Chapter 13: Liquids and Solids

In our study of gases, we related the physical properties of gases to the behavior of the molecules that make up the gas through the KINETIC - MOLECULAR THEORY.

We are now going to do a similar comparison between physical properties and molecule behavior for liquids and solids. Then we will look at the changes that occur when a substance changes phase ie   gas ⇌ liquid ⇌ solid.

There are 3 states of matter: gas   liquid   solid

fluid   condensed : particles are in close contact with each other
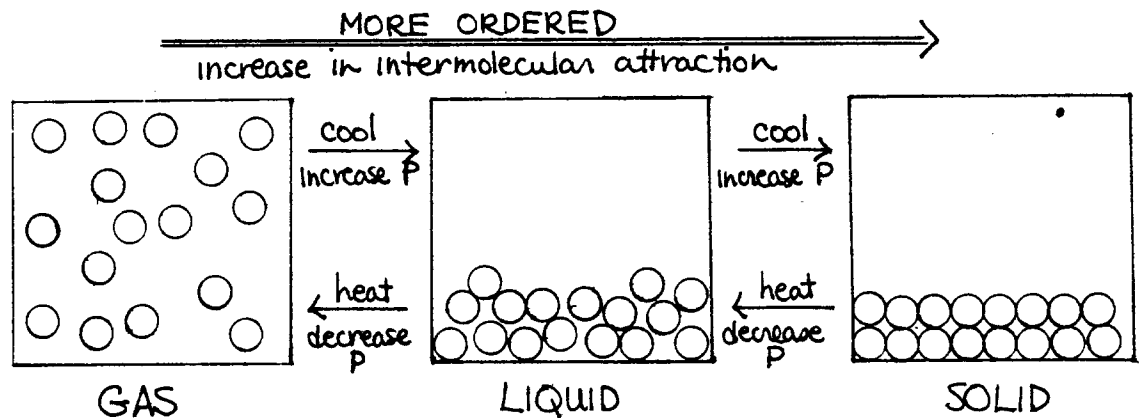
If we could look at molecules:

MORE ORDERED ⟶

increase in intermolecular attraction

Fig 13-1

GAS — cool / Increase P → ← heat / decrease P — LIQUID — cool / Increase P → ← heat / decrease P — SOLID

GAS	LIQUID	SOLID
1. no shape	1. no shape	1. definite shape
2. compressible	2. not very compressible	2. not compressible
3. low density	3. medium density	3. high density
4. diffuse rapidly	4. diffuse thru liquids	4. very slow diffusion
5. disordered	5. disordered	5. ordered

Effect of pressure :   think of P as forcing the molecules together.

Effect of temperature :   As T decreases, kinetic energy of molecules decrease until forces of attraction between molecules overcomes KE. ⇒ liquifaction but there is still some disorder.
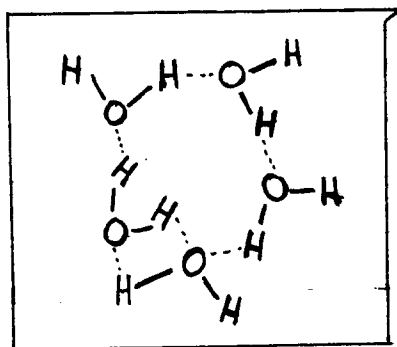
As T continues to decrease, there are stronger forces of attraction

which cause ordering to occur and at low enough temperatures, the liquid solidifies or freezes.

But what are these intermolecular forces in gases and liquids?

First, let's illustrate what we are discussing.

Consider a beaker of water (illustration of hydrogen bonding) $H_2O = H \overset{\cdot\cdot}{\underset{H}{O}}$

⋯ intermolecular forces are forces <u>between</u> individual particles

— intramolecular forces are within each molecule. These are strong covalent bonds that bind the atoms together in molecule.

Intermolecular forces operate over short distances. If not for these forces, the condensed phases (liquids & solids) would not exist; gases would never change to liquids and solids.

Kinds of Intermolecular Forces in Liquids

1. ion-ion interaction : <u>molten</u> salts ($NaCl$, $MgBr_2$, $KClO_4$ etc in molten state)
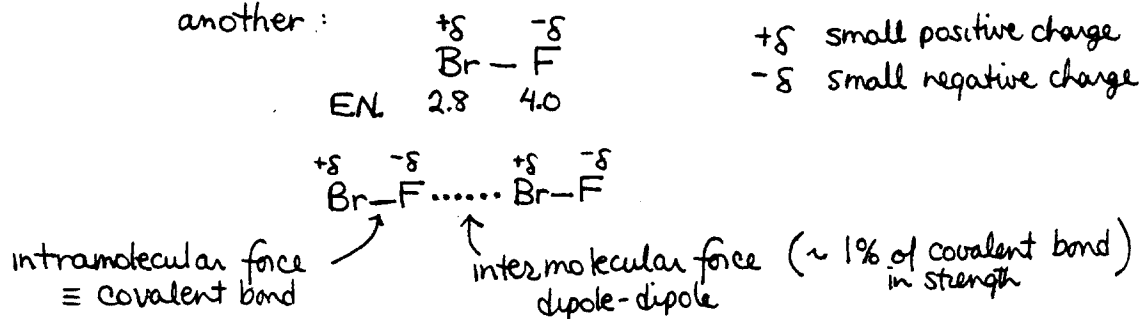
very strong interaction

force of attraction between 2 oppositely charged ions — governed by

$$\text{Coulomb's Law}: \quad F \propto \frac{q^+ q^-}{d^2}$$

where q^+ charge on cation
q^- charge on anion
d distance between them

characteristics of molten salts:
  (1) have high boiling points because ion-ion interaction is strong
  (2) ionic substances with multiple charges (Al^{3+} , Mg^{2+} , O^{2-} , S^{2-}) have higher B.P. than those with singly charged ions (Cl^- , Na^+ , etc) due to Coulomb's Law.
  (3) conduct electricity well since ions are mobile.

