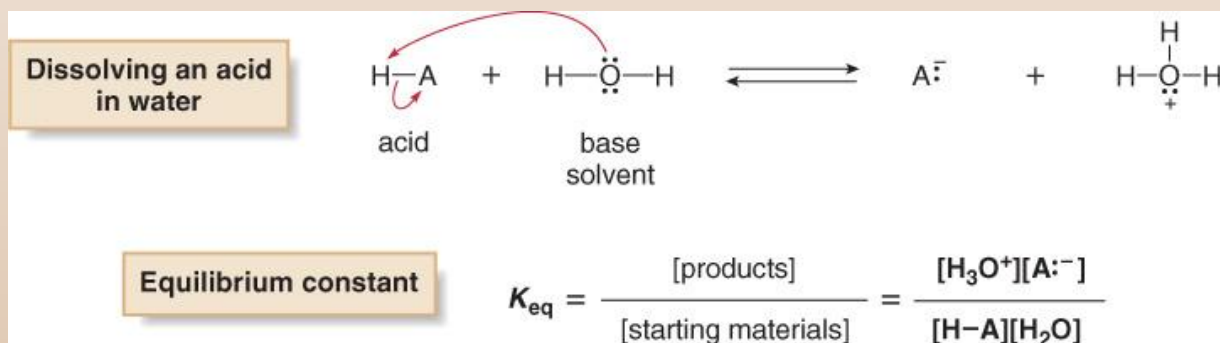


Acids and Bases – 2 - Strength

Dr. Sapna Gupta

Acid Strength and pKa

- Acid strength is the tendency of an acid to donate a proton.
- The more readily a compound donates a proton, the stronger an acid it is.
- Acidity is measured by an equilibrium constant.
- When a Brønsted-Lowry acid H—A is dissolved in water, an acid-base reaction occurs, and an equilibrium constant can be written for the reaction.



$$\text{Acidity constant} = K_a = [\text{H}_2\text{O}]K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H-A}]}$$

- It is more convenient to use “pK_a” values than K_a values.

Definition: pK_a = -log K_a

pKa Table

| | Acid | Approximate pK _a | Conjugate Base | |
|----------------|---|-----------------------------|--|----------------|
| Strongest acid | HSbF ₆ | < -12 | SbF ₆ ⁻ | Weakest base |
| | HI | -10 | I ⁻ | |
| | H ₂ SO ₄ | -9 | HSO ₄ ⁻ | |
| | HBr | -9 | Br ⁻ | |
| | HCl | -7 | Cl ⁻ | |
| | C ₆ H ₅ SO ₃ H | -6.5 | C ₆ H ₅ SO ₃ ⁻ | |
| | (CH ₃) ₂ OH ⁺ | -3.8 | (CH ₃) ₂ O | |
| | (CH ₃) ₂ C=OH ⁺ | -2.9 | (CH ₃) ₂ C=O | |
| | CH ₃ OH ₂ ⁺ | -2.5 | CH ₃ OH | |
| | H ₃ O ⁺ | -1.74 | H ₂ O | |
| | HNO ₃ | -1.4 | NO ₃ ⁻ | |
| | CF ₃ CO ₂ H | 0.18 | CF ₃ CO ₂ ⁻ | |
| | HF | 3.2 | F ⁻ | |
| | CH ₃ CO ₂ H | 4.75 | CH ₃ CO ₂ ⁻ | |
| | H ₂ CO ₃ | 6.35 | HCO ₃ ⁻ | |
| | CH ₃ COCH ₂ COCH ₃ | 9.0 | CH ₃ COCH ⁻ COCH ₃ | |
| | NH ₄ ⁺ | 9.2 | NH ₃ | |
| | C ₆ H ₅ OH | 9.9 | C ₆ H ₅ O ⁻ | |
| | HCO ₃ ⁻ | 10.2 | CO ₃ ²⁻ | |
| | CH ₃ NH ₃ ⁺ | 10.6 | CH ₃ NH ₂ | |
| | H ₂ O | 15.7 | OH ⁻ | |
| | CH ₃ CH ₂ OH | 16 | CH ₃ CH ₂ O ⁻ | |
| | (CH ₃) ₃ COH | 18 | (CH ₃) ₃ CO ⁻ | |
| | CH ₃ COCH ₃ | 19.2 | ⁻ CH ₂ COCH ₃ | |
| | HC≡CH | 25 | HC≡C ⁻ | |
| | H ₂ | 35 | H ⁻ | |
| | NH ₃ | 38 | NH ₂ ⁻ | |
| | CH ₂ =CH ₂ | 44 | CH ₂ =CH ⁻ | |
| Weakest acid | CH ₃ CH ₃ | 50 | CH ₃ CH ₂ ⁻ | Strongest base |

