Chapter 11: Intermolecular Forces and Liquids and Solids

What we will learn:

- Theory of liquids and solids
- Intermolecular forces
- Properties liquids
- Crystal structure
- X-ray diffraction
- Types of crystals
- Phase changes
- Phase diagrams

Kinetic Molecular Theory of Liquids and Solids

Gases

- Molecules are far apart, they easy can move (very weak interactions between molecules)
- Very low density
- Very compressible

Liquids

- Molecules are closer, they can move (stronger interactions between molecules)
- High density
- Slightly compressible

Solids

- Molecules are very close, they can not move (very strong interactions between molecules)
- Very high density
- Incompressible

A phase

• A homogenous part of the system separated from another part by a boundary

Density

$$d = m / V$$

m - mass (g) V - volume (mL)

Density of solids is bigger than density of liquids

Exception

Ice floating on water



SOLID





The bigger the mass, the bigger density. The bigger the volume, the smaller density

Intermolecular forces

- Attractive forces between molecules
- Weaker than forces within molecules between atoms (intramolecular)
- Stronger in solids and liquids than in gases
- Responsible for non-ideal properties of gases

van der Waals forces

- Dipole dipole
- Dipole induced dipole
- Dispersion

Dipole moment

 A vector showing how an electron cloud is moved from one part of a molecule to another part



Example

• A permanent dipole moment of H₂S

• A permanent dipole moment of HBr

• A zero resultsant dipole moment of CBr₄





Polarizability of a molecules

• A tendency of an electron cloud to be moved from one side of a molecule to another side

An ability to respond to an external perturbation, for example an electrostatic fileId

The bigger the polarizability, the bigger movement of an electron cloud





An electron cloud of CH_{A}

Induced dipole moment

• A temporary dipole moment which occurs in a molecule, in a presence of another charge or another dipole moment



A temporary dipole moment induced by a presence of a point charge



1. Dipole - dipole forces

- Weak forces between polar molecules
- Electrostatic interactions between dipole moments
- The bigger the dipole moments, the stronger forces
- Example: HBr and HF

The dipole - dipole forces depend on the orientation of the interacting molecules (dipole moments)

The molecule reorient themselves to maximize the attractive forces

Coulomb's law

A positive pole of one dipole is attracted by a negative pole of another dipole









2. Ion - dipole forces

- Forces between an ion (cation, anion) and a polar molecule
- Electrostatic interaction involving a charge and a dipole moment
- The bigger the charge (dipole moment), the stronger interaction
- Example: Na⁺ and HCl

Hydration

• Interactions between ions and water molecules

 $F = -405 \text{ k} \text{ l/mol} (\text{Na}^+)$

The bigger the charge, the bigger energy of hydration The bigger the ion radius, the smaller energy of hydration

$$E_{hydr} = -1926 \text{ kJ/mol } (Mg^{2+})$$

$$Na^{+} \text{ ion hydrated by water molecules}$$

- 3. Dipole induced dipole forces
- Weak forces between a polar molecule and a non-polar molecule
- Electrostatic interactions between a dipole moment and an induced dipole moment
- Depend on polarizability of a nonpolar molecule
- Example: H₂S...N₂





4. Dispersion forces

- Universal forces between molecules or atoms
- Electrostatic interactions between a temporary induced dipole moment of one molecule and a temporary induced dipole moment of another molecule
- The bigger the polarizability, the stronger dispersion forces
- The larger intermolecular contact, the bigger dispersion forces
- Example: He...He, N₂...N₂



Dispersion forces and polarizability

- The larger the number of electrons, the bigger polarizability
- The more diffuse the electron cloud, the bigger polarizablity



Dispersion forces and melting points

- The bigger the molecular mass, the bigger number of electrons
- The bigger the number of electrons, the bigger polarizability
- The bigger the polarizability, the higher melting point

Compound	Melting point (C)
CH	-182.5
CF	-150.0
CCİ	-23.0
CBr	90.0

Dispersion forces can be bigger than dipole-dipole forces

Example (boiling points)

$$T_{b} = -78.4 \text{ C} (\text{CH}_{3}\text{F})$$

$$T_{b} = 76.5 \text{ C} (\text{CCl}_4)$$



5. Hydrogen bonding

- Interaction involving a hydrogen atom in a polar bond and an electronegative atom
- Includes a strong dipole dipole interaction and strong dispersion forces
- Can form long chains
- Very important in proteins and DNA
- Example: H₂O...H₂O, NH₃...H₂O

