

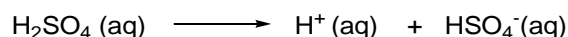
## Module 2 Acids and Bases

### Lecture 3 Acids and Bases

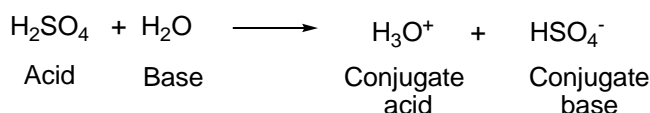
#### 2.1 Concepts

A compound is classified as an acid or a base based on certain properties. At present there are several theories which define the concepts of acidity and basicity. Some important concepts are detailed below.

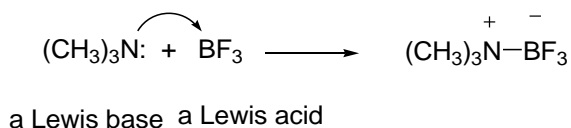
**Arrhenius concept of acids and bases:** The Arrhenius definition of acids says that they are compounds that give off  $H^+$  ions in water and that bases are compounds that give off  $OH^-$  ions in water. Thus, according to this theory only protic acids are allowed and only hydroxide bases are allowed to be classified as an acid or a base.



**Bronsted-Lowry definition:** The Bronsted-Lowry definition of acids is that acids are compounds that give off  $H^+$  ions when they react with another compound. Likewise, this definition says that bases are compounds that accept  $H^+$  ions from other compounds. Furthermore, it also brings a new concept of conjugate acids and conjugate bases. Since an acid after donating its proton is technically a base according to this definition and is referred to as a conjugate acid. So every acid has its conjugate base and vice versa. Also, the stronger is an acid, the weaker is its conjugate base and vice versa.

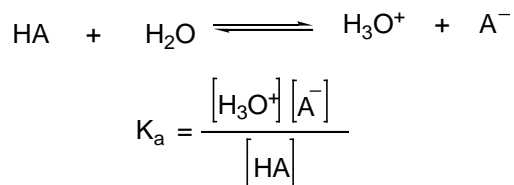


**Lewis concept of acids and bases:** Acids are electron pair acceptors while bases are electron pair donors. Thus, electron deficient species like  $BF_3$  are Lewis acids while electron rich species such as tertiary amines are Lewis bases. Lewis acids may combine with Lewis bases to generate a salt.



## 2.2 pH and pKa

The strength of an acid depends on its degree of dissociation in water and can be determined from the equilibrium expression (Scheme 1).



$$-\log K_a = -\log [\text{H}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

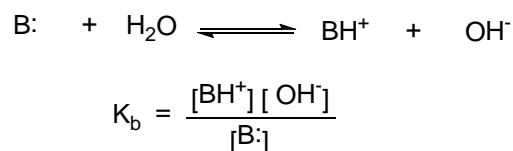
$$\text{or } \text{p}K_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\boxed{\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}}$$

Scheme 1

This equation is known as **Henderson-Hasselbach equation** and relates a relationship between the concentration of hydrogen ions in solutions and acid strength. Thus, pH is a measurement of the  $\text{H}^+$  concentration in a liquid. If there is a high  $\text{H}^+$  concentration, the pH indicates that it is a very acidic solution. If the solution is neutral, there is only a small  $\text{H}^+$  concentration, and the pH reflects that. If the solution is basic, there is almost no  $\text{H}^+$  concentration, and you can tell that by the pH number.

As with acids, a similar scale may be derived for bases based on the equilibrium of the protonated form of the base and base itself (Scheme 2).

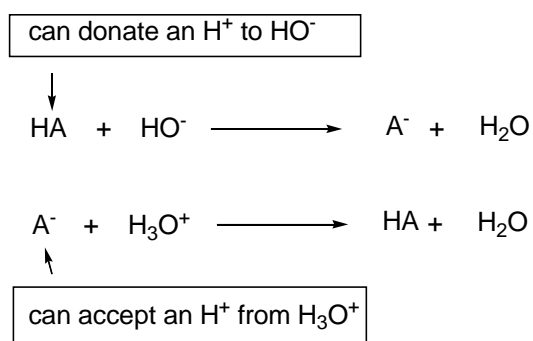


Scheme 2

However, such an expression creates two separate scales for the determination of strengths of acids and bases. Instead the strength of the conjugate acid is determined then a common scale in terms of  $pK_a$  may be used for both acids and bases. Thus, the lower the value of  $pK_a$ , stronger is the acid. Similarly, higher is the value of  $pK_a$  of base, more basic it is.

