ACIDS AND BASES

At first times, substances that have sour taste were called as acids and substances that have bitter taste were called as bases. Later acids and bases determined by looking the change in colour of the litmus paper. In the late 18th century, Lavoisier said that ''Oxygen is the element gives substances their acidic property''. He investigated the combustion of C, S and P elements and when these elements were burned, formed products showed acidic property in H_2O*. That is why he said that "Oxygen determines the acidity of substances". Davy suggested that the hydrogen element has given the acidic property to the substances, by investigating HCl acid, which is composed of only hydrogen and chloride elements. Acid-base chemistry was explained in molecular term at first time, as a result of studies about aqueous solutions of Ostwald and Arrhenius and also especially the ionization theory of Arrhenius between the years 1880-1890. The first scientifically accepted acid-base definition was done by Arrhenius. Lots of other definitions were suggested between the years 1920 and 1940. However, in the last years, studies that correlate acidity - basicity with molecular structure and electron density by using MO theory became important.*

ACID - BASE DEFINITIONS

1. *Arrhenius Definition*
2. *Brønsted-Lowry Definition*
3. *Definition according to solvent system*
4. *Lewis Definition*
5. *Gutman Definition*
6. *Lux-Flood Definition*
7. *Usanovich Definition*
8. *Soft-Rigid Acid-Base Definition*
9. *Generalized Definition*
10. *Ingold-Robinson Definition*

ARRHENIUS DEFINITION

Classical Definition: *Acids are written as HX and when they decompose, they form protium* (H^+) *ion in water. Bases are written as MOH (M= metal) and when they decompose in water, they form hydroxide (* OH^- *) ion.*

Modern Definition: *In 1884, Arrhenius suggested that water ionizes itself (self - ionization) according to the theory of electrolytic dissociation and made acid-base definition according to that theory.*

$$H_2O \rightarrow H^+(aq) + OH^- (aq) \quad K= 1.10^{-14}$$

Therefore, compounds that give a H^+ *ion in aqueous solution (or compounds that increase* H^+ *ion concentration) are called as ACID, and compounds that give* OH^- *ion (or compounds that increase* OH^- *ion concentration) are called as BASE.*

BRØNSTED - LOWRY DEFINITION

In 1923, British Lowry and Danish Brønsted said that substances that give proton to the matter which they interact are called acids, and substances that take proton from the matter that they interact are called bases. As with the Arrhenius acids, a Brønsted-Lowry acid is shown as H_nA. So all Arrhenius acids are also Brønsted-Lowry's acid. Brønsted-Lowry base should be considered a chemical species that contains an electron pair that it can easily give to bind the proton. Generally they are shown as B:

Brønsted-Lowry acid-base reaction can be shown as follows:

$$\underset{\text{Acid-1}}{H\text{-}A} \quad + \quad \underset{\text{Base-2}}{B:} \leftrightarrow \underset{\text{Acid-2}}{[H\text{-}B]^+} + \underset{\text{Base-1}}{A:^-}$$

NOTE: *Compounds that act as both Brønsted-Lowry acid and Brønsted-Lowry base are called AMPHIPROTIC SUBSTANCES. Ex: H_2O. Since H_2O is amphiprotic, the balance of proton transfer can occur without acid or base.*

DEFINITION ACCORDING TO SOLVENT SYSTEM

Acids are substances that increase the characteristic cation concentration of the solvent, while bases are those which increase the characteristic anion concentration of the solvent. Many solvents are self-ionizing. This ionization is called the autoionization of the solvent.

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

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

$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$

$2POCl_3 \rightleftharpoons POCl_2^+ + POCl_4^-$

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

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

$2CH_3OH \rightleftharpoons CH_3OH^+ + CH_3O^-$

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

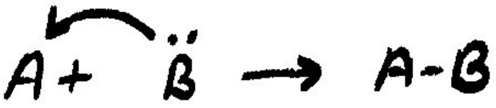
LEWIS DEFINITION

In 1923, Lewis proposed an acid-base definition that is not connected to protons, ions and solvent reactions in the solvent. According to this, substances that can take an electron pair (substances that can coordinate the electron pair) are acids, and substances that can give electron pair are bases. All transition metal cations are Lewis acid.

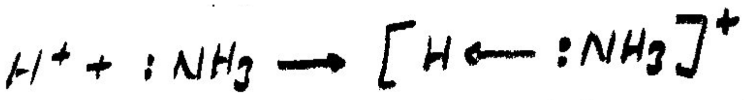
For a substance to be Lewis acid:

There must be an octet space. There must be empty orbitals that can accept an electron pair. The structure must have π bonds and the octet must be incomplete.

