Inorganic Chemistry

Acids, Bases and Non-Aqueous Solvents

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Keywords
Arrhenius theory, Bronsted-Lowry theory, Solvent-system concept

Introduction

The terms ‘acids’ and ‘bases’ have been defined in many ways. According to Arrhenius, probably the oldest, acids, and bases are the sources of H^+ and OH^- ions respectively. A somewhat broader but closely related definition (Bronsted – Lowry) is that an acid is a substance that supplies protons and a base is proton acceptor. Thus in water an acid increases the concentration of hydrated proton ($H3O^+$) and a base lowers it or increases the concentration of OH^-. In addition to Bronsted-Lowry concept there are others like solvent-solvent definition and the Lux and Flood definition but each one has its own limitations. One of the most general and useful of all definitions in reference to complex formations was due to G. N. Lewis. Lewis defined acid-base in terms of electron pair donor-acceptor capability. This definition includes Bronsted- Lowry definition as a special case. Some- what related to Lewis concept was an approach developed by Pearson, who generalized complex formation in terms of hard-soft acids and bases.

All these concepts will be discussed in detail. Attempt will also be made to highlight some of the structural and theoretical aspects regarding these concepts of few non-aqueous solvent systems as they are relevant in this context.

1. **Arrhenius Concept**

The first modern approach to acid-base concept was advanced in 1878 by Swedish chemist Svante Arrhenius, according to which an acid is defined as a hydrogen compound which in water solution gives hydrogen ions and a base is a hydroxide compound which in water solution yields hydroxide ions.

Examples:

HCl , HNO_3 , H_2SO_4	(acids)
$NaOH$, KOH, $Ba(OH)_2$	(bases)

The reactions of an acid with a base represented a neutralization of the characteristics of both. The Arrhenius theory has been subjected to many objections, the chief among them beings:

(1) The theory defined an acid or a base in terms hydrogen or hydroxyl compounds only.
(2) It offered no satisfactory explanation for the acid property of various substances such as $AlCl_3$, NH_4NO_3, etc.
(3) A bare proton cannot exist in solution.
(4) The theory does not include non-aqueous solvents.

Arrhenius’s ideas had to be extended as several substances are capable of releasing hydrogen ions by reacting with water, though they themselves do not contain hydrogen, e.g, SO_3, N_2O_5, Cl_2O_7, etc. Similarly, there are compounds which may form OH^- ions on their reaction with water. e.g. Na_2O, K_2O, etc.

In spite of the objections Arrhenius theory is still unrivalled in its simplicity and is found adequate for an elementary approach.

2. **Bronsted – Lowry Concept of Acids and Bases**

A general definition of acids and bases was given independently by Bronsted and Lowry in 1923. According to this concept an acid is defined as a compound or ion which gives a proton and a base is a compound or ion which accepts a proton from an acid. Thus the definition applies to protonic systems; those in which proton transfer can occur. A general equation expressing proton transfer in aqueous solutions is :

$$AH_{(aq)} + B_{(aq)} \rightarrow A^-_{(aq)} + BH^+_{(aq)}$$

where AH is a general acid with a proton which is dissociable and B is a general base which can accept a proton. In the reverse process where the proton is donated by BH^+ ions to the anion A^-, BH^+ is called the acid and the anion A^- the base. Further, when a substance that on reaction with water releases proton (H^+) is an acid and any substance that accepts proton (H^+) from water is a base. Thus

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

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
(Base)

HCl is an acid and NH_3 a base. To HCl , H_2O is a base and to NH_3, water is an acid, Hence, we are led to the idea that when acid reacts with a base, there are two <u>conjugate</u> <u>acid-base</u> pairs i.e. for every acid there exists a base which is produced when the acid loses its proton and for every base there exists an acid which is produced when the base accepts proton. The acid or base so related are said to be conjugate to be one another. Thus

HA	+	B	→	BH^+	+	A^-
Conjugate Acid$_1$		Conjugate Base$_2$		Conjugate Acid$_2$		Conjugate Base$_1$

This concept is illustrated for a series of common acids and bases.

Acid$_1$		Base$_2$		Acid$_2$		Base$_1$
HCl	+	H_2O	→	H_3O^+	+	Cl^-
HNO_3	+	H_2O	→	H_3O^+	+	NO_3^-
$HClO_4$	+	H_2O	→	H_3O^+	+	ClO^-_4
H_2SO_4	+	H_2O	→	H_3O^+	+	HSO^-_4
H_2S	+	H_2O	→	H_3O^+	+	HS^-
HCN	+	H_2O	→	H_3O^+	+	CN^-
$CH_3\overset{O}{\underset{OH}{C}}$	+	H_2O	→	H_3O^+	+	$CH_3\overset{O}{\underset{O-}{C}}$
NH^+_4	+	H_2O	→	H_3O^+	+	NH_3
H_2O	+	CN^-	→	HCN	+	OH^-
H_2O	+	CO^{2-}_3	→	HCO^-_3	+	OH^-

In general, stronger the acid, the weaker is its conjugate base; conversely stronger the base, the weaker is its conjugate acid.

Actually no acid surrenders its proton unless it comes in contact with another substance (may be the solvent) of higher proton affinity acting as a base. Thus a base accepts a proton from a water molecule releasing hydroxyl ion,

$$H_2O + B \rightarrow BH^+ + OH^-$$

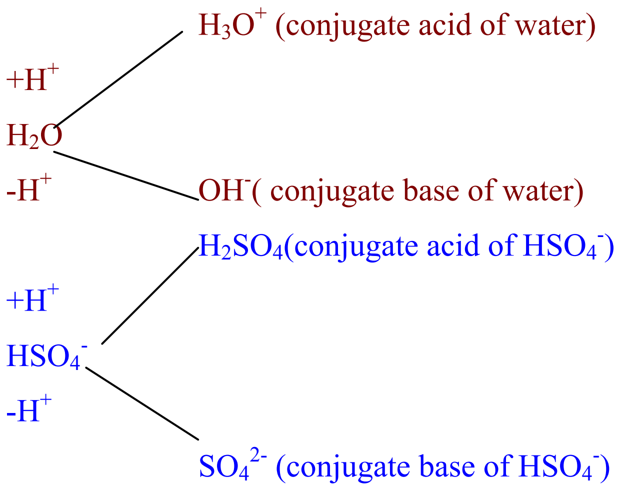
Many anions are bases and take up proton to from a neutral molecule. Basic behaviour in aqueous solution results in an increase in hydroxyl ion concentration and hence, a decrease in hydronium ion concentration. The oxide of electropositive metals are well known bases. The oxide ion present in them has great affinity for proton, i.e.

$$Na_2O \rightarrow 2Na^+ + O^{2-}$$

$$H_3O^+ + O^{2-} \rightarrow H_2O + OH^-$$

Metal hydroxides which ionize in water to produce hydroxyl ions directly are also classified as bases.

Certain species may be either acids or bases, depending on the way they behave in a given reaction. These are regarded as amphoteric substances. Thus water and HSO_4^- ion may either lose or gain proton; their nature is then decided by the other acidic or basic species present in solution:



Reactions involving the transfer of proton are known as protolytic reactions. The substances which can function both as an acid and a base such as water or alcohol are designated as amphiprotic or amphoteric.

3. Solvent –System Concept

The Lowry-Bronsted concept of acid-base phenomenon is much broader than the one provided by Arrhenius. In this concept the acid-base behaviour is neither restricted to nor dependent upon any particular solvent. In fact the Bronsted concept applies to many of the solvents that contain hydrogen. Liquid ammonia is another solvent most widely studied. Ammonia like water produces charges bearing particles as:

$$\begin{array}{lllllll} NH_3 & + & NH_3 & \Leftrightarrow & NH_4^+ & + & NH_2^- \\ \text{acid} & & \text{base} & & \text{acid} & & \text{base} \end{array}$$

Compare $H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$

When water is added in liquid ammonia

$$\begin{array}{lllllll} H_2O & + & NH_3 & \Leftrightarrow & NH_4^- & + & OH^- \\ \text{acid} & & \text{base} & & \text{acid} & & \text{base} \end{array}$$

Water becomes a weak acid. The acid properties of ammonia are much less known; when chlorine dissolves in ammonia

$$\begin{array}{lllllll} 2NH_3 & + & Cl_2 & \Leftrightarrow & NH_2Cl & + & NH_4Cl \\ \text{acid} & & \text{base} & & \text{base} & & \text{acid} \end{array}$$

From the above reactions it is clear that when a substance acts as an acid or a base it acts in such a way as to furnish a particular type of ion characteristic of the solvent. Thus in the solvent-system concept (Franklin, 1935) an acid is defined as a *species that increases the concentration of the characteristic_cation of the solvent and a base as a species that increases the concentration of the characteristic anion.* The usefulness of this concept is primarily in terms of convenience. One may treat nonaqueous solvents by analogy with weather.

