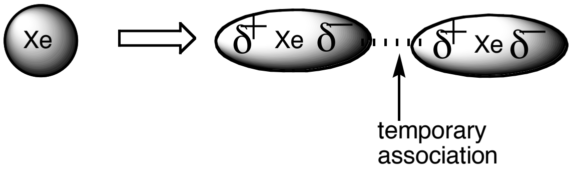
London Forces (Temporary Dipoles):

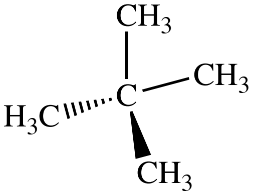
- Also know as London dispersion forces
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

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

CH_4 associates with CH_4 due to London forces

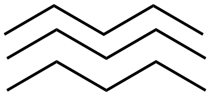


Neopentane (C_5H_{12})

C_5H_{12} hydrophobic bonding

$\mathbf{H_3C{-}CH_2{-}CH_2{\cdot}CH_2{-}CH_3}$ n-pentane

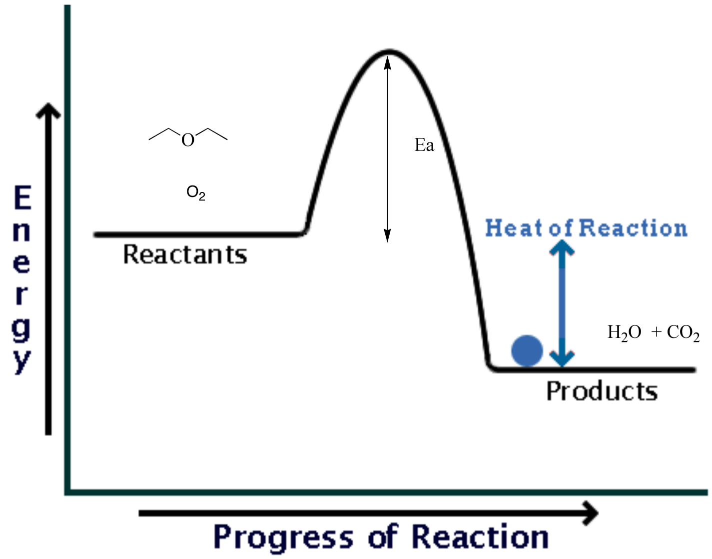
n= Normal=straight



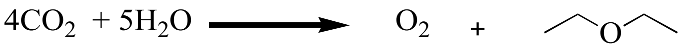
n-pentane is a liquid at 20° C - why is it a liquid? Because its temporary dipoles – it is not miscible in water – water would rather hydrogen bond to itself – like dissolves like

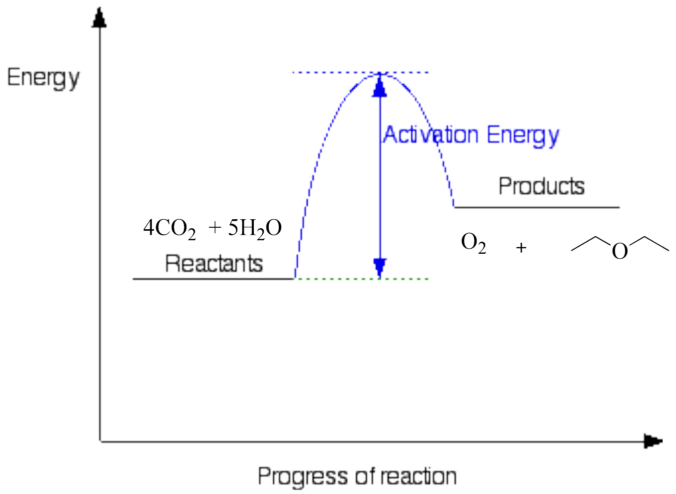
Reactivity/ Reactions

Diethyl ether
or Ethyl Ether or
simply called Ether



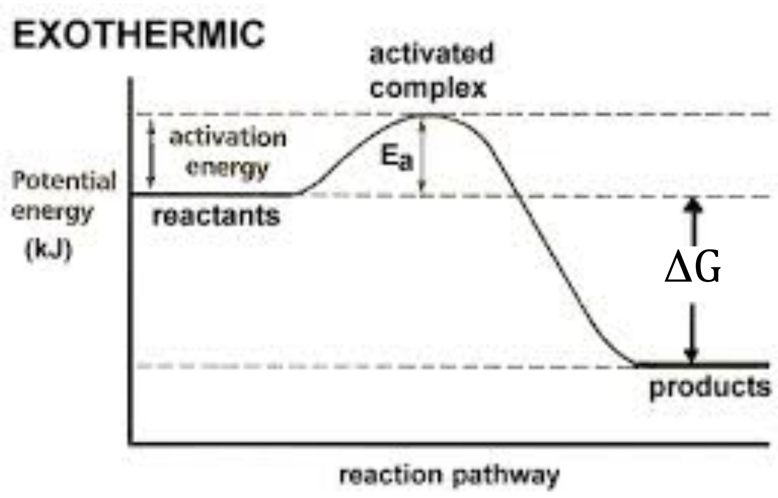
Progress of reaction is also called Reaction Coordinate
S.M. = starting material or reactants (e.g. diethyl ether, oxygen)





$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$

Energy diagram for the reaction:



Reaction coordinate => progress of reaction

Reactants or starting material (S.M.): CH_4 and O_2
Products: CO_2 and H_2O

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

- This reaction is an exothermic reaction, heat is released during reaction
- ΔG = negative for an exothermic (heat releasing) reaction, positive 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 = $0.082 \dfrac{L\cdot atm}{mol\cdot K}$

T = Temperature in ^{o}K

ΔG = Change in energy of system (determines equilibrium)

E_a = Activation energy → determines rate of reaction

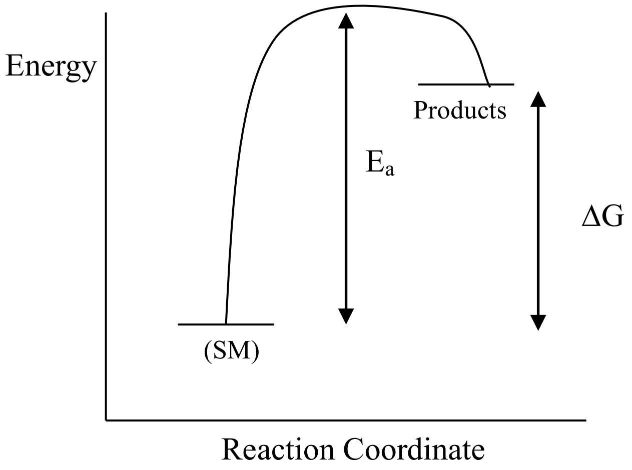
$$A + B \rightleftharpoons C + D$$

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

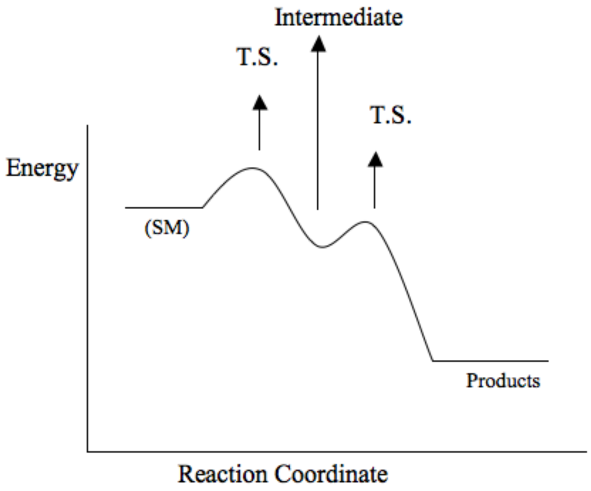
$$Keq = \frac{[CH_4][O_2]^2}{[CO_2][H_2O]^2}$$

Hence ΔG determines product concentrations at equilibrium
Ea determines rate of reaction

Endothermic Reaction: Positive ΔG.



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.

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

Exothermic ΔG = Negative

Endothermic ΔG = Positive
TS = Transition State: Point where bonds are partially broken and partially formed
Intermediate: Short live species

<u>Bond Energy</u>

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:

$$\begin{aligned} &4 \text{ x C-H bonds} = 4 \text{ x } 99 &&= 396 \text{ kcal/mol} \\ &2 \text{ x O=O} = 2 \text{ x } 119 &&= \underline{238 \text{ kcal/mol}} \\ &\Delta E_{SM} &&= 634 \text{ kcal/mol} \end{aligned}$$

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

For products:

$$\begin{aligned} &2 \text{ C=O} = 2 \text{ x } 179 &&= 358 \text{ kcal/mol} \\ &4 \text{ H-O} = 4 \text{ x } 111 &&= \underline{444 \text{ kcal/mol}} \\ &\Delta E_{pdt} &&= 802 \text{ kcal/mol} \end{aligned}$$

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).

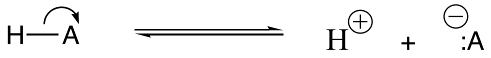
Lewis Acid/Base:

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

Examples of Lewis acids:

$$\mathbf{H^+ \quad AlCl_3 \quad BH_3 \quad FeCl_3}$$

- 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) Methane:

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

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

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

Ex # 2) Ammonia Gas:

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

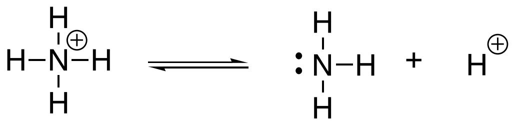
$$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$$

$$pK_a = 36$$

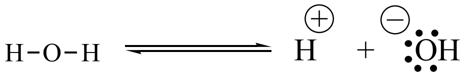
- Ammonia gas is a better acid compared to methane (bigger K_A), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

NB: The lower the pKa the more acidic

“pKa of Ammonia” in biological system

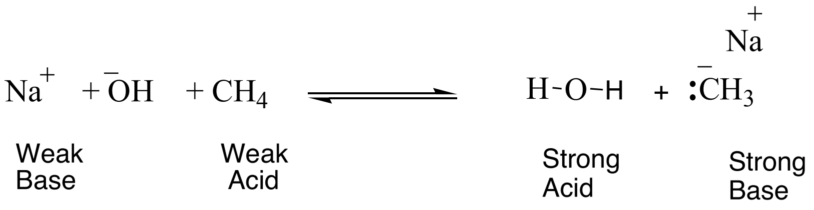


Ex #3) Water:



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

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



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