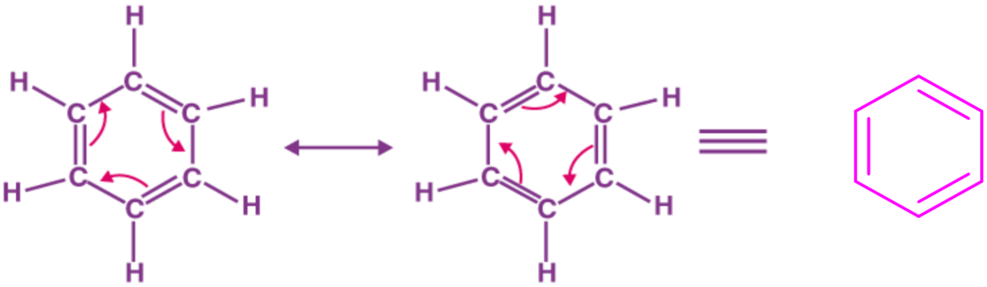
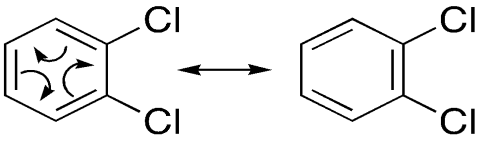
RECALL:

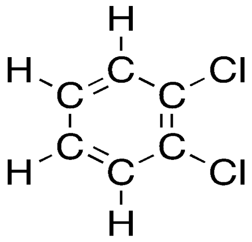
More examples of resonance structures

e.g. **1. Benzene**



2. 1, 2-dichlorobenzene

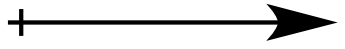




Intermolecular Forces (forces present between molecules):

There are three attractive intermolecular forces

- i) Hydrogen bonding
  - Donors: H on O, N, or halogen
  - Acceptors: Lone pair on O, N, or halogen
- ii) Dipole-dipole interaction



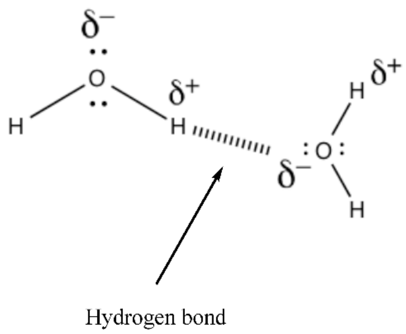
δ^+ δ^-

- iii) London forces (temporary dipole; hydrophobic bonding)

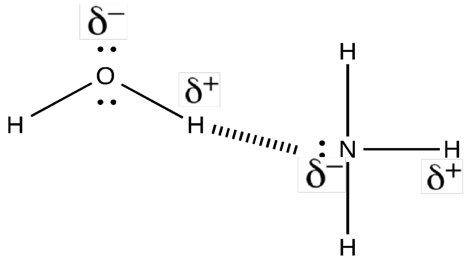
Hydrogen Bonding:

- Strongest intermolecular attractive force
- Need H directly attached to a very electronegative atom (N, O, F, Cl, Br, I)
  - Known as **donors**
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
  - Known as **acceptors**

e.g. **1. H-O-H (water)**

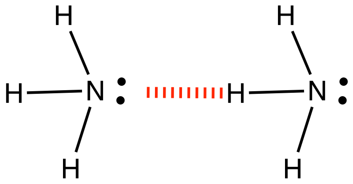


- Oxygen is electronegative and it is sp^3 hybridized
- The partial positive charge on H and the partial negative charge on O lead to their attraction
- Results in high boiling point (100 C) and high melting point by self-association
- HF, H_2O and NH_3 form hydrogen bonds

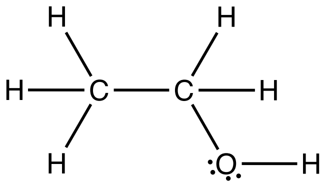


- Water is a liquid at RT while ammonia is a gas
- Oxygen is more e-neg than nitrogen, so the protons on water have a higher positive partial charge than the protons on ammonia
- In an ammonia solution, water would be the hydrogen bond donor and ammonia would be the acceptor
- Water dissolves ammonia very well – up to 18M