2. <u>Dipole-dipole interactions</u> : polar covalent molecules ($CHCl_3$, BrF, SO_2)
   medium strength interaction — less strong than ion-ion attraction
   force of attraction between $+\delta$ end of one molecule and $-\delta$ end of
   another :

$$\overset{+\delta \quad -\delta}{Br - F}$$

$$EN \quad 2.8 \quad 4.0$$

$+\delta$ small positive charge
$-\delta$ small negative charge

$$\overset{+\delta \quad -\delta}{Br-F} \cdots \cdots \overset{+\delta \quad -\delta}{Br-F}$$

intramolecular force ↗
≡ covalent bond

↑ intermolecular force ($\sim 1\%$ of covalent bond in strength)
   dipole-dipole

characteristics of liquids of polar covalent molecules
   (1) Boiling points are lower than for molten salts since
       dipole-dipole interactions are weaker than ion-ion interactions
   (2) ∴ these liquids are more volatile.

3 <u>Hydrogen bonding</u> : polar covalent molecules composed of H bonded to a small highly E.N. atom such as O, N, F
   special case of dipole-dipole interactions
   stronger interaction than dipole-dipole interactions.
   force of attraction between $+\delta$ end of molecule (H) and $-\delta$ end
   of another (small, highly electronegative element such as O, F, N.

examples : HF, H_2O, NH_3, CH_3OH, CH_3COOH

$$\overset{++\delta \quad =\delta}{H-F} :::::: \overset{++\delta \quad =\delta}{H-F}$$
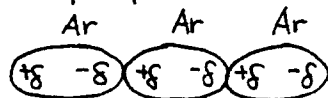
characteristics
(1) strength of H bond may be as high as 10% of covalent bond
(2) compounds having H bonding have anomalously high boiling
    points.

4. <u>London forces</u> : non polar covalent molecules (Ne, CO_2, Cl_2, CH_4)
   (also named Van der Waals attraction, dispersion forces, dipole-induced dipole
   attractive forces that exist over very short distances ($F \propto \frac{1}{d^7}$)
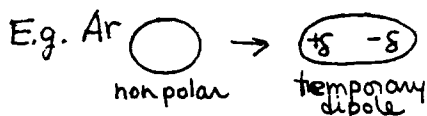
E.g. Ar ◯ → ⬭ $+\delta$ $-\delta$ but at any instant, a non-polar molecule
    non polar   temporary   is a temporary dipole
                 dipole

a temporary dipole can induce a dipole in other atoms.

Ar   Ar   Ar
$+\delta$ $-\delta$ $+\delta$ $-\delta$ $+\delta$ $-\delta$

Characteristics

more polarizab[le]

(think of water balloons)

(1) the larger the molecule, the easier it becomes to induce dipoles since the electron cloud is larger and more easily distorted.

∴ London forces are more important in larger molecules (molecules with higher MW's) and are oftentimes more important in determining physical properties of liquids than permanent dipole-dipole interactions.

Example: Table 13-3 H-Cl   permanent dipole-dipole energy 3.3 kJ/mol
                                London energy   17.8 kJ/mol

Lets consider some examples to illustrate these intermolecular forces:

Consider the boiling points of the noble gases as a function of molecular size:

Noble Gas	Molecular Weight*	BP (°C)
He	4	−268.9
Ne	20	−246.0
Ar	40	−185.7
Kr	84	−152.3
Xe	131	−107.1
Rn	222	−61.8

* as a measure of size

The increase in b.p. as function of molecular size can be interpreted as it becoming more and more difficult to break the intermolecular forces between molecules in the liquid to form isolated molecule in the gas. ∴ more + more energy is required to do this as molecules get larger.

The intermolecular forces in this case are London Forces.

Liquid   → +energy   Gas
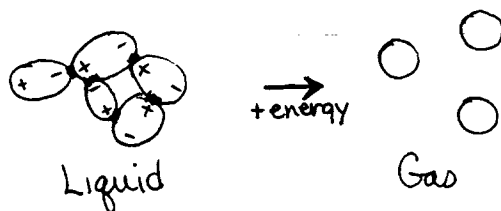
Another series of nonpolar molecules are the hydrocarbons. Boiling point increases due to increasing London forces.

Formula	Name	Structure	Molecular Wt.	B.P.(°C)
CH_4	methane	$-\overset{\shortmid}{\underset{\shortmid}{C}}-$	16	−164
C_2H_6	ethane	$-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-$	30	−88.6
C_3H_8	propane	$-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-$	44	−42.1
n-C_4H_{10}	normal butane	$-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-$	58	−0.5
n-C_5H_{12}	normal pentane	$-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-\overset{\shortmid}{\underset{\shortmid}{C}}-$	72	36.1

The following is more complicated: the hydrides of IVA, VA, VIA and VIIA elements
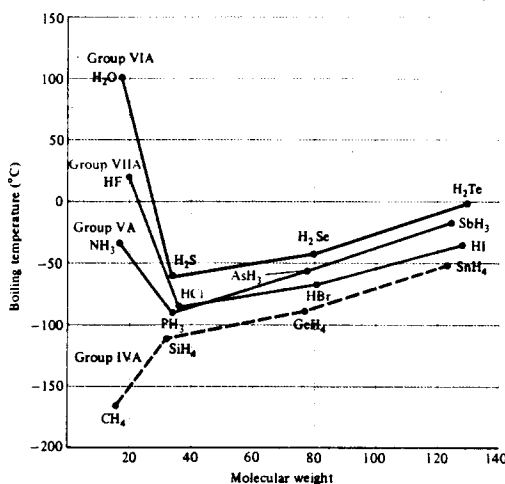

FIGURE 13-5 Boiling points of some hydrides as a function of molecular weight. The anomalously high boiling points of NH_3, H_2O, and HF compared with those of other hydrides of the same groups are due to hydrogen bonding. The electronegativity difference between H and C is small and there are no lone pairs on C; thus, CH_4 is not hydrogen bonded.

Group IVA hydrides: $CH_4 < SiH_4 < GeH_4 < SnH_4$ in size ; these are nonpolar.

∴ London forces are operating and become stronger as molecules get larger.

∴ <u>B.P. increases as molecular weight increases.</u>

Group VA hydrides: $NH_3 < PH_3 < AsH_3 < SbH_3$ in size

• these are polar $H\overset{}{\diagup}\overset{-\delta}{\underset{\underset{H}{\shortmid}}{\ddot{N}}}\diagdown H_{+\delta}$ and dipole-dipole interactions are expected.

