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<u>ACIDS AND BASES</u>

1.1 Introduction

Acids and bases play a central role in chemistry because, with the exception of redox reactions, every chemical reaction can be classified as an acid-base reaction. Our understanding of chemical reactions as acid-base interactions comes from the wide acceptance of the Lewis definition of acids and bases, which supplanted both the earlier Bronsted-Lowry concept and the first definition--the Arrhenius model. Arrhenius first defined acids as proton (H^+) producers in aqueous solution and bases as hydroxide (OH^-) producers. Although this model is intuitively correct, it is limited to substances that include proton and hydroxide groups. Bronsted and Lowry proposed the more general definitions of acids and bases as proton donors and acceptors, respectively. Unlike the Arrhenius conception, the Bronsted-Lowry model accounts for acids in solvents other than water, where the proton transfers do not necessarily involve hydroxide ions. But the Bronsted-Lowry model fails to explain the observation that metal ions make water more acidic. Finally, Lewis gave us the more general definition of acids and bases that we use today. According to Lewis, acids are electron pair acceptors and bases are electron pair donors. Any chemical reaction that can be

represented as a simple exchange of valence electron pairs to break and form bonds is therefore an acid-base reaction.

Acid-base chemistry is important to us on a practical level as well, outside of laboratory chemical reactions. Our bodily functions, ranging from the microscopic transport of ions across nerve cell membranes to the macroscopic acidic digestion of food in the stomach, are all ruled by the principles of acid-base chemistry. Homeostasis, the temperature and chemical balances in our bodies, is maintained by acid-base reactions. For example, fluctuations in the pH, or concentration of hydrogen ions, of our blood is moderated at a comfortable level through use of buffers. Learning how buffers work and what their limitations are can help us to better understand our physiology. We will start by introducing fundamentals of acid-base chemistry and the calculation of pH, and then we will cover techniques for measuring pH. We learn about buffers and see how they are applied to measure the acidic content of solutions through titration.

1.2 Different Types of Acid-Base Concepts and Solvents

Various concepts of acids and bases were developed from time to time, through each concept has its limitation. Latter on, G. N. Lewis listed the following based upon which the definition are to be developed to avoid limitations.

(a) The process of neutralization is a rapid one.

(b) Acid and bases can be titrated one against the other in presence of indicator.

(c) A stronger acid or base can displace a weaker acid or base during reaction.

(d) Acid and bases act as a catalyst in various reaction.

In addition to these Faraday's recognition that the ions carry current and acids-bases are electrolytes, led much foundation for the development of semi-modern and modern concept of acids and bases.

There are six concepts regarding acids and bases, which are discussed below with their advantages and limitations.

1.2.1 Arrhenius Concept or Water Ion Concept

According to Arrhenius "acids are hydrogen containing substances which gives H^+ ions in aqueous solution whereas bases are substances which gives OH^- ions in aqueous solution."

The process of neutralization amounts to the combination of H^+ with OH^- to form water.

ACID: $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

BASE: $NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H2O$

Neutralization: $H^+ + OH^- \rightleftharpoons H_2O$

Advantages: (i) This concept readily explains that the heat of neutralization of a strong acid by a strong base should be constant.

(ii) The concept offered a means of co-relating catalytic behavior with the concentration of H^+ ion.

Limitation: (i) Acid base behavior is restricted to the presence of solvent water only. But acid-base behavior observed in other solvents as well as in absence of solvent.

(ii) The concept can not explain the acidic character of certain salt like $AlCl_3$ in aqueous solution.
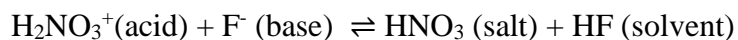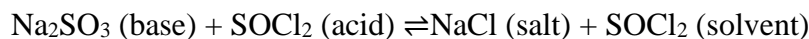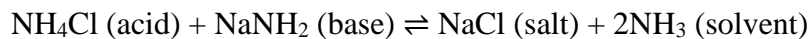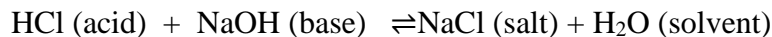
1.2.2 Solvent System Concept

In this model, the autoionization of the solvent is considered and any substance capable of increasing the concentration of the cation (i.e. lyonium) produced by the autoionization of the solvent is regarded as an acid in that solvent. On the other hand, the species which can enhance the concentration of the anion (i.e. lyate) produced in the autoionization of the solvent is considered as a base in that solvent. Hence to characterize the substances as acid or base in a particular solvent, it is required to know the mode of autoionization of the solvent under consideration. Some common solvents with their autoionization modes are given below.

Solvent		Acid		Base
$H_2O + H_2O$	$\rightleftharpoons$	H_3O^+	$+$	OH^-
$NH_3 + NH_3 \rightleftharpoons$		NH_4^+	$+$	NH_2^-

$$SO_2 + SO_2 \rightleftharpoons \quad\quad SO^{2+} + SO_3^{2-}$$

$$HF + HF \rightleftharpoons \quad\quad H_2F^+ + HF^-$$

In liquid H_2O, NH_3, SO_2, HF typical acid base reaction are:

HCl (acid) + NaOH (base) $\rightleftharpoons$ NaCl (salt) + H_2O (solvent)

NH_4Cl (acid) + $NaNH_2$ (base) $\rightleftharpoons$ NaCl (salt) + $2NH_3$ (solvent)

Na_2SO_3 (base) + $SOCl_2$ (acid) $\rightleftharpoons$ NaCl (salt) + $SOCl_2$ (solvent)

$H_2NO_3^+$ (acid) + F^- (base) $\rightleftharpoons$ HNO_3 (salt) + HF (solvent)

Advantage: It can extend the concept of acid-base interaction in both protic and aprotic solvents

Limitation: (i) It pays an excessive attention to the idea of autoionization of the solvents ignoring the other physical and chemical properties of the solvents. It even ignores the properties arising from the dielectric constant which in fact, determines the possibility of autoionization.
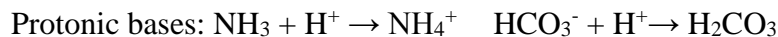
(ii) It cannot explain many acid-base reactions occurring in the absence of any solvent.

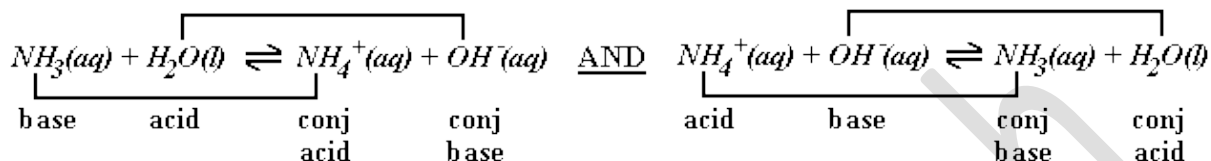(iii) Many acid base reactions involving the neutral molecules cannot be explained in this model.

1.2.3 Bronsted-Lowry Concept or Protonic Concept

Bronsted and Lowry in 1923 independently proposed a more fruitful concept for acid and bases. According to them " An acid is defined as any hydrogen containing molecule or ions that can release a proton (H^+) to any other substance and a base is any molecule or ion which can accept a proton." In short " An acid is a proton donor and base is a proton acceptor."

Following are some examples:

Protonic acids: HCl $\rightarrow H^+ + Cl^-$, $\quad\quad\quad [Al(H_2O)_6]^{3+} \rightarrow H^+ + [Al(H_2O)_5OH]^{3+}$

Protonic bases: $NH_3 + H^+ \rightarrow NH_4^+$ $HCO_3^- + H^+ \rightarrow H_2CO_3$

An acid and a base that are related by the gain and loss of a proton are called a conjugate acid-base pair. For example, NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate base of NH_4^+. Every acid has associated with it a conjugate base. Likewise, every base has associated with it a conjugate acid.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad \underline{AND} \quad NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

| base | acid | conj acid | conj base | | acid | base | conj base | conj acid |

Advantage: (i) According to this concept acid-base behavior is not made dependent upon the presence or absence of any particular solvent.

(ii) This concept is useful in according for the acidic or alkaline nature of aqueous solution of certain salts like $FeCl_3$ or Na_2CO_3. The acidic or alkalinity character develop due to hydrolysis.

$$FeCl_3 + 6H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{3+} + H^+$$
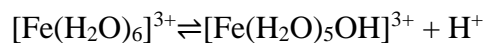
(iii) This concept gives idea regarding the relative strength of acids and bases (both qualitative and quantitative).

Limitation: (i) It gives too much emphasis on the proton although the common acids are protonic in nature, yet there are many acids which are not protonic e.g, $AlCl_3$, CO_2, SO_2, etc.
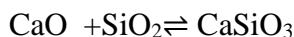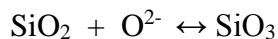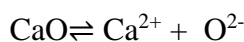
(ii) Although this concept gives a major of the relative strength from the determined K values with respect to a common base or acid. Yet it fails to compare the relative strength of the so called common strong acids like HCl, H_2SO_4, HNO_3 etc. due to the levelling effect of the solvent. In aqueous solution these acids behave equally stronger due to levelling effect of water.

1.2.4 Lux-Flood Concept

They put forward a concept for defining acid base character of oxides, according to them acids are oxide ion acceptor and bases are oxide ion donor.

$$Acid + O^{2-} \rightleftharpoons Base$$

$$CO_2 + O^{2-} \rightleftharpoons CO_3$$

$$SO3 + O^{2-} \rightleftharpoons SO_3$$
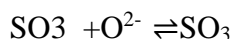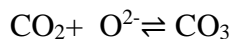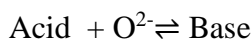
This view is particularly-useful in high temperature chemistry, as in the field of ceramics and metallurgy:

$$CaO \rightleftharpoons Ca^{2+} + O^{2-}$$

$$\underline{SiO_2 + O^{2-} \leftrightarrow SiO_3}$$

$$CaO + SiO_2 \rightleftharpoons CaSiO_3$$

$$Base + Acid \qquad Salt$$

Zinc oxides shows amphoterism as it can both donate or accept oxide ions.

$$Base: ZnO + S_2O_7^{2-} \rightleftharpoons Zn^{2+} + 2SO_4^{2-}$$

$$Acid: Na_2O + ZnO \rightleftharpoons Na_2ZnO_2$$
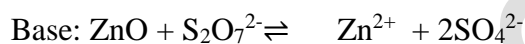
This concept is very much limited and it gained very little importance. This concept is unable even to explain the acidic and basic character of very common acids and bases such as HCl, H_2SO_4, HNO_3 etc.

