Acids and Bases
2 – Strength of Acids and Bases

Dr. Sapna Gupta

Acid Strength and pKa

Strength of an acid is the ease of an acid to donate a proton. The more readily a compound donates a proton, the stronger the acid. Acidity can be measured by pH or pK_a. pH can be used for both strong and weak acids, however it is easier to use pK_a for the weak acids.

- **pH**: Is the negative log of hydronium ion concentration. This works well for strong acids where there is complete dissociation of the proton.

$$\boxed{pH = -\log[H_3O^+]}$$

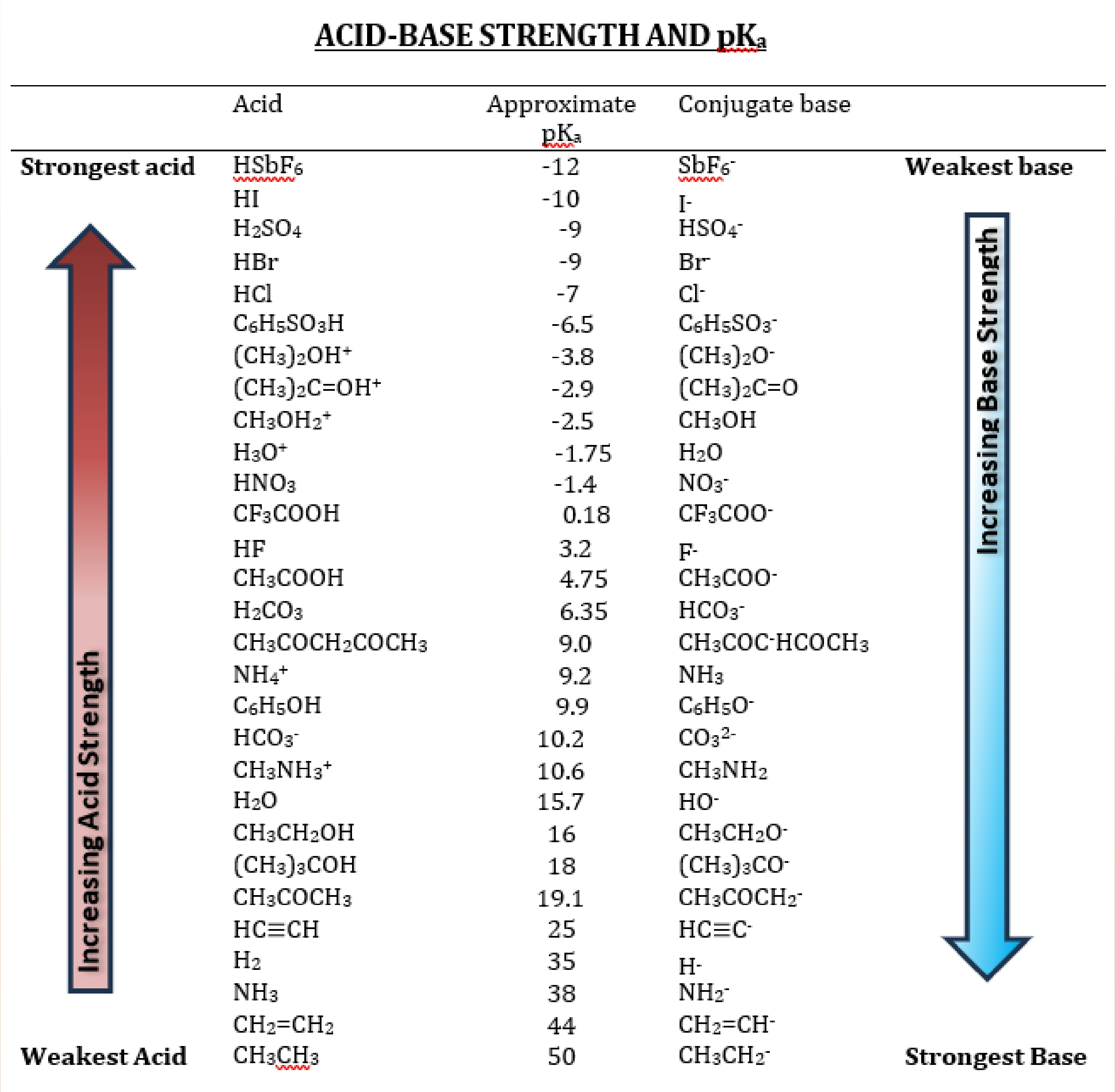
- **pK_a**: In case of weak acids there an equilibrium where equilibrium constant (K_a) is calculated. It is more convenient to use "pK_a" values (negative log of K_a) than K_a to determine strength of acids/bases.
- An equation for Brønsted-Lowry acid H—A dissolved in water can be written as shown below.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad \boxed{pK_a = -\log K_a}$$

pKa Table

- This table gives pK_a values of common mineral and organic acids.
- Most mineral acids are stronger than organic acids due to complete dissociation of H^+ ion.
- The right column is the conjugate base formed, whose strength increases as the acid strength decreases.