For example:

$$Kw = [H_3O^+] [OH^-] = 10^{-14}$$

$$K_{AB} = [A^+] [B^-]$$

where $[A^+]$ and $[B^-]$ are the concentrations of the cationic and anionic species characteristic of a particular solvent. Similarly, pH scale of water may be constructed with the neutral point equal to $-1/2\log K_{AB}$. The “levelling” effect follows quite naturally from this viewpoint. All acids and bases stronger than the characteristic cation and anion of the solvent respectively will be “levelled” to the latter; acids and bases weaker than those of the solvent system will remain in equilibrium with them. For example

$$H_2O + HClO_4 \rightarrow H_3O^+ + ClO_4$$

but $H_2O + CH_3COOH \rightarrow H_3O^+ + CH_3COO^-$

Similarly

$$NH_3 + HClO_4 \rightarrow NH_4^+ + ClO_4^-$$

and $NH_3 + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$

but $NH_3 + NH_2CONH_2 \rightarrow NH_4^+ + NH_2CONH^-$

This solvent system has been used extensively as a method of classifying solvolysis reactions. For example, one can compare the hydrolysis of non-metal halides with their solvolysis by non-aqueous solvents:

$H_2 + OPCl_3 \rightarrow OP(OH)_3 + 3HCl$

$3ROH + OPCl_3 \rightarrow OP(OR)_3 + 3HCl$

$6\,NH_3 + OPCl_3 \rightarrow OP(NH_2)_3 + 3\,HCl$

The solvent is actually a reagent in many reactions behaving sometimes as an acid sometimes as a base.

The solvents which contain hydrogen and from which proton can be derived are known as protic solvents, e.g. water, liquid ammonia and hydrogen fluoride. Solvents which have no tendency to accept or release protons are known as aprotic solvents, e.g. benzene, chloroform, CCl_4, etc.

4. Aprotic Acids and Bases

The Bronsted concept of acids and bases obviously cannot be applied to solvents which do not contain bound hydrogen. Nevertheless, some of the general features of acid base theory find analogies in the other solvents such as liquid BrF_3, liquid SO_2 and liquid N_2O_4. Each of these solvents is a conductor of electricity; the ions arise from the self ionization of the solvents.

$2BrF_3 \Leftrightarrow BrF_2^+ + BrF_4^-$

$2SO_2 \Leftrightarrow SO^{2+} + SO_3^{2-}$

$N_2O_4 \Leftrightarrow NO^+ + NO_3^-$

Carrying the analogies further, the cations correspond to acids and anions to bases. Thus in liquid BrF_3 silver fluoride is a strong base and SbF_3 is a strong acid, leading to the following:

$AgF + BrF_3 \Leftrightarrow Ag^+ + BrF_4^-$

$SbF_5 + BrF_3 \Leftrightarrow BrF_2^+ + SbF_6^-$

Thus, substances which give rise to BrF_2^+ ions in BrF_3 solvent behave as acids and those producing BrF_4^- act as bases.

Zinc dissolves in liquid N_2O_4 liberating NO and forming the ions NO^+ and $[Zn(NO_3)_4]^{2-}$

$4N_2O_4 + Zn \Leftrightarrow [Zn(NO_3)_4]^{2-} + 2NO^+ + 2\,NO$

5. Lux- Flood Acid- Base Concept

In contrast to the Bronsted-Lowry theory that emphasizes the proton as the principal species in acid-base reactions, the definition proposed by H. Lux and extended by H. Flood describes the acid-base behaviour in terms of oxide ion. This acid-base concept was advanced to treat nonprotonic systems which were not amenable to the Bronsted- Lowry definition. For example, in solid state reactions at high temperatures (inorganic melt reactions) the following reaction takes place:

$$\underset{\text{base}}{CaO} + \underset{\text{acid}}{SiO_2} \rightarrow CaSiO_3$$

The base is an oxide donor and the acid is an oxide acceptor. The usefulness of the Lux – Flood definition is mostly limited to systems such as molten oxides. This approach emphasizes the acid – base concepts in the chemistry of anhydrides certainly useful though generally neglected. The Lux-Flood base is a basic anhydride:

$$Ca^{2+} + O^{2-} + H_2O \rightarrow Ca^{2+} + 2OH^-$$

and the Lux-Flood acid is an acid anhydride:

$$SiO_2 + H_2O \rightarrow H_2SiO_3$$

A general definition of acid-base behaviour might be developed by identifying metal and nonmetal oxides as acids and bases.

6. Strength of Bronsted Acids and Bases

In Bronsted term the strength of an acid is determined by its tendency to donate protons, and that of a base is dependent on its tendency to receive protons. The reaction proceeds virtually

$$\begin{array}{lllllll} \text{Acid} & & \text{Base} & & \text{Acid} & & \text{Base} \\ HCl & + & H_2O & \rightarrow & H_3O^+ & + & Cl^- \end{array}$$

to completion (from left to right). It may be concluded that HCl is a stronger acid than H_3O^+ and so also H_2O is a stronger base than Cl^- since HCl has stronger tendency to lose proton and H_2O has stronger tendency to receive proton. The strong acid HCl, has a weak conjugate base Cl^-.

A strong acid, which has a greater tendency to lose protons, is necessarily conjugate to a weak base, which has a smaller tendency to gain and hold protons. Hence, the stronger the acid, the weaker its conjugate base. Conversely, strong base attracts protons strongly and is necessarily conjugate to a weak acid. The stronger the base, the weaker its conjugate acid.

Acetic acid in 1.0 M aqueous solution is 0.42 per cent ionzed at 298 K. The equilibrium represented as:

$$\begin{array}{lllll} \text{Acid} & \text{Base} & & \text{Acid} & \text{Base} \\ HC_2H_3O_2 & H_2O & \Leftrightarrow & H_3O^+ & C_2H_2O_2^- \end{array}$$

is displaced to the left. This reaction may be understood as representing a competition between bases, acetate ions and water molecules, for protons. The position of the equilibrium shows that the acetate ion $C_2H_3O_2^-$ is a stronger base than H_2O; at equilibrium more protons form acetic acid, $HC_2H_3O_2$ molecules than form H_3O^+ ions. It may also be concluded that H_3O^+ is a stronger acid than acetic acid $HC_2H_3O_2$; at equilibrium more H_3O^+ ions than acetic acid, HC2H3O2 molecules have lost protons. From these examples it is noted that the stronger acid H_3O^+ is conjugate to a weaker base H_2O and the stronger base, acetate C2H3O2$^-$ is conjugate to the weaker acid, acetic acid $HC_2H_3O_2$.

Another conclusion may be drawn that the position of equilibrium favours the formation of the weaker acid and weaker base. Thus in the reaction of HCl and H_2O the equilibrium concentrations of H_3O^+ and Cl^- (the weaker acid and base respectively) are high, whereas in the solution of acetic acid the equilibrium concentration of H_3O^+ and $C_2H_3O_2^-$ (the stronger acid and base respectively) are low.

7. Relative Strengths of Acids and Bases (Quantitative Aspect)

It is very useful to have a quantitative measure of the tendency of an acid to lose a proton and a base to gain one, i.e. of the acid and base strengths. For a protonic acid HX the following equilibrium is established in aqueous solution

$$HX + H_2O \Leftrightarrow X^- + H_3O^+$$

The equilibrium constant of this system, κ_a, expresses the relative tendencies of HX and H_3O^+ to donate a proton.

$$K_a = \frac{{}^aX^- \times H_2O^+}{{}^aHX \times {}^aH_2O}$$

Note: ${}^a(X)$ is the activity of X, its effective thermodynamic concentration in the solution at equilibrium. Where thermodynamic precision is not required or when concentrations are very low activities of solutes are replaced molar concentrations [X].

${}^aH_2O$ is virtually constant for dilute solutions and it is usual to define a second constant K, as

$$K_a = \frac{{}^aX^- \times {}^aH_3O^+}{{}^aHX}$$

Ka denotes the acid strength, that is, the extent to which HX is ionized. In water the conjugate base X^- can undergo the reaction.

$$X^- + H_2O \rightarrow HX + OH^-$$

$$K_b = \frac{{}^aXH \times {}^aOH^-}{{}^aX^-}$$

$K_aK_b = K_w(= {}^aH_3O^+ \times {}^aOH^-)$ the ionic product of water which has the value , $K_{w} = 1.0 \times 10^{-14}$ at 298.1 K.

