

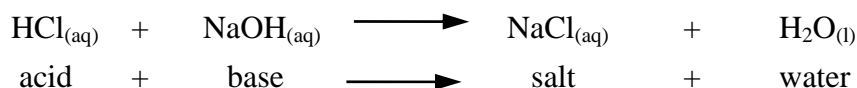
Chemistry 12

Unit IV – Acids, Bases and Salts

Notes

IV.1 – The Arrhenius Theory Of Acids and Bases

- **Acid:** any substance which releases H^+ (aq) in water.
- **Base:** any substance which releases OH^- (aq) in water.
- **Salt:** is the neutralization product which results when an acid and a base react:



In more general terms, a salt is any *ionic* compound which is neither an acid nor a base.

- The following is a more simple way to think of Arrhenius acids, bases and salts. (There are some exceptions)

An **ACID** is any *ionic* species whose formula starts with an “H”.

Examples: HCl, HNO₃, H₂SO₄

A **BASE** is any *ionic* species whose formula ends with an “OH”

Examples: NaOH, KOH, Ca(OH)₂, Zn(OH)₂

A **SALT** is any *ionic* species which does not start with an “H” or end with an “OH”.

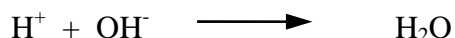
Examples: KBr, FePO₄, Li₂CO₃

How to write and balance acid-base neutralization reactions.

- Since we know that: ACID + BASE \longrightarrow SALT + WATER, we can use the following procedure.

All neutralization reactions are based on the fact that acids produce H^+ and bases produce OH^- .

Therefore, the main reaction which occurs in every instance is just:



Example: Write the neutralization reaction that occurs between HCl and Ca(OH)₂.

- General Properties of Acids and Bases

The presence of H^+ accounts for these properties of **acids**:

- a) acids react with bases.
- b) acids are electrolytes.
- c) acids react with some metals to produce $\text{H}_2(\text{g})$.
- d) acids turn litmus paper RED.
- e) acids taste SOUR. (e.g. lemon juice, vinegar)

The presence of OH⁻ accounts for these properties of **bases**:

- a) bases react with acids.
- b) bases are electrolytes.
- c) bases feel slippery. (React with your fat to make soap.)
- d) bases turn litmus paper **BLUE**.
- e) bases taste **BITTER**. (e.g. baking soda)

A mnemonic for remembering the litmus colours:

Litmus paper is: **RED** in **ACID**
BLUE in **BASE**

Examples:

1. August 2003

Which of the following is a property of **all** acidic solutions at 25°C?

- A. They have a pH less than 7.0.
- B. They have a pH greater than 7.0.
- C. They cause phenolphthalein to turn pink.
- D. They release hydrogen when placed on copper metal.

2. June 2004

Which of the following best describes an acidic solution?

	Litmus Colour	Reaction with Zn
A.	red	reaction
B.	red	no reaction
C.	blue	no reaction
D.	blue	reaction

3. August 1998

Both acidic and basic solutions

- A. taste sour.
- B. feel slippery.
- C. conduct electricity.
- D. turn blue litmus red.

4. August 2001

Which of the following reactions is not a neutralization reaction?

- A. $\text{KOH} + \text{HF} \rightarrow \text{KF} + \text{H}_2\text{O}$
- B. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- C. $\text{Ca}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
- D. $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$

*****Do Hebden Questions #1 - 4, pgs 110 - 112*****

IV.2 - Some Common Acids and Bases

- Sulphuric Acid (H_2SO_4) Commercial names: oil of vitriol, “battery acid”

Properties:

- good dehydrating agent (removes water from substances)
- strongly exothermic reaction when mixed with water
- chars some types of organic material (e.g., sugars) when in concentrated form, as a result of dehydrating action (turns skin black on contact)
- reacts with some metals, but often slowly
- good electrolyte (conducts electricity)
- concentrated Sulphuric acid is 98% H_2SO_4 and 2% water (18 M H_2SO_4)

Common uses:

- production of sulphates
- manufacturing fertilizers, explosives, plastics, insecticides,
- used in car batteries as an electrolyte

- Hydrochloric Acid (HCl) Commercial name: muriatic acid

Properties:

- concentrated HCl turns skin white on contact
- good electrolyte
- concentrated solutions have a choking odour
- reacts with some metals, but often slowly
- concentrated hydrochloric acid is 37% HCl in water (12 M)

Common uses:

- production of chlorides
- cleaning metal products (removes metal oxides)
- “stomach acid” is a dilute solution of HCl ; stomach acid
- activates a protein-digesting biological catalyst “enzyme”
- removing scale from boilers (“boiler scale” consists of calcium and magnesium carbonate)

- Nitric Acid (HNO_3) Commercial name: (none, other than “nitric acid”)

Properties:

- colours protein yellow (this is a non-specific test for the presence of protein). Hence, turns skin yellow on contact.
- very reactive, quickly attacks almost all metals
- concentrated nitric acid is 69% HNO_3 in water (16 M)

Common uses:

- production of nitrates
- manufacturing fertilizers, explosives, dyes

- Acetic Acid (CH_3COOH) Commercial name: 5% aqueous solution is called “vinegar”

Properties:

- non-electrolyte when concentrated (99 - 100%, 17 M); weak electrolyte when diluted
- corrosive, burns skin
- only affects highly reactive metals

Common uses:

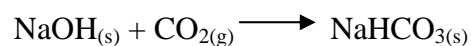
- food preservation (“pickles”)
- manufacturing textiles and plastics

Common Bases

- Sodium Hydroxide (NaOH) Commercial names: lye, caustic soda

Properties:

- very corrosive (caustic) to animal and plant tissues
- highly exothermic reaction when mixed with water
- rapidly “deliquesces”; that is, absorbs H₂O from the air
- rapidly absorbs CO₂(g) from the air to form carbonates:



Common uses:

- making soap and other cleaning products such as oven cleaner, drain cleaner
- manufacturing glass, pulp and paper, plastics, aluminium
- neutralizing acids during industrial reactions

- Potassium Hydroxide (KOH) Commercial name: caustic potash

Properties:

- much the same as NaOH, but melts at a lower temperature

Common uses:

- manufacturing liquid soap (potassium soaps have a lower melting temperature than sodium soaps)
- absorbing CO₂(g)
- making potassium salts
- electrolyte in alkaline batteries

- Ammonia (NH₃) Commercial name: NH_{3(aq)} is called “ammonium hydroxide”

Properties:

- colourless gas with pungent odour
- highly toxic, corrosive, alkaline gas
- highly soluble in water

Common uses:

- manufacturing explosives, fertilizers, synthetic fibres
- used as a refrigeration gas

Example:

1. August 2004

Which of the following is a common base found in drain cleaners?

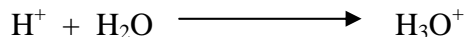
- A. bleach
- B. vinegar
- C. milk of magnesia
- D. sodium hydroxide

*****Do Hebden Questions #5 - 9, pg 114*****

IV.3 - The True Nature of H⁺_(aq): (Background Theory)

- The hydrogen atom consists of a proton surrounded by a single electron. If we remove the electron, so as to create H⁺, we are left with a “naked” proton. Since this tiny nuclear particle has an enormous charge concentration (it has a +1 charge concentrated in a very small region of space - the diameter of the proton is 5X10⁻¹⁴cm), this highly concentrated positive charge is very strongly attracted to any region where negative charges exist.

All the H⁺ present in water will attach itself to water molecules:



- Definitions

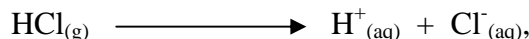
H⁺ is called the **proton**.

H₃O⁺ is called the **hydronium ion**, or the hydrated proton.

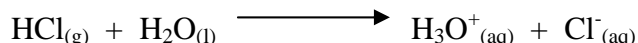
- What we previously have been calling H⁺_(aq) is actually H₃O⁺_(aq). Using H₃O⁺_(aq) instead of H⁺_(aq) will mean that in the future we will have to rewrite the way we show the IONIZATION of an acid.

Example:

When HCl(g) is added to water to produce a hydrochloric acid solution, HCl_(aq), we previously would write:



but we should now write:



Notice that what we have done to our first equation is to add H₂O to both sides of the equation. However, on the right hand side we combined the added H₂O with H⁺ to produce H₃O⁺.

Examples:

1. April 2004

Which of the following is a general characteristic of Arrhenius acids?

- A. They produce H⁺ in solution.
- B. They accept an H⁺ from water.
- C. They turn bromthymol blue a blue colour.
- D. They react with H₃O⁺ ions to produce H₂.