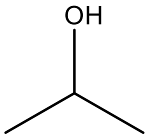
2. Ammonia
- both H-bond acceptor and donor
- H-bond is weaker than the H-bond of water because N is less electronegative than O
- BP: -36 °C



3. Ethanol
- both H-bond acceptor and donor
-BP: 78.5 °C

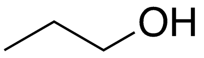


4. Isopropyl alcohol



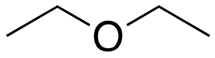
Isopropyl alcohol

- both H-bond acceptor and donor



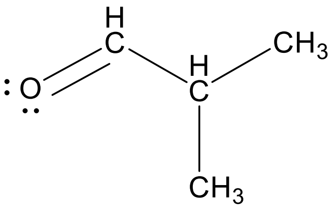
n-Propanol
(1-Propanol)

- Can hydrogen bond to itself
  - Has H directly attached to oxygen
- Has a high boiling points relative to its size due to hydrogen bonding
- Can dissolve in water very well



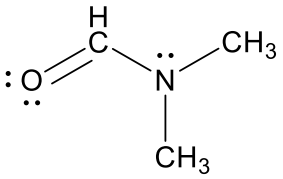
Diethyl Ether

- Cannot hydrogen bond to itself
  - Has no H directly attached to oxygen (No donor)
  - Can H-bond to water because it has an acceptor
- Has a low boiling point
  - Will not dissolve in water very well(not miscible with water) (although a little bit will be dissolved)



Isobutyraldehyde

vs



Dimethylformamide

Can't form H-bonds with itself (not a H-bond donor)
Lone pairs on O can form H-bonds with water (H-bond acceptor)
Poorly soluble in water

Can't form H-bonds with itself (not a H-bond donor)
Lone pairs on O and N can form H-bonds with water (H-bond acceptor)
Infinitely soluble (miscible) in water

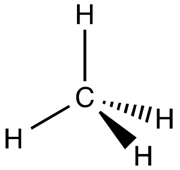
Note: The more H-bonds it can form, the more soluble it is in water

Dipole-Dipole Interactions:

Dipole drawing convention:

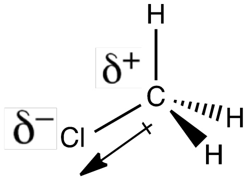
Partial positive charge is the “plus” end, partial negative charge is the arrow head

1. Methane; CH_4



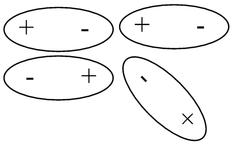
- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole); gas at room temperature
- Low BP -164 °C (this is relatively low compared to water at 100 °C)
- Low MP -182 °C

2. Chloromethane, methyl chloride; CH_3Cl

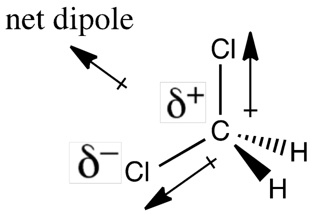


- H and C have similar electronegativity values (non-polar bond)
- Cl is very electronegative due to the fact that it only needs one electron to get inert gas configuration.
- Electron density is pulled toward the chlorine atom, creating a net dipole toward chlorine atom. A net dipole is the vector sum of individual bond dipoles.
- Has a higher MP and BP than methane

Dipoles in different molecules tend to line-up temporarily with each other (partial positive / negative charge on the molecule) – causes molecules to “stick” to each other

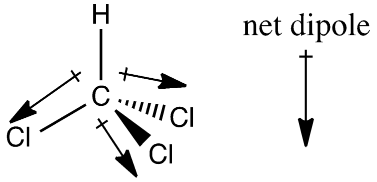


3. Dichloromethane, methylene chloride; CH_2Cl_2



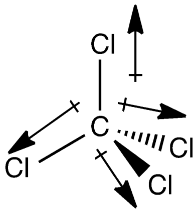
- Liquid at room temperature BP 40 °C MP – 95 °C
- More polar than chloromethane
- Not miscible with water

4. Trichloromethane, chloroform; $CHCl_3$



- More polar than methylene chloride BP 61 °C MP – 64 °C
- Higher than dichloromethane due to dipole dipole interaction