1. H^+ *ion*
2. *Main element cations with a large charge/radius ratio*
3. *Transition metal cations*
4. *Molecules that do not obey octet rule*
5. *Molecules that contain empty d orbital*
6. *Molecules containing multiple bonds between atoms that have different electronegativities*
7. *Some transition elements*



The Lewis acid has low-energy LUMOs. The Lewis base has high energy HOMOs. What makes different a Lewis acid-base reaction from the two electron-transfer oxidation-reduction (redox) reactions is the formation of a coordinate-covalent bond. Oxidation numbers of atoms in the formation of coordinated-covalent bonds are not changed. However, the characteristic of redox reactions is that the oxidation numbers are changing.

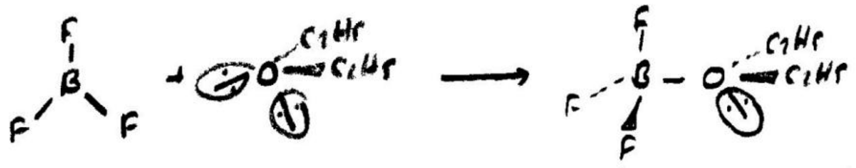


HCl is a Lewis acid. Because it takes a pair of electrons from a base such as water and ionizes.

$$H_2O + HCl \longrightarrow [H_2O: \rightarrow HCl] \longrightarrow H_3O^+ + Cl^-$$

$$Ag^+ + 2:NH_3 \longrightarrow [H_3N: Ag : NH_3]^+$$

In these reactions, silver ions (or other cations) act as acids and ammonia (and other electron pairing agents) act as bases. Another example is the BF_3*-*NH_3 *adduct. The* BF_3 *molecule has a triangular planar structure. Each B-F bond has some degree of double bond character. Because the electronegativity of the fluorine atom is large, there is a positive charge (+) on the boron atom. The boron atom is generally defined as the electron poor atom. The free electron pair of the* NH_3 *molecule in HOMO combines with the empty LUMO of the boron to form an addition product. B-F bonds are bent to form a uniform tetrahedral structure around the boron atom.*



When one of the free electron pair is connected to the boron atom, transforms the geometry around the boron atom from trigonal planar to tetrahedral. As a result, adduct (B.P -125-126 °C) is formed from BF_3 *(B.P -99.9 °C) and diethyl ether (B.P -34.5 °C).*

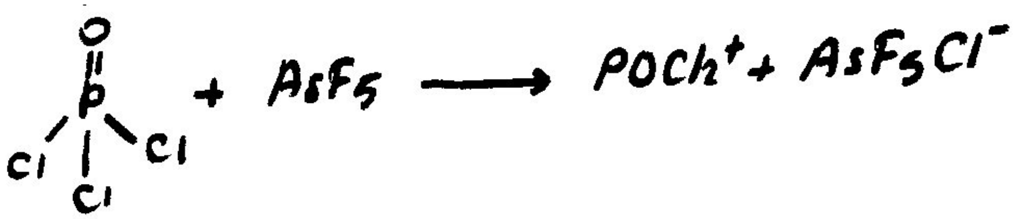
For a substance to be Lewis base:

Each chemical species that contains an uncompleted pair of electrons or an electron pair that it can easily give (e.g; Π-bond electrons) is called a Lewis base. The MO theory explains the Lewis basicity of a chemical species with HOMO (highest occupied MO).

1. *H^- ion (hydride ion*
2. *VA group hydrides, conjugate bases and their derivatives*
3. *VIA group hydrides, conjugate bases and their derivatives*
4. *Halogens and oxa-anions*
5. *Some molecules that have two atoms*
6. *Singlet carbenes*
7. *Akenes*

GUTMAN DEFINITION

Substances that give Cl^- ion are bases and substances that take Cl^- ion are acids.



$POCl_3 + AsF_5 \longrightarrow POCl_2^+ + AsF_5Cl^-$

$CsCl + FeCl_3 \longrightarrow Cs^+ + FeCl_4^-$

base acid

LUX-FLOOD DEFINITION

Substances that give oxide (O^{2-}) are bases and substances that take oxide are acids.

