

SOLIDS and LIQUIDS

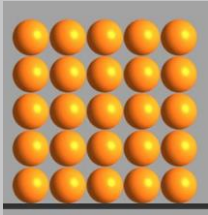
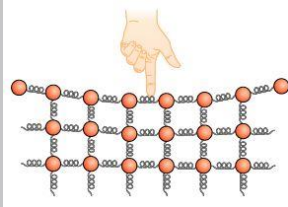
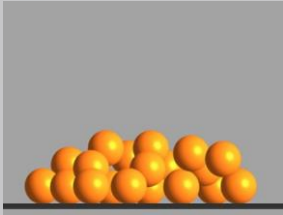
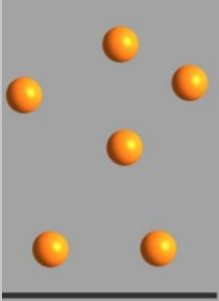
Lectures 11 and 12



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SOLIDS AND LIQUIDS

Phase	Macroscopic	Sub-microscopic
Solid	Definite volume Definite shape 	Particles attracted strongly Regular arrangement/structure 'balls held with springs' 
Liquid	Definite volume Shape of container 	Particles attracted weakly More random arrangement 'balls held with wires/bands'
Gas	Volume of container Shape of container 	Particles not attracted at all Totally random arrangement 'balls not attached at all'



INTERPARTICLE FORCES (IPF)

Two broad Categories
(focus on solids):

Infinite Arrays (IPF)

- IONIC BONDS
- METALLIC BONDS
- COVALENT BONDS

Discrete molecules (IMF)

- DIPOLE-DIPOLE
- LONDON DISPERSION FORCES
- HYDROGEN BONDING

Interparticle forces are the forces that hold particles (atoms, ions) in a molecule

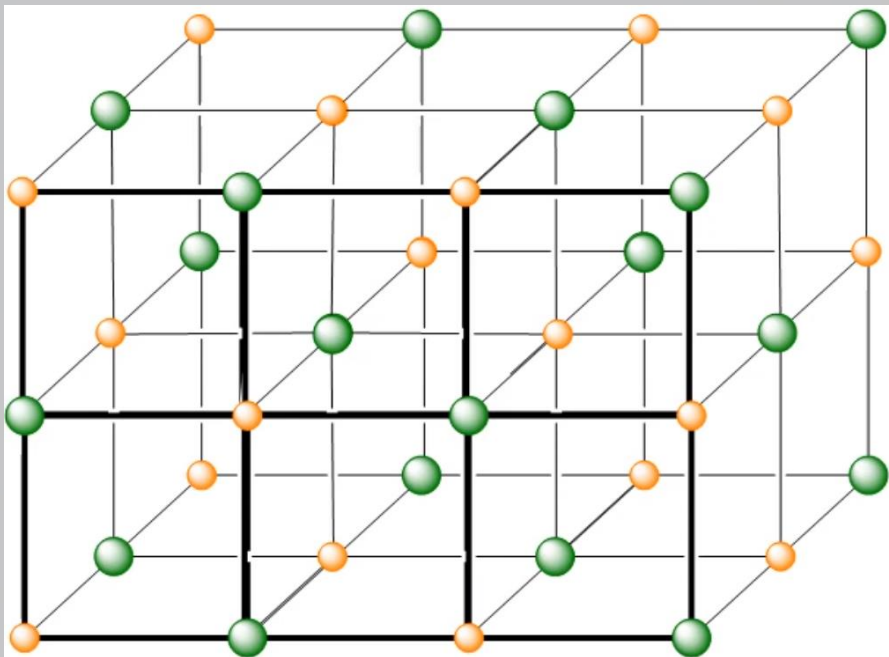
Intermolecular forces are the forces that hold molecules in a substance (between discrete molecules – relatively weak)



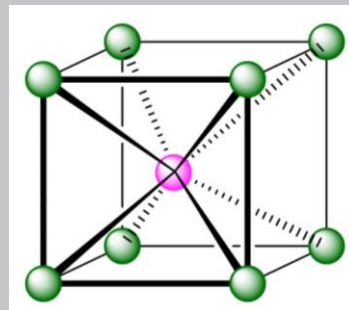
IPF – IONIC COMPOUNDS

IPF – ionic bonds

SODIUM CHLORIDE



CAESIUM CHLORIDE



$$PE = q_1 q_2 / 4\pi\epsilon_0 r$$

q_1 and q_2 separated by r
(charge on electron – $1,602 \times 10^{-19}$ C)

ϵ_0 - permittivity of a medium

Ionic bond is the electrical attraction between the opposite charges of cations and anions.

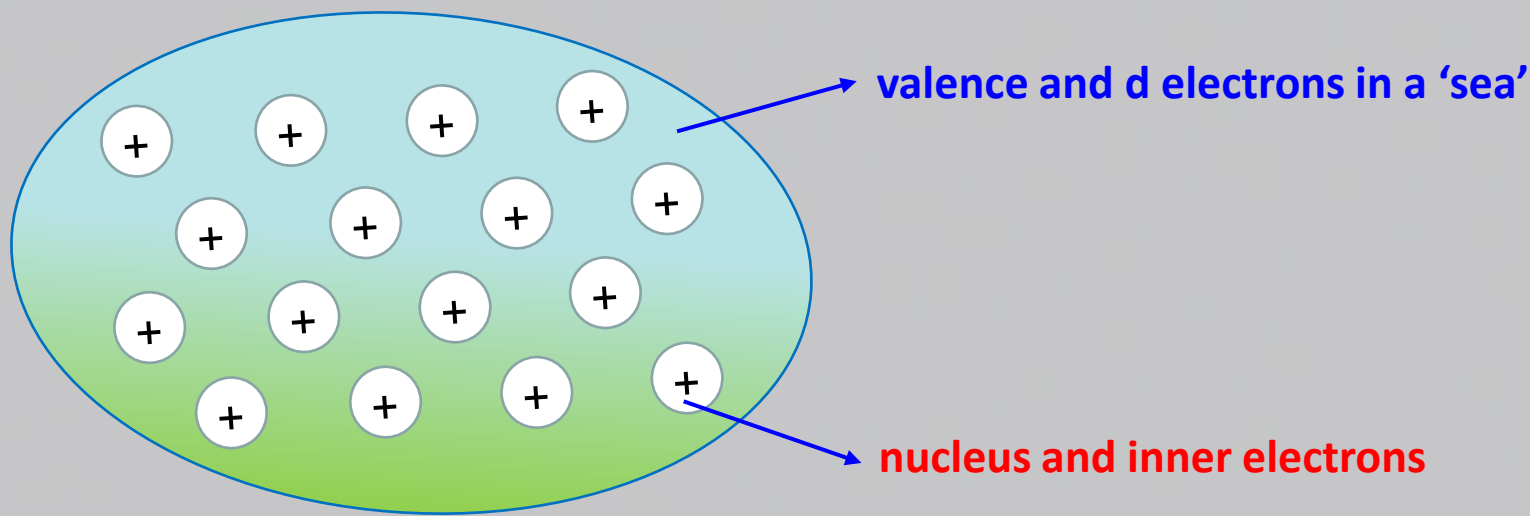
It forms when the valence electrons of one atom are transferred permanently to another atom.

