CHEM 261 January 19, 2023

RECALL:

There are three attractive intermolecular forces

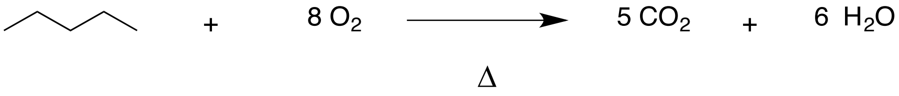
- i) Hydrogen bonding
  - Donors: H on O, N, or halogen
  - Acceptors: Lone pair on O, N, or halogen
- ii) Dipole-dipole interaction

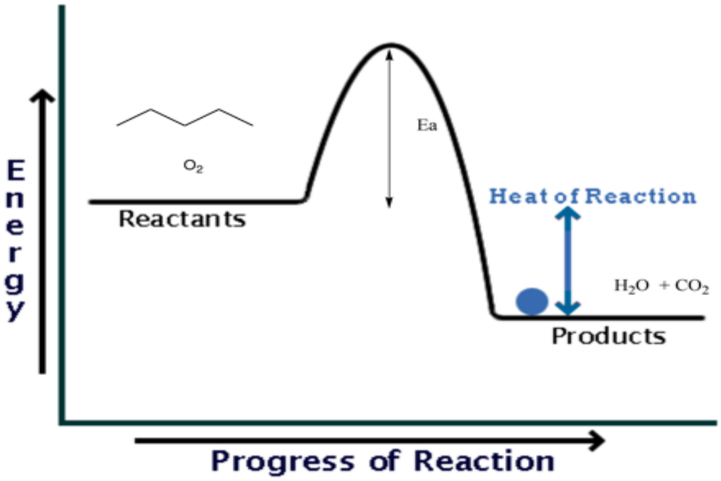
- iii) London forces (temporary dipole; hydrophobic bonding)

Reactivity/ Reactions

Exothermic Reaction: Negative ΔG

Example: Combustion of Pentane

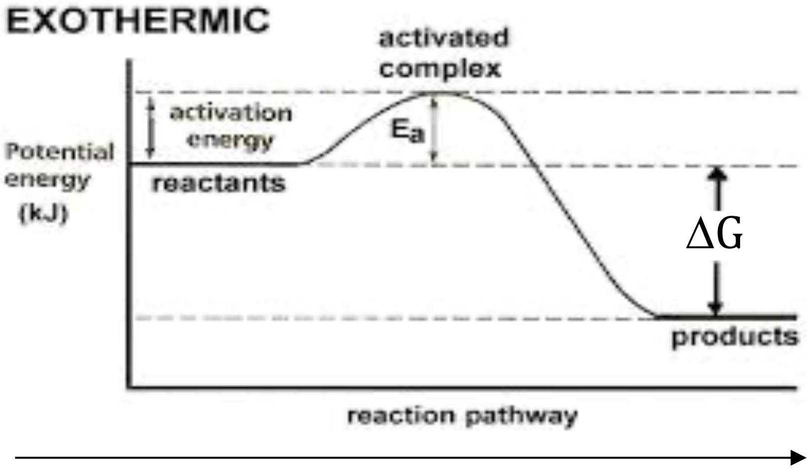




Progress of reaction is also called Reaction Coordinate

S.M. = starting material or reactants (e.g. pentane, oxygen)

Energy diagram for the reaction:



Reaction coordinate => progress of reaction

$\Delta E = \Delta G$: 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. 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.

<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

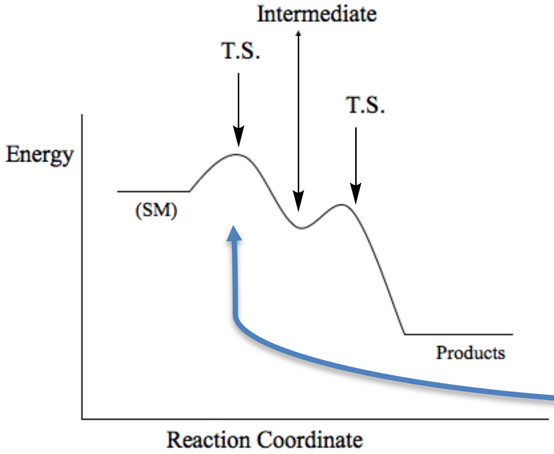
$\Delta G = -RT \ln K_{eq}$
R = Gas constant = 0.082 $\frac{L\cdot atm}{mol\cdot K}$
T = Temperature in °K
ΔG = Change in energy of system (determines equilibrium)
E_a = Activation energy → determines rate of reaction

