CHEM 261 September 18, 2018

RECALL:

There are three attractive intermolecular forces

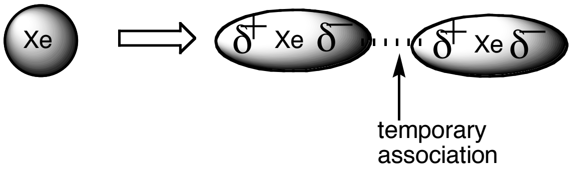
- i) Hydrogen bonding
  - Donors: H on O, N, or Halogen
  - Acceptors: Lone pair on O, N, or halogen
- ii) Dipole-dipole interaction

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

London Forces:

- Also know as dispersion forces
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

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



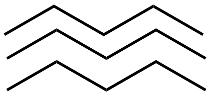
- The larger the atom (expanded electron density), the easier the formation of temporary dipoles

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

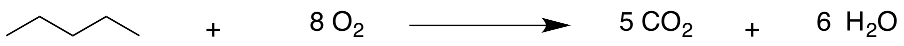


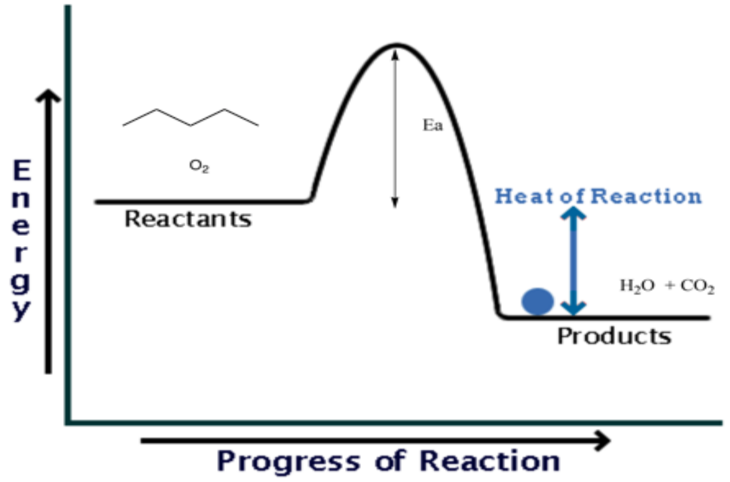
n-Pentane has a boiling point of 35 ^{o}C; therefore, it is a liquid at room temperature - why is it a liquid? Because its temporary dipoles – it is not miscible in water – water would rather hydrogen bond to itself – like dissolves like.

Reactivity/ Reactions

Exothermic Reaction: Negative ΔG

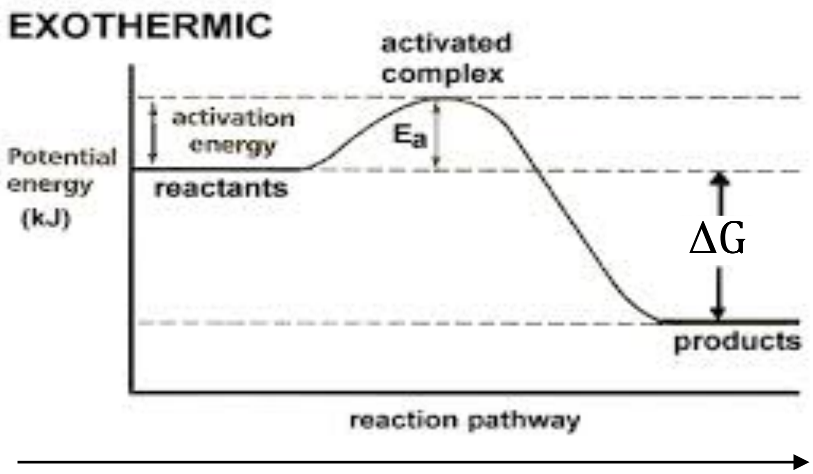
Example: Combustion of Pentane





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

Energy diagram for the reaction:



Reaction coordinate => progress of reaction

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

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

Temperature in ^{o}K
(^{o}K = ^{o}C + 273)

↑

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

↙ ↘

Change in enthalpy
= bond energy

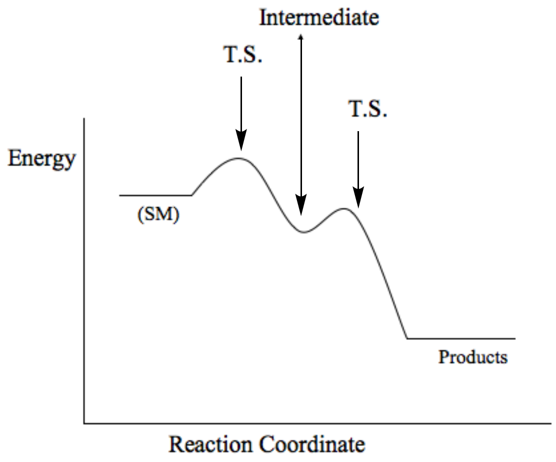
Change in entropy
= measure of disorder in system

