#### 1. 1,2-Dichlorobenzene



8. Benzene



#### **Intermolecular Forces: (forces present between molecules)**

- Attractive intermolecular forces:
  - i) Hydrogen bonding strongest on per atom basis (e.g. base recognition in forming DNA helix) (also in RNA)
     Linus Pauling development of H bonding
  - ii) **Dipole-dipole interaction** (Intermediate strength)
  - iii) **London forces** (temporary dipole; hydrophobic bonding) weakest on per atom basis distortion of inner shells.

#### **Electronegativity:**

- An atom's desire for electrons (negative charge).
- On the periodic table, electronegativity increases as you go from left to right (up to inert gases, which are not electronegative) and as you go from down to up
- Halogens (F, Cl, Br, I) are highly electronegative
  - i.e. Fluorine is the most electronegative atom (wants to gain the inert gas configuration of Ne) and is small (has few electrons)

- It influences acidity of H's attached, as well as the intermolecular forces between molecules.

#### **Hydrogen Bonding:**

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- Strongest intermolecular attractive force
  - Need H directly attached to a very electronegative atom (N, O, F, Cl, Br, I) • Known as <u>donors</u>
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
  - Known as acceptors

e.g. H-O-H (water)



Hydrogen bond





(1-Propanol)

- Can hydrogen bond to itself
  - Has H directly attached to oxygen
- Has a high boiling points relative to its size due to hydrogen bonding
- Can dissolve in water very well

- Oxygen is electronegative and it is sp<sup>3</sup> hybridized
- The partial positive charge on H and the partial negative charge on O lead to their attraction
- Results in high boiling point (100 C) and high melting point by self-association
- HF, H<sub>2</sub>O and NH<sub>3</sub> form hydrogen bonds
- Water is a liquid at RT while ammonia is a gas
- Oxygen is more e-neg than nitrogen, so the protons on water have a higher positive partial charge than the protons on ammonia
- In an ammonia solution, water would be the hydrogen bond donor and ammonia would be the acceptor
- Water dissolves ammonia very well up to 18M



**Diethyl Ether** 

- Cannot hydrogen bond to itself
  - Has no H directly attached to oxygen (No donor)
  - Can H-bond to water because it has an acceptor
- Has a low boiling point
- Will not dissolve in water very well (although a little bit will be dissolved)



Can't form H-bonds with itself (not

Lone pairs on O can form H-bonds

with water (H-bond acceptor)

Poorly soluble in water

 $: O \xrightarrow{H} C \xrightarrow{C} CH_3$  $: O \xrightarrow{C} N$  $| CH_3$ 

Dimethylformamide

Can't form H-bonds with itself (not a H-bond donor) Lone pairs on O and N can form H-bonds with water (H-bond acceptor) Infinitely soluble (miscible) in water

Note: The more H-bonds it can form, the more soluble it is in water

#### **Dipole-Dipole Interactions:**

Dipole drawing convention:

 $\delta^+$   $\delta^-$ 

Partial positive charge is the "plus" end, partial negative charge is the arrow head

1. Methane; CH<sub>4</sub>

a H-bond donor)



- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole); gas at room temperature
- Low BP -164 °C (this is relatively low compared to water at 100 °C)
- Low MP -182 °C
- 2. Chloromethane, methyl chloride; CH<sub>3</sub>Cl



- H and C have similar electronegativity values (non-polar bond)

- Cl is very electronegative due to the fact that it only needs one electron to get inert gas configuration.
- Electron density is pulled toward the chlorine atom, creating a net dipole toward chlorine atom. A net dipole is the vector sum of individual bond dipoles.
- Has a higher MP and BP than methane

Dipoles in different molecules tend to line-up temporarily with each other (partial positive / negative charge on the molecule) – causes molecules to "stick" to each other



3. Dichloromethane, methylene chloride; CH<sub>2</sub>Cl<sub>2</sub>



- Liquid at room temperature BP 40 °C MP 95 °C
- More polar than chloromethane
- Not miscible with water
- 4. Trichloromethane, chloroform; CHCl<sub>3</sub>



- More polar than methylene chloride BP 61 °C MP 64 °C
- Higher than dichloromethane due to dipole dipole interaction
- 5. Tetrachloromethane, carbon tetrachloride; CCl<sub>4</sub> (toxic)



- Non-polar molecule (net-zero dipole)

- Has temporary dipoles since chlorine is polarizable (see below), BP ~77 °C
- Historically used as a dry-cleaning fluid

#### **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

$$\delta^+$$
  $\delta^-$ 

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	
Ar	-186 °C	
Kr	-153 °C	↓
Xe	-108 °C	Large atom/ High polarizability



Steric effect: interaction of a filled shell of electrons. Causes repulsion. • The larger the atom (expanded electron density), the easier the formation of temporary dipoles.

This is the reason why CH<sub>4</sub> associates with CH<sub>4</sub>, due to London forces

temporary association

#### C<sub>5</sub>H<sub>12</sub> hydrophobic bonding:



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 $\Delta G$

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 -  $\Delta G$  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:**



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

$$\Delta G$$
 determines product concentrations at equilibrium  $E_a$  determines rate of reaction

#### **Reaction proceeding through an intermediate**



Reaction Coordinate

### **Endothermic Reaction**: Positive $\Delta G$

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** energy needed to break bond into two

Example:

Radicals

Change in enthalpy = bond energy

 $H-CH_3 \iff H \bullet + \bullet CH_3$ 

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