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

$$A + B \rightleftarrows C + D$$

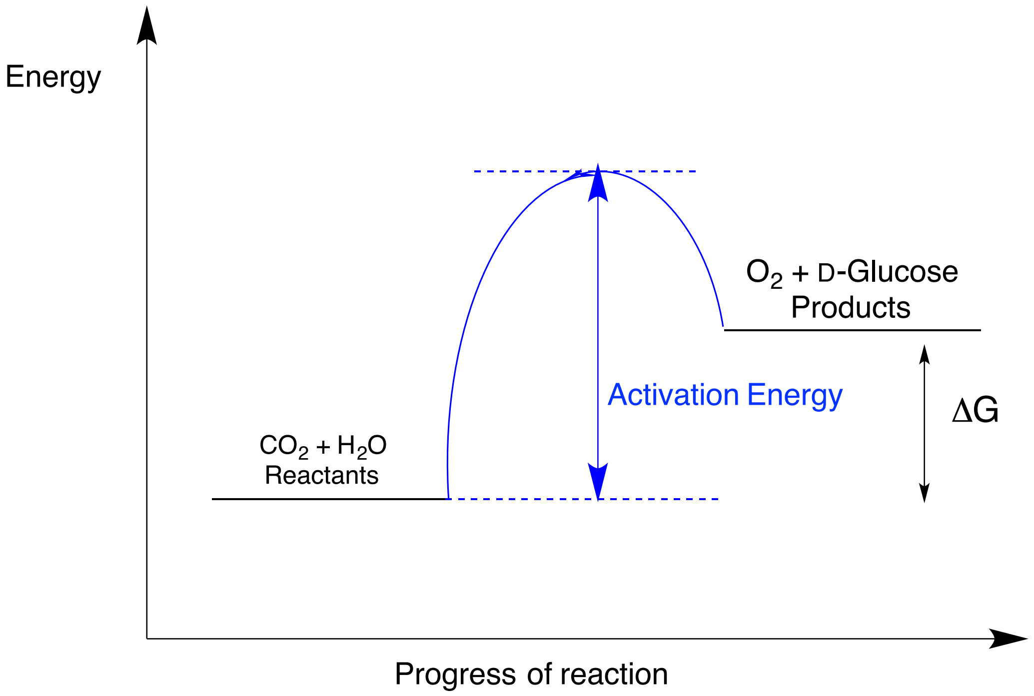
ΔG determines product concentrations at equilibrium
E_a determines rate of reaction

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.

Endothermic Reaction: Positive ΔG



Summary:

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

$$\Delta G = \underset{\downarrow}{\Delta H} - T\overset{\substack{\text{Change in Entropy}\\ \downarrow}}{\Delta S} \text{ (2nd law of thermodynamics)}$$

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

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

e.g.) Methane (CH_4)

$CH_4 + 2\ O_2 \xrightarrow{\Delta} CO_2 + 2\ H_2O$ – 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 = $\underline{238\ \text{kcal/mol}}$
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 = $\underline{444\ \text{kcal/mol}}$
ΔE_{pdt} = 802 kcal/mol

ΔE_{pdt} = sum of bonds formed

$\Delta E_{reaction}$ = 634 kcal/mol – 802 kcal/mol = -168 kcal/mol (a negative energy result means it is an exothermic reaction, energy released). This is the enthalpy ΔH.

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).

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

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

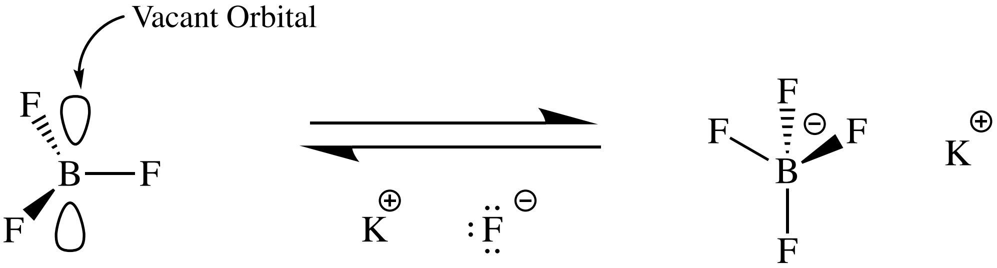
$$HCl + NaOH \longrightarrow NaCl + H\text{-}OH$$

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

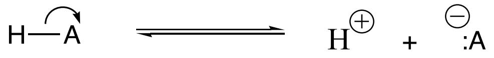
Boron tetrafluoride
-sp^3
-Tetrahedral
-109° bond angle

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:

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



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

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

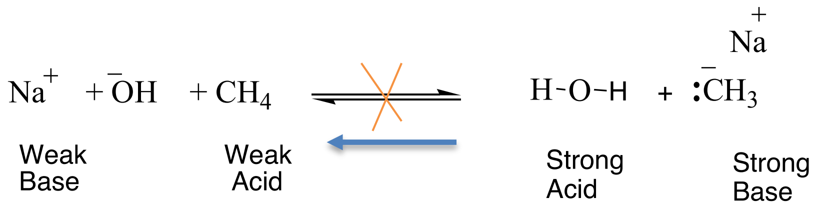
C-H > N-H > OH > F-H
Not acidic. Very acidic

