Acid Base Theory

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THEORIES OF ACIDS AND BASES

- Arrhenius, Bronsted-Lowry, and Lewis theories of acids and bases,

- And explains the relationships between them.

- It also explains the concept of a conjugate pair - an acid and its conjugate base, or a base and its conjugate acid.

The Arrhenius theory is of historical interest only, and you are unlikely to need it unless you are doing some work on the development of ideas in chemistry.

Arrhenius Concept

- One of the properties that acids and bases have in common is that **they are electrolytes**--they form ions when they dissolve in water.

- Svante Arrhenius, a Swedish chemist who received a Nobel prize in 1903 for his work on electrolytes, focused on **what ions were formed** when acids and bases dissolved in water.

- He came up with the concept or idea that **acids** dissociated in water to give **hydrogen ions** and that **bases** dissociated in water to give **hydroxide ions**.

- This definition is very useful when we talk about acids and bases as being electrolytes in solution.

The Arrhenius Theory of acids and bases

Acids are substances which produce hydrogen ions in solution.

Bases are substances which produce hydroxide ions in solution.

Neutralisation happens because hydrogen ions and hydroxide ions react to produce water.

$HCl \leftrightarrow H^+ + Cl^-$ **(in presence of water)**

$NaOH \leftrightarrow Na^+ + OH^-$

$H^+ + OH^- \rightarrow H_2O$

UTILITY

i) Since it's a neutrlaistion reaction involves the combination of H^+ and OH^- ions molar heat of neutralisation would be expected.

It can be well understood by heat of neutralisation of a strong acid by a strong base.

ii) this concept also gives a correlating behaviour with the concentration of the H^+ ion

LIMITATIONS

i) HCl is an acid only when dissolved in H_2O and not in some other solvent such as C_6H_6 or when it exists in the gaseous form.

ii) It cannot account the acidic and basic character of the materials in non aqueous solvents.
    for e.g., NH_4NO_3 in liquid NH_3 acts as an acid though it does not give H^+ ions.

    similarly organic compounds and NH_3 which do not give OH^- ions but shows basic character.

iii) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, but some reactions involves the formation of salt in many other solvents and even in the absence of solvents.

iv) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

- Consider reaction also happens between ammonia gas and hydrogen chloride gas.

- In this case, there aren't any hydrogen ions or hydroxide ions in solution - because there isn't any solution. The

- Arrhenius theory wouldn't count this as an acid-base reaction.

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$

The Bronsted-Lowry Theory of acids and bases

- Johannes Bronsted & Thomas Lowry - took a new approach to acids and bases in 1923

- The Bronsted-Lowry concept considers the _role_ of acids and bases in reactions rather than the properties of their aqueous solutions

- This allows scientists to describe, explain _and predict_ many reactions, including those that take place outside of the water environment

- However, does not explain _why_ a proton is donated or accepted and therefore is not a comprehensive theory.

In general, we can say that Bronsted-Lowry acids are substances that donate a proton to another substance:

e.g. $HCl_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

H^+

Bronsted-Lowry bases are substances that accept a proton from another substance

e.g. $NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

H^+
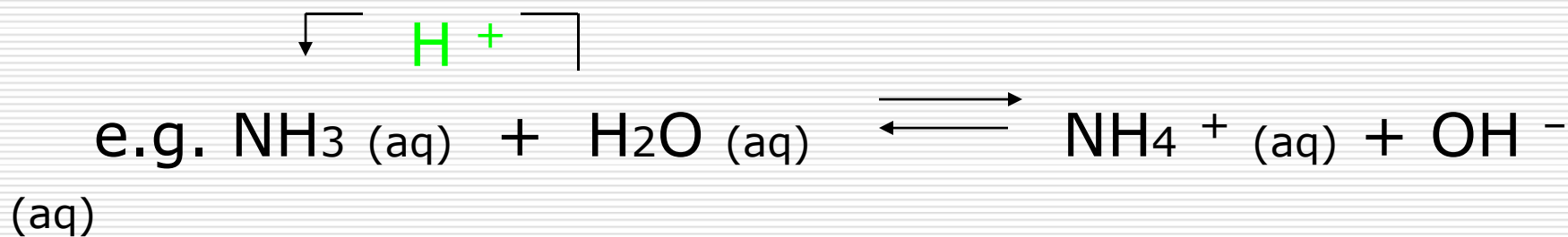
An additional benefit to the Bronsted-Lowry concept is that we no longer need to worry about what is _formed_, only what a substance _does;_ thus water does not even have to be present
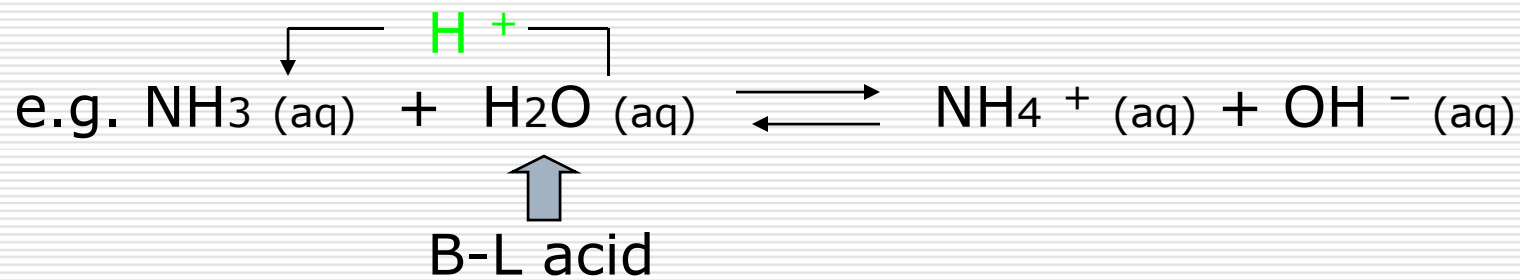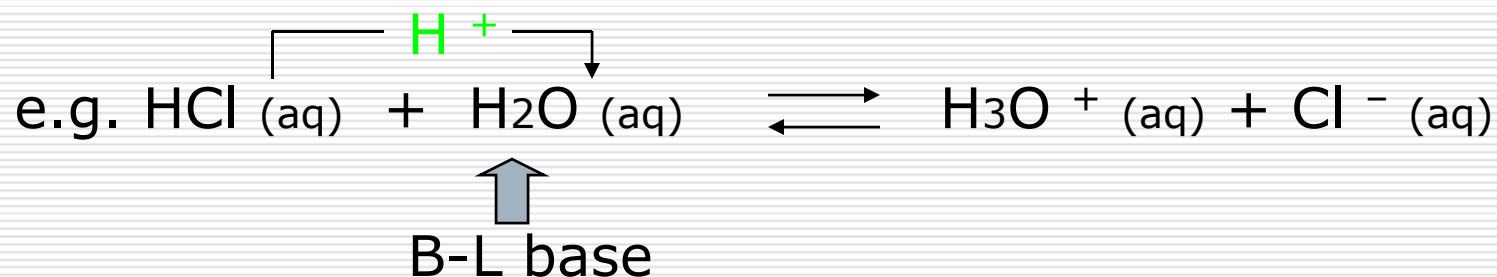
$$H^+$$