2. June 2002

An Arrhenius base is defined as a substance that

- A. releases H⁺_(aq)
- B. releases OH⁻_(aq)
- C. accepts a proton
- D. donates a proton

*****Do Hebden Questions #10, pg 115*****

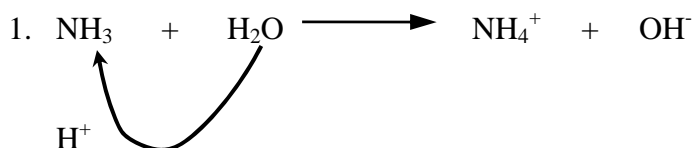
IV.4 - The Bronsted-Lowry Theory of Acids and Bases

- The Bronsted-Lowry theory...
 - More general than the Arrhenius theory
 - Incorporates all of the Arrhenius theory into a more general scheme
 - Allows for the effect of equilibrium reactions and permits us to extend our ideas of acids and bases to a wider range of species.
- According to the Bronsted-Lowry theory:
An **ACID** is a substance which **DONATES A PROTON**.
A **BASE** is a substance which **ACCEPTS A PROTON**.

An ACID is a PROTON DONOR (gives away an H^+) and A BASE is a PROTON ACCEPTOR (gets an H^+)

- Here are 2 typical Bronsted-Lowry acid-base reactions equations:

Examples:



In the above Reaction:

NH_3 reacts to become NH_4^+

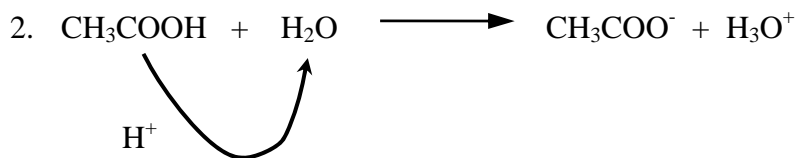
NH_3 has gained an extra "H" and a "+" charge

NH_3 is acting as a **BASE**: it has "accepted a proton" (H^+).

If the NH_3 accepted a proton (H^+) then it had to get the H^+ from something - the H_2O

H_2O must have donated a proton and hence must be an **ACID**

H_2O has lost (that is, donated) an H^+ , and produced an OH^-



In the above Reaction:

CH_3COOH donated (loses) and H^+ to become CH_3COO^-

CH_3COOH must be acting as an **ACID** (The fact that acetic acid acts as an acid should make sense!)

H_2O accepted a proton to become H_3O^+

H_2O must be acting as a **BASE**

Types of Acids

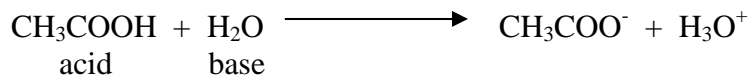
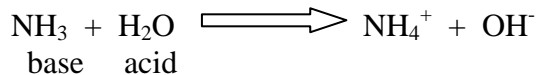
Monoprotic Acid: A MONOPROTIC ACID is an acid which can supply only one proton. Example: HCl

Diprotic Acid: A DIPROTIC ACID is an acid which can supply up to two protons. Example: H₂SO₄

Triprotic Acid: TRIPROTIC ACID is an acid which can supply up to three protons. Example: H₃PO₄

Polyprotic Acid: POLYPROTIC ACID is a general term for an acid which can supply more than one proton. Examples: H₂SO₄, H₃PO₄

Look at these reactions...notice anything?

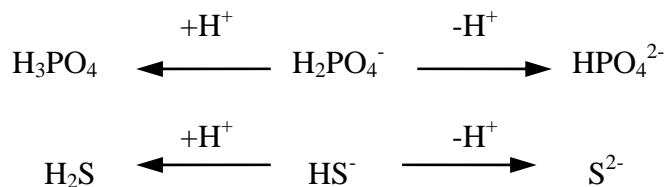


Conclusion: In some circumstances a substance may act as a Bronsted-Lowry acid, whereas in other circumstances the same substance may act as a Bronsted-Lowry base. Water acts as a Bronsted-Lowry base when it is forced to react with an acid, but will act as an acid when forced to react with a base.

Such a substance is said to be **amphoteric** or **amphiprotic**.

An **amphoteric (amphiprotic)** substance is a substance which can act as either an acid or a base. Some amphiprotic substances are H₂O, H₂PO₄⁻, HS⁻, HCO₃⁻.

Examples:

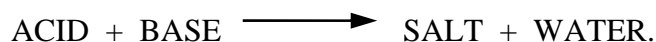


If a substance:

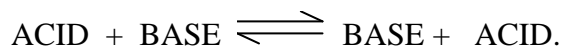
- possesses a **NEGATIVE CHARGE**, and
- still has an easily removable **HYDROGEN**, then the substance will be **AMPHIPROTIC**.

• Comparing Bronsted-Lowry and Arrhenius Reactions

In the old **Arrhenius theory**:

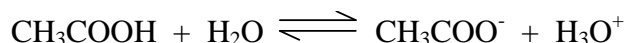


Now, in the **Bronsted-Lowry theory**:



In every case of a Bronsted-Lowry reaction we will have an acid and a base on both sides of the equation.

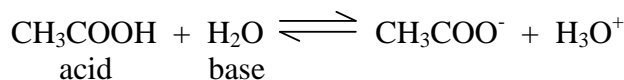
• Identifying ACIDS and BASES in Bronsted-Lowry Reactions.



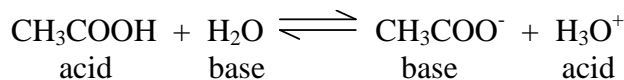
Determine the identity of one species on the reactant side, by seeing whether it gains or loses a proton. For example, CH₃COOH here is acting as an acid since it is losing a proton.

You can automatically determine the identity of the “similar species” on the product side. It will be the opposite (for example, BASE) of the species you first identify (for example, ACID).

To this point we now have



- Use the fact that each side must have both an ACID and a BASE to complete our assignment. For example:



Examples:

1. January 2004

What is a general characteristic of all Brønsted-Lowry bases?

- A. They all accept H⁺.
- B. They all accept OH⁻.
- C. They will turn litmus a pink colour.
- D. They will react with acids to produce H₂ gas.

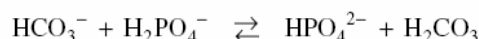
2. August 2002

A Brønsted-Lowry acid is defined as a substance that

- A. releases H⁺_(aq)
- B. releases OH⁻_(aq)
- C. accepts a proton
- D. donates a proton

3. June 2004

Consider the following equilibrium:



What are the Brønsted-Lowry acids in this equilibrium?

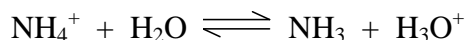
- A. HCO₃⁻ and H₂CO₃
- B. HCO₃⁻ and HPO₄²⁻
- C. H₂PO₄⁻ and H₂CO₃
- D. H₂PO₄⁻ and HPO₄²⁻

*****Do Hebden Questions #11 - 14, pgs 117 - 119*****

IV.5 - Conjugate Acids and Bases

- **Conjugate Acid-Base Pair:** A conjugate acid-base pair (or conjugate pair) is a pair of chemical species, which differ by only one proton.
- **Conjugate Acid:** A conjugate acid is the member of the conjugate pair which has the extra proton.
- **Conjugate Base:** A conjugate base is the member of the conjugate pair which lacks the extra proton.

Example: In the equilibrium reaction



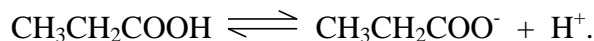
there are *two* conjugate pairs:

conjugate pair

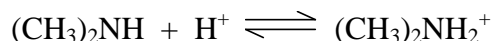
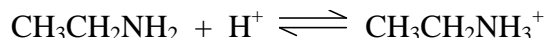
conjugate acid

conjugate base

- If we are asked to find the **CONJUGATE ACID** of NH_3 , then we want to know the formula of the acid which has **ONE MORE** proton than NH_3 (which is assumed to be a base). Hence, we add H^+ to NH_3 to get NH_4^+ .
- If we are asked to find the **CONJUGATE BASE** of NH_3 , then we want to know the formula of the base which has **ONE LESS** proton than NH_3 (which is assumed to be an acid). Hence, we take away an H^+ from NH_3 to get NH_2^- .
- Note: simple **organic acids** end with a **COOH** group, and the H at the end of the group is acidic.



organic bases contain an **NH₂** group or an **NH** group. The nitrogen atom will accept an extra proton.



Conclusion: A Bronsted-Lowry acid-base reaction just involves a proton transfer.

Example: Write the acid-base equilibrium that occurs when H_2S and CO_3^{2-} are mixed in solution.

Examples:

1. April 2003

In which of the following is HSO_3^- acting as a Brønsted-Lowry acid?

- A. $\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + \text{OH}^-$
- B. $\text{NH}_3 + \text{HSO}_3^- \rightarrow \text{NH}_4^+ + \text{SO}_3^{2-}$
- C. $\text{HSO}_3^- + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{SO}_3 + \text{PO}_4^{3-}$
- D. $\text{H}_2\text{C}_2\text{O}_4 + \text{HSO}_3^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{SO}_3$

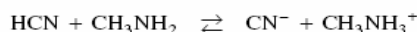
2. August 2005

What is the conjugate acid of the base HAsO_4^{2-} ?