VERY, VERY STRONG



IPF – METALLIC COMPOUNDS

- **metallic bond** - force that holds closely packed atoms together in a metallic substance
- the **valence electron** shell of each atom overlaps with a large number of neighbouring atoms so the **valence electrons** move from one atom to another and are not associated with any specific pair of atoms
- **valence electrons** are nonlocalized, moving freely throughout the entire crystal
- the atoms that the **electrons** leave behind become positive ions, and the interaction between such ions and valence electrons gives rise to the binding force that holds the metallic crystal together

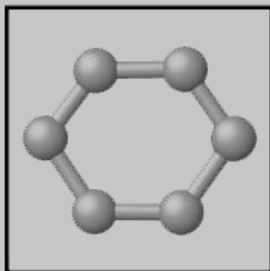


STRONG TO VERY, VERY STRONG

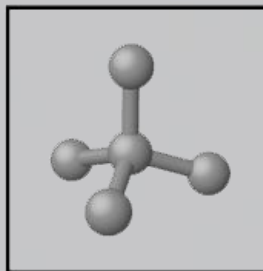
IPF – COVALENT BONDS

network covalent bonds found in large, rigid three-dimensional arrangements of atoms held together by strong covalent bonds

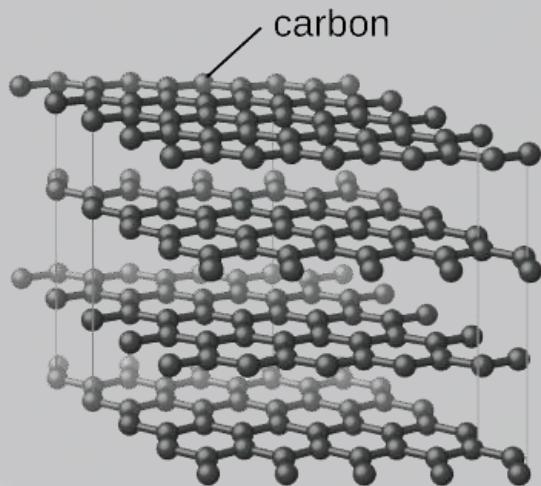
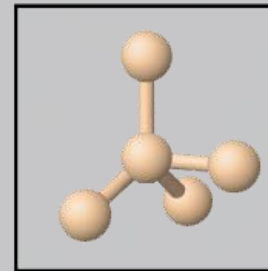
trig.planar



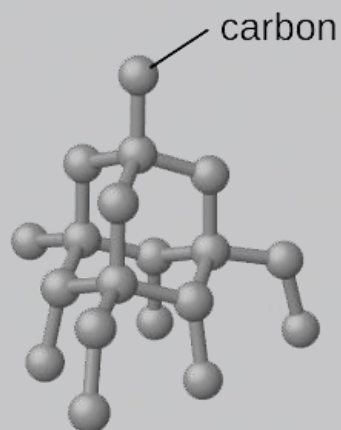
tetrahedral



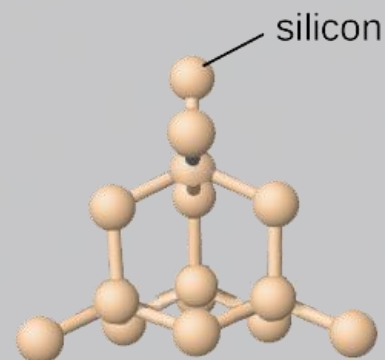
Si tetrahedral
held by O atoms



graphite



diamond



silicon

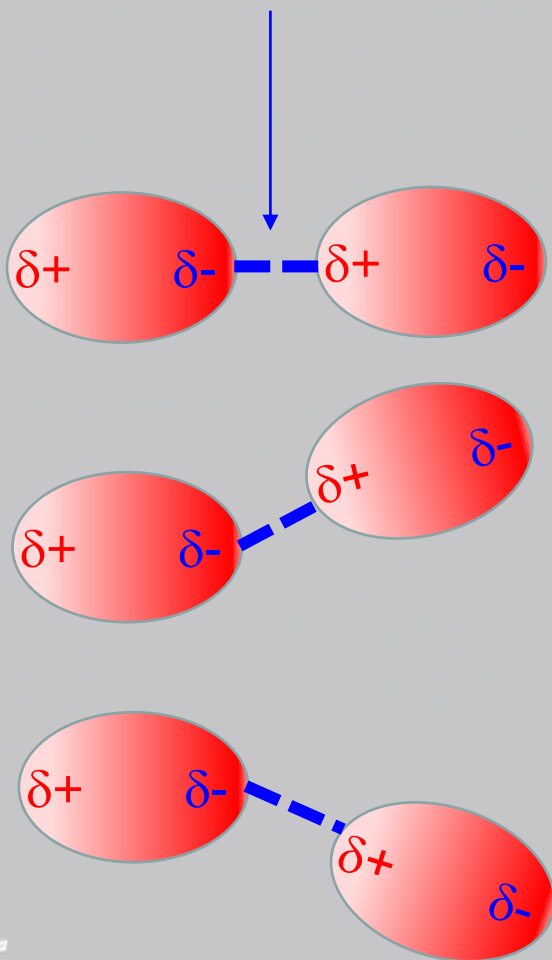
allotropes



VERY, VERY STRONG

IMF – POLAR COVALENT MOLECULES

IMF – dipole-dipole forces



- between two discrete molecules
- whole molecule that has a dipole moment interacts with another dipole molecule
- weaker than IPF
- undirected, slightly negative interaction
- affect the molecules