### 2.3 Buffer Solution

A solution of a weak acid and its conjugate base is referred as a buffer solution. A buffer solution has the ability to resist to a small change of pH, because the weak acid can donate a proton to any  $HO^-$  added to the solution, and its conjugate base can accept any  $H^+$ , which is added to the solution.

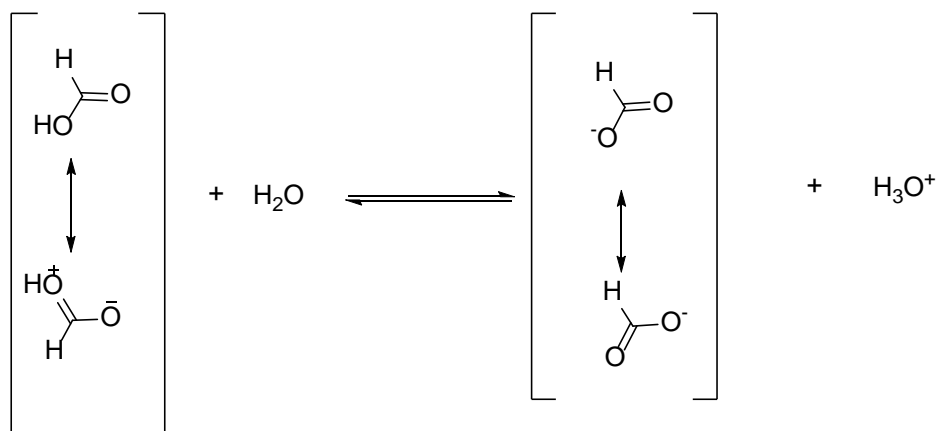


A common example of buffer is a solution of sodium acetate in acetic acid. Human blood is also a buffered solution and maintains a pH close to neutrality.

## 2.4 The Effect of Structure on $pK_a$

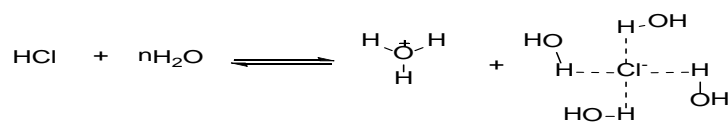
There are several factors which decide the relative strength of an acid (H-A). The strength of the H-A bond, the electronegativity of  $A^-$  and the factors stabilizing  $A^-$  with respect to HA are some of these factors. The first one is usually not much relevant but may be the cause of difference in acid strengths of  $CH_3OH$  (16) vs  $CH_4$  (43).

- The stabilization of the anion with respect to the undissociated molecule is however of quite importance. As an example, in case of formic acid, the anion generated is greatly stabilized due to effective delocalization of the charge into the two canonical structures of identical energy. Such delocalization is not possible in the formic acid itself without leading to separation of charges (Scheme 3).



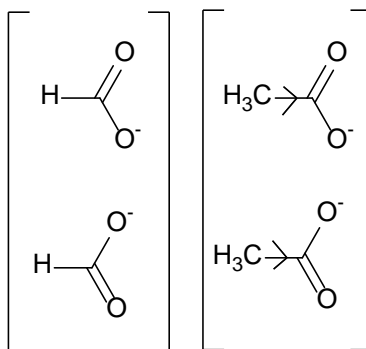
Scheme 3

- Similarly, the solvent plays an important role. The solvation of the species generated in the solvent could lead to an increase or decrease in acidity. As an acid or base is dissociated, more charges develop which may be better stabilized in solvent having a high dielectric constant and a greater degree of hydrogen bonding ability. Thus, HCl when dissolves in water is very strong acid as the ions it generates are suitably solvated by the water molecules but if the solvent is changed to toluene, there is hardly any dissociation (Scheme 4).