- A. AsO_4^{3-}
- B. $\text{H}_2\text{AsO}_4^{2-}$
- C. H_2AsO_4^-
- D. H_3AsO_4

3. August 2003

Consider the following reaction:

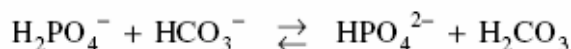


Which of the following describes a conjugate acid-base pair in the equilibrium above?

	Acid	Base
A.	CN^-	HCN
B.	CH_3NH_3^+	CN^-
C.	HCN	CH_3NH_3^+
D.	CH_3NH_3^+	CH_3NH_2

4. August 2004

Identify the two conjugate pairs in the equilibrium provided.

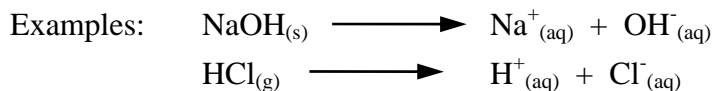


	Pair 1	Pair 2
A.	$\text{H}_2\text{PO}_4^- / \text{H}_2\text{CO}_3$	$\text{HCO}_3^- / \text{HPO}_4^{2-}$
B.	$\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$	$\text{HCO}_3^- / \text{H}_2\text{CO}_3$
C.	$\text{HCO}_3^- / \text{HPO}_4^{2-}$	$\text{H}_2\text{PO}_4^- / \text{H}_2\text{CO}_3$
D.	$\text{H}_2\text{PO}_4^- / \text{HCO}_3^-$	$\text{HPO}_4^{2-} / \text{H}_2\text{CO}_3$

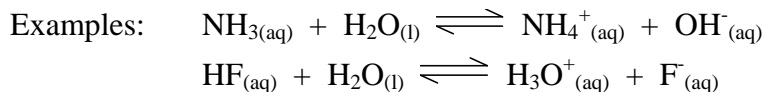
*****Do Hebden Questions #15 - 19, pgs 119 - 121*****

IV.6 - “Strong and Weak” Acids and Bases

- **Strong Acid or Base:** A STRONG acid or base is an acid or base which is 100% ionized in solution.



- **Weak Acid or Base:** A WEAK acid or base is an acid or base which is LESS THAN 100% ionized in solution.



- **NOTE:**

- a) Weak acids and bases are involved in equilibrium reactions, strong acids and bases **ARE NOT**.
- b) The definition of a weak acid implies that an acid which is 99.9% ionized will be “weak”, while an acid which is 100% ionized is “strong”.
- c) The terms **weak** and **strong** refer to the percentage of ionization. The terms **dilute** and **concentrated** refer to the molarity of a solution.

The terms **WEAK** and **STRONG** refer to the percentage of ionization

The terms **DILUTE** and **CONCENTRATED** refer to the molarity of a solution

Examples:

10.0 M $\text{HF}_{(aq)}$ is concentrated and weak

0.001 M $\text{HCl}_{(aq)}$ is dilute and strong.

- HClO_4 , HI, HBr, HCl, HNO_3 , $\text{H}_2\text{SO}_4 \rightleftharpoons$ disassociate 100% (Strong Acids)...**ALL** products, no reactants.

The Acid-Base Table (“Relative Strengths of Bronsted-Lowry Acids and Bases”)

- At this point it is appropriate to introduce a table that will be very important to us in this unit. Look at the table found in your data booklet (handout) as you read the following.

The Strong Acids:

The strong acids are the top six acids listed on the “**Relative Strengths of Bronsted-Lowry Acids and Bases**”, namely:

Name	Formula
Perchloric acid	HClO_4
Hydriodic acid	HI
Hydrobromic acid	HBr
Hydrochloric acid	HCl
Nitric acid	HNO_3
Sulphuric acid	H_2SO_4

(Note: H_2SO_4 is only strong for the first dissociation: $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$)

The Strong Bases:

Strong bases that are not metal hydroxides include O^{2-} and NH_2^- both are found on the acid-base table. The hydroxide ion, OH^- , found on the lower right side of the table, is a strong base. **All metal hydroxides** are 100% dissociated in solution, and thus are strong bases.

For example:

Name	Formula
Sodium hydroxide	NaOH
Potassium hydroxide	KOH
Magnesium hydroxide	Mg(OH) ₂
Iron(III) hydroxide	Fe(OH) ₃
Zinc hydroxide	Zn(OH) ₂

(**Note:** These are just a few of the metal hydroxides that are considered to be strong bases.)

The Weak Acids:

All the acids listed on the left side of the table in the white section are “weak” acids.

The Weak Bases:

All the bases found on the right side of the table in the white section are “weak” bases

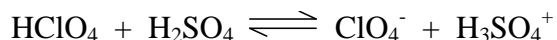
Some other relationships found on the table.

1. The higher an acid is on the left side of the table, the stronger the acid.
2. The lower a base is on the right side of the table, the stronger the base
3. The stronger an acid, the weaker its conjugate base (and vice versa.)
4. When a substance acts as an acid with water, H₃O⁺ is always produced. The stronger the acid, the greater the [H₃O⁺]
5. When a substance acts as a base with water, OH⁻ is always produced. The stronger the base, the greater the [OH⁻] produced.

Special Note: HPO₄²⁻ and HCO₃⁻ can be found on both the left and right sides of the table. This is because they are amphoteric and can act as weak acids and weak bases.

The Levelling Effect:

- H₃O⁺ is the strongest acid that can exist in a solution. Why?
- HClO₄, HI, HBr, HCl, HNO₃, H₂SO₄ don't exist in solution. Why?
- On the “chart”, the top left shows the strong acids. The higher the acid, the stronger it is.
- If we take a pure strong acid such as HClO_{4(l)} and dissolve it in another pure strong acid, such as H₂SO_{4(l)}, with no other solvent present, we will find:

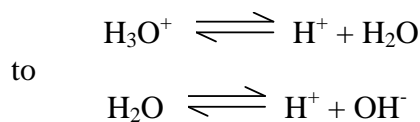


What do you notice? Which behaves like an acid and which a base?

- Combining strong acids allows us to establish the relative order of strengths among the strong acids.
- In water, all strong acids will be 100% dissociated with water taking the H⁺ forming H₃O⁺.
- We say that water has “**levelled**” all the strong acids to the same strength.

Therefore, the strongest acid that can exist in aqueous solution is H₃O⁺.

- So HClO₄, HI, HBr, HCl, HNO₃, H₂SO₄ are all levelled to the same strength as H₃O⁺.
- Therefore, the central portion of the table form:



shows the reactions which can occur in aqueous solution: the top six reactions are levelled to produce H₃O⁺ and the bottom two reactions are levelled to produced OH⁻.

Examples:

1. April 2003

Which of the following is correct if the four solutions listed are compared to one another?

	Concentration	Relative Conductivity	Ionization	
A.	strong acid	0.50 M	highest	complete
B.	weak acid	0.50 M	lowest	complete
C.	strong base	1.0 M	highest	complete
D.	weak base	1.0 M	lowest	complete

2. April 2004

Which of the following best describes a weak acid?

- A. Its 0.10 M solution will have pH = 1.00.
- B. It may be very soluble, but only partly ionized.
- C. It must be very soluble and completely ionized.
- D. It must be of low solubility and completely ionized.

3. April 1998

Which of the following 0.1 M solutions will have the greatest electrical conductivity?

- A. HNO₂
- B. H₂SO₃
- C. H₃PO₄
- D. C₆H₅OH

4. August 2004

What is the main difference between a strong acid and a weak acid?

- A. their degree of ionization
- B. their reactivity with platinum
- C. their concentration in solution
- D. their effect on phenolphthalein

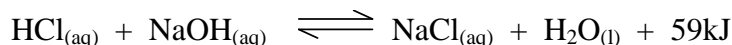
*****Do Hebden Questions #20 - 27, pgs 122 - 126*****

IV.7 - The Equilibrium Constant for the Ionization of Water

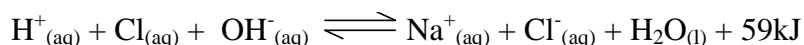
- Acidic Solution: has $[H_3O^+] > [OH^-]$
- Basic Solution: has $[H_3O^+] < [OH^-]$
- Neutral Solution: has $[H_3O^+] = [OH^-]$

Example: A typical acid-base reaction: $HCl + NaOH$

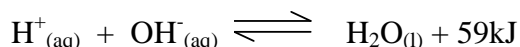
Formula Equation:



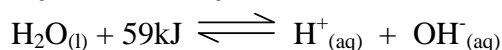
Total Ionic Equation:



Net Ionic Equation:



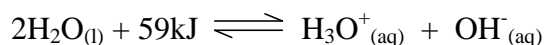
Therefore, the *self-ionization of water* can be written as:



The equilibrium expression (K_w) for this reaction is:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

- We can also write the self-ionization of water as follows:



so that the equilibrium expression (K_w) is:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

Recall that $[H_2O_{(l)}]$ is a constant and not included in the expression.