e.g. $NH_{3 (g)}$ + $HCl_{(g)}$ $\longrightarrow$ $NH_4^+Cl^-_{(s)}$

B-L base   B-L acid

(H^+ acceptor)   (H^+ donor)
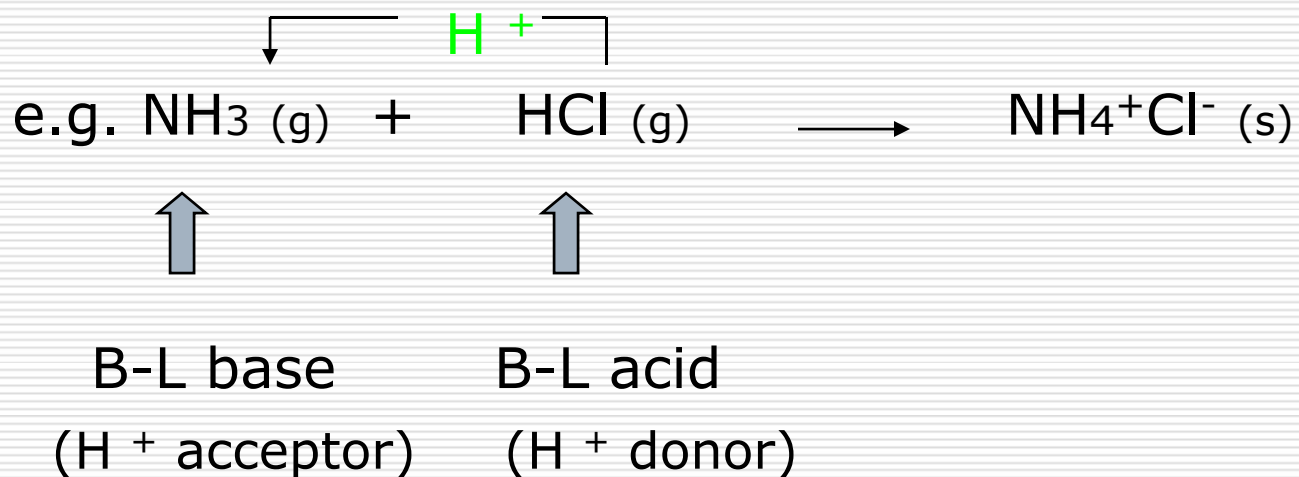
The theory

- An acid is a proton (hydrogen ion) donor.
- A base is a proton (hydrogen ion) acceptor.

Amphiprotic Substances

Substances which can act as B-L acids in one reaction situation and B-L bases in another reaction situation are called amphiprotic; e.g. water
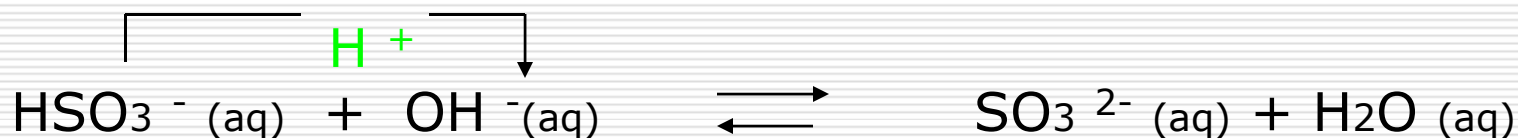
H^+

e.g. $HCl_{(aq)}$ + $H_2O_{(aq)}$ ⇌ $H_3O^+_{(aq)}$ + $Cl^-_{(aq)}$

B-L base

H^+

e.g. $NH_3_{(aq)}$ + $H_2O_{(aq)}$ ⇌ $NH_4^+_{(aq)}$ + $OH^-_{(aq)}$

B-L acid

Amphiprotic Substances

In general, substances which are hydrogen-containing anions can all be amphiprotic.

$$HSO_3^-\ _{(aq)}\ +\ H_3O^+\ _{(aq)} \rightleftharpoons H_2SO_3\ _{(aq)} + H_2O\ _{(aq)}$$

H $^+$

B-L base

$$HSO_3^-\ _{(aq)}\ +\ OH^-\ _{(aq)} \rightleftharpoons SO_3^{2-}\ _{(aq)} + H_2O\ _{(aq)}$$

H $^+$

B-L acid

The relationship between the Bronsted-Lowry theory and the Arrhenius theory

The Bronsted-Lowry theory doesn't go against the Arrhenius theory in any way - it just adds to it.

Hydroxide ions are still bases because they accept hydrogen ions from

acids and form water.

An acid produces hydrogen ions in solution because it reacts with the water molecules by giving a proton to them

When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule.

A co-ordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the HCl. Hydroxonium ions, H_3O^+, are produced.