ACID-BASE STRENGTH AND pK_a

	Acid	Approximate pK_a	Conjugate base	
Strongest acid	$HSbF_6$	-12	SbF_6^-	**Weakest base**
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2OH^+$	-3.8	$(CH_3)_2O^-$	
	$(CH_3)_2C{=}OH^+$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3OH_2^+$	-2.5	CH_3OH	
	H_3O^+	-1.75	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3COOH	0.18	CF_3COO^-	
	HF	3.2	F^-	
	CH_3COOH	4.75	CH_3COO^-	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3COC^-HCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	$C_6H_5O^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	HO^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.1	$CH_3COCH_2^-$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest Acid	CH_3CH_3	50	$CH_3CH_2^-$	**Strongest Base**

Factors Determining Acid Strength

One cannot have pKa tables available all the time, hence there has to be some criteria that we can use to determine the strength of acids and bases. We will cover acids in detail because as we have learned, once you know the strength of acid, the conjugate base strength is just the opposite. Below are all the criteria will learn about acid strength.

1. Size of the anion: Size of anion increases down the group, e.g. HF, HCl, HBr, HI. (*The larger the anion the more stable it is*).
2. Electronegativity: Electronegativity of the atom attached to the acidic proton, e.g. H_2O vs CH_4 (*The more electronegative the element the more acidic it is*).
3. Number of oxygen: The number of oxygen in oxoacids, e.g. HNO_2 vs HNO_3. (*More oxygens cause more electronegativity hence its easier for acidic H to leave*).
4. Inductive effects: The pull or push of electrons over bonds. e.g. CH_3COOH vs $CH_2ClCOOH$. (*Pull of electrons away from acidic protons makes it easy to dissociate*).
5. Resonance: Causes stabilization of conjugate base, e.g. CH_3COOH vs CH_3OH.
6. Hybridization: Acidity of hydrocarbons due to delocalization of e^- in conjugate base, e.g.$CH\equiv CH$, $CH_2=CH_2$, CH_3CH_3 (*sp has more delocalization than sp^2 than sp^3*).

1) Size of Anion

Within a column of the Periodic Table, acidity is related to the size of 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.

	CH_3SH	CH_3OH
pKa	7.0	16
Conjugate base	CH_3S^-	CH_3O^-

After dissociation, the CH_3S^- ion is more stable than CH_3O^- due to the large size of sulfur ion, hence the proton will stay dissociated, causing CH_3SH to be stronger acid than CH_3OH.

2) Electronegativity in the Row

Electronegativity increases to the right of periodic table. Within a row, the greater the electronegativity of the atom bearing the negative charge stabilizes the anion and the acid is stronger. Below are examples of some similar compounds with atoms of increasing electronegativity.

Acidity Increasing →

Acid	δ^- δ^+ $\mathbf{H_3C\text{-}H}$	δ^- δ^+ $\mathbf{H_2N\text{-}H}$	δ^- δ^+ **HO-H**	δ^- δ^+ **F-H**
pK_a	48	38	15.7	3.2
Conjugate base	H_3C^-	H_2N^-	HO^-	F^-

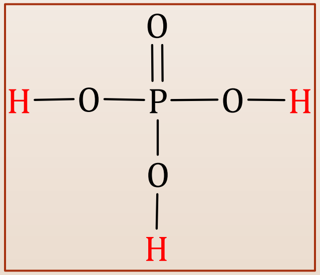
Acidity Increasing →

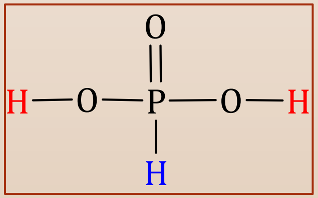
Acid	δ^- δ^+ $\mathbf{H_3CH_2\text{-}H}$	δ^- δ^+ $\mathbf{CH_3NH\text{-}H}$	δ^- δ^+ $\mathbf{CH_3O\text{-}H}$
pK_a	51	38	16
Conjugate base	$H_3CH_2^-$	CH_3NH^-	CH_3O^-

3) Number of Oxygen Atoms and Electronegativity

In all Bronsted acids the dissociating proton is bonded to oxygen.