$MgO + SO_3 \xrightarrow{1000°C} MgSO_4$

base acid

$SiO_2 + H_2O \longrightarrow H_2SiO_3$

base acid

$CO_2 + CaO \longrightarrow CaCO_3$

acid base

USANOVICH DEFINITION

All chemicals that react with bases, give cations, accept anions or electrons are acids. All the chemical substances that react with the acids, anions, electrons or can connect with cations are bases.

INGOLD-ROBINSON DEFINITION

The electrophile and nucleophile approach is the Lewis theory. However, the terms used here is related with reactivity. Electrophilic reagents are acid, nucleophilic reagents base.

GENERALIZED DEFINITION

Acidity is a positive character and the ability of interest to negatives, whereas basicity is a negative character and the ability to interest to positives.

SOFT-HARD ACID-BASE DEFINITION:

In 1963 R.G. Pearson defined the soft and the hard concepts. For both acids and bases, the term hard is defined by atoms, ions and molecules, whose electrons are strongly held by the nucleus and that are electrically difficult to migrate and are low in polarity.

For acids:

HARD	BORDERLINE	SOFT
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}	Cu^+, Ag^+, Au^+, Hg^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}	CH_3Hg^+, Pd^{2+}, Pt^{2+}
BF_3, $B(OR)_3$, $AlCl_3$, $Al(CH_3)_3$, AlH_3	SO_2, Ru^{2+}, Ir^{3+}, Cd^{2+}	Hg^{2+}, BH_3, CH_2
CO_2, RCO^+, CH_3Sn^{3+}	BBr_3, $B(CH_3)_3$	R_2C^+, Br_2, I_2
Al^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}	R_3C^+, NO^+	Π-acceptor
Co^{3+}, Ti^{4+}, Zr^{4+}		
Cl^{3+}, Cl^{7+}, I^{5+}, I^{7+}		

For bases:

HARD	**BORDERLINE**	**SOFT**
NH_3, RNH_2, N_2H_4	N_2, N_3^-, NO_2^-	H^-, CN^-, SCN^-, $S_2O_3^{2-}$, I^-, R^-
H_2O, ROH, R-O-R	C_5H_5N, $C_5H_5NH_2$	RS^-, R_2S, CO, C_2H_4, RNC, RSH
OH^-, NO_3^-, ClO_4^-, CO_3^{2-}	Br^-, SO_3^{2-}	C_6H_6, $S_2O_3^{2-}$,
SO_4^{2-}, O^{2-}, PO_4^{3-}		R_3P, $(RO)_3P$, R_3As
F^-, Cl^-, CH_3COO^-		

AlF_6^{3-}	hard-hard	most strong bond	$AlF_6^{3-} \rightleftharpoons Al^{3+} + 6F^-$	$K_F = \frac{[Al^{3+}][F^-]^6}{[AlF_6]^{3-}}$
$AlCl_6^{3-}$	hard-hard	↓	"	"
$AlBr_6^{3-}$	hard-soft		"	"
AlI_6^{3-}	hard-soft	most weak bond	"	"

$$K_F < K_{Cl} < K_{Br} < K_I$$

The most stable complex is AlF_6^{3-}

HgF_4^{2-}	soft-hard	most weak bond
$HgCl_4^{2-}$	soft-hard	↓
$HgBr_4^{2-}$	soft-soft	
HgI_4^{2-}	soft-soft	most strong bond

$$K_I < K_{Br} < K_{Cl} < K_F$$

The most stable complex is HgI_4^{2-}

FeF_6^{3-}	hard-hard	most strong bond
$FeCl_6^{3-}$	hard-hard	↓
$FeBr_6^{3-}$	hard-soft	
FeI_6^{3-}	hard-soft	most weak bond

$$K_F < K_{Cl} < K_{Br} < K_I$$

The most stable complex is FeF_6^{3-}

AgF	*soft-hard*	↓ *Solubility decreases*
$AgCl$	*soft-hard*	
$AgBr$	*soft-soft*	
AgI	*soft-soft*	

VF_4^{3-}
VF_4^{-}
VF_4^{+} → *most stable*

$Mn(SCN)_4^{2-}$ → *most stable*
$Fe(SCN)_4^{2-}$
$Co(SCN)_4^{2-}$
$Ni(SCN)_4^{2-}$
$Cu(SCN)_4^{2-}$
$Zn(SCN)_4^{2-}$

$PbBr_4^{2-}$ y-y → *most stable*
SnF_4^{2-} y-s
$GeCl_6^{4-}$ ygo-sge
SiI_6^{2-} yso-y