These should decrease as MW ↑ since ΔEN between VA element and H decrease. The result : BP ↓ as MW ↑. This is <u>not</u> seen.

• B.P. increases since size of molecule increases and London forces increase

• the higher B.P. for NH_3 is due to H-bonding.

Group VIA and VIIA hydrides: same trend as VA: HF and H_2O have anomolously high B.P. due to H-bonding.

To summerize,

(1) without intermolecular forces, liquids and solids would not exist.

(2) these forces affect physical properties of liquids

(3) the relative strengths of the forces are as follows:

London forces ~ dipole-dipole interactions < hydrogen bonding < ion-ion interaction

Example: Arrange the following substances in order of increasing boiling point

$$C_2H_6 \quad NH_3 \quad Ne \quad NaCl \quad AsH_3 \quad MgO$$

lowest BP	Ne	<	C_2H_6	<	AsH_3	<	NH_3	<	NaCl	<	MgO
	monatomic molecule (small)		nonpolar covalent molecule (larger)		polar covalent molecule (even larger)		polar covalent molecule		ionic		ionic

Forces: London   London   London   London   ion-ion   ion-ion

                                              dipole-dipole   H-bonding   (contains ions with greater charge

$$F \propto \frac{q_1 q_2}{d^2}$$

Note: all covalent compounds have London dispersion forces.

The Liquid State − Properties (depend on intermolecular forces)

(1) viscosity : a measure of the resistance to flow

       e.g. molasses in January (sugar has much H-bonding) has higher viscosity than gasoline (C_8H_{18})

       depends on intermolecular forces, size and shape of molecules

       is a function of temperature: as T ↑, intermolecular forces ↓, viscosity ↓

(2) surface tension : a measure of inward forces that must be overcome to expand the surface area of liquid. Surface tension is what allows bugs to "walk" on water and water drops to be spheres.

particle 2 is equally attracted to all its neighbors

particle 1 at the surface is NOT completely surrounded by neighbors and holds more tightly to the ones it has.
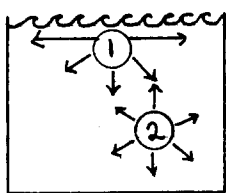
(3) capillary action : the process by which a liquid may climb a small diameter
tube (e.g. roots of plants)

the result of adhesive forces (force of attraction between
the liquid and another surface) being greater than
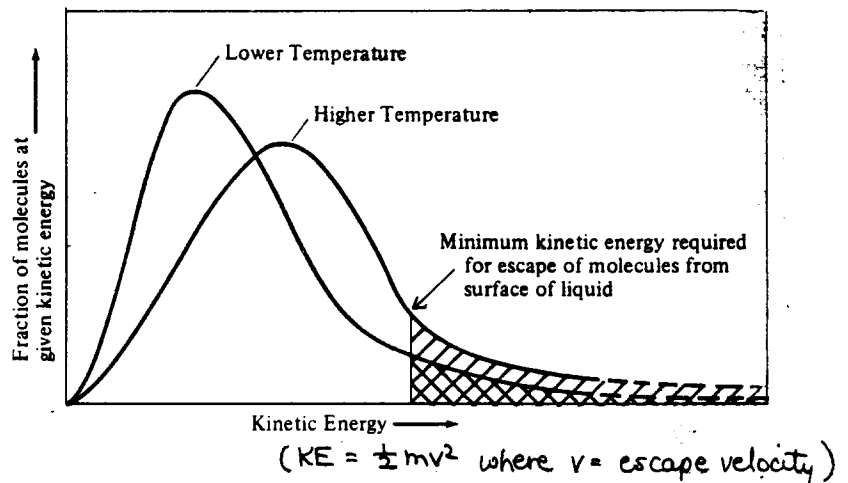cohesive intermolecular forces (forces holding the
liquid together)

consider the meniscus:

H_2O

Hg

adhesion > cohesion   cohesion > adhesion
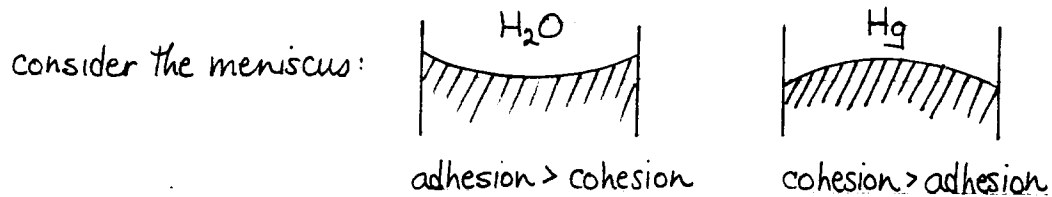
Evaporation, Vapor Pressure and Boiling Point of Liquids

What is involved when a liquid changes to a gas?

Evaporation : the process by which molecules break away from the surface of a liquid
and become a gas

molecules need a minimum amount of kinetic energy ($\propto$ absolute T)
in order to do this.

FIGURE 13-10 Distribution of kinetic energies of molecules in a liquid at different temperatures. At the lower temperature, a smaller fraction of the molecules has the energy required to escape from the liquid, so evaporation is slower at the lower temperature.

Lower Temperature

Higher Temperature

Fraction of molecules at given kinetic energy

Minimum kinetic energy required for escape of molecules from surface of liquid

Kinetic Energy

(KE = $\frac{1}{2}mv^2$ where v = escape velocity)

When the temperature is higher, there is a greater fraction of molecules with
the necessary kinetic energy to escape from the liquid.
∴ the rate of evaporation is higher at higher temperatures. (sensible)

the reverse process is called <u>condensation</u>.

In a closed container, a dynamic equilibrium is set up after a period of time.
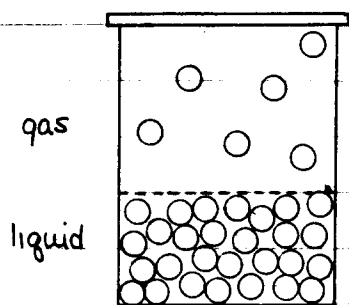
molecules in liquid $\underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}}$ molecules in vapor

at equilibrium, the rate at which molecules in liquid become molecules in gas (vapor) is equal to the rate at which gaseous molecules become liquid.