$\Delta G = -RT \ln K_{eq}$
R = Gas constant = 0.082 $\frac{L\cdot atm}{mol\cdot K}$
T = Temperature in ^{o}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

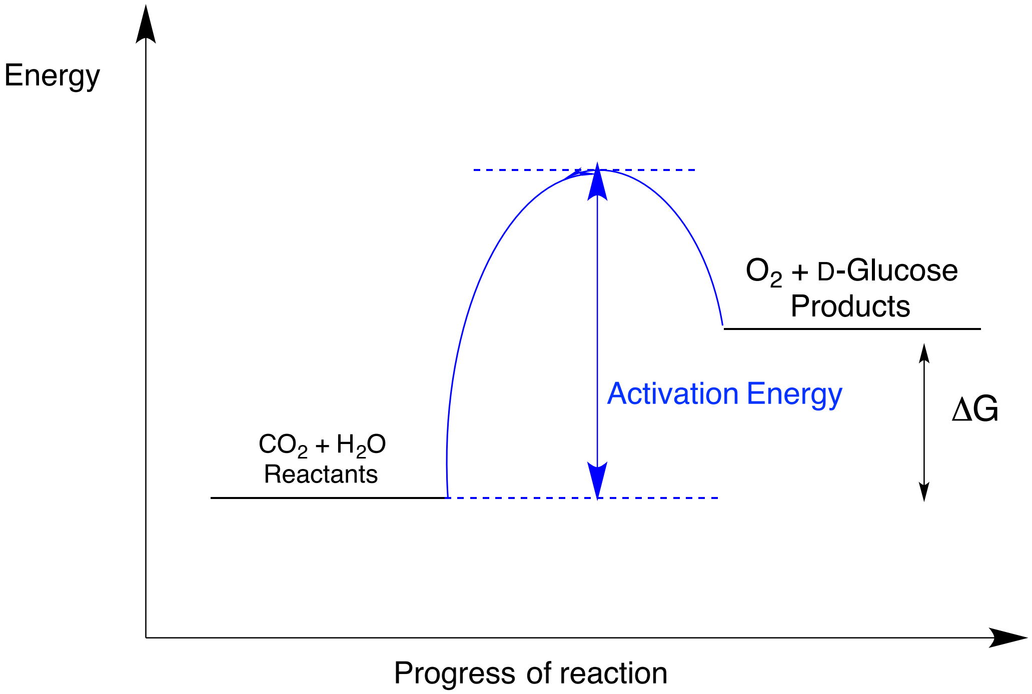
ΔG determines product concentrations at equilibrium
Ea determines rate of reaction

Reaction proceeding through an intermediate



NB: 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.

Endothermic Reaction: Positive ΔG



Summary:

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

$$\Delta G = \underbrace{\Delta H}_{\text{Change in enthalpy = bond energy}} - T\overbrace{\Delta S}^{\text{Change in Entropy}} \text{ (2nd law of thermodynamics)}$$

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

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

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

e.g.) $CH_4 + 2\,O_2 \xrightarrow[\Delta]{} CO_2 + 2\,H_2O$ – Exothermic reaction (releases Energy (E))

$\Delta E_{reaction} = \Delta E_{SM} - \Delta E_{pdt}$

For CH_4:
4 x C-H bonds = 4 x 99 = 396 kcal/mol
2 x O=O = 2 x 119 = 238 kcal/mol
ΔE_{SM} = 634 kcal/mol

ΔE_{SM} = sum of bonds broken (enthalpy)

For products:
2 C=O = 2 x 179 = 358 kcal/mol
4 H-O = 4 x 111 = 444 kcal/mol
ΔE_{pdt} = 802 kcal/mol

ΔE_{pdt} = sum of bonds formed

$\Delta E_{reaction}$ = 634 kcal/mol – 802 kcal/mol = -168 kcal/mol (exothermic reaction, energy released)

Acids and Bases

Bronsted – Lowry :

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

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

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

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

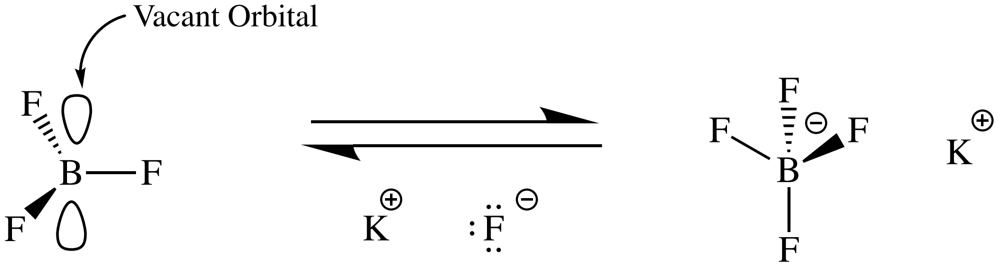
- Very fast reaction as HCl is a strong acid and NaOH is a strong base. NaCl is a weak base (weak conjugate base) and H_2O is a weak acid (weak conjugate acid).