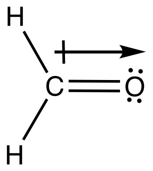
5. Tetrachloromethane, carbon tetrachloride; CCl_4 (toxic)



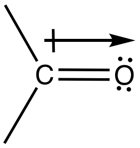
NO net dipole

- Non-polar molecule (net-zero dipole)
- Has temporary dipoles since chlorine is polarizable (see below), BP ~77 °C
- Historically used as a dry-cleaning fluid

6. Formaldehyde
- toxic
-polar and miscible in water



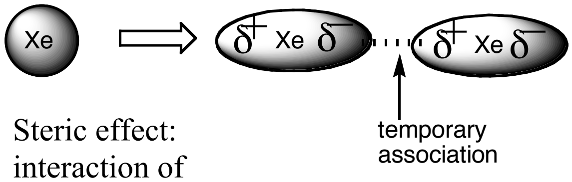
7. Acetone
   -polar and miscible in water



London Forces:

- Also known as dispersion forces, temporary dipoles or Van der Waals forces (less good)
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

Atoms	Boiling Point	
He	-269 ^{o}C	Small atom/ Low polarizability
Ne	-246 ^{o}C	↓
Ar	-186 ^{o}C	
Kr	-153 ^{o}C	
Xe	-108 ^{o}C	Large atom/ High polarizability



Steric effect: interaction of a filled shell of electrons. Causes repulsion.

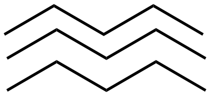
- The larger the atom (expanded electron density), the easier the formation of temporary dipoles.

This is the reason why CH_4 associates with CH_4, due to London forces

C_5H_{12} hydrophobic bonding:

$H_3C-CH_2-CH_2\cdot CH_2-CH_3$ n-pentane

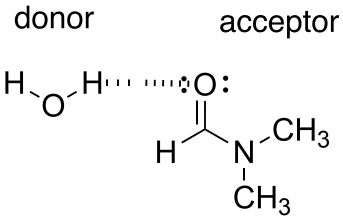
n= Normal=straight



Hydrophobic bonding

n-Pentane has a boiling point of 35 °C; therefore, it is a liquid at room temperature - why is it a liquid? Because its temporary dipoles – it is not miscible in water – water would rather hydrogen bond to itself – like dissolves like.

Example: DMF - dimethylformamide



soluble in water

<u>Reactivity/ Reactions</u>

<u>Thermodynamics of a chemical reaction:</u>

T= Temperature in °K
(°K = °C + 273)

↑

$\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)

↙ ↘

ΔH =Change in enthalpy = bond energy (large)

ΔS =Change in entropy = measure of disorder in system

$\Delta G = -RT \ln K_{eq}$

R = Gas constant = 0.082 $\frac{L\cdot atm}{mol\cdot K}$

T = Temperature in °K

ΔG = Change in energy of system (determines equilibrium)

E_a = Activation energy → determines rate of reaction

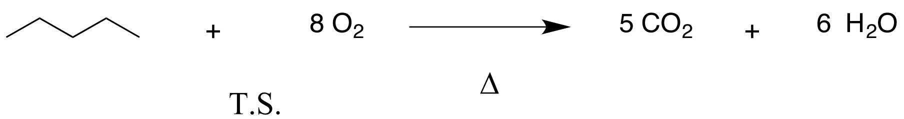
K_{eq} = equilibrium constant = $\frac{[C][D]}{[A][B]}$ [C] = concentration of compound C

