

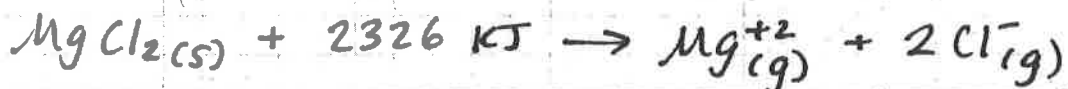
Quantum part 2 (Chapter 8)

- (17.) a) AlF_3 b) K_2S c) Y_2O_3 d) Mg_3N_2

(21) (a) lattice energy is the energy required to transform 1 mole of an ionic compound from a solid to individual gas phase ions.

(or, it is the energy released when the gas phase ions form one mole of the ionic solid..)

For example, $MgCl_2$ has a lattice enthalpy of 2326 kJ/mole.



(lattice enthalpy isn't directly measured though)

(b) The stronger the attractive forces between ions, the higher the lattice enthalpy. These attractive forces can be estimated with Coulomb's Law:

$$F = \frac{k q_1 q_2}{r^2}$$

← The higher the ion charges, the higher the lattice enthalpy.

↑
The shorter the bond length, the higher the lattice enthalpy.

charges usually have more impact on the lattice energy than size differences, since ion radii are (mostly) with a factor of 2 of each other, for example:

$Li^{+1} = .90 \text{ \AA}$	$F^{-} = 1.19 \text{ \AA}$
$Rb^{+1} = 1.66 \text{ \AA}$	$I^{-1} = 2.06 \text{ \AA}$

but just doubling the charge of 1 ion can double the force, if all other factors are constant.

(c) Compounds with higher lattice energies tend to have higher melting points.

23 Look up lattice enthalpies of KF, CaO, ScN (page 293), and explain

KF	808	KJ/mole	+1	and	-1	ions	in	1:1	ratio
CaO	3414	"	+2	and	-2	ions	in	1:1	ratio
ScN	7547	"	+3	and	-3	ions	in	1:1	ratio

all ions are from period 4 elements, so the radii are fairly similar, but the higher the charge on the ions, the stronger the coulomb attractive forces, and the higher the lattice enthalpy.

(The numbers work pretty well: if the bond lengths, etc., were the same, then CaO would have 4x the attractive forces as KF, and ScN would have 9x the attractive forces.

$$808 : 3414 : 7547$$

$$= 1 : 4.2 : 9.3$$

b) given: BaS, CaO, KCl, MgO, NaCl, SrO

have these mp, but not in order: 770, 993, 1200, 2351, 2613, and 2852 (all in °C)
which is which? justify choices.

MgO	2852 °C
CaO	2613 °C
SrO	2351 °C
BaS	1200 °C

all of these have +2 / -2 charges. but Mg⁺², O⁻² have the smallest radii of the group, and Ba⁺²/S⁻² have the largest radii; the list is ranked by radii. I assumed that charge was more important than size; it usually is, so these 4 cpds would have stronger attractive forces than those with only +1/-1 charges.

NaCl	993 °C
KCl	770 °C

these two only have +1/-1 charges, so should have lower mp than the other 4 cpds, due to weaker coulomb forces. Na⁺¹ has a smaller radius than K⁺¹, so NaCl has shorter bond lengths, and stronger attractive forces, than KCl, therefore so NaCl has a higher melting point (mp)

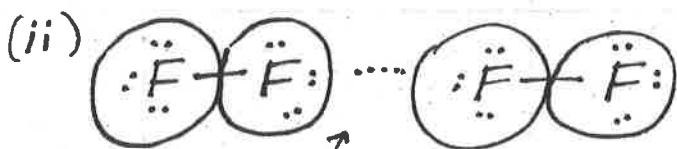
1. The picture shows a Liquid.

The molecules are relatively close together: much closer together than they would be in a gas, but not as close as they would be in a solid. Also, it can't be a solid since the molecules are disorganized - there is no uniform spacing.

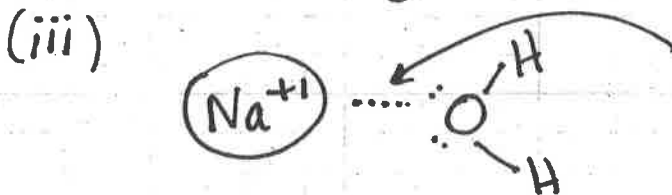
2. (a) What type of intermolecular attractive force in each pair:



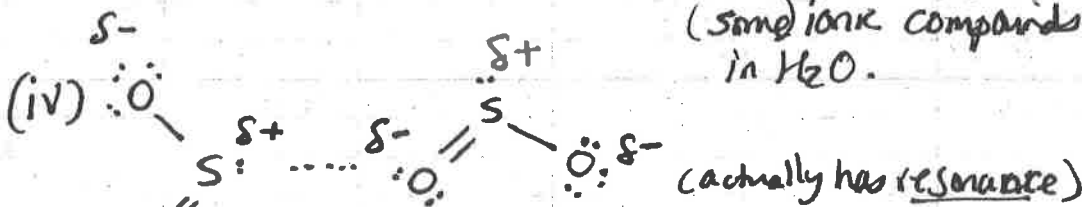
this is a "hydrogen bond": an attractive force between two very polar molecules



F₂ is nonpolar, so the attractive force is London Dispersion Force though F₂ has no permanent dipole, it can have a temporary dipole due to asymmetric distribution of e⁻ in the orbitals. The two molecules can "shift" their temporary polarities in conjunction with e⁻/o⁺ so that they are attracted to e⁻/o⁺.



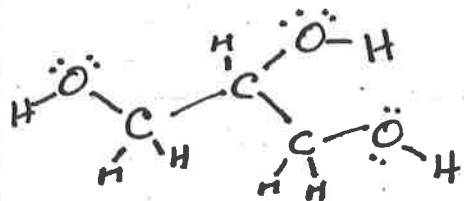
The attractive force here would be an "ion-dipole" force. This is the attractive force that allows (some) ionic compounds to dissolve in H₂O.



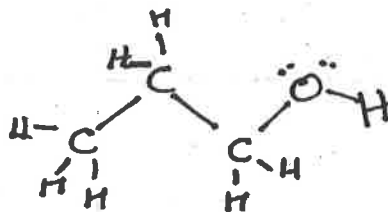
Since SO₂ is polar, the force here would be Dipole-Dipole

b) the forces in F₂ are probably the weakest, since it only has London Forces.

3. Which would have the higher viscosity: glycerol or 1-propanol?



glycerol (aka glycerine)
 $C_3H_8(OH)_3$



1-propanol C_3H_7OH

glycerol would have the higher viscosity.

Since glycerol has 3 O-H bonds compared to propanol's 1 O-H bond, glycerol has stronger intermolecular attractive forces; the glycerol molecules stick to each other, and have more resistance to flow. Glycerol molecules have more sites for forming "hydrogen bonds" attractive forces with other glycerol molecules, when compared to propanol. Glycerol/glycerine is used in shampoos, cough syrup, medicines.. It tastes sweet and has a syrupy consistency. cosmetics, other

11. Arrange CCl_4 , Si, Ar in order of increasing boiling point.

Ar has the lowest b.p., then CCl_4 , then Si has the highest bp

Ar and CCl_4 both have only London Dispersion Forces, since both are nonpolar. However, CCl_4 has more electrons and would therefore be more polarizable, and CCl_4 would be expected to have more surface area than Ar. For both of those reasons, CCl_4 would be expected to have stronger London Forces than Ar.

Silicon forms a Covalent Network Solid similar to diamond (but w/ Si, not C) since every Si is sigma/single covalently bonded to 4 other Silicons. So it has very strong cohesive forces compared to the other two substances.

(Note: Ar is a gas @ room temp, CCl_4 is a liquid, and Si is a solid (!))

12. Arrange in order of increasing bp: Ga, Ne, Br₂

Well, we can already tell from the periodic table that Ga, Ne, and Br₂ are solid, gas, and liquid phase (respectively) at room temperature... but also,

Ga is a metal, so it has metallic bonding, and so would be expected to have stronger forces than Ne and Br₂, since these two only have London Dispersion Forces, since they are nonpolar molecules. But Br₂ would be expected to have stronger London forces than Ne, since Br₂ has more e⁻ than Ne, and so is more polarizable than Ne and has more surface area.

So, Ne has the lowest bp, then Br₂, then Ga has the highest bp.

13. at STP, "molar volume" (volume occupied by one mole of substance) of Cl₂ is 22.06 L, and that of NH₃ is 22.40 L.

(a) The molar volumes are very close since both Cl₂ and NH₃ are gases at STP. In a gas, the gas molecules themselves occupy a very tiny fraction of the overall volume, so the size and attractive forces of the molecules have only a minor effect on the molar volume. If both gases were perfectly ideal, they would have exactly the same molar volumes. The size and IMF of molecules aren't quite insignificant so the molar volumes are slightly different.

(b) at 160 K, both are crystalline solids. how will this affect the molar volumes?

Solids are much more dense than gases, so at 160 K, both substances will have much smaller molar volumes than they did at STP, when they were gases. Probably about 1000x smaller?

(c) Cl₂ Density = 2.02 g/cm³ at 160 K, NH₃: D = 0.84 g/cm³

$$\text{Cl}_2: \left(\frac{70.906 \text{ g}}{\text{mole}} \right) \left(\frac{1 \text{ cm}^3}{2.02 \text{ g}} \right) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = \boxed{0.0351 \text{ Liter/mole}} \text{ Cl}_2$$

$$\text{NH}_3: \left(\frac{17.0304 \text{ g}}{\text{mole}} \right) \left(\frac{1 \text{ cm}^3}{0.84 \text{ g}} \right) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = \boxed{0.020 \text{ L/mole}} \text{ NH}_3$$

(cont'd, next page)

(13) cont'd from last page..

(d) no, though NH_3 and Cl_2 had very similar molar volumes as gases at STP, they have fairly different molar volumes as solids at 160K: $0.020 \frac{\text{L}}{\text{mole}}$ and $0.0351 \frac{\text{L}}{\text{mole}}$ respectively.

As gases, the molecules were far apart, so the volumes that the molecules themselves occupy is nearly insignificant, so the molar volumes were similar.

But as solids, the molecules themselves occupy more than 50% of the crystal lattice (perhaps $\approx 70\%$) so larger molecules will have a larger molar volume. Since Cl is in period 3, and N and H are in period 2/1, Cl_2 would have a larger molecular volume, and so a larger molar volume, than NH_3 .

(e) I would expect the molar volumes in liquid state to be close to the solid molar volumes than to the gas molar volumes. Though not generally quite as dense as solids, liquids have molecules that are relatively close together, like solids do.

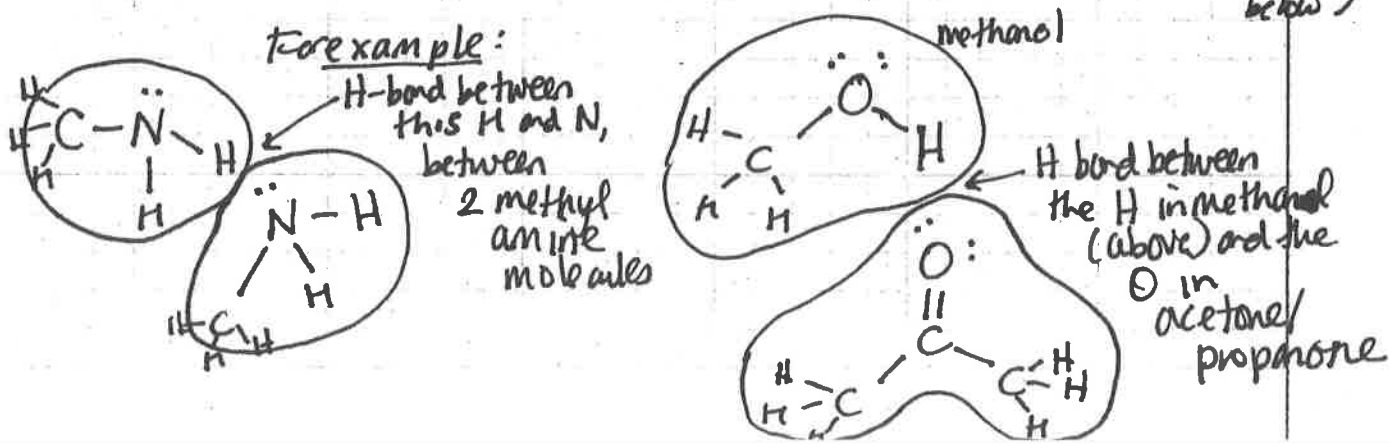
(15) What type of IMF operate:

(a) between all molecules: London Dispersion Forces

(b) between polar molecules: Dipole - Dipole Forces

(c) between the hydrogen atom of a polar bond and a nearby small, electronegative atom: Hydrogen Bond/Bonding.

(The "small, electronegative atom would be N, O, or F")
(usually the N/O/F is also covalently bonded to an H, as in the left example) but it won't always be so.. \rightarrow for example \rightarrow example below

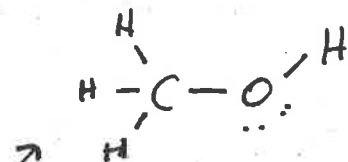


18 Explain differences in terms of IMF:

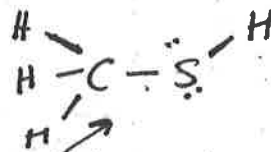
(a) CH_3OH : bp 65°C

vs

CH_3SH bp : 6°C



can form hydrogen bonds
(Its IMF is "hydrogen bonding")
so has stronger IMF than CH_3SH



has only Dipole-Dipole forces - barely, since ΔEN on the S-H bond is 0.5

(b) Xe is a liquid at 120 K
Ar is a gas at 120 K

Both Xe and Ar have only London Dispersion Forces
Xe has more e- and has a larger radius, so Xe is more polarizable and has more surface area, so Xe has stronger London Forces than Ar.

(c) Kr (84 amu) bp = 120.9 Kelvin

Cl_2 (71 amu) bp = 238 Kelvin

Both have only London Forces, but $\text{Cl}-\text{Cl}$ is more cylindrical, and Kr is more spherical.

so Cl_2 has more surface area than Kr.



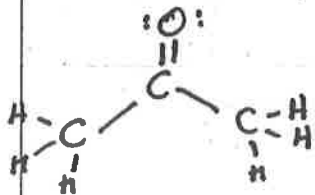
vs



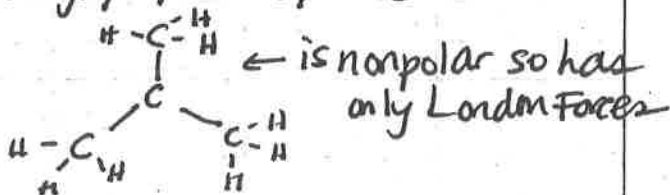
Two Cl_2 molecules can make more contact than two Kr molecules, which allows Cl_2 to have stronger London forces.

(d) Acetone bp 56°C

2 methyl propane bp -12°C



acetone is polar because of the C=O bond, so it has Dipole-Dipole Forces

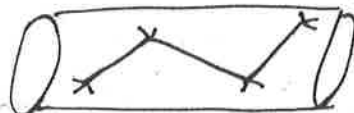


← is nonpolar so has only London Forces

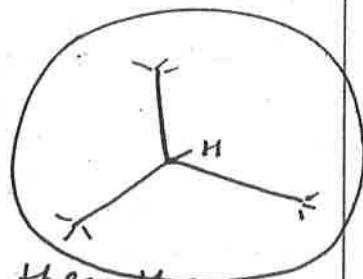
(and acetone has London forces of similar strength to 2 methyl propane since they are similar size). But only acetone has the Dipole-Dipole Forces so acetone has stronger IMF and higher BP.

23 explain why butane has a higher boiling point than 2-methylpropane. (-0.5°C vs -11.7°C)

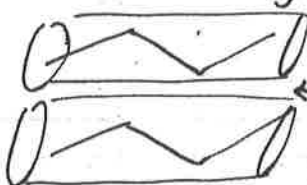
Both have the formula C_4H_{10} . Both are nonpolar, so only have London Dispersion Forces as their IMF (Intermolecular Force). Since they have the same formula, they have the same # of electrons and similar polarizability. However butane's shape is somewhat similar to a cylinder



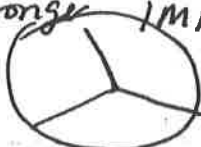
and 2-methylpropane's shape is more spherical



therefore butane has a larger surface area than methyl propane, so two butane molecules can have a stronger IMF between them than two methylpropane



more surface contact



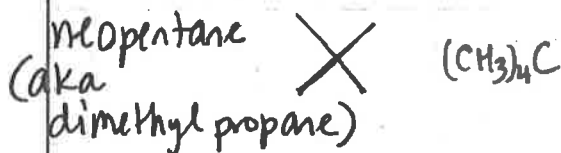
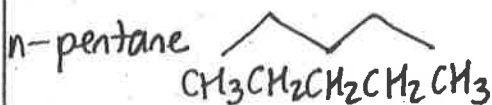
less surface contact

since more surface contact is possible; the temporary dipole can be concentrated along a longer/larger surface.

38 n-hexane has a viscosity of $3.26 \times 10^{-4} \text{ kg/m-s}$ at 270 K. how would n-pentane's viscosity compare to hexane's? how would neopentane, $(CH_3)_4C$ compare to that of n-pentane? the viscosity of

Viscosity = a fluid's resistance to flow.

Liquids with stronger attractive forces tend to have higher viscosities, since more strongly attracted molecules will drag/pull on each other.



All 3 of these have only London Dispersion Forces since they are nonpolar.

pentane has fewer C's and H's than hexane (C_5H_{12} vs C_6H_{14}), so pentane is less polarizable, and has less surface area, than hexane, so pentane would be expected to have weaker IMF, and lower viscosity, than hexane.

neopentane and pentane are both C_5H_{12} , so they have similar polarizabilities, but pentane is more cylindrical, and neopentane is more spherical, so neopentane has less surface area, and would be expected to have weaker IMF, and lower viscosity, than pentane.

(19) (a) polarizability refers to a molecule's ability to have a temporary polarity due to asymmetric distribution of charge/electrons within its orbitals. usually, the more e- a molecule has, the higher the polarizability, and, therefore, the stronger the London Dispersion forces.

(b) out of N, P, As, Sb, I would expect Sb to have the highest polarizability. It is the largest atom, and has the most electrons.

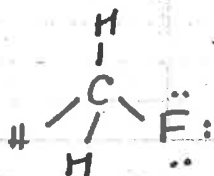
(c) Rank GeCl_4 , CH_4 , SiCl_4 , GeBr_4 acc to polarizability

$\text{CH}_4 < \text{SiCl}_4 < \text{GeCl}_4 < \text{GeBr}_4$ most polarizable highest boiling pt
 (I just ranked acc to molar mass)

(d) lowest boiling point (The order of polarizability is the same as the order of boiling points.)

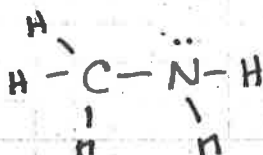
(25) (a) To form hydrogen bonds with a molecule of its same kind, a molecule must contain a H bonded covalently to a N, O, or F atom; it must contain an O-H, N-H, or F-H bond.

(b) CH_3F

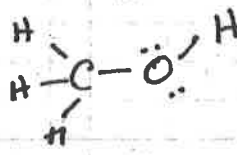


↑
has H and F, but not bonded together. can not H-bond.

CH_3NH_2

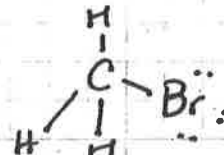


CH_3OH



↑ only these two can H-bond.

CH_3Br



can not H bond

(26) (a) HF (bp 20°C) vs HCl (bp -85°C)

HF can H-bond, HCl can not. HCl has only Dipole-Dipole Forces (both have London forces)

(b) CHCl_3 (61°C) vs CHBr_3 (150°C)

CHCl_3 is slightly more polar than CHBr_3 , due to the higher ΔEN in the C-Cl bonds than in C-Br, but CHBr_3 will have stronger London Forces since it is more polarizable and has greater surface area.

(c) Br_2 vs ICl
 (59°C) (97°C)
 (160amu) (162amu)

These two have similar London Forces, but Br_2 only has London Forces. ICl has Dipole-Dipole forces (it is polar, with ΔEN of ≈ 0.5) so has stronger forces. Br_2 has no dipole-dipole forces since it is non-polar.

31 Many salts containing BF_4^- ion are ionic liquids (meaning that they are liquid phase at room temperature) but salts containing SO_4^{2-} ion do not form ionic liquids (they must be solids at room temp, which is far more typical for ionic compounds).

SO_4^{2-} is a larger tetrahedral ion than BF_4^-

Q: explain why only BF_4^- salts, not SO_4^{2-} salts, form ionic liquids.

Nearly all ionic compounds are solid phase at room temp, because they have very strong cohesive forces.

Acc to Coulomb's Law, Attractive forces between oppositely charged ions will be strongest when

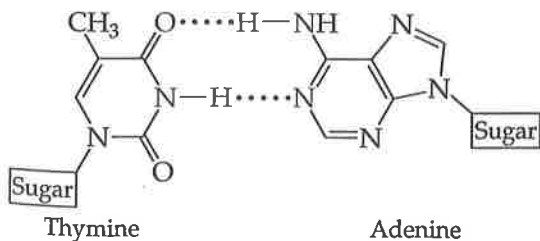
(1) The charges are relatively high, and

(2) The ions are relatively close together / the bond lengths are relatively short.

If SO_4^{2-} is a larger ion than BF_4^- , this alone would cause larger bond distances, and weaker attractive forces between ions. However, SO_4^{2-} has twice the negative charge of BF_4^- . This will cause stronger attractive force between ions, which means SO_4^{2-} salts will be less likely to be liquid / more likely to be solid / than BF_4^- salts.

78.