Increasing acid strength

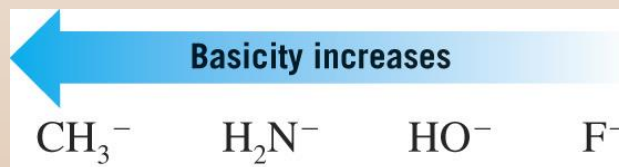
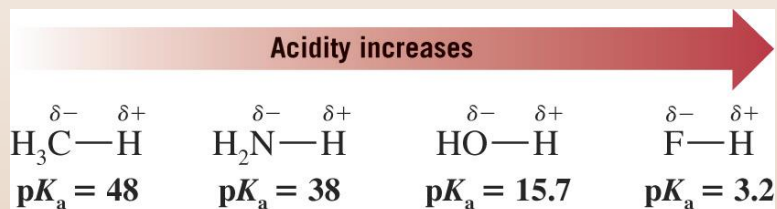
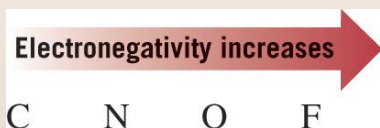
Increasing base strength

Factors Determining Acid Strength



1. Electronegativity: Across the row, e.g. H_2O vs CH_4 (the more electronegative the element the more acidic it is)
2. Size of the anion: down the group, e.g. HF , HCl , HBr , HI (the larger the anion the more stable it is)
3. Number of oxygen, e.g. HNO_2 vs HNO_3 (more oxygen cause more electronegativity hence easier for H to leave)
4. Inductive effects, e.g. CH_3COOH vs CH_2ClCOOH
5. Resonance stabilization of conjugate base, e.g. CH_3COOH vs CH_3OH
6. Acidity of hydrocarbons due to delocalization of e^- in conjugate base, e.g. $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{CH}_2$, CH_3CH_3
7. Solvent effect: more polar solvents will support more bronstead-lowry type acids because of ions formed during reactions.

1) Electronegativity in the Row

Within a row, the greater the electronegativity of the atom bearing the negative charge stabilizes the anion and the acid is stronger.

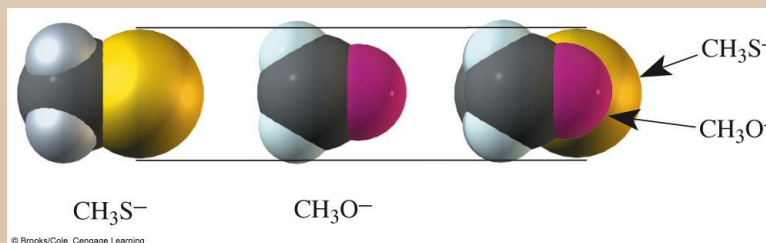
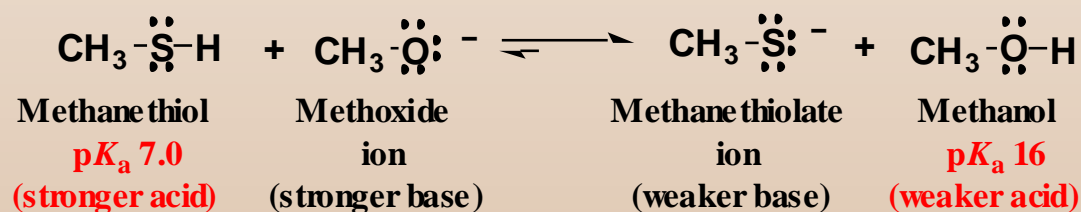


| Acid | Conjugate base |
|---|--|
| Methanol $\text{p}K_a$ 16 $\text{CH}_3-\ddot{\text{O}}-\text{H}$ | $\text{CH}_3-\ddot{\text{O}}:^-$ Methoxide ion |
| Methylamine $\text{p}K_a$ 38 $\text{CH}_3-\ddot{\text{N}}-\text{H}$ | $\text{CH}_3-\ddot{\text{N}}:^-$ Methylamide ion |
| Ethane $\text{p}K_a$ 51 $\text{CH}_3-\text{C}-\text{H}$ | CH_3-C^- Ethyl anion |

 increasing acidity
 increasing basicity

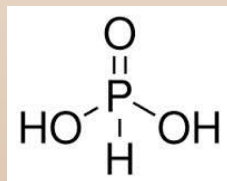
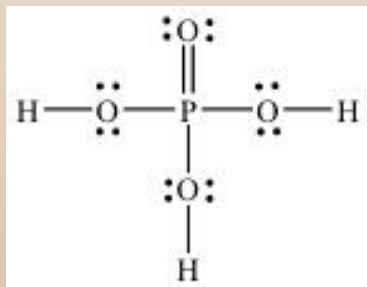
2) Size of Anion

- Within a column of the Periodic Table, acidity is related to the size of the the atom bearing the negative charge.
- Atomic size increases from top to bottom of a column.
- The larger the atom bearing the charge, the greater its stability.



