Winter 2025

January 23, 2025

RECALL:

Bond Energy

Example:

Radicals

+ •CH₃

Change in enthalpy = bond energy

| Bond | Bond Energy (kcal/mol) |
|------|------------------------|
| H-C | 99 |
| H-O | 111 |
| C-C | 83 |
| C=O | 179 |
| 0=0 | 119 |

At room temperature: there is an available energy of 15-20 kcal/mole

 $H-CH_3 \longrightarrow H_{\bullet}$

e.g.) Methane (CH₄)

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

 $\Delta E_{reaction} = \Delta E_{SM}$ - ΔE_{pdt} (SM=starting material, pdt= product)

| For CH ₄ : | 4 x C-H bor | $nds = 4 \ge 99$ | = 396 kcal/mol | ΔE_{SM} = sum of bonds |
|-----------------------|-----------------|------------------|-----------------------|--------------------------------|
| | 2 x O=O | = 2 x 119 | = <u>238 kcal/mol</u> | broken (enthalpy) |
| | ΔE_{SM} | | = 634 kcal/mol | |

| For products: | 2 C=0 = 2 x 17 | 79 = 358 kcal/mol | $\Delta E_{pdt} = sum of bonds formed$ |
|---------------|-------------------|--------------------------------------|--|
| | 4 H-O = 4 x 1 | $1 = \frac{444 \text{ kcal/mol}}{1}$ | |
| | ΔE_{pdt} | = 802 kcal/mol | |

 $\Delta E_{\text{reaction}} = 634 \text{ kcal/mol} - 802 \text{ kcal/mol} = -168 \text{ kcal/mol}$ (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 + H₂O H₃O⁺ + 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 H₂O is a weak acid (weak conjugate acid).

HCI \longrightarrow H⁺ + CI⁻

NaOH \longrightarrow Na⁺ + OH⁻

HCI + NaOH → NaCI + H-OH

Lewis Acid/Base:

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



BF₃ 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: + B^O + HB HA $\begin{array}{c} & & \\ & &$ н—А C-H > N-H > OH > F-HNot acidic. Very acidic Ex #1) Methane: H-CH₃ \longrightarrow H⁺ + CH₃⁻ $K_a = [H^+][CH_3^-] = 10^{-46}$ $pK_a = -logK_a = 46$ [HCH₃] +Na $Na^+ + OH + CH_4$ Н-О-Н + :СН₃ Weak Acid Weak Strong Strong Base

 $pK_a CH_4 = 46$ $pK_a H_2O = 15.7$

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

Ex #2) Ionization of HF

$$HF \longrightarrow H^{\oplus} + F^{\ominus}$$
$$pK_a = -10$$
$$K_a = 10^{10}$$

Acid

Base

HF when solvated has a pKa of 3.5

Ex # 3) Ammonia Gas:

H-NH₂
$$\longrightarrow$$
 H + $\stackrel{\bigcirc}{\overset{\frown}{NH_2}}$ $K_a = [\underline{H^+}][\underline{NH_2}] = 10^{-36}$
[NH₃]
 $pK_a = 36$



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 pK_a 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.

 $NH_4CI + NaOH$ $H_3 + H_2O$

Stronger acid Stronger base

NaCl Weaker base Weaker acid

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

Ex #4) Water:

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

 $pK_a = -logK_a = 15.7$



Stronger acid Stronger base Weaker base Weaker acid

Ex #5) Strong acid/base



Another example:

 $\begin{array}{rcl} LiNH_2 & + & H_2O & \rightarrow & LiOH & + & NH_3 \\ & & pKa=15.7 & & pKa=36 \\ & & stronger \ acid & & Weaker \ acid \end{array}$

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

NaOH + NH₃ \longrightarrow H-OH + Na⁺ + NH₂ pKa=36 pKa=16

Weaker base Weaker acid Stronger acid Stronger base The lower the pK_a the more acidic the compound

Examples of strong acids:

| Acid | pKa |
|------|-----|
| HI | -10 |
| HBr | -9 |
| HCl | -7 |

| CHEM 261 | | Winter 2025 | January 23, 2025 |
|------------------------|-------|-------------|--|
| HF H2O ⁺ | -10 | | Can go up to +3.17 in a diluted solution (in |
| 1130 | -1.75 | | 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 its conjugate acid will be

Electromagnetic Radiation:

Infrared (IR) Spectroscopy – Background only:

 $E = hc/\lambda = hv$, energy is quantized

- E = Energy
- h = Planck's Constant= 6.6×10^{-34} joules/sec
- v = Frequency
- $\lambda = Wavelength$
- $c = Speed of light = 3.0 X 10^{10} cm/sec$



NB: There is an inverse relationship between wavelength and frequency.