1.2.5 Lewis Electronic Concept

Lewis concept was proposed in 1923 by Gilbert N. Lewis which includes reactions with acid-base characteristics that do not involve a hydron transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid-base reactions involve hydron transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids.

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
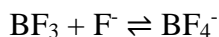
In the first example BF_3 is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Brønsted theory because there is no hydron transfer. The second reaction can be described using either theory. A hydron is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion. Lewis acids and

bases are defined in terms of electron pair transfers. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor. An organic transformation (the creation of products from reactants) essentially results from a process of breakingbonds and forming new ones. This process basically amounts to electron pair transfers. Ionic mechanisms involve electron pair transfers andare therefore described by the Lewis acid-base theory.The Lewis definition implies the presence of high electron density centers in Lewis bases, and low electron density centers in Lewis acids. In a reaction between a Lewis acid and a Lewis base the electron pair donated by the base is used to form a new sigma bond to theelectron deficient center in the acid. The identification of Lewis basesfollows basically the same guidelines as the identification of Bronsted bases. They frequently contain atoms that have nonbonding electrons, or *lone pairs*. On the other hand, Lewis acids frequently contain atomswith an incomplete octet, a full positive charge, or a partial positive charge.Water is an example of a Lewis base. Carbocations are examples of Lewis acids. When water reacts with a carbocation as shown below, oneof the electron pairs from oxygen is used to form a new sigma bond to the central carbon in the carbocation. As with Bronsted acid-basereactions, curved arrow is used to indicate the movement of electron pairs during the reaction process. The arrow always originates with the Lewis base and moves towards the area of electron deficiency in the Lewis acid. To avoid confusion between the Lewis and the Bronsted definitions of acids and bases, Lewis bases are sometimes called nucleophiles, and Lewis acids are called electrophiles. In the example above, water acts as a nucleophile (donates electrons), and the carbocation acts as an electrophile (receives electrons). Since Bronstedacids and bases are a subcategory of the more encompassing Lewisdefinition, it can be said that most Bronsted basesare also nucleophiles, and that the proton is a Lewis acid, or an electrophile. There are however some subtle differences to keep in mind.

Lewis base   Lewis acid   Addition product
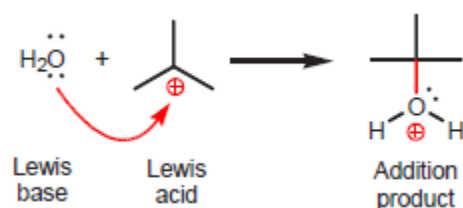
Recognizingnucleophiles: For the most part, the same criteria used for identifying Bronsted bases can also be used to identifynucleophiles. Here is a summary.

1. The most common type of nucleophiles are those containing atoms with unshared electron pairs, such as the following.Notice that nonbonding electrons are frequently omitted from formulas.

Always remember their presence on oxygen, nitrogen, and negativelycharged carbon atoms. H_2O, OH^-, NH_3, RNH_2, CN^-
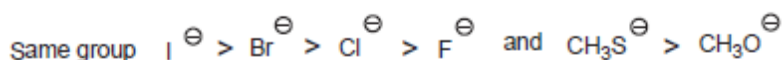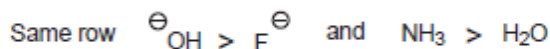
2. A negatively charged species is usually a stronger nucleophile or base than its neutralanalog. Thus, hydroxide ion is stronger, both as abase and as a nucleophile, than water.

3. Carbon bonded to a metal has strong negative character, revealed when writing resonance structures. The carbon atom in such moleculesis considered a strong nucleophile. Recall the structures of *n*-butyllithium and Grignard (organo-magnesium) reagents from previous notes.

4. The pi bond is a region of high electron density. Pi bonds are not as strong as sigma bonds, which means that pi electrons are more availablefor reactions because pi bonds are more easily broken. Molecules containing pi bonds are considered weak nucleophiles or bases, becausethey can react with strong acids or electrophiles. See examples under Bronsted acid-base chemistry.

5. Periodic trends in nucleophilicity are such that, other factors being similar, nucleophilicity increases from right to left across the same row,and from top to bottom across the same period or group. Make a note that this trend is different from the basicity trend, which increases inthe same way across a row, but from bottom to top within a period.

Nucleophilicity trends

Same row $\quad ^{\ominus}OH > F^{\ominus} \quad$ and $\quad NH_3 > H_2O$

Same group $\quad I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus} \quad$ and $\quad CH_3S^{\ominus} > CH_3O^{\ominus}$

6. Basic vs. nucleophilic behavior. There are some differences between Bronsted bases and nucleophiles. First, the term base is reservedfor substances seeking acidic protons, whereas the term nucleophile is used for substances seeking electron-deficient centers, be they protonsor other atoms (most commonly carbon).

Second, in acid-base reactions the size (or bulk) of the base seldom matters. In nucleophilic reactions, the size of the nucleophile can be an important (steric) factor. Smaller is more effective. Thus, although the nucleophilic atom in the two species below is the same (oxygen) and they have similar structures, methoxide ion is a more effective nucleophile than *t*-butoxide ion, even though they are about equally effective as bases. The larger *t*-butoxide ion has more difficulty reaching an electrophilic center, which is typically a carbon buried at the core of the molecular structure. That is not a problem when it acts as a base because acidic protons usually lie in the periphery of the molecule and areeasily accessible.

methoxide ion
smaller ion,
better nucleophile

t-butoxide ion
larger ion,
poorer nucleophile
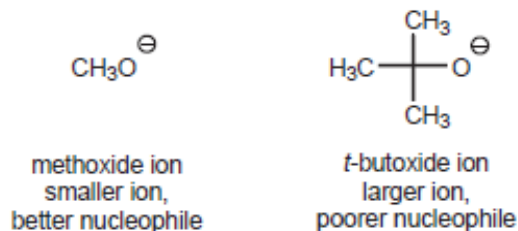
Recognizing electrophiles: There are two requirements for a molecule to be considered a good electrophile. First, it must contain an electrophilic center or atom. Second, the electrophilic atom must be able to accommodate a new sigma bond. Please keep in mind the difference between electrophile and electrophilic center. The term electrophile refers to the molecule. The term electrophilic center refers to the particular part of the molecule susceptible to nucleophilic attack. To avoid confusion, the term *substrate* is frequently used in reference to electrophiles. This term denotes a molecule being acted upon by

another agent. For example, an enzyme substrate is a molecule being modified by an enzyme. Likewise, an electrophile can be thought of as the substrate of a nucleophile when the latter "attacks" its electrophilic center. *Electrophilic centers are areas of low electron density*. Most often they are atoms which (a) *contain an incomplete octet*, and/or (b) *carry a full or a partial positive charge*. A partial positive charge can be revealed by writing resonance structures, or by identifying a polar bond.

   1. The following are examples of electrophiles containing atoms with incomplete octets:

proton

Molecules containing group III
elements or transition metals

carbocations
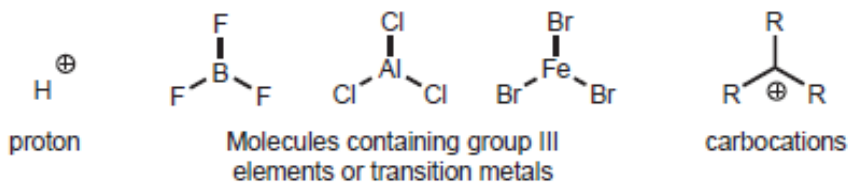
   2. These are examples of electrophiles containing atoms with partial positive charges:
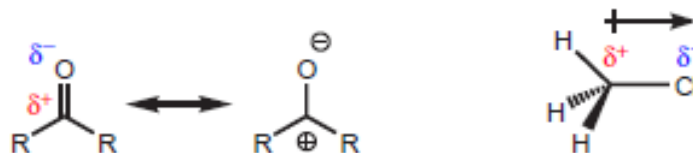
   3. Atoms of the second row like oxygen and nitrogen, which are more electronegative than carbon, seldom act as electrophilic centers, even if they carry a positive charge. In that situation they seek to lessen their positive character by sharing the charge with adjacent

atoms, causing them go become acidic (protons) or electrophilic (carbon for instance). Resonance structures can reveal this shift of positive charge.

Hydronium ion, $pK_a \sim -1.7$ Ammonium ion, $pK_a \sim 9$
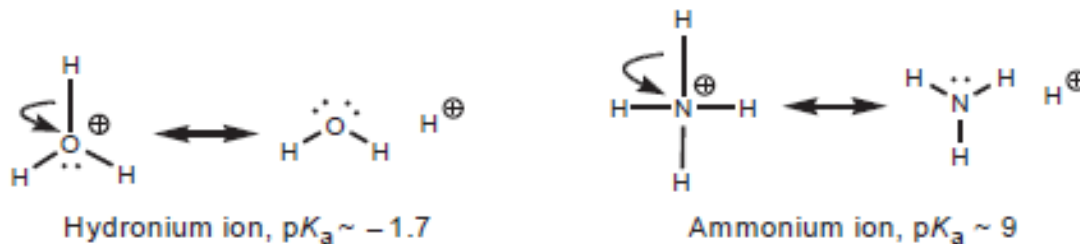
The ammonium and hydronium are of moderate high acidity because the highly negative oxygen and nitrogen seek to transfer the positive charge to adjacent proton, to make acidic. In addition, those atoms cannot accommodate another bond without violating the octate rule.
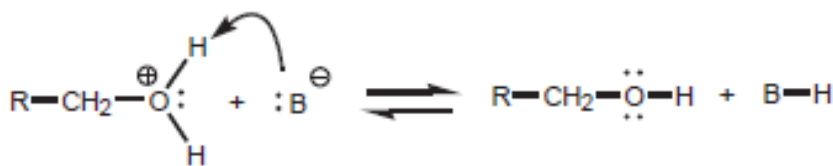
The reaction with a base (B^-) is an equilibrium process that normally has low activation energy and is therefore relatively fast.