3) Number of Oxygen Atoms and Electronegativity

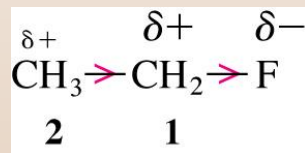
- In all Bronsted acids the proton that dissociates is bonded to oxygen.
- Compare the Lewis structures of phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4). Phosphoric acid is triprotic and all three protons are bonded to oxygen whereas phosphorous is diprotic as it has only 2 protons bonded to oxygen, the third one, bonded to P, does not ionize. The bond between oxygen and hydrogen is more polar than between hydrogen and phosphorous due to electronegativity difference.



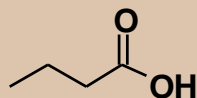
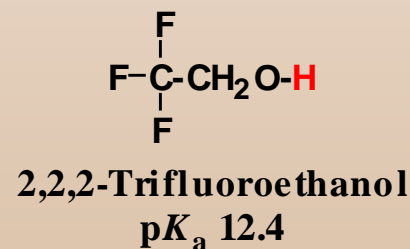
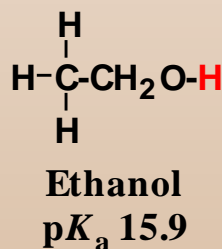
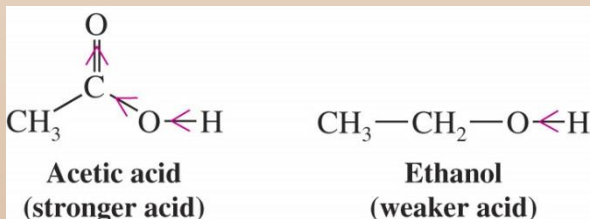
- For mineral acids more oxygen atoms means they are the more acidic e.g. $\text{HNO}_3 > \text{HNO}_2$ and $\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$
- For organic acids $\text{CH}_3\text{COOH} > \text{CH}_3\text{OH}$

4) Inductive Effect

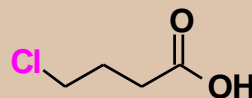
- Electronic effects that are transmitted through space and through the bonds of a molecule due to the electronegativity of an adjacent covalent bond.
- Stabilization by the inductive effect falls off rapidly with increasing distance of the electronegative atom from the site of negative charge in the conjugate base.



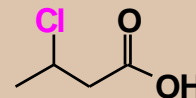
- We also see the operation of the inductive effect in the acidity of alcohols and acids and also the halogen substituted alcohols and carboxylic acids.



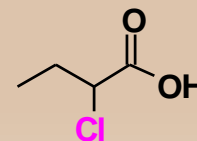
Butanoic acid
 $\text{p}K_a$ 4.82



4-Chlorobutanoic acid
 $\text{p}K_a$ 4.52



3-Chlorobutanoic acid
 $\text{p}K_a$ 3.98

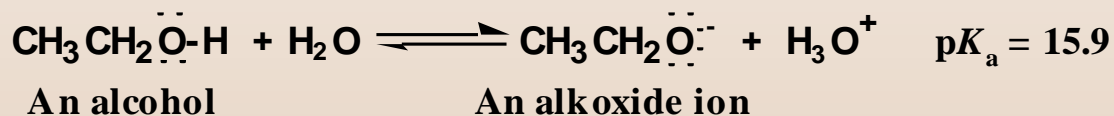


2-Chlorobutanoic acid
 $\text{p}K_a$ 2.83

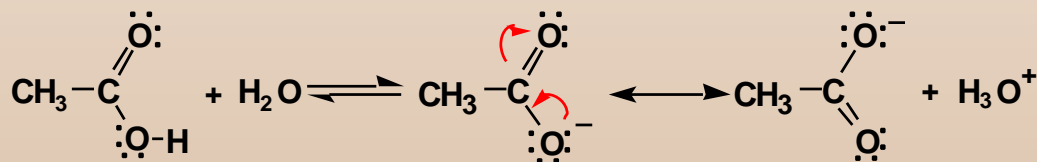
5) Resonance

Resonance delocalization of charge in A⁻. The more stable the anion, the more the position of equilibrium is shifted to the right.