Lewis Acid/Base:

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

e.g.) BF_3

- Lewis Acid

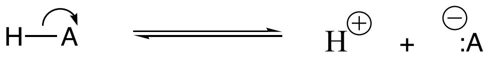


Boron trifluoride
-sp^2
-Trigonal planar
-120° bond angle

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.



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

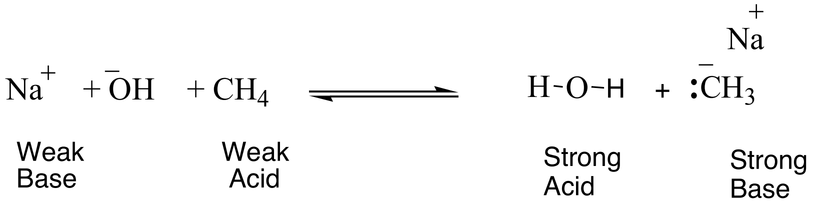
K_a = acidity constant
$pK_a = -\log K_a$

Ex #1) Water:

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

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

$$pK_a = -\log K_a = 15.7$$



$$Na^+ + {}^-OH + CH_4 \rightleftharpoons \text{H-O-H} + \overset{Na^+}{:\overset{-}{C}H_3}$$

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

Ex # 2) Ammonia Gas:

$$\text{H-NH}_2 \rightleftharpoons \overset{\oplus}{\text{H}} + \overset{\ominus}{\ddot{\underset{\cdot\cdot}{\text{N}}}\text{H}_2}$$

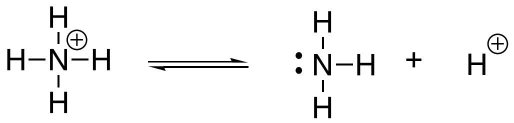
$$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$$

$$pK_a = 36$$

Ammonia gas is a better acid compared to methane (bigger K_A), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

NB: The lower the pKa the more acidic

pKa of "Ammonia" in biological system



$$NH_4^{\oplus} \rightleftharpoons :NH_3 + H^{\oplus}$$

Ammonium Cation

$pK_a = 9.3$

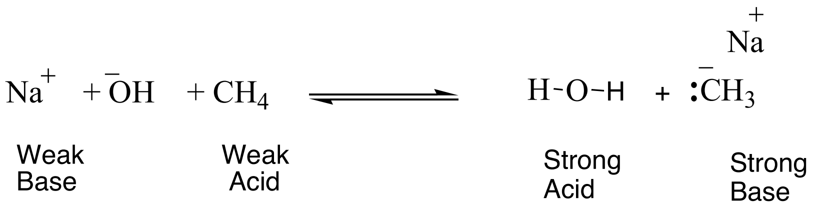
Ex #3) Methane:

$$\text{H-CH}_3 \rightleftharpoons H^+ + CH_3^-$$

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

$$pK_a = -\log K_a = 46$$

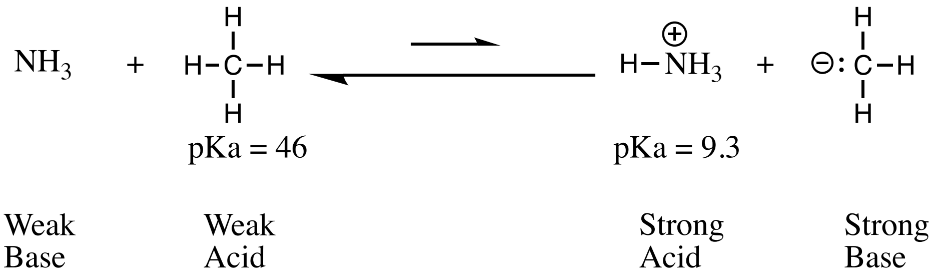
NB: Oxygen is more electronegative than nitrogen, which makes water more acidic than ammonia. Nitrogen more electronegative than carbon and that makes ammonia more acidic than methane.



$$Na^{+} + {}^{-}OH + CH_4 \rightleftharpoons H{-}O{-}H + {:}\overset{-}{C}H_3\ Na^{+}$$

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

Ex #4) Strong acid/base



$$NH_3 + CH_4 \rightleftharpoons H{-}\overset{\oplus}{N}H_3 + \ominus{:}CH_3$$

The reaction lies far (exclusively) to the left since ammonia is not a strong enough base to deprotonate methane