Advantage: (i) This concept is more general than the other concepts because the acid base behavior is not dependent upon the presence or absence of any solvent.

(ii) It explains the long accepted basic properties of metallic oxides and acidic properties of nonmetallic oxides.

(iii) This theory can explain those acid-base reaction which occur at the high temperature in the gas phase and in absence of solvent.

Limitation:(i) Since the strength of Lewis acids and bases depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

(ii) According to phenomenological criteria the process of neutralization is a rapid one. But those are many reaction Lewis acid-base reactions are slow.

1.2.6 Usanovich Concept

Actually, this concept (1934) extents and generalizes the idea of Lewis acid-base concept. It does not get confined within the domain of electron pair donation and acceptance. It defines acids bases as follows.

An acid is a substance capable of accepting anions or electrons or giving up cations, and a base is a substance which can combine with the cations or give up anions or electrons. Thus the redox reactions (i.e. electron transfer reactions) are also regarded as acid-base reactions.

Here it is worth mentioning that both the Lewis and Usanovich concepts are identical in terms of kind but they may differ on the degree of the process. In Lewis acid base interactions, the donated electron pair is commonly shared by the reactants in the adduct but in Usanovich concept, the electrons might be completely or partially transferred. There are some reactions which may be considered as redox reactions (i.e. Usanovich's acid base reactions) as well as Lewis acid base adduct formation. These are,

$$O + :SO_3^{2-} \rightleftharpoons SO_4^{2-}, \quad C_6H_5N: + O \rightleftharpoons C_6H_5N^+ \rightarrow O^-$$

Practically, Usanovich concept includes all the reactions as acid-base reactions. These are illustrated by considering some specific examples.

(i) $SiO_2 + CaO \rightleftharpoons Ca^{2+}SiO_3^{2-}$ Here SiO_2 takes up the anion, O^{2-} which is given up by CaO

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$ Here Fe^{2+} combines with the anion CN^-

(iii) $2 Fe^{3+} + Sn^{2+} \rightleftharpoons Sn^{2+} + 2 Fe^{2+}$ Here Sn^{2+} gives up electrons which are taken up by Fe^{3+}. Thus Sn^{2+} act as a base while Fe^{3+} act as an acid.

1. 3. The Drago-Wayland Equation

Consider the gas phase reaction: $A(g) + :B(g) \rightarrow A\text{-}B(g)$

Drago and Wayland proposed the equation: $-\Delta H = E_A E_B + C_A C_B$

where ΔH is the standard enthalpy of the reaction, and E_A, E_B and C_A, C_B values represent the abilities of the acid and base to participate respectively in ionic and covalent interactions. Large enthalpies result from combinations of acids and bases with either large E or large C values. Predictions using this equation typically agree with experimental values (for uncharged species) unless there is special interference of groups attached to the donor or acceptor atoms.

#### Drago-Wayland E and C Parameters for Uncharged Lewis Acids and Bases

Acid	Acceptor atom	E_A	C_A	C/E
Iodine	I	1.00	1.00	1.00
Iodine monobromide	I	2.41	1.56	0.65
Iodine monochloride	I	5.10	0.830	0.16
Sulfur dioxide	S	0.92	0.808	0.88
Antimony pentachloride	Sb	7.38	5.13	0.70
Chlorotrimethylstannane	Sn	5.76	0.03	0.01
Boron trifluoride	B	9.88	1.62	0.16
Trimethylborane	B	6.14	1.70	0.28
Trimethylalane	Al	16.9	1.43	0.08
Trimethylgallium	Ga	13.3	0.881	0.07
Trimethylindium	In	15.3	0.654	0.04
Water	H	1.64	0.571	0.35
Phenol	H	4.33	0.422	0.10
Thiophenol	H	0.99	0.198	0.20
Ethanol	H	3.88	0.451	0.12
(Tetraphenylporphyrinato)zinc(II)	Zn	5.15	0.620	0.12
(Tetraphenylporphyrinato)cobalt(II)	Co	4.44	0.58	0.13

Base	Donor atom	E_B	C_B	C/E
Dimethyl selenide	Se	0.217	8.33	38.4
Dimethyl sulfide	S	0.343	7.46	21.8
Diethyl sulfide	S	0.339	7.40	21.8
Diethyl ether	O	0.936	3.25	3.5
Acetone	O	0.937	2.33	2.5
Ethyl acetate	O	0.975	1.74	1.8
Tetrahydrofuran	O	0.978	4.27	4.4
Trimethylphosphine	P	0.838	6.55	7.8
Trimethylamine	N	0.808	11.54	14.2
Pyridine	N	1.17	6.40	5.5
Dimethylamine	N	1.09	8.73	8.0
Methylamine	N	1.30	5.88	4.5
Ammonia	N	1.15	4.75	4.1
Acetonitrile	N	0.886	1.34	1.5
1-Azabicyclo[2.2.1]octane	N	0.700	13.2	18.9
Benzene	C	0.280	0.590	2.1

1. 4. Levelling and Differentiating Effect of Solvent

In water, no stronger than H_3O^+ can survive. Thus, water levells off all such stronger acids to the acids to the acidity of H_3O^+. The effective proton affinity of H_2O in water is 1130 kJ mol^{-1}. Hence, all acids (HA) for which effective proton affinity of their conjugate bases (A$^-$) is smaller than 1130 kJ mol-1 are levelled off in water (i.e. HA + $H_2O \rightarrow H_3O^+$ +A$^-$).

In water, any base stronger than OH$^-$ cannot survive. The effective proton affinity of OH$^-$ in water is 1188 kJ mol^{-1}. Thus any base (B) for which the effective proton affinity is greater than 1188 kJ mol^{-1} will be completely converted into the conjugate acid (BH$^+$) with the release of OH- in water (B + $H_2O \rightarrow BH^+$ + OH$^-$).

This is why, we cannot study NH_2^- or CH_3^- in water as these get completely protonated as follows:

$LiCH_3 + H_2O \rightarrow Li^+ + OH^- + CH_4$
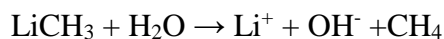
For liquid NH_3, the proton affinity of NH_3 is greater than that of H_2O and consequently the acids which are weaker and differentiated in water may be levelled off in liquid NH_3. The proton affinity of NH_2^- is greater than that of OH^- and consequently, the stronger bases which are levelled off in water may not be levelled off in liquid NH_3.

1. 5. Relative Strength of Different Acids and Bases

To measure the proton donating strength of an acid, a refence must be taken into consideration, as the extent of proton transfer definitely depends on two factors: (i) the proton donating power of the acid and (ii) the proton accepting power of the reference base participated in proton transfer equilibrium. Generally, to measure the proton donating strength (i.e acid strength) of an acid, the solvent is taken as the refence base. This is an aqueous solution the following proton transfer equilibrium is to be considered.

$Acid_1\ (A_1) + Base_2\ (H_2O) \rightleftharpoons Base_1\ (B_1) + H_3O^+ + (Acid_2)$
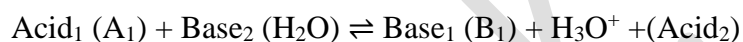
$K_{eq} = [H_3O^+][B_1]/[A_1][H_2O]$

The extent of proton transfer is measured by the equilibrium constant (in dilute solution), K. The conventional acid dissociation constant (K_a) is given by:

$K_a = K_{eq}[H2O] = [H_3O^+][B_1]/[A_1]$

In dilute solution $[H_2O]$ can be taken as 55.5 moles per litre. Thus, $K_a = K_{eq}$x 55.5. Thus in general, the acid dissociation constant can be defined as follows:

The acid dissociation constant is the product of the equilibrium constant of the proton transfer process and the concentration of the reference base (generally the pure solvent) with respect to which the extent of proton transfer is being measured.

Strongest acids are classified as Ka > 1 and usually Ka >>1 (i.e. negative pKa values), while weak acids are classified as Ka < 1 (i.e. positive pKa values).

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

HA(aq)+H₂O(l)⇌H₃O⁺(aq)+A⁻(aq)
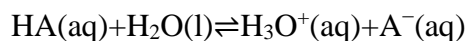
Water is the base that reacts with the acid HA, A⁻ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A⁻ when the acid ionizes in water; Table 1 lists several strong acids. A weak acid gives small amounts of H_3O^+ and A⁻.

Table 1: Some of the common strong acids and bases are listed here.