co-ordinate bond

$$H_2O \ + \ HCl \longrightarrow H_3O^+ \ + \ Cl^-$$
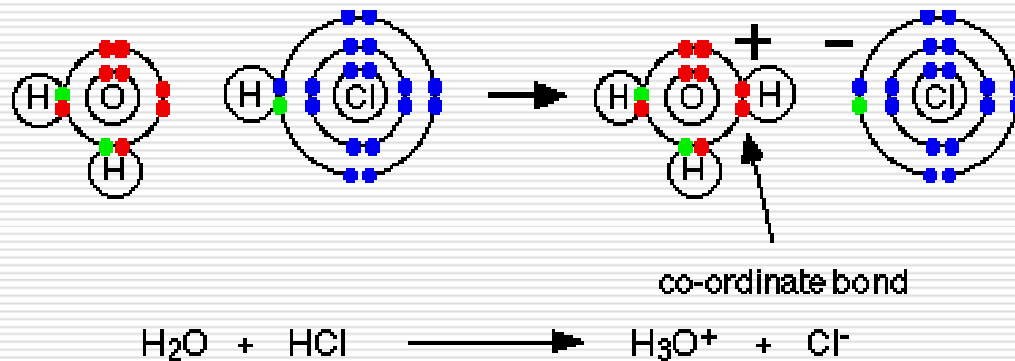
When an acid in solution reacts with a base, what is actually functioning as the acid is the hydroxonium ion. For example, a proton is transferred from a hydroxonium ion to a hydroxide ion to make water.
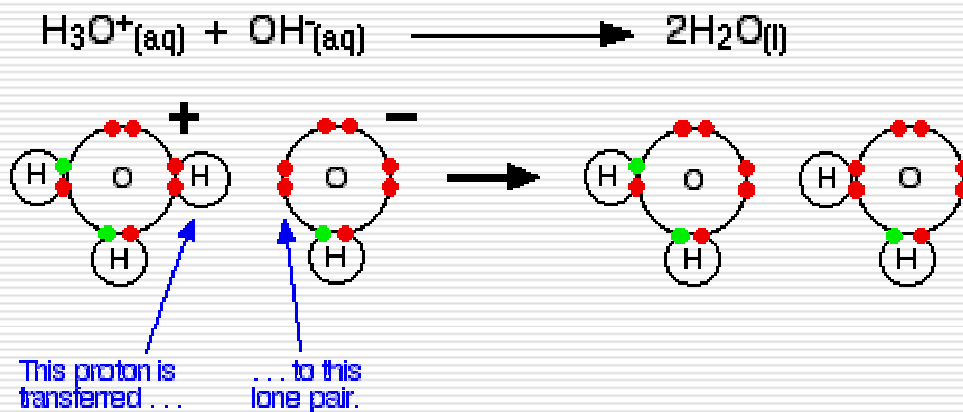
It is important to realize that whenever we talk about hydrogen ions in solution, $H^+(aq)$, what you are actually talking about are hydroxonium ions.

The hydrogen chloride / ammonia problem

The reaction in solution or in the gas state, ammonia is a base because it accepts a proton (a hydrogen ion). The hydrogen becomes attached to the lone pair on the nitrogen of the ammonia via a co-ordinate bond.

Incoming hydrogen ion attaches to this lone pair . . .
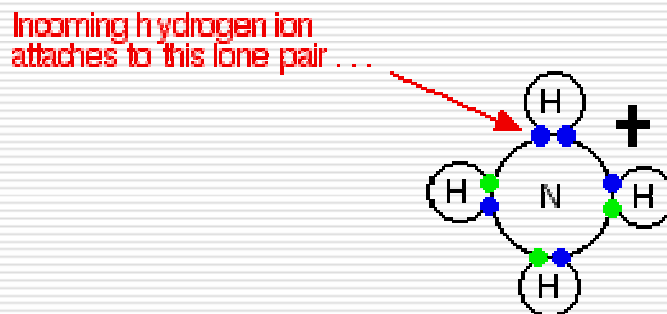
. . . and forms an ammonium ion.

If it is in solution, the ammonia accepts a proton from a hydroxonium ion:

$$NH_{3(aq)} + H_3O^+_{(aq)} \longrightarrow NH_4^+_{(aq)} + H_2O_{(l)}$$

If the reaction is happening in the gas state, the ammonia accepts a proton directly from the hydrogen chloride:

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4^+_{(s)} + Cl^-_{(s)}$$

Either way, the ammonia acts as a base by accepting a hydrogen ion from an acid.

Conjugate pairs

When hydrogen chloride dissolves in water, almost 100% of it reacts with the water to produce hydroxonium ions and chloride ions. Hydrogen chloride is a strong acid, and we tend to write this as a one-way reaction:

$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

In fact, the reaction between HCl and water is reversible, but only to a very minor extent. In order to generalise, consider an acid HA, and think of the reaction as being reversible

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Think about the *forward reaction:*

- The HA is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the HA.

But there is also a *back reaction* between the hydroxonium ion and the A- ion:

- The H_3O^+ is an acid because it is donating a proton (hydrogen ion) to the A- ion.

- The A- ion is a base because it is accepting a proton from the H_3O^+.

one conjugate pair

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

the other conjugate pair
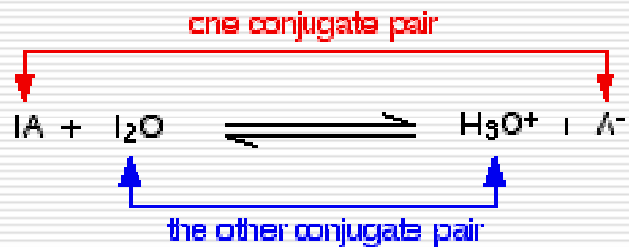
The reversible reaction contains *two* acids and *two* bases. The pairs are called **conjugate pairs**.

When the acid, HA, loses a proton it forms a base, A-.

When the base, A-, accepts a proton back again, it obviously reforms the acid, HA. These two are a conjugate pair.

Members of a conjugate pair differ from each other by the presence or absence of the transferable hydrogen ion.

If we thinking about HA as the acid, then A- is its conjugate base.
If we thinking about A- as the base, then HA is its conjugate acid.

The water and the hydroxonium ion are also a conjugate pair. If water is considered as a base, the hydroxonium ion is its conjugate acid because it has the extra hydrogen ion which it can give away again.

If the hydroxonium ion as an acid, then water is its conjugate base. The water can accept a hydrogen ion back again to reform the hydroxonium ion.
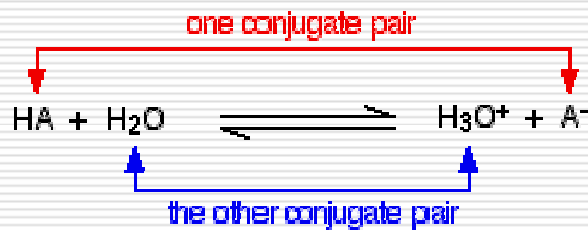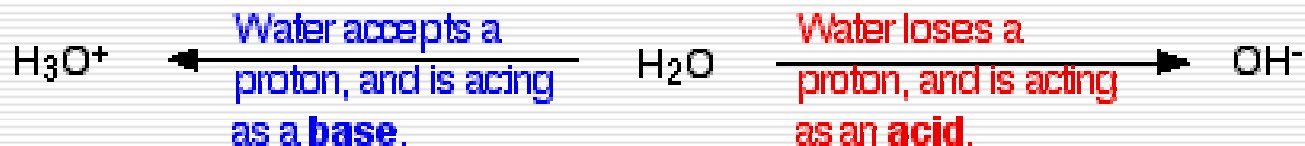
A second example of conjugate pairs

- This is the reaction between ammonia and water. Think first about the forward reaction. Ammonia is a base because it is accepting hydrogen ions from the water. The ammonium ion is its conjugate acid - it can release that hydrogen ion again to reform the ammonia.