Electromagnetic Spectrum:

NB: 1nm = 10 angstrom



NEXT SECTION: Lecture Outline 2: ALKANES

<u>Hydrocarbons</u> – Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C), sp³
- Alkenes = contains C=C and has sp² hybridization (e.g. olefins)
- Alkynes = contains $C \equiv C$ and has sp hybridization (acetylenes)

<u>Alkanes</u>

- All carbons are sp³ hybridized (optimal bond angle of 109°)
- Single bonds (σ bonds).
- Tetrahedral geometry at every carbon
- Held together by London (dispersion) forces



NOTE: Propane has a boiling point of -42°C, which is higher than methane because it's chain-like structure allows for more surface area for London dispersion forces to take effect.

Ex #5) C₄H₁₀, isobutane or i-Butane



- 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) second type: stereoisomers (diastereomers and enantiomers) – will talk about more

structural isomer = constitutional isomer

Ex #6) Pentane C₅H₁₂





(isopentane or 2-methylbutane)

n - pentane Neopentane

Neo Group



Systematic (IUPAC) Nomenclature

RULES:

- 1. Find the longest straight chain
- 2. Number from end of the chain, so that the 1st branch point has the lowest number
- 3. Name the chain, then add prefixes (for the groups attached) with number and name the groups attached
- 4. Separate numbers and names by dash



Note: iso = second-to-last carbon of the chain is disubstituted (2 methyl groups) neo = second-to-last carbon of the chain is trisubstituted (3 methyl groups)

Prefixes for naming: Di (2), Tri (3), Tetra (4), Penta (5), Hexa (6) etc.

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>

(i) Methyl group - CH3



(ii) Ethyl group - CH₂CH₃



(iii) Isopropyl group



СН₃ | H—С—ОН | СН₃

iso-propyl group

iso-propyl alcohol

(iv) *n*-Propyl group





n-propyl chain

n-propyl alcohol

(v) *tert*-Butyl group (t-butyl)



tert-Butyl chain

tert-Butyl chloride

(vi) neo group





neo chain

2,2-dimethylbutane

Naming Examples:





2,3,3-trimethylpentane

3,5-diethyl-4-methyloctane

Cycloalkanes:

General Molecular Formula of Alkanes

- Linear alkanes: general formula is $C_NH_{2N} + 2$
- Each degree of unsaturation "removes" 2 hydrogens from the C_NH_{2N} +2 formula
- (if there are no nitrogens in the molecule, there will always be an even # of hydrogens)
- Cylcoalkanes always have at least 1 degree of unsaturation

e.g.

- $\circ~1$ Degree of unsaturation : $C_{N}H_{2N}~$ Alkanes with one ring or double bond
- $\circ~2$ Degrees of unsaturation : $C_{N}H_{2N\text{-}2}$ Alkanes with two rings or double bonds, or one each

Note: Ring Structure Naming

- Parent ring is the largest one
- Prefix with "cyclo"
- Start with numbering at point of maximum branching/most important functional group
- Number so as to give next branch/functional group lowest number

Cyclopropane, C₃H₆



- One degree of unsaturation (*n*-propane is C_3H_8)
 - Not a structural isomer (different molecular formula)
- C-C-C bond angle (60°)

- Highly reactive due to ring strain (sp³ carbons prefer to be 109°)







Cyclopentane, C5H10

Cyclohexane, C₆H₁₂



Examples of Naming Cycloalkanes: Basic rule: (1)Start at maximum branch (2)lowest No. to the next branch



Degree of Unsaturation= 1

1-methylcyclopentane (structural isomer of hexane)

Ex #2) C7H14



1,3-dimethylcyclopentane

Degree of Unsaturation= 1