline $\text{C}_6\text{H}_5\text{NH}_2(\text{aq})$ is closely related to ammonia and is also a weak base. If the pH of a 0.10 mol/L aniline solution was found to be 8.81, what is its K_b ? (ans: $K_b = 4.2 \times 10^{-10}$)
- What would the pH and pOH of $\text{CN}^-(\text{aq})$ be if 4.58 grams of sodium cyanide is dissolved into 120 mL of distilled water? (ans: pH = 11.55)

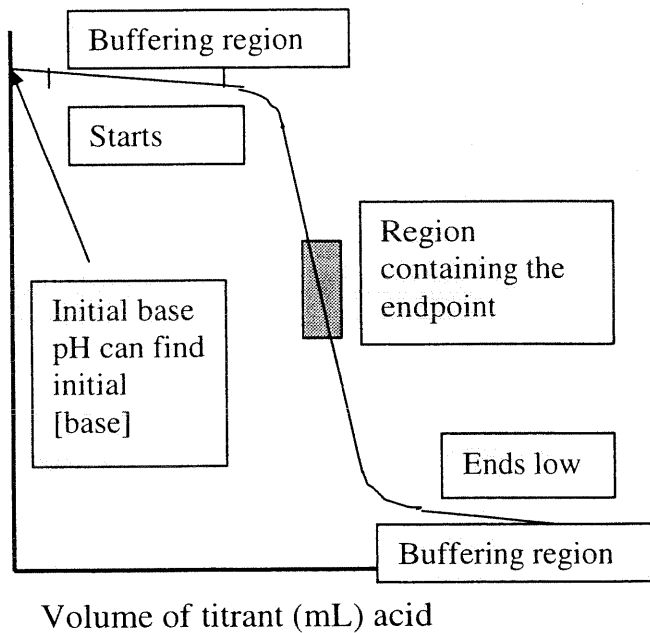
Interpreting pH Curves

pH curve - a graph of the pH of a reaction solution versus the volume of titrant added

Titration of a Acid with a Base



Titration of a Base with a Acid



Buffering region -

- the initial region of a pH curve that maintains a near constant pH through the addition of relatively large amounts of titrant
- buffering occurs even though a large amount of titrant has been added. This titrant has reacted with the acid or base present and is converted to water.

Equivalence point

- refers to that point in any chemical reaction when chemically equivalent amounts of reactant have been combined.
- The endpoint is defined(theoretically) by the stoichiometric ratio from the reaction equation
- At this point NO reactant is in excess.

Indicator endpoint

- Refers to that point in a titration analysis where the addition of titrant is stopped.
- The endpoint is defined (empirically) by the observed colour change.

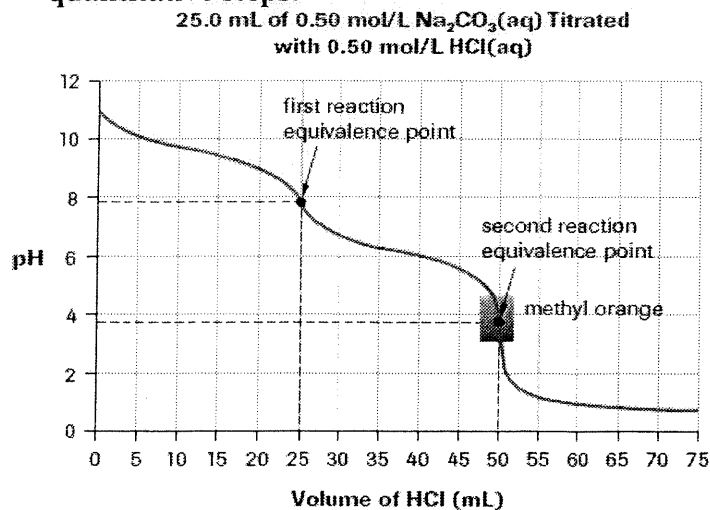
Polyprotic Entities and Sequential Reactions.