Strong acid		Strong base	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:
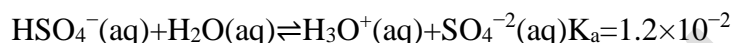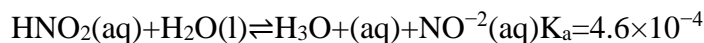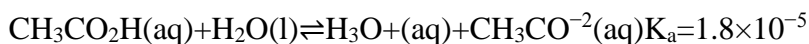
$$HA(aq)+H_2O(l)⇌H_3O^+(aq)+A^-(aq)$$
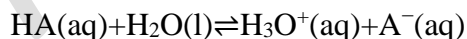
we write the equation for the ionization constant as:

$$K_a=[H_3O^+][A^-]/[HA]$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include [H₂O] in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A⁻ relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength $CH_3CO_2H <$ $HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+CH_3CO^{-2}(aq) K_a=1.8\times10^{-5}$$

$$HNO_2(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+NO^{-2}(aq) K_a=4.6\times10^{-4}$$

$$HSO_4^-(aq)+H_2O(aq)\rightleftharpoons H_3O^+(aq)+SO_4^{-2}(aq) K_a=1.2\times10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\text{ionization}= ([H_3O^+]_{eq}/[HA]_0)\times100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq)+H_2O(l)\rightleftharpoons HB^+(aq)+OH^-(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

Table 2: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^-+H_2O\rightleftharpoons H_3O^++SO_4^{2-}$	1.2×10^{-2}
$HF+H_2O\rightleftharpoons H_3O^++F^-$	3.5×10^{-4}

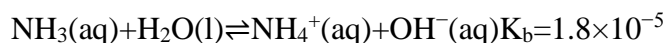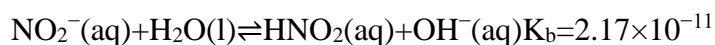|	
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$,

we write the equation for the ionization constant as:

$K_b = [HB^+][OH^-][B]$

where the concentrations are those at equilibrium. Again, we do not include [H_2O] in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) K_b = 2.17 \times 10^{-11}$

$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) K_b = 5.6 \times 10^{-10}$

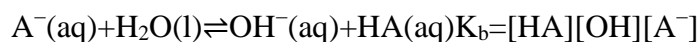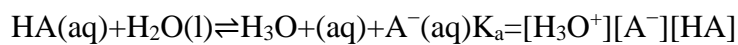$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) K_b = 1.8 \times 10^{-5}$

A table of ionization constants of weak bases appears in Table 3. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.
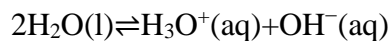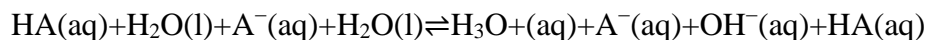
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Table 3.: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.3×10^{-10}

Consider the ionization reactions for a conjugate acid-base pair, HA $^-$ A$^-$:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + A^-(aq) \quad K_a = [H_3O^+][A^-][HA]$$

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \quad K_b = [HA][OH][A^-]$$

Adding these two chemical equations yields the equation for the autoionization for water:

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

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = [H_3O^+][A^-][HA] \times [HA][OH^-][A^-] = [H_3O^+][OH^-] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($CH3COO-$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = Kw$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A⁻, of the acid. If A⁻ is a strong base, any protons that are donated to water molecules are recaptured by A⁻. Thus there is relatively little A⁻ and H_3O^+ in solution, and the acid, HA, is weak. If A⁻ is a weak base, water binds the protons more strongly, and the solution contains primarily A⁻ and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 1)

Relative acid strength

Stronger acids	H_3O^+	$HClO_2$	HF	H_2CO_3	CH_3COOH	NH_4^+	HPO_4^{2-}	H_2O	Weaker acids
K_a	1.0	10^{-2}	10^{-4}	10^{-6}	10^{-8}	10^{-10}	10^{-12}	10^{-14}	

Relative conjugate base strength

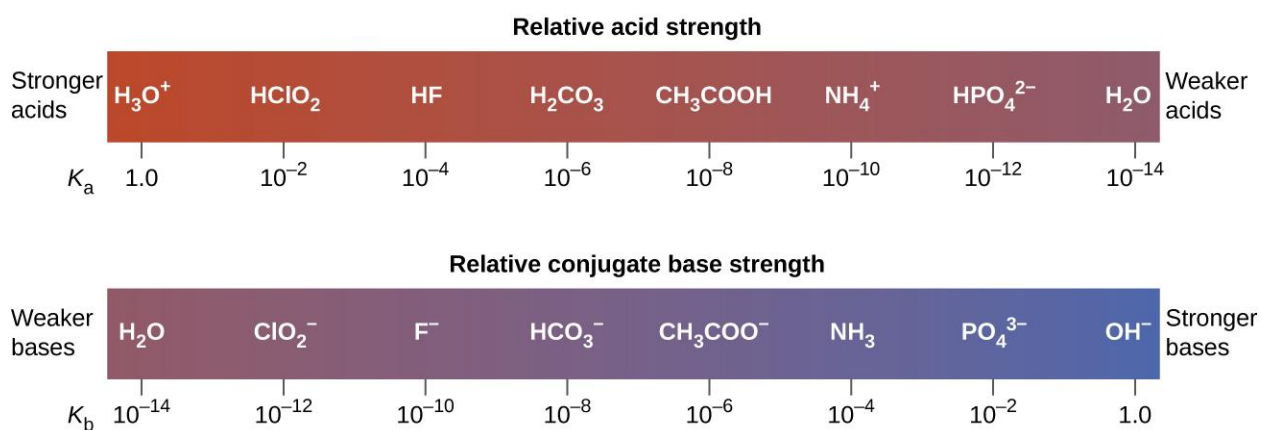| Weaker bases	H_2O	ClO_2^-	F^-	HCO_3^-	CH_3COO^-	NH_3	PO_4^{3-}	OH^-	Stronger bases
K_b	10^{-14}	10^{-12}	10^{-10}	10^{-8}	10^{-6}	10^{-4}	10^{-2}	1.0	

Figure 1: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 3. lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.
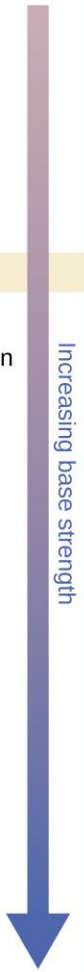
Acid				Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion	
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion	
hydrogen iodide	HI			I^-	iodide ion	
hydrogen bromide	HBr			Br^-	bromide ion	
hydrogen chloride	HCl			Cl^-	chloride ion	
nitric acid	HNO_3			NO_3^-	nitrate ion	
hydronium ion	H_3O^+			H_2O	water	
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion	
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion	
hydrogen fluoride	HF			F^-	fluoride ion	
nitrous acid	HNO_2			NO_2^-	nitrite ion	
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion	
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion	
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion	
ammonium ion	NH_4^+			HN_3	ammonia	
hydrogen cyanide	HCN			CN^-	cyanide ion	
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion	
water	H_2O			OH^-	hydroxide ion	
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion	
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion	
ammonia	NH_3			NH_2^-	amide ion	
hydrogen	H_2			H^-	hydride ion	
methane	CH_4			CH_3^-	methide ion	

Increasing acid strength → (upward) Increasing base strength ↓ (downward)

Figure .3: The chart shows the relative strengths of conjugate acid-base pairs.

The first six acids in Table 1 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Table 2 exhibit no observable acidic

behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Table.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

1.6. Relative Strength of Mononuclear Oxyacid: Pauling Rule

In H_nXO_m all the oxygen atoms are directly linked with the central atom X and some of which are present as OH groups. Thus from the structural view point H_nXO_m can be represented as $O_{m-n}X(OH)_n$. Hence it is assumed that all H-s exist as OH groups. Each X-OH bond is formed by using one X electron and one O electron while in each $X\rightarrow O$ bond, there is a net loss of electron from X. In this way, the formal positive charge accumulated on the central atom is given by the number of $X\rightarrow O$ bonds and it becomes (m-n). With the increase of (m-n), the central atom becomes more and more electron deficient and it facilitate the removal of the proton from the -O-H bonds due to the enhanced electron withdrawing inductive effect towards the central atom. An empirical relationship between the values of (m-n) and acid strength measured by pK_1(i.e. first acid dissociation constant) has been proposed by Pauling as follows: $pk_1 \approx 8 - 5(m-n)$

(m-n)	0	1	2
pk_1(observed)	~8.5	~2.8	$<< 0$
k_1 (observed)	~$10^{-8} - 10^{-9}$	~$10^{-3} - 10^{-4}$	very strong

The successive pK values differ by 5 units. In many cases, the prediction has been supported experimentally.

Relative strength of oxyacids, H_nXO_m

(m-n)	Acid	pK_1	pK_2	pK_3
0	$HClO_4$	7.5	-	-
	$HBrO_4$	8.7	-	-
	H_3AsO_3	9.2	-	-
	H_6TeO_6	8.8	-	-
	H_3PO_3	1.8	6.15	-
1	H_3PO_4	2.1	7.2	12.0
	H_3PO_2	2	-	-
	H_3AsO_4	3.5	7.2	12.5
	H_5IO_6	3.3	6.7	-
	H_2SO_3	1.9	7.3	-
	H_2SeO_3	2.6	6.6	-
	HNO_2	3.3	-	-
	H_2CO_3	6.4	10.3	-
2	HNO_3	Highly negative	-	-
	H_2SO_4	Do	1.9	-
	H_2SeO_4	Do	2.0	-
3	$HClO_4$	Do	-	-
	$HMnO_4$	Do	-	-

1.7   Hammett Acidity Function and Super Acid

The concept of pH measuring the acidity is only meaningful in aqueous dilute solutions of acid and bases. But in concentrated solutions of the so-called strong acids and bases and in nonaqueous media, a new parameter called the Hammett acidity function (H) has been defined to measure the acidity of the solution. To express the Hammett acidity function, protonation-deprotonation equilibria of an indicator base (B) are to be considered. Depending on the charge of the indicator base, the Hammett acidity function are denoted by H_0, H_+, H_- for neutral (B), cationic (B^+) and

anionic (B^-) indicator bases respectively. To measure the H_0, p-nitroanilline (a neutral base) is used. For a particular solution, H_0, H_+ and H_- values differ but these run parallel.

Let us illustrate H_0 (i.e. reference base is neutral) by considering the following equilibrium:

$BH^+ \rightleftharpoons B + H^+$
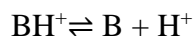
$K_{BH^+} = a_B a_{H^+}/a_{BH^+} = (a_{H^+}[B] f_B)/([BH^+] f_{BH^+})$

$H_0 = -\log (a_{H^+} f_B)/(f_{BH^+}) = -\log h_0 = pK_{BH^+} + \log [B]/[BH^+]$

Here, a denotes the activity term and f denotes the corresponding activity coefficient. In dilute solutions, the ratio of activity coefficients (i.e. f_B/f_{BH^+}) becomes unity and it leads to:

$H_0 = -\log a_{H^+} = pH = pK_{BH^+} + \log [B]/[BH^+]$

Which is the Henderson's equation.