A number of experimental methods are available for the measurement of acid and base strengths; reference should be made to a textbook of Physical Chemistry for details of these. The values of K vary through many powers of ten for different acids and bases. It is generally more convenient to express strengths as negative logarithm of dissociation constants, ${}_pK_a(=-\log_{10} K_a)$

A large value of ${}_pK_a$ means that the acid is little dissociated and therefore weak; a small value is found for ${}_pK_a$ when the acid is strong, ${}_pK_a$ values of some weak acids are given in Table .1 in aqueous medium.

Table 1: ${}_pK_a$ values for Some Weak Acids in Aqueous Solution (298 K)

Acid	${}_pK_a$	Acid	${}_pK_a$
H_3AsO_3	9.2	HNO_2	3.3
H_3AsO_4	2.3	$CH_3NH^+_3$	10.7
H_3BO_3	9.2	$N_2H_3^+$	8.0
H_2CO_3	6.4	$HONH_3^+$	5.0
HOOCH	3.7	H_2O_2	11.8

$HOOCH_3$	4.7	H_3PO_2	2.0
CNH	9.3	H_3PO_4	1.8
HClO	7.2	H_2PO_4	2.1
$HClO_2$	2.0	$H_2PO_4^-$	7.3
HF	3.3	H_2S	7.0
HIO	10.0	H_2SO_3	1.9
H_5IO_6	1.6	HSO_3^-	7.2
HN_3	4.7	HSO_4^-	1.9
$H_2N_2O_2$	7.1	H_2Te	2.6

Instead of aqueous solution if different solvents are chosen, then the acid strengths will be different. Thus, in strongly acid solvents such as sulphuric acid the normally strong i.e. completely dissociated, acids like perchloric and hydrochloric are not as strong as the acid $H_3SO^+_4$; and hence have $_pK_a$ values in sulphuric acid greater than unity. The $_pK_a$ value for perchloric acid is about +4 whereas in aqueous solution it is about -10, a difference of fourteen powers of ten in K_a. In a more basic solvent such as liquid ammonia, there is a much greater levelling effect and even a weak acid such as formic acid, HCOOH, with $_pK_a = 3.68$ in water acts as a strong acid.

$$HCOOH\,(sol) + NH_3(l) \rightarrow \quad NH_4^+\,(sol) + HCOO^-\,(sol)$$

The levelling effect on acids in liquid ammonia occurs for acids with a $_pK_a$ (in water) less than about 4. The levelling effects on acids differ from solvent to solvent systems.

8. Solvent Leveling and Discrimination in Water

Any acid stronger than H_3O^+ in water donates a proton to water and forms H_3O^+. Consequently no acid stronger than H_3O^+ can survive in water and no experiment conducted in water can tell us which is the stronger acid of HCl and HBr because both react essentially completely to give H_3O^+ . Water is said to have levelling effect. Since the effective proton affinity of H_2O in water is 1130 kJ mol^{-1} all acids with conjugate bases having effective proton affinity smaller than 1130 kJ mol^{-1} are levelled in water.

A base strong enough to react completely with water to give the OH^- ion will be levelled; hence OH^- is the strongest base that can exist in water. The proton affinity of OH^- in water is 1188 kJ mol^{-1} . Any base with an effective proton affinity greater than 1188 kJ mol^{-1} will be converted into the conjugate acid HA, producing OH^- ion in the process. For this reason we cannot study NH_2^- or CH_3^- in water by dissolving their salts because both generate OH^- quantitatively and are fully protonated to NH_3 and CH_4. The range of acidity that can be studied in water lies approximately between the effective proton affinities of 1130 kJ mol^{-1} and 1188 kJ mol^{-1} , a range of 58 kJ mol^{-1}. If the proton affinity A^- is less than 1130 kJ mol^{-1} HA will be converted to A^- and all the protons will be present as H_3O^+ . If the proton affinity is greater than 1188 kJ mol^{-1} the solute will exist only as HA at the expense of forming OH^- ions from water.

It is interesting to express the acidity range as equilibrium constant. The contribution of the reaction entropy is important in solution and we must use $\Delta G^o = +\,81$ kJ mol^{-1} in place of + 58 kJ mol^{-1} in

$$\Delta G = -2.303\ RT \log K$$
$$= 2.303\ RT\ {}_pK$$

This gives $_pK = 14$ which is the value of $_pK_w$. The window of unlevelled strengths which in terms of proton affinities span 58 kJ mol^{-1} as can be interpreted as the value PK_w.

For any solvent, the range over which acid and base strength can be discriminated is given by its antroprotolyis constant. For water, the range is 14. For liquid ammonia $_pK_w = 33$

$$NH_3\ (1) + NH_3\ (1) \Leftrightarrow NH_4^+\ (am) + NH_2^-\ (am)$$

So the range of discrimination is considerably wider. It is quite easy to understand the physical basis of this. Since the proton affinity of NH^-_2 is considerably higher than that of OH^-, strong bases that are levelled in water will not be levelled in ammonia. However, the proton affinity of NH_3 is distinctly greater than that of H_2O, so the acids that are weak in water may be levelled in ammonia. Hence the basic solvent ammonia has a window for measurement of acid strengths that is widened and shifted towards weaker acids.

The converse is also true. Thus going from water to a more strongly acid solvent, such as CH_3COOH moves the range of distinguishable acids toward stronger acids. The proton affinity of CH_3COOH is less than that of OH^- so acids that transfer proton completely to water do not do so completely to CH_3COOH. Since CH_3COO^- has a lower proton affinity that OH^-, weaker bases may convert CH_3COOH quantitatively to CH_3COO^-.

The window for dimethyl sulphoxide (DMSO) solvent is wide because $_pK$ for DMSO is (37) quite large. Consequently it can be used to study a wide range of acids (from H_2SO_4 to phosphine (PH_3)).

9. Amphoterism

An amphoteric oxide (from Greek word meaning both) is an oxide that reacts with both acids and bases. Thus Al_2O_3 reacts with acids and alkalies:

$$Al_2O_3 + 6H_3O^+(aq) + 3H_2O(1) \rightarrow 2\ Al\ (H_2O)_6{}^{3+}(aq)$$
$$Al_2O_3 + 2OH^-(aq) + 3H_2O(1) \rightarrow 2\ Al\ (OH)\ 4]^-(aq)$$

Amphoterism is observed for lighter elements of Groups 2 and 13 as illustrated by BeO, Al_2O_3, _ Ga_2O_3. It is also observed for some of the d-block elements such as TiO_2 and V_2O_5 and some of the heavier elements of Group 14 and 15 e.g. SnO_2, As_2O_5 and Sb_2O_5.

10. Trends in Acid Strength of various Bronsted Acids

(1) **Polyprotic acids:** They are capable of dissociating into more than one proton e.g. H_2SO_4, H_3PO_4. They dissociate in steps. The tendency to dissociate in water follows the order

$H_2SO_4 > HSO^-_4$

$H_3PO_4 > H_2PO^-_4 > HPO^-_4$

(2) In acids with the same central atom containing different number of oxygen atoms, the acid strength increases as the oxidation number of central atom increases:

$HC1O_4 > HC1O_3 > HC1O_2 > HC1O$

$H_2SO_4 > H_2SO_3$

$HNO_3 > HNO_2$

The more positive central atom will attract its bonding electrons with the oxygen to a greater extent than does the hydrogen atom.

(3) Acids with different central atoms containing oxygen: All oxygen atoms attached to central atom, lesser the number of hydrogenated oxygen atoms, greater the acid strength.

$HClO_4 > H_2SO_4 > H_3AsO_3$

The rule is similar to rule (2)

(4) Acids containing oxygen and central atoms having the same oxidation state: The acid strength decreases as the size of the central atom increases.

$HClO_4 > HBrO_4 > HIO_4$

$H_2SO_4 > H_2SeO_4 > H_2TeO_4$

$H_3PO_4 > H_3AsO_4$

Smaller the size of central atom greater is the charge density, the more easily it will attract electrons from the electronegative oxygen.

(5) Hydrogen acids. The acid strength increases with increase in the size of atoms. The per cent ionic character of the bonds in these compounds is in the reverse order to their acid strengths, e.g.

$HI > HBr > HCl > HF$

$H_2Te > H_2Se > H_2S > H_2O$

The gas phase acidity increases across a period and down a group in the *p*-block binary acids, HF is a stronger acid than H_2O and HI is the strongest of the hydrogen halides.

All these halide ions except F^- have proton affinity smaller than H2O which is constant with all the hydrogen halides except HF, being strong acids in water.

Another factor in proton transfer is hydrogen bonding. Thus water has great stabilizing effect on small, highly electronegative ions, particularly for F^-, Cl^-, OH^- to which it can act as hydrogen-bond acceptor. NH^+_4 is stabilized by hydrogen bonding and has reduced acidity. An example is the increased acidity of HCl in CH_3OH which can stabilize Cl^- by forming Cl… $H\text{-}OCH_3$ in comparison with HCl in dimethylformamide $(CH_3)_2NCHO$ which does not have significant hydrogen-bond donor properties.