Polyprotic Acids Acid species that are capable or have the ability of donating or losing more than one hydrogen during a reaction

Polybasic Species Base species that are capable or have the ability of accepting or gaining more than one hydrogen during a reaction

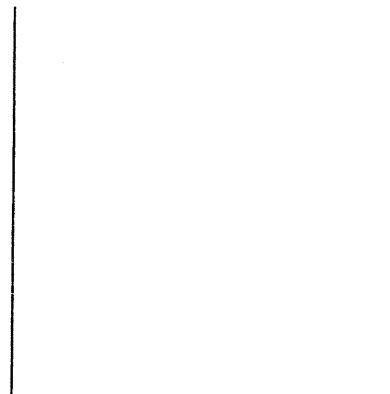
Substances that are polyprotic produce a pH curve that has more than one sudden rise or fall (humps)

Eg#1. Sodium Carbonate is titrated with Hydrochloric Acid, the graph produced shows two quantitative steps.



Write the Bronsted-Lowry equation for the above reaction.

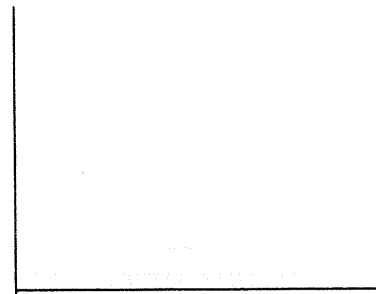
e.g.#2. A solution of sodium hydroxide is continually added to phosphoric acid. Appropriate indicators show two endpoints. Write a Bronsted-Lowry equation showing all steps. Sketch a pH curve for the reaction.



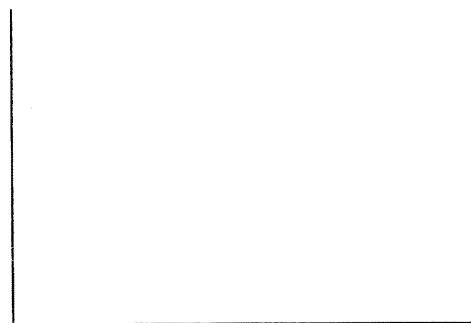
Questions - Polyprotic Species

For each of the following reactions, write a Bronsted-Lowry equation showing all quantitative steps.

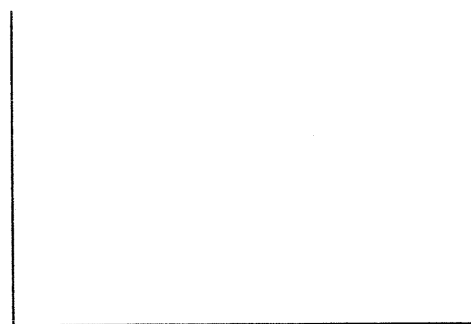
1. Potassium hydroxide is continuously added to a sodium hydrogen sulfate solution. When a pH curve is drawn, one hump appears on the graph. Include a pH curve.



2. A perchloric acid solution is continually added to a solution of potassium ascorbate ($K_2C_6H_6O_6(aq)$) and two equivalence points are observed. Include a pH curve.



3. Aqueous barium hydroxide is continuously added to an oxalic acid solution producing a pH curve with two sudden rises in pH.



Indicator End point

Usually only one indicator is used in a titration, regardless of whether the substance being titrated is monoprotic or polyprotic. If the acid or base is polyprotic, the last equivalence point is usually chosen to coincide with the indicator endpoint. Why? One reason is, the greater the volume of titrant used, the smaller the experimental error overall.

5. An imaginary acid $H_3X(aq)$ is titrated using sodium hydroxide solution. Equivalence points are detected at pH of 4.5, 7.7 and 9.6.
- Sketch a pH curve of this reaction

b. Which equivalence point would be the best choice to coincide with the indicator endpoint? Explain.

c. Based on your response to question b. , what indicator(s) would you chose to highlight the indicator endpoint? What colour change would identify the indicator endpoint chosen?

d. Write a Bronsted-Lowry net ionic equation for each of the steps that correspond to the equivalence points given for $H_3X(aq)$.

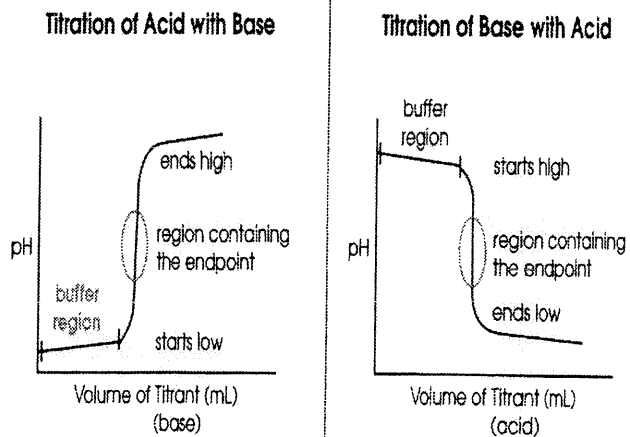
pH Curves versus Acid and Base Strength

Possible acid-base combinations

- strong acid - strong base
- weak acid - strong base
- strong acid - weak base

Shape of pH Curves -Clues to look for:

- Determine which substance in the titrant
 - acid titrant - begin with base only
- high pH initially
 - base titrant - begin with acid only
- low pH initially



2. What are the species in the solution at the equivalence point (ie. what substances were produced by the reaction and what substances were never part of the reaction).

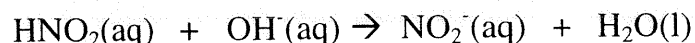
If the solution after the quantitative reaction is :

- neutral (ie. water and/or some neutral substance) equivalence point = 7
- a weak acid is produced (ie $\text{CH}_3\text{COOH}(\text{aq})$), the equivalence point < 7
- a weak base is produced (ie. $\text{NO}_2^-(\text{aq})$), the equivalence point > 7

pH Curves

1. **Strong base added to a weak acid** eg. $\text{HNO}_2(\text{aq})$ & $\text{NaOH}(\text{aq})$

- species: $\text{HNO}_2(\text{aq})$, $\text{Na}^+(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{H}_2\text{O}(\text{l})$
- initial low pH due to the acid only before titration



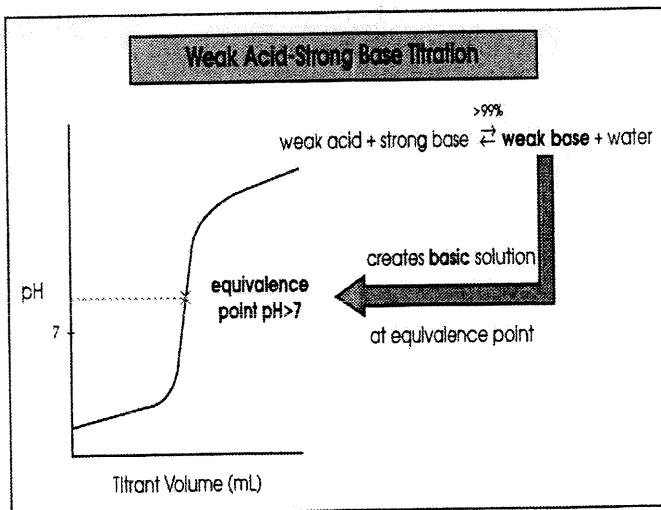
Species at the equivalence point: $\text{Na}^+(\text{aq})$, $\text{NO}_2^-(\text{aq})$, $\text{H}_2\text{O}(\text{l})$

The weak conjugate base $\text{NO}_2^-(\text{aq})$ produces a weak base solution at the equilibrium by reacting with water in the following reaction:



As a result the equilibrium pH is > 7 for this reaction.

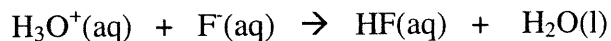
Note: The reverse reaction will produce the same equilibrium pH. The only change is the initial pH will be low due to the weak acid being by itself initially



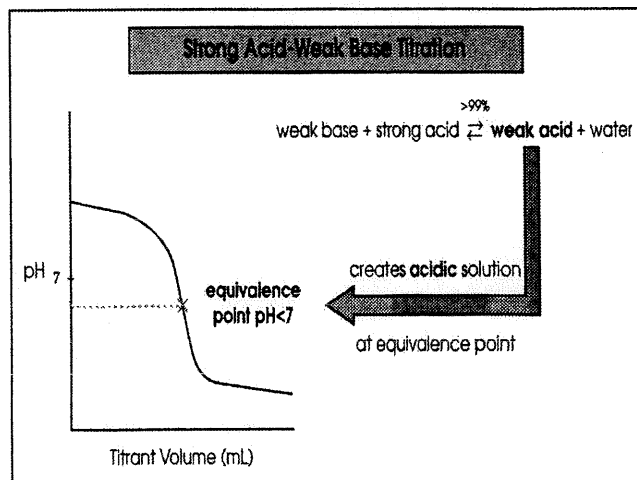
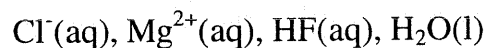
2. **Strong acid added to a weak base** eg. $\text{HCl}(\text{aq})$ & $\text{MgF}_2(\text{aq})$