$$PE = - \frac{0.66(\mu_1\mu_2)^2}{(4\pi\epsilon_0)^2k_B T} \times \frac{1}{r^6}$$

μ – dipole moment on a molecule
 k_B – Boltzman constant

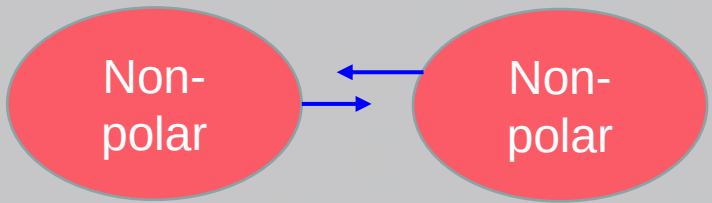
PE decreases when the distance increases r^6



WEAK

IMF – LONDON DISPERSION FORCES

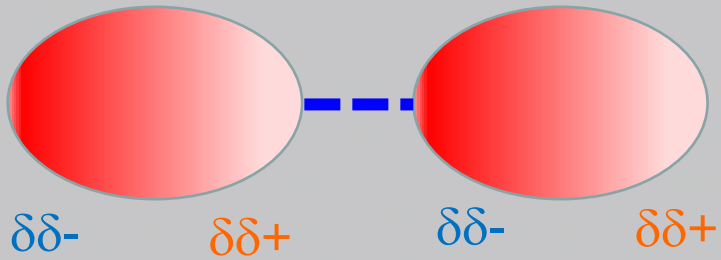
Non-polar Covalent Molecules



- the weakest intermolecular force
- a temporary attractive force that results from temporary dipoles

POLARIZABILITY: relative tendency of an electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field, caused by the presence of a nearby ion or dipole

Induced dipole
Proximity of electron cloud



‘Squishiness of molecules’
Bigger molecules more squishy
Larger LD forces

$$PE = - \frac{1.5(\alpha_1\alpha_2)^2}{(4\pi\epsilon_0)^2} \times \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{1}{r^6}$$

α – polarizability
 I – ionisation energy

Van der Waals forces are ALL intermolecular forces
London dispersion forces are an example of Van der Waals forces

VERY VERY WEAK



PRACTICE PROBLEMS

PRACTICE PROBLEM 1: Which type of intermolecular/interparticle force exists in all solid substances?

- a) Ionic
- b) London Dispersion
- c) Dipole-dipole
- d) None - there are different types of IMF/IPF depending on the substance

PRACTICE PROBLEM 2: Which type of intermolecular force ("interparticle force") is the most important in $\text{PF}_3(\text{l})$?

- a) London Dispersion
- b) Ion-dipole forces
- c) Dipole-dipole forces
- d) Ionic bonds

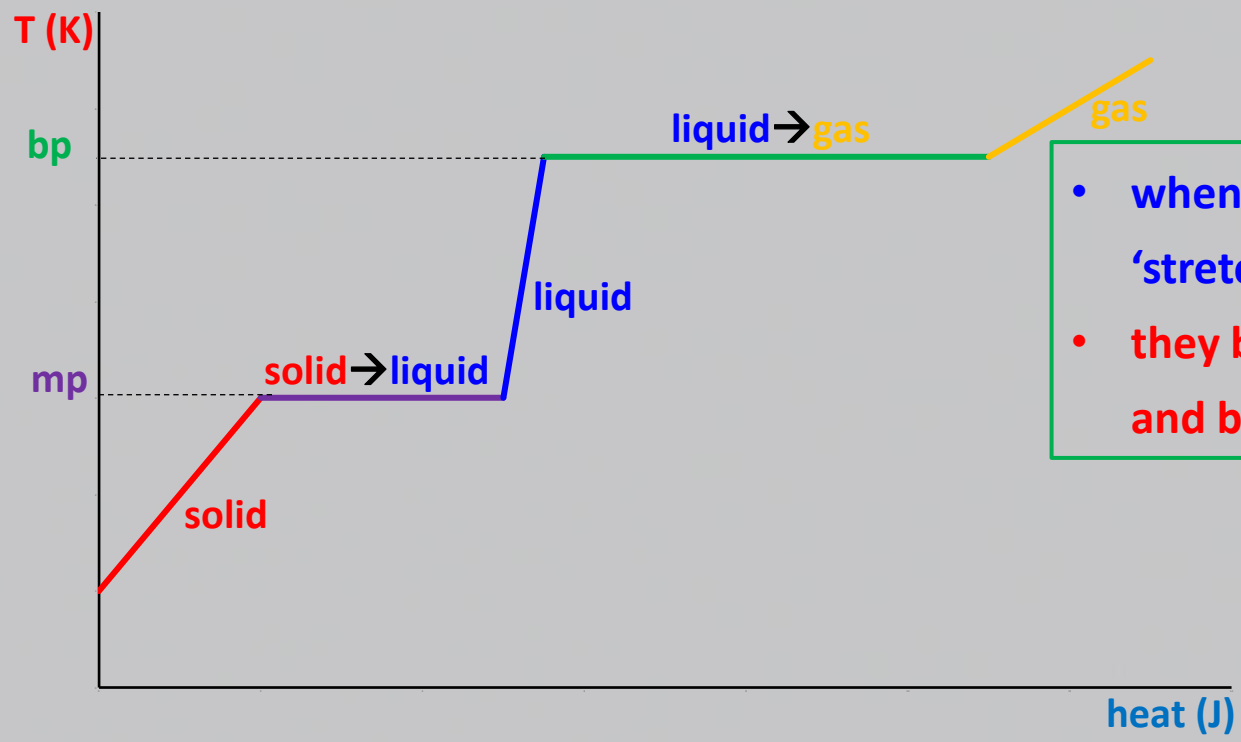
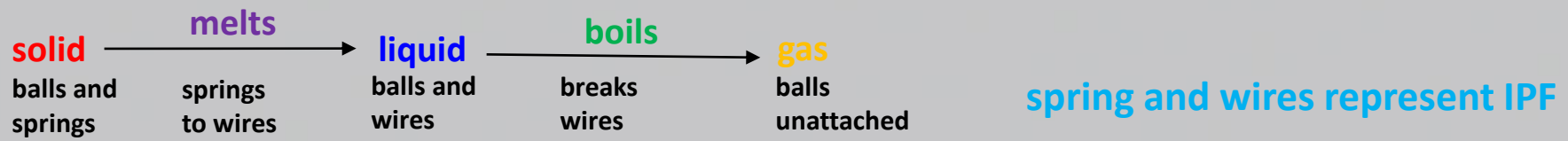
PRACTICE PROBLEM 3: Identify the kinds of intermolecular forces that might be present between molecules of the following substances