Generally dipole - dipole interactions are stronger than dispersion interactions

Exception: CCl₄ (a nonpolar molecule) has stronger dispersion forces than CH₃F (a polar molecule)

Electronegative atom:

• An atom which likes electrons. These are atoms from the upper right corner of the periodic table (not involving noble gases)

Group Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																		2 He 4.0026
2	3 Li 6.94	4 Be 9.0122												5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305												13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 CI 35.45	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078		21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62		39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 OS 190.23	77 ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 1 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 HS [277.15]	109 Mt [276.15]	110 DS [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 FI [289.19]	115 Uup [288.19]	116 LV [293]	117 Uus [294]	118 Uuo [294]
				57	58	59	60	61	62	63	64	65	66	67	68	69	70		
*Lai	nthanoi	ds	*	La 138.91	Ce 140.12	Pr 140.91	Nd 144.24	Pm [144.91]	Sm 150.36	EU 151.96	Gd 157.25	Tb 158.93	Dy 162.50	HO 164.93	Er 167.26	T M 168.93	Yb 173.05		
**/	Actinoid	S	**	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 ES [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		

Nature of hydrogen bonds

- Hydrogen bond is an effective interaction between a polar bond involving a hydrogen atom, and an electronegative atom
- The stronger the polar bond, the stronger hydrogen bond
- The more electronegative the atom, the stronger hydrogen bond
- Hydrogen bond involves dipole dipole and dispersion interactions of the three atoms arranged in a linear form



A - H ... B

- A H Polar bond
- A H ... A A, B Electronegative atom

Examples of hydrogen bonding



Hydrogen bonding in water is responsible for unusual properties of water

- Water is liquid at room temperature (H₂S is gas)
- Density of ice is smaller than a density of liquid water (opposite to almost all other compounds)
- Water has a relatively high boiling point (H₂S has much smaller)
- Water has a very high specific heat (can cumulate a lot of energy)

Density of water

Water is an exception showing that a density of solid water (ice) is smaller than a density of liquid water

In a liquid water there are hydrogen bonds between water molecules, however water molecules are not so separated as in ice

Hydrogen bonding between water molecules in ice form a complex three dimensional structure keeping water molecules apart from each other



Questions

- 1. What is the predominate intermolecular force in each of the following substances?
 - Solid CO₂ (the molecule does not have a permanent dipole moment, therefore the dispersion interaction is the only interaction between two molecules)
 - Liquid CH₃CH₂OH (the molecule has a polar bond "O-H" and an electronegative atom "O", therefore the hydrogen bond will be the strongest interaction between two molecules)
 - Liquid SCl₂ (the molecule has a permanent dipole moment, therefore the dipole-dipole interaction will be the strongest interaction between two molecules)

- MgCl₂ dissolved in liquid SCl₂ (when MgCl₂ is dissolved in SCl₂ it dissociates into Mg²⁺ cation and Cl⁻ anions. Those ions interact with a permanent dipole moment of SCl₂, therefore the ion-dipole interaction will be the strongest)
- CO₂ dissolved in SCl₂ (the CO₂ molecule does not dissociate into ions and does not have a permenent dipole moment, when is dissolved in SCl₂. Therefore there will be an interaction between a permanent dipole moment of SCl₂ and an induced dipole moment of CO₂)
- NaCl dissolved in water (NaCl dissociates into Na⁺ cation and Cl⁻ anion. The ions interact with a permanent dipole moment of water. The ion-dipole interaction is the strongest)

- 2. Which molecules can form hydrogen bonding:
 - H₂S (The molecule has a polar bond "S-H" and an electronegative atom "S", therefore it can form a hydrogen bond)
 - C₆H₆ (The molecule does not have a polar bond nor an electronegative atom, it can not form a hydrogen bond)
 - CH₃OH (The molecule has a polar bond "O-H" and an electronegative atom "O", it can form a hydrogen bond)
 - CO₂ (The molecule has a polar "C-O" bond, but it does not have a hydrogen atom, it can not form a hydrogen bond)