- The water is acting as an acid, and its conjugate base is the hydroxide ion. The hydroxide ion can accept a hydrogen ion to reform the water.

- Looking at it from the other side, the ammonium ion is an acid, and ammonia is its conjugate base. The hydroxide ion is a base and water is its conjugate acid.

one conjugate pair

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

the other conjugate pair
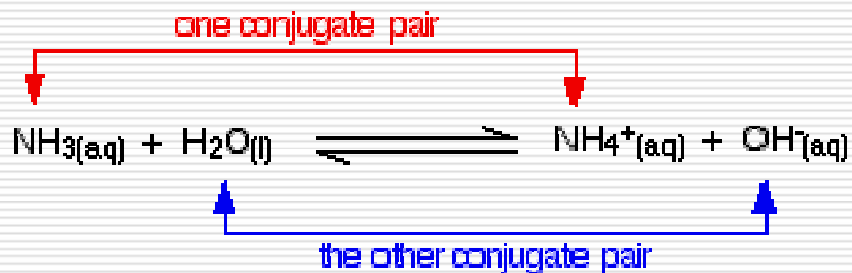
Amphoteric substances

we may possibly have noticed that in one of the last two examples, water was acting as a base, whereas in the other one it was acting as an acid.

A substance which can act as either an acid or a base is described as being *amphoteric*

H_3O^+ ← Water accepts a proton, and is acing as a **base**. H_2O Water loses a proton, and is acing as an **acid**. → OH^-

Amphiprotic and amphoteric

An *amphiprotic* substance is one which can both donate hydrogen ions (protons) and also accept them. Water is a good example of such a compound. The water acts as both an acid (donating hydrogen ions) and as a base (by accepting them).

The "protic" part of the word refers to the hydrogen ions (protons) either being donated or accepted. Other examples of amphiprotic compounds are amino acids, and ions like HSO_4^- (which can lose a hydrogen ion to form sulphate ions or accept one to form sulphuric acid).

But as well as being amphiprotic, these compounds are also *amphoteric*. Amphoteric means that they have reactions as both acids and bases. So what is the difference between the two terms?

All amphiprotic substances are also amphoteric - but the reverse isn't true. There are amphoteric substances which don't either donate or accept hydrogen ions when they act as acids or bases.

A new definition of acid-base behaviour (the Lewis theory) which doesn't necessarily involve hydrogen ions at all.
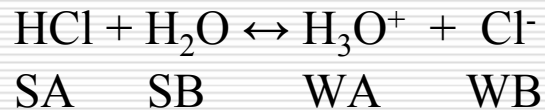
Important rule

A strong acid and a strong base reacts to form weak acid and weak base

Acid base reactions proceed in a direction to form the weak acid and weak base.

strong acid + weak base $\rightarrow$ conjugte acid base pair

strong base + weak acid $\rightarrow$ conjugte acid base pair

$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$
SA   SB   WA   WB

HCl is a strong acid its conjugate base is Cl^- ion is weak base – conjugate acid base pair

H_3O^+ is a weak acid and H_2O is another conjugate strong base – conjugate acid base pair

thus conjugate base of a strong acid always a weak base and the conjugate acid of a strong base is always a weak acid.

Dual behaviour of water

water can act as an acid and as a base. for example H_2O acts as a acid towards NH_3 and acts as a base towards HCl

$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$

$H_2O + HCl \leftrightarrow H_3O^+ + Cl^-$
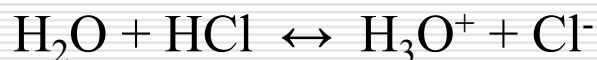
when $NaCO_3$ is dissolved in water CO_3^{2-} ion being a strong proton acceptor acts as a base and H_2O molecule which loses the proton behaves as an acid. thus OH- ions are produced and these ions make the solution alkaline.

$H_2O + CO_3^{2-} \leftrightarrow HCO_3^- + OH^-$
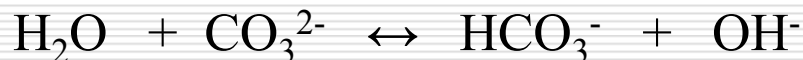
Aqueous solution of the salts of Fe^{3+}, Al^{3+}, cations are strongly hydrated and highly charged small cations are strong proton donors and hence readily give up a proton to H_2O. Due to the presence of H_3O^+ cations the solution is acidic.

$$[Fe(H_2O)_6]^{3+} \; + \; H_2O \; \rightarrow \; H_3O^+ \; + \; [Fe(H_2O)_5(OH)]^{2+}$$

Lewis concept - Electron donor –Acceptor system

An acid is any species which can accept an electron pair and a base is any species that can donate an electron pair.

A lewis acid is an electrophile – accept electron pair

They may be positive charge species H^+, RCO^+, and metal cations, and molecules CO_2, BF_3, SO_2 Or metals in zero oxidation states.

A lewis base is a nucleophile – donating electron pair

They may be OH^-, F-, NH_2, or electron rich molecules NH_3, H_2O

Neutralisation reactions in terms of lewis concept

The process of neutralisation is simply the formation of coordinate bond between acid and base. the product formed is called a neutralisation product or an adduct.

$$H^+ \quad + \quad :NH_3 \rightarrow [H^+ \leftarrow NH_3]^+$$

The proton H+ accepts one electron pair from $:NH_3$ molecule and is an acid whereas NH_3 donates an electron pair is a base. The adduct is NH_4^+ion.
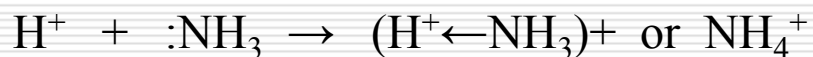
Arrhenius Acids vs Lewis Acids

Arrhenius considered those substances as acids which could dontae proton(H+). Since proton can accept an electron pair from base ALL ARRHENIUS ACIDS ARE LEWIS ACIDS.

BRONSTED BASE VS LEWIS BASE

Bronsted base is which accepts proton while Lewis base is which can donate an electron pair .

Bronsted base can accept proton only when it has an unshared pair of electrons in it.