If the top of the beaker were removed, the system could <u>NOT</u> reach equilibrium and the water would evaporate as the system <u>tried</u> to reach equilibrium. (An illustration of Le Chatelier's principle — a system at equilibrium will react to undo any stress put on the system.

<u>Vapor Pressure</u> : partial pressure of vapor above the surface of the liquid AT EQUILIBRIUM with the vapor.

• as temperature increases, the vapor pressure increases.
• vapor pressures of different liquids are different due to their having different intermolecular forces.
• in general, liquids with strong intermolecular forces (molten salts, H_2O etc) have low vapor pressures and high boiling points.

<u>Boiling Point</u> : the temperature at which the vapor pressure of the liquid equals the applied pressure — usually atmospheric pressure.

∴ at the boiling point,   vapor pressure = applied pressure

at this temperature, bubbles of vapor form beneath the surface of the liquid and rise to the surface. In other words, evaporation occurs EVERYWHERE in the liquid, not just at the surface.
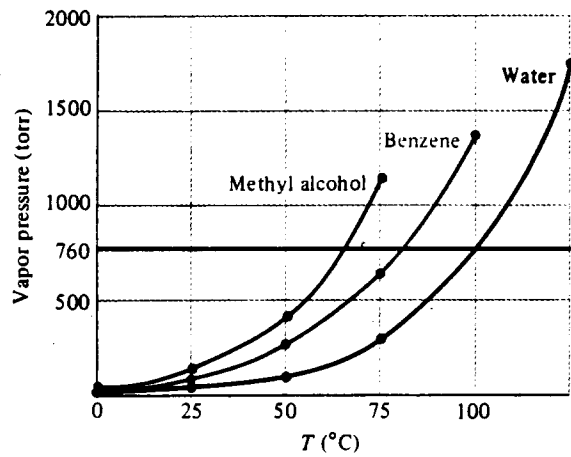
These are plots of vapor pressure of some liquids vs temperature. The <u>NORMAL</u> boiling point of these liquids occurs at the temperature where their vapor pressure equals 1 atm (760 torr) (Figure 13-13)

at the boiling point, the liquid and vapor exist in equilibrium.

$$\text{liquid} \underset{\text{condensing}}{\overset{\text{boiling}}{\rightleftharpoons}} \text{vapor}$$
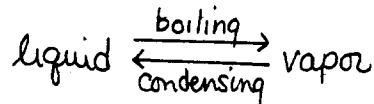
Since different liquids have different intermolecular attractions, they have different vapor pressures and different boiling points at the same applied pressure. It is possible to separate a mixture of liquids into its components by exploiting their different boiling points. This process is called DISTILLATION. The liquid with the lowest boiling point is separated out first (Fig 13-14)

<u>The Solid State</u> – An Introduction

Just as the intermolecular forces in liquids (ion-ion, dipole-dipole, hydrogen-bonding, London) must be broken for the liquid to become a gas, the intermolecular forces existing in solids (more later) must be overcome for a solid to become a liquid.

<u>Melting Point (Freezing Point)</u> : the temperature at which liquid and solid exist together at equilibrium

At the melting point, $\text{solid} \underset{\text{freezes}}{\overset{\text{melts}}{\rightleftharpoons}} \text{liquid}$ dynamic equilibrium

the <u>normal</u> melting point is the melting point at 1 atm pressure.

How do we break the intermolecular forces holding solids and liquids together?

ANS. We add heat!!!

(Figure 13-15)
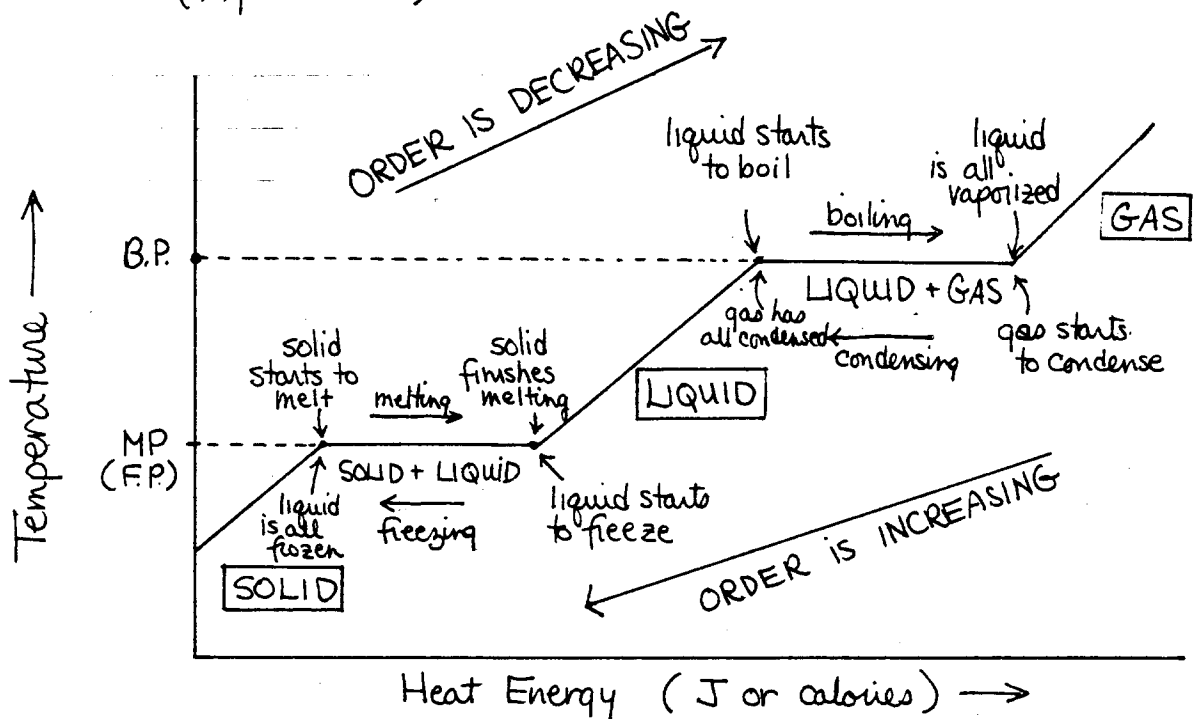
Heat is absorbed by system as solid ⟶ liquid ⟶ gas.
   This process of breaking intermolecular forces is ENDOTHERMIC.
Heat is released by system as gas ⟶ liquid ⟶ solid
   This process is EXOTHERMIC.