$Ni(CO)_4$ → *most stable*
$Ni(CO)_5^{2+}$

* MnF_6^{4-}
FeF_6^{4-}
TiF_6^{2-}
VF_6^{-} → *most stable*
WF_6

* SO_4^{2-} → *most stable*
SeO_4^{2-}
TeO_4^{2-}
PoO_4^{2-}

* VH → *most stable*
VH_2
VH_3
VH_4
VH_5

* $Ni(CO)_4$
$Pd(CO)_4$
$Pt(CO)_4$ → *most stable*

ACID AND BASE STRENGTH

Proton Affinity (PA)

The acidity or basicity of a chemical species depends on two main factors. The first is the properties of the chemical species, the second is the chemical environment. Data on the first factor are obtained in the best gas phase. The second factor is associated with solution chemistry. The proton affinity and electron affinity, which are measured in the gas phase, are very useful. The acidity or basicity of a chemical species in the solution depends not only on the chemical species but also on the solvent. The acid base strength in the solution is understood by the equilibrium constant.

The proton affinity of a chemical species is the enthalpy of the reaction in which the chemical species react with H^+ *in the gas phase.*

$B(g) + H^+ \rightarrow BH+ (g) \quad \Delta H = PA$

IE sequence $CH_4 > NH_3 < H_2O < HF$ *(Hyrides of second period elements)*
PA sequence $CH_4 < NH_3 > H_2O > HF$

The ionization energies of the 7A group elements are $I < Br < Cl < F$*. Hydrides;* $HF > HCl > HBr > HI$*. The alkalinity of the alkali metal hydroxides having the acid-base strength in the aqueous solution in the gaseous phase is* $LiOH < NaOH < KOH < CsOH$*.*

$H_2Se > H_2S > H_2O$
Conjugate bases of large molecules (SeH^-*,* SH^-*,* OH^-*) have a low charge density and therefore have smaller pulling forces for* H^+ *ion (bond force sequence: O-H > S-H > Se-H).*

$HF > H_2O > NH_3$
The -1 charged NH_2^- *ion has two lone pairs of electrons and there is a -1/2 charge on each lone electron pairs. Similarly, in the* OH^- *ion there is a -1/3 charge on each non electron pair. There is -1/4 load with* F^- *ion. Therefore,* NH_2^- *(amide) ion has the largest proton pulling force.*

The Acidity of the Ametal Hydrides

CH_4	NH_3	H_2O	HF
SiH_4	PH_3	H_2S	HCl
GeH_4	AsH_3	H_2Se	HBr
		H_2Te	HI

→ *The acidity of the ametal hydrides increases.*

↓ *The acidity of the ametal hydrides increases.*

Inductive Effect and Resonance

NF_3 NCl_3 NH_3

NH_3 CH_3NH_2 $(CH_3)_2NH$ $(CH_3)_3N$

CF_3CH_2OH CCl_3CH_2OH CH_3CH_2OH

→ *The proton affinity increases. In the first two series, the central atom is nitrogen, and in the third series the central atom is oxygen. The electron withdrawing ability of the substituent decreases. The inductive effect depends on the distance from the central atom. The distance from the central atom decreases the inductive effect. For example, the proton affinity of* $CH_3CHClCOOH$ *is higher than the proton affinity of* CH_2ClCH_2COOH*.*

Alkyl groups are electron donor groups. In the amines, the alkyl groups provide electrons to the nitrogen and increase the negative character of the nitrogen, making it a stronger base. Therefore, the basic order; $NHMe_2 > NH_2Me > NH_3$*.*

Boron halides do not comply with the inductive effect rule. Because BF_3 *and* BCl_3 *have Π-bonds that significantly increase the electron density on the boron atom. According to the inductive effect* BF_3 *is expected to be the strongest acid. In fact, the acidity order is* $BF_3 < BCl_3 \leq BBr_3$*.*

Hydration Effect

The proton affinity of the SH$^-$ ion is lower than that of F$^-$ ion. This indicates that the F$^-$ ion is a stronger base than the SH$^-$ ion. As the conjugate acid of the strong base is weak, H_2S is stronger acid than HF. However, in aqueous solution, HF is a stronger acid. This is due to the fact that the F$^-$ ion gives a strong H bond with water. As a result, the hydration energy of F$^-$ is considerably higher than that of the SH$^-$ ion. As the hydration of the ions shows the increasing acidity effect, HF acts more acidic in aqueous solution than the gas phase.