It is evident that the Hammett acidity function measures the effective pH of the solution and it is formally equivalent to

$H_0 = -\log h_0 = -\log (a_{H^+} f_B)/(f_{BH^+})$

Similarly, H_+ and H_- may be defined as follows:

$$B^+ + H^+ \rightleftharpoons BH^{2+}$$
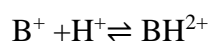
$H_+ = -\log (a_{H^+} f_B^+)/(f_{BH^{2+}}) = -\log h_+ = pK_{BH^{2+}} + \log [B^+]/[BH^{2+}]$

$$B^- + H^+ \rightleftharpoons BH$$
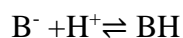
$H_- = -\log (a_{H^+} f_B^-)/(f_{BH}) = -\log h_- = pK_{BH} + \log [B^-]/[BH]$

In general, organic bases used as indicator bases posses different colours in their protonated and deprotonated forms. Thus the ratio $[B]/[BH^+]$ or $[B^+]/[BH^{2+}]$ or $[B^-]/[BH]$ can be determined spectrophotometrically. By using suitable organic bases, it is possible to determine the Hammett

acidity functions of different solutions. Acidity functions of some solutions are given below in table.

In aqueous media, the strongest acid which can survive is H_3O^+. Hence, the idea of superacid only exists in nonaqueous media. Generally, the superacids are 10^6 to 10^{10} times more acidic than the fairly concentrated (1M) aqueous solution of strong acids like H_2SO_4, HNO_3, etc. The powerful proton donating property of superacids can protonate even very weak bases and stabilize the species susceptible to the base attack. Superacids are produced by concentrated solutions of very strong Bronsted cids like $H_2S_2O_7$(i.e. SO3 + H_2SO_4) , FSO_3H or combination of a Bronsted acid and Lewis acid (e.g. SbF_5) acting as the acceptor of conjugate base of the Bronsted acid.

Hammett acidity function of some solutions

Solution/Pure acid	H_0	Solution	H_-
6M HNO_3 (aq)	-1.5	5 M KOH (aq)	15.4
HSO_3H + SbF_5(14.1 mol %)	-26.5	10 M KOH (aq)	16.9
HSO_3H	-15.0	15 M KOH (aq)	18.2
HF + SbF_5(0.6 mol%)	-21.1		
HF	-11.0		
HF + NaF (1M)	-8.4		
7 M HCl (aq)	-2.0		
8 M $HClO_4$ (aq)	-2.63		
H_2SO_4 (63% in water)	-4.9		
H_2SO_4	-12.0		
Oleum	-15.0		
F_3CSO_3H	-15.1		
H_3PO_4	-5.0		
HCO_2H	-2.2		

(i)   Bronsted acid + Lewis acid: It is noticed that the acidity of HF increases by the addition of Lewis acid SbF_5.

$2HF \rightleftharpoons H_3F^+ + F-$, $SbF_5 + F- \rightleftharpoons SbF_6-$

(ii)   Strong Bronsted acid + Lewis acid: SbF5 also increases the acidity of fluorosulfonic acid (HSO_3F) and it produces superacid.

$$2HSO_3F + SbF_5 \rightleftharpoons H_2SO_3F^+ + FSO_2O\text{-}SbF_5^-$$

(iii)   Triflic acid (F3CSO3H) can act as powerful strong acid ($H_0 = -15.1$). It is act as like superacid.

1.8   Hard and Soft Acid-Base (HSAB) Principle and its Application

According to Lewis concept acid base reaction involves the formation of coordination complex. A strong acid and strong base will form a stable complex.

$$A + :B = A \leftarrow B$$
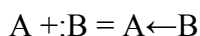
R. G. Pearson (1963) introduced the soft and hard or hard and soft concept of acids and bases for determining the strengths of Lewis acids and bases. According to this concept, " a hard acid prefers to combine with a hard base and a soft acid prefers to combine with a soft base to form a more stable adduct." This is known as SHAB or HSAB concept. Hardness and softness refer to firmly and loosely bound electron respectively.

For the determining the hardness and softness of bases R. G. Pearson measured the equilibrium constant of the following exchange reaction.

$$BH^+ + CH_3Hg(H_2O) \rightleftharpoons [CH_3HgB]^+ + H_3O^+$$
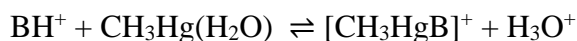
It was found that bases having more electronegative donors (O, N, and F) prefer to bind to the proton but bases with less electronegative donors (P, S, I, Br, Cl) prefer to bind to CH_3Hg^+. The former bases are hard bases and the later are soft bases.

1.8.1. Classification of Acids and Bases

From the measured K values R. G. Pearson classified Lewis bases as hard and soft having the following criteria. Bases with intermediate character are said to be boarder line.

Hard base	Soft base
(i) High electronegativity	(i) Low electronegativity
(ii) Low polarisibility	(ii) High polarisibility
(iii) Presence of filled orbital, empty orbital may exist at higher energy level	(iii) Parially filled orbitals, empty orbitals are low lying.
e. g, H_2O, OH^-, F^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, NH_3, R-NH_2, R-OH, R_2O, etc.	e. g, H^-, I^-, SCN^-, $S_2O_3^{2-}$, CO, C_2H_4, C_6H_6, R2S, R_3P, etc.

Border line: C_6H_5-NH_2, C_5H_5N, N_2, N_3^-, NO_2^-, Br^-, etc.

Lewis acids also classified as hard, soft and boarder line having the following characteristics:

Hard acid	Soft acid
(i) Small size	(i) Large size
(ii) High positive oxidation stae	(ii) Zero or low positive oxidation stae
(iii) Absence of any outer electrons which are easily excited to higher states.	(iii) Presence of several exicitable valency electrons.
e. g, H^+, Li^+, Na^+, K^+, Mg^{2+}, Fe^{3+}, CO_2, SO_3, BF_3, $AlCl_3$, etc.	e. g, Cu^+, Ag^+, Hg^+, Hg^{2+}, I^+, I_2, Cl, M^0, etc.

Border line: Fe^{2+}, CO^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2, etc.

1.8.2 Usefulness of SHAB Principle

Hard -hard and soft-soft principle can be used as guide lines for predicting various chemical reactions. Following are some examples.

(i) BF_3 being a hard acid prefer to combine with hard base F^- and BH_3 being a soft acid prefer to combine a soft base H^-. So the following reactions are proceeds to the right.

$$BF_3H^- + BH_3F^- \rightarrow BF_4^- + BH_4^-$$
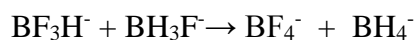
For similar reason the following reaction proceeds to the right.

$$CF_3H + CH_3F \rightarrow CF_4 + CH_4$$
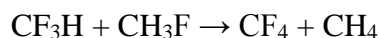
(ii) Hard-hard and soft-soft combination can be used to explain the 'Pearson-Pauling paradox' of chemistry. According to the Pauling concept of electronegativity, Cs and Hg should form more stable bond with F as their electronegativity difference is greater. So the following reaction should not proceed to the right.

$$LiI + CsF \rightleftharpoons LiF + CsI$$

$$HgF_2 + BeI_2 \rightleftharpoons BeF_2 + HgI_2$$
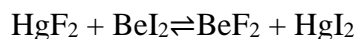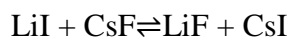
In fact both the reactions proceed to the right and this anomaly can be explained by SHAB principle. On the left hand side there hard-soft and soft-hard combination (Li^+ - hard acid, I^- -soft base, Cs^+ - soft acid, F^- - hard base). To attain more stable hard-hard and soft-soft combination these reactions proceeds to the right.

(iii) The concept can explain the existance and non-existance of certain ion like AgI_2^-, is known for soft-soft combination whereas AgF_2^- does not exist as it involves soft -hard combination.

(iv) SHAB principle can be used to explain the existance of certain type of compounds as metal ores and non-existance of others. Thus hard acid like Mg^{2+}, Ca^{2+} and Al^{3+} occur in nature as $MgCO_3$, $CaCO_3$ and Al_2O_3i. e combining with a hard bases (CO_3^{2-}, O^{2-}). But they do not occur as sulphides because S^{2-} is a soft base. Soft acids such as Cu^+, Ag^+ and Hg^{2+} occur as their sulphides for soft-soft combination. On the otherhand border line acids like Ni^{2+}, Cu^{2+}, Pb^{2+} occur in nature both as carbonates and sulfides.

1.9. Acid -Base Equilibria in Aqueous Solution

We are going to be working with acid-base equilibria in aqueous solution, and we will use the Brønsted-Lowry definitions that an acid is a source of H^+ and a base is an acceptor of H+.

Acid ionization constant Ka

A convenient way to write the reaction of an acid HA in water is

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
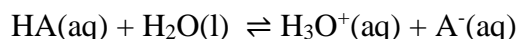
Here water is acting as a base, accepting the H^+; the result, H_3O^+, called the conjugate acidof H_2O,since H_3O^+ can donate H^+ to reform H_2O. In a similar way, A^- is called the conjugate baseof theacid HA, since A^- can accept H^+ to reform HA. The equilibrium constant is known as the acidionization constant Ka,

$$K_a = [H3O^+][A^-]/[HA]$$

with the understanding that [...] stands for the numerical value without units of the concentrationin mol/L. As usual, K_a is unit-less.

