Chem 161 Sept 21, 2006

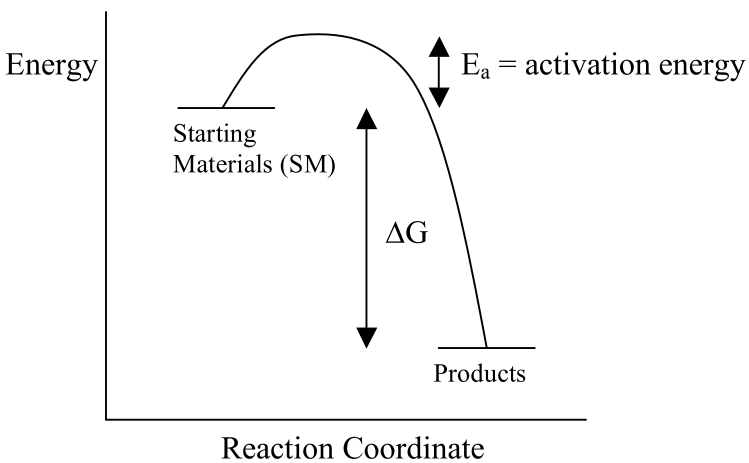
Energy

- Kinetic (movement) in molecule = Heat
    - Translation → movement forward and backward
    - Rotation → Tumbling
    - Bending and stretching → Measure by infrared radiation (IR)

- Potential energy → Reactivity and bond energy

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

Ex) $CH_4 + 2\ O_2 \xrightarrow{\Delta} CO_2 + 2\ H_2O$ – Exothermic reaction (releases Energy (E))



- ΔG = change in energy of system or change in Gibbs free energy.

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

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

For CH_4:

4 x C-H bonds = 4 x 99	= 396 kcal/mol		ΔE_{SM} = sum of bonds broken (enthalpy)
2 x O=O = 2 x 119	= <u>238 kcal/mol</u>		
ΔE_{SM}	= 634 kcal/mol		

For products:

2 C=O = 2 x 179 = 358 kcal/mol		ΔE_{pdt} = sum of bonds formed
4 H-O = 4 x 111 = <u>444 kcal/mol</u>		
ΔE_{pdt} = 802 kcal/mol		

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

ex)

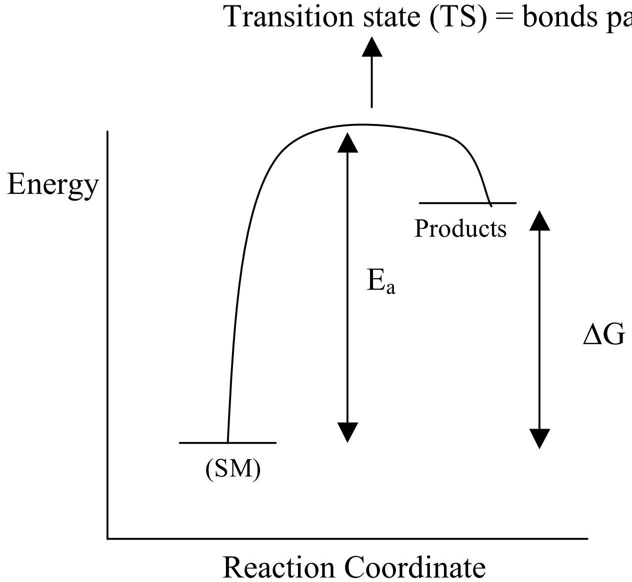
$$A + B \rightleftharpoons C + D$$

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

$\Delta G = -RT\ln K_{eq}$
R = gas constant = 0.082 $\frac{L\cdot atm}{mol\cdot K}$
T = temperature in ^oK
ΔG = change in energy of system (determines equilibrium)
E_a = activation energy → determines rate of reaction

<u>Endothermic Reaction</u>

Transition state (TS) = bonds partially made/broken



Rate = k_f[A][B] k_f = forward rate constant
Rate = k_r[C][D] k_r = reverse rate constant

rates are not directly dependent on ΔG

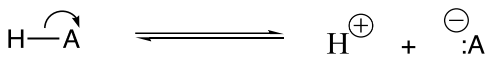
at equilibrium rate forward = rate reverse
hence $K_{eq} = k_f / k_r$

Acids – Bases

- Bronsted – Lowry
    - An acid donates proton (H^+)
    - A base accepts a proton

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

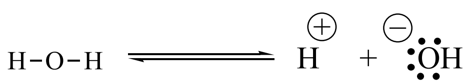
Definition



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

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

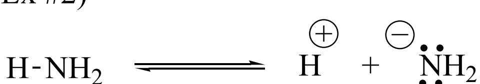
Ex



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

$pK_a = -\log K_a = 15.7$

Ex #2)



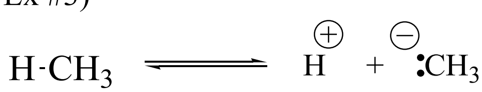
Ammonia gas

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

$pK_a = 36$

- NH_3 is less acidic than H_2O by a factor of $\sim 10^{20}$ because N is less electronegative than O.