- Compare the Lewis structures of phosphoric acid (H_3PO_4) and phosphorous acid (H_3PO_3). 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.



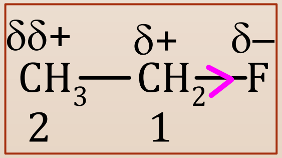


- In general, for mineral acids more oxygen atoms means higher acidity e.g., $HNO_3 > HNO_2$ and $H_2SO_4 > H_2SO_3$. The reason is as above for phosphoric and phosphorous acid. Lewis structures will show how all the protons are bonded.
- For organic acids $CH_3COOH > CH_3OH$.

4) Inductive Effect

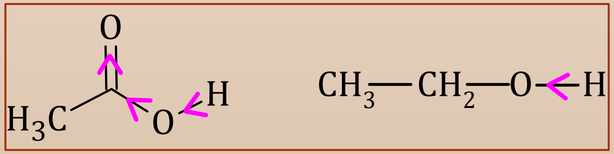
Inductive effect is an electronic effect that is transmitted through space and through the covalent bonds of a molecule due to the electronegativity or high electron density of an adjacent covalent bond.

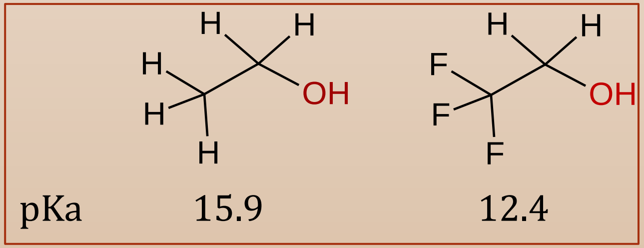
- Inductive effect decreases with increasing distance of the electronegative atom from the site of negative charge in the conjugate base e.g., in the structure below, carbon 1 feels more electronic effect than carbon 2. (*δ means small, δ δ means very very small*).

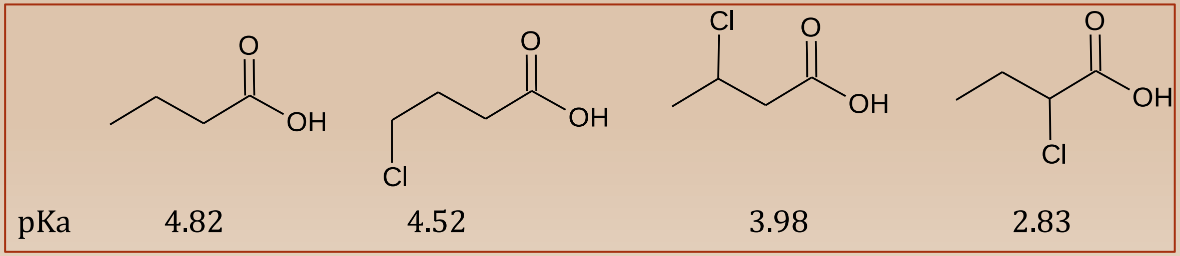


$$\overset{\delta\delta+}{\underset{2}{CH_3}}-\overset{\delta+}{\underset{1}{CH_2}}\rightarrow\overset{\delta-}{F}$$

- Similar inductive effect can be seen in the acidity of alcohols and acids and in the halogen substituted alcohols and carboxylic acids.







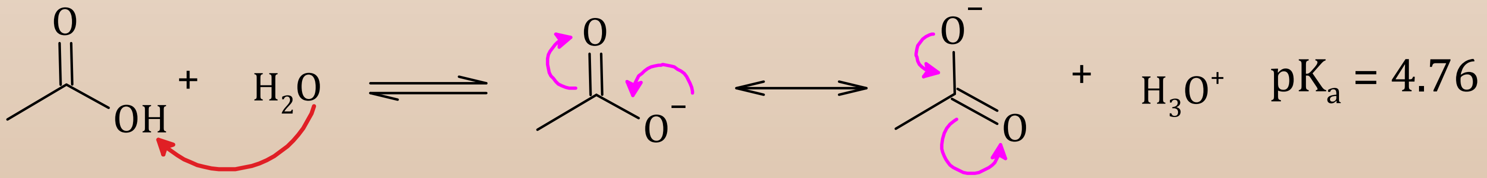
5) Resonance

Resonance causes delocalization of charge in the anion conjugate base, A^-. The more stable the anion, the more the position of equilibrium is shifted to the right.