Properties of Liquids



Forces between molecules of a liquid are stronger than the forces between a molecule of the liquid and a molecule of the glass container Forces between molecules of a liquid are weaker than the forces between a molecule of the liquid and a molecule of the glass container

Surface tension

Surface tension is the energy required to increase the surface of a liquid

Liquids with strong intermolecular forces have high surface tensions

LIQUID

Hydrophobic surface

• A surface which is repulsive to water

Hydrophilic surface

• A surface which is attractive to water

Examples

- · bugs walking on water
- water beads on an apple

Cohesion

• The intermolecular attraction between molecules of the same substance

Adhesion

• The intermolecular attraction between molecules of different substances

Adhesion > Cohesion

Adhesion < Cohesion



Viscosity

• It is a measure of a fluid's resistance to flow. The bigger the viscosity, the fluid flows more slowly



Intermolecular interactions are stronger in a fluid with bigger viscosity than in a fluid with smaller viscosity

Example

• Water does not flow down from a narrow tube



The viscosity of a liquid usually decreases as the temperature increases

Thermal motions decrese the attractive interactions between molecules of a liquid, and decrese the viscosity of the liquid



Crystal structure

• A solid state which possesses rigit and long range order; its atoms, molecules or ions occupy specific positions

Unit cell

• A basic structural unit, which repeats in a crystalline solid



Packing spheres

- Arrangement of spheres in a three dimensional space
- Simple cubic
- Body-centered cubic
- Face-centered cubic

Coordination number

 The number of atoms surrounding an atom in a crystal lattice



X-ray diffraction of crystals

• The scattering of X rays by the units of a crystalline solid

Bragg equation

 $2 d \sin \tau = n \lambda$

- d distance between adjacent planes
- λ wavelength of the X ray
- τ angle between the X ray and the plane of crystal
- n integer number 1, 2, 3, ...



2 d sin τ = n λ

Types of crystals

- Ionic; they are composed of charged atoms (cations, anions), they are held together by electrostatic interactions
- Covalent; they are composed of neutral atoms, they are held together by covalent bonds
- Molecular; they are composed of neutral molecules, they are held together by van der Waals (dispersion) forces or hydrogen bond forces
- Metalic; they are composed of metal atoms, they are held together by delocalized electrons





METAL



GCh11-34

Amorphous solids

• A solid which lacks a regular three-dimensional arrangement of atoms

Example

- Glass an optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystalization. Glass behaves more like an overcooled liquid rather than a solid
- Rubber
- Polymers

Phase Changes

A phase

• A homogenous part of a substance separated from another part by a boundary

Melting

• Change from a solid to a liquid

Evaporation

• Change from a liquid to a gas

Sublimation

• Change from a solid to a gas

Phase change

• Transformation of a substance from one phase to another

Freezing

• Change from a liquid to a solid

Condensation

• Change from a gas to a liquid

Desublimation

• Change from a gas to a solid

Liquid-vapor equilibrium

• A dynamic equilibrium where the rate of evaporation is balanced by the rate of condensation

In equilibrium a number of molecules which are going from a liquid to a gas, is the same as a number of molecules which are going from the gas to the liquid, at the same time

Vapor pressure

The equilibrium pressure of vapor over the liquid at a particular temperature

Molar heat of vaporation

 The energy (in kilojules) which required to vaporize 1 mole of a liquid [ΔH_{vap}]



 $q = n \Delta H_{vap}$

q - heat (energy)
 n - number of moles
 △H_{vap} - molar heat of vaporation

Clausius-Clapeyron equation

$$ln P = - (\Delta H_{vap}) / (RT) + C$$

- P vapor pressure
- ΔH_{vap} molar heat of vaporation
- R gas constant (8.314 J / K mol)
- T absolute temperature
- C constant

The Clausius-Clapeyron equation is used to calculate the vapor pressure of the liquid at a particular temperature