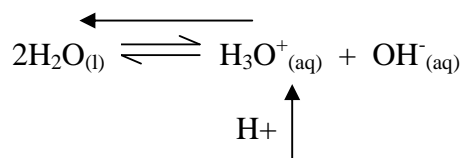
- What happens if the temperature increases?

Increased $[H_3O^+]$ and $[OH^-]$, increased electrical conductivity

- What happens if temperature is decreased?

Decreased $[H_3O^+]$ and $[OH^-]$, decreased electrical conductivity

- As $[H_3O^+]$ increases $[OH^-]$ decreases, keeping K_w at a constant 1.00×10^{-14}
- As $[H_3O^+]$ decreases $[OH^-]$ increases, keeping K_w at a constant 1.00×10^{-14}
- If we add an acid, $[H_3O^+]$ will increase and the water equilibrium will shift to use up some of the additional H_3O^+ .



- However, the $[H_3O^+]$ and $[OH^-]$ are very low in neutral water:

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}M$$

so that very little of this additional H_3O^+ can be neutralized by this small amount of OH^- . The $[\text{H}_3\text{O}^+]$ builds up while the $[\text{OH}^-]$ decreases. BUT even in acidic solution (lots of H_3O^+) a small amount of OH^- will be present.

Unless you are told otherwise, you should always assume the temperature is 25 °C and therefore the value of $K_w = 1.00 \times 10^{-14}$.

Try these...

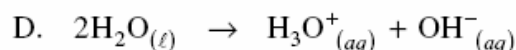
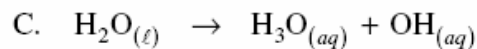
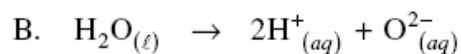
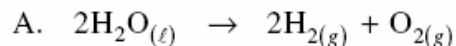
1. What is the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in 0.0010 M $\text{HCl}_{(aq)}$?

2. What is the $[\text{H}_3\text{O}^+]$ of a 0.01 M NaOH at 25°C?

3. Find $[\text{H}_3\text{O}^+]$ at 25°C of 2.0 M $\text{Sr}(\text{OH})_2$?

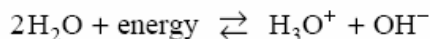
4. January 2002

The ionization of water can be represented by



5. January 1999

Consider the following equilibrium:



In pure water at a temperature of 50°C,

A. $\text{pH} < 7$

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

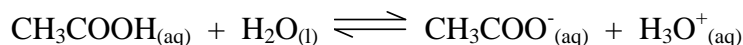
C. $K_w = 1.0 \times 10^{-14}$

D. $[\text{OH}^-] < 1.0 \times 10^{-7}$

*****Do Hebden Questions #28 - 30, pg 127*****

IV.8 - K_A and K_B

- When a **WEAK acid** like CH_3COOH reacts with water we find:

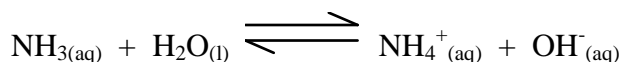


This process is called **acid ionization**. The equilibrium expression for the ionization is given by:

$$K_A = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

K_A is called the **acid ionization constant**.

- When a **WEAK base** such as NH_3 reacts with water we find:



This process is called **base ionization**. The equilibrium expression for the ionization is given by:

$$K_B = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.79 \times 10^{-5}$$

K_B is called the **base ionization constant**.

- From the Table of “*relative strengths of Bronsted-Lowry acids and bases*”, we can see that the greater the value of K_A , the stronger the acid. For a “strong acid”, the value of K_A is not defined since the acid is 100% ionized and the concentration of the unionized acid in the denominator of the K_A expression is effectively zero. Basically, K_A for a strong acid is **HUGE!**
- Similarly, the greater the K_B value for a base, the stronger the base. The table does not list K_B values but calculate the K_B values for bases by using the K_A values in the table.

Examples:

1. April 2004

What is the equilibrium expression for the predominant equilibrium in $\text{NaHCO}_3(aq)$?

- A. $K_a = \frac{[\text{HCO}_3^-]}{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}$
- B. $K_b = \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3][\text{OH}^-]}$
- C. $K_a = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$
- D. $K_b = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]}$

*****Do Hebden Questions #31 - 34, pg 128*****

IV.9 - K_A and K_B for Conjugate Pairs

- For a **conjugate pair** we have:

$$K_A (\text{conjugate acid}) \times K_B (\text{conjugate base}) = K_W$$

- Now we have a way to calculate K_B values for the weak bases on the Table of “relative strengths of Bronsted-Lowry acids and bases”.
- DO NOT USE THE WRONG K_A VALUE!** If you are required to find K_B for H_2PO_4^- then **look on the right-hand side of the table**, where H_2PO_4^- is acting as a BASE.

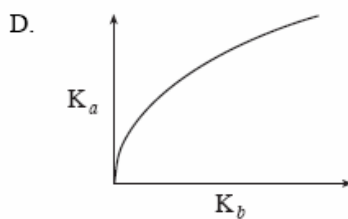
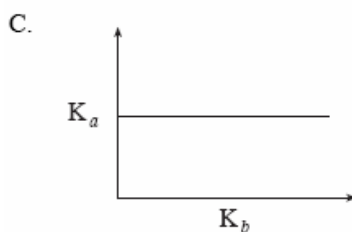
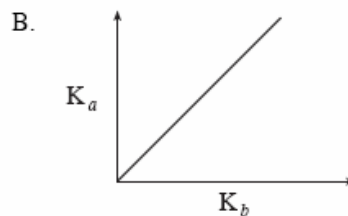
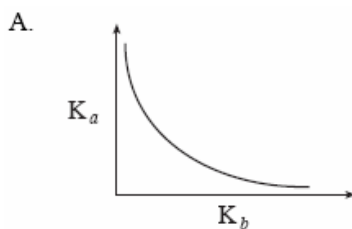
Examples:

1. What is the value of K_b for ammonia, NH_3 ?

2. What is K_b of H_2PO_4^- ?

3. August 2000

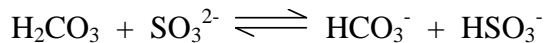
Which of the following graphs describes the relationship between K_a and K_b for all conjugate pairs?



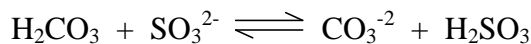
*****Do Hebden Questions #35 - 37, pg 130*****

IV.10 - Relative Strengths of Acids and Bases

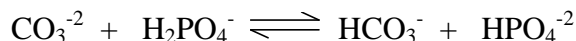
- If we mix solutions containing H_2CO_3 and SO_3^{2-} , the SO_3^{2-} can only act as a base (since it has no protons) and we find:



In Chemistry 12 we will only study the transfer of ONE proton. We will not deal with two-proton transfers such as:



- Consider what happens when we mix CO_3^{2-} and H_2PO_4^- :



We have set up a “proton competition” in solution.

- There are two acids in equilibrium, H_2PO_4^- and HCO_3^- , each trying to donate a proton.
- There are two bases in equilibrium, CO_3^{2-} and HPO_4^{2-} , each trying to accept a proton.
- The stronger of the two acids involved will be more successful in donating a proton than the weaker.
- From the Acid-Base Table we see that H_2PO_4^- ($K_a = 6.2 \times 10^{-8}$) is a stronger acid than HCO_3^- ($K_a = 5.6 \times 10^{-11}$).
- As a result, H_2PO_4^- has a greater tendency to donate a proton than does HCO_3^- . Therefore, there will be MORE PRODUCTS than reactants (“products are favoured”)

*****In a Bronsted-Lowry acid-base equilibrium, the side of the equilibrium that has the WEAKER ACID will be favoured*****

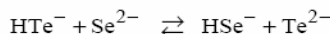
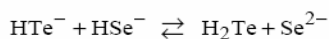
Try this....

When HS^- and HCO_3^- are mixed, does the resulting equilibrium favour the reactants or products?

Examples:

1. June 1998

Consider the following equilibria:



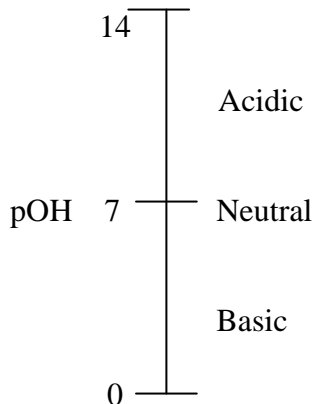
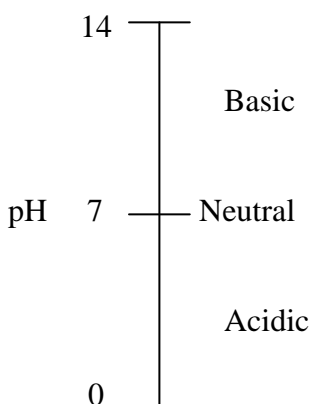
Reactants are favoured in both equilibria. The order of acids from strongest to weakest is

- A. HTe^- , HSe^- , H_2Te
- B. HSe^- , H_2Te , HTe^-
- C. H_2Te , HTe^- , HSe^-
- D. H_2Te , HSe^- , HTe^-

*****Do Hebden Questions #38 - 46, pg 133*****

IV.11 - pH and pOH

- $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log_{10}[\text{OH}^-]$



Converting from $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ to pH and pOH

Example 1: If $[\text{H}_3\text{O}^+] = 3.94 \times 10^{-4} \text{ M}$, what is pH?

