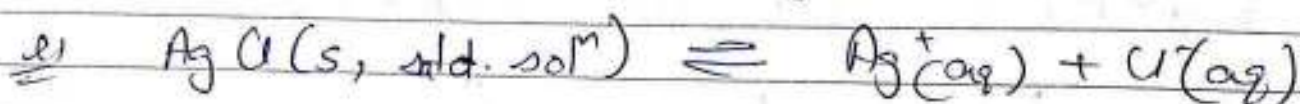


Solubility Product

In a saturated solⁿ of a salt, there exists a dynamic equilibrium b/w the excess of the solute and the ions furnished by that part of the solute which has gone in solⁿ.



$$K = \frac{a_{\text{Ag}^+} \times a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

Since activity of a solid is taken as unity.

$$\therefore K_{sp} = a_{\text{Ag}^+} \times a_{\text{Cl}^-}$$

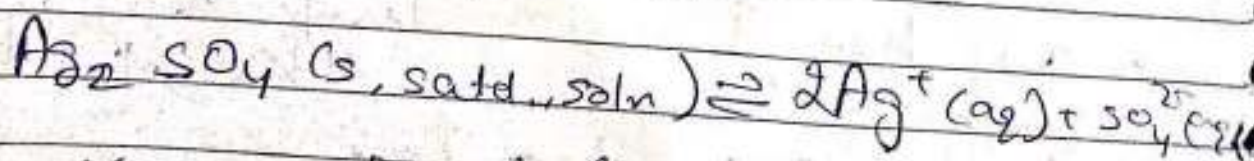
Solubility product of AgCl
concentration solubility product

$$\rightarrow K'_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

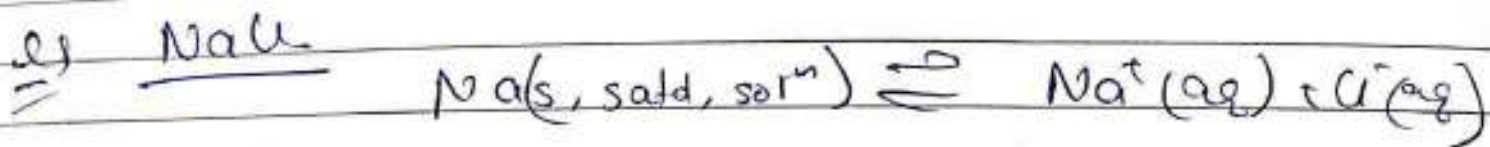
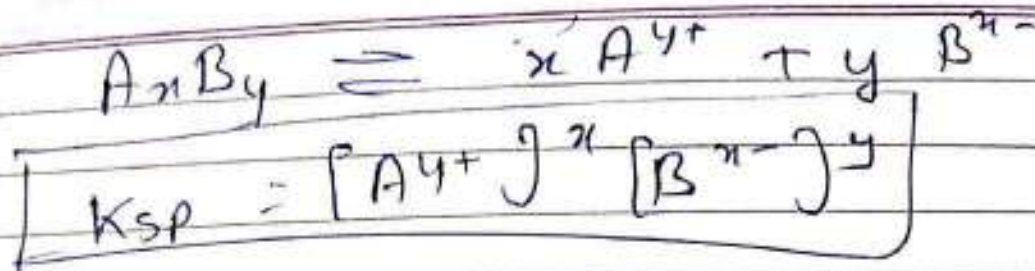
If in case of sparingly soluble salt like AgCl, ionic concⁿ are v. low, hence, activity of each ion is almost equal to its concⁿ.

$$\therefore K_{sp} = K'_{sp}$$

$$\therefore K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$



$$K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$



$$K_{sp} = a_{Na^+} \times a_{Cl^-}$$

$$K'_{sp} = [Na^+][Cl^-]$$

$$K_{sp} \neq K'_{sp}$$

This is due to high ionic concⁿ which enhances the interionic effects which reduces the activities.