A liquid with stronger intermolecular forces has a small vapor pressure

A liquid with weak intermolecular forces has a big vapor pressure



At higher temperature, the vapor pressure is bigger

The the same temperature the vapor pressure of a liquid with stronger intermolecular forces, is smaller than the vapor pressure of a liquid with weaker intermolecular forces If we know the value of ΔH_{vap} and P of a liquid at one temperature, we can calculate the vapor pressure of the liquid at different temperature

$$In P_{1} = -(\Delta H_{vap}) / (RT_{1}) + C$$

$$In P_{2} = -(\Delta H_{vap}) / (RT_{2}) + C$$

$$In P_{1} - In P_{2} = (\Delta H_{vap}) / R (1/T_{2} - 1/T_{1})$$

$$In (P_{1} / P_{2}) = (\Delta H_{vap}) / R (1/T_{2} - 1/T_{1})$$

Problem

Calculate the vapor pressure of diethyl ether ($CH_3CH_2-O-CH_2CH_3$) at 32 C. The vapor pressure of diethyl ether is 401 mmHg at 18 C, the molar heat of its vaporization is 26 kJ/mol.

Data

$$\ln (P_{1}/P_{2}) = (\Delta H_{vap}) / R (1/T_{2} - 1/T_{1})$$

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\Delta H_{vap} = 26 \text{ kJ/mol}

T_1 = 18 \text{ C} = 291 \text{ K}

T_2 = 32 \text{ C} = 305 \text{ K}

P_1 = 401 \text{ mmHg}
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In $(401/P_2) = (26000 \text{ J/mol}) / (8.314 \text{ J/K mol}) (1/305 \text{ K} - 1/291 \text{ K})$ In $(401/P_2) = -0.493$ $401/P_2 = e^{-0.493}$ $P_2 = 656 \text{ mmHg}$

Specific heat

• It is amount of heat needed to raise the temperature of one gram of the substance by one degree of Celsius

A substance with a big specific heat cumulates more energy than a substance with a small specific heat

 $q = m s \Delta t$

Examples

q - heat (energy)
m - mass
s - specific heat
∆t - temperature change

Specific heat (J/g C) Al 0.900 Cu 0.385 H_2O 4.184

Heat

• Energy Transfer between substances of different temperature



A bigger specific heat indicates on stronger interactions betweem molecules

Temperature is a measure of molecular moves. The more the molecular moves, the higher temperature

The stronger the intermolecular forces, the less molecular moves



Boiling point

- The temperature when a liquid is changing into a gas
- The vapor pressure of a liquid is equal to the external pressure

A GAS D LIQUID THEAT

A higher boiling point indicates on stronger interactions between molecules in a liquid

Substance	Boiling Point (C)	∆H _{vap} (kJ/mol)
Benzene	80.1	31
Ethanol	78.3	39
Methane	-164	9.2
Water	100	40.8



The bigger the number of electrons, the higher boiling point

The more the branched molecule, the lower boiling point

A bigger number of electrons is responsible for bigger plarizability and bigger disspersion forces between atoms or molecules, which inceases a boiling point

There are more attractive interactions between linear molecules rather than branched molecules, which yields in a higher boiling point of a linear molecule

Liquid - Solid equilibrium

• A dynamic process of melting and freezing, which takes place at the same time



In equilibrium a number of molecules which are going from liquid to solid, is the same as a numer of molecules which are going from solid to liquid, at the same time

Freezing point

• The temperature when a liquid is changing into a solid

A higher freezing point indicates on a stronger interaction between molecules in a solid

Molar heat of melting (fusion)

• The energy (in kilojules) which is required to melt 1 mole of a solid $[\Delta H_{fus}]$

Substance	Melting Point (C)	∆H _{fus} (kJ/mol)
Benzene	5.5	10.9
Ethanol	-117.3	7.6
Methane	-183	0.86
Water	0	6.01

Supercooling

• An unstable state of a liquid where the liquid is temporary cooled to below the freezing point

Addition of a small "seed" cristal transforms the supercooled liquid to a solid

Solid - Vapor equilibrium

• A dynamic process of sublimation and desublimation, which takes place at the same time

In equilibrium a number of molecules which are going from solid to gas, is the same as a numer of molecules which are going from gas to solid, at the same time

Molar heat of sublimation

 The energy (in kilojules) which is required to sublimate 1 mole of a solid [ΔH_{sub}]

Illustration of Hess's law

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

for the phase changes at the same temperature



Examples

- Naphtalene
- lodine
- Carbon dioxide

Phase diagram

• A diagram showing coexistence of a vapor, a liquid and a solid phase of a substance

