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Prepared by:- SUSIE ZIGALE (Msc)

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ACID-BASE CHEMISTRY

1. Introduction

Acids and bases are the most prominent inorganic compounds .Some of the most important process in chemical and biological systems are acid base concepts .since they are too familiar in real life situation ,used to many industrial process .a number of familiar materials ,such as aspirin and vitamin Care acidic .vinegar is a dilute solution of acetic acid ,lemonde contains citric acid, the battery in the car contains sulpheric acid .milk of magnesia is basic ,as are baking soda and washing soda.

Generally ,acids and bases are the most important classes of compounds and necessary in biology and chemistry enviroment.

- Acids & Bases Found in Homes

- ✓ Citrus Fruits- Oranges and lemons, for instance, contain citric acid, which makes them acidic home products.
- ✓ Toothpaste- Toothpaste is a Base, and it has an alkaline composition. As soon as we eat, the food breaks down and releases acid. We use toothpaste to brush our teeth to counteract the acidic influence in our mouths.
- ✓ Carbonated Beverages. –carbonic Acid
- ✓ Vinegar – weak acetic acid
- ✓ Lemon juice – citric acid and some ascorbic acid
- ✓ Any citrus fruit – citric acid and some ascorbic acid
- ✓ Most other fruits – citric acid, possibly tartaric, oxalic, or malic acid
- ✓ Carbonated soda – phosphoric, carbonic, and sometimes citric acid
- ✓ Battery acid – sulfuric acid
- ✓ Aspirin – acetylsalicylic acid
- ✓ Muriatic acid – hydrochloric acid
- ✓ Sour candies – citric acid
- ✓ Yogurt – lactic acid
- ✓ Brewed coffee or tea- Tannic acid
- ✓ Most alcoholic beverages- Acetic acid
- ✓ Stomach acid and vomit – hydrochloric acid
- ✓ Urine (only slightly acidic)
- ✓ Baking soda – sodium bicarbonate
- ✓ Washing soda – sodium carbonate
- ✓ Soap – Either sodium or potassium hydroxide
- ✓ Chalk – calcium carbonat

1. Definition of Acids and Bases

The term 'acid' is derived from the Latin word 'ACERE' which means sour while base is derived from a latin word "alquili" ,which mean ash of plant.

1.1.Traditional definition of Acid and base

An acid is any substance that in water solution tastes sour, changes blue litmus paper to red, reacts with some metals to liberate hydrogen, reacts with bases to form salts, and promotes chemical reactions (acid catalysis).

The basic definition of Acids and Bases are categorized to three classes. Arrhenius definition, Bronsted lowry definition and Lewis definitions will study next.

1.2. Arrhenius Definitions

The Swedish chemist ***svante Arrhenius*** framed the first successful concept of Acids and Bases. The Arrhenius definition states that **an acid produces H^+ in solution and a base produces OH^-**. This theory was developed by Svante Arrhenius in 1883. Later, two more sophisticated and general theories were proposed. These are the Brønsted-Lowry and the Lewis definitions of acids and bases.

According to Arrhenius,

An acid is a substance that, when dissociate in water, increase the concentration of hydroium ion, $H3O^+(aq)$

A base is a substance that, when dissociate in water increase the concentration of hydroxide ion OH^- (aq) . For more general, Arrhenius concept is aqueous dependent, some typical Arrhenius Acids are HCl, HNO_3, H_2SO_4, $HClO_4$ and some typical bases are NH_3, HaOH, $Ca(OH)_2$, $Ba(OH)_2$,

$HCl(q) + H_2O+(aq) \rightarrow Cl^-(aq)+H^+(aq)$: HCl is Arrhenius Acid

$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$: NH_3 is Arrhenius base

Despite in success, the Arrhenius definition of acid and base is limited to *aqueous* solutions. but there are number of reactions that occurs in other solvents and in the gas phase, example, when benzene solution of Acetic Acid and ammonia are mixed, acetic acid react with ammonia to form ammonium acetate,

$CH_3COOH\ (l) + NH_3(g) \rightarrow CH_3COONH_4(s)$

Ammonia and hydrogen chloride react as a base and an acid in the gas phase to form ammonium chloride.

$NH_3\ (g) + HCl \rightarrow NH_4Cl(s)$

Therefore, a more general definition of acids and bases that include reaction in the gas phase and in non aqueous solvent is needed.

Advantages of Arrhenius Theory

The various advantages of Arrhenius theory are that it provides knowledge about:

- It was also the first theory on acids and bases that acknowledged the significance of solvents in neutralization and water formation during the reaction.
- The properties of acids and bases
- The strength of acids and bases
- Concept of neutralization and hydrolysis

Limitations of Arrhenius Theory

1. Arrhenius Theory is limited to the study of acids and bases in aqueous solution only and not applicable in gaseous and non-aqueous solutions.
2. Arrhenius theory is applicable only to acids having ionizable hydrogen (HA). For example: HCl, HBr. It is not applicable for SO_2, CO_2, and $AlCl_3$.
   Activity: What does it mean ionizable/non-ionizable hydrogen?
3. Arrhenius theory is only applicable to bases having the formula BOH. For example: NaOH, KOH. It is not applicable for Na_2CO_3, NH_3 and pyridine. In fact, the need to prove the relationship between base and OH ion led to the proposal of the formula NH4OH as base of ammonia in water, the actual formula being NH_3.
4. Arrhenius definition is failed to explain the extent of definition
5. This theory fails to explain the properties of acids and bases in any solvents)like benzene or acetone) or gases, other than water.
6. According to Arrhenius, all salts should produce solutions that are neither acidic nor basic.

❖ However, there are some exceptions to this and Arrhenius theory fails to explain this, e.g

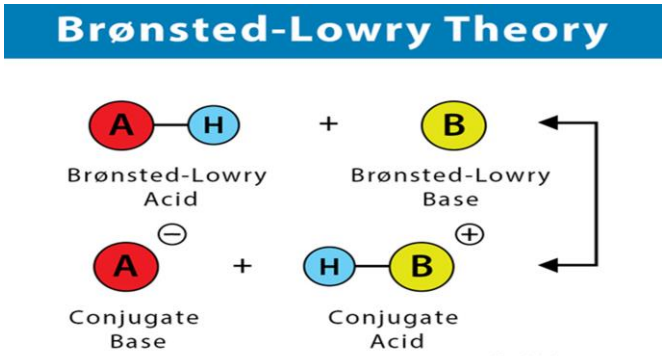
- ✓ Equal amounts of HCL and ammonia yield a slightly acidic solution

- ✓ Equal amounts of acetic acid and sodium hydroxide yield a slightly basic solution

7. According to this idea, solvents play no role in determining the acidic or basic constitution of substances. For instance, hydrochloric acid is weak when dissolved in benzene but strong when dissolved in water.
8. According to this theory, hydrogen ions release in the aqueous solution and remain there, increasing the concentration of hydrogen ions in the solution. However, this is not true because hydrogen can never exist freely as hydrogen ions. It exists as hydronium ion (H_3O^+).
   (i.e. failed to explain the existence of hydrogen ion)