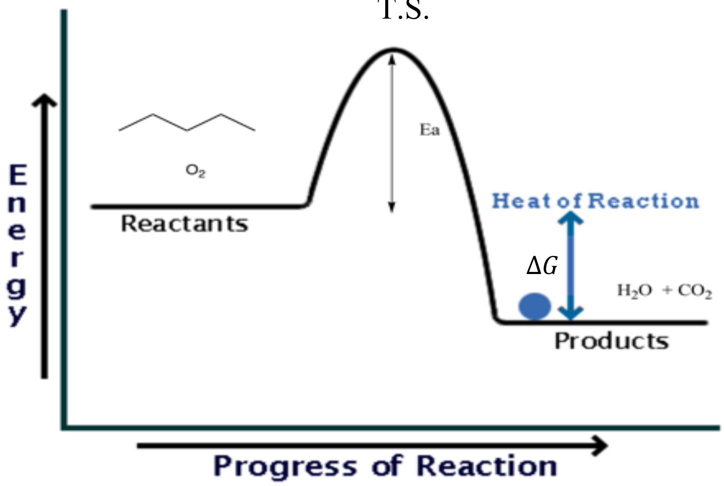
$$A + B \rightleftharpoons C + D$$

ΔG determines product concentrations at equilibrium
E_a determines rate of reaction

Exothermic Reaction: Negative ΔG

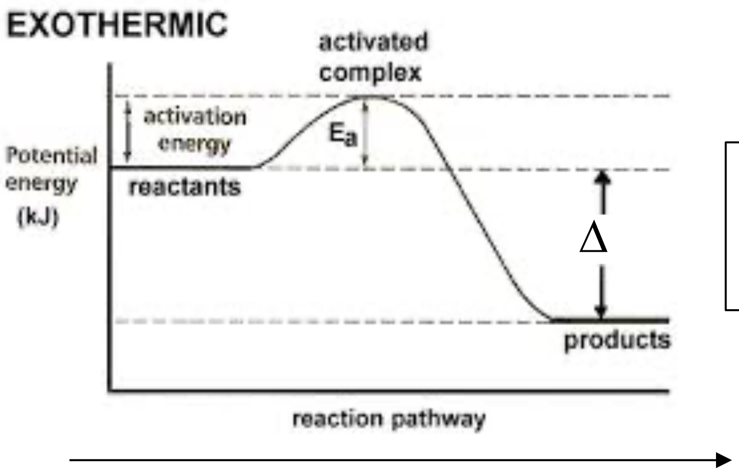
Example: Combustion of Pentane





Progress of reaction is also called Reaction Coordinate
S.M. = starting material or reactants (e.g. pentane, oxygen)

Energy diagram for the reaction:



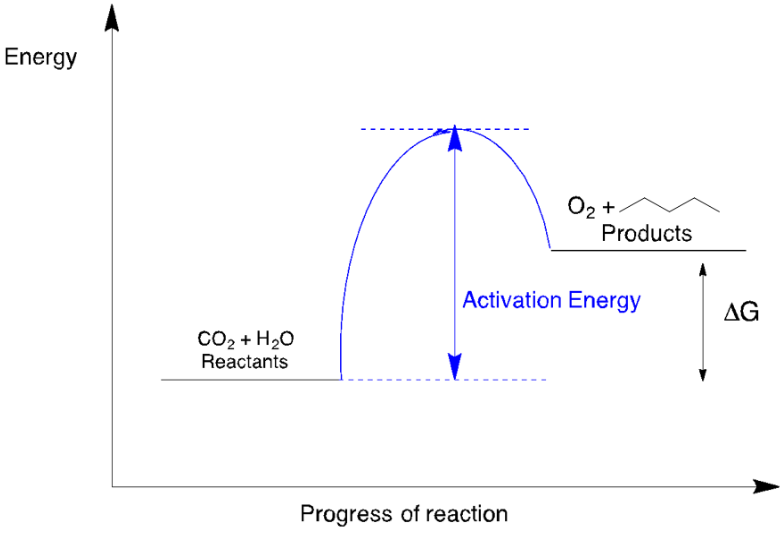
ΔE = ΔG: Gibbs free energy (total) change for the reaction