The amount of heat absorbed or released by a system during phase changes
   can be accurately calculated.

Terminology:
Joule and calorie are units of heat.   1 calorie = 4.184 J
Specific heat of a substance in a certain phase (gas, liquid, solid)
      is the amount of heat required to raise the temperature of 1 g
      of the substance by 1 °C. with no change in state.
         Specific heat has units of (J/g °C).   Heat = Sp. H. × mass × ΔT
Heat of fusion : the amount of heat required to melt 1 g of a solid
      at its melting point .   Units : (J/g).   It is also the amount
      of heat released when 1 g of a liquid freezes at its
      freezing point.
                Amount of Heat = heat of fusion × mass

Extra

Difference Between Specific Heat $(\frac{J}{g \cdot c})$ and Heat of Fusion/Vaporization $(\frac{J}{g})$

Specific heat is a constant particular to a certain substance in a specific phase which relates how much heat in joules is necessary to change the temperature of a certain amount of the substance (without changing its phase).

Example: If 15.0 g of iron(s) cools from 35.0°C to 9.0°C, thereby releasing 173 J of heat, what is the specific heat of iron(s)?

$$\text{Specific heat} \left(\frac{J}{g \cdot C}\right) = \frac{\text{heat (J)}}{\text{mass(g)} \times \Delta T (°C)} = \frac{173 \text{ J}}{15.0 \text{ g} \times (35.0-9.0)°C}$$

$$= 0.444 \text{ J}/g°C$$

Heat of Fusion/Vaporization $(\frac{J}{g})$ is a constant particular to a certain substance that is changing phase at the temperature where the phase change occurs:

Heat of fusion	solid ⇌ liquid	occurs at freezing/melting pt
Heat of vaporization	liquid ⇌ gas	occurs at boiling point

The constant relates how much heat is necessary for the phase change to occur at the phase change temperature for a certain mass of compound.

Example: If 327 J of heat are removed from 3.00 g of CH_3CH_2OH (ℓ) at -117°C, what is the heat of fusion of ethanol? The freezing point of ethanol is -117°C.

$$\text{Heat of Fusion} \left(\frac{J}{g}\right) = \frac{\text{heat (J)}}{\text{mass (g)}} = \frac{327 \text{ J}}{3.00 \text{ g}} = 109 \text{ J}/g$$

Note: temperature or temperature change is not involved in the calculation for heat of fusion or heat of vaporization because the process is occurring at the phase change temperature.

Heat of vaporization: the amount of heat required to vaporize 1 g of a liquid to a gas at its boiling point. Units: (J/g). H is also the amount of heat released when 1 g of vapor condenses to 1 g of liquid at the boiling point.   Amount of heat = heat of vap. × mass

Example: How many joules of energy must be absorbed by 500 g of H_2O at 50°C to convert it to 500 g of steam at 120°C?

Given: Specific heat H_2O (l) : 4.18 J/g°C
Specific heat H_2O (g) : 2.03 J/g°C
Heat of vaporization H_2O: 2.26×10^3 J/g
B.P. H_2O : 100°C

liquid $\xrightarrow{①}$ liquid $\xrightarrow{②}$ gas $\xrightarrow{③}$ gas
50°C   100°C   100°C   120°C
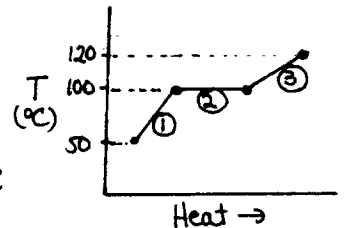
where ① heat needed to raise T of 500 g H_2O to its B.P. at 100°C
② heat needed to change all water into steam at 100°C
③ heat needed to raise T of steam from 100°C to 120°C

Total Heat Absorbed = ① + ② + ③

$$= \left[Sp.\ H.\ H_2O(l) \times mass\ H_2O \times \Delta T \right] + \left[H.\ of\ vap. \times mass\ H_2O \right]$$
$$+ \left[Sp.\ H.\ of\ H_2O(g) \times mass\ H_2O \times \Delta T \right]$$

$$= \left[4.18 \frac{J}{g°C} \times 500g \times (100-50°C) \right] + \left[2.26 \times 10^3 \frac{J}{g} \times 500g \right]$$
$$+ \left[2.03 \frac{J}{g°C} \times 500g \times (120-100°C) \right]$$

= 104 kJ + 1130 kJ + 20 kJ
= 1250 kJ
= 1.25×10^6 J

Note that the energy required to break the intermolecular bonds in liquid water is very high due primarily to hydrogen bonding.

Example: How much heat (in kJ) must be removed when cooling 155 g of benzene, C_6H_6, at 120.0°C to solid benzene at 5.48°C?

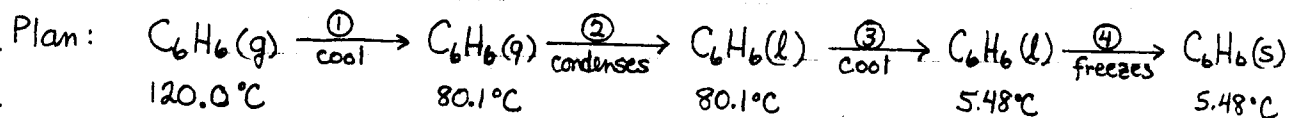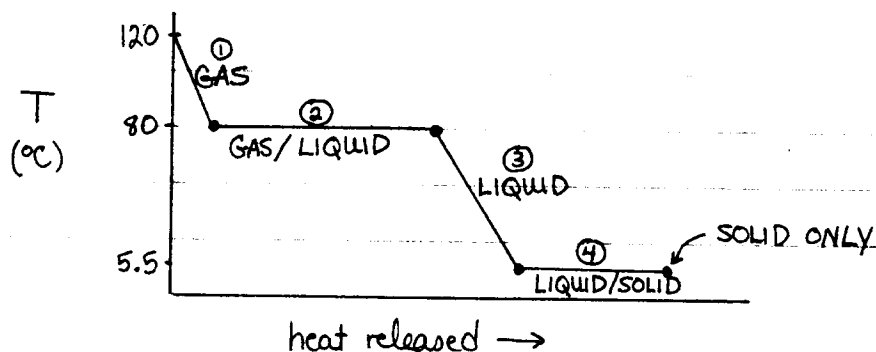Given for benzene: b.p. at 1 atm : 80.1°C
                     m.p. at 1 atm : 5.48°C

specific heat (l): 1.74 J/g°C
specific heat (g): 1.04 J/g°C
heat of fusion : 127 J/g
heat of vaporization: 395 J/g

heat released →

Plan: C_6H_6 (g) $\xrightarrow[cool]{①}$ C_6H_6 (g) $\xrightarrow[condenses]{②}$ C_6H_6 (l) $\xrightarrow[cool]{③}$ C_6H_6 (l) $\xrightarrow[freezes]{④}$ C_6H_6 (s)