2.2. Bronsted lowery Definition

A somewhat more general approach was that proposed independently in 1923 by the Danish chemist, *J.N bronsted* and the British chemist *T.M lowry*
according to Bronsted lowry definition;



- An acid is proton donor, any substance that can donate a proton, H^+ is an acid which must contain H in its formula; HCl, H_2SO_4, HF, HNO_3, $HClO_4$ are examples of an acids.
- All *Arrhenius* acids are *bronsted Lowry acids*, but the reverse may not be true
- A base is proton acceptor, any species that can accept a proton is base.
- A base must contain a lone pair of electrons to bind the H^+, eg NH3, F^- ,HSO_4^-, HCO_3^-, H_2PO4^-, $HPO4^{-2}$

According to Bronsted lowry definition the only requirement for an acid base reaction is that one species donates a proton and another species accepts it. Thus an acid base reaction is a proton transfer process.
eg. $HCl(g) + H_2O(L) \rightarrow Cl^-(aq) + H_3O^+(aq)$,in such reaction proton is transferred from HCl to H_2O thus :

HCl is proton donor, an acid
H_2O is proton acceptor, a base

The *bronsted lowry* definitions provides a new way to looks at acid-base reactions, because it focuses on the reactant and product in certain reaction. example

$H_2S + NH_3 \rightarrow HS^- + NH4^+$;

In the forward reaction, H_2S act as acid by donating proton, H^+ to NH_3, which act as a base

In the reverse reaction, $NH4^+$ act as acid while HS^- act as a base. Notice that, in forward reaction, the acid H_2S, become a base, HS^- and the base NH3, become an acid NH_4^+. According to *bronsted t*erminology, H_2S and HS^- are conjugated acid-base pair.

i.e. HS^- is the conjugated base of acid, H_2S Hence, when acid loses a proton, form a conjugated base.

similarly, NH_3 and $NH4^+$are a conjugated acid - base pairs. NH_4^+ is the conjugated acid of the base NH_3, hence, when a base accept a proton, it forms a conjugated acid of base. A conjugate acid, base pairs consist of two species that differ from each other by the presence of one H^+ unit. i.e.

- the conjugated base of the pair has one fewer H and one more negative charge than the acid
- The conjugated acid of the pair has one more H and one fewer negative charge than the base.

A *Bronsted-lowry* acid-base reaction occurs when an acid and a base react to form their conjugate base and conjugate acid respectively;

$$Acid_1 + Base_2 \leftrightharpoons Bas_1 + Acid_2$$

- ✓ Base1 is the conjugated base of Acid1
- ✓ acid 2 is the conjugated acid of base2

Examples, in the following reactions, label each species as an acid or a base and show the conjugated acid-base pairs.

A. $H_2PO_4^-(aq) + CO_3^{-2}(aq) \leftrightharpoons HCO^{-3}(aq) + HPO_4^{2-(}aq)$
B. $H_2O(L) + SO_3^{2-}(aq) \leftrightharpoons OH^-(aq) + HSO_3^-(aq)$
C. $HCOOH(l) + CN^-(aq) \rightleftharpoons HCOO^-(aq) + HCN(l)$

Acid	Base	Conjugated acid	Conjugated base	Conjugated Acid-Base pair
$H_2PO_4^-$	CO_3^{2-}	HCO_3^-	HPO_4^{2-}	$H_2PO_4^-/HPO_4^{-2}$ CO_3^{-2}/HCO_3^-
H_2O	SO_3^{2-}	HSO_3^-	OH^-	H_2O/OH^- SO_3^{2-}/HSO_3^-
HCOOH	CN^-	HCN	$HCOO^-$	$HCOOH/HCOO^-$ CN^-/HCN

Limitations of Brønsted–Lowry Theory

- ❖ Brønsted–Lowry Theory concept **cannot explain the reactions occurring in non-photonic solvents** such as $COCl_2$, SO_2, N_2O_4, etc.
- ❖ It cannot explain reactions of acid and basic oxides which can take place even in the absence of solvents.
- ❖ It does not explain the reactions between acidic oxides and basic oxides. $CaO + CO_2 \rightarrow CaCO_3$

2. 3. Lewis concept of acid and base

G.N Lewis an American chemist suggested a broader acid-base definition in 1938. According to lewis concept

An Acid is a species with avacant orbital capable of accepting an electron pair

A Base a species with an excess of electron which can donate an electron pair to form coordinative covalent bond.

In other word, Lewis acids are electron pair acceptor

Lewis bases are electron pair donor

Example :$BF_3+NH_3 \rightarrow BF_3NH_4$; BF3 is Lewis acid(accept electron) while NH_3 is Lewis base (donate electron)

The lewis theory, thus, extends the range of base reaction to include those that don't involve proton transfer.

Aproton itself is *lewis* acid. Lewis concept is the most general one

NB; Substance that are classified as *Bronsted Lowery* base are also bases according to Lewis system. Chemical substance that can included the following Lewis concepts

I. Molecules or atoms that have vacant orbital Or an incomplete octet of electrons are acid e.g. BF_3, $AlCl_3$
II. Many simple cat ions are Lewis Acids. example, Fe^{3+} has vacant orbital and reacts strongly with cyanide ion to form the ferric cyanide ion, $Fe^{3+} + 6C\equiv N \rightarrow [Fe(CN)6]^{3-}$. Thus Fe^{3+} has a vacant orbital that accept pair of electrons donated by CN^-
III. Some compounds with multiple bonds can behave as lewis acid
IV. Some metal can function as acids in the formation of compound such as carbonyls, which are produced by the reaction of metal with carbon monoxide is lewis acid $Ni + 4CO \rightarrow Ni(CO)_4$
V. Compounds that have central atoms capable of expanding their valance shells are

Lewis Acid e.g. $SiCl_4$, PF_5, SbF_5

$SiCl_4 + 2Cl^- \rightarrow [SiCl_4]^{2-}$

$PF_5 + F^- \rightarrow [PF_6]^-$

Any species which is negatively charged or having lone pair are Lewis base e.g. NH_3, F^-, Cl^-, H_2O

The following table will summarize the three definitions of acid and base

Types of Definition	Bases of definition	Description
Arrhenius definition	Aqueous dependent	*Acid* increase concentrations of H^+ *Base* increase concentration of OH^-
Brondted Lowry definition	proton transfer	*Acid* are proton donor *Base* are proton acceptor
Lewis defination	Electron transfer	*Acids* are e- pair acceptor *Bases* are e- pair donor

2. Acid-Base equilibrium and strength

Auto-ionization and Ion-product of water

Auto-ionization is the reaction process occurs between two the same species one act as An acid while other act as a base.