10.1 Acids Strength and Molecular Structure: In order to understand the relationship between acid strength and molecular structure, acids may be divided into two types, hydrides and oxoacids.

(i)Hydrides: Two factors influence the acid strength of the hydride of an element- the electro negativity of the element and the atomic size of the element. These may be understood by making a comparison of the hydrides of the element in a period and in a group.

(a) Hydrides of the elements of a period: Consider the hydrides of nitrogen, oxygen and fluorine of the second period. The electronegativity of these element increases in the order.

$$N < O < F$$

And acid strength 0f the hydrides increases in the same order

$$NH_3 < H_2O < HF$$

Similarly, the electronegativities of the elements of the third period change in the order

$$P < S < Cl$$

The acid strength of the hydrides of these elements increases in the same order

$$PH_3 < H_2S < HCl$$

PH_3 does not react with water, H_2S is a weaker acid and HCl is a strong acid.

(b) Hydrides of the elements in a group: The acidity of the hydrides of the elements of a group increases with increasing size of the central atom. Consider the hydrides of group 16 and 17 elements

$$H_2O < H_2S < H_2Se < H_2Te$$

$$HF < HCl < HBr < HI$$

This order is the reverse of that expected on the basis of the electronegativity. The first hydrides of each series (H_2O and HF) is the weakest acid of the series and is formed by the element with the highest electronegativity.

Two factors that influence acid strength are the electronegativity of the central atom and the size of the central atom. When these factors work against each other, the effect of atomic size outweighs the electronegativity effect. A proton is more easily removed from a hydride in which the central atom is larger than from the one in which the central atom is small.

Consider for example the hydrides of carbon, sulphur, and iodine. The electronegativity of C, S and I, which belong to different groups are about the same (2.5). The atomic radius of C is 77 pm, of S is 103 pm and of I is 133 pm. There is a marked increase in the acidity of the hydrides with increase in size of the central atom. Methane, CH_4, does not dissociate in water, H_2S is a weak acid, and HI is a strong acid.

(ii) Oxoacids: Oxoacids are the compounds derived from

$$H \overset{a}{-} O \overset{b}{-} Z$$

In each of these compounds, the acidic hydrogen is bonded to an O atom and the variation in the size of this atom is very small. The key to the acidity of the oxoacids lies with electronegativity of the atom Z. If Z is an atom of a metal with a low electronegativity, the electron pair marked *b* will belong completely to the O atom, which has high electronegativity. The compound will be an ionic hydroxide – a base. Sodium hydroxide ($HO^- Na^+$, written as $Na^+ OH^-$) falls into this category.

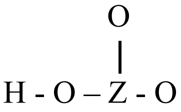
If Z is an atom of a nonmetal with a high electronegativity, the situation is different. The bond marked *b* will be a strong covalent bond not an ionic bond. Instead of adding to the electron density around the O atom, Z will tend to reduce the electron density even though itself is highly electronegative. The effect will be felt in bond *a*. The O atom will draw the electron density of this H-O bond away from the H atom, which will allow the proton to dissociate and make the compound acidic. Hypochlorous acid, HOCl, is an acid of this type.

The higher the electronegativity of Z, the more the electrons are drawn away from the H atom and the more readily proton is lost. In the series

$$HOI < HOBr < HOCl$$

the electrnegativity of Z increases (I < Br < Cl), and the acid strength increases in the same order.

In some molecules additional O atom are bonded to Z, For example.



$$H-O-\overset{\overset{O}{|}}{Z}-O$$

These O atoms draw electrons away from Z atom and make it more positive. The Z atom, therefore, becomes more effective in withdrawing electron density. In turn, electrons of the H – O bond are drawn more strongly away from the H atom. The net effect makes it easier for the proton to dissociate and increases the acidity of the compound. With more number of 0 atoms bonded to Z, the compound becomes a stronger acid. The effect is illustrated in the following series of acids, which are arranged by increasing order of acid strength.

Notice the formal charge on the central atom increasing in the series. As the formal charge on the Cl increases, electron density of the H – O bond shifts away from the H atom. As a result the acidity increases.

Sometimes the acid strength of a series of oxoacids such as this is correlated with oxidation number of the central atom rather than with the formal charge of the central atom as has been done here. In the series of the oxo-acids of chlorine, formal charge and oxidation number increase in the same order so that it may appear that either could be used.

	$HOCl$	$HOClO$	$HOClO_2$	$HOClO_3$
formal charge of Cl	0	1+	2+	3+
oxidation number of Cl	+1	+3	+5	+7

In some cases, however, oxidation number is not a reliable indicator – formal charge must be used. The oxoacids of phosphorus, for example, are all weak acids –about of equal strength.

	H_3PO_2	H_3PO_3	H_3PO_4
formal charge of P	1+	1+	1+
oxidation number of P	+1	+3	+5

The acid strength of compounds of this type can also be rated by counting the number of O atoms bonded to Z but not bonded to H atoms.

HNO_3 is a stronger acid than HNO_2

H_2SO_4 is a stronger acid than H_2SO_3

In general the strength of acids that have general formula

$(HO)_m\ ZO_n$ can be related to the value of the n

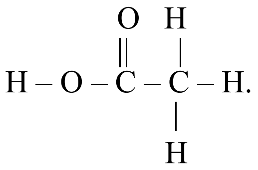
(a) If $n = 0$, the acid is very weak HOCl, $(OH)_3$ B

(b) If $n = 1$,the acid is weak HOClO, HONO

(c) If $n = 2$, the acid is strong $HOClO_2$, $HONO_2$

(d) If $n = 3$, the acid is very strong, $HOClO_3$, $HOIO_3$,

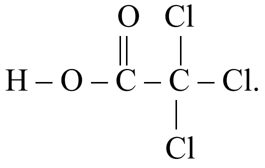
The effect of electron-withdrawing group is also seen in organic chemistry. e.g.
Acetic acid



$$H-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H.$$

is a weak acid. If one or more of H atoms that are bonded to C in acetic acid are replaced by highly electronegative atoms (such as Cl), the acidity is increased.

Tricholoroacetic acid, for example



$$H-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-Cl.$$

is a much stronger acid than acetic acid. Trends in base strength are readily derived from conjugate relationship. For example, it is possible to predict that S^{2-} is a weaker base than O^{2-} since H_2S is a stronger acid than H_2O.

10.2. Strength of Mononuclear Oxoacids- Pauling's Rules: The two rules derived by Pauling are:

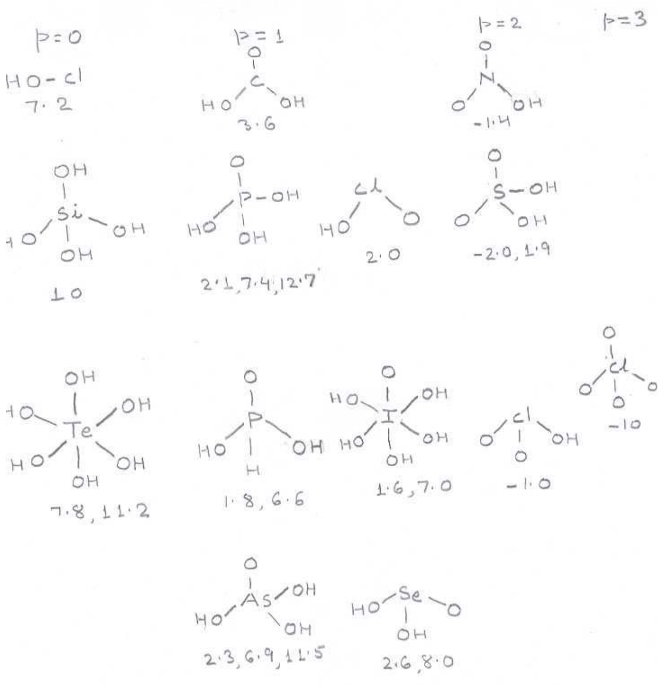
1. For oxoacid $O_pE(OH)_q$, $_pK_a = 8-5$

   Neutral hydroxoacids with $_p= 0$ have $_pK_a \approx 8$, with one oxo group $_pK_a \approx 3$ and acid with two oxo groups $_pK_a \approx 2$.

2. The successive $_pK_a$ values for polyprotic acids (those with q>1) increase by 5 units for each successive proton transfer. Sulphuric acid, $O_2S(OH)_2$ has $_p = 2$ and q = 2 and $_pKa_{1=}$-2 $_pKa_2 = +3$

   The success of these simple rules may be gauged by inspection of the acid given here in which acids are grouped according to $_p$, the number of oxogroups.