Experiment

Water is heated in a closed cylinder. By moving the pistion, we can change the pressure. Then we measure the temperature and the pressure



We plot the pressure versus the temperature, and we report a presence of the solid, liquid and the vapor phases

Triple point

• The solid, the liquid and the vapor phases exist at the same time



In the triple point all three phases are in equilibrium with one another

Questions

- Can we have solid water (ice) at the temperature higher than 0 C
- Yes, if we decrease the pressure
- Can we have liquid water at the temperature lower than 0 C
- Yes, if we increase the pressure



Phase diagram and critical points

At the temperature higher than the critical point temperature, there is no liquid phase

At the temperature smaller than the critical point temperature, there are the liquid and the vapor phases



A vapor can be condensed into a liquid by increasing the external pressure at a particular temperature. However there is a temperature (critical temperature) that this process can not occur

Critical temperature

• The temperature above which a gas phase can not be condenced into a liquid, no matter how great the applied pressure

Critical pressure

• The minimum pressure that corresponds to the critical temperature

Substance	T _c (C)	P _c (atm)
Benzene	Ž88	48
Ethanol	243	63
Methane	-83	45.6
Water	374	219.5

Phase diagram of carbon dioxide

The liquid phase is not stable below 5.2 atm, so that only the solid and vapor phases can exist under atmospheric conditions



Problem

• Calculate the amount of energy needed to heat 12.6 g of liquid water from the room temperature (20 C) to the boiling point (100 C).

Data

 $q = m s \Delta t$

- q energy; m mass;
- Δt temperature change;
- s specific heat (liquid water = 4.184 J/g C)

Solution

Energy needed to heat water from 20 to 100 C

 $q = m s \Delta t$

= (12.6 g) (4.184 J/g C) (100 C - 20 C)

= 4217 J = 4.217 kJ

Problem

 Calculate the amount of energy needed to heat 346 g of liquid water from 0 to 182 C.

Data

$$q = m s \Delta t$$
 $q = n \Delta H_{vap}$ $q = q_1 + q_2 + q_3$

- q heat (energy); m mass; n number of moles of water
- Δt temperature change
- ΔH_{vap} molear heat of vaporation (water = 40.79 kJ/mol)
- s specific heat (liquid water = 4.184 J/g C; water steam = 1.99 J/g C)
- q_1 energy needed to heat water from 0 to 100 C
- q_2 energy needed to evaporate of water at 100 C
- q_3^- energy needed to heat steam from 100 to 182 C

Solution

Step 1. Energy needed to heat water from 0 to 100C

$$q_1 = m \ s \ \Delta t$$

= (346 g) (4.184 J/g C) (100 C - 0 C) n = 1 mol x 346 g/18.02 g
= 145 kJ = 19.2 mol

Step 2. Energy needed to evaporate of water

$$q_2 = n \Delta H_{vap}$$

= (19.2 mol) (40.79 kJ/mol)
= 783 kJ

Number of water moles:

Step 3. Energy needed to heat steam from 100 C to 182 C

The total energy:

$$q = q_1 + q_2 + q_3$$

= 984.5 kJ

Problem

Calculate the heat released when 68 g of steam at 124 C is converted to water at 45 C

Data

 $q = m s \Delta t$ $q = n \Delta H_{vap}$ $q = q_1 + q_2 + q_3$

- q heat (energy); m mass; n number of moles of water
- ∆t temperature change
- ΔH_{van} molear heat of vaporation (water = 40.79 kJ/mol)
- s specific heat (liquid water = 4.184 J/g C; water steam = 1.99 J/g C)
- q_1 energy released from cooling steam from 124 to 100 C
- q_2 energy released from condensation of steam to water at 100 C
- q_3^- energy released from cooling water from 100 to 45 C

Step 1. Energy released from cooling steam from 124 to 100 C

 $q_1 = m \ s \ \Delta t$ = (68 g) (1.99 J/g C) (100 C - 124 C) = - 3.24 kJ

Step 2. Energy released from condensation of steam into water at 100 C

 $q_2 = n \Delta H_{vap}$ = (3.77 mol) (- 40.79 kJ/mol)

= - 153.9 kJ

Step 3. Energy released from cooling water from 100 to 45 C

The total energy:

$$q = q_1 + q_2 + q_3$$

= -172.78 kJ