An example acid ionization is

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$
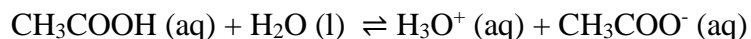
$$K_a = [H3O^+][CH_3COO^-]/[CH_3COOH]$$

If Ka is much greater than 1, the acid is mostly dissociated and so is said to be a *strong acid*. If Ka ismuch less than 1, the acid is dissociated only to a small extent and so is said to be a *weak acid*.
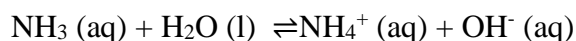
Base Ionization Constant Kb

Similarly, we can write the reaction of a base B in water as

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
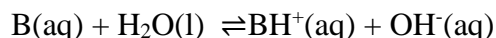
Here water is acting as an acid, donating the H^+; the result, OH^-, is called the conjugate base of H_2O, since OH^- can accept H^+ to reform H_2O. Analogously, HB^+ is called the conjugate acid of the base B, since HB^+ can donate H^+ to reform B. The equilibrium constant is known as the base ionization constant K_b,

$K_b = [HB^+][OH^-]/[B]$

where we have used the abbreviated form. Here is an example base ionization,

NH_3 (aq) + H_2O (l) $\rightleftharpoons NH_4^+$ (aq) + OH^- (aq)

$K_b = [NH_4^+][OH^-]/[NH_3]$

If K_b is much greater than 1, the base reacts nearly completely with water and so is said to be a strong base. If K_b is much less than 1, the base reacts hardly at all with water and so is said to be a weak base.

Water Autoionization Constant K_w

In this analysis of acid and base ionization we see that water in one case plays the role of a base and the other plays the role of an acid. Indeed, the role that water plays in an aqueous equilibrium can be used as another definition of acid or base. A consequence of this dual role of water is that its equilibrium with H_3O^+ and OH^- is the reference standard against which aqueous acidity and basicity are defined.

Here is how this works. A general base ionization reaction is

$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq), \quad K_b$

and the ionization reaction of its conjugate acid is

$HB^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq), \quad K_a$
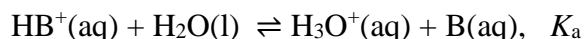
The sum of these two reactions is $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq), \quad K_w$

This equation is called the autoionization of water and its equilibrium constant is known as the water autoionization constant Kw. At 25°C it is equal to

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Now, we have seen that the equilibrium constant of a sum of two reactions is the product of the equilibrium constants of the summed reactions. Therefore, we know that water autoionization constant can be expressed as $K_w = K_aK_b$.

This means we can compute the base ionization constant from the ionization constant of its conjugateacid,

$K_b = K_w/K_a = 10^{-14}/K$a , where the last equality is for 25°C. It is for this reason that base ionization constants are generally not tabulated.

1.10. pH

Because K_w is so small, water is ionized only very slightly. We can compute the concentration of H3O+ and OH- by solving the autoionization equilibrium.

	$[H_3O^+]/M$	$[OH^-]/M$
Initial	0	0
Equilibrium	x	x

Initial and equilibrium activities for the autoionization of liquid water. The equilibrium expression is then $K_w = 1.0 \times 10^{-14} = x^2$ and so the concentration of H_3O^+ and OH^- are each 1×10^{-7} M at 25°C.

Now, as we will see in a moment, strong acids can have H_3O^+ concentrations of 1 M or more. This means that H_3O^+ varies over many powers of 10 (orders of magnitude), and so it is convenient to measure $[H_3O^+]$ on a logarithmic scale. Also, for weak acids and bases, which is what we will beinterested in primarily, concentrations of H_3O^+ and OH^- are generally much less than 1 M, whichmeans their logarithms are negative, and so it is more convenient to work with the negativelogarithmsso that we have a positive quantity.and in particular pH and pOH are defined

aspH = -log$_{10}$ H$_3$O$^+$, andpOH = -log$_{10}$OHwhere in each case the second equality is written with understanding that […] stands for thenumerical value—without units—of the concentration in mol/L.

Since acids produce additional H_3O^+, their pH is always less than 7. Similarly, since bases produceadditional OH$^-$, their pOH is always less than 7. We can relate pH and pOH, by calculating pK$_w$.

pK$_w$
$= -\log_{10}K_w$
$= -\log_{10}$ (H$_3$O$^+$ +OH$^-$)
$= -\log_{10}$H$_3$O$^+$- $\log_{10}$OH$^-$
$=$ pH + pOH
This means that at 25°C
pH = 14 - pOH.
so that bases have pH greater than 7, at 25°C.

It is important always to be mindful of the temperature being used. The reason is that equilibrium constants in general, and the value of K_w in particular, are different at different temperatures. This means that the pH of pure water will be different at different temperatures. For this reason, saying a solution has pH = 7 does not, by itself, mean the solution is "neutral" (has equal concentrations ofH$_3$O$^+$ and OH$^-$. More generally, the acidic or basic character of a solution is due to the relative concentrations of H_3O^+ and OH$^-$, rather than a particular numerical value of pH.

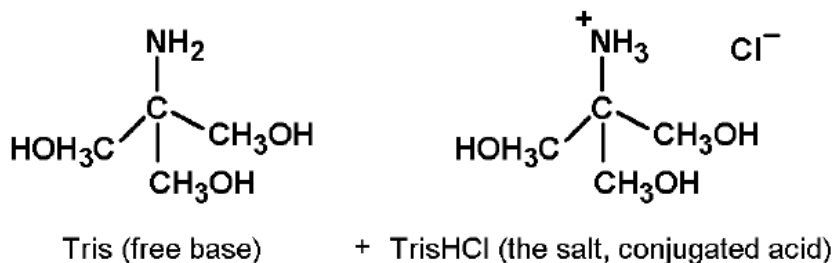## 1.11. Buffer and buffer capacity

Before we get into what a buffer capacity is, we should first understand buffers. A buffer is a compound that resists changes in pH when a limited amount of acid or base is added to it. The chemical composition of a buffer solution usually entails a weak acid or a weak base accompanied by its conjugate salt.
For example:
Acetate buffer: CH$_3$COOH (the weak acid) + CH$_3$COONa (the salt, conjugated base)

Phosphate buffer: NaH_2PO_4 (the weak acid) + Na_2HPO_4 (the salt, conjugated base)

Tris buffer*:*

Tris (free base)   + TrisHCl (the salt, conjugated acid)

(Tris: Tris [2-amino-2-(hydroxymethyl)-propan-1,3-diol)], an organic base)

Now, Buffer Capacity can be defined as the measure of the efficiency of a buffer in resisting its change in pH. This definition does present a bit of a problem as to 'what is the significant change?' Sometimes, a change of 1 unit does not bring about any significant change. At other times, even a 0.1-unit change can cause a significant difference. So, to giveclear definition, buffer capacity may be defined as the quantity of a strong acid or strong base that must be added to one liter of a solution to change it by one pH unit. The buffer capacity equation is as follows:

$$\beta = dn/dpH$$

where n is some equivalents of added strong base (per 1 L of the solution). Note that the addition of n moles of acid will change the pH by the same value, but in the opposite direction. We will derive a formula connecting buffer capacity with pH, pK_a and buffer concentration.

It can be shown that the buffer capacity is maximum when the concentration of the weak acid and the base participating in the major proton transfer process in the buffer solution are same.

Let us have a buffer solution prepared by by mixing a weak acid (HA) with a strong base (MOH) having their initial equivalent concentration a and b (where a > b) respectively. Thus in the buffer prepared, concentrations of the unconsumed weak acid and its conjugate base are: [HA] = a − b; [A] = b. From the the Henderson's equation,

$pH = pK_A + log [A^-]/[HA] = pK_A + log [b/(a − b)]$

$pH = pK_A + (1/2.303) \ln [b/(a − b)]$

Therefore, $d(pH)/db = (1/2.303) [(a − b)/b] [a/(a − b)^2]$

$d(pH)/db = (1/2.303) [a/(a − b)b]$

$db/d(pH) = 2.303 [b(a − b)/a]$

β = 2.303 [b(a – b)/a]

dβ/db = 2.303(a – 2b)/a

for maximum β, dβ/db = 0, Then b = a/2

Hence, for b = a/2 (i.e., at half neutralization), β is maximum or minimum. Therefore, at half neutralization, the buffer capacity is maximum.

Importance of Buffer Solution

(1) In biological processes: The pH of our blood is maintained constant inspite of various acid and base producing reactions going on in our body. The buffer action is due to the presence of carbonic acid , bicarbonate ion and carbon dioxide in the blood.

(2) In industrial processes: The use of buffers is an important part of many industrial processes, e.g.,in electroplating, in the manufacture of leather, dyes, photographic materials.

(3) In analytical chemistry: (i) in the removal of acid radicals such as phosphate, oxalate and borate which interfere in the precipitation of radicals of group 3.(ii) in complexometric titration(iii) to calibrate the pH metres

(4) In bacteriological research, culture media are generally buffered to maintain pH required for the growth of the bacteria being studied.