Reaction coordinate => progress of reaction

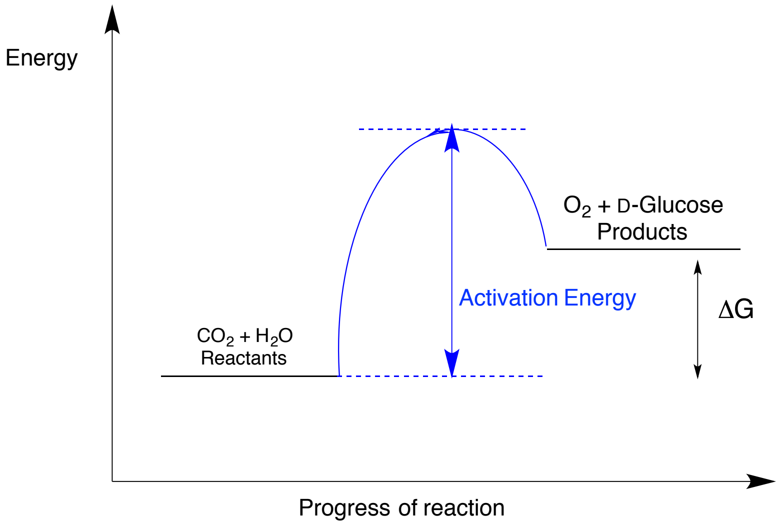
- The above reaction is an exothermic reaction, heat is released during reaction
- ΔG will be negative ($\Delta G < 0$) for an exothermic (heat releasing) reaction but will be positive ($\Delta G > 0$) for endothermic reaction.
- E_A= Activation energy: minimum amount of energy required to activate molecules or atoms to be able to undergo a chemical reaction. Controls the rate of the reaction.
- Activated complex **or transition state (T.S):** Highest energy point in a reaction pathway in which bonds are being formed and broken simultaneously. A T.S. cannot be observed or isolated. Should not be confused with and an intermediate.

Endothermic Reaction: Positive ΔG

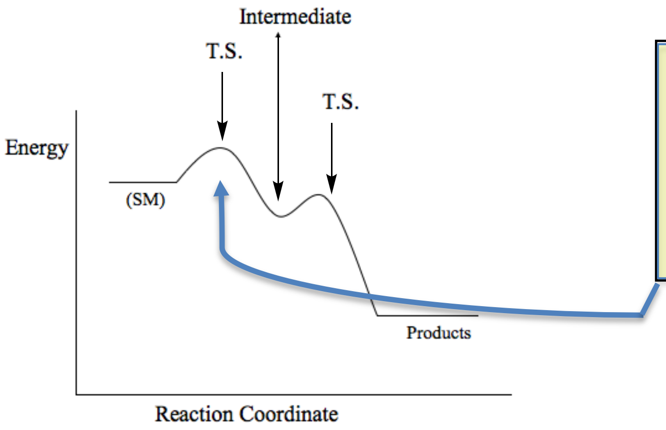
If the reverse of the combustion of pentane were to happen:



Another example:



Reaction proceeding through an intermediate



The Rate Determining Step is the TS with the larger E_A, which will be the slowest step; that is for the diagram to the left, the first step is the rate determining step.

Exothermic reaction,
ΔG= negative

Summary:

$\Delta E = \Delta G$: Gibbs free energy (total) change for the reaction

Change in Entropy
↓
$\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)
↓

Exothermic reactions have ΔG = Negative

Endothermic reactions have ΔG = Positive

TS = Transition State: Point where bonds are partially broken and partially formed

Intermediate: Short lived species

Bond Energy

Example:

Radicals

Change in enthalpy
= bond energy

$$H{-}CH_3 \rightleftharpoons H\bullet + \bullet CH_3$$

Bond	Bond Energy (kcal/mol)
H-C	99
H-O	111
C-C	83
C=O	179
O=O	119

At room temperature: there is an available energy of 15-20 kcal/mole

Acids and Bases

Bronsted – Lowry :

- An acid **donates proton (H^+)**
- A base **accepts a proton (H^+)**

Ex) $HCl + H_2O \quad H_3O^+ + Cl^-$

- Very fast reaction as HCl is a strong acid and NaOH is a strong base. NaCl is a weak base (weak conjugate base) and H_2O is a weak acid (weak conjugate acid).