Example 2: If $[\text{OH}^-] = 9.51 \times 10^{-12} \text{ M}$, what is pOH?

Converting from pH and pOH to $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

Since $\text{pH} = -\log[\text{H}_3\text{O}^+]$

We need to undo all the procedures that have been applied to $[\text{H}_3\text{O}^+]$, so that we have only $[\text{H}_3\text{O}^+]$ on the right hand side.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad \text{OR} \quad [\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH})$$

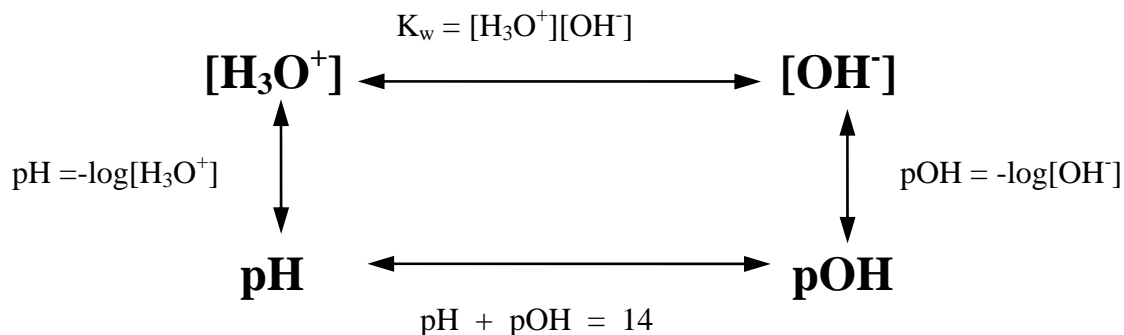
Example 3: If $\text{pH} = 3.405$, what is $[\text{H}_3\text{O}^+]$?

Example 4: If $\text{pOH} = 11.022$, what is $[\text{OH}^-]$?

Converting from pH to pOH and from pOH to pH.

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

Now we can convert between pH, pOH, $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ as follows:



Example 5: If $\text{pH} = 9.355$, what is pOH ?

Example 6: If $\text{pH} = 6.330$, what is $[\text{OH}^-]$?

One More Special Relationship Involving Logarithms.

$$\text{p}K_w = -\log(K_w) = -\log(1.00 \times 10^{-14})$$

so that $\text{p}K_w = 14.000$, at 25°C

Therefore, $\text{p}K_w = \text{pH} + \text{pOH}$

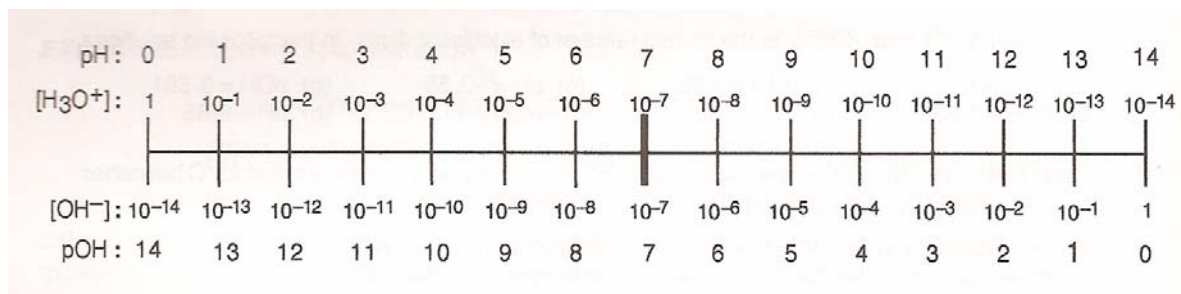
A Special Note on Significant Digits

In pH or pOH notation, only the digits after the decimal are significant digits. The digits before the decimal come from the “non-significant” power of 10 in the original $[\text{H}_3\text{O}^+]$.

Example 7: If $[\text{H}_3\text{O}^+] = 5.28 \times 10^{-5} \text{ M}$, what is pH?

The pH scale:

The relationship between pH, pOH, $[H_3O^+]$ and $[OH^-]$ are shown on the diagram below.



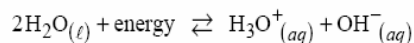
- The pH scale INCREASES as the pOH scale decreases.
- Acidic solution when pH is less than 7; basic solution when pH is greater than 7. Acidic solution when pOH is greater than 7; basic solution when pOH is less than 7. A neutral solution has $pH = pOH = 7$.
- At any point, $pH + pOH = 14$ and $[H_3O^+][OH^-] = 10^{-14}$.
- It is possible to have a pH of -1 and 15 , the pH scale is meant for a range between 0 and 14. A pH of -1.00 is better shown as $[H_3O^+] = 10 \text{ M}$.

When pH is *increased* by 1, the $[H_3O^+]$ is *decreased* by 10.

Examples:

1. August 1998

Consider the following equilibrium:



When the temperature of water is changed, the pH decreases. Which of the following explains this pH change?

- A. Temperature and K_w both increase.
- B. Temperature and K_w both decrease.
- C. Temperature increases and K_w decreases.
- D. Temperature decreases and K_w increases.

2. January 2004

Which of the following equations can be used to calculate pOH ?

- A. $pOH = -\log K_w$
- B. $pOH = pK_w + pH$
- C. $pOH = pK_w - pH$
- D. $pOH = -\log [H_3O^+]$

*****Do Hebden Questions #49 - 57, pgs 139 - 141*****

IV.12 - Mixtures of Strong Acids and Bases

- When we mix an acid and a base, we can obtain an acidic, basic or neutral solution depending on the relative amounts of reactants involved.

To do these problems you will need **ONE** of the following equations:

$$[\text{H}_3\text{O}^+]_{\text{XS}} = [\text{H}_3\text{O}^+]_{\text{ST}} - [\text{OH}^-]_{\text{ST}} \quad \text{or} \quad [\text{OH}^-]_{\text{XS}} = [\text{OH}^-]_{\text{ST}} - [\text{H}_3\text{O}^+]_{\text{ST}}$$

*****Don't forget to do DILUTION CALCULATIONS*****

Examples:

1. If we add 10.0 ml of 0.100 M HCl to 90.0 ml of 0.100 M NaOH, what is the pH of the resulting solution?

2. How many moles of $\text{HCl}_{(\text{g})}$ must be added to 40.0 mL of 0.180 M NaOH to produce a solution having $\text{pH} = 12.500$, if we assume that there is no change in volume when the HCl is added?

3. 40.0 mL of 2.61 M $\text{Sr}(\text{OH})_2$ is mixed with 70.0 mL of 2.61 M HNO_3 . Find the pOH and pH.

4. April 2004

What $[\text{H}_3\text{O}^+]$ results when 25.0 mL of 1.0M HCl is mixed with 15.0 mL of 0.30 M KOH ?

- A. 0.020 M
- B. 0.51 M
- C. 0.70 M
- D. 0.82 M

*****Do Hebden Questions #58 - 68, pgs 143 - 144*****

IV.13 - Hydrolysis

- **Hydrolysis:** a reaction between a salt and water to produce an acidic or basic solution.
- **All salts are considered to be 100% ionized in water.** Therefore, the ions making up the salt will be of concern to us, not the salt itself.
- First, we need to identify the ions that **do not react with water** to produce an acidic or basic solution . . . **spectator ions.**
- Spectator ions are ions that are the conjugates of strong acids or bases.

Spectator Cations: are the ions of the alkali metals (column I of the periodic table) and the ions of the alkaline earth metals (column II)

Spectator anions: are the first five anions found at the top right of the table of relative strengths of acids:
 ClO_4^- , I^- , Br^- , Cl^- and NO_3^- (HSO_4^- is not a spectator since it is a weak acid)

*****Memorize the spectators...you will be using them A LOT 😊*****

- 3 Steps to Determining the Behaviour of a Salt in Water
 1. Determine the ions produced when the salt dissociates.
 2. Ignore the spectators.
 3. Of the ions that remain,
 - They will act as an acid if they are found on the acid (left) side of the table.
 - They will act as a base if they are found on the base (right) side of the table.

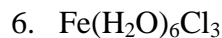
Examples:

1. NaCl

2. NH_4Cl

3. NaF

4. NaHC_2O_4



7. August 2003

Which of the following solutions has the highest pH ?