Applicatⁿ of Solubility Product

① Determinatⁿ of solubilities of Sparingly Soluble salts

If we divide Eq. (2) by Eq. (1), we get

$$[\text{OH}^-] = \frac{1.3 \times 10^{-37} \text{ M}^5}{5.0 \times 10^{-33} \text{ M}^4} = 2.6 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log \{[\text{OH}^-]/\text{M}\} = -\log (2.6 \times 10^{-5}) = 4.6$$

or

$$\text{pH} = 9.4$$

(b) Here $\text{Al}(\text{OH})_3$ will be completely converted into Al^{3+} . Thus

$$\text{Al}^{3+} = 1.0 \times 10^{-3} \text{ M}$$

and $[\text{Al}^{3+}][\text{OH}^-]^3 = 5.0 \times 10^{-33} \text{ M}^4$

which gives

$$[\text{OH}^-] = \left(\frac{5.0 \times 10^{-33} \text{ M}^4}{1.0 \times 10^{-3} \text{ M}} \right)^{1/3} = 1.71 \times 10^{-10} \text{ M}$$

Thus, $\text{pOH} = -\log \{[\text{OH}^-]/\text{M}\} = -\log (1.71 \times 10^{-10}) = 9.78$ and hence

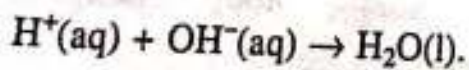
$$\text{pH} = 14 - \text{pOH} = 4.22$$

4.35 SOME CONCEPTS OF ACIDS AND BASES

One of the most important equilibrium in chemistry involves acids and bases. Various attempts have been made to define these acids and bases, starting from the phenomenological basis to the molecular composition and structure of the compound. Three of the currently accepted concepts are discussed in the following.

Arrhenius classified a substance into an acid or a base in terms of the characteristic ions of water which it produces in aqueous solution. Thus, *an acid is a substance which ionizes in water to produce $\text{H}^+(\text{aq})$ or the hydronium ion; a base is a substance which produces hydroxide ion $\text{OH}^-(\text{aq})$.* The strength of an acid is defined in terms of the concentration of $\text{H}^+(\text{aq})$ that is present in the aqueous solution of a given concentration of the acid. Likewise, the strength of a base depends upon the relative concentration of $\text{OH}^-(\text{aq})$ in an aqueous solution of the base.

The neutralization of an acid with base is explained in terms of the equation



This reaction is exothermic, as 57.32 kJ of heat is liberated when one mole of a strong acid combines with one mole of a strong base. If a weak acid and/or a weak base is involved, then the heat evolved is less than 57.32 kJ.

The principle of Arrhenius-water concept has been extended to incorporate the reactions in nonaqueous media. An acid is a substance that gives the cation characteristic of the solvent and a base that gives the anion characteristic of the solvent. The reaction of an acid and a base yields the solvent as one of its products. Table 4.35.1 includes some of the solvent systems.

Table 4.35.1 Some Solvent Systems

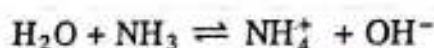
Solvent	Acid ion	Base ion	Typical acid	Typical base
H ₂ O	H ₃ O ⁺	OH ⁻	HCl	NaOH
NH ₃	NH ₄ ⁺	NH ₂ ⁻	NH ₄ Cl	NaNH ₂
CH ₃ -C(=O)-OH	H ₂ C ₂ H ₃ O ₂ ⁺	C ₂ H ₃ O ₂ ⁻	HCl	CH ₃ -C(=O)-ONa
SO ₂	SO ₂ ⁺	SO ₃ ⁻	SOCl ₂	CaSO ₃
N ₂ O ₄	NO ⁺	NO ₂ ⁻	NOCl	AgNO ₃
COCl ₂	COCl ⁺	Cl ⁻	(COCl)AlCl ₃	CaCl ₂

The Brönsted-Lowry Concept

J. Brönsted and T. Lowry independently proposed a broader concept of acids and bases. According to them, a substance is known as an acid if it can donate a proton and as a base if it can accept a proton. The substance may be a molecule or an ion. The reaction of an acid with a base constitutes the transfer of a proton from the acid to the base.