  120.0°C   80.1°C   80.1°C   5.48°C   5.48°C

Total heat released = ① + ② + ③ + ④

① heat released = Sp. Ht (g) × mass × ΔT = 1.04 J/g°C × 155 g × (120.0 - 80.1°C) = 6.43 kJ

② heat released = Ht vap. × mass = 395 J/g × 155 g =   = 61.2 kJ

③ heat released = Sp. Ht (l) × mass × ΔT = 1.74 J/g°C × 155 g × (80.1 - 5.48°C) = 20.1 kJ

④ heat released = Ht fusion × mass = 127 J/g × 155 g =   = 19.7 kJ

∴ total heat released = ① + ② + ③ + ④ = 107.4 kJ

Example: If 500 g of lead at 200°C are placed in 100g of water at 20°C in an insulated container, what will be the temperature when the lead and water are at the same temperature?

Given: Specific heat of H_2O (l) : 4.18 $\frac{J}{g°C}$
Specific heat of Pb(s) : 0.159 $\frac{J}{g°C}$

$$H_2O \;(l) \longrightarrow H_2O(l) + Pb\,(s) \longleftarrow Pb(s)$$

20°C T_f 200°C
100g   500g
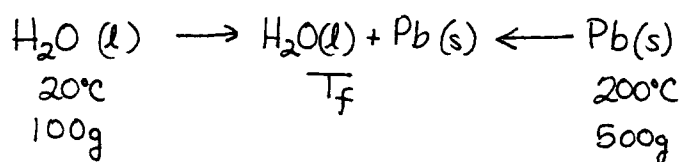
heat gained by water = heat lost by Pb

$$4.18 \;\tfrac{J}{g°C} \times 100g \times (T_f-20) = 0.159 \;\tfrac{J}{g°C} \times 500g \times (200-T_f)$$

$$418\,T_f - 8360 \;J = 15900\,J - 79.5\;T_f$$

$$498\,T_f = 24260 \;J$$

$$T_f = 48.7 \;°C$$

When substances at different temperatures are mixed, heat is transferred from the warmer substance to the cooler substance and the final temperature of the mixture is intermediate between the original temperatures of the substances.

Example: If 5000 J of heat are removed from 500 g of H_2O (l) at 62°C what will be its final temperature?

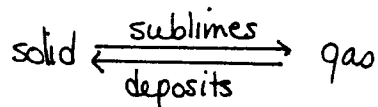$$5000 \;J = 4.18 \;\tfrac{J}{g°C} \times 500g \times (62-T_f)$$
$$5000 \;J = 130,000 \;J - 2090\,T_f$$
$$2090\,T_f = 125000 \;J$$
$$T_f = 59.8 \;°C$$

In these calculations we have used the following equilibrium situations

$$solids \xrightleftharpoons[\text{freezes}]{\text{melts}} liquid \qquad\qquad liquid \xrightleftharpoons[\text{condenses}]{\text{boils}} gas$$
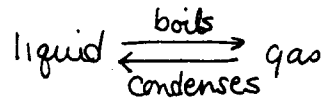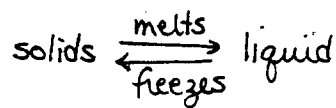
Some solids (iodine, dry ice: CO_2 (s)) change directly to a gas at atm. pressure.

$$solid \xrightleftharpoons[\text{deposits}]{\text{sublimes}} gas$$

All these changes of one phase to another are dependent on both T & P.

One useful way of summenizing all this data regarding phase transitions for any pure substance is the PHASE DIAGRAM, which gives pressure-temperature relationships for all phases at equilibrium.

Consider the phase diagram for H_2O (not to scale)
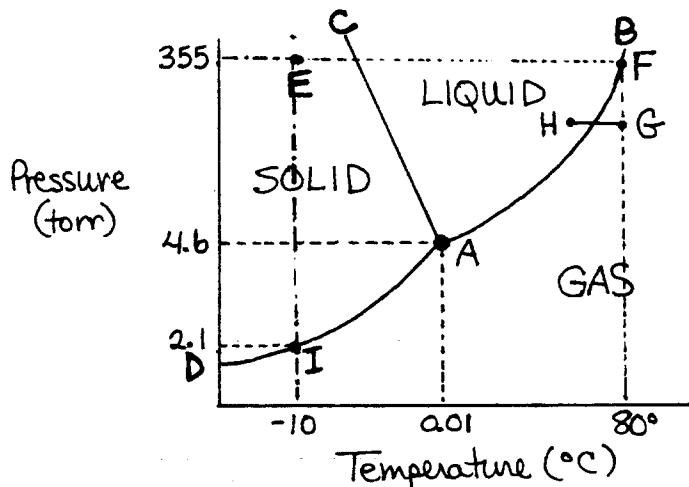
A: triple point

AB: vapor pressure curve
AC: melting curve
AD: sublimation curve.