Structures and $_p$K$_a$ values of oxoacids



* Numbers are successive $_pK_a$ values.

The estimates are good to about ± 1 and in excellent agreement with the arguments. The variation down a group is not large and complex and perhaps canceling effects of changing structures allow the rules to work moderately well.

11. Lewis Acids and Bases

To broaden the Bronsted's ideas, G. N. Lewis in 1923 defined acids and bases in terms of electron pair acceptor donor. Thus a Lewis acid is a substance that acts as electron pair acceptor and a Lewis base is a substance that acts as an electron pair donor. If a Lewis acid is denoted by A and a Lewis base by: B, often omitting any other lone pairs that may be present, the fundamental reaction of Lewis acids and bases is the formation of a complex. A-B, in which A and :B bond together by sharing the electron pair supplied by the base.

(i)Examples of Lewis acids and bases: The proton is a Lewis acid because it can attach to an electron paid donor. It follows, therefore, that any Bronsted acid, since it provides protons, exhibits Lewis acidity too. All Bronsted bases are Lewis bases, since a proton acceptor is also an electron pair donor. However, since proton is not a part of the definition, a wider range of substances can be classified as Lewis acids and bases than can be classified in the Brosnted scheme.

There are many examples of the Lewis acid but one should consider the following possibilities:

1. A metal cation can bond to an electron pair supplied by the base:An example is the hydration of Cu^{2+} where the O atom of H_2O providing a lone pair (acting as Lewis base) attaches to the central cation. The cation is therefore a Lewis acid.

2. A molecule with incomplete octet can complete its octet by accepting an electron pair: An example is $B(CH_3)_3$, which can accept electron pair of NH_3 or any other donor, hence $B(CH_3)_3$ is a Lewis acid.

3. A molecular or ion with a complete octet can rearrange its valence electrons and accept an additional electron pair : An example is CO_2 which acts as a Lewis acid when it forms HCO^-_3 by accepting an electron pair from O atom in OH^- ion.

4. A molecule or ion may be able to expand its octet (or simply be large enough) to accept electron pair: An example is the formation of complex $[SiF_6]^{2-}$ when two F^- ions (the Lewis bases) bond to SiF_4 (the acid).

5. A closed-shell molecule may be able to use one of its antibonding molecular orbital to accommodate an incoming electron pair. An example of this behaviour is the ability of tetracyanoethylene (TCNE) to accept a lone pair into its π^* orbital, and hence to act as an acid*.
   (* Such acids are known as π - acids. Many of the π - complexes are formed in this way.)

6. Molecules having carbon to carbon double bond: The terms acids and bases are reserved for discussions of the equilibrium position of the reactions. If the electron donation is involved in a kinetic process determining the rate of reaction; the term base is replaced by the term nucleophile and an electron pair acceptor, acid is an electrophile.

(ii) Strength of Lewis Acids and Bases: The proton (H^+) is the key ion in the discussion of Bronsted acid and base strengths. In the Lewis theory, we have to allow a greater variety of electron-pair acceptors and hence a greater variety of factors that influence strength. Nevertheless it turns out that we can discuss some general trends by focusing on a few central aspects. Since the elementary acid-base reaction is

$$A + :B \Leftrightarrow A \rightarrow B$$

The strength of the acid A can be expressed thermodynamically in terms of the equilibrium constant (or Gibbs free energy) for this formation reaction.

$$K_f = \frac{[AB]}{[A][B]} \qquad \Delta G^o = -RT \ln K_f$$

One can then set up a scale of strengths by choosing a common acid A and arranging the bases: B in order of their K_f values (or $_pK_f$ values where $_pK_f = -\log K_f$). It is important to remember, though, that different reference bases might yield different scales. When the reference acid is H^+, $K_f = 1/K_a$ where K_a is acidity constant.

(iii)Contributions to Lewis acid and base strengths: Four contributions are largely responsible for the magnitude of ΔG^o. One is the dependence of the strength of A-B bond, second is the rearrangement of the substituents of the acid and base that may be necessary to permit formation of the complex. The third is the steric interaction between the substituents on the acid and the base. Finally, in solution, we must take into account the solvation of the acid, the base and the complex. Some of these are considered in detail here.

(iv)Factor's Governing the Lewis acid and base strengths: Acid and base strengths in the Lewis concept are not fixed, as far as inherent properties of the species concerned, but vary somewhat with the nature of the partner. That is the order of base strength of a series of Lewis bases may change when the type of acid with which they are allowed to combine changes. For a given donor or acceptor atom basicity or acidity can be influenced greatly by the nature of substituents. This influence can be either electronic or steric in origin.

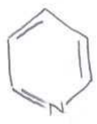
Electronic Effects: The electronegativity of the substituents contributes to the acidity / basicity orders. Consider the following for examples:

Bases: $(CH_3)_3N > H_3N > F_3N$

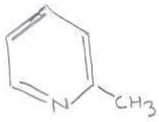
Acids: $(CH_3)_3B < H_3B < F_3B$

The more electron-withdrawing (electronegative) the substituents the more it enhances Lewis acidity and diminishes Lewis basicity. However, some more subtle electronic factors can also be important. Take for example, the halides of baron. On simple electronegativity grounds the following order of acid strength would be predicted: $BF_3 > BCl_3 > BBr_3$. Experimentally this prediction is found to be incorrect. This can be understood when the existence of π interactions in the planar BX_3 molecules is taken into account, and when it is noted that after the Lewis acid has combined with a base the BX_3 group becomes pyramidal with the absence of the π interaction between X and B. The B-X π interactions will decrease in strength in the order F> Cl> Br. Therefore, BF_3 is a weaker Lewis acid than BCl_3 because in the planar BF_3 molecule π interaction is of much greater magnitude than that in BCl_3.

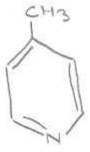
Steric Effects: These may be of several kinds. In the following compounds the base strength toward the proton increases from I to II and is virtually the same for II and III.



I



II



III

But with respect to $B(CH_3)$, the order of basicity is

I $\approx$ III >> II

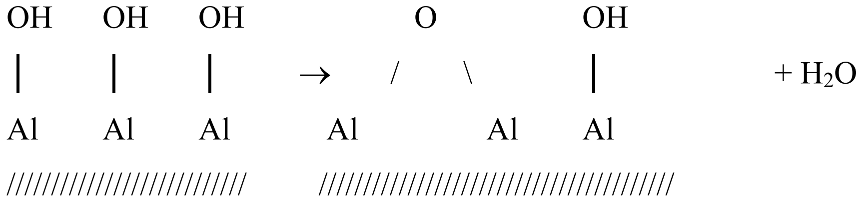
This results from steric hindrance between ortho-methyl group of the base and the methyl group of $B(CH_3)$. For similar reason quinuclidine is a far stronger base toward $B(CH_3)_3$ than triethylamine

A different type of steric effect may be observed if the size of R group on the boron atom in BR_3 is increased. As the size of R group increases or it is branched the B atom should be less strongly acidic.

This can be well understood when we realize that the alkyl groups on the B atom move closer on forming a complex as BR_3 changes from planar to pyramidal. This explains that if the substituents are branched then also the B atom should be less strongly acidic which is experimentally observed.

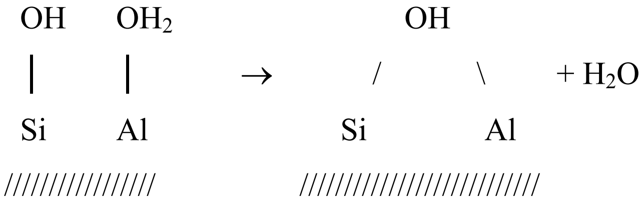
(v) Solid Surface Activity: Some of the important reactions involving Lewis acidity of inorganic compound occur at solid surfaces. Such surface acids with a high surface area and Lewis acid sites are used as catalysts in petroleum industry for isomerization and alkylation of aromatic compounds. Surface acidity is also important in the chemistry of soil and natural water.

Alumina (Al_2O_3) , for example is a surface acid on account of high charge (+3) of Al. When freshly precipitated hydrous aluminium oxide is heated above 150°C, the dehydration begins and the surface undergoes changes such as



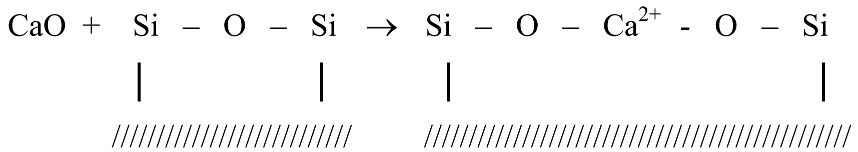
The Al^{3+} ions created at the surface act as Lewis acids and the unprotonated O^{2-} ions produced act as Lewis bases. Though the acid-base pair is produced together the Lewis acid sites are more important surface catalysis.