- In comparing 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.

$$CH_3CH_2O\text{-}H + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+ \qquad pK_a = 15.9$$

- Ionization of a carboxylic acid gives a resonance-stabilized anion.



$pK_a = 4.76$

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

6) Hybridization

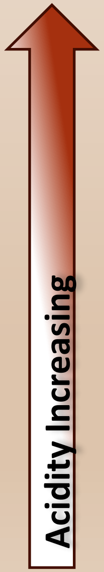
In anions differing only in the hybridization of the charged atom, the greater the % s character to the hybrid orbital of the charged atom, the more stable the anion, therefore more acidic ($sp > sp^2 > sp^3$). There is more delocalization of the negative charge over the pi electrons.

More acidic $HC{\equiv}CH > H_2C{=}CH_2 > H_3C{-}CH_3$

More basic $H_3C{-}CH_2{:}^- > H_2C{=}CH{:}^- > HC{\equiv}C{:}^-$

- Consider the acidity of alkanes, alkenes, and alkynes (given for comparison are the acidities of water and ammonia).

Weak Acid		Conjugate base	pK_a
Water	HO – **H**	HO^-	15.7
Alkyne	HC ≡ C-**H**	$HC \equiv C^-$	25
Ammonia	H_2N-**H**	H_2N^-	38
Alkene	CH_2=CH-**H**	$CH_2=CH^-$	44
Alkane	CH_3CH_2-**H**	$CH_3CH_2^-$	51



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.

- Methanol (CH_3OH), is a weak acid so methoxide (CH_3O^-) is a strong conjugate base; alkane is a weaker acid (than methanol) and its conjugate base is even stronger than methoxide.

Acidity Increasing →

Acid	$\delta^- \delta^+$ **H_3CH_2-H**	$\delta^- \delta^+$ **CH_3NH-H**	$\delta^- \delta^+$ **CH_3O-H**
pK_a	51	38	16
Conjugate base	$H_3CH_2^-$	CH_3NH^-	CH_3O^-

← **Basicity Increasing**

- It is best to remember acidity rules and then you will know that bases are opposite to acids in strength.

Solved Problem: Strength of Acid-Base

Determine the stronger acid or base in the following pairs of compounds. Give a brief reason for your choice.

		ANSWER
a)	CH_3OH or CH_3COOH	*CH_3COOH is stronger because it has more oxygens.*
b)	$CH_3CH_2CH_3$ or $HC\equiv CCH_3$	*Alkyne is stronger acid because it is sp hybridized.*
c)	$^{-}C\equiv CCH_3$ or $CH_3CH_2CH_2^{-}$	*The conjugate base of alkane is stronger base because it is the conjugate base of a weaker acid.*
d)	CH_3O^{-} or $CH_3CH_2O^{-}$	*CH_3CH_2O is stronger base because it has more electron density from the carbons.*
e)	NH_3 or CH_3NH_2	*CH_3NH_2 is stronger base because it has more electron density from the carbons.*
f)	$CH_3CH_2ClCOOH$ or CH_2ClCH_2COOH	*$CH_3CH_2ClCOOH$ is stronger acid because of inductive of Cl closer to the acidic proton.*