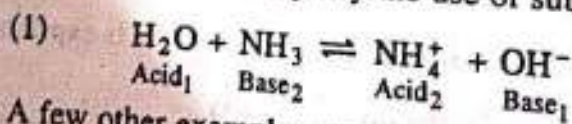
Conjugate Acid-Base Pair

The dissolution of ammonia in water may be represented by the equation

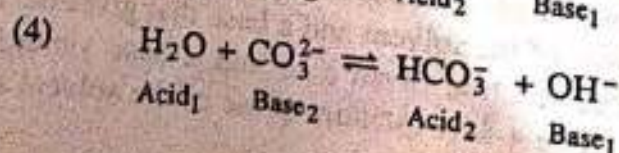
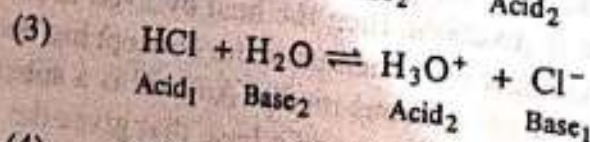
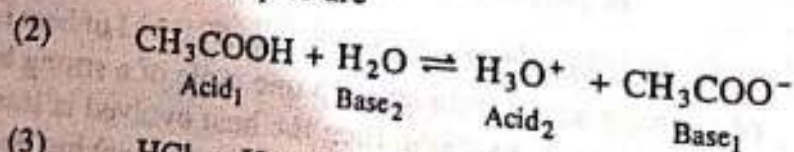


In this reaction, H₂O is serving as an acid and is donating a proton to the base NH₃. If a solution of an ammonium salt is made strongly alkaline, ammonia gas is released. The reaction is, therefore, reversible and the system exists in equilibrium.

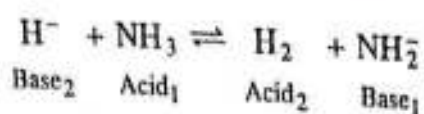
In the reverse reaction, NH₄⁺ is serving as an acid and OH⁻ as a base. It follows, then, that in this Brönsted acid-base reaction, two acids (H₂O and NH₄⁺) and two bases (OH⁻ and NH₃) are involved. The base NH₃ gains a proton and thereby forms the acid NH₄⁺ which on the loss of a proton forms the base NH₃. Such an acid-base pair, related through the loss or gain of a proton, is called a *conjugate pair*. NH₄⁺ is the conjugate acid of the base NH₃, and NH₃ is the conjugate base of the acid NH₄⁺. In like manner, the acid H₂O and the base OH⁻ constitute a second conjugate pair in the preceding reaction. We may indicate conjugate relationships by the use of subscripts in the following manner:



A few other examples are



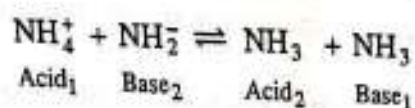
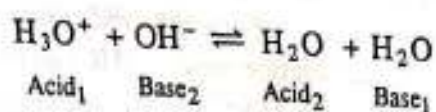
Similar type of reactions can be written in a nonaqueous medium:



Amphiprotic Species

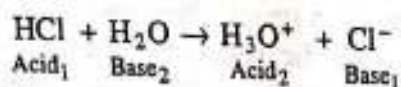
There are many molecules and ions that can function as acids in certain reactions and as bases in other reactions. Such species are called *amphiprotic*. For example, H_2O acts as an acid in reactions (1) and (4) and as a base in reactions (2) and (3).

Arrhenius acid-base type reactions are also covered by the Brønsted-Lowry reactions:



Strength of Brønsted Acids and Bases

The strength of a Brønsted acid is determined by its tendency to donate a proton, and the strength of a Brønsted base is determined by its tendency to accept a proton. Consider the reaction

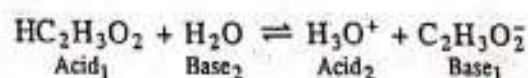


This reaction proceeds virtually to completion, i.e. the reactants are completely converted into products. It can be concluded that:

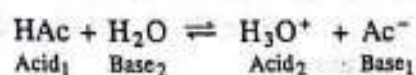
- (i) The acid HCl is stronger than H_3O^+ ion, since HCl has a greater tendency to lose a proton than the H_3O^+ ion.
- (ii) The base H_2O is stronger than Cl^- ions, since in the competition for holding the proton, H_2O shows larger tendency and thereby is converted to H_3O^+ .