The familiar example for such rxns are

$H_2O(l) + H_2O(l) \leftrightharpoons H3O^+(aq) + OH^-(aq)$

$NH_3(l) + NH_3(l) \leftrightharpoons NH_4^+(aq) + NH_2^-(aq)$

For the reaction ; $H_2O(l) + H_2O(L) \leftrightharpoons H_3O^+(aq) + OH^-(aq)$, according to Bronsted lowry theory, the reaction is viewed as a proton transfer from one water molecule to other. Since water act as both acid & base called amphoteric. The reaction is reversible, and H_2O, H_3O^+ and OH^- are at equilibrium. In pure water at 25^0C, $[H^+] = [OH^-] = 1 \times 10^{-7}$. These are low concentration and tell us that very few H_2O molecule are ionized and that the equilibrium lie to the left at equilibrium. the product of $[H^+]$ and [OH-] equals constant called ion product constant for water Kw

i.e. $2H_2O(l) \leftrightharpoons H_3O^+ + OH^-$

$Kc = [H3O^+][OH^-]/[H_2O]$

$Kc\,[H_2O]^2 = [H3O^+]\,[OH^-]$

Since, pure liquid H_2O has constant Concentration

$Kc.\ K = [H_3O^+]\,[OH^-]$

$Kw = [H_3O^+]\,[OH^-]$

$[OH\text{-}] = [H3O^+]$

$1 \times 10^{-14} = [OH^-]\,[OH^-]$

$1 \times 10^{-14} = [OH^-]^2$

$[OH^-] = 1 \times 10^{-14}$

$[OH^-] = [H3O^+]$

$[H3O^+] = 1 \times 10\text{-}7$

- $Kw = [H_3O^+]\,[OH^-]$

At 25^0C, $Kw = 1 \times 10^{-14}$ and $[H_3O^+]\,[OH^-] = 1 \times 10^{-14}$ for dissociation of pure water

The value of Kw applies to all aqueous solution at 25^0C when an acid is added to water, the $[H^+]$ increase. Therefore the $[OH^-]$ must decrease in order for Kw to remain constant. i.e in acidic solution, $[H^+] > [OH^-]$, similarly when a base is added to water and $[OH^-]$ increase the $[H^+]$ must decrease for the same reason.

Acidic, basic and neutral solutions are characterized as follows

Neutral solution	*Acidic Solution*	*Basic Solution*
$[H^+] = [OH^-]$	$[H^+] > [OH^-]$	$[OH^-] > [H^+]$
$[H^+] = 1 \times 10^{-7}$	$[OH^-] < [H^+]$	$[OH^-] > 1 \times 10^{-7}$
$[OH^-] = 1 \times 10^{-7}$	$[H^+] > 1 \times 10^{-7}$	$[H^+] < 1 \times 10^{-7}$

For two different acids of equal concentrations, the stronger acids produces, the greater quantity of hydrogen ion. Thus the concentration of hydrogen ion is a measure of relative strength of two acid similarly, stronger base will contain a large concentration of hydroxide ion than the solution of weaker base if both solution are of equal concentrations.

3. The PH and POH scale

3.1. The PH scale

The Measurement and Meaning of Hydrogen Ion Concentration in Enzymatic Processes

- PH stands for power of hydrogen
- It is defined as the negative logarithm of hydrogen ion concentration
- The concentration of hydrogen ion in a solution can be expressed interms of pHscale . Recall that the logarithm of a number is the power to which 10 must be raised in order to equal the number

e.g. $100 = 10^2$ $log 100 = 2$

first find the PH of neutral solution

in pure water at 25^0C; $[H^+] = 1 \times 10^{-7}$

PH = -log $[H^+]$, PH = -log(1×10^{-7}) = 7

❖ The PH of neutral solution is 7

Likewise, for an acidic solution where, for example the $[H^+]$ is 1×10^{-5} M the PH is 5,

PH = -log (1 x 10-5) = -(-5)=5

Therefore for acidic solution PH<7

3.2. The POH scale

POH-stands for power of hydroxyl

The concentration of OH^- describe POH

POH is defined as the negative logarithm of hydroxide ion POH= $-log[OH^-]$

For a basic solution where, for example the $[OH^-]$ if 1 x 10-4, the POH is 4,

POH= $-log[OH^-]$ = -log (1×10^{-4})= -(-4) = 4

For therefore a basic solution POH <7

It is important to notice that a change in PH of one unit corresponds to a 10 fold change in $[H^+]$. As $[H^+]$ drops from 10^{-8} to 10^{-9}M, for instance PH changes from 8 to9.

A change of 2.0 PH units corresponds to 100 fold changes in $[H^+]$ never say

"A PH of 2 is twice acidic as PH of 4". It is really 100 times more acidic

e.g. the PH values of two solutions A and B are 2 and 4 respectively, by how much factors the $[H^+]$ in solution A is greater than solution B?

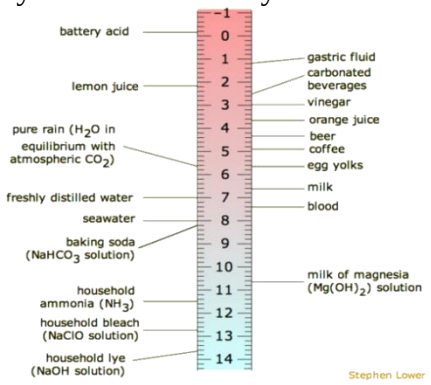
solution A	Solution B
PH=2	PH= 4
$[H^+] = 10^{-PH}$	$[H+] = 10^{-PH}$
$[H^+] = 10^{-2}$	$[H+] = 10^{-4}$

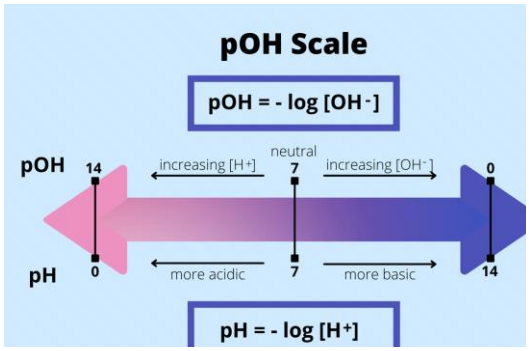
Therefore ,the concentration of hydrogen ion in solution A (1×10^{-2}) is greater than B($1x10^{-4}$) by factor of 100.

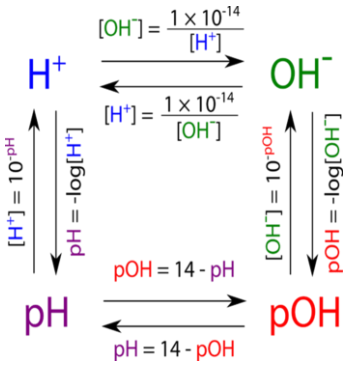
3.3. The Effective Range of the pH Scale

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14, but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of

concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar.
Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0 to 14 provides sensible (but not absolute) "bookends" for the scale. One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar.







- If pH >7, the solution is basic. The pOH should be looked in the perspective of OH^- instead of H^+. Whenever the value of pOH is less than 7, then it is considered basic. And therefore there are more OH^- than H^+ in the solution.
- At pH 7, the substance or solution is at neutral and means that the concentration of H^+ and OH^- ion is the same.
- If pH < 7, the solution is acidic. There are more H^+ than OH^- in an acidic solution.
- The pH scale **does not** have an upper nor lower bound.