- Compare the acidity alcohols and carboxylic acids.
- Ionization of the O-H bond of an alcohol gives an anion for which there is no resonance stabilization.



- Ionization of a carboxylic acid gives a resonance-stabilized anion.
- The pK_a of acetic acid is 4.76



equivalent contributing structures;
the carboxylate anion is stabilized by
delocalization of the negative charge.

- Carboxylic acids are stronger acids than alcohols as a result of the resonance stabilization of the carboxylate anion.

6) Hybridization

- For anions differing only in the hybridization of the charged atom, the greater the % s character to the hybrid orbital of the charged atom, the more stable the anion, therefore more acidic.
- Consider the acidity of alkanes, alkenes, and alkynes (given for comparison are the acidities of water and ammonia).

More acidic $\text{HC}\equiv\text{CH} > \text{H}_2\text{C}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}_3$

More basic $\text{H}_3\text{C}-\text{CH}_2:^- > \text{H}_2\text{C}=\text{CH}:^- > \text{HC}\equiv\text{C}:^-$

| Weak Acid | | Conjugate Base | $\text{p}K_{\text{a}}$ |
|-----------|------------------------------------|-----------------------------|------------------------|
| Water | $\text{HO}-\text{H}$ | HO^- | 15.7 |
| Alkyne | $\text{HC}\equiv\text{C}-\text{H}$ | $\text{HC}\equiv\text{C}^-$ | 25 |
| Ammonia | $\text{H}_2\text{N}-\text{H}$ | H_2N^- | 38 |
| Alkene | $\text{CH}_2=\text{CH}-\text{H}$ | $\text{CH}_2=\text{CH}^-$ | 44 |
| Alkane | $\text{CH}_3\text{CH}_2-\text{H}$ | CH_3CH_2^- | 51 |

↑ Increasing acidity



7) Effect of Solvent

- Acidity values in gas phase are generally very low
- It is difficult to separate the product ions without solvent molecules to stabilize them
- Acetic acid has pKa of 130 in the gas phase
- A protic solvent is one in which hydrogen is attached to a highly electronegative atom such as oxygen or nitrogen e.g. water
- Solvation of both acetic acid and acetate ion occurs in water although the acetate is more stabilized by this solvation

Strength of Bases

- Bases are opposite of acids in strength; a strong acid will give a weak conjugate base and a weak acid gives a strong conjugate base.
- E.g. HCl is a strong acid so Cl^- is a weak conjugate base; methanol (CH_3OH) is a weak acid so methoxide (CH_3O^-) is a strong conjugate base.

| Acid | Conjugate base |
|---|--|
| Methanol pK_a 16 $\text{CH}_3-\ddot{\text{O}}-\text{H}$ | $\text{CH}_3-\ddot{\text{O}}:^-$ Methoxide ion |
| Methylamine pK_a 38 $\text{CH}_3-\ddot{\text{N}}-\text{H}$ H | $\text{CH}_3-\ddot{\text{N}}:^-$ Methylamide ion H |
| Ethane pK_a 51 $\text{CH}_3-\text{C}-\text{H}$ H | $\text{CH}_3-\text{C}:^-$ Ethyl anion H |