Thus, we see that the strong acid HCl has a weak conjugate base Cl^- ion and the strong base H_2O has a weak conjugate acid H_3O^+ . The fact that a strong acid has a weak conjugate base and vice versa is always true since a strong acid with a high tendency to lose a proton is necessarily conjugate to a weak base with a small tendency to gain and hold a proton. Similarly, a strong base with a strong tendency to attract a proton is necessarily conjugate to a weak acid with a lower tendency to lose a proton.

An aqueous solution of 0.1 M acetic acid is only 1.33 per cent ionized at 25 °C. The reaction is



or briefly



which is largely displaced to the left. Once again, we can conclude that:

(i) The H_3O^+ is a stronger acid than HAc since at equilibrium more H_3O^+ ions than HAc molecules have lost protons.

(ii) The Ac^- is a stronger base than water since it shows greater tendency to attract a proton than H_2O , thus converting itself into HAc.

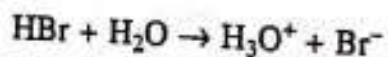
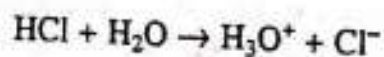
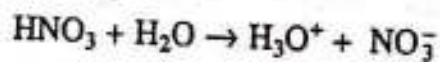
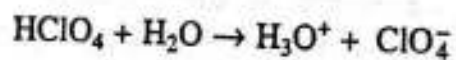
In the above example, we again notice that the stronger acid H_3O^+ is conjugate to the weaker base H_2O and the stronger base Ac^- is conjugate to the weaker acid HAc. From the above two examples, one more conclusion can be drawn. This can be stated as follows: *In a given reaction, the position of equilibrium favours the formation of a weak acid and a weak base.*

Thus, in the reaction between HCl and H_2O , the equilibrium concentrations of the weaker species H_3O^+ and Cl^- are high, whereas in the solution of acetic acid, the equilibrium concentrations of the stronger species H_3O^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ are low.

Arrhenius concept of a strong and a weak acid in aqueous solution can be explained by the Brønsted concept. In Arrhenius theory, a strong acid is virtually 100% ionized in aqueous solution and thus produces very high concentration of H_3O^+ . In the Brønsted system, acids are classified according to their ability to donate protons to a specific base under consideration. It is obvious that if water is used as the specific base, then the acid strengths of the Arrhenius concept can be explained in terms of the Brønsted concept. Thus, strong Arrhenius acids are those substances that are stronger acids than H_3O^+ and weak Arrhenius acids are those substances that are weaker acids than H_3O^+ . Table 4.35.2 records some common conjugate acid-base pairs showing the interdependent relationship of their strengths.

Levelling Effect

In Brønsted system, it is obvious that the strength of an acid is influenced by the solvent water. All those acids which are stronger than H_3O^+ will essentially be completely ionized in aqueous solution. For Example:



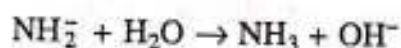
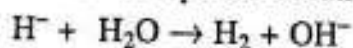
Thus, the acids HClO_4 , HNO_3 , HCl and HBr of the same concentration appear to have the same acid strength (equally stronger). Water is said to have a levelling effect on acids stronger than H_3O^+ . The strongest acid that can exist in water solution is the conjugate acid of water, i.e. H_3O^+ ion.

Acids that are weaker than H_3O^+ are not levelled by water. Thus, the weaker acids such as HAc, H_3PO_4 , HNO_2 and H_2S show a wide variation in their degree of ionization.