Ex #1) Methane:

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

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

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



pK_a CH_4 = 46
pK_a H_2O = 15.7

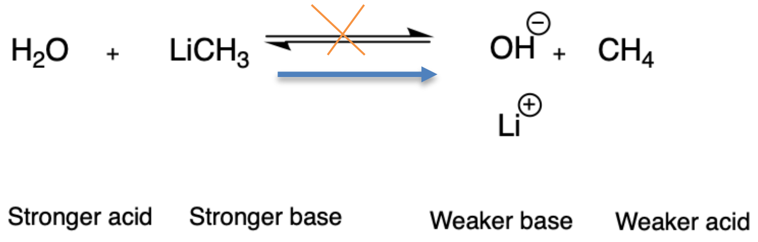
The equilibrium above lies far (exclusively) to the left. Hydroxide will NOT deprotonate methane.

Ex #2) Water:

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

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

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



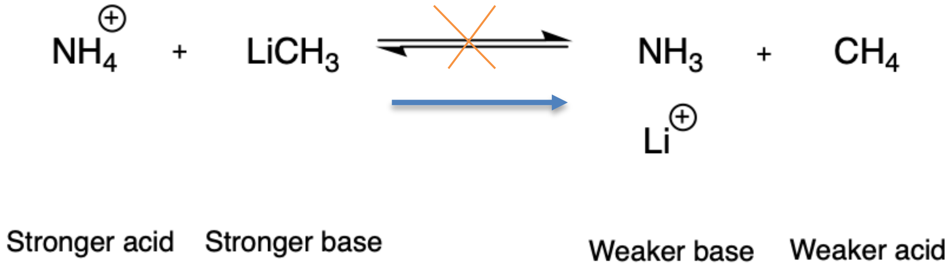
Ex # 3) Ammonia Gas:

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

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

$$pK_a = 36$$

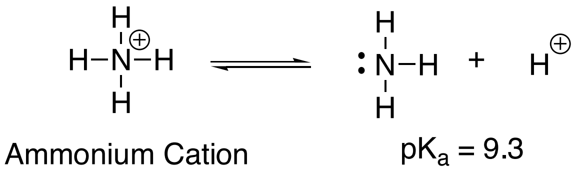
Biology of ammonium ion



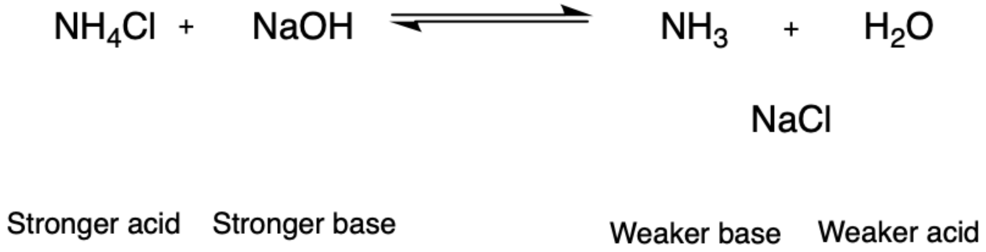
Ammonia gas is a better acid compared to methane (bigger K_A), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

NB: The lower the pKa the more acidic

pKa of “Ammonia” in biological system

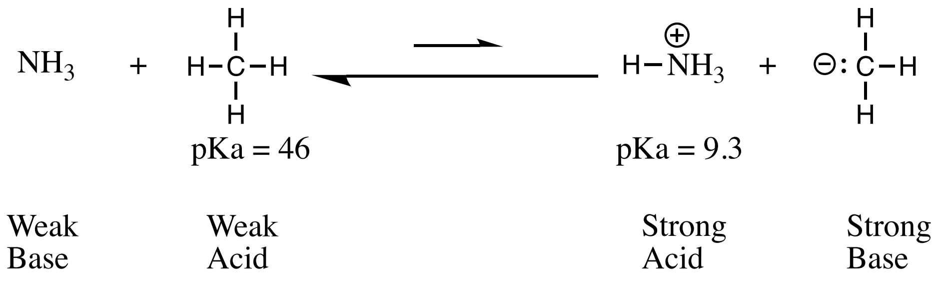


NB: Oxygen is more electronegative than nitrogen, which makes water more acidic than ammonia. Nitrogen more electronegative than carbon and that makes ammonia more acidic than methane.



pK_a H_2O = 15.7 (weaker acid)
pK_a NH_4 = 9.3 (stronger acid)

Ex #4) Strong acid/base



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

The lower the pKa the more acidic the compound

Examples of strong acids:

Acid	**pKa**
HI	-10
HBr	-9
HCl	-7
HF	-10
H_3O^+	-1.75

Can go up to +3.17 in a diluted solution (in water)

Two factors that affect acidity of the above acids:

1) Electronegativity – the more electronegative the atom, the better it can hold a negative charge
2) Solvation – the larger the ion, the better solvated it can be and so the more acidic it's conjugate acid will be