- a) Cl_2
- b) HCl
- c) C_6H_6
- d) $\text{C}_6\text{H}_5\text{Cl}$



HEATING CURVE

effect of IPF on microscopic behaviour of a substance upon heating



- when heated springs and wires 'stretch'
- they break when melting/fusing and boiling/vaporising

Stronger these forces $\rightarrow$
Higher melting point
Higher boiling point



melting point - the constant temperature at which a solid changes into liquid
boiling point - the constant temperature at which a liquid starts changing into gas

DEPEND ON IPF !!!

MELTING POINTS

melting point - the constant temperature at which a solid changes into liquid

Lithium Fluoride
Magnesium Oxide

845 °C
2852 °C

IONIC

strong IPF – high mp

Tungsten
Mercury

3422 °C
- 39 °C

METALLIC

liquid Hg – IMF weaker than in solid

Diamond

3550 °C

COVALENT NETWORK

Acetone
polar

-95 °C

Fluorine

-220 °C

Chlorine

-101 °C

Bromine

-7 °C

Iodine

114 °C

MOLECULAR

increase in
mass

increase in
polarizability

In halogens there are only LD forces but high polarizability makes them strong

F
9
Cl
17
Br
35
I
53

increase in melting
point



MELTING POINTS

hydrides

O
8
S
16
Se
34
Te
52

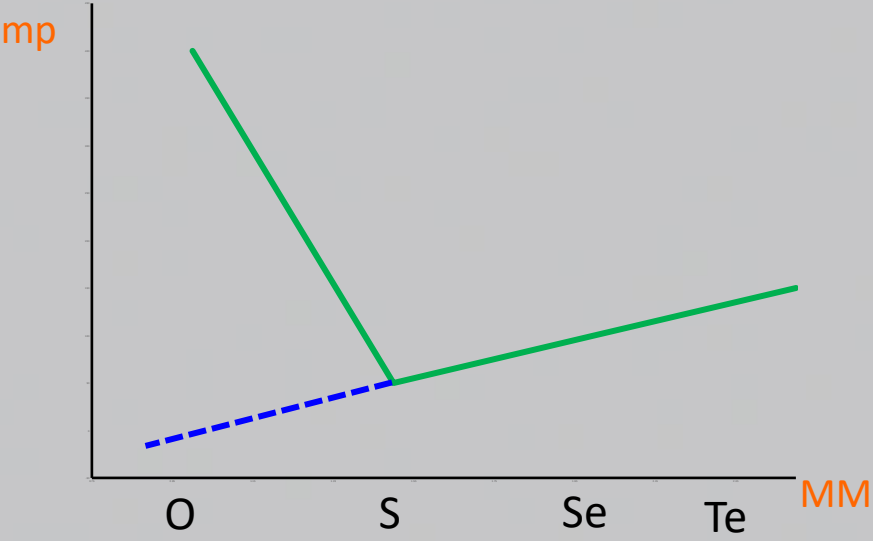
H₂O 0 °C ???

H₂S -82 °C

H₂Se -66 °C

H₂Te -49 °C

mp increases with
size but not for water



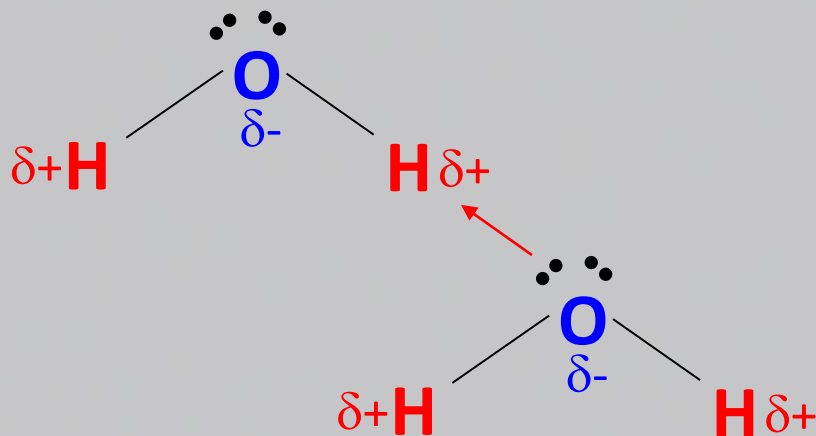
polar molecules – dipole-dipole + LD

H₂S – gas at room temperature even though it has more electrons than water and so stronger LD forces



IMF – HYDROGEN BONDS

A hydrogen bond consists of a hydrogen atom lying between two small, strongly electronegative atoms with lone pairs of electrons (N, O or F)



Small size of H

Small size of O

Very large charge density

Very polar O-H bonds

Very directed
Tetrahedral

How does it form? – O-H bond is polar; the electronegative O pulls the electrons from H creating a large $\delta+$ on H; such H is strongly attracted to the lone pair of electrons on O atom on other H_2O molecule to form a **HYDROGEN BOND**



DOMINATES ALL OTHER IMF !!!