3.4. The relationship of PH and POH

The ion product constant of water is applicable to all aqueous solutions.

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

$K_w = [H^+][OH^-] = 1 \times 10^{-14}$ at 25^0C, take $-log$ in both side

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

$-\log K_w = (-\log[H^+] + (-\log[OH^-]))$,

by mathematical principles log xy= log x + logy

$log\ kw = Pkw$, $-log\ [H+] = PH$, $-log[OH-] = POH$, $-log\ (1x\ 10^{-14}) = 14$

$Pkw = PH + POH = 14$

4. Strength of acids and Base

4.1 Strong acid & strong base

- The sronger the acid, the more completely it ionizes in water producing, $H_3O^+(aq)$ and anion

Strong acids are strong electrolytic and are assumed to ionize completely in water e.g. $HBr + H_2O \rightarrow H_3O^+ + Br^-$

The seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.

•These are, by definition, strong electrolytes and exist totally as ions in aqueous soluti on (i.e.,they are 100% ionic in solution)

•For the monoprotic strong acids, the concentration of $H_3O^+$is equal to the concentrat ion of the acid: $[H_3O^+]$ = [acid]

Like a strong acid, a strong base is one that ionizes completely in aqueous solution e.g. $KOH(aq) + H_2O(l) \rightarrow K^{+(}aq) + OH^-(aq)$

- In water, some acids are better proton donors than other and some bases are better proton acceptor than others

4.2. Weak Acids and Weak base

Weak Acids are that is only particularly ionized in water HF is typically weak acid in water. Weak acids are much less than 100% ionized in water (usually 5% ionic or less) One of the best known weak acids is acetic acid, CH_3CO_2H

$HF(aq) + H_2O(l) \leftrightharpoons H_3O+ (aq) + F^-(aq)$

Since HF is ionized partially, the concentration of HF molecules is much greater than the concentration of H^+ (aq) and F^-(aq) weak acid and base ionize a few percent.

$NH_3(aq) + H_2O(l) \leftrightharpoons NH_4^+(aq) + OH^-(aq)$ Generally, strong acid and strong base ionize nearly 100% weak acid and weak base ionize partially.

4.3 Strength of conjugated Acid-Base

According to Bronsted lowry theory, the strength of Acid and base are related to the strength of its conjugate base and acid respectively.

- The stronger the acid, the weaker its conjugate base
- The stronger the base, the weaker its conjugate acid
- The weaker the acid, the stronger its conjugated base
- The weaker the base, the stronger its conjugate Acid

Let us compare the ionization of HCl, strong acid and HF a weak acid,

$HCl(aq) + H_2O(l)$ H3$\rightarrow O^+(aq) + Cl^-(aq)$

$HF(aq) + H2O(l) \leftrightharpoons H3O^+(aq) + F^-(aq)$

Chloride ion is the conjugate base of HCl here we see that it must be a very weak base because it has no tendency to accept a proton from H_3O^+ in the reverse reaction In the ionization of a weak acid HF, the reverse reaction occurs to a much greater extent than Cl^-. The conjugated bases of strong acid has no measurable base strength when comparing the strength of different acids we see that; As acid strength increase, the strength of conjugate base decrease similarly as the strength of base increase the strength of its conjugated acid decrease.

e.g. In acid strength, $HClO_4 > HCl > HNO_3 > H_3O^+ > HF > HNO_2 > HCN > H_2O$

conjugate base strength; $ClO_4^- < Cl^- < NO_3^- < H_2O < F^- < NO_2^- < CN^- < OH^-$

5. Conjugate Pairs

- The*Arrhenius* definition of an acid is a species that produces a proton (H^+) in water.
  A base is a species which produces a hydroxide ion (OH^-) in water.

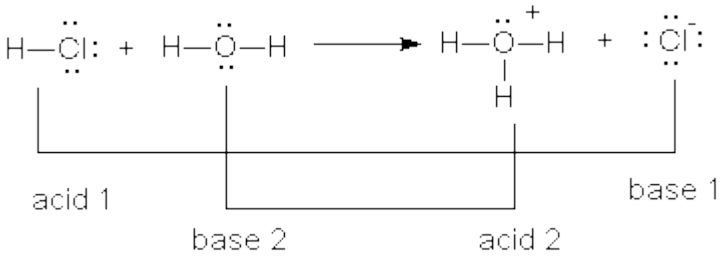
- These only describe reactions taking place in water and there are many other solvents available, so a more general definition is required.
- According to the *Brønsted* definition, an acid is a substance capable of donating a proton, and a base is a substance capable of accepting a proton.
- This means that all Brønsted bases must possess a *lone pair of electrons*, in order to form a bond to the proton they are accepting.

This is shown in the reaction between hydrochloric acid (HCl) and water.



The proton leaves HCl, leaving both bonding electrons on the Cl, forming the Cl^- ion, with four lone pairs.
The proton bonds to the water molecule, using one of the lone pairs, producing H_3O^+.

An extension of this definition is the concept of *conjugate acid-base pairs*, which are defined as an acid and its conjugate base or a base and its conjugate acid.
They differ from each other by a proton.
These pairs are identified in the HCl water reaction:



HCl is an acid because it can lose a proton. When it loses that proton it becomes Cl^-, a base, with four lone pairs of electrons. It is a base because it has lone pairs that can potentially bind a proton.

Water is behaving like a base in this reaction. It has two lone pairs of electrons. One lone pair is used to bond the proton from HCl, forming H_3O^+, which is an acid, since it can potentially lose a proton.
HCl is an acid and Cl^- is its conjugate base. They are one proton different from each other.
In this example, water is a base and H_3O^+ is its conjugate acid. They differ by one proton.

5.1. Strong Acids

Some acids are better proton donors than others.

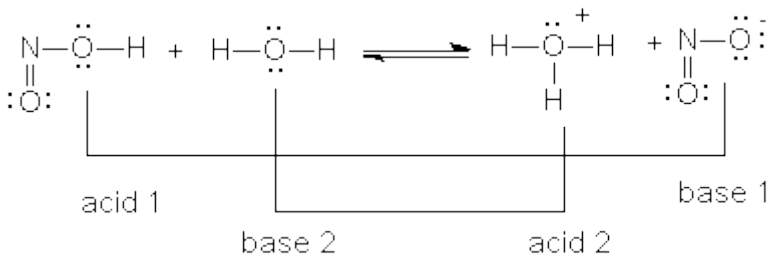
The strength of an acid can be measured by the fraction of the acid molecules that undergoes ionization (loses a proton).

Strong acids are those that ionize completely in water, that is, they give up their protons completely.
In the example above, HCl is a strong acid.
Its reaction with water goes to completion.
It is not an equilibrium process.
HCl is converted completely to Cl^- and H_3O^+
This is because the conjugate base, Cl^-, has virtually no tendency to gain a proton, so there is no reverse reaction.
The stronger the acid, the weaker its conjugate base.
H_3O^+ is the strongest acid that can exist in aqueous solutions.
Acids stronger than H_3O^+ react completely with water to form H_3O^+ and their conjugate bases.
These strong acids are HCl, HBr, HI, and the oxyacids, HNO_3, $HClO_4$ and H_2SO_4.
Their *conjugate bases*, Cl^-, Br^-, I^-, NO_3^-, ClO_4^- and HSO_4^- have no activity as bases, no tendency to gain protons.