In contrast to alumina, aluminosilicates can display strong Bronsted acidity. The formation of acid sites may be thought of as condensation of $Si(OH)_4$ units with hydrous aluminum units, $H_2O\ Al(OH)_3$. Thus



This produces a strong Bronsted acid site where the protons are retained to balance the positive charge of the Al^{3+} ion.

(vi) Solid and Molten Acids in Industrial processes: The Lewis acid concept systematizes many reactions in molten salt solutions. The reactions often involve the transfer of a basic anion, such as O^{2-}, S^{2-} or Cl^-, from one cationic acid centre to another. For example, the reactions of CaO with Si O_2 s to give Ca^{2+}salt of the polyanion [$SiO^{2-}{}_3$] can be considered as the transfer of the base O^{2-} ion from the weak acid Ca^{2+} to the stronger acid Si^{4+}, Thus



$$CaO + Si - O - Si \rightarrow Si - O - Ca^{2+} - O - Si$$

This reaction occurs in slag formation, which removes silicates from the molten iron phase in the production of iron in a blast furnace. Similar reactions are involved in the formation of glass and ceramics. In these alkali metal oxides or hydroxides transfer a basic O^2 ion to the acid silicate centre.

12. Hard and Soft Acids and Bases

In Bronsted – Lowry concept, we encountered the trends in basicity that is found when we consider the single acid H^+. We saw that strong bases are found in compounds which the electron-pair donor atom comes from the upper and right of the p-block. When we consider more general acids, we find that there are excellent correlation between the order of affinity for bases obtained with them and the order obtained when H^+ is used as the acid. Thus the value of $_{p}K_f$ for the formation of complexes of carboxylate ions and Se^{3+} ions is proportional to the $_{p}K_a$ of the carboxylic acid.

However, not all acids behave like H^+, if we are to deal with all the elements of the periodic table, we need to consider all the metal ions which can be sorted into two type (a) and (b) according to their preference for various ligands. Consider for examples the ligands formed by the elements of groups 15, 16 and 17. For group 15 we might take a homologous series such as R_3N, R_3P, R_3As, R_3Sb and for group 17 we take the anions F^-, Cl^-, Br^- and I^-

For type (a) elements the metals complexes are most stable with the lightest ligands and less stable as each group is descended. For the type (b) elements the trend is just the opposite. Thus

Type (a) bond in the order

(i) $I^- < Br^- < Cl^- < F^-$
(ii) $R_3Sb < R_3As < R_3P < R_3N$

Type (b) bond in the order

(i) $F^- < Cl^- < Br^- < I^-$
(jj) $R_3N < R_3P < R_3As < R_3Sb$

Type (a) metals include principally

1. Alkali metal ions
2. Alkaline earth metal ions
3. Lighter and more highly charged ions, e.g. Ti^{4+} ,Fe^{3+} , Co^{3+}, Al^{3+}
4.

Type (b) metal ions include principally

1. $Hg^{2+}{}_2$, Hg^{2+}, Pt^{2+}, Pt^{4+} Ag^+, Cu^+
2. Low valent metal ion such as the formally zero valent metals in metal carbonyls.

This empirical ordering proved very useful in classifying and to some extent predicting relative stabilities of complexes. Later, R.G. Pearson (1963) introduced a more generalized correlation to include broader range of acid – base interactions. He observed that the type (a) metal ions (acids) were small, compact and not very polarizable and that they preferred ligands (bases) which were also small and less polarizable. He called these acids and bases "hard". Conversely the type (b) metal ions and the ligands they prefer tend to be larger and more polarizable, he called these acids and bases as "soft". The empirical relationship could then be expressed qualitatively, by the statement that hard acids prefer hard bases and soft acids prefer soft bases. When a series of acids and bases is analyzed with these rules in mind, it is possible to identify the following classification.

Table 2: Classification of Hard and Soft Acids and Bases

	Hard	Border Line	Soft
Acids	H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}	Cu^+, Ag^+, Au^+, $Tl^{+,}$
	Be^{2+}, Mg^{2+}, Ca^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+},	Hg^{2+}, Hg^+, Pd^+,
	Cr^{3+}, SO_3, BF_3	SO_2, Br_2	Cd^{2+}, Pt^{2+}, BH_3
Bases	F^-, OH^-, H_2O, NH_3	NO^-_2, SO^{2-}_3, Br^-	H^-, R^-, CN^-, CO, I^-
	CO^{2-}_3, NO^{2-}_3, O^{2-}	N^-_3, N_2	SCN^-, R_3P, C_6H_6
	SO^{2-}_4, PO^{3-}_4, ClO^-_4	C_6H_5N, SCN^-	R_2S

(i)The Interpretations of Hardness: Hard acids and bases are generally best described in terms of ionic interactions. Soft acids bases are more polarizable than hard acids and bases and are more richly covalent. We can interpret molecular hardness and softness in terms of frontier orbitals in much the same way as we do for atomic hardness. When the frontier orbital separation is small the electron distribution is easily rearranged by a perturbation and the molecule is soft. When the separation is large, the electron distribution resists the rearrangement even when the perturbation is moderately strong.

(ii) Chemical Consequences of Hardness: The concepts of hardness and softness help to rationalize a great deal of inorganic chemistry. For example, they are relevant to the compounds that constitute the structure of the earth. The tendency of soft acids to prefer soft bases and hard acids to prefer hard bases explains two categories of modes of occurrences in the earth crust. The lithophile elements, which are found in association with hard base O^{2-} in silicate minerals include hard acids like Li, Na, Al and Cr. The chalcophile elements which include soft acids Ag, Cu, Cd, Pb, Sb, Bi are found principally in association with soft bases S^{2-}.

The concept of hardness and softness is also useful for choosing experimental conditions and predicting the directions of reactions. Elements with high oxidation numbers generally provide hard acid centres and hence are stabilized by hard bases such as F^- and O^{2-}. Hardness can also be used as a guide to the outcome of metathesis reactions. Thus R_3Si^+ is a hard acid and salts of the form AgX^- convert R_3SiX to R_3SiX' if X' is harder than X. This is because the harder base X' prefers the hard Si atom, whereas the softer base X prefers the softer acid Ag^+. An illustration of these preferences is found in the following sequence

$$R_3SiX \xrightarrow{AgCl} R_3SiCl \xrightarrow{AgF} R_3SiF$$

Another type of illustration concerns the way in which an ambident at ligand base (a molecule or ion that can donate an electron pair from more than one atom) functions. For example the SCN^- ion is a base by virtue of both the harder N atom and the softer S atom; the ion binds , to the hard atom through N and to the soft atom through S. Thus with a soft acid such as a metal ion in low oxidation state the ion binds through S. For examples Pt (II) forms Pt - SCN.

Although the concepts of hardness and softness are useful, it must be appreciated that they are qualitative and that they focus on electronic factor mainly. That being so, we must develop an appreciation of their limitations and reliability in different chemical contexts.

13. Autoionization of Solvents

In order to have a clear understanding of reactions in different solvents, it is important to understand how these solvents undergo autoionization. Water, ammonia and sulphuric acid (pure liquid) are examples of liquids in which autoionization occurs. The process is one of proton transfer between two molecules in the liquid phase as indicated by the equilibria shown below:

$$2H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)} \qquad (i)$$

$$2NH_3(l) \Leftrightarrow NH_4^+{}_{(solvent)} + NH^-_{2(solvent)} \qquad (ii)$$

$$H_2SO_4 \Leftrightarrow H_3SO_4^+{}_{(solvated)} + HSO^-_{4(solvated)} \qquad (iii)$$

In the three cases the positive ion is solvated proton (or hydrogen ion),the negative ion being the solvated molecule minus hydrogen ion. The extent of autoionization differs in the three cases and in none is extensive. The autoprotolysis constants (the equilibrium constants for the processes described by equations (i), (ii) and (iii) and which are sometimes referred to as ionic products) are:

1×10^{-14}(298K), (ii) 1×10^{-30} (223K) and 1.7×10^{-4} (283K).

The magnitude of autoprotolysis constant is related to the dielectric constant (i.e. the permittivity) of the liquid. The permittivity of sulphuric acid, water and ammonia are 101(298K), 78.5(298K) and 22 (240K) respectively. It is to be expected that the greater the permitivity of the solvent is, the larger will be the value of the solvation energy of the ions produced in that solvent by autoionization. A larger value of solvation energy of an ion will result in a greater stabilization of the ion and lead to higher concentration of it in the solvent.

Let us now consider reactions in some non-aqueous solvents.