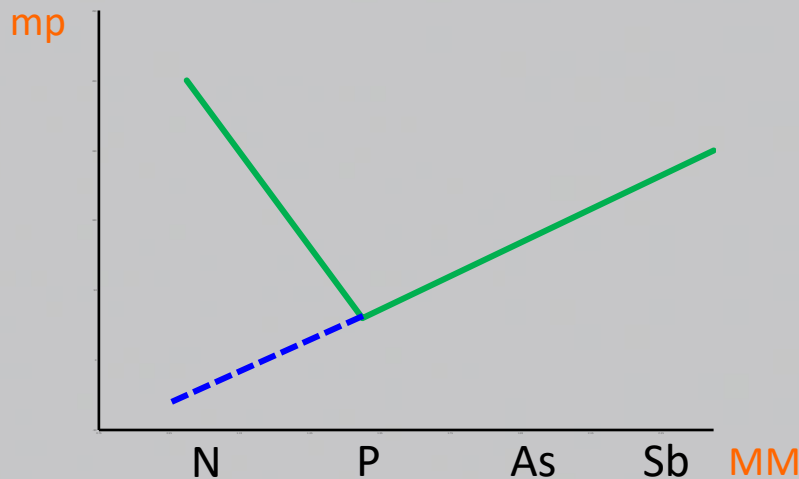
BETTER THAN WEAK

MELTING POINTS

N
7
P
15
As
33
Sb
51

NH ₃	-78 °C	HF	-84 °C
PH ₃	-133 °C	HCl	-114 °C
AsH ₃	-111 °C	HBr	-87 °C
SbH ₃	-88 °C	HI	-51 °C

F
9
Cl
17
Br
35
I
53



Generally: O-H
N-H Hydrogen bonds
F-H

NH₃ and HF have higher boiling points than PH₃ and HCl because of hydrogen bonds



PRACTICE PROBLEMS

PRACTICE PROBLEM 1: Which of ethane and ethanol experience London Dispersion forces in the solid and liquid states?

- a) both ethane and ethanol
- b) ethane only
- c) ethanol only
- d) neither ethane nor ethanol

PRACTICE PROBLEM 2: Which of the following substances has the highest melting point and why?

- a) HCl
- b) HI
- c) HBr
- d) HF

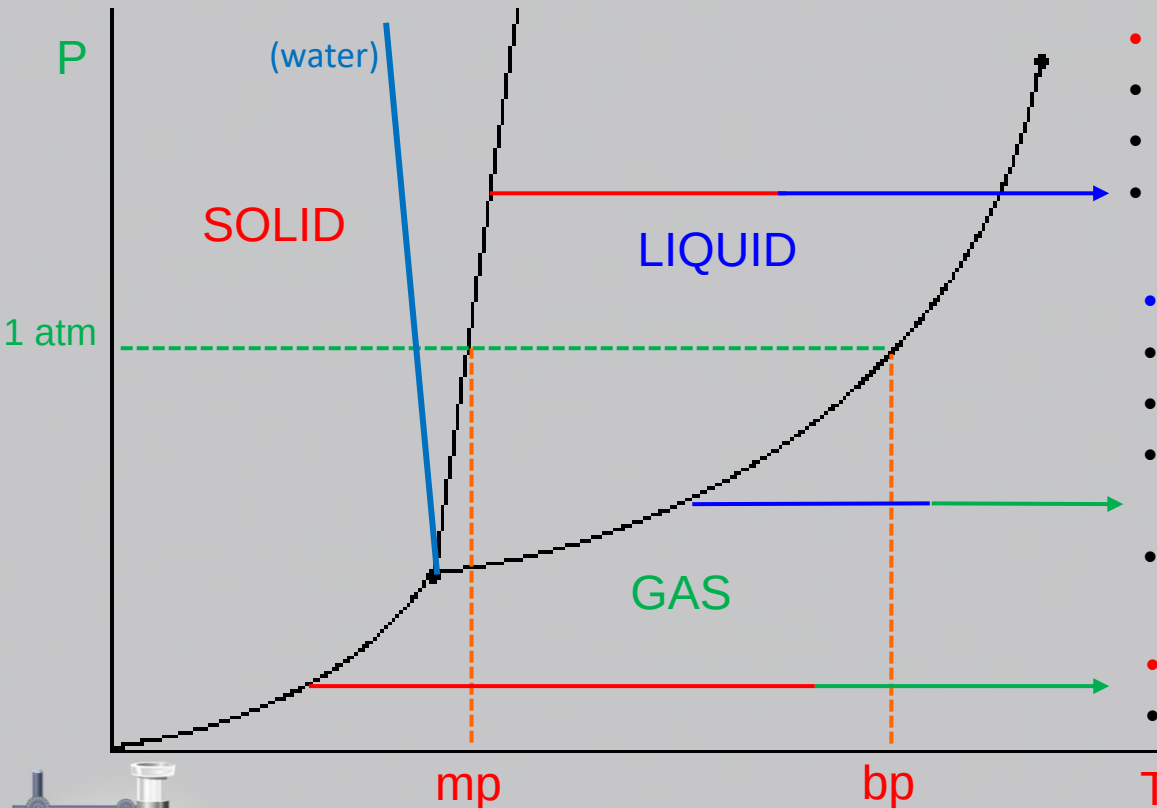
PRACTICE PROBLEM 3: Which of the following substances are able to form hydrogen bonds?

- a) HF
- b) CH₄
- c) NH₃
- d) CH₃OH



PHASE DIAGRAM

The phase diagram is a summary of the temperatures and pressures at which the various solid, liquid and vapour phases of pure substance exist/coexist

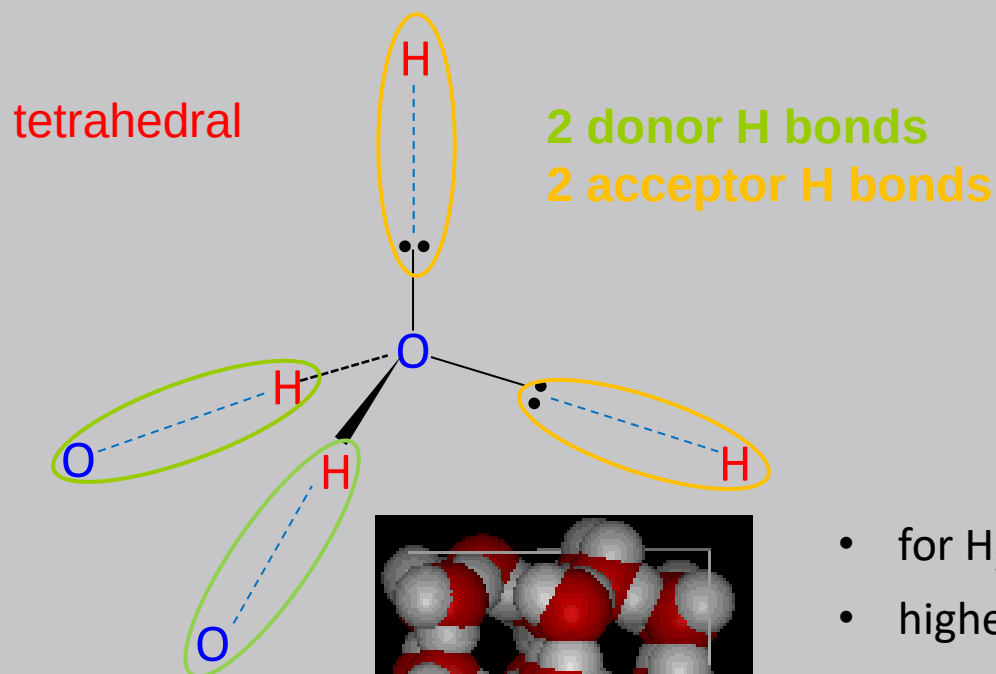


- **solid** to **liquid**: both phases can coexist
- freezing $\leftrightarrow$ melting
- almost vertical
- mp hardly changes with pressure
- **liquid** to **gas**: both phases can coexist
- condensation $\leftrightarrow$ boiling/vaporisation
- very pressure dependent.
- shows vapour pressure of liquid at different temperatures
- bp when $v_p = \text{external pressure}$.
- **solid** to **gas**: both phases can coexist
- deposition $\leftrightarrow$ sublimation



WATER

Ideal Hydrogen Bond Formation

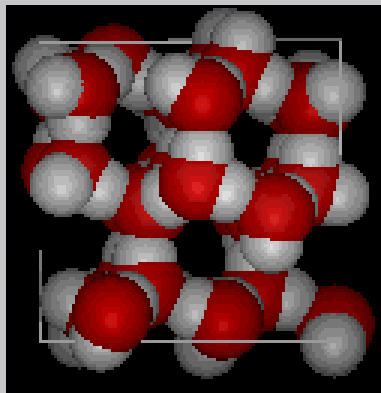


Only in ice

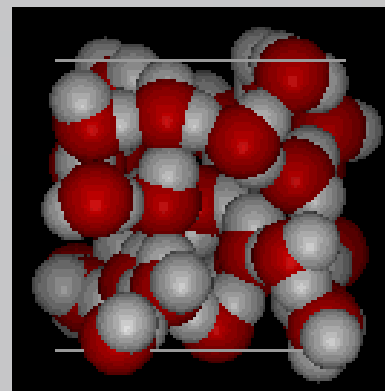
Rigid

Further apart

Less compact (flows in water)



Liquid 2-3 H bonds at a given time



Less rigid

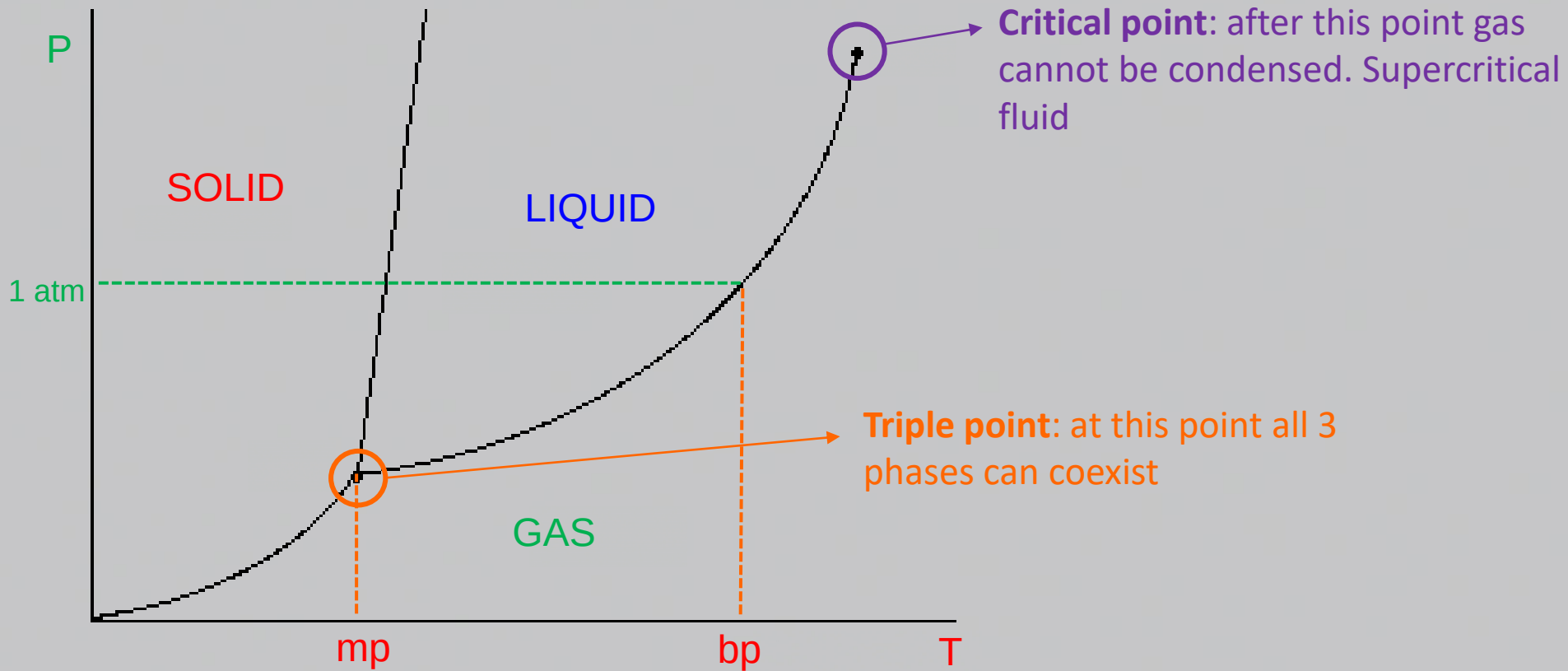
Closer together

More compact

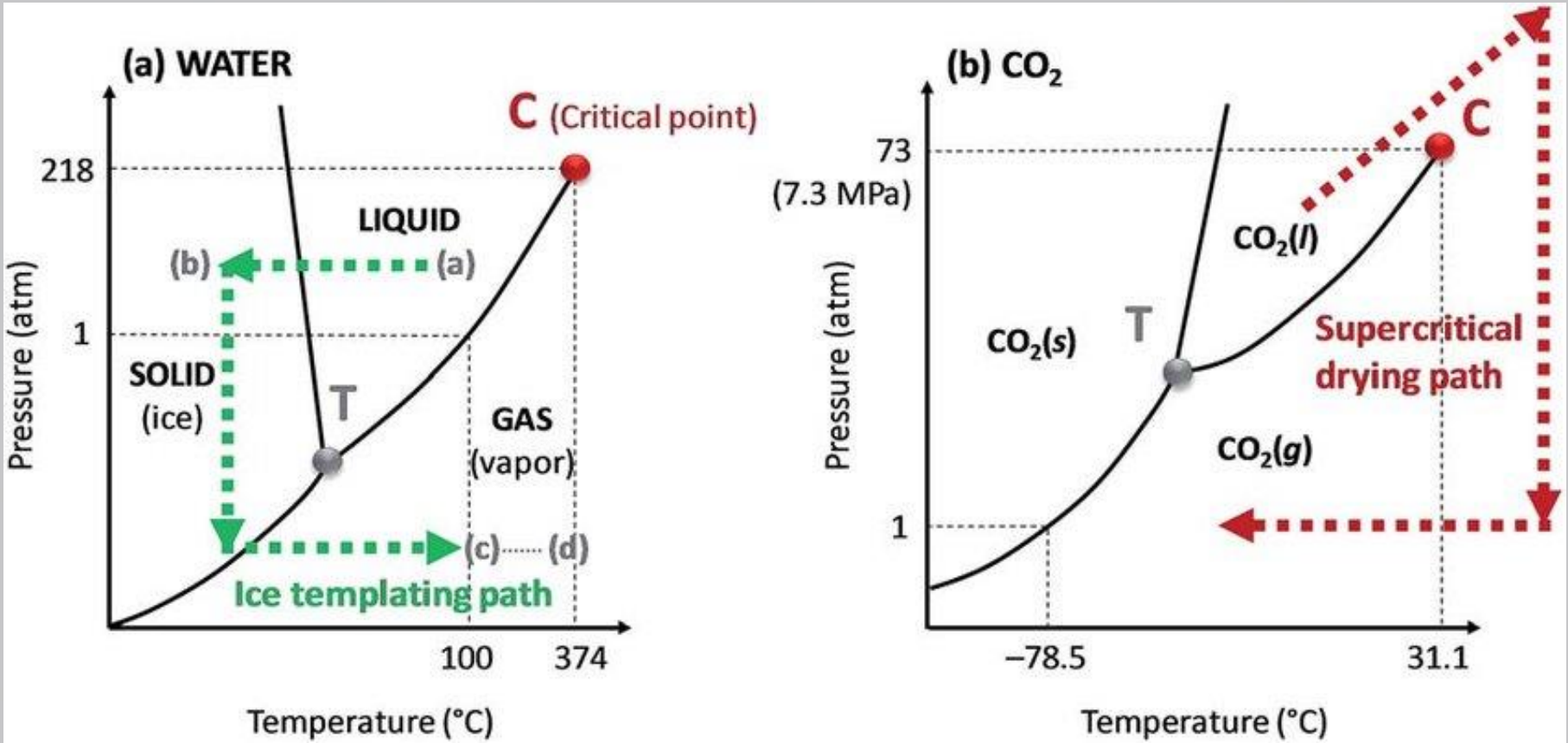
- for H_2O mp decreases when pressure increases
- higher pressure on H_2O (l) makes it harder for the molecules to move apart and form tetrahedral ice structure
- to allow this more compact structure H_2O must be cooled more



PHASE DIAGRAMS



PHASE DIAGRAMS



MACROSCOPIC PROPERTIES

	IONIC	METALLIC	MOLECULAR
Melting/boiling points	High	Usually high	Low
Hardness	Hard and brittle	Malleable and ductile	Soft
Electrical conductance	None in solid In liquid or aqueous solution	In solid and liquid	None
Solubility in polar solvent	Some	None	Very few
Solubility in non-polar solvent	None	None	Most

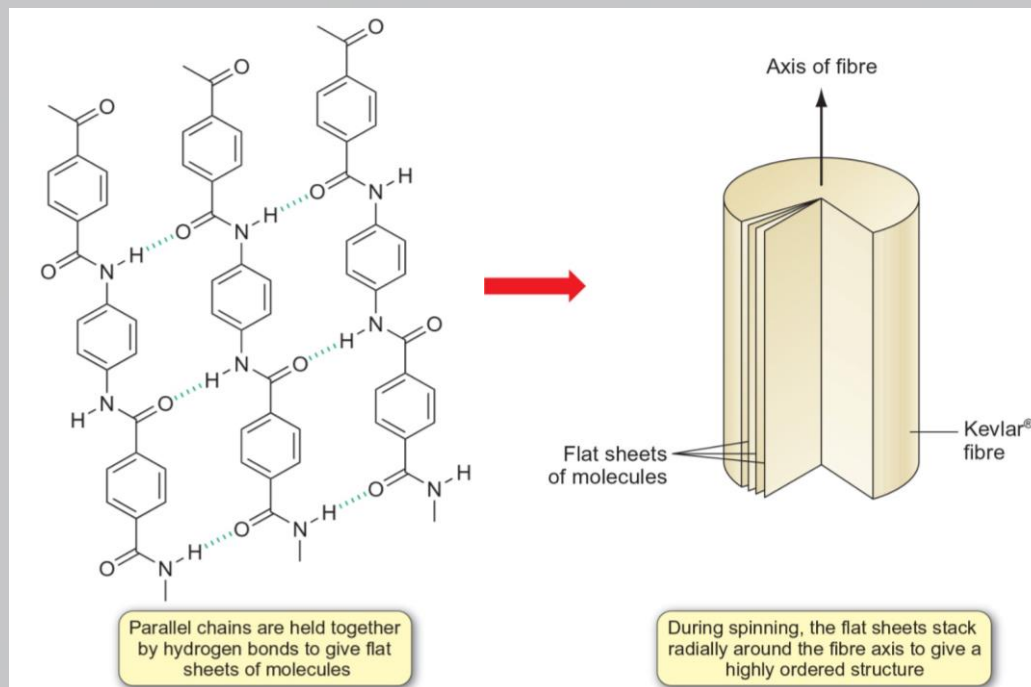
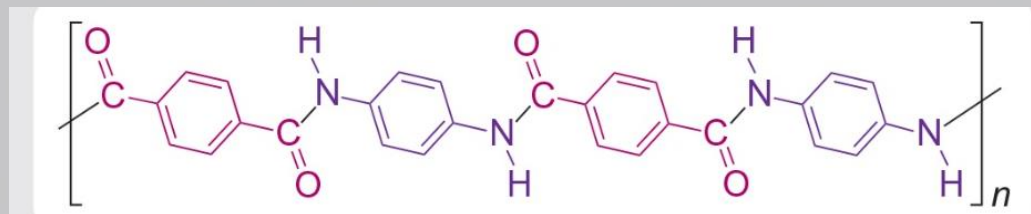


WHY IS KEVLAR SO STRONG?

- DuPont, 1965
- lightweight, flexible, resistant
- 5 times stronger than steel

**highly ordered,
crystalline structure**

1. Benzene rings linked by amide group – rigidity (limited bond rotation)
2. Hydrogen bonding between the chains – prevents slipping
3. The chains orientate themselves along the fibre axis with H-bonding linking adjacent chains



EXAMPLES

Question 1

Which pair is mismatched?

- a) ionic - low vapor pressure
- b) dipole moment - dipole-dipole forces
- c) N—H or O—H bonds - hydrogen bonding
- d) polarizability - ionic forces
- e) polarity - dipole moment

Question 2

Which type of intermolecular force ("interparticle force") is the most important in $\text{SiBr}_4(\text{l})$?

- a) Hydrogen bonds
- b) Ionic bonds
- c) London Dispersion
- d) Ion-dipole forces
- e) Dipole-dipole forces

Question 3

Which of the following molecules would be expected to exhibit hydrogen bonding?

- a) hydrogen sulfide
- b) methanol
- c) hydrogen chloride
- d) methane

Question 4

Which of the following substances has the highest melting point?

- a) PH_3
- b) NH_3
- c) AsH_3
- d) SbH_3

Question 5

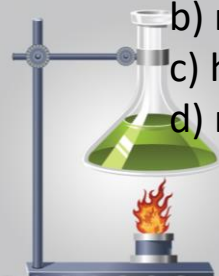
For solid substances of the same approximate formula mass the lowest molar heat of vaporization is to be expected for

- a) non-polar covalent substance
- b) network covalent substance
- c) polar covalent substance
- d) metallic substance
- e) ionic substance

Question 6

A certain substance, X, has a triple point temperature and pressure of 20°C and 2.0 atm and a critical point temperature and pressure of 210°C and 150 atm. The equilibrium line between solid and liquid phase has a positive slope. Which one of the following statements cannot be true?

- a) X cannot exist as a liquid below 2 atm
- b) X can exist as a gas at 25°C and 1 atm.
- c) X can exist as a solid below 25°C and 2 atm
- d) X can only exist as a solid above 20°C
- e) X can exist as a liquid above 20°C



PRACTICE PROBLEMS

PRACTICE PROBLEM 1: A diamond film forms on a surface from gaseous carbon atoms in a vacuum. What is this phase change called (Enter the letter of your choice.)?

- a. melting (fusion)
- b. sublimation
- c. condensation
- d. crystallization (freezing)
- e. evaporation
- f. deposition

PRACTICE PROBLEM 2: The critical temperature of water is the:

- a) temperature at which water vapor condenses
- b) temperature at which solid, liquid and gaseous water can coexist
- c) minimum temperature at which liquid water can exist
- d) minimum temperature at which a good cup of tea can be made
- e) maximum temperature at which liquid water can exist

PRACTICE PROBLEM 3: According to the phase diagram of methanol shown, which statement is correct?

- a) Solid methanol sublimates at atmospheric pressure.
- b) Water and methanol have the same relationship between freezing point and pressure as they both have hydrogen bonding
- c) Solid, liquid, and gaseous methanol can only coexist at pressures above 1 atm.
- d) At 1.25 atm pressure, the boiling point of methanol is greater than 64.7 °C
- e) At 200 °C and 1 atm pressure, methanol is a supercritical fluid