Steric Effects

When large groups are forced to form the addition compound, mutual pushing of large groups makes the reaction difficult. If the pussing between large groups makes it difficult for acids and bases to approach each other and prevents their orbital overlapping, this is called as ''front strain''. If large groups interfere with each other and change the geometry of the central atom, this is called as ''back strain''. The effects of different types of electronic structures of similar molecules are called as ''internal strain''.

2,6-dimethyl pyridine > 2-methly pyridine > 2-t-butyl pyridine > pyridine

This sequence is compatible with the sequence of the inductive effect of alkyl groups. However, the reaction of with large acids such as BF_3 and BMe_3 gives the basicity sequence: pyridine > 2-methylpyridine > 2,6 dimethylpyridine > 2-t-butylpyridine. As the molecules approach to each other, the larger F atoms bound to the boron atom or the ortho groups of pyridines substituted with Me groups push each other. The order of steric effect is 2 methyl > 2,6 dimethyl > 2-t butyl.

Oxides

BeO
MgO
CaO
SrO
BaO ↓ Basicity increases

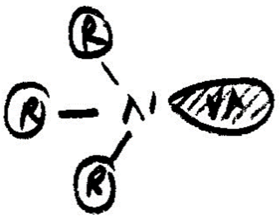
Na_2O MgO Al_2O_3 SiO_2 P_2O_5

→ Basicity decreases

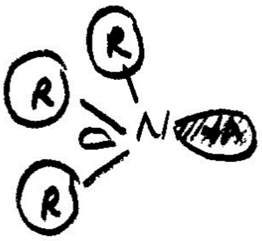
Basicity and Steric Effect of Nitrogenous Compounds

Binding the electron-withdrawing groups to the nitrogen atom affects the base in the decreasing direction, while the electron-donating groups act in an increasing manner. The displacement of H atoms in the NH_3 *molecule with electron withdrawing groups such as F, OH and* NH_3 *decreases the basicity. The OH group withdraws more electrons group than the* NH_2 *group, therefore hydroxylamine is weaker base than hydrazine. Since the methyl and ethyl groups are electron donor groups, they increase the electron density on the nitrogen atom and increase the basicity. This tendency is seen until the binding of the second methyl or ethyl group. Addition of the third group, the basicity decreases.*

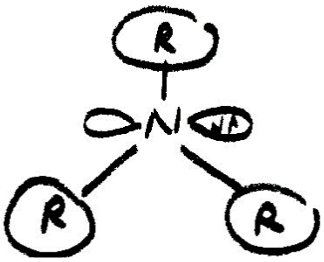
secondary amine > primary amine > tertiary amine



R is a small alkyl group
(sp^3)



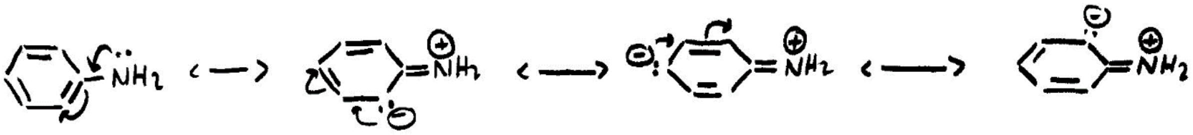
R is a medium-sized alkyl group
(geometry is slightly distorted)



R is a big alkyl group
(geometry from tetrahedral to trigonal planer)
(sp^2+p)

In non-aromatic cyclic amines, the alkyl groups are interconnected in chain form and away from the lone pairs of electrons of nitrogen. There is no steric effect on the basic character of such amines. Therefore, they are more basic than open chain amines. For example, pyrrolidine is stronger than dimethylamine and quinuclidine is stronger than diethylamine.

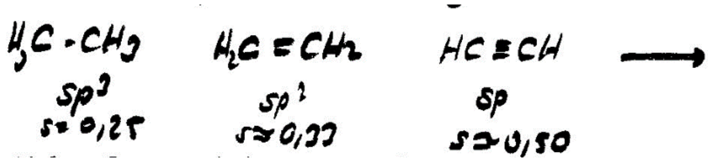
Another factor that affects the basic character of amines is the resonance. The lone pair of electrons of the nitrogen is delocalized on the molecule with resonance, and the basic character decreases.



Because the cyclohexane does not have any resonance, it is a stronger base than aniline. The base of the amines in the aqueous solution also depends on the hydration. Hybridization is effective on basicity.

Effect of s Character on Acidity

The higher the s character in the hybridization of the carbon atom, the higher the electronegativity. As the s character increases, acidity increases.