1.11. Acid – Base Neutralization Curves and Choice of Indicators

Acid – base titration, which is sometimes called neutralization titration is used to titrate any species having an acidic characteristic enough ($K_a > 1 \times 10^{-8}$) where it can be titrated with a standard solution of a strong base. Like wise any species that has basic property enough ($K_b > 1 \times 10^{-8}$) can be titrated with a standard solution of a strong acid. The most important characteristics of a neutralization titration can be summarized in the titration curve (usually pH as a function of volume of the titrant). The titration curve can be calculated theoretically, whereupon conclusion can be drawn from it for the feasibility and the expected accuracy of a titration, and the selection of the proper indicator. The most common approach for the calculation of titration curves is based on approximations depending on the relative strength of the acid and base, the concentration levels, and the actual region of the titration curve relatively to the equivalence point.
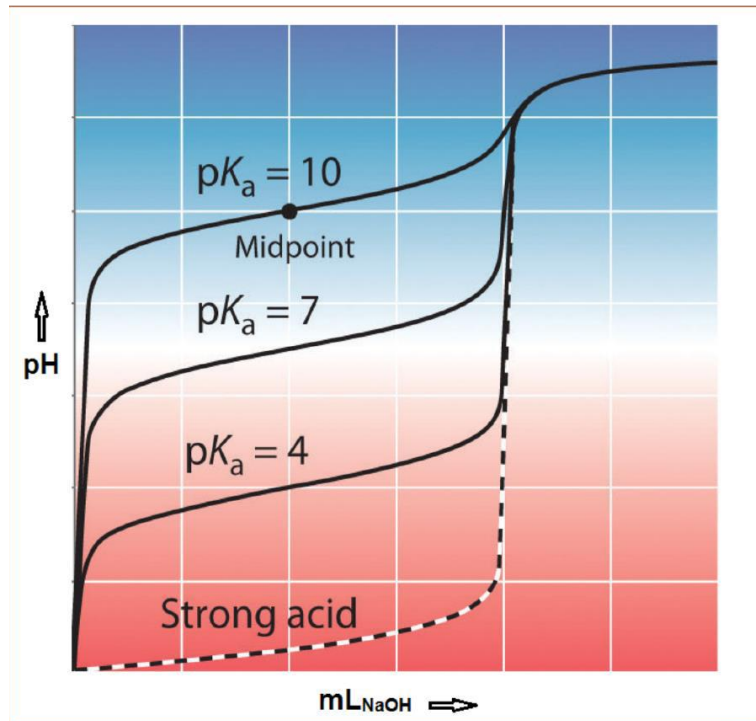
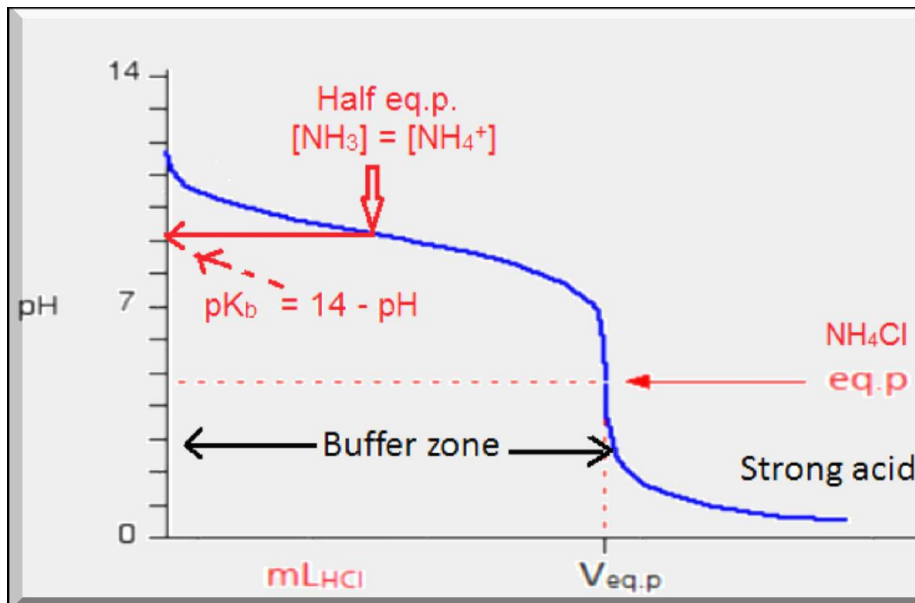### 1.11.1   Strong Acid and Strong Base Titration Curve
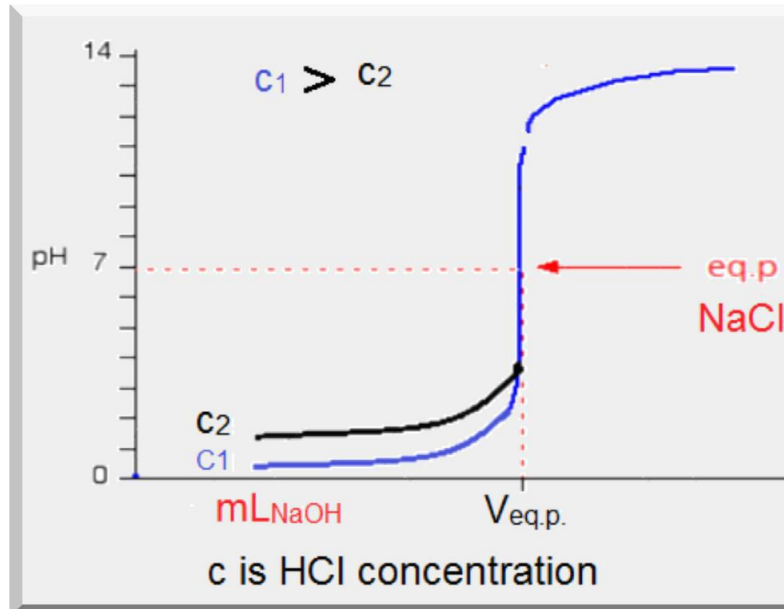
1.11.2   Weak Acid and Strong Base Titration Curve
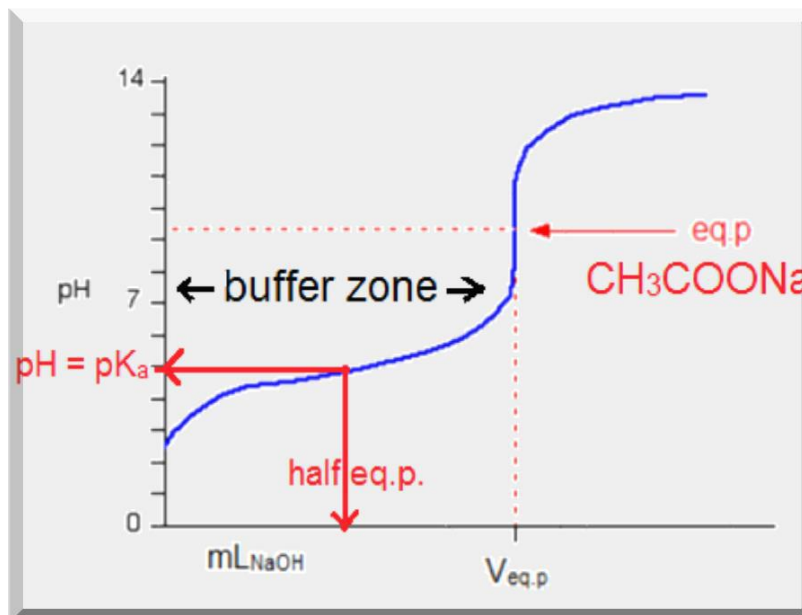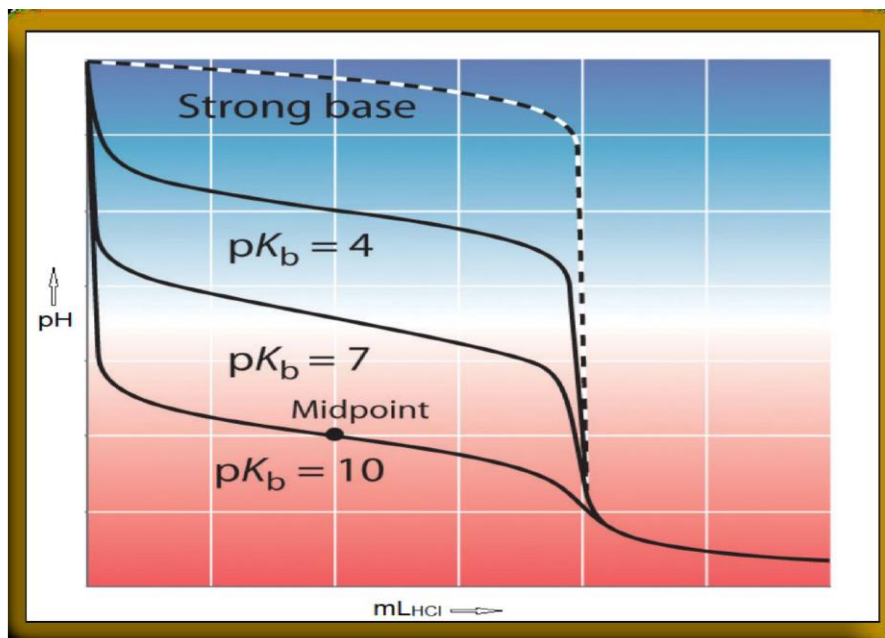
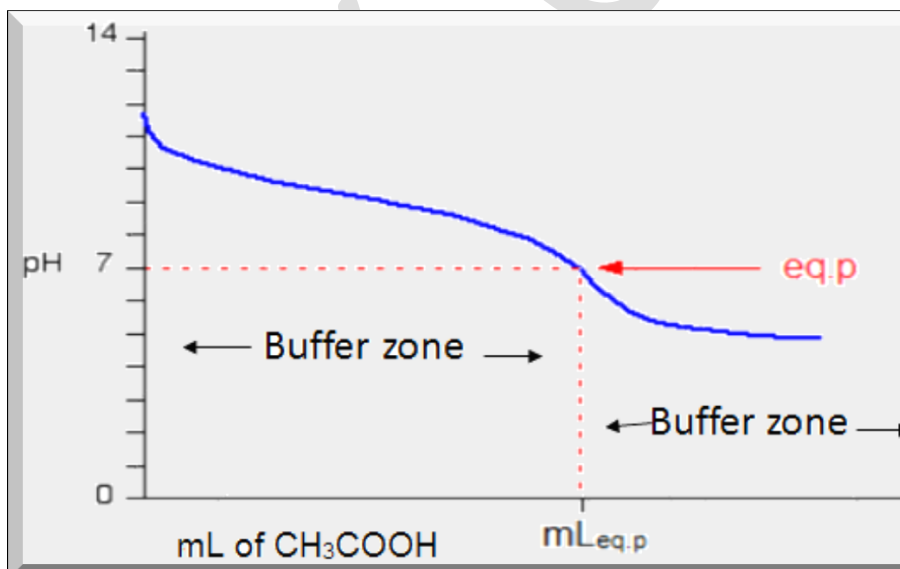### 1.11.3   Weak Acid and Strong Base Titration Curve