These are not equilibrium reactions.

5.2. Weak Acids

Weak acids are those that only partly dissociate in water.
Nitrous acid, HNO_2 is an example.



In its reaction with water, there is an equilibrium mix of all of the species, HNO_2, H_2O, NO_2^- and H_3O^+.
The stronger of the two acids is H_3O^+, which the strongest acid that can be present in water.
Because H_3O^+ has a stronger tendancy to lose a proton than HNO_2 the *reverse* reaction is favored in this equilibrium.
This means that the equilibrium constant ([products]/[reactants]) for this reaction will be small.

The conjugate base of this weak acid, NO_2^- , is a fairly strong base, with some ability to gain protons.
This is what drives the reverse reaction.
The weaker the acid, the stronger its conjugate base.
An equilibrium constant, K_a, can be used to describe this process.

$$K_a = \frac{[NO_2^-]\,[H_3O^+]}{[HNO_2]} = 4.0 \times 10^{-4}$$

It is a number much smaller than 1, meaning that the reverse reaction is favored and that relatively little product will be formed. It will follow all of the rules that we developed for equilibrium processes (Le Châtelier).

- Water does not appear since it is a pure substance whose concentration cannot change.
- This is the value of the equilibrium constant, K_a, at 25°. Its value will change with temperature, depending on the sign of ΔH.
- If the product, NO_2^- is added to water, making Q > K, the reverse reaction will proceed, as predicted by LeChâtelier, to form more reactant, HNO_3.

Here is a link to a list of the K_a values for a number of weak acids.
The larger the equilibrium constant, the more complete the dissociation of the acid, the stronger the acid.
We can think of proton transfer reactions as being governed by the relative ability of two acids to transfer protons. This can be shown by the reaction between an acid, HA and water.



We can compare the strength of $acid_1$ and $acid_2$. If HA is a stronger acid than H_3O^+, the HA will transfer its proton to water more effectively than H_3O^+ will transfer its proton to A^-. The equilibrium will lie far to the right, so far, that it will no longer be considered an equilibrium process. This is the case with the "strong acids".

If HA is a weaker acid than H_3O^+, the reverse reaction will have a stronger tendency to take place, an equilibrium will be established. This happens with all acids, except those defined to be strong acids.
As demonstrated in the examples, above, the H^+ ion (proton) released by the acid is hydrated in aqueous solutions. The reaction between water and H^+ is usually represented as:

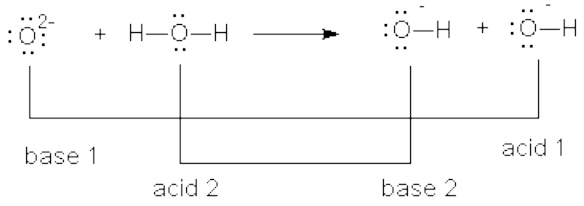
$$H^+ (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq)$$

The proton may be associated with more than one water molecule. It can be written as H^+, H_3O^+or $H_7O_4^+$, to show the high degree of hydrogen bonding. We will usually refer to it as H^+, but writing it as H_3O^+ demonstrates that water is a Brønsted base (proton acceptor).

5.3. Strong Bases

The strongest acid that can exist in water is H_3O^+.
The strongest base that can exist in water is OH^-.
There are relatively few common strong bases.
The most common strong bases are the soluble ionic hydroxides of the alkali metals (Group I) and the alkaline earth metals (Group II), like NaOH, KOH and $Ca(OH)_2$. These species simply dissolve in water to create the OH^- ion.

Strongly basic solutions are also created by substances that react with H_2O to form OH^-.The most common of these is the oxide ion, O^{2-}.



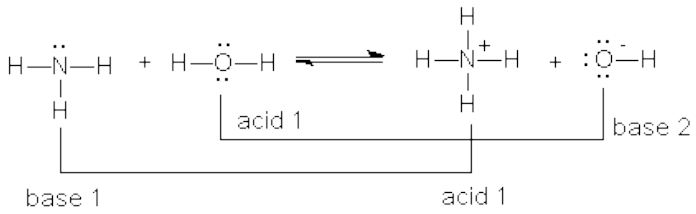
$O^{2-}$is a stronger base than OH^- so the reaction will proceed completely to the right.

It is interesting to note that in this reaction one OH^- is labelled as a base and the other as an acid.
This is completely compatible with the Brønsted definistion of acid acids and bases:
acids lose protons, H^+. OH^- could, in theory, lose a protons to form the oxide ion, O^{2-}, and
bases have lone pairs that can bind a proton. OH^- has two lone pairs that can bind a proton to form water.
Species, like OH^- that can gain or lose a proton are said to be *amphoteric*.
In the base reaction with the oxide ion, water behaves like an acid. In the acid reactions, it behaves like a base. Water is also amphoteric, since it can lose protons (acid) or gain protons (base).

5.4. Weak Bases

Most weak bases are analogs or ammonia, NH_3. One, two or all three of the H on ammonia can be replaced by organic groups, composed of C and H.

Shown below is the reaction between ammonia, NH_3, and water. Ammonia is a base because of the lone pair of electrons on N, which can form a bond with a proton.



The strongest acid that can exist in aqueous solutions is H_3O^+.
The strongest base that can exist in aqueous solutions is OH^-.
In the reaction between ammonia, NH_3 and water, ammonia is a base that accepts a proton from water to form the ammonium ion, NH_4^+, its conjugate acid.
As shown, this is an equilibrium reaction. Ammonia is a much weaker base than OH^-, so the equilibrium will lie to the left and not much product will form.

The equilibrium constant for this type of reaction is called the K_b and is given by:

$$K_b = \frac{[BH^+]\,[OH^-]}{[B:]}$$

The larger the value of K_b, the stronger the base, the more OH^- will be formed at equilibrium.

6. Factors that affect the strength of acid and Base

The strength of any acids & base are decided by different factors concentration of H^+, OH^- ,PH ,POH, percent of ionization, Ka & Kb are mostly familiar factors.

6.1. Concentration of Hydrogen ion and Hydroxide ion

Strong acid are ionize sufficiently, increase the concentration of hydrogen ion. i.e. the strong the acid the higher $[H^+]$
The stronger the base the higher $[OH^-]$
So, for strong acid $[H^+] >>> [OH^-]$ and vice versa

6.2. PH and POH

PH and POH are the quantitative measure of Acid & base strength.
The lower PH value implies the stronger the acid ,The higher PH value implies that the weaker the acid so, for strong Acid PH<< POH
For strong base PH >> POH

6.3. Percent of ionization

The strength of acid and base are also reflected in its percent ionization. It defined as

Percent ionization= $\frac{concentration\ of ionized\ acid\ /base}{initial\ concentration\ of acid/base}$ X 100%

the concentration of H^+ ions (or that of A^- ions) at equilibrium thus

% of ionization= $\frac{[H+]}{[HA]}$ X 100%

The higher percent of ionization, the stronger the acid/base

The lower percent of ionization, the weaker the acid/Base

6.4. Ionization constant Ka & Kb

Ionization constant: weak acid and weak base are ionized only small extent in an aqueous solution. In both case, the ionization reaction is reversible and equilibrium is reached. For a hypothetical weak Acid, HA, $HA + H_2O \leftrightharpoons A^- + H_3O^+$ at equilibrium, all [HA], $[A^-]$, $[H_3O^+]$ are there

$$Ka= \frac{[A-][H3O+]}{[HA]}$$

For strong acid the acid ionize sufficiently the value of numerator > denominator so Ka become large and vice versa. Generally, for higher Ka and Kb value the stronger acid and base respectively.