Table 4.35.2 Common Conjugate Acid-Base Pairs

Acid		Conjugate base	
Name	Formula	Formula	Name
Perchloric acid	HClO_4	ClO_4^-	Perchlorate ion
Sulphuric acid	H_2SO_4	HSO_4^-	Hydrogen sulphate ion
Hydroiodic acid	HI	I^-	Iodide ion
Hydrobromic acid	HBr	Br^-	Bromide ion
Hydrochloric acid	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogen sulphate ion	HSO_4^-	SO_4^{2-}	Sulphate ion
Phosphoric acid	H_3PO_4	H_2PO_4^-	Dihydrogen phosphate ion
Nitrous acid	HNO_2	NO_2^-	Nitrite ion
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	Acetate ion
Carbonic acid ($\text{CO}_2 + \text{H}_2\text{O}$)	H_2CO_3	HCO_3^-	Bicarbonate ion
Hydrogen sulphide	H_2S	HS^-	Hydrosulphide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Water	H_2O	OH^-	Hydroxide ion
Ammonia	NH_3	NH_2^-	Amide ion

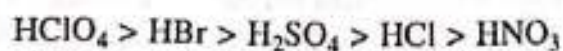
Similarly, bases that are stronger than the OH^- ion are levelled by water. For example, H^- and NH_2^- ions are stronger than OH^- ion and therefore they are levelled to OH^- in aqueous solution.



Thus, the above reactions are essentially complete. The bases that are weaker than OH^- are not levelled in water. Examples include NH_3 and anilinium ion.

The levelling effect is basically due to the fact that water acts as too strong a base with respect to those acids which are stronger than H_3O^+ and also too strong an acid with respect to those bases which are stronger than OH^- . If we want to differentiate these acids and bases, we will have to choose a less basic (more acidic) and less acidic (more basic) solvent than water, respectively. For example:

(i) In acetic acid medium, the strength of some of the acids described above were found to be



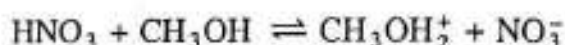
(ii) In liquid ammonia, out of H^- and NH_2^- ions, the former is found to be stronger than the latter.

The levelling effect is also observed for solvents other than water. For example, in liquid ammonia solvent, the strongest acid that can exist is the

conjugate acid of NH_3 , i.e. NH_4^+ ion, and the strongest base that can exist is the conjugate base of NH_3 , i.e. NH_2^- ion. Thus, any acid that is stronger than NH_4^+ ion will be levelled and any base that is stronger than NH_2^- will also be levelled. For example, HAc is a stronger acid than NH_4^+ and thus will be levelled, which will give us:

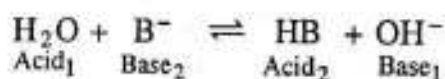


Nitric acid in methanol (CH_3OH) solution is incompletely dissociated since HNO_3 is a weaker acid than the conjugate acid of methanol, CH_3OH_2^+ :



Hydrolysis of Anions

The reaction of an ion with water in which either H_3O^+ or OH^- is produced is called hydrolysis. Such reactions are Brønsted acid-base reactions. Anions that function as bases in water solution are hydrolyzed as follows:



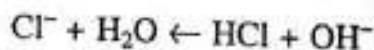
The extent of hydrolysis of a given anion depends upon the base strength of the anion, and an indication of the degree of hydrolysis is given by the concentration of OH^- relative to the concentration of anion present in the solution.

The following are the factors which determine the extent of hydrolysis of anions:

Complete hydrolysis The anion which is a stronger base than OH^- and the conjugate acid of the anion much weaker acid than H_2O will show complete hydrolysis. This is, in fact, the levelling effect of water on bases stronger than OH^- , e.g. H^- shows complete hydrolysis. For such a reaction, we have

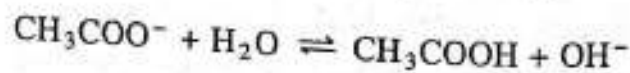


No hydrolysis The anion which is a weaker base than OH^- and its conjugate acid stronger than both H_2O and H_3O^+ does not hydrolyze. For example Cl^- ion:



If fact, HCl is levelled in water to H_3O^+ and, therefore, the HCl molecules do not exist in solution. The Cl^- ion is simply too weak a base to accept a proton from water. Thus, anion that have conjugate acids stronger than H_3O^+ do not hydrolyze.

Hydrolysis to a limited extent The anion which acts as a weaker base than OH^- ion and the conjugated acid stronger than H_2O but weaker than H_3O^+ , shows hydrolysis to a limited extent. Example is CH_3COO^- ion:



Other examples are CN^- , NO_2^- , and S^{2-} .

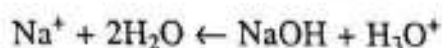
Hydrolysis of Cations

Cations, like anions, also show hydrolysis. The extent of hydrolysis depends upon the following factors:

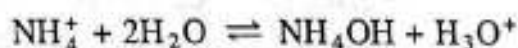
Complete hydrolysis The cation which is a stronger acid than H_3O^+ and its conjugate base very much weaker than H_2O will show complete hydrolysis. Example is PH_4^+ ion:



No hydrolysis The cation which is a weaker acid than H_3O^+ and its conjugate base stronger than both H_2O and OH^- does not hydrolyze. Example is Na^+ ion:



Hydrolysis to a limited extent The cation which is a weaker acid than H_3O^+ ion and its conjugate base stronger than H_2O but weaker than OH^- , shows hydrolysis to a limited extent. Example is NH_4^+ ion:

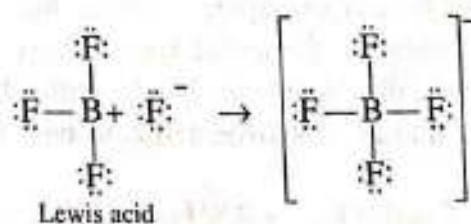


The Lewis Concept

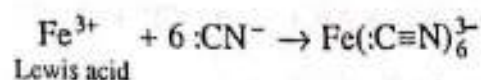
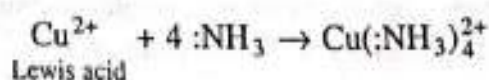
The Brönsted-Lowry concept of acids and bases which involves the transfer of a proton from an acid to a base was broadened by Lewis to include substances whose reactions do not involve loss or gain of a proton. According to him, a base has an unshared electron pair which enables it to form a covalent bond with an atom, molecule or ion. An acid is a substance that can form a covalent bond by accepting an electron pair from a base.

The following are a few examples of Lewis acids:

(i) Molecules or atoms that have incomplete octets:

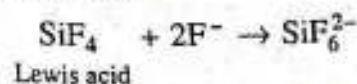
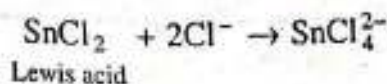


(ii) Simple cations:

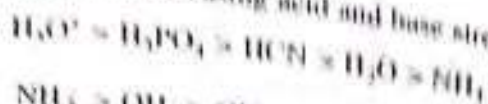


Here, the strength of the acid is determined by the positive charge density on the cation. Thus, the acid strength would increase with increasing charge and decreasing radius.

(iii) Compounds having central atoms capable of expanding their valence shells:



Thus, the order of decreasing acid and base strengths are

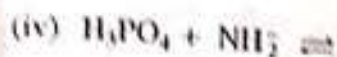
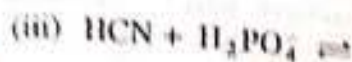
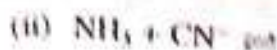
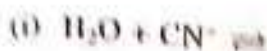


and

$$\text{NH}_2^- > \text{OH}^- > \text{CN}^- > \text{H}_2\text{PO}_4^- > \text{H}_2\text{O}$$

Example 4.35.4

Based upon knowledge about the relative strength of acids in Example 4.35.3, would you expect an appreciable reaction (i.e. over 50%) to occur in the following (complete the reaction yourself).



Solution

The complete reactions along with the designations as acids and bases and the relative strengths of these are as follows.

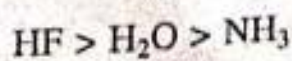
				Acid strength comparison	Base strength comparison		
(i)	$\text{H}_2\text{O} + \text{CN}^- \rightleftharpoons \text{HCN} + \text{OH}^-$	Acid ₁	Base ₂	Acid ₂	Base ₁	$\text{H}_2\text{O} < \text{HCN}$	$\text{CN}^- < \text{OH}^-$
(ii)	$\text{NH}_3 + \text{CN}^- \rightleftharpoons \text{HCN} + \text{NH}_2^-$	Acid ₁	Base ₂	Acid ₂	Base ₁	$\text{NH}_3 < \text{HCN}$	$\text{CN}^- < \text{NH}_2^-$
(iii)	$\text{HCN} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_3\text{PO}_4 + \text{CN}^-$	Acid ₁	Base ₂	Acid ₂	Base ₁	$\text{HCN} < \text{H}_3\text{PO}_4$	$\text{H}_2\text{PO}_4^- < \text{CN}^-$
(iv)	$\text{H}_3\text{PO}_4 + \text{NH}_2^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{PO}_4^-$	Acid ₁	Base ₂	Acid ₂	Base ₁	$\text{H}_3\text{PO}_4 > \text{NH}_3$	$\text{NH}_2^- > \text{H}_2\text{PO}_4^-$

Only reaction (iv) is expected to proceed in the forward direction since both the reactants are stronger than the products.

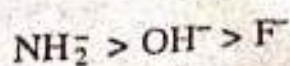
36 ACID AND BASE STRENGTHS AND STRUCTURE

The correlation between molecular structure and acid or base strength involves many factors. Some of them are listed below.

(1) The acid strength of the hydrogen compounds of the elements in a particular period increases as the atomic number is increased. This is primarily due to the increase of electronegativity of the atom attached to hydrogen. Thus, the decreasing order of acid strength of the last three elements of second period is

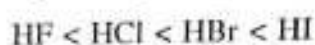
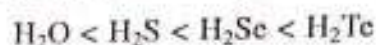


The conjugate base strength will, however, follow opposite trend, that is



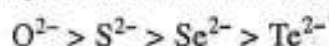
Thus, the base strength decreases with increasing electronegativity. Here size difference of the atom is small compared with the electronegativity difference.

(2) There is an increase in acid strength of the hydro-acids of the elements in any group of the periodic classification with increasing atomic size of the electronegative elements. For example, the hydrogen compounds of the Group 16 and 17 elements arranged according to increasing acid strength are



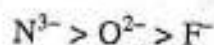
This is, primarily due to increase in atomic radius of the element in a group.

Trends in a base-strength will be opposite to the above trends. Thus, the decreasing order of base-strength will be



that is for monatomic anions of similar charge, base strength decreases with increasing size.

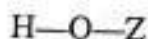
(3) As the negative charge on the ion decreases, its base strength also decreases. Thus



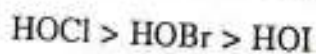
Acid Strength of Oxoacids

The oxoacids have been studied more extensively than any other type of acids.

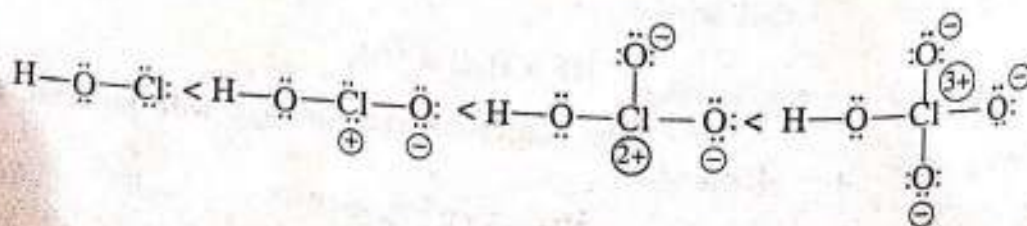
(1) For acids with the structure



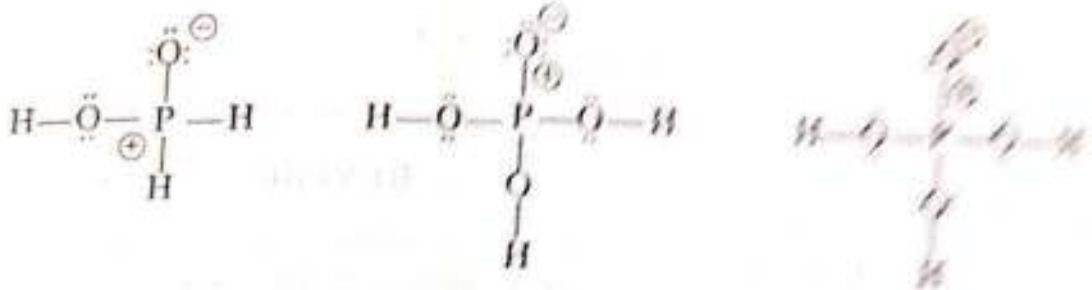
the acid strength increases with increasing electronegativity of Z. The higher the electronegativity of Z, the more electrons of the bonds are displaced towards Z and thus more readily is the proton removed. For example, in the hypohalous acids, the order of decreasing acidity is



(2) In compounds in which additional oxygen atoms are bound to Z, the electron withdrawing power of the group bonded to hydrogen is increased. Thus, the proton is more readily removed. This effect is illustrated by the series in which acidity increases with increasing oxidation state of chlorine (from +1 in HOCl to +7 in HClO₄). However, the formal charge of the central atom of an oxoacid is a better indicator of acid strength than oxidation number.



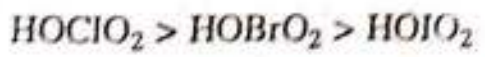
In the above series, the increasing formal charge on the chlorine atom leads to an increase in the oxidation number of the chlorine atom and hence to increasing acid strength. However, for the oxoacids of phosphorus, the oxidation number fails to give a true indication of acid strength. The acids are approximately of equal strength, and in each case, the formal charge on the phosphorus atom is +1.



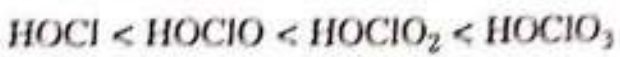
The number of oxygen atoms bonded to the central atom but not bonded to H atoms influence the formal charge on the central atom and, therefore, a qualitative indication of the strength of acids of general formula $(HO)_nX$, is provided by the value of n in the formula. In general, we have

- $n = 3$ very strong acid $\text{HOClO}_3, \text{HOIO}_3$
- $n = 2$ strong acid $\text{HOClO}_2, (\text{HO})_2\text{SO}_2, \text{HOBrO}_2$
- $n = 1$ weak acid $\text{HOClO}, (\text{HO})_2\text{PO}, \text{HOBO}$
- $n = 0$ very weak acid $\text{HOCl}, (\text{HO})_3\text{B}$

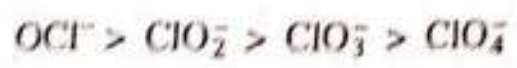
Within a particular group, acid strength increases with increase in electronegativity of the central atom. Thus,



This increasing acid strength will show a parallel decreasing base strength of the conjugate base. Thus, for the series



the order of the base strength of the anions is



Which compound in each of the following pairs is the stronger acid and why?

- (i) H_3PO_4 or H_3AsO_4 , (ii) H_3AsO_3 or H_3AsO_4 , (iii) H_2SO_4 or H_2SeO_4
 - (iv) H_3BO_3 or H_2CO_3 , (v) H_2Se or HBr
- (i) $\text{H}_3\text{AsO}_4 > \text{H}_3\text{PO}_4$ P and As belong to the same group, but size of As is larger than P.
 (ii) $\text{H}_3\text{AsO}_4 > \text{H}_3\text{AsO}_3$ More number of oxygen atoms attached to As in H_3AsO_4 .
 (iii) $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4$ More number of oxygen atoms attached to S in H_2SO_4 .
 (iv) $\text{H}_2\text{CO}_3 > \text{H}_3\text{BO}_3$ Same period, electronegativity of C is greater than that of B.
 (v) $\text{HBr} > \text{H}_2\text{Se}$ Electronegativity of Br is greater than that of Se.