14. Reactions in Non-Aqueous Solvents

Many inorganic substances dissolve in a solvent with chemical change, that is undergo solvolysis. A particular example is the hydrolysis of salts in aqueous solution. Alternatively, the solvent itself may not be involved in the reaction but is merely used as a medium in which to carry out the reaction. Some nonaqueous solvents which are of special interest are now discussed in detail.

(i)Liquid Ammonia: Ammonia like water is highly associated in liquid state, association arising presumably from intermolecular hydrogen bonding. However, the melting and boiling points of ammonia are correspondingly lower than those of water. Ammonia is a good solvent for many nitrogen containing solutes like nitrates and for organic compounds such as amines, phenols and carboxylic acids which can form hydrogen bonds with solvent molecules. The salts of transition metals such as copper, nickel, zinc and silver often have much greater solubilities in ammonia than in water because of the tendency of ammonia to coordinate strongly with these metals. Silver halides show appreciable solubilities in ammonia for this reason.

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$$

Ammonolysis occurs with many solutes. The tetrahalides of silicon and germanium except (fluorides) are readily and completely converted to the amides at low temperatures.

$$SiCl_4 + 8NH_3 \xrightarrow{223K} Si(NH_2)_4 + 4NH_4Cl$$

The comparable solvolysis with water is the conversion to hydrated silica. Tin (IV) and transition metal halides like $TiCl_4$, $ZnCl_4$, VCl_4, and $MoCl_5$ are only partially ammonolysed, e.g.,

$$SiCl_4 + 6NH_3 \xrightarrow{240K} SnCl(NH_2)_3 + 3NH_4Cl$$

Reactions of chlorine, bromine and iodine with ammonia are typified by

$$Cl_2 + 2NH_3 \rightarrow NH_2Cl + NH_4Cl$$

Neutralization reaction occurs between an acid and a base. Representative reactions of these types are between ammonium halide (acid) and a metal amide, or nitride (base).

$$NH_4Cl + KNH_2 \rightarrow KCl + 2NH_3$$

$$2NH_4I + PbNH \rightarrow PbI_2 + 3NH_3$$

$$3NH_4I + BiN \rightarrow BiI_3 + 4NH_3$$

The course of such reactions may be followed by conductometric titration methods and sometimes by the use of the indicators. For example, the alkali amides can be titrated with ammonium salt in liquid ammonia with phenolphthalein as indicator in exactly the same way as acids can be titrated with alkalies in aqueous solution. Sometimes it is preferable to carry out a reaction in liquid ammonia rather than in water. For instance ammonia bromide in liquid ammonia gives a better yield than aqueous hydrochloric acid in the preparation of silanes from magnesium silicide.

$Mg_2Si + HCl$ (in H_2O) = Silanes (Si_2H_6 etc) 25 per cent yield

$Mg_2Si + NH_4Br$ (in $NH_{3)}$ = Silanes (chiefly SiH_4 Sir_2H_6) 70- 80 percent yield

Extensive hydrolysis of the products reduces the yield in aqueous solution, but ammonolysis is less extensive than hydrolysis because the N – H bonds of ammonia are less easily broken than the O- H bonds of water.

The alkali metals dissolve in ammonia, without the evolution of hydrogen, giving the blue, strongly conducting solutions.these colors are ascribed to solverted electrosis. In dilute solutions the cation appears to be Na^+ , probably solvated as $Na(NH_3)_n^+$, and the anion i.e. solvated electron, in this case ammoniated electron $e(NH_3)^-_n$, which contributes the colour. Metals such as platinum and iron catalyse decomposition of the solution with the formation of sodium amide and the liberation of hydrogen:

$$2Na + eNH_3 \rightarrow 2NaNH_2 + H_2$$

A solution of sodium in liquid ammonia furnishes a useful reducing agent. Many compounds which cannot be made in the presence of water have been prepared using metal ammonia solutions to effect reduction. Solutions of sodium in ammonia, for instance, can reduce many compounds to the free elements and sometimes to intermetallic compounds; silver salts are reduced to the metal; bismuth triiodide, on the other hand, is reduced to the metal and various intermetallic substances which have been assigned the formulate Na_3Bi, Na_2Bi_3, and Na_3Bi_5.

Reactions of special interest are those which lead to the preparation of compounds of metals showing an unusual oxidation state. One of the best known examples is the reduction of the complex cyanide $K_2M(CN)_{4=}$ (where M is Ni, Co or Pd) using potassium in liquid ammonia. In the case of nickel, reduction of Ni^{ii} 9 $(CN)^{2-}{}_4$ proceeds via [$Ni(CN)_3]_4^{4-}$ to $[NI(CN)_4]^{4-}$ which the nickel is zero valent.

$$2[Ni(CN)_4]^{2-} + 2e^- \rightarrow [Ni(CN)_3]_2^{4-} + 2CN^-$$

$$[Ni(CN)_3]_2^{4-} + 2CN^{--} + 2e^- \rightarrow 2[Ni(CN)_4]^{4-}$$

The corresponding tetracyno complexes of Co^0 and Pd^0, $[Co(CN)_4]^{4-}$ and $[Pd(CN)_4]^{4-}$ respectively are also known.

(ii) Hydrogen Fluoride: The solvent HF has a very high dielectric constant ($\in$ 84); it is an excellent ionizing solvent and dissolves many inorganic and organic compounds to give highly conducting solutions. Its uses as a solvent in NMR experiments of biological compounds are well known. It is a strongly acid solvent. It dissolves water, ethers, ketones, aliphatic acids and even nitric acid, all of them functioning as bases.

$$H_2O + HF \Leftrightarrow H_2O^+ + F^-$$

$$Et_2O + HF \Leftrightarrow Et_2OH^+ + F^-$$

$$HNO_3 + HF \Leftrightarrow H_2NO_3^+ + F^-$$

The self ionization of hydrogen fluoride may be written as

$$2HF \Leftrightarrow H_2F^+ + F^-$$

Ionic fluorides like KF dissolve readily and are bases because they increase the concentration of fluoride ion in solution.

$$NaCl + HF \rightarrow Na^+F^- + HCl(gas)$$

The reaction proceeds further with salts of oxo-acids, such as nitrates

$$KNO_3 + 2HF \rightarrow K^+ \; H_2NO_3^+ + 2F^-$$

Some non-metal fluorides dissolve to give acid solutions:

$$AsF_3 + 2HF \Leftrightarrow H_2F^+ + AsF_6^-$$

Solvolysis occurs with sulphuric acid which produces fluorosulphuric acid

$$H_2SO_4 + 2HF \rightarrow HSO_3F + H_3O^+ + F^-$$

One of the many preparations which have been carried out in anhydrous hydrogen fluoride as solvent is that of anhydrous silver tetrafluoroborate, $AgBF_4$. This is strongly hygroscopic and is precipitated when silver nitrate and boron trifluoride solutions in HF are mixed. On the assumption that BF_3 acts as an acid, the reaction my be written as

$$AgNO_3 + 2HF \rightarrow Ag^+ + H_2NO_3^+ + 2F^-$$

$$BF_3 + 2HF \rightarrow H_2F^+ + BF_4^-$$

$$Ag^+ + BF_4^- \rightarrow AgBF_4$$

(iii) Sulphur Dioxide: The liquid sulphur dioxide solvent is used industrially as a refrigerant and as an extractive solvent in petroleum refining. It is thus readily available and extensive chemical investigations have been carried out using it. The relatively low dielectric constant of sulphur dioxide accords with its property of dissolving covalent rather than ionic compounds. A wide variety of covalent compounds are soluble in liquid SO_2. For example, compounds such as CCI_4, $SiCl_4$, $SnCl_4$, $TiCl_4$, CS_2, Et_2O,C_6H_6, C_6H_5Cl, alcohols, esters, ketones and aldehydes have been described as either very soluble or soluble in liquid SO_2,. Iodides and thiocyanates are the most soluble inorganic salts. Liquid SO_2 is very poor conductor of electricity; in this respect it is similar to water. Early workers attributed the conductivity to autoionization of the solvent,

$$2SO_2 \Leftrightarrow SO^2 + SO^{2-}_3$$

drawing the parallel to the process responsible for the conductivity of pure water. In this aprotic analogy to the autoionization of water, SO^{2+} and SO^{2-}_3 ions were assumed to play the roles of the acidic and basic species respectively. Substances that increase the concentration of SO^{2+} are acids while metal sulphites (M_2SO_3) are bases. Indeed there are many reactions reported which fit this pattern. For example, the reaction between $SOCl_2$ and Cs_2SO_3 can be followed conductometrically in liquid SO_2, a break in the curve occurring at a 1:1 mole ratio off reactants. This has been formulated as