The Kb of a base is related to ka of its conjugated Acid the Ka and Kb for any conjugate acid-base pair are always related by the equation kw=Ka+Kb

For hypothetical reaction, $HA(aq) + H_2O (l) \leftrightharpoons A^-(aq) + H_3O^+(aq)$

A^- Is the conjugated base of a weak acid HA undergo, Hydrolysis reaction:

*$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^- (aq)$

*$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

$$Kb= \frac{[HA][OH-]}{[A-]}$$

$$Ka.Kb= \frac{[H3O+[A-]}{[HA]} \text{ X } \frac{[HA][OH-]}{[A-]} = \boldsymbol{[H_3O^+]\,[OH^-] = Kw}$$

Kw= Ka.Kb …..take log in both side

-log(Kw= Ka.Kb) , $-\log Kw= (\log Ka) + (-\log Kb)$

$$\boldsymbol{Pkw= Pka+ PKb}$$

The higher Ka values,the lower PKa implies the stronger the acid and vice verse

The higher Kb values, the lower Pkb implies the stronger the base and vice versa

7. Prediction of Direction of Reactions:

Think of the reaction as a competition between the bases for the H+ - the stronger base will win!!

Stronger acid/base pair → weaker acid/base pair is the direction the reaction will favor

Example 2: The pH of a 0.010 M solution of formic acid is 2.92. What are K_a and percent ionization?

	$HCOOH\ (aq)$	⇌	$H^+\ (aq)$	+	$HCOO^-\ (aq)$
[Initial]	0.010 M		0		0
[Change]	-x		+x		+x
[Equil]	(0.010-x)		x		x

$$K_a = \frac{x^2}{(0.010 - x)} \qquad pH = -\log [H^+] = -\log (x) = 2.92 \qquad x = 0.00120$$

$$K_a = \frac{(0.00120)^2}{(0.010 - 0.00120)} = \frac{(0.00120)^2}{0.0088} = 1.636 \times 10^{-4} = \boxed{1.6 \times 10^{-4}}$$

Two types: (a) given conc's, find K_a ; (b) given K_a, find conc's.

Method: Write balanced equation and set up reaction table - let x be the unknown conc. Solve. Use quadratic equation if necessary.

Remember: If we are told the pH, we will know $[H^+]$ (i.e. $[H_3O^+]$)

	$HA\ (aq)$	⇌	$H^+\ (aq)$	+	$A^-\ (aq)$
[Initial]	1.0 M		0		0
[Change]	-x		+x		+x
[Equil]	(1.0-x)		x		x

** Ignore H^+ from self-ionization of water unless [HA] is very small **

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{(1.0 - x)}$$

Given x (e.g. from pH), can calculate K_a
Given K_a, can calculate x, and then pH

Example 1: K_a for HNO_2 is 7.1×10^{-4}. What are $[H_3O^+]$, $[NO_2^-]$, and $[OH^-]$ in 0.50 M HNO_2? What is the pH?

	$HNO_2\ (aq)$	⇌	$H^+\ (aq)$	+	$NO_2^-\ (aq)$
[Initial]	0.50 M		0		0
Change	-x		+x		+x
[Equil]	(0.50 -x)		x		x

$$K_a = 7.1 \times 10^{-4} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} \qquad \text{(Assume } x \ll 0.50\text{)}$$

~3.8% of 0.50
∴ good assumption)

$\therefore x^2 = (0.50)(7.1 \times 10^{-4}) = 3.55 \times 10^{-4} \qquad \therefore x = 1.88 \times 10^{-2} = 1.9 \times 10^{-2}$ M (sig. figs!)

$\therefore [H_3O^+] = [NO_2^-] = 1.9 \times 10^{-2}$ M

Name of the Acid	Formula	K_a
Acetic acid	CH_3COOH	1.8×10^{-5}
Ascorbic acid	$C_6H_8O_6$	8.0×10^{-5}
Benzoic Acid	C_6H_5COOH	6.5×10^{-5}
Formic acid	$HCOOH$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hypobromous acid	$HOBr$	2.5×10^{-9}
Hypochlorous acid	$HOCl$	3.0×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}

Base	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	4.0×10^{-10}
Ethylamine	$C_2H_5NH_2$	4.7×10^{-4}
Hydrazine	C_2H_4	1.7×10^{-6}
Hydroxylamine	NH_2OH	1.1×10^{-6}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}

1. **The dissociation constant of an acid HA is 1×10−5. The pH of 0.1 molar solution of the acid will be approximately:**
2. **K_a value for the acid HA is 1×10^{-6}. The value of K for $A^- + H_2O \rightarrow HA + OH^-$ is**

K_a, K_b and percent ionization: Practice

1. Determine the K_a of a weak acid if a 0.300 M solution has a pH of 1.94.
2. What is K_b for N_2H_4 (hydrazine) if a 0.500 M solution has the following concentrations at equilibrium? $[N_2H_4] = 0.499$ M, $[OH^-] = 1.23 \times 10^{-3}$M, $[N_2H_5^+] = 1.23 \times 10^{-3}$
3. A solution of 1.00 M HA in water ionizes 2.00 %. Find K_a.
4. A 0.250 M solution of a weak acid is 1.75 % ionized. Determine the pH and K_a of this solution.
5. What is more acidic, a solution 0.100 M boric acid or a 0.100 M solution of nitrous acid? (see data booklet)
6. C_5H_5N is a weak base. A 0.125M solution of this base has a pH of 9.10. Find the K_b.

7. Benzoic acid (C_6H_5COOH) is a weak acid. If K_a of benzoic acid is 6.46×10^{-5} then find: a) the pH of a 0.0125 M solutionb) the % ionization of this solution
8. What is the percent ionization in 0.0200 M HClO? $K_a = 3.16 \times 10^{-8}$
9. What is the ethanoate ion concentration in a 0.0178 M solution of ethanoic acid?
10. What would be the hydrogen ion concentration in a 0.884 M solution of

8. Common ion effect

- Common ion effect is shifting of ionic equilibrium caused by the addition of absolute that provides an ions that takes part in equilibrium
- Consider the solution of acetic acid, CH3COOH
- $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + H_3O^+(aq)$

Suppose we add strong electrolyte substance which contains CH_3COO^-, CH_3COONa

$CH_3COOH(aq) + H_2O(l) \leftrightharpoons CH_3COO^-(aq) + H_3O^+(aq)$

$Ch_3COONa \rightarrow CH_3COO^-(aq) + Na^+$

on addition of CH_3COONa, the concentration of acetate ion increase as a result it consumes more $H3O^+$. According to ***lechatlier*** principle the equilibrium lies to the left as a result dissociation extent of Acetic acid decrease. This suppression of the dissociation of acetic acid is called *common ion effect*.