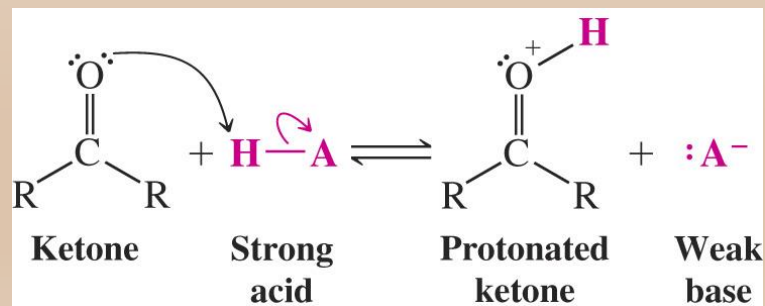
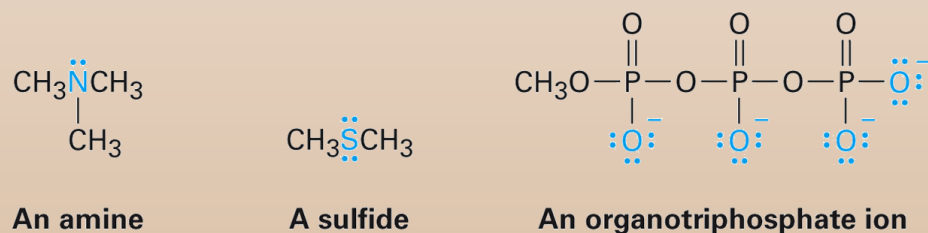
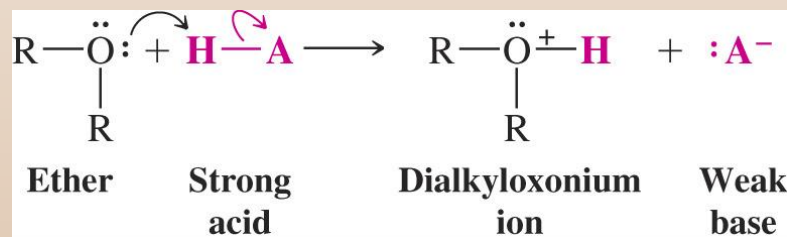
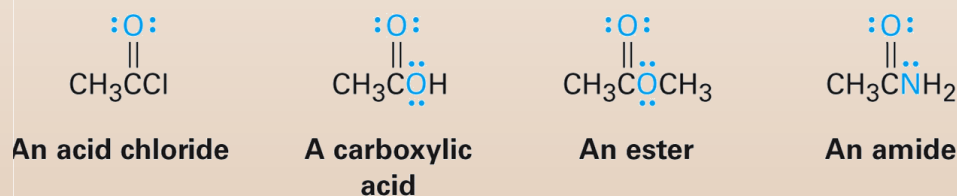
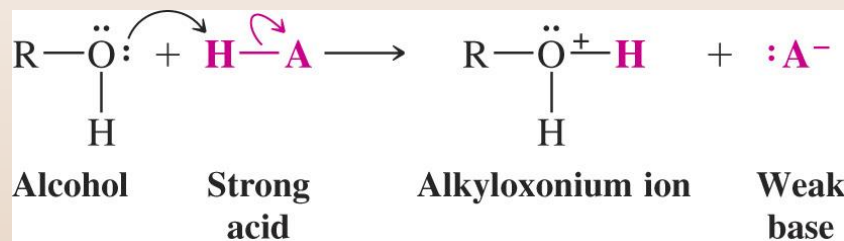
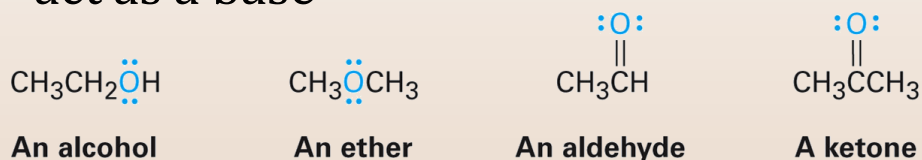
- It is best to remember acidity rules to remember bases also.

Lewis Acids and Bases

- Lewis acid: A molecule/ion that can accept a pair of electrons.
- Lewis base: A molecule/ion that can donate a pair of electrons.
- There is no pKa scale for these acids and bases. Their effectiveness is determined by how well they donate or accept electrons.
- Examples of Lewis Acids
 - Group 3A elements, such as BF_3 and AlCl_3 , are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases
 - Transition-metal compounds, such as TiCl_4 , FeCl_3 , ZnCl_2 , and SnCl_4 , are Lewis acids
 - In case of organic compounds, any carbocation (carbon with a positive charge) would be a Lewis acid.

Organic Compounds as Lewis Bases

- Any organic compound containing an atom with a lone pair (O,N) can act as a base



Solved Problems

Which of the following is a Lewis base?

- a) BCl_3
- b) Cu^{2+}
- c) SH^-**
- d) Mn^{2+}
- e) NH_4^+

Iodine trichloride, ICl_3 , will react with a chloride ion to form ICl_4^- . Which species, in this reaction, is the Lewis base?

- a) ICl_4^-
- b) ICl_3
- c) Cl^-**
- d) the solvent

Which one of the following is a Lewis acid but not a Brønsted-Lowry acid?

- a) Fe^{3+}**
- b) H_3O^+
- c) HSO_4^-
- d) NH_3

Which of these species will act as a Lewis acid?

- a) NH_3
- b) NH_4^+
- c) H_2O
- d) BF_3**
- e) F^-

Key Words/Concepts

- Why acid base reactions take place
- Factors determining acid strength
- Factors determining base strength
- Lewis acids and bases