$$SOCl_2 + Cs_2SO_3 \rightarrow 2CsCl + 2SO_2$$

where it was supposed that $SOCl_2$ would undergo ionization

$$SOCl_2 \rightarrow SO^{2+} + 2\,Cl^-$$

The acidic species formed in this process would react with the base SO^{2-}_3

$$SO^{2+} + SO^{2-}_3 \rightarrow 2SO_2$$

Thus a thionyl compound would be defined as an acid and a sulphite as a base in the sulphur dioxide solvent system. Experiments with labelled sulphur and with labelled oxygen in the $SO_2 - SOCl_2$ system indicate that neither the sulphur not the oxygen atoms exchange between the solute and solvent. Thus many of the reactions that have been interpreted as acid-base reactions probably would occur in any solvent in which these compounds are soluble. Evidence exists that sulphur dioxide does not form solvents, but promotes the ionization of some covalent species such as SO_2X(X= Cl, Br, I), X_2 (X= Br, Cl), IBr, ICl, and ($C_6H_5)_3$ CX (X = Cl, Br). It appears likely that many of the earlier observations which were interpreted in terms of solvolysis reactions actually arise because of the presence of molecular oxygen, water, or both substances. Sulphur dioxide forms numerous solvates in which it acts as an electron pair acceptor (R_3 N. SO_2), but SO_2 can also act as Lewis base (e.g. BF_3. SO_2, $2TiCl_4.SO_2$, $2SnBr_4.SO_2$ and Al_2 Cl_6 SO_2).

(iv) Sulphuric acid: Sulphuric acid has high dielectric constant and is a good solvent for electrolytes. For example, alkali metal-sulphates are fully ionized in solution in sulphuric acid. They give rise to the hydrogen sulphate ion, HSO^-_4 and are classed as strong bases

$$KHSO_4 \rightarrow K^+ + HSO^-_4$$

Normal sulphates are converted into hydrogen sulphates and hence are the analogues of metal oxides in water.

$$K_2\,SO_4 + H_2SO_4 \quad \rightarrow \quad 2K^+ + 2\,HSO^-_4$$

Acids in the sulphuric acid solvent system are limited in number. Many compounds which behave as acid solutes in water are readily protonated in sulphuric acid. Thus phosphoric acid acts as a strong base:

$$H_3PO_4 + H_2SO_4 \rightarrow H_4PO_4^+ + HSO^-_4$$

Many organic compounds are similarly protonated, e.g.

$$R\text{-}COOH + H_2SO_4 \rightarrow R.\,COOH_2^+ + HSO^-_4$$

Sulphuric acid is so strongly protogenic that most compounds of oxygen and nitrogen accept proton from it to some extent. Not only amines but ethers and ketones given twice the normal freezing point depression suggesting that such reactions as

$$R_2O + H_2SO_4 \rightarrow R_2OH^+ + HSO^-_4$$

go virtually to completion. Many carboxylic acids dissociate as bases in sulphuric acid (above) and even perchloric acid ionizes like a weak acid in sulphuric acid:

$$^a(H_3\,SO^-_4) \times {}^a\,(ClO^-_4) / {}^a\,(H_2SO_4) \times {}^a\,(HClO_4) \approx 10^{-4} \text{ at } 298\text{ K} \qquad (a = \text{activity})$$

Some other substances acting as weak acids are disulphuric acid $H_2S_2O_7$ and the higher polysulphuric acid present in oleum. Certain substances, however, undergo reactions more complicated than proton transfer when dissolved in sulphuric acid. Nitric acid, for example, gives the nitronium ion which is the active agent in aromatic nitration.

$$HNO_3 + 2H_2SO_4 \Leftrightarrow NO^-_4 + H_3O^+ + 2HSO^-_4$$

This solvent has also been used to prepare stable solutions of ions which cannot exist in more basic solvents like water. For example, when I_2 and HIO_3 in the mole ratio of 7 : 1 are dissolved in sulphuric acid, the I_3^+ cation is formed.

$$HIO_3 + 7I_2 + 8H_2SO_4 \rightarrow 5I_3^+ + 3H_3O^+ + 8HSO_4^-$$

Iodic acid alone dissolves in sulphuric acid to produce iodyl hydrogen sulphate, IO_2, HSO_4.

$$HIO_3 + H_2SO_4 \rightarrow IO_2HSO_4 + H_3O^+ \ HSO_4^-$$

However, iodylsulphate is a polymeric compound and there is no evidence for the existence of simple ion, IO_2^+.

(v) Acetic Acid: The autodissociation of acetic acid may be written as:

$$2CH_3COOH \Leftrightarrow CH_3COOH_2^+ + CH_3COO^-$$

Hence, substances like metal acetate producing acetates ion are basic in this medium. Due to the greater proton donating ability of acetic acid than that of water, bases such as ammonia and many amines are essentially completely ionized in acetic acid.

$$CH_3COOH + NH_3 \rightarrow NH_4^+ + \underset{\text{base}}{CH_3COO^-}$$

However, acetic acid is much poorer proton acceptor than water so acids such as HCl and HNO_3 are only partially dissociated. From conductance studies the relative order of acid strengths in acetic acid has been found to be $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$. Titrations of amines which are very weak bases in H_2O may be carried out with strong acid dissolved in acetic acid using crystal violet indicator. Zinc chloride shows amphoteric character in acetic acid, just as zinc ion does in many other solvents. Addition of sodium acetate first precipitates zinc acetate from solution of $ZnCl_2$ in acetic acid and then dissolves the precipitate with the formation of a teraacetatozincate ion.

15. Discrimination in non-aqueous solvents

For any solvent, the range over which acid and base strengths can be discriminated is given by its autoprotolysis constant. For water, the range is 14, for liquid ammonia

$$NH_3(I) + NH_3(I) \Leftrightarrow NH^+_{4(am)} + NH^-_{2(am)} \quad pK_{am} = 33$$

so the range of discrimination is considerably wider. It is quite easy to understand the physical basis of why this is so. Since the proton affinity of NH_2^- is distinctly greater than that of OH^-, strong bases that are levelled in water will not be levelled in ammonia. However, the proton affinity of NH_2 is distinctly greater than that of H_2O, so acids that are weak in water may be levelled in ammonia. Hence the basic solvent ammonia has a window for the measurement of acid strengths, that is widened and shifted toward weaker acids.

The reverse is also true, going from water to a more strongly acid solvent, such as CH_2COOH, moves the range of distinguishable acids towards stronger acids. The proton affinity of CH_3COOH is less than that of water, so acids that transfer proton to water completely do not do so completely to CH_3COOH. Since CH_3COO^- has a lower proton affinity than OH^- weaker bases may convert CH_3COOH to CH_3COO^-.

To determine the acidity constants of strong acids such as HCl, we need data from acidic solvents such as acetic acid. To study data of strong bases, such as NH_2^-, we need data from basic solvents such as liquid ammonia.

In general, higher the pK value of the auto protolysis of the solvent, wider will be its range for levelling. For example, pK of dimethylsulphoxide (dmso) is

$$\mathrm{CH_3\overset{\overset{O}{||}}{S}CH_3 + CH_3\overset{\overset{O}{||}}{S}CH_3} \Leftrightarrow \mathrm{CH_3\overset{\overset{O}{||}}{S}CH_2^- + CH_3\overset{\overset{O}{||}}{S}CH_4^+}, \ pK=37$$

very large consequently dmso can be used to study a wide range of acids (from H_2SO_4 to PH_3)

In the end it may be pointed out that the concepts of acids and bases encampas a vast area of chemical systems and are very useful in deciding the course of chemical reactions. There are numerous physical and structural parameters which rationalize the strengths and reactivity of substances acting as acids or bases. In this connection, the roles of solvents are very important, indeed. By far the most important solvent is undoubtedly water. However, the importance of non-aqueous solvents in carrying out specific reactions involved in certain industrial processes can well appreciated.

Suggested Readings

1. Bell, R. P. , Proton in Chemistry , 2nd Ed., Chapmaon Hall, (1973).
2. Drago, R. S., Modern Approach to Acid base Chemistry, J. C.Chem. Educ., 51, 300 (1974)
3. Gillespie, R. R., Proton acids, Lewis acids, hard acids, soft acids and super acids. Chapman and Hall (1975)
4. Jensen, W.B.,The Lewis Acid-Base Concepts, Wiley, New York (1980)
5. Marcus, Y. Ion Solvation, Wiley (1985)
6. Nicholls, D. Inorganic Chemistry in Liquid Ammonia, Elsevier (1979)
7. Pearson, R. G., Ed., Hard and Soft Acids and Bases, Dowden, Hutchinson (1973)
8. Waddington, T. C. Non-aqueous Solvents, Nelson London (1969)