- species: $\text{H}_3\text{O}^+(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{Mg}^{2+}(\text{aq})$, $\text{F}^-(\text{aq})$, $\text{H}_2\text{O}(\text{l})$

- initial high pH due to presence only weak base



Species at the equivalence point:



The conjugate acid HF(aq) produces hydronium ions as it forms an equilibrium with water in the following reaction;



As a result, the pH at equilibrium for this reaction is <7

Note: The reverse reaction will produce the same equilibrium pH. The only change is the initial pH will be low due to the strong acid being by itself initially.

3. Strong acid added to a strong base eg. NaOH(aq) & HCl(aq)

- species: Na(aq), OH(aq), H₃O⁺(aq), Cl⁻(aq), H₂O(l)

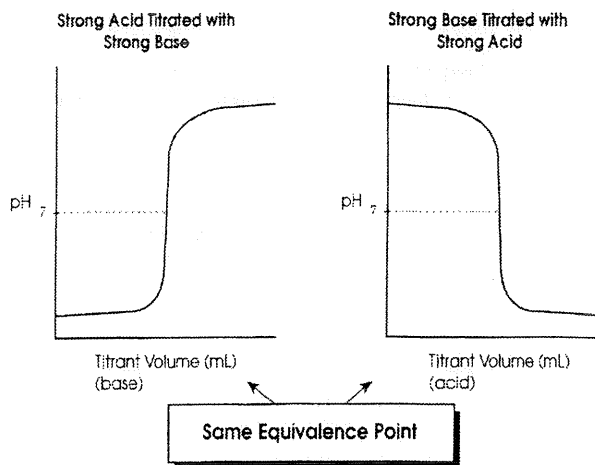
- initial high pH due to base only present



Species at the equivalence point is

a) H₂O(l), Na⁺(aq), and Cl⁻(aq)

Since the strongest base or acid at the equivalence point is water, the solution is neutral and the pH is = 7 as shown earlier



Questions

1. The first quantitative reaction in each of the following acid-base titrations, predict (where possible) whether the equivalence point pH will be greater than, less than, or equal to 7. Support your answer. Which of the following indicators; methyl orange, bromothymol blue or phenolphthalein would be appropriate to identify the endpoint?

a. hydroiodic acid + aqueous sodium hydrogen phosphate →

b. aqueous sodium hydrogen sulfate + aqueous potassium hydroxide →

c. hydrochloric acid + solid magnesium hydroxide →

pH Curve Buffering Regions and Buffer Solutions

Buffer systems consist of:

- weak acid and its conjugate base, its weak salt – form an acidic buffer with a pH below 7.00

$\text{CH}_3\text{COOH}(\text{aq}) / \text{CH}_3\text{COO}^{1-}(\text{aq})$ Acetic acid-acetate ion buffer system

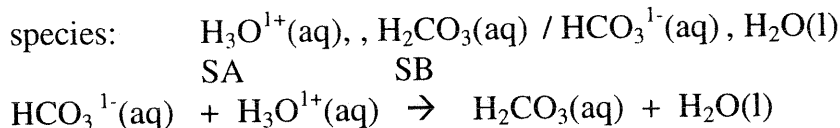
$\text{H}_2\text{CO}_3(\text{aq}) / \text{HCO}_3^{1-}(\text{aq})$ For example, carbonic acid, $\text{H}_2\text{CO}_3(\text{aq})$, is a weak acid, and its conjugate base is the hydrogen carbonate ion, $\text{HCO}_3^{1-}(\text{aq})$. This buffer is found in the blood

The most efficient buffers are made from equal concentrations of an acid and its conjugate base or equal concentrations of a base and its conjugate acid.

- **How buffering works?**

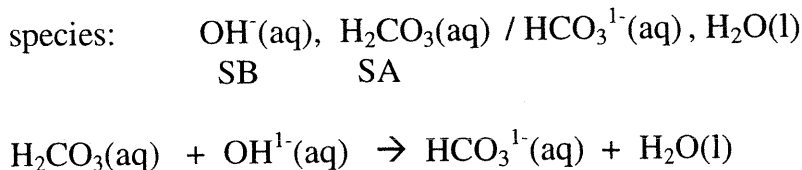
Buffer systems reacts as Bronsted-Lowry acids and bases.