$H^+ + :NH_3 \rightarrow (H^+\leftarrow NH_3)+$ or NH_4^+

NH_3 behaves both as Bronsted base as well as Lewis base.

All Bronsted bases are also Lewis bases.

Bronsted Acids vs Lewis Acids

There are many Lewis acids which cannot be treated as Bronsted acids.

The central atom of these acids is electron deficient and hence can accept a pair of electrons from a base to complete its octet.
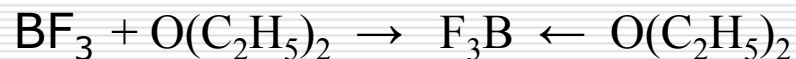
for ex. Halides of B, Al, Fe(III) and Zn

HCl is a Bronsted acid cannot be called a Lewis acid, since it has no vacant orbital to accept an electron pair from a base.

Classification of Lewis Acids

1. Molecules containing a central atom with incomplete octet.

    This class of acids are electron deficient molecules such as alkyls and halides of Be, B, Al.

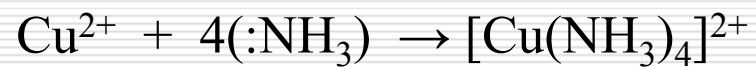 $$BF_3 + O(C_2H_5)_2 \rightarrow F_3B \leftarrow O(C_2H_5)_2$$

2. Molecules containing a central atom with vacant d-orbital

    The central atom of the halides such as SiX_4, GeX_4, TiX_4, SnX_4, PX_3, PF_5, SF_4, $TeCl_4$ have vacant d orbital.

3.   Simple cations

All simple cations are potential Lewis acids

$$Cu^{2+} + 4(:NH_3) \rightarrow [Cu(NH_3)_4]^{2+}$$

UTILITY

i)   This concept also includes those reactions in which no protons are involved

ii) Its more general than Bronsted – Lowry concept. The acid base behaviour is not dependent on the presence of one particular element or presence or absence of a solvent.

iii) Its also accepted basic properties of metallic oxides and acidic properties of non metallic oxides.

iv) This theory also includes many reactions such as gas phase, high temperature and non solvent reactions.

Limitations

The relative strengths of acids and bases cannot be explained on the basis of lewis concept. It does not arrange acids and bases according to their strength.

For ex. Fluoride complex of Be^{2+} is more stable than that of Cu^{2+} indicating Be ion is more acidic than that of Cu ion. On the other hand amine complex of Cu is more stable than Be ion indicating that Cu is more acidic than Be.

Acid base reaction should be a rapid reaction. But there are many Lewis acid base reactions which are slow.

The Lewis concept is too general and includes all reactants which can form coordination bonds.

Even metals in their zero oxidation state (Fe, Ni, Co, Mn) are termed as Lewis acids in their complexes with pi acceptor ligands such as CO, cyclopentadiene and olefins.

HSAB theory

The **HSAB concept** is an acronym for 'hard and soft acids and bases'. Also known as the **Pearson acid base concept**, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways.

It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species.

'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable.

'Soft' applies to species which are big, have low charge states and are strongly polarizable.

The theory is used in contexts where a qualitative, rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions

This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

HSAB theory is also useful in predicting the products of metathesis reactions.

The sensitivity and performance of explosive materials can be explained on basis of HSAB theory.

Ralph Pearson introduced the HSAB principle in the early 1960s as an attempt to unify inorganic and organic reaction chemistry.

The gist of this theory is that soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases.

certain ligands tend to form stable complexes with heavier ions such as Ag^+, Hg^{2+}, Pd^{2+}, Pt^{2+} etc. some other ligands prefer to form stable complexes with lighter ions such as Li^+, Be^{2+}, Al^{3+}, SC^{3+} etc.

Based on this preferential tendency to form stable complexes, the ions as well as ligands have been classified into two categorised as hard and soft acids, the anions and neutral ligands are catergorised as hard and soft bases.

Hard acids and **hard bases** tend to have:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity
- energy low-lying HOMO (bases) or energy high lying LUMO (acids).

Examples of hard acids are: H^+, alkali ions, Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3.

Examples of hard bases are: OH^-, F^-, Cl^-, NH_3, CH_3COO^-, CO_3^{2-}.

The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and **soft bases** tend to have:

- large atomic/ionic radius
- low or zero oxidation state
- high polarizability
- low electronegativity
- energy high-lying HOMO (bases) and energy-low lying LUMO (acids).

Examples of soft acids are: CH_3Hg^+, Pt^{4+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, Cd^{2+}, BH_3.

Examples of soft bases are: H^-, R_3P, SCN^-, I^-.

The affinity of soft acids and bases for each other is mainly covalent in nature.

Acids				Bases			
hard		**soft**		**hard**		**soft**	
Hydronium	H^+	Mercury	CH_3Hg^+, Hg^{2+}, Hg_2^{2+}	Hydroxyl	OH^-	Hydride	H^-
Alkali metals	Li^+,Na^+,K^+	Platinum	Pt^{4+}	Alkoxide	RO^-	Thiolate	RS^-
Titanium	Ti^{4+}	Palladium	Pd^{2+}	Halogens	F^-,Cl^-	Halogens	I^-
Chromium	Cr^{3+},Cr^{6+}	Silver	Ag^+	Ammonia	NH_3	Phosphine	PR_3
Boron trifluoride	BF_3	borane	BH_3	Carboxylate	CH_3COO^-	Thiocyanate	SCN^-
Carbocation	R_3C^+	P-chloranil		Carbonate	CO_3^{2-}	carbon monoxide	CO
		bulk Metals	M^0	Hydrazine	N_2H_4	Benzene	C_6H_6
		Gold	Au^+				
Table 1. Hard and soft acids and bases							

For example the I- ion (a soft base) has a very high polarisability.

Ammonia is a hard base.

The presence of easily polarisable aromatic ring makes both aniline and pyridine to behave as nearly soft bases.

All the species in any category are not equally hard or soft.

Cu^{2+} ion behaves as a harder acid than Mn^{2+} ion because of the smaller size of the former.

Li^+ ion is a harder acid than Cs^+ ion because of the smaller size of the former.

similarly bases such as $C_6H_5NH_2$, $(C_6H_5)_2NH$, NH_3, C_6H_5N all containing N are not equally hard.

NH_3 is harder than $C_6H_5NH_2$ which in turn is harder than $(C_6H_5)_2NH$, is a soft base.

There is no sharp line between soft and hard species and a number of border line cases also exist.

For instance transition metal ion such as Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} behave as border line acids .