- A. 0.1 M HCl
- B. 0.1 M NaF
- C. 0.1 M NaHS
- D. 0.1 M NH_4Cl

8. August 2004

What is the predominant net ionic equation for the hydrolysis of $(\text{NH}_4)_2\text{HPO}_4(aq)$?

- A. $\text{NH}_4^+(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)$
- B. $\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq)$
- C. $(\text{NH}_4)_2\text{HPO}_4(aq) \rightleftharpoons 2\text{NH}_4^+(aq) + \text{HPO}_4^{2-}(aq)$
- D. $\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq)$

9. June 2000

In a solution of 0.10 M NaCN, the order of ion concentration, from highest to lowest, is

- A. $[\text{Na}^+] > [\text{OH}^-] > [\text{CN}^-] > [\text{H}_3\text{O}^+]$
- B. $[\text{Na}^+] > [\text{CN}^-] > [\text{OH}^-] > [\text{H}_3\text{O}^+]$
- C. $[\text{H}_3\text{O}^+] > [\text{OH}^-] > [\text{CN}^-] > [\text{Na}^+]$
- D. $[\text{OH}^-] > [\text{Na}^+] > [\text{CN}^-] > [\text{H}_3\text{O}^+]$

*****Do Hebden Questions #69 - 73, pg 148*****

IV.14 - Calculations Involving K_A

- When a weak acid, HA (hypothetical weak acid), is put into water, some of the acid ionizes. As a result of the ionization, a certain amount of H_3O^+ is produced. The amount of H_3O^+ produced depends on the K_A value of the weak acid, the larger the K_A value the more H_3O^+ produced. None of the acid ionizes until it reaches the water, therefore there will be “**a sense of time passing**” while the acid ionizes. As in the Equilibrium Unit, when there is **a sense of time passing** we use an “**ICE Table**”.
- There are only 3 major pieces of information that a completely solved problem will contain:
 - [HA], the original concentration of the weak acid.
 - K_A for the acid.
 - [H_3O^+] or pH of the acid solution.
- The acid ionization (K_A) expression is the only equation that can be used to solve weak acid problems that involve unknowns.

The K_A expression will be used to:

 - Find [H_3O^+] or pH, given [HA] and K_A .
 - Find K_A , given [HA] and [H_3O^+] or pH.
 - Find [HA], given K_A and [H_3O^+] or pH.

Examples:

1. If $K_a = 1.8 \times 10^{-5}$ for CH_3COOH , what is the pH of a 0.50 M solution of CH_3COOH ?

2. If $\text{pH} = 1.70$ for a 0.100 M solution of an unknown weak acid, HA , what is K_{A} for HA ?

3. What mass of NH_4Cl will produce 2.00 L of a solution having a pH of 4.75 ?

4. August 2005

What is the $[\text{H}_3\text{O}^+]$ in 0.70 M HCN ?

- A. 0.70 M
- B. $1.9 \times 10^{-5} \text{ M}$
- C. $1.0 \times 10^{-7} \text{ M}$
- D. $3.4 \times 10^{-10} \text{ M}$

*****Do Hebden Questions #74 - 83, pg 152*****

IV.15 - Calculations Involving K_B

- When a weak base, A^- (hypothetical weak base), is put into water, some of the base ionizes. As a result of the ionization, a certain amount of OH^- is produced. The greater the value of K_B , the more OH^- formed.
- Calculations involving bases are very similar to weak acid calculations with two important changes:
 - K_B will have to be calculated, it cannot be taken directly from the table.
 - The resulting solution will be basic, not acidic, which means we will be using $[OH^-]$ rather than $[H_3O^+]$.

Examples:

1. What is the pH of a 0.10 M solution of NaCN?

2. The pOH of a 0.50 M solution of the weak acid is 10.64. What is K_B for X^- ?

*****Do Hebden Questions #84 - 93, pgs 153 - 154*****

IV.16 - Acid - Base Titrations

- **Titration** is an analytical method used to determine the concentration of a substance. It involves the use of a standard solution of known molarity to titrate against a solution of unknown molarity.
- The goal of a titration is to stop adding the titrant (“**end point**”) when stoichiometrically equivalent amounts of the two reactants have combined. This is called the “**equivalence point.**”

But how do we know when we should stop a titration?

- An *indicator* is required to mark the end point of the titration. An indicator is simply a chemical that has a different colour at different pH values. When the indicator changes colour, we end the titration.
- All titration problems involve at least FIVE different values.

Concentration of acid
Volume of acid

Concentration of base
Volume of base

Acid / Base mole ratio

- Pay special attention to significant figures in titration calculations. The purpose of titrations is to get accurate and precise values of unknown concentrations.
- Titrations must be repeated as an accuracy check. The volumes added from the burette should be within ± 0.02 “ish” of each other. If the volumes do not agree, then the titration must be repeated until good agreement between the volumes is found.

For example: Consider the following volumes...

Volume from titration #1 = 23.90 mL

Volume from titration #2 = 24.66 mL

Volume from titration #3 = 23.88 mL

What do you notice? The volumes from titration #1 and #3 agree with each other, but what about #2? The 2nd titration is way off and **MUST BE DISCARDED**. Therefore, the volume used will be an **AVERAGE** of the other two results.

$$\text{Average volume} = \frac{(23.90 \text{ mL} + 23.88 \text{ mL})}{2} = 23.89 \text{ mL}$$

Examples:

1. Three 10.00 mL samples of HCl of unknown concentration were titrated with 0.1000 M NaOH to find the [HCl]. Phenolphthalein will be used as an indicator.

Volume of 0.1000 M NaOH Used

Titration #1 25.58 mL

Titration #2 24.10 mL

Titration #3 24.08 mL

2. Find the concentration of sulphuric acid if three 25.00 mL samples of the acid were titrated with 0.2055 M sodium hydroxide yielding the following results:

Volume of 0.2055 M NaOH Used

Titration #1 23.80 mL

Titration #2 23.23 mL

Titration #3 23.23 mL

3. A 2.295 g sample of an unknown diprotic acid was dissolved and diluted to 250.0 mL. Three titrations were done using 25.00 mL samples of the unknown acid and an average of 23.39 mL of 0.2000 M KOH was used to reach the end point.
- What is the concentration of the unknown acid?
 - What is the molar mass of the unknown acid?
 - Is the unknown acid H_2SO_3 , H_2CO_3 , or H_2SO_4 ?

4. An equivalence point is reached by reacting 25.00 mL of 0.1255 M NaOH with 38.74 mL of 0.02700 M $\text{H}_4\text{P}_2\text{O}_7$. How many protons are removed from the $\text{H}_4\text{P}_2\text{O}_7$ on average and what is the balanced equation for the reaction? (Partial Neutralization example...calculating the mole ratio)

5. A 3.4786 g sample of impure NaHSO_4 is diluted to 250.0 mL. A 25.00 mL sample of the solution is titrated with 26.77 mL of 0.09974 M NaOH. What is the percent purity of the NaHSO_4 ?

$$\% \text{ purity} = \frac{\text{Actual Concentration}}{\text{Expected Concentration}} \times 100\%$$

6. A 3.2357 g sample of unknown Monoprotic acid is diluted to 250.0 mL. A 25.00 mL sample of the acid solution is titrated with 16.94 mL of 0.1208 M KOH. What is the molar mass of the acid?

7. June 2004

A 25.0 mL sample of a diprotic weak acid is titrated with 20.2 mL of 0.10 M NaOH.
What is the concentration of the acid?

- A. 0.040 M
- B. 0.080 M
- C. 0.16 M
- D. 0.12 M

*****Do Hebden Questions #94 - 107, pgs 158 - 159*****

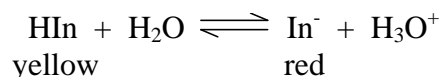
IV.17 - Indicators

- An **indicator** is an organic weak acid or base having different colours for its conjugate acid and conjugate base forms.
- Indicators are usually very complex molecules so we will use abbreviations such as:

HIn to represent the conjugate acid of the indicator.

In⁻ to represent the conjugate base of the indicator.

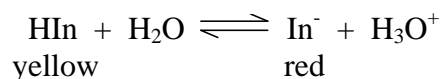
Example:



Indicator in acidic solution: when in an acidic solution, the excess H_3O^+ shifts the equilibrium to the left, causing the solution to turn **YELLOW**.

Conclusion: An indicator will always be in its CONJUGATE ACID form when in HIGHLY ACIDIC solutions.

Let's consider the some example again...



Indicator in basic solution: when in an basic solution, the $[\text{H}_3\text{O}^+]$ is very low so that the equilibrium shifts to the right and turns the solution **RED**.

Conclusion: An indicator will always be in its CONJUGATE BASE form when in HIGHLY BASIC solutions.

- In summary, (for the above indicator):

In acidic solutions we find $[\text{HIn}] > [\text{In}^-]$

That is we have more YELLOW than RED molecules, and the solution appears YELLOW.

In basic solutions we find $[\text{HIn}] < [\text{In}^-]$

That is we have more RED than YELLOW molecules, and the solution appears RED.