In blood, this conjugate acid-base pair carbonic acid – hydrogen carbonate ion undergoes reactions to help control the pH. When excess hydronium ions, $\text{H}_3\text{O}^{1+}(\text{aq})$, enters the blood, the hydrogen carbonate ion undergoes the following reaction to reduce the $[\text{H}_3\text{O}^{1+}(\text{aq})]$



In this way, excess $\text{H}_3\text{O}^{1+}(\text{aq})$ cannot build up and drastically affect the pH. In this situation the buffer converts a very strong acid to a very weak acid result in a very little change in pH

Whenever excess hydroxide ions, $\text{OH}^{1-}(\text{aq})$, form in the blood they have a strong affinity (attraction) for $\text{H}^{1+}(\text{aq})$. Carbonic acid provides a source of protons (hydrogen) for the $\text{OH}^{1-}(\text{aq})$, and the following reaction occurs.



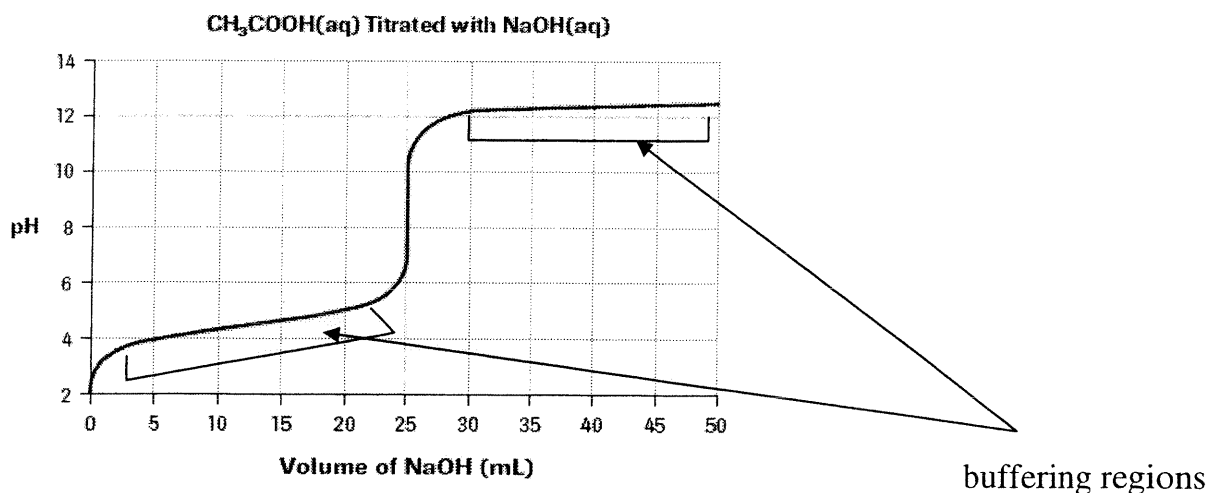
The result is the conversion of a very strong base($\text{OH}^{1-}(\text{aq})$) to a weak base ($\text{HCO}_3^{1-}(\text{aq})$) resulting in a near constant pH. (neutralizing effect)

Just as your body uses a weak acid and conjugate base pair for buffering, chemists use this same concept to make buffers in the lab.

eg. Hydrochloric acid is added to the acetic acid / acetate ion buffer system

eg. Sodium hydroxide is added to the acetic acid / acetate ion buffer system

The same logic discussed with buffers and how they work can be used to explain a buffering region in a titration reaction



- Buffering occurs initially because as any of the strong base $\text{OH}^{\text{-(aq)}}$ is added it immediately reacts with the acetic acid and is converted to water.
- The concentration of the acetic acid decreases slowly and this is shown by a slow increase in the pH.
- As we approach the equivalence point this “leveling” effect of the pH fails as excess hydroxide has been added.
- As we approach the 2nd buffering region, an excess of $\text{OH}^{\text{(aq)}}$ has been added and this is shown with a high pH.
- Adding more $\text{OH}^{\text{(aq)}}$ does not change the nature of the solution as it only increases the hydroxide concentration slightly.

Questions:

1. One of the most important body buffers is the carbonic acid – hydrogen carbonate ion system. Write the equation for the quantitative reaction that occurs when $\text{HNO}_3(\text{aq})$ is added to the buffer system described.
2. Write the equation for the quantitative reaction that occurs when $\text{LiOH}(\text{aq})$ is added to the buffer system described in question #1.