For the dissociation of formic acid $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$ what is the effect of adding strong acid, HCl on dissociation reaction

$HCOOH + H2O \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$

$HCl(aq) \rightarrow H_3O^+(aq) + Cl^-$

* H_3O^+ is common ion

So on addition of HCl

- $[H_3O^+]$ increase
- PH decrease
- Acidity increase

***** What is the effect of adding NH_4Cl to dissociation of NH_3?

$NH_3(aq) + H_2O(l) \rightleftharpoons NH4+(aq) + OH^-$

$NH4Cl(aq) \rightarrow NH4+ + Cl^-$, So on addition of NH4Cl

- $[NH_4^+]$ increased
- $[OH^-]$ decreased, more OH^- decreased more OH^- consumed

- Equilibrium shift to left
- POH increase
- PH decrease
- Acidity increase
- Basicity decrease

9. Buffer solution

Any solution like the preceding one, which contains both weak acid (HF) and its conjugate base (F^-) has ability to neutralize added strong acid and bases with very little change in PH such solution is called *buffer solution*. Because it resists significant changes in the PH value a buffer must contains an acid to react with any OH^- ions that may be added and a base to react with any added H^+ ions. Buffer solution is prepared from weak Acid and its conjugated base and weak base and its conjugate acid

A buffered solution is one that resists a change in its pH when either hydroxide ions or protons (H_3O^+) are added. Very little change in pH is witnessed even when a strong acid or base is added.

Buffered solutions are solutions of weak acids or bases containing a common ion.The pH calculations on buffered solutions are the same as last chapter.

When a strong acid or base is added to a buffered solution, do the stoichiometric calculation first.

The components of a buffer are a conjugate acid-base pair.

- Buffer solution is prepared from weak acid and its salt or weak bas with its salt
  e.g. NH_3/NH_4Cl
  - CH3COOH/CH_3COONa
  - HF/NaF

When asmall amount of strong acid is added to buffer, it is neutralized by the weak base. Also when a small amount of strong base is added to buffer it is neutralized by the weak base. E.g. In HF/F^- buffer for example the following neutralization reactions takes place.

- On addition of strong base, the neutralization reaction takes place as follows
- $OH^- + HF \rightarrow H_2O + F^-$
- On addition of strong acid the neutralization reaction is $H^+ + F^- \rightarrow HF$

In order to be most effective the amount of weak acid and weak base used to prepare the buffer must be considerably greater than the amount strong acid or strong base that may be added later.

Buffer capacity refers to the amount of acid/base that can be neutralized by a buffer solution before its PH is appreciably affected.

10. How Buffers Work

10.1 PH of buffer solution

To calculate the PH of buffer requires that the concentration of the weak acid (such as HF) and a soluble salt of a weak acid (NaF) be substituted into the ionization constant expression for a weak acid.

For a solution to be buffer ,the ratio of base concentration to the acid concentration soud not be less than 0.1 or more than 10.this conclusion follows from handerson Hasselbalch equation ,for a concentration ranging from 1:10 to 10:1implies a pH also ranging

$PH=Pka+\log 10^{-1}$ =pka-1 , pH=pka+log10=pka+1

The PH of buffer solution calculate using ***Hhanderson- Hasselbalch*** equation to derive this equation let us consider a buffer made up of weak acid HA and its conjugated base A^-

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

$Ka = \frac{[H3O+][A-]}{[HA]}$, $[H_3O^+] = Ka \frac{[HA]}{[A-]}$ .....take -log in both side

$-\log[H_3O^+] = -log ka - \log \frac{[HA]}{[A-]}$)

$PH = Pka + \log \frac{[A-]}{[HA]}$

More generally, $PH = Pka + \log \frac{[base]}{[salt]}$ .....Handerson hasselbalch equation

$A(aq) + H_2O(l) \rightleftharpoons HA + OH^-(aq)$

$Kb = \frac{[HA][OH-]}{[A-]}$, $[OH^-] = Kb \frac{[A-]}{[HA]}$.....take –log

$-\log [OH^-] = -\log kb + -\log \frac{[A-]}{[HA]}$

$POH = PKb + \log \frac{[HA]}{[A-]}$

More generally, $POH = Pkb + \log \frac{[Acid]}{[Base]}$

When [Acids] = [Base],

PH = PKa + log 1 , POH= PKb + log 1

PH = Pka ***POH= Pkb***

This phenomena is called maximum buffer capacity (when PH= Pka & POH= Pkb)

e.g. what ratio of $[F^-]$ to [HF] would you use to make a buffer of PH= 2.85? solution use *handerson Hassalbach* equation

$PH = Pka + \log \frac{[conjugate\ bases]}{[acids]}$

10.2 physiological buffer

Biological fluids ,such as human blood ,are usually solutions ;the control of pH is vital to proper functioning of these fluids.the oxygencarrying function of blood depend on its pH. the normal human blood is maintained very near pH of 7.4. If the PH were to change by tenth of unit ,the capacity of the blood carry oxygen would be lost .human blood contains H_2CO_3 and HCO_3^- as other well as other conjugate acid base pair. The two important characterized of buffer are its PH and buffer capacity. the normal HCO_3^- to H_2CO_3 in the blood is 20:1. When the concentration of HCO_3^- increase relative to H_2CO_3,blood pH rises. If this increase is sufficient to cause blood pH to excess the normal range, the condition is called *acidosis. When a person is burned, blood plasma leaks from the circulatory system into injured area, produce swelling (edema)and reduce the blood volume . If the burned are is large, this loss of blood volume may be sufficient to reduce blood flow and oxygen supply to all the body tissues.lack of oxygen,in turn causes the tissues to produces an excessive amount of*

lactic acid which enters the blood stream reacts with bicarbonate ion to produce H2CO3,and shift the ratio of HCO_3^- to H_2CO_3 to a .to lower value . to minimum the consequent decrease the pH called metabolic acidosis

10.3. Buffer capacity

Buffer capacity represents the amount of protons or hydroxide ions the buffer can absorb without significantly changing the pH.

The pH of a buffered solution is determined by the ratio of [A-]/[HA].

The capacity of a buffered solution is determined by the magnitudes of [HA] and $[A^-]$.

The most effective buffers have equal concentrations or weak acid to conjugate base or

The most effective buffers have equal concentrations or weak acid to conjugate base or $[A^-]/[HA] = 1$

$pH = pK_a + \log([A^-]/[HA])$

$\log(1) = 0$

The pK_a of the weak acid used should be as close as possible to the desired pH of the buffered solution.

The pKa of the weak acid used should be as close as possible to the desired pH of the buffered solution.

