



**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.

Change in Entropy  $\Delta G = \Delta H - T\Delta S$  (2nd law of thermodynamics)  $\downarrow$ Change in enthalpy = bond energy

Exothermic  $\Delta G = Negative$ 

Endothermic  $\Delta G = Positive$ 

## **Bond Energy**

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 <sub>4</sub> :	4  x C-H bonds = 4  x  99		= 396 kcal/mol	$\Delta E_{SM} = sum of bonds$
	2 x O=O	$= 2 \times 119$	= 238 kcal/mol	broken (enthalpy)
	$\Delta E_{SM}$		= 634 kcal/mol	

For products:	2 C = O = 2	2 x 179 = 358 kcal/mol	$\Delta E_{pdt}$ = sum of bonds formed
	4  H-O = 1	4 x 111 = <u>444 kcal/mol</u>	-
	$\Delta E_{pdt}$	= 802 kcal/mol	

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

## Acids and Bases

### **Bronsted** – Lowry :

- An acid donates proton (H<sup>+</sup>)
- A base accepts a proton (H<sup>+</sup>)

HCI  $\longrightarrow$  H<sup>+</sup> + CI<sup>-</sup> NaOH  $\longrightarrow$  Na<sup>+</sup> + OH<sup>-</sup>

HCI + NaOH → NaCI + H-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<sub>2</sub>O 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:

#### $\mathbf{H}^+$ AlCl<sub>3</sub> BH<sub>3</sub> FeCl<sub>3</sub>

• 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.

$$H \xrightarrow{\frown} A \qquad \qquad H^{\oplus} + \stackrel{\bigcirc}{:} A \qquad \qquad K_{eq} = K_a = [H^+][A^-] \qquad \qquad K_a = acidity constant [HA] \qquad \qquad FK_a = -\log K_a$$

Ex #1) Methane:

H-CH<sub>3</sub> 
$$\longrightarrow$$
 H<sup>+</sup> + CH<sub>3</sub><sup>-</sup>  
 $K_a = [H^+][CH_3^-] = 10^{-46}$   
[HCH<sub>3</sub>]  
 $pK_a = -logK_a = 46$ 

$$pK_a = -logK_a$$

Ex # 2) Ammonia Gas:

H-NH<sub>2</sub> 
$$\longrightarrow$$
 H +  $\stackrel{\bigcirc}{\overset{\frown}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}}}$   $\overset{\frown}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}}}} H_2$   $K_a = [\underline{H^+}][\stackrel{\frown}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}}} H_2] = 10^{-36}$  [NH<sub>3</sub>]

 $pK_a = 36$ 

٠ Ammonia gas is a better acid compared to methane (bigger K<sub>A</sub>), because nitrogen is more electronegative than carbon. It can hold a negative charge easier than carbon.

"pKa of Ammonia" in biological system



Ex #3) Water:

H-O-H 
$$\longrightarrow$$
 H +  $\bigcirc$   
H +

Ex #4)



Ex #5)



These Lewis acids are not Bronsted acids: Note BF4<sup>-</sup> is not a Lewis acid, althogh BF3 is



Infrared (IR) Spectroscopy – Background only

 $\mathbf{E} = \mathbf{h}\mathbf{c}/\lambda = \mathbf{h}\mathbf{v}$ 

E = Energy

h = Planck's Constant=  $6.6 \times 10^{-34}$  joules/sec

- v = Frequency
- $\lambda =$  Wavelength
- $c = Speed of light = 3.0 \times 10^{10} cm/sec$



# **Electromagnetic Spectrum:**



uv and visible light: conjugated double bond systems infrared radiation: bond stretching and bending

# **NEXT SECTION: Lecture Outline 2: ALKANES**

# Hydrocarbons – Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C)
- Alkenes = Olefins (C=C)
- Alkynes = Acetylenes ( $C \equiv C$ )

# <u>Alkanes</u>

- All carbons are sp<sup>3</sup> hybridized (optimal bond angle of 109°)
- Single bonds ( $\sigma$  bonds).
- Tetrahedral geometry at every carbon
- Held together by London (dispersion) forces

Ex #1) CH<sub>4</sub>, methane

Ex #2) C<sub>2</sub>H<sub>6</sub>, ethane



 $CH_4 \quad H_4C \quad CH_3\text{-}H \qquad \qquad C_2H_6 \quad CH_3\text{-}CH_3 \quad H_3C\text{-}CH_3$ 



n-Butane: normal straight chain butane

# Ex #5) $C_4H_{10}$ , isobutane



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

-	iso	-	meros		
	same	-	parts		
one type: structural (same as constitutional)					



structural isomer = constitutional isomer

## **Groups** (part of an alkane structure)

- In naming the particular group, drop the "ane" part and add "yl" to the name
- For example, meth<u>ane</u>  $\rightarrow$  meth<u>yl</u>



(ii) Ethyl group -CH<sub>2</sub>CH<sub>3</sub>

34

(iii)

(iv)



n-propyl chain

℃ H<sub>2</sub>

 $H_2$  $H_3C$  C C $H_2$ 

n-propyl alcohol