Metals and non metals in lower oxidation state behave as soft acids while the same species in higher oxidation state behave as hard acids.

According to Pearson's hard soft [Lewis] acid base (HSAB) principle:

Hard [Lewis] acids prefer to bind to Hard [Lewis] bases
and
Soft [Lewis] acids prefer to bind to Soft [Lewis] bases

This principle does not state that hard-soft or soft-hard combinations cannot not exist.

It only states that if there is a choice a hard –hard or a soft – soft combination would be preferred to a soft- hard or hard – soft combination.
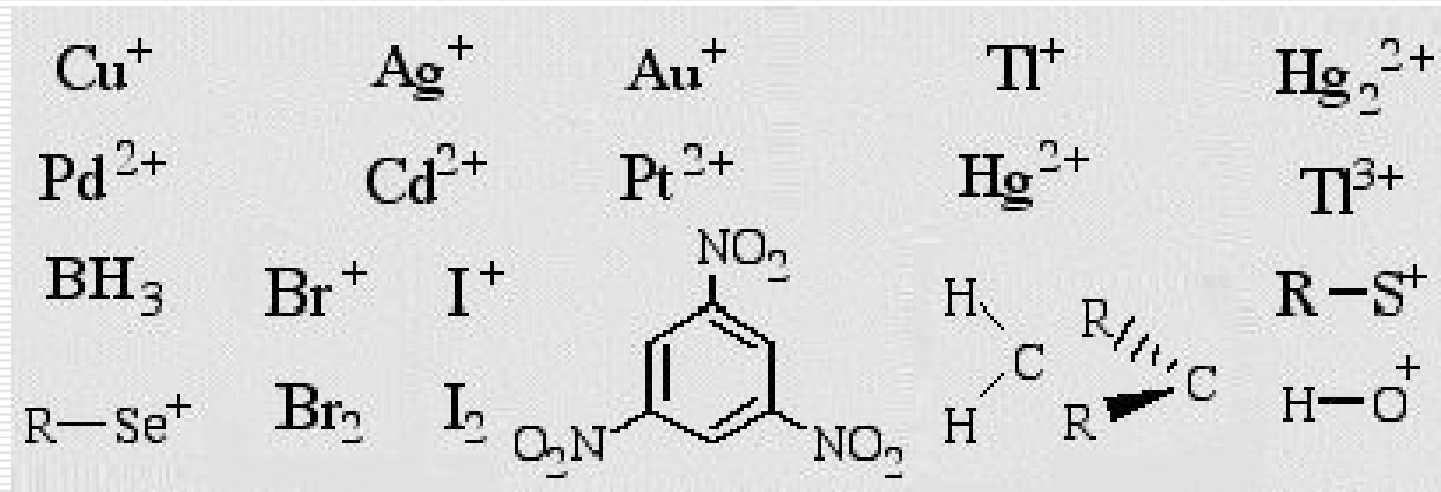
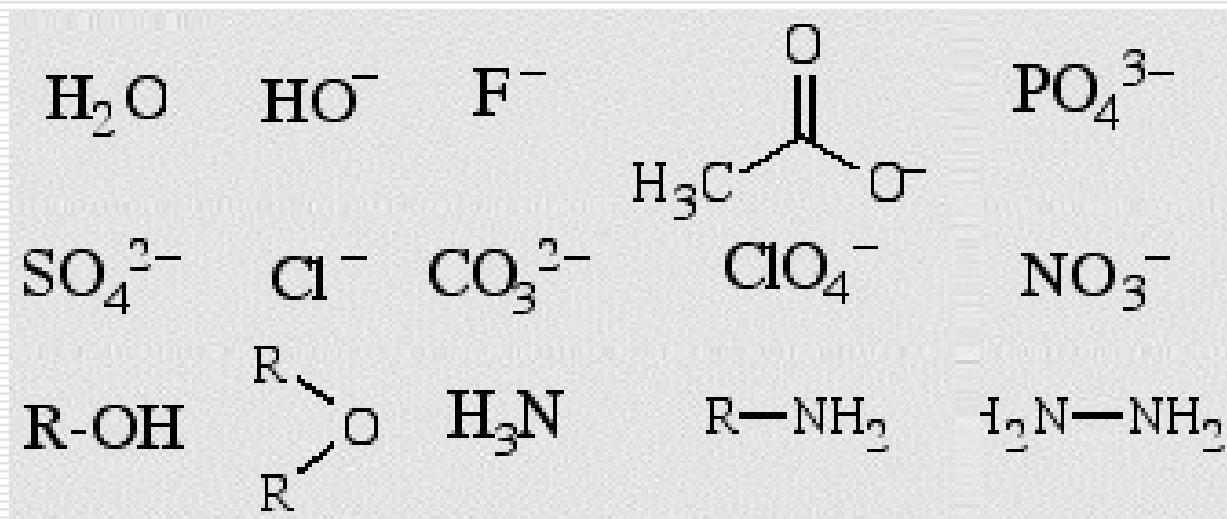# Pearson's HSAB Species
Pearson's Hard Lewis Acids:

$$H^+ \quad Na^+ \quad K^+ \quad Be^{2+} \quad Mg^{2+}$$

$$Ca^{2+} \quad Mo^{3+} \quad Mn^{2+} \quad Al^{3+} \quad Sc^{3+}$$

$$In^{3+} \quad Cr^{3+} \quad Co^{3+} \quad Fe^{3+} \quad Ti^{4+}$$

$$Zr^{4+} \quad U^{4+} \quad Ce^{3+} \quad Sn^{4+} \quad BF_3$$

$$AlCl_3 \quad AlH_3 \quad SO_3 \quad NO_2^+ \quad CO_2$$

Pearson's Soft Lewis Acids:
Pear

Cu^+ Ag^+ Au^+ Tl^+ Hg_2^{2+}

Pd^{2+} Cd^{2+} Pt^{2+} Hg^{2+} Tl^{3+}

BH_3 Br^+ I^+ $R-S^+$

$R-Se^+$ Br_2 I_2 $H-O^+$

Pearson's Hard Lewis Bases:

H_2O HO^- F^- PO_4^{3-}

$H_3C-C(=O)-O^-$

SO_4^{2-} Cl^- CO_3^{2-} ClO_4^- NO_3^-

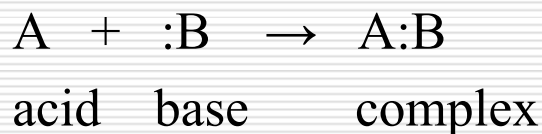$R-OH$ R_2O (R—O—R) H_3N $R-NH_2$ H_2N-NH_2