Previous Diploma Exam Questions:

1. When a small amount of base is absorbed into the blood, the $\text{H}_2\text{CO}_3(\text{aq})/\text{HCO}_3^{1-}(\text{aq})$ buffer maintains blood pH at approximately 7.3 because the base reacts with
 - a. $\text{H}_2\text{CO}_3(\text{aq})$
 - b. $\text{HCO}_3^{1-}(\text{aq})$
 - c. $\text{CO}_3^{2-}(\text{aq})$
 - d. $\text{H}_2\text{O}(\text{l})$
2. Which of the following would produce a buffer solution when added to 1.0 mol/L $\text{NH}_3(\text{aq})$?
 - a. $\text{HNO}_3(\text{aq})$
 - b. $\text{KNH}_2(\text{aq})$
 - c. $\text{NaOH}(\text{aq})$
 - d. $\text{NH}_4\text{Cl}(\text{aq})$
3. A few drops of strong acid are added to 1.0 L of a pH 8.0 buffer solution. The resulting solution will have an approximate pH of
 - a. 5.6
 - b. 7.0
 - c. 7.9
 - d. 8.1

4. A student prepares a buffer by placing ammonium chloride in a solution of ammonia. Equilibrium is established according to the equation:



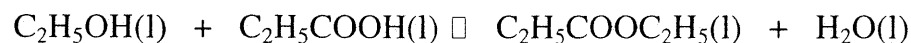
When a small amount of base is added to the buffer, the base reacts with the

- a. $\text{NH}_3(\text{aq})$ and the pH decreases
- b. $\text{NH}_4^{1+}(\text{aq})$ and the pH decreases
- c. $\text{NH}_3(\text{aq})$ to keep the pH relatively constant
- d. $\text{NH}_4^{1+}(\text{aq})$ to keep the pH relatively constant

Ans: 1. A 2. D 3. C 4. D

Previous Diploma Written Response Questions

The unique flavour of fruits and berries is due to the presence of esters, chemical compounds that are easily synthesized in the laboratory. For example, ethyl propanoate is responsible for the flavour characteristics to pineapple. It is produced by the reaction



When 7.71 mol of $\text{C}_2\text{H}_5\text{OH}(\text{l})$ and 7.37 mol of $\text{C}_2\text{H}_5\text{COOH}(\text{l})$ are reacted in a beaker, 4.80 mol of $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5(\text{l})$ are present when equilibrium is established and the total volume is exactly 1.0L.

a. Calculate K_c for this system

b. Are the reactants or products favoured at equilibrium? Justify your choice.

2. An unidentified acid with a concentration of 1.0 mol/L has been given to you to identify. The acid appears in your data booklet on the relative strengths of acids and bases table. The following test results were recorded:

- Methyl violet is yellow when added to the acid.
- The acid did not form a precipitate when a solution containing $\text{Ag}^+(\text{aq})$ was added to it.
- The solution turned blue and a gas was formed when the strip of copper was added to the acid.

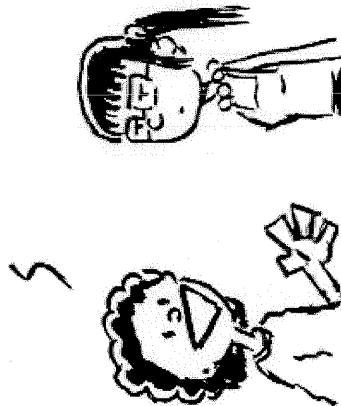
Based on these test results, identify the acid and justify your choice. Your answer should include equations and/or calculations where appropriate.

HIGH SCHOOL COMICS - CLAUDIO PATTO & RODRIGO CHAVES

SORRY SIR, BUT
I DON'T LIKE
BIOLOGY. I LIKE
CHEMISTRY...



SORRY MRS, BUT
I DON'T LIKE
CHEMISTRY. I
LIKE PHYSICS...



SORRY SIR, BUT
I DON'T LIKE
PHYSICS. I LIKE
BIOLOGY...



SO, FIFI SAID
SHE LIKES
BIOLOGY?

AND SHE SAID
SHE LIKES
CHEMISTRY?



FIFI REALLY
SAID SHE LIKES
PHYSICS?

Good Luck on your Diploma Exam!!!