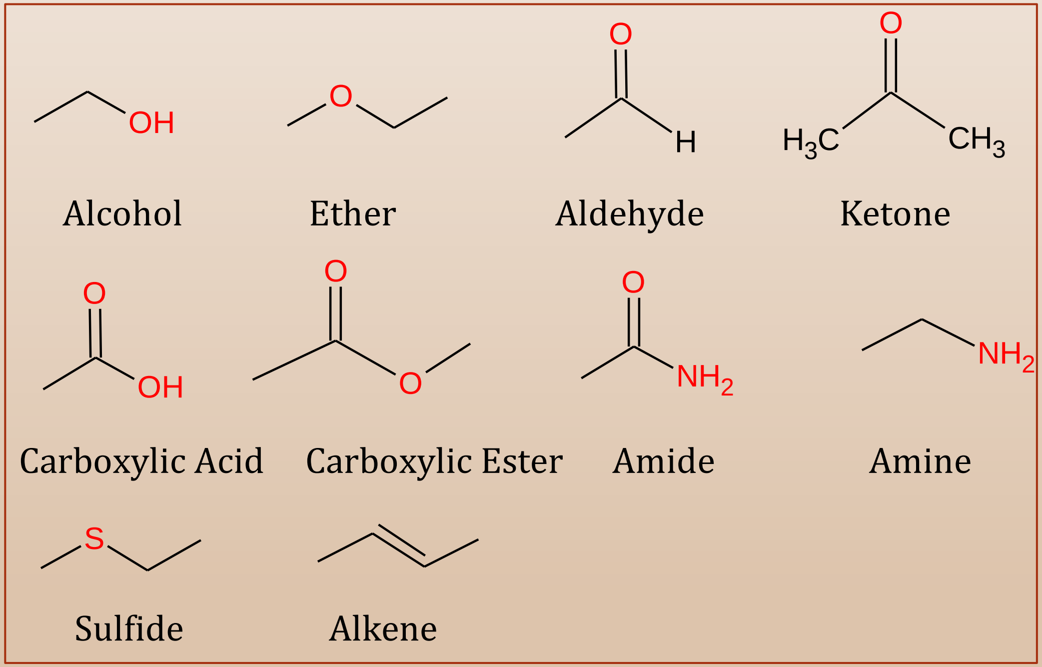
Lewis Acids and Bases

- 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.

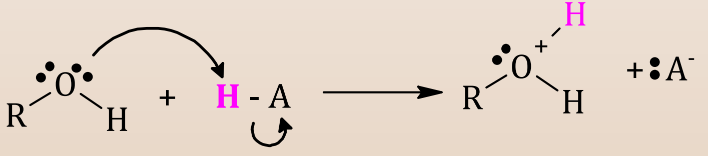
- **Examples of Lewis Acids**
  - Group 3A elements, such as BF_3 and $AlCl_3$, are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases
  - Transition-metal compounds, such as $TiCl_4$, $FeCl_3$, $ZnCl_2$, and $SnCl_4$, are Lewis acids
  - In case of organic compounds, any carbocation (carbon with a positive charge) would be a Lewis acid.

Organic Compounds as Lewis Bases

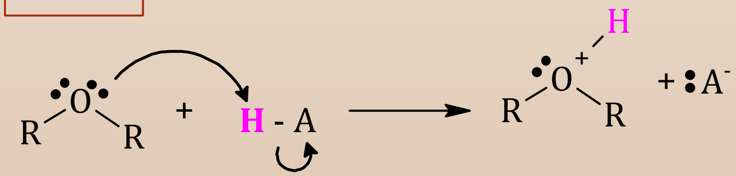
- Any organic compound containing an atom with a lone pair (O,N) can be a Lewis base.
- A double bond is also a Lewis base.



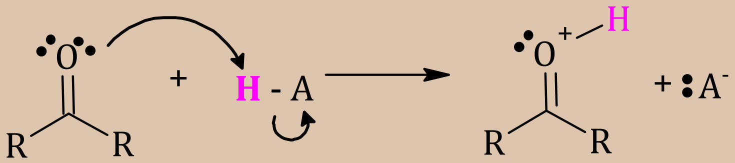
Alcohol



Ether

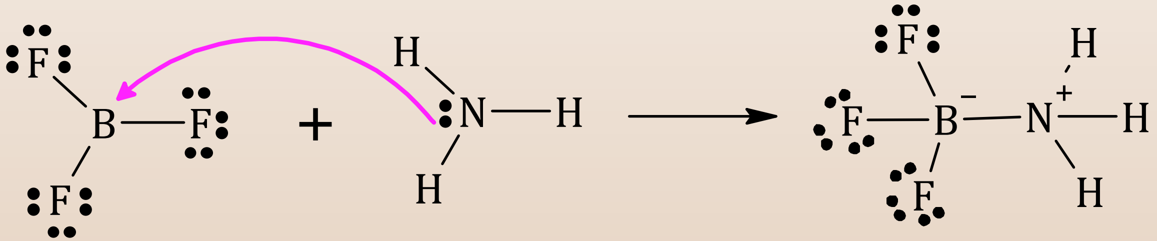


Ketone



Lewis Acid Base Reaction

- Start the arrow from where the electrons are on the Lewis base and end it at the atom that is lacking the electrons on the Lewis acid.



Lewis Acid Lewis Base

- You will not form water in LA and LB reactions as there is no proton and hydroxide ions.

Solved Problems: Lewis Acid/Base

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, is the Lewis base this reaction?

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