- If we add a base to an acidic solution at some point we will have:

$$[\text{HIn}] = [\text{In}^-]$$

and an equal number of YELLOW and RED molecules give an ORANGE solution. This point at which an indicator is half way through its colour change is called the **end point** or **transition point**.

- At the end point we have:

$$K_A = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = [\text{H}_3\text{O}^+] \quad \text{since } [\text{HIn}] = [\text{In}^-]$$

Conclusion: The $[\text{H}_3\text{O}^+]$ at which an indicator changes colour will be equal to the value of K_A for the indicator.

Recall we made the previous definition: **$\text{p}K_A = -\log K_A$**

$$K_A = \frac{[H_3O^+]}{[H_2O]}$$

$$-\log K_A = -\log \frac{[H_3O^+]}{[H_2O]}$$

$$pK_A = pH$$

Conclusion: An indicator will be at the midpoint of its colour change when the pH of the solution equals the pK_A of the indicator.

- **Note:** The end point is the point in the titration where the colour of the indicator changes. The equivalence point is the point in the titration where the stoichiometry of the reaction is balanced. If we choose our indicator correctly, the indicator should change colour at or very close to the **stoichiometric point**, and there will be a negligible difference between the **end point** and the **equivalence point**.
- An indicator does not change colour instantly at some magic pH value; the colour change takes place over a range of about 2 pH units.

Examples:

1. Ethyl orange is red at $pH < 3.4$, yellow at $pH > 4.8$ and an intermediate orange at $pH = 4.1$. What is the approximate value of K_A for ethyl orange?
2. Alizarin Yellow R changes from red to yellow at $pH = 11$. If $Aliz^-$ ion is red what colour is Alizarin Yellow R in $1 \times 10^{-4} M NaOH$?

- Often we need to quickly determine the pH of a solution. A pH meter can be used to get an accurate pH value but it is a slow process to get out a meter, calibrate it and determine the pH. For quick measurements requiring only an approximate pH value, we use a “**universal indicator**.”
- A **universal indicator** is a solution which changes colour several times over a range of pH values.

Example:

1. A universal indicator can be made using the following indicators:

Indicator	pK_A	Acid Form Colour	Base Form Colour
methyl orange	3.8	red	yellow
bromothymol blue	6.8	yellow	blue
phenolphthalein	9.1	colourless	pink

What will be the colour- pH behaviour of this universal indicator?

2. August 2000

What is the $[\text{H}_3\text{O}^+]$ at the transition point for an indicator with a K_a of 3.9×10^{-8} ?

- A. 1.0×10^{-14} M
- B. 3.9×10^{-8} M
- C. 1.0×10^{-7} M
- D. 2.6×10^{-7} M

3. January 2003

Which of the following chemical indicators has a $K_a = 2.5 \times 10^{-5}$?

- A. methyl orange
- B. phenolphthalein
- C. thymolphthalein
- D. bromocresol green

*****Do Hebden Questions #108 - 120, pgs 162 - 163*****

IV.18 – Practical Aspects of Titrations

- *Standard Solutions*

To perform an acid-base titration we must have a solution having an accurately known concentration. Such a solution is called a standard solution or a standardized solution.

There are two main ways to prepare a standard solution:

- a) Use a substance that can be obtained in pure and stable form, which does not absorb water or carbon dioxide from air and which has a known molar mass. With these conditions met the standard solution can be prepared to an exact concentration by determining the exact mass required for a certain volume. Such a substance is called a *primary standard*.

Example: Potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$; molar mass = 204.23 g/mol) is used as a primary standard. Weighing out exactly 20.423 g and diluting to 1.000 L can make a solution of exactly 0.1000 M.

- b) Titrate an “unreliable” base with an acid primary standard, or titrate an “unreliable” acid with a base primary standard. Once the concentrations of these unreliable are known they can be used as standards.

Example: NaOH should not be used as a primary standard because solid NaOH is only 95-98% pure and rapidly absorbs water upon exposure to air. If NaOH is to be used as a standard for a titration it must first be made to an approximate concentration then standardized with an acidic primary standard.

Acidic Primary Standards:

1. Potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$
2. Oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

Basic Primary Standard

1. Sodium carbonate, Na_2CO_3

*****Do Hebden Questions #121 - 123, pg 165*****

- *Types of Titration Curves*

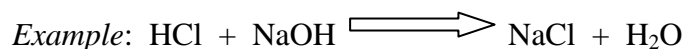
In an acid base titration, the pH at the equivalence point is the same as that of the salt solution formed during the neutralization.

a) Titration of a STRONG ACID with a STRONG BASE



Choosing an indicator:

The salt of a strong acid and strong base is **NEUTRAL** in solution.



As a result the equivalence point will be at about $\text{pH} = 7$ and an indicator with a transition point at about this pH is needed. Therefore, choose an indicator with pK_A of about 7.

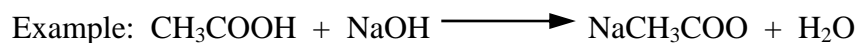
- pH rises slowly, until it is near the equivalence point
- Before base is added, pH is determined by the $[\text{H}_3\text{O}^+]$ in the acid (HCl)
- Before the equivalence point, pH depends on the unreacted HCl ($[\text{H}_3\text{O}^+]$)
- At the equivalence point, the number of moles of acid = moles of base
- After the equivalence point, pH depends on the excess $[\text{OH}^-]$

b) Titration of a WEAK ACID with a STRONG BASE



Choosing an indicator:

The salt of a weak acid and strong base is BASIC in solution.



As a result the equivalence point will be above $\text{pH} = 7$ and an indicator with a transition point at above $\text{pH} 7$ is needed. Therefore, choose an indicator with pK_A above 7.

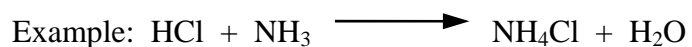
- Before base is added, pH is determined by the weak acid
- At the equivalence point, the pH is higher than 7 because the salt is slightly basic.
- Higher initial pH
- Short abrupt pH rise at the beginning
- Shorter / less steep around the equivalence point

c) Titration of a STRONG ACID with a WEAK BASE



Choosing an indicator:

The salt of a strong acid and weak base is ACIDIC in solution.



As a result the equivalence point will be below $\text{pH} = 7$ and an indicator with a transition point below $\text{pH} 7$ is needed. Therefore, choose an indicator with pK_A below 7.

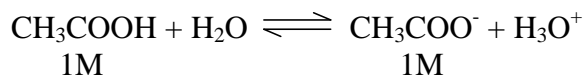
- Before base is added, pH is determined by the weak base
- At the equivalence point, the pH is lower than 7 because the salt is slightly acidic
- Short abrupt pH decline at the beginning

*****Do Hebden Questions #124 - 125, pgs 167-176*****

IV.19 - Buffers

- **Buffer:** is a solution containing *appreciable* amounts of a **weak acid** and its conjugate **weak base**.

Example: Acetic Acid / Acetate buffer



- Buffers resist pH changes
- Used whenever a constant pH is required
- Write the K_a for the above example

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Remember that this buffer has equal concentrations of $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COO}^-]$.

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$$

therefore, $\text{pH} = \text{p}K_a$

- When **equal concentrations** of a weak acid and its conjugate base are added to water, the pH of the resulting buffer will equal the $\text{p}K_a$ of the weak acid.
- Overall, buffers have a relatively large concentration of both a weak acid and its conjugate base and a *small* concentration of $[\text{H}_3\text{O}^+]$.
- **Note:** A solution of CH_3COOH by itself is not a buffer. There **MUST** be substantial amounts of both the conjugate acid and conjugate base.
- Diluting a buffer has no effect on pH. Here is why...

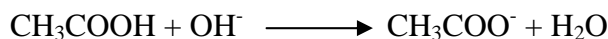
$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] = 1.0 \text{ M}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[1.0][\text{H}_3\text{O}^+]}{[1.0]} = [\text{H}_3\text{O}^+]$$

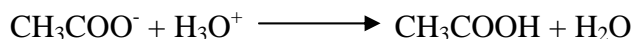
Dilute...affects both sides equally

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[0.1][\text{H}_3\text{O}^+]}{[0.1]} = [\text{H}_3\text{O}^+]$$

- Buffers work because the value of the ratio of between the conjugate acid and conjugate base does not change much when reacted with small amounts of acids or bases.
- Conjugate acid neutralize added OH^-



- Conjugate base neutralize added H_3O^+



- Making an Acidic Buffer...

Mix 1.0 mol of acetic acid (CH_3COOH) and 1.0 mol of sodium acetate (NaCH_3COO) and dilute to 1.0 L (make sure the salts are soluble!!!)