Ex #3)



$$K_a = \frac{[H^+][^-CH_3]}{[CH_4]} = 10^{-46}$$

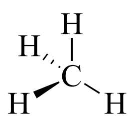
$pK_a = 46$

C is less electronegative than N or O

<u>Alkanes</u> (Hydrocarbons) – Lecture Outline and Assignment 2

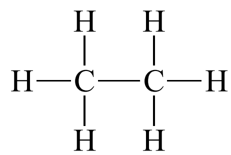
- Contain C and H (hydrocarbons)
- Contain only single bonds (C-H, C-C)
- All carbons are sp^3 hybridized (bond angle of 109°)
- Held together by London (dispersion) forces

Ex #1) CH_4 , methane



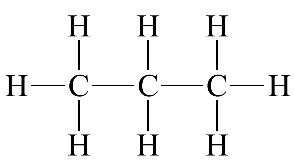
Bp = 161°C

Ex #2) C_2H_6 , ethane



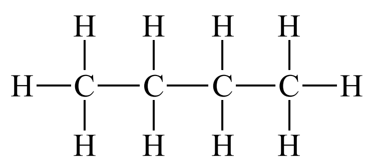
Bp = -88°C

Ex #3) C_3H_8 , propane

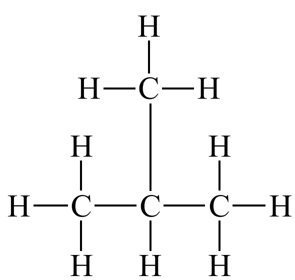


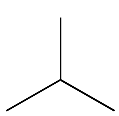
Bp = -42°C

Ex #4) C_4H_{10} , butane



Ex #5) C_4H_{10} , isobutane



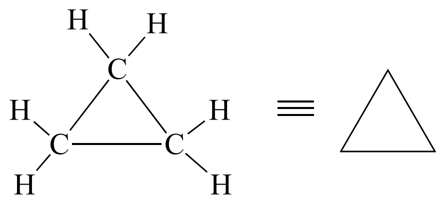


- Isomers (structural or constitutional) are different compounds that have same molecular formula. They have different physical properties (e.g. mp, bp, odour, biological effects)

- No rings: general formula is C_NH_{2N+2}
  - ex) $C_{10}H_{22}$ → Decane

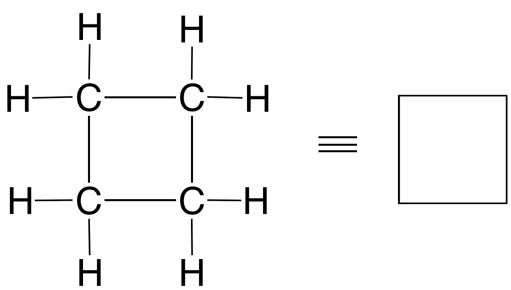
Cycloalkanes

Ex #1) Cyclopropane, C_3H_6

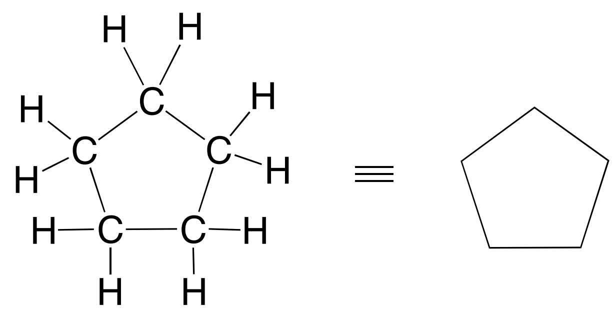


- C-C-C Bond angle (^{o}60)
- Highly reactive due to angle strain.

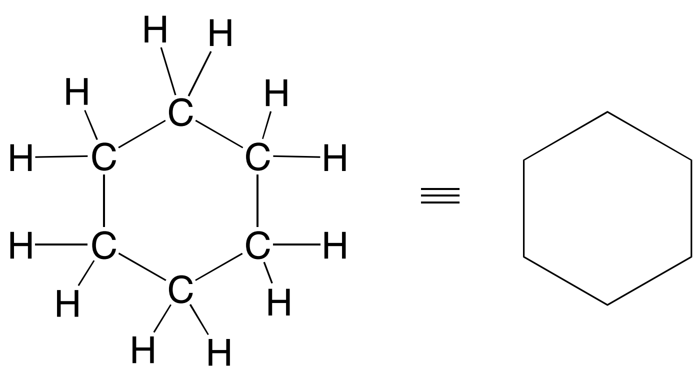
Ex #2) Cyclobutane, C_4H_8



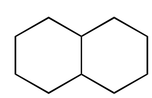
Ex #3) Cyclopentane, C_5H_{10}



Ex #4) Cyclohexane, C_6H_{12}



1 ring = C_NH_{2N}
2 rings = C_NH_{2N-2}

ex) 

$C_{10}H_{18}$

Has 2 degrees of unsaturation

Each deviation of 2 hydrogens from the C_NH_{2N+2} formula is a degree of unsaturation (means ring or double bond in hydrocarbon)