Any solution is said to be buffere iff the pH value is in the range of P^H_{-1} to P^H_{+1}

10.4. Preparation of buffer solution

In the preparation of a buffer solution with a given PH,we select aweak acid or weak base with a pka or pkb that is within one pH unit of desired pH.

Buffer solution is prepared from weak Acid and its conjugated base and weak base and its conjugate acid

11. Diprotic and polyprotic acids

Acids are classified into three categories depends on the no of ignitable proton

Monoprotic- Acid with only one dissociable proton

e.g. CH_3COOH, HCl, HNO_3

Acetic acid contains four hydrogen atoms per molecules but it is still monoprotic because only one of them is ionized in solution. The atoms bonded to the carbon atoms do not ionize because the electro negativity difference between C and H is not greater enough to produce sufficient positive charge on the hydrogen atoms.

Diplopic Acid- Acids that contains two ionizable Hydrogen atoms e.g. sulphuric acid (H_2SO_4) is a diprotic acid e.g. H_2SO_4, H_2CO_3, H_2C_2O

Poly protic acid- Acid which contains three or more ionizable proton

The ionization reaction for diprotic & polyprotic acids occurs in step wise the conjugate base in the first step becomes the acid in the second step of ionization.

•Have more than one ionizable H

•A common polyprotic acid is sulfuric acid, H2SO4

•The dissociation of a polyprotic acid is written to take place in steps:

H_2SO_4- (aq) + H_2O (l)→HSO_4^-(aq) + H_3O^+(aq) HSO_4^-(aq) + H_2O (l)→SO_4^{2-} (aq) + $H_3O^{+(}$aq)

•For a weak acid or weak base, all the ions shown in the equation are present in solution

step wise dissociation of H_3PO_4 is as follows

1. $H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ ka1
2. $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$ Ka2
3. $HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$ ka3

This example is typically Ka1 > Ka2> Ka3

It is more difficult to remove an H^+ molecule such as H^3PO4.

The K overall= Ka1× Ka2× Ka3

12. The Leveling and differentiating effect

•The pH scale ranges from 0 to 14 *Can an acid or base have a pH lower than 0 or higher than 14?

•When a strong acid, such as HCl, is dissolved in water, it reacts to form H_3O^+in the following reaction:

$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

•Any acid that is stronger than H_3O^+reacts with H_2O to form H_3O^+; therefore, no acid can be stronger tha n H_3O^+ in H_2O.

•In the same way, a base which is stronger than the conjugate base of water,such as sodium oxide, will r eact with water to give the weaker base which is the hydroxide ion,

$Na_2O(s) + H_2O \rightarrow 2OH\ (aq) + 2Na^+(aq)$

Note: The actual base here is the oxide ion since the sodium ion is an extremelyweak acid •All bases wh ich are stronger than the hydroxide ion will react with water to produce hydroxide ion.

•Although oxide ion, amide ion, ethoxide ion, and methoxide ion are all stronger bases than hydroxide i on, their strength in aqueous solution is leveled to of hydroxide ion.

•Any base that is stronger than OH^-reacts with H_2O to form OH^-

; therefore, no base can be stronger than OH^-in H_2O.

Can the strengths of strong acids or bases can be differentiated?

•The leveling effect operates in any protonic solvent. If a solvent other than water is used, differences b etween strengths of strong acids or bases can be measured.

•In liquid ammonia, for example, all acids are levelled to the strength of the ammonium ion, NH_4^+, and all bases are leveled to the strength of the amide ion,

$NH_2^- + 2\ NH_3 \rightarrow NH_4^+ + NH_2^-$

•Many of the acids which are weak in water act as strong acids in liquid ammonia becaue they are stron ger than ammonium ion.

•Not all of the bases which are strong in water are also strong in liquid ammonia.

•Glacial acetic acid is another protonic solvent in which the leveling effect takes place.

$HC_2H_3O_2 \rightarrow H^+ + C_2H_3O^{2-}$

•Glacial acetic acid can be used to show that hydrogen chloride is a weaker acid than is perchloric acid, since hydrogen chloride behaves as a weak acid in glacial acetic acid.

•Methanol is also a protonic solvent in which some of the acids which are strong (completely dissociate) in water are found partially in molecular form

Generally, a solvent (eg ammonia) which can dissolve certain acids equally is called levelling effect while a solvent(H_2O) which can dissolve certain acids/bases unequally is called differentiating effect.

13. Acid–Base Indicators

Acid-base indicators are weak organic acids or weak organic bases that indicate whether a solution is acidic, basic or neutral.

Let us consider a weak organic acid that is denoted by HIn. In order to be effective indicators, HIn, and its conjugate base, In–, must have different colours. In solution, the acid ionizes as follows: If the indicator is in sufficiently acidic medium, the equilibrium, according to Le Chatelier's principle, shifts to the left and the predominant colour of the indicator is that of nonionized form (HIn). On the other hand, in a basic medium, the equilibrium shifts to the right and the colour of the solution will be that of the ionized form (In–).

Since the indicator molecule is a weak acid, the ratio of HIn and In– is governed by the[H3O+] of the test solution.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging this equation gives

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{K_{In}}$$

To illustrate how an indicator works, consider an indicator that has a yellow colour in acid form (HIn) and a red colour in basic form (In^-). K_{In} is 1.0×10^{-6}. Thus, we have

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{1.0 \times 10^{-6}}$$

The colour we observe in a solution of this indicator depends on the ratio of [HIn] to $[In^-]$. In a solution of pH = 4.0, $[H_3O^+]$ is 1×10^{-4}, so

$$\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = \frac{100}{1}$$

This means that the concentration on HIn is 100 times that of In^-, and so the solution appears yellow.

A solution having a pH of 5, $[H_3O^+] = 1.0 \times 10^{-5}$

$\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-5}}{1.0 \times 10^{-6}} = \frac{10}{1}$, still appears yellow.

At pH of 6.0, $[H_3O^+]$ is 1×10^{-6}, and $\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-6}}{1.0 \times 10^{-6}} = \frac{1}{1}$

Equal concentrations of HIn and In^- give the solution an orange colour.

At pH = 7.0, $[H_3O^+]$ is 1×10^{-7}, and $\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-7}}{1.0 \times 10^{-6}} = \frac{1}{10}$

Here the concentration of In^- is 10 times that of HIn, and so the solution appears red.

Indicators are used in the laboratory for estimating the pH of a solution and to reveal the equivalence point of a titration. Equivalence point is the point at which stoichiometrically equivalent quantities of an acid and a base have been brought together.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underbrace{HIn_{(aq)}}_{\text{red}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underbrace{In^-_{(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, In^-, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60–90% or more) is present as In^-, then we see the color of the In^- ion, which would be yellow for methyl orange. If most is present as HIn, then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[In^-]}{[HIn]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[H_3O^+]}$$

This shows us how the ratio of $[In^-]/[HIn]$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right)$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right)$$

$$-\text{pH} + \text{p}K_a = -\log\left(\frac{[In^-]}{[HIn]}\right)$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[In^-]}{[HIn]}\right) \text{ or } \text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

The last formula is the same as the Henderson-Hasselbalch equation, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH.

In all cases, though, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.