$$HCl \longrightarrow H^+ + Cl^-$$

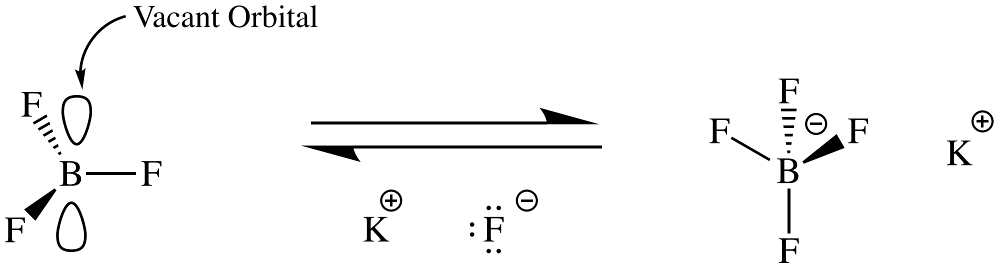
$$NaOH \longrightarrow Na^+ + OH^-$$

$$HCl + NaOH \longrightarrow NaCl + H{-}OH$$

Lewis Acid/Base:

- An **acid accepts a pair of electrons**
- A **base donates a pair of electrons**

e.g) BF_3
- Lewis Acid



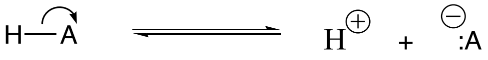
Boron trifluoride
-sp^2
-Trigonal planar
-120° bond angle

Boron tetrafluoride
-sp^3
-Tetrahedral
-109° bond angle

BF_3 can react with potassium fluoride (KF) to obtain an inert gas configuration. However, BF_4^- is unhappy with a formal negative charge, so the reaction is reversible.

- Every Bronsted-Lowry acid/base is also a Lewis acid/ base. The converse statement is not true; not all Lewis acids/bases can be classified as a Bronsted-Lowry acids/bases.
- **A general acid/base reaction:**

$$HA + B^{\ominus} \rightleftharpoons A^{\ominus} + HB$$



$$H{-}A \rightleftharpoons H^{\oplus} + :A^{\ominus}$$

$$K_{eq} = K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a = acidity constant
$pK_a = -\log K_a$

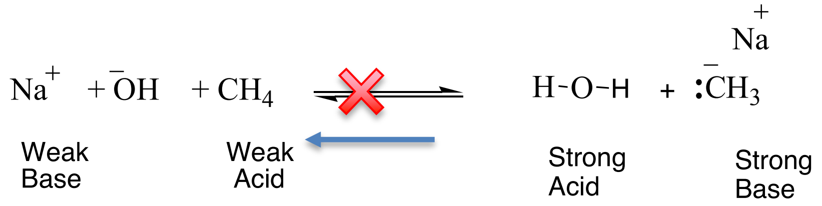
C-H > N-H > OH > F-H
Not acidic. Very acidic

Ex #1) Methane:

$$H{-}CH_3 \rightleftharpoons H^+ + CH_3^-$$

$$K_a = \frac{[H^+][CH_3^-]}{[HCH_3]} = 10^{-46}$$

$pK_a = -\log K_a = 46$



$$Na^+ + {}^-OH + CH_4 \rightleftharpoons H{-}O{-}H + :CH_3^- \; Na^+$$

pK_a CH_4 = 46
pK_a H_2O = 15.7

The equilibrium above lies far (exclusively) to the left. Hydroxide will NOT deprotonate methane.

Ex # 2) Ammonia Gas:

$$H{-}NH_2 \rightleftharpoons \overset{\oplus}{H} + \overset{\ominus}{\ddot{\underset{\cdot\cdot}{N}}}H_2$$

$$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$$

$pK_a = 36$

Ex #3) Water:

$$H{-}O{-}H \rightleftharpoons \overset{\oplus}{H} + \overset{\ominus}{:\ddot{\underset{\cdot\cdot}{O}}}H$$

$$K_a = \frac{[H^+][^-OH]}{[HOH]} = 10^{-15.7}$$

$pK_a = -\log K_a = 15.7$

Ex #4) Ionization of HF

$$HF \longrightarrow H^{\oplus} + F^{\ominus}$$

$pK_a = -10$

$K_a = 10^{10}$

HF when solvated has a pKa of 3.5

$$\underset{\text{strong base}}{NaOH}+\underset{\text{strong acid}}{HCl} \longrightarrow \underset{\text{weak base}}{NaCl}+\underset{\text{weak acid}}{H_2O}$$