$\text{NaCH}_3\text{COO}_{(s)} \longrightarrow \text{Na}^+ + \text{CH}_3\text{COO}^-$ (Na^+ is a spectator) therefore the following equilibrium is set up

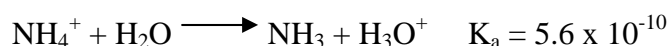


$$\text{pH} = \text{pK}_a = -\log(1.8 \times 10^{-5}) = 4.74$$

This is referred to as an acidic buffer since it buffers the pH in the acidic region

- Making a Basic Buffer...

1 mol of ammonia (NH_3) and 1.0 mol of ammonium nitrate (NH_4NO_3) and dilute to 1.0 L.



$$\text{pH} = \text{pK}_a = -\log(5.6 \times 10^{-10}) = 9.25$$

This is referred to as a basic buffer since it buffers pH in the basic region.

- There is a limit to the amount of H_3O^+ and OH^- that can be neutralized.
- If there is 1 mol of conjugate base present, a maximum of 1 mol of H_3O^+ can be neutralized. 1 mol of conjugate acid implies maximum of 1 mol OH^- .
- ***Whenever a weak acid OR weak base is titrated, a buffer solution will occur in the middle portion of a titration curve. (See page 181).***

Examples:

1. June 1999

Consider the following:

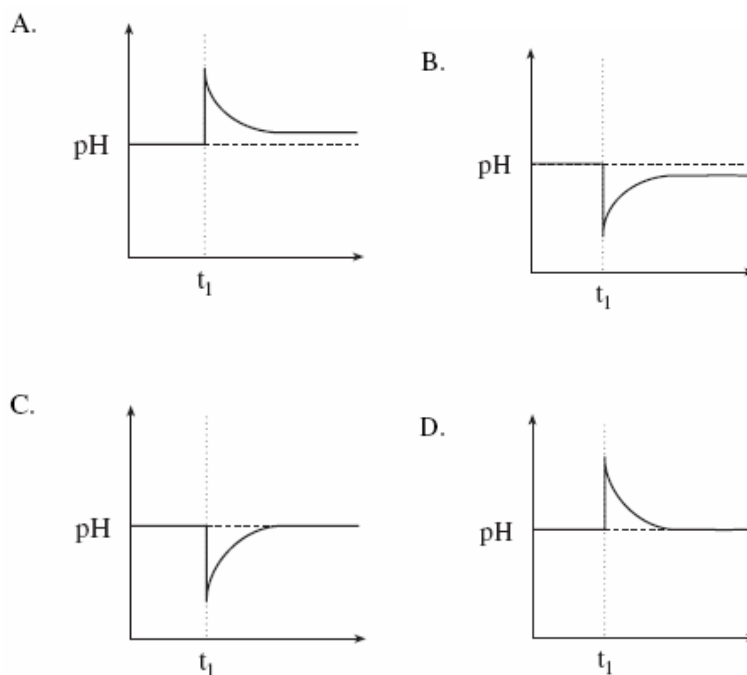
I.	H_3O^+
II.	CH_3COO^-
III.	CH_3COOH

The purpose of a buffer system consisting of CH_3COOH and CH_3COONa is to maintain a relatively constant concentration of

- A. I only.
- B. I and II only.
- C. II and III only.
- D. I, II and III.

2. January 2004

Which of the following graphs best describes the effect on the pH of a buffer solution when a small amount of acid is added at t_1 ?



3. August 2003

Which of the following pairs of chemicals could be used to make a buffer solution?

- A. NH_3 and H_2O
- B. HCl and NaCl
- C. NH_3 and NH_4Cl
- D. CH_3COOH and HCl

4. April 2003

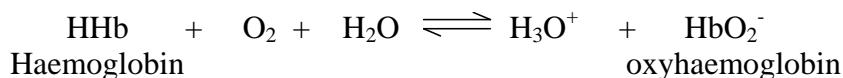
Which of the following acids could **not** be present in a buffer solution?

- A. HF
- B. HNO_2
- C. H_2SO_3
- D. HClO_4

*****Do Hebden Questions #131 - 140, pgs 181-182*****

IV.20 – Buffers in Biological Systems

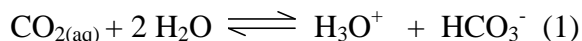
- Buffers are very important in biological systems because they provide a way to prevent the systems from being overwhelmed by changes in acidity or basicity of their environment.
- Haemoglobin is the oxygen carrier in blood and is involved in the following equilibrium...



The optimum pH for the blood is 7.35.

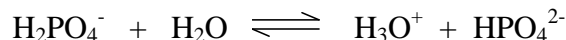
- If the pH < 7.20, = Acidosis. The $[\text{H}_3\text{O}^+]$ is very high and the equilibrium shifts left. As a result, O_2 does not bind as well with the haemoglobin.
- If the pH > 7.50, = Alkalosis. The $[\text{H}_3\text{O}^+]$ is too low and the equilibrium shifts to the right. As a result, O_2 is not released from the oxyhaemoglobin.
- Obviously it is important to regulate blood pH. If no there were no buffers in the blood we would die from drinking lemon juice or eating a tomato.

The $\text{CO}_2 / \text{HCO}_3^-$ System



- An increase in CO_2 (cell metabolism) or decrease in CO_2 (breathing out) upsets the $[\text{H}_3\text{O}^+]$ in (1). Because $\text{CO}_{2(\text{aq})}$ and HCO_3^- in 1 create a buffer, the loss of CO_2 or the build-up HCO_3^- of has a minimal effect on blood pH.

The $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ System



- The metabolic by-products of cell growth are acidic and this buffers prevents a build-up of acid.
- H_2PO_4^- and HPO_4^{2-} are present in the blood and to a greater extent in cells.

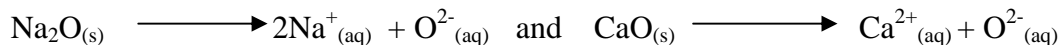
*****Do Hebden Questions #141 - 143, pgs 181-182*****

IV.21 – Applied Acid / Base Chemistry

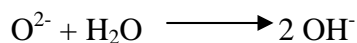
A. Aqueous Solutions of Metal and Non-Metal Oxides

Metal Oxides

- When a metal oxide is mixed with water, the following occurs...



Na^+ and Ca^{2+} are spectators and O^{2-} is a strong base.



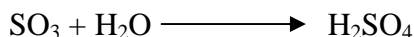
Thus, a **basic solution** is produced.

- Only ionic metal oxides form basic solutions. Oxides of **group I** and **group II** are highly ionic and are the only metal oxides considered in chemistry 12.

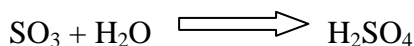
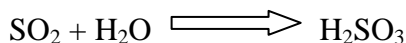
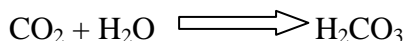
Example: Write the equation for the reaction between Na_2O and water

Non-Metal Oxides

- When a non-metal reacts with water, the water bonds to the existing oxide molecule to form an **acidic solution**.



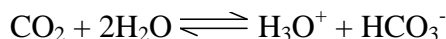
- Covalent oxides form acidic solutions. Know the following...



*****Do Hebden Questions #144 - 145, pg 185*****

B. Acid Rain

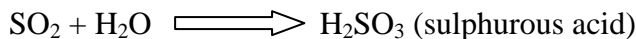
- Because of dissolved CO_2 , rain is normally slightly acidic with a pH of about 5.6



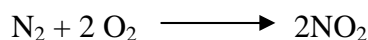
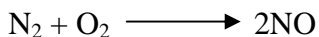
- Any precipitation with $\text{pH} < 5.6$ is called “Acid rain”

- *Sources of acid rain...*

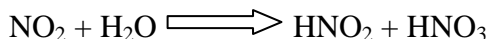
- Sulphur containing substances...most fuels, including coal and oil. When fuels are burned, sulphur is converted to sulphur dioxide, SO_2 .
- Sulphur dioxide reacts with air to produce, $\text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$
- When the gases SO_2 and SO_3 (non-metal oxides!!!) react with water vapour, acids are formed.



- Mixtures of SO_2 and SO_3 is often referred to as “ SO_x ”
- Also, combustion reactions (i.e. automobiles) cause small amounts of N_2 to react with air, NO and NO_2 is produced.



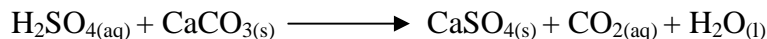
- NO_2 reacts with water...



- Mixtures of NO and NO_2 are referred to as “ NO_x ”

- *Protection from acid rain...*

- Lakes have a $\text{CO}_2 / \text{HCO}_3^-$ buffer capacity, but if a large amount of acid rain goes into the lake, the buffer capacity is exceeded and the ecosystem can be harmed.
- There is still hope, if the acid rain stops, the absorption of CO_2 from the atmosphere can eventually reverse the effects of acid rain.
- Limestone (in some lakes) can neutralize the acidity of acid rain.



- *Problems associated with acid rain...*

- Fish and plant growth affected
- Leaches minerals out of the rocks and soils.
- Limestone building damaged

*****Do Hebden Questions #146 - 147, pg 188*****