A is called the TRIPLE POINT. At 4.6 torr and 0.01°C, H_2O exists at equilibrium as a solid, liquid and gas. From this point we draw the lines   AB defines the P-T boundary where   liquid ⇌ gas
AC defines the P-T boundary where   solid ⇌ liquid
AD defines the P-T boundary where   solid ⇌ gas

From the phase diagram:
(1) H_2O cannot exist as a liquid if P < 4.6 torr
(2) Point E at 355 torr and -10°C shows H_2O to be a solid
If the T ↑ as P constant, to point F, the solid will melt at the intersection of AC to a liquid and will start to boil at Point F

∴ at point F we have equilibrium liquid ⇌ gas at 355 tor, 80°C
If the temperature is held constant and pressure is decreased, H_2O vapour
   exists solely as a gas. (Point G). If temperature is decreased
   to 70°C (Point H) the gas condenses to a liquid.
Starting at Point E, and decreasing the pressure to Point I on
   the sublimation curve keeping the temperature at T= -10°C,
   we have solid ⇌ gas at equilibrium at 2.1 tor + -10°C.
   If the pressure is reduced further, the solid sublimes to a gas
   (process is called freeze-drying).

The Solid State Revisited:

Solids can be defined as being
   (1) amorphous : no well-defined crystal structure, lacking internal regularity,
          examples : rubber, some plastics, glass (also called supercooled liquid)

   (2) crystalline : compact ordered arrangement of particles.
                  • X-ray diffraction - discussed in text - can determine the
                    positions of atoms, ions, molecules in the structure.

All crystals are polyhedra having regularly repeating arrays of atoms,
   molecules or ions.
The smallest unit of volume of a crystal showing all the characteristics
   of its lattice is called the UNIT CELL. The unit cell fits into one
   of seven crystal systems (Table 13-9, p482). There are 14 possible
   crystal lattices (Figure 13-22, p483). A unit cell is the repeating
   unit in a crystal.
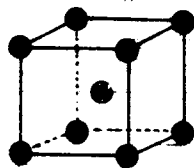Let's discuss three simple unit cells: (For Interest Only)
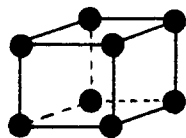
(1) cubic   If all atoms are the same, how many atoms in
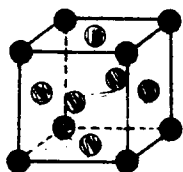   the unit cell: $8 \times \frac{1}{8} = 1$ atom/unit cell

(2) body centered cubic

atoms in unit cell: corners $8 \times \frac{1}{8} = 1$

center $1 \times 1 = 1$

$\underline{}$

2 atoms/unit cell

(3) face centered cubic

atoms in unit cell: corners $8 \times \frac{1}{8} = 1$

faces $6 \times \frac{1}{2} = 3$

$\underline{}$

4 atoms/unit cell

side view —o—

A crystal has the same geometry as the unit cell.

Isomorphous : different substances that crystallize in the same kind of lattice.

eg Li Br + NaCl crystallize in face centered cubic lattice.

polymorphous : a single substance that crystallizes in more than one form.

e.g. $CaCO_3$: calcite   (density : 2.710)

aragonite (density : 2.930)

For Interest Only:

Example: An unknown metal crystallizes in a body centered cubic lattice with a unit cell edge length of 3.301 Å (1 Å $= 1 \times 10^{-8}$ cm). Its density is 8.569 g/cm³ at 20°C. Identify the metal.

The unit cell of a body centered cubic lattice contains 2 atoms/unit cell. (see above)

volume of unit cell = (edge length)³ = $(3.301 \times 10^{-8} cm)^3$ = 35.97×10^{-24} cm³.

Density = $\frac{g}{cm^3}$ ∴ # g = D × volume in cm³   = mass of unit cell. (2 atoms)

= 8.569 $\frac{g}{cm^3}$ × 35.97×10^{-24} cm³

= 3.082×10^{-22} g / 2 atoms

∴ 1 atom weighs $\frac{3.082 \times 10^{-22} g}{2}$ = 1.541×10^{-22} g

1 mole of atoms weighs $1.541 \times 10^{-22} \frac{g}{atom}$ × $6.022 \times 10^{23} \frac{atoms}{mole}$ = 92.81 $\frac{g}{mole}$

∴ 92.81 g/mole is the molecular weight   ∴ $_{41}$Nb is the element

Classification of Crystalline Solids

This is based on (1) types of particles making up the lattice
(2) types of bonding found in the lattice

	Solids	Particles	Interparticle Forces	Properties	Examples
1.	molecular	molecules or noblegases (atoms)	London, dipole-dipole H-bonding	soft poor conductors of heat, electricity low melting point	CH_4, Ar PH_3, NH_3 H_2O
2.	covalent or network	atoms	covalent bonds (strong)	very hard poor conductor high melting point	C (diamond) C (graphite) SiO_2 (quartz)
3.	ionic	cations + anions	electrostatic	hard, brittle poor conductor high melting point	NaCl $CaBr_2$ + other salts
4.	metallic	metal ions in a cloud of electrons	metallic bonds: (electrical attraction between cation and electrons)	soft → hard good conductors wide range of melting points	Li, K Ca, Cu and other metals

Using the periodic table to identify types of solids:

Ionic Solids (metal + nonmetal)

Metallic Solids

Molecular Solids

Covalent Solids (composed of some C, Si, Ge substances)
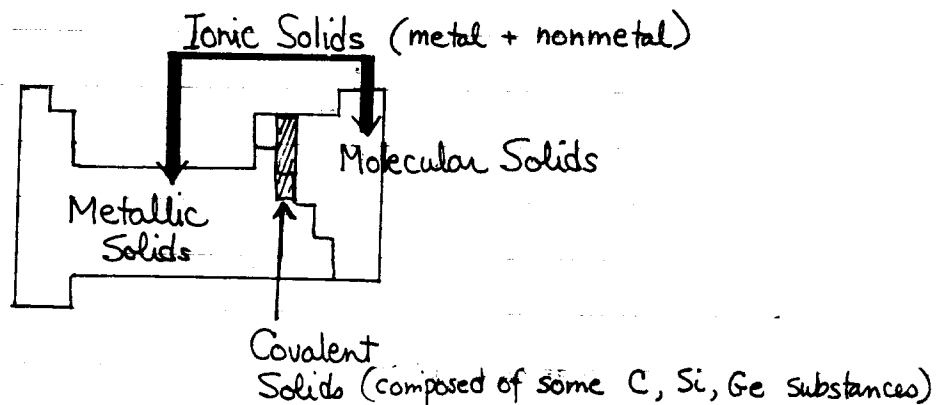
Melting Points for solids, like boiling points for liquids, give information about the strength of attractive forces between particles in solids : the higher the m.p. the stronger the interparticle forces in solids.
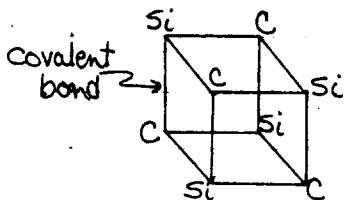
1. molecular solids : low melting points because the attractive forces between the molecules are weak: London, dipole-dipole, hydrogen bonding.