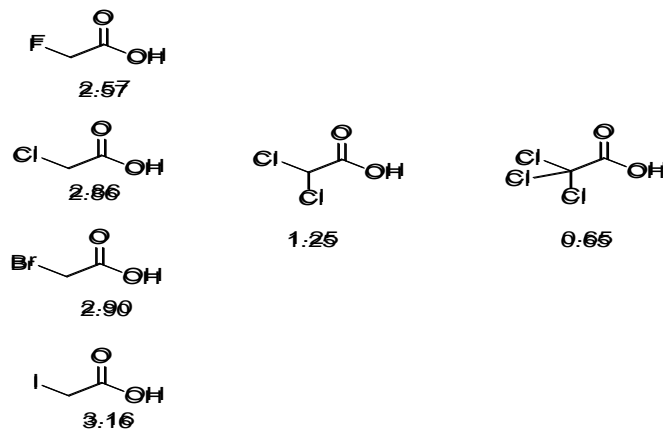


Scheme 4

- It is also expected that electron withdrawing and electron donating groups will have a profound effect on the acid strength of a substance. Thus, electron donating group substituted carboxylic acids are less acidic than those without them. In comparison of the acid strengths of methanoic and ethanoic acids, it is observed that the former has  $pK_a$  of 3.77 while for the later has only 4.84. The difference has been explained by the electron donating inductive effects of the methyl group of ethanoic acid. However, it is to be noted that the inductive effect falls off quickly with the increase in the chain length and other factors become dominant on going down the series.

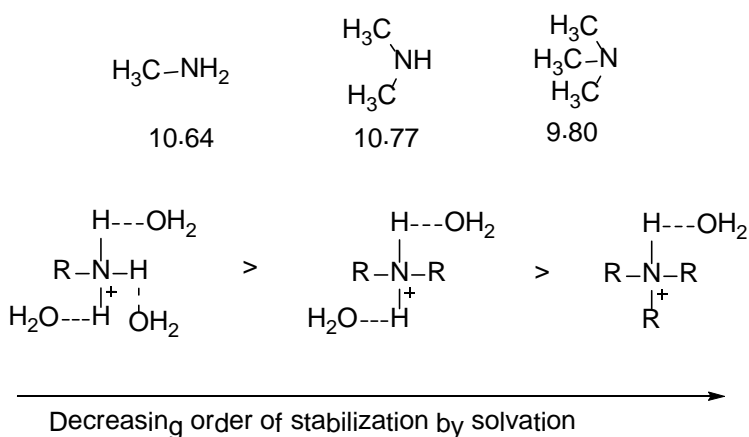


- Similarly, substitutions by electron withdrawing groups tend to increase the acidity of an acid. Thus, in the following series of halo acids it is observed that the  $pK_a$  decreases with increasing number of halogen atoms. Furthermore, it is also observed that among the monosubstituted halo acids the value of  $pK_a$  decreases with increase in electronegativity of the halogen. This indicates that the more is the electron withdrawing power of a group, the lower is the  $pK_a$  (Scheme 5).



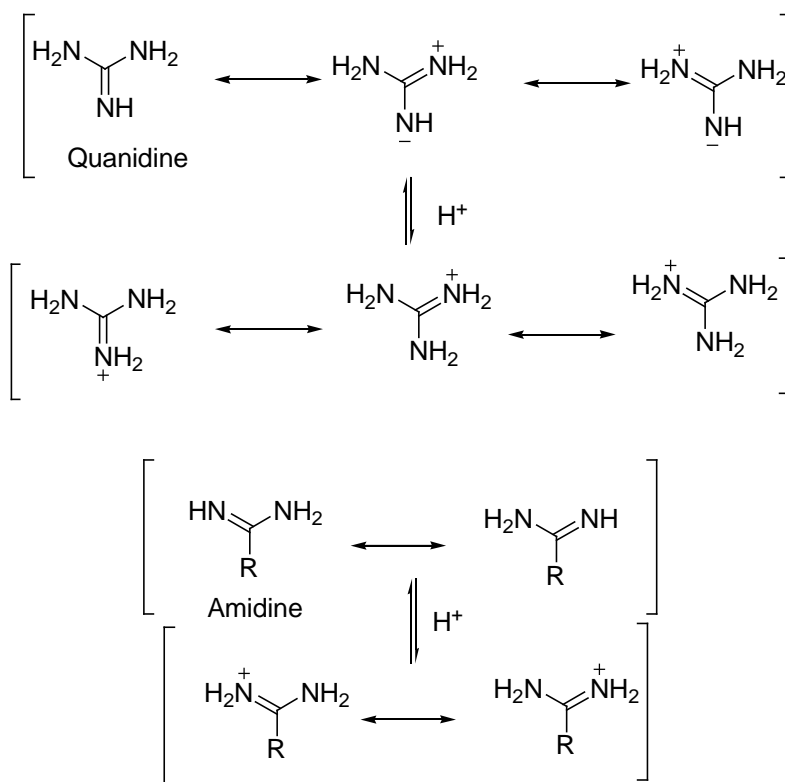
Scheme 5

- In case of aliphatic bases, it is thus expected that the increase in the number of alkyl groups will increase the basicity. Thus, basicity is supposed to increase on going from primary to secondary to tertiary amines. In fact, it is observed that in a solution of water, the basicity does increase on going from the primary amine to secondary amine but drops slightly on going to the tertiary amine. This drop is explained by considering the factor of stabilization of the conjugate acid by solvation. As the number of alkyl groups increase, there is a decrease in the number of hydrogen atoms capable of forming hydrogen bonds with water. This in turn has an adverse effect on the stabilization by solvation. If however, the basicities are measured in solvent where stabilization by solvation is insignificant, then the basicity does increase on going from secondary amine to tertiary amine (Scheme 6).