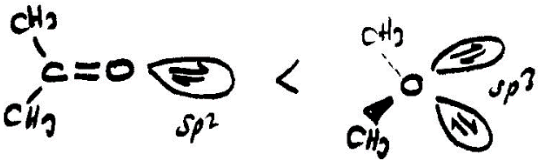


acidity increases

$$HC\equiv C-COOH > CH_3CH_2COOH$$

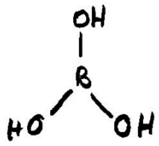
pyridine

piperidine

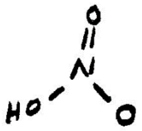


Oxyacids

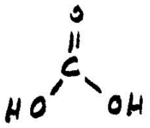
Acids [(HO)pXOq (p=1,2,…; q=0,1,2,...)] in which oxygen atoms and OH groups are around the central atom (ametal) is called oxyacids. According to Paules, the first acidity force of the acids is dependent on q. As the q increases, the acidity strength increases. When the number of more electronegative oxygen atoms bonded to the central atom, the H-O bond is weaker.



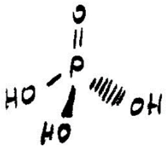
(H_3BO_3)
p=3, q=0



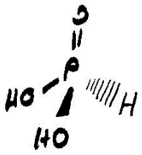
(HNO_3)
p=1, q=1



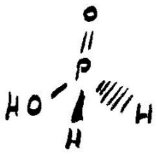
(H_2CO_3)
p=2



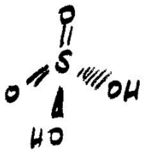
(H_3PO_4)
p=3, q=1



(H_3PO_3)
p=2, q=1

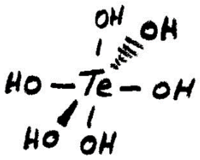


(H_3PO_2)
p=1, q=1

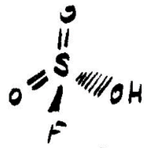


(H_2SO_4)
p=2, q=2

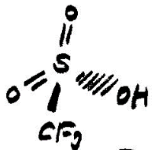
$(HClO_4)$
p=1, q=3



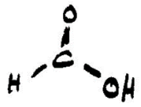
(H_6TeO_6)
p=6, q=0



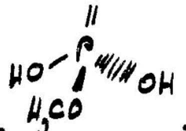
(HSO_3F)
p=1, q=2
Florosülfonik asit



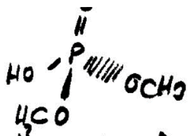
$(HSO_3(CF_3)]$
p=1, q=2
Triflorometansülfonik asit



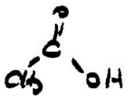
HCOOH
p=1, q=1



$[(OH)_2(OCH_3)PO]$
p=2, q=1



$[(OH)(OCH_3)_2PO]$
p=1, q=1



(CH_3COOH)
p=1, q=1

SUPER ACIDS

About 10^6 to 10^{10} times stronger acidic liquids than known as the strongest acids, such as HNO_3 and H_2SO_4, are called super acids. Super acids are absolutely anhydrous systems. It is necessary to define a scale other than the normal pH scale to measure the super-acidity. Hammett acidity function (H_o) is a scale developed based on experimental data for very strong acids.

$$\underset{\text{base}}{B} + H^+ \longrightarrow BH^+$$

$$BH^+ \rightleftharpoons B + H^+ \qquad K_{BH^+} = \frac{[B][H^+]}{[BH^+]}$$

$$[H^+] = K_{BH^+} \cdot \frac{[BH^+]}{[B]} \Rightarrow$$

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

Super acid: Protonated form of base (BH^+)

[BH+]/[B] ratio can be measured by spectrophotometrically.

$$\underset{\text{base}}{H_2SO_4} + \underset{\text{acid}}{H_2SO_4} \rightleftharpoons \underset{\text{Super acid}}{H_3SO_4^+} + HSO_4^-$$

$$H_3SO_4^+ \longrightarrow H^+ + H_2SO_4$$

$\downarrow$

strong proton donor

Many cationic species, which cannot be isolated by other methods and degraded even by weak bases, can be prepared in the presence of super acids.

$$(CH_3)_3COH \xrightarrow{\text{superacid}} (CH_3)_3C^+ + H_3O^+$$

$$I_2 \longrightarrow I_2^+ \text{ or } I_3^+$$

$$Se_8 \longrightarrow Se_4^{2+} \text{ or } Se_8^{2+}$$