London forces →

eg H_2O (s)   mp. 0°C

NH_3 (s)   m.p. -77°C
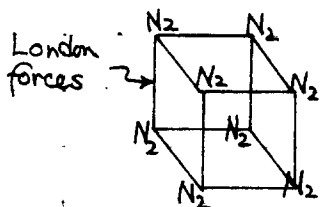
N_2 (s)   m.p. -209°C

N_2 crystallizes in cubic structure

2. covalent solids : very high melting points since in order to melt the solid it is necessary to break covalent bonds.

covalent bond →

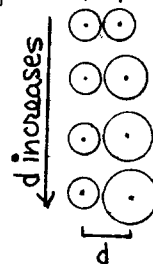eg SiO_2 (s)   mp 1610°C

$C_{diamond}$ (s)   m.p. >3550°C

SiC (s)   m.p. 2700°C   cubic structure

3. ionic solids : high melting point due to electrostatic forces

electrostatic bond →
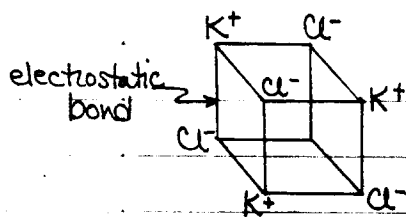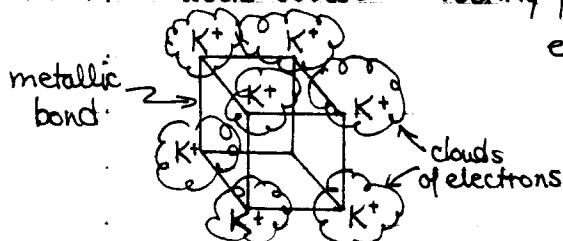
eg KF (s)   mp 846 °C

KCl (s)   mp 776 °C

KBr (s)   mp 730 °C

KI (s)   mp 686°C

d increases ↓

The halide ions increase in diameter, d increases
Therefore, the electrostatic force decreases $F \propto \dfrac{g^+ g^-}{d^2}$

4. metallic solids : melting point is variable

metallic bond →

clouds of electrons

eg K (s)   mp 64°C

Pb (s)   mp 327°C

Al (s)   mp 660°C

Example: Identify the following crystalline solids:

Crystalline Solid	m.p.	Electrical Conductivity		Type
		solid	liquid	
C (graphite)	high	poor	poor	covalent
NaCl	high	no	yes	ionic
Na	high	yes	yes	metallic
O_2	low	no	no	molecular

Metallic Bonding and Band Theory

Most metals crystallize in close packed lattices.
    ∴ we know that the attractive interparticle forces are great.

Why is this? According to theories we have used, representative metals and d-transition metals do not have enough valence electrons to account for this.

A new theory was developed, <u>Band Theory</u>, which accounts for bonding and properties of metallic solids (Section 13-17). It explains the differences between conductors (metals), semi-conductors and insulators.

Metallic bonding is thought to result from the electrical attractions among positively charged metal ions and mobile, delocalized electrons belonging to the crystal as a whole.

Note: There is some confusion about differences between a molecular solid and a covalent solid. Consider CO_2 and SiO_2. Both C and Si are IVA elements but
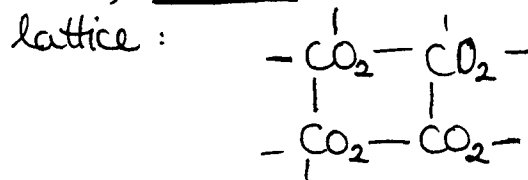
CO_2 forms a molecular solid   m.p. $-56.6\,°C$ @ 5.2 atm.
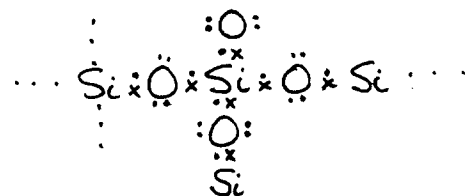SiO_2 forms a covalent solid   m.p. $1610\,°C$
(quartz)

Why?

I CO_2 :   the Lewis dot structure is $\ddot{O}::C::\ddot{O}$ or $:O=C=\ddot{O}$
it is a non polar molecule
∴ the only interparticle forces at work are London forces
which are very weak and very easily broken, hence low m.p.
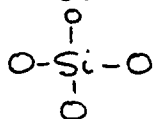as a solid, molecules are at the corners of the crystalline
lattice :

$$-\overset{|}{C}O_2-\overset{|}{C}O_2-$$
$$-\underset{|}{C}O_2-\underset{|}{C}O_2-$$

II SiO_2 or $(SiO_2)n$:   since Si does not form double bonds, the Lewis structure is

$$\begin{array}{c} :O: \\ \cdots Si : \ddot{O} : Si : \ddot{O} : Si \cdots \\ :O: \\ Si \end{array}$$

Note: Si does not form double bonds with oxygen, like its fellow IVA element C does, because of its larger size. The p orbitals on Si are just too far away from the p orbitals on oxygen to effectively overlap side-on to form a π bond.

and we have a solid in which all the atoms are covalently bonded together in a network.

$$\begin{array}{c} -O-\underset{|}{Si}-O-\underset{|}{Si}- \\ O \quad\quad O \\ -O-\underset{|}{Si}-O-\underset{|}{Si}- \\ O \quad\quad O \end{array}$$
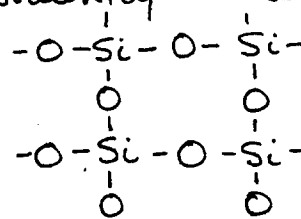
each Si is the center of a tetrahedron:

$$\begin{array}{c} O \\ | \\ O-Si-O \\ | \\ O \end{array}$$

if we count the atoms
Si : 4
O   8
and ratio gives SiO_2