Scheme 6

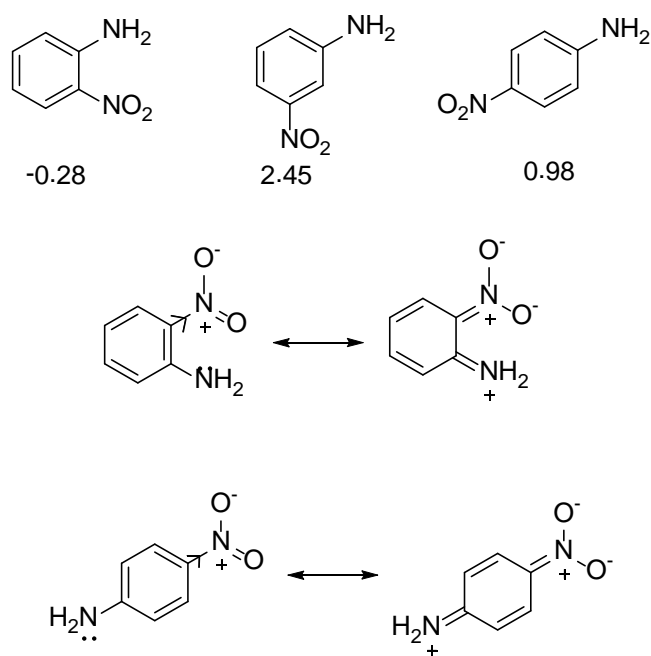
- There is also an effect of stabilization by delocalization in case of strength of bases (like the case of methanoic acid vs ethanoic acid). Thus, it is found that guanidine is much stronger base than amidine which in turn is stronger than urea. The high basic strength is explained by the formation of 3 identical canonical structures of similar energy for guanidinium ion. This results in lowering in energy of the molecule and gives stability to the species. A similar case occurs for amidinium ion where there are two such structures of identical energy. In case of urea, there are no such structures of identical energy and thus it is the least basic of the three (Scheme 7).



Scheme 7

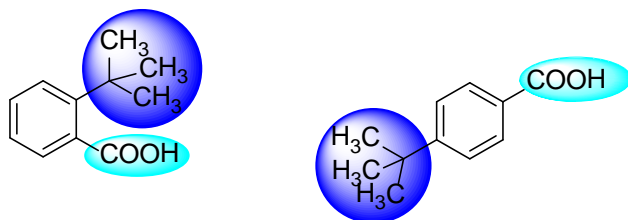


- Electron withdrawing and electron donating mesomeric effects also have influence on the strengths of acids and bases. In the series of *o*-, *m*-, *p*-nitroanilines it is observed that the *ortho* and *para* isomers have extremely high acidity as compared to the *meta* isomer. In fact the *o*-nitroaniline is a stronger acid than *p*-nitroaniline. This is explained in terms of electron withdrawing mesomeric effect which is operational only in the *ortho* and *para* isomers but not in the *meta* isomer. The extra base weakening effect, when the substituent is in *ortho* position in part due to the short distance over which its inductive effect is operating and also to the direct interaction between the nitro and amino group by hydrogen bonding (Scheme 8).



Scheme 8

- Steric considerations may also affect the strength of an acid or base. Such an instance is observed in case of *o*-*t*-butyl benzoic acid which is ten times stronger than its *para* isomer. This is totally unexpected since the electron donating inductive effect should be stronger in the *ortho* isomer compared to the *para* isomer. However, in this case, the carboxyl group is forced out of the plane of the ring by the bulky *t*-butyl group in *ortho* position.



- Steric effects can also be caused by other types of strain. 1,8-Bis(diethylamino)-2,7-dimethoxynaphthalene is an extremely strong base for a tertiary amine, but proton transfers to and from the nitrogen are exceptionally slow; slow enough to be followed by a UV spectrophotometer. This is because the compound is severely strained and the two nitrogen lone pairs are forced to be near each other. Protonation relieves the strain: one lone pair is now connected to hydrogen, which forms a hydrogen bond to the other lone pair.