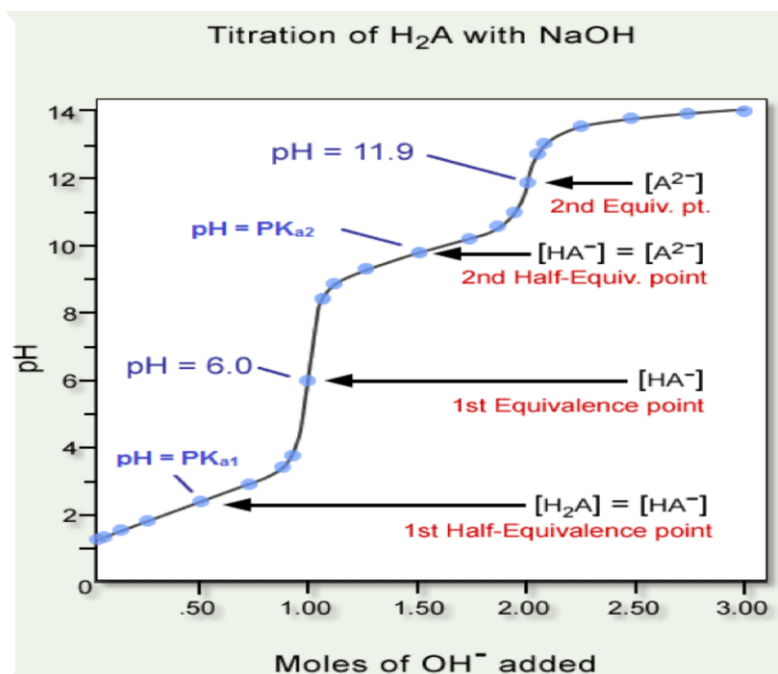### 1.11.4 Weak Base and Strong Acid Titration Curve

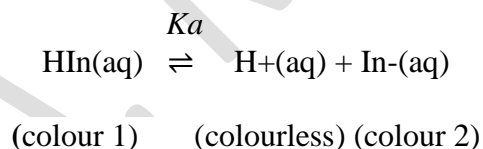## 1.11.5. Weak Base and Weak Acid Titration Curve

1.11.5. Curves for Polyprotic Acids Titration

Titration of H₂A with NaOH

1.12. Choice of Indicators in Acid–base Titrations

Acid-base titration indicators are usually weak acids (HIn) which ionise as follows:

$$\text{HIn(aq)} \underset{}{\overset{Ka}{\rightleftharpoons}} \text{H+(aq) + In-(aq)}$$

(colour 1)   (colourless) (colour 2)

$$\text{pH} = \text{p}Ka + \log[\text{In}^-\text{(aq)}]/[\text{HIn(aq)}]$$

For the reaction mixture to impart colour 1 with confidence,[In- (aq)]/ [HIn(aq)]has to be ≤ 1/10

For the reaction mixture to impart colour 2 with confidence,[In- (aq)]/ [HIn(aq)]has to be ≥10.

In other words, for the reaction mixture to impart colour 1 with confidence, pH value of the solution should be pKa- 1 or lower, and for the reaction mixture to impart colour 2with confidence, pH value of the solution should be pKa+1 or higher. Hence pH range of an indicator = pKa± 1.
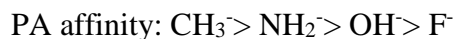
1.13. Gas Phase Acidity

The proton affinity and gas phase acidity are quite similar in this contest. The term proton affinity of a species B is determined from the enthalpy change of the following process:

$B_{(g)} + H^+_{(g)} \rightleftharpoons BH^+_{(g)}$, $-\Delta Hp = PA$ of B; $HA_{(g)} \rightleftharpoons H^+_{(g)} + A^-_{(g)}$, (Gas phase acidity of HA)
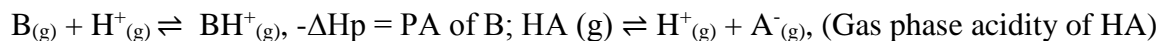
ΔHp can be estimated by constructing a suitable Born-Haber cycle. If A^- is the conjugate base of HA, then the higher proton affinity of A- indicates the weaker gas phase acidity of HA. In terms of Born – Haber cycle, gas phase acidity of HA depends on the three energy terms i.e. HA bond dissociation energy, ionization energy of H and electron affinity (EA) of A. Higher stability of A- (g) will enhance the gas phase acidity of HA. In the case of aqueous phase acidity, solvation of the involved species is to be considered.

Gas phase acidity of the hydrides of 2nd period elements run as:

PA affinity: $CH_3^- > NH_2^- > OH^- > F^-$

Gas phase acidity: $HF > H_2O > NH_3 > CH_4$, (same sequence in aqueous phase)

Beside the A-H bond strength (which does not change remarkably in a period), the electron affinity of A is also an important factor to determine the gas phase acidity. The higher electron affinity (or electronegativity roughly) of A will favour the process more. In a period, EA increases from left to right. This is reflected in above series.

A-H bond strength decreases for the heavier congeners in aparticular group because of the increasing trend of A – H bond length. In fact, the heavier congeners, the valence orbitals of larger size cannot effectively overlap with the small 1s orbital of H. Thus the bond strength decreases in the following sequence:

$H – O (H_2O) > H – S (H_2S) > H – Se > H – Te (H_2Te)$;

$H – N (NH_3) > P – S (PH_3)$; $H – F > H – Cl > H – Br > H – I$
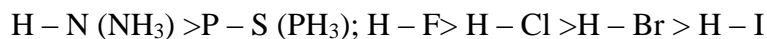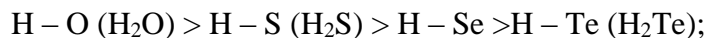
Gas phase acidity: $H_2Te > H_2Se > H_2S > H_2O$; $HI > HBr > HCl > HF$; $PH_3 > NH_3$

Proton affinity: $OH^- > HS^- > HSe^- > HTe^-$; $F^- > Cl^- > Br^- > I^-$; $NH_2^- > PH_2^-$

In a group, in general electron affinity decreases in moving from top to bottom. Thus in terms EA, hydrides of heavier congeners should show reduced gas phase acidity. The observed reverse sequence can be explained by considering the bond strength which decreases for the heavier congeners, Thus we can conclude:

(i)   In a period, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases in moving from left to right and it is mainly due to the increasing trend of electron affinity.

(ii)   In a group, the gas phase acidity (and also aqueous phase acidity) of the hydrides increases from top to bottom and it is governed mainly by the bond strength sequence through opposed by the electron affinity sequence.

Gas phase acidity: $C_2H_5OH > CH_3OH > H_2O$ (opposite sequence in aqueous phase)

The alkyl groups are the better electron pushing groups compared to hydrogen. Thus H_2O is expected to be stronger acid than ROH but it is not true in gas phase. To explain the sequence, we are consider the relative stability of the conjugate bases i.e. $C_2H_5O^-$, CH_3O^- and OH^-. Now let us consider the inherent group electronegativity(a1) and charge capacity parameters ($\sigma \propto 1/b$)

a: H (2.1) < Me (2.3) < Et (2.32); σ : H(1) < Me (2.8) < Et (3.9)

Thus inherent electronegativities of the groups H, Me and Et are more or less the same but their charge capacity parameters are quite different. In terms of the σ values, the charge accommodating capacity of the groups is in the sequence: Et > Me > H. The ion induced dipole interaction due to the polarization of the R-group in R-O$^-$ also follows the same trend. Thus stability of the conjugate bases due to charge delocalization through the polarization of R runs in the sequence: $EtO^- > MeO^- > OH^-$.

Gas phase acidity order of primary, secondary and tertiary alcohols: It runs in the sequence $R(3°)OH > R(2°)OH > R(1°)OH$.

The sequence can not be explained in terms of simple electron pushing inductive effect of R but it can be explained in terms of electron capacity charge parameters of the R groups and the resultant stability sequence of the conjugate bases. The charge capacity is large for the more branched chain alkyl groups and consequently such alkyl groups are the better moieties to accommodate the charge. Thus the stability order of the conjugate base in terms of charge delocalization run as $R(3°)O^- > R(2°)O^- > R(1°)O^-$

Gas phase acidity $CH_3OH > H_2O$ but $CH_3SH < H_2S$

The size of the orbitals of carbon and sulfur differ significantly while the orbitals of carbon and oxygen are comparable in size. Thus stabilization of CH_3S^- through charge delocalization by hyperconjugation is not efficient but CH_3O^- is efficiently stabilized by through charge delocalization by hyperconjugation.

Similarly, the gas phase acidity orders are $CHCl_3 > CHF_3$; $C_6H_5CH_3 > CH_4$; $CH_3NO_2 > CH_4$

1.14   Questions

(1) What are the different types of Lewis acids and bases? Discuss the merits and demerits of Lewis concept.

(2) What are the basic features of Bronsted –Lowery concept of acids and bases? Discuss its merits and demerits.

(3) Discuss the basic idea of Lux-Flood concept of acids and bases?

(4) What do you mean by the leveling effect of water? How do you express the acid strength?

(5) Discuss the relative strength and factors of mononuclear oxyacids?

(6) What do you mean by the Hammett acidity function (H_0)? What do you mean by H_0, H_+, H_-? What do you mean by the superacids?

(7) Discuss the basic concept of SHAB principle. What are the basic characteristics of hard and soft species?

(8) What do you mean by buffer? How does a buffer show its action? Show that buffer capacity is maximum at the pH close to the pKa value of the conjugate weak acid.

(9) Discuss the basic principle involved in selecting the indicator in acid base titration.

(10) What do you mean by gas phas acidity? Which factor affecting the strength of gas phas acidity?

1.15   Answers

(1) See the section 1.2.5

(2) See the section 1.2.3

(3) See the section 1.2.4

(4) See the section 1.4 and 1.5

(5) See the section 1.6

(6) See the section 1.7

(7) See the section 1.8 and 1.8.1

(8) See the section 1.11

(9) See the section 1.12

(10) See the section 1.13

1.16   References

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