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

 δ^+ δ^-

iii) London forces (temporary dipole; hydrophobic bonding)

London Forces:

- Also known as dispersion forces, temporary dipoles or Van der Waals forces (less good)
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

Atoms	Boiling Point	
Не	-269 °C	Small atom/ Low polarizability
Ne	-246 °C	1
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.

This is the reason why CH₄ associates with CH₄, due to London forces

C₅H₁₂ hydrophobic bonding:

a filled shell of electrons. Causes repulsion.



n-Pentane has a boiling point of 35 °C; therefore, it is a liquid at room temperature - 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.

Example: DMF - dimethylformamide

donor acceptor

soluble in water

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

- 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.

Thermodynamics of a chemical reaction:



 $\Delta G = Change in energy of system (determines equilibrium)$ $E_a = Activation energy \rightarrow determines rate of reaction$ $K_{eq} = equilibrium constant = [C][D] \quad [C] = concentration of compound C$ [A][B] $A + B \xrightarrow{} C + D$

$$\Delta G$$
 determines product concentrations at equilibrium

E_a determines rate of reaction

Reaction proceeding through an intermediate



Reaction Coordinate

Endothermic Reaction: Positive ΔG

If the reverse of the combustion of pentane were to happen:





<u>Summary:</u>

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

Change in Entropy

$$\downarrow$$

 $\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)
 \downarrow

Exothermic reactions have $\Delta G = Negative$

Endothermic reactions have $\Delta G = Positive$

TS = Transition State: Point where bonds are partially broken and partially formed

Intermediate: Short lived species

Bond Energy

Example:

Radicals

 $H-CH_3 \longrightarrow H \bullet + \bullet CH_3$

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

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}

For CH ₄ :	4 x C-H bond	$ls = 4 \ge 99$	= 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 179 = 358 kcal/mol	$\Delta E_{pdt} = sum of bonds formed$
	4 H-O = 4	x 111 = 444 kcal/mol	
	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:



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

Ex #2) Water:

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

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



Stronger acid Stronger base Weaker base Weaker acid

Ex # 3) Ammonia Gas:

H-NH₂
$$\stackrel{\textcircled{}}{\longrightarrow}$$
 $\stackrel{\bigoplus}{H}$ $\stackrel{\bigoplus}{+}$ $\stackrel{\bigoplus}{NH_2}$ $K_a = [\underline{H^+}][\underline{\cdot}N\underline{H_2}] = 10^{-36}$
[NH₃] $pK_a = 36$
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 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.



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) 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 pK_a the more acidic the compound

Ex #5) Ionization of HF

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

Examples of strong acids:

Acid	pK _a]
HI	-10	
HBr	-9	$Con = un t_0 + 2.17 $
HC1	-7	a diluted solution (in
HF	-10	water)
H_3O^+	-1.75	

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:



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

Electromagnetic Spectrum:

NB: 1nm = 10 angstrom



UV and visible light: conjugated double bond systems

e.g. C=C bonds absorb UV light and some visible light

Infrared Radiation: bond stretching and bending modes

-Measured in wavenumbers (cm⁻¹)

- Defined as cycles/second
 - e.g. O-H bond can be seen around ~3400cm⁻¹ in an IR spectrum



NEXT SECTION: Lecture Outline 2: ALKANES

Hydrocarbons - Compounds that contain only C and H

- Alkanes contain only single bonds (C-H, C-C), sp³
- Alkenes = contains C=C and has sp^2 hybridization (e.g. olefins)
- Alkynes = contains $C \equiv C$ and has sp hybridization (acetylenes)

Alkanes

- 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

Ex #1) CH₄, methane



BP = -164 °CCH₄ H₄C CH₃-H



$$BP = -88 \ ^{\circ}C$$

$$C_{2}H_{6} \qquad CH_{3}\text{-}CH_{3} \qquad H_{3}C\text{-}CH_{3}$$

Ex #3) C₃H₈, propane



 C_3H_8 $CH_3CH_2CH_3$ \frown H_3C



Ex #4) C₄H₁₀, butane



 $BP = -42 \ ^{\circ}C$

n-Butane: normal straight chain butane

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) C_4H_{10} , 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

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one type: structural (same as constitutional) second type: stereoisomers (diastereomers and enantiomers) – will talk about more

structural isomer = constitutional isomer





(isopentane or 2-methylbutane)

n - pentane Neopentane

 $-+C_{H_2}$ Neo Group

Ex #7) Hexane C₆H₁₄

n-hexane

Isohexane

neohexane