Pearson's Soft Lewis Bases:
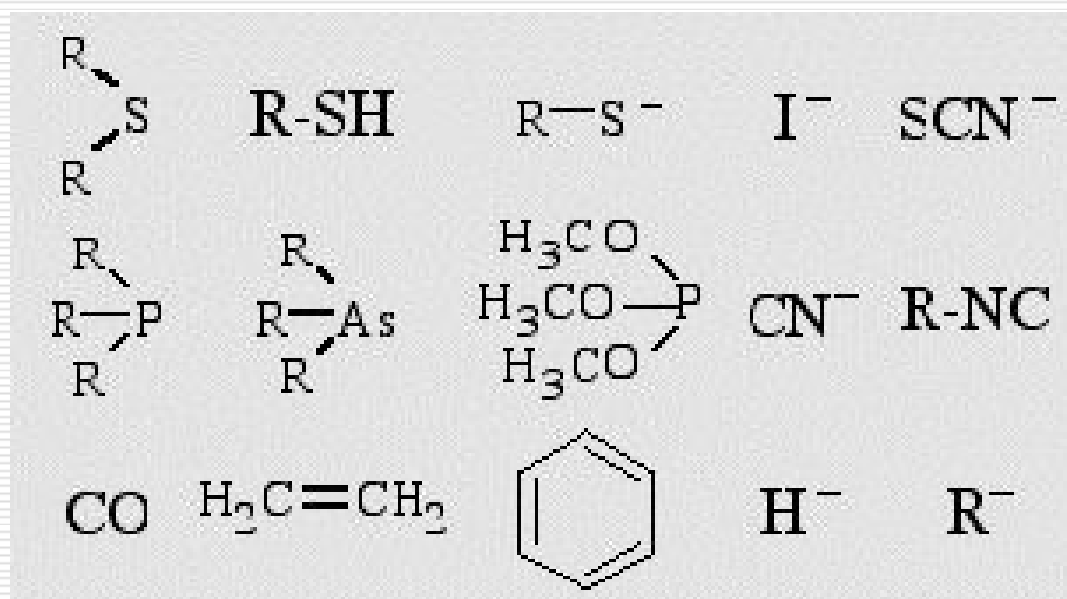
Applications of HSAB principle

1. Stability of complexes.

   Pearson in 1963 explained the relative stability of complexes on the basis of HSAB principle. A complex A:B formed as follows,

   A + :B → A:B

   acid   base   complex

   if A and B is either both hard or both soft the complex would be stable

   The complex would be less stable if A is harder than B and is soft or vice versa.

For example while AgI_2^- exists as a stable compound AgF_2^- does not exist.

Ag+ is a soft acid. its interaction with I- ion , a soft base yields a stable complex

AgI_2- whereas its interaction with F- ion hard base yields an unstable complex AgF_2-.

Ag+   +   2I   → AgI_2-
Soft acid   soft base   stable complex

Ag+   +   2F   → AgF_2-
Soft acid   hard base   unstable complex
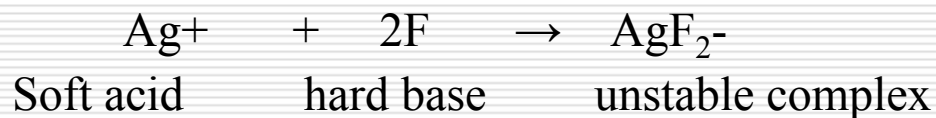
With similar reasons we can explain why $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$

PREDICTION OF COORDINATION IN COMPLEXES OF AMBIDENTATE LIGANDS

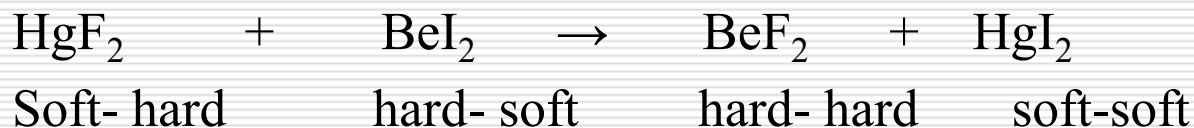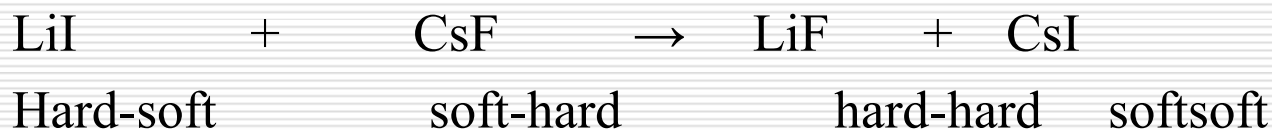We can predict the formation of various metal ion complexes with ambidentate ligands.

An ambidentate ligands is one which although unidentate may coordinate to the metal ion through either of its two coordinating atoms.

For example [SCN]- is an ambidentate ligand, it coordinates through N atom to form the complex $[Co(NCS)_4]^{2-}$ where as it coordinates through S atom to form the complex $[Pd(SCN)_4]^{2+}$.

The reason for the above is : Pd^{2+} is a soft acid so that it prefers to coordinate through the S atom to form Pd-SCN linkage.

Co^{2+} is a hard acid so that it prefers to coordinate through the harder N atom to form the Co-NCS linkage.

Predicting feasibility of a reaction

The reaction between LiI and CsF to give LiF and CsI is an interesting example of preferential combination of soft- soft and hard-hard species.

LiI   +   CsF   →   LiF   +   CsI

Hard-soft   soft-hard   hard-hard   softsoft

HgF_2 + BeI_2 → BeF_2 + HgI_2

Soft- hard   hard- soft   hard- hard   soft-soft

Combination of hard ligands or of soft ligands with a metal ion is more favourable than the combination of a mixture of hard and soft ligands with the metal ion.

It is easy to understand why the complexes $[Co(CN)_5I]^{3-}$ and $[Co(NH_3)_5F]^{3-}$ are stable while the complexes $[Co(CN)_5F]^{3-}$, and $[Co(NH_3)I]^{2+}$ are unstable.

the CN- and I- are both soft bases while NH_3 and F- are both hard bases.

In 1968, G. Klopman quantified Pearson's HSAB principle using frontier molecular orbital(FMO) theory. Klopman proposed that:

Hard [Lewis] Acids bind to Hard [Lewis] Bases to give charge-controlled ionic complexes.

and

Soft [Lewis] Acids bind to Soft [Lewis] Bases to give FMO-controlled covalent complexes.

Combining Pearson's and Klopman's ideas:

Hard Lewis acids:

Atomic centres of small ionic radius and with net positive charge.

Species do not contain electron pairs in their valence shells, they have a low electron affinity and are likely to be strongly solvated.

High energy LUMO.

Soft Lewis acids:

Large radius, low or partial (delta+) positive charge.

Electron pairs in their valence shells. Easy to polarise and oxidise.

Low energy LUMOs but large magnitude LUMO coefficients.

Hard Lewis bases:

Small, highly solvated, electronegative atoms: 3.0-4.0.
Species are weakly polarisable and are difficult to oxidise.
Low energy HOMO.

Soft Lewis bases:

Large atoms of intermediate electronegativity: 2.5-3.0.
Easy to polarise and oxidise.
High energy HOMOs but large magnitude HOMO coefficients.

Effect of solvent on relative strength of Acids and Bases

Effect of solvent on acid strength.

The term acid strength is a relative term. According to the concept of Lowry and Bronsted, it depends on the substance which acts as a base. consider the general equation

Acid1 + Base2 $\leftrightarrow$ Acid 2 + Base1
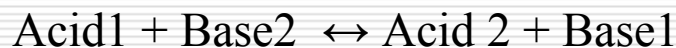
The capacity of the acid to ionise (i.e to donate protons) depends upon the base strength (i.e. the capacity to accept protons) of the solvent which acts as a base.

To illustrate this point ionization in three solvents namely glacial acetic acid water and liquid ammonia of increasing basic character may be considered.

Ioniztion in Acetic acid

Although acetic acid is normally an acid it is also able to some extent to accept a proton and thus acts as a base as well.

The ionization of strong acid HA in this medium is represented as

$$HA + CH_3COOH \rightarrow CH_3COOH2+ + A-$$
acid   base   acid   base

but the equilibrium cannot lie very much to the right since acetic acid has only a small tendency to accept protons. Thus even strong acids are only feebly ionised in acetic acid.

The degree of ionization of a number of acids when dissolved in glacial acetic acid have been determined from conductance.

Some of the common acids have been arranged in the following order of decreasing strength

$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$ - This is the correct order of decreasing strength of these acids.

Ionisation in water

Water is much stronger than acetic acid i.e., it has much greater tendency to accept protons than acetic acid.

Therefore the ionisation equilibrium of a strong acid in water represented as

$$HA \ + \ H_2O \ \rightarrow \ H_3O+ \ + \ A-$$
acid   base   acid   base

It lies very much to the right. All the five acids ($HClO_4$,HBr, H_2SO_4,HCl, HNO_3) reacts almost completely with water to form hydronium ion H_3O+.

Therefore all strong acids in aqueous solutions appear almost equally strong. Their relative strengths in aqueous solutions cannot be compared. This phenomenon is known as the levelling effect.

Ionisation in liquid ammonia

liquid ammonia has strong basic character (strong tendency to take up protons) that even a weak acid, like acetic acid, ionise to a considerable extent in liquid ammonia and thus behaves as a strong acid . The ionic equilibrium lies very much to the right.

$$CH_3COOH \;\; + \; NH_3 \;\; \rightarrow \;\; NH_4^+ \;\; + \; CH_3COO\text{-}$$
 acid   base   acid   base
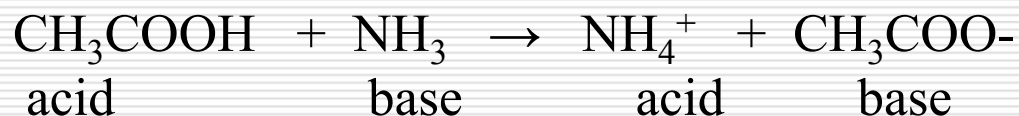
By conductance measurements it has been found that all acids, which in aqueous solution behave stronger than acetic acid, appear to be of about the same strength when dissolved in ammonia.

Thus such strong acids hydrochloric and nitric and such weak acids as acetic acid appear to be almost equal strength when dissolved in ammonia.

Ionisation in HF

Hydrogen fluoride has strong acidic properties and no basic.(i.e proton accepting). so the strongest acid is incapable of ionising as an acid when dissolved in hydrogen fluoride.

some of the acids have tendency to accept protons, ionise as bases when dissolved in HF.

$HNO_3 + HF \leftrightarrow H_2NO_3^+ + F-$
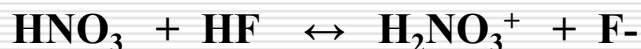
even a strong acid like HNO_3 behaves as a base(weak base) when dissolved in HF.

acetic acid has greater tendency to accept a proton ionise readily as a base in HF solution.

$CH_3COOH + HF \leftrightarrow CH_3COOH_2^+ + F-$
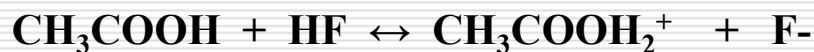
The acetic acid behaves as a strong base than nitric acid when dissolved in HF

What are the different kinds of Lewis bases?

(i) All the anions can acts as Lewis acids because they have tendency to donate electron pairs.

For example, oxides (O^{2-}), hydroxide (OH^-), halides (X^-) amides(NH_2^-) etc. act as Lewis bases.

The greater the charge density on the anion the stronger the base.

(ii) Substances having unshared or lone pair of electrons acts as Lewis bases. For example water ($H2O$) ammonia ($NH3$), ether($R2O$), ketones ($R2C=O$), etc act as electron donors.

What is extended Lewis definition of acid and base?

LEWIS ACID

(i) The extended Lewis acids include unsaturated species like CO2 and CS2, where central atom is bonded to atoms of different electronegativities by one or more multiple bonds.

(ii) Although both molecules lack acceptor character of the central atom because carbon atom cannot extend its octet yet these are indirectly treated as Lewis acid.

(iii) This is due to polarization of the Π electron cloud, the polarization leads to a partial +ve charge on C and partial –ve charge on the more electronegative atom like O.

(iv) The +vely charged carbon then acts as an electron acceptor in the raection of CO2 with lewis base.

LEWIS BASE

The extended Lewis base include substance like CO and unsaturated hydrocrbons like alkenes, alkynes, butadienes, benzene etc.

These may be treated as Lewis bases because of a lone pair on :CO or donation from above mentioned hydrocarbons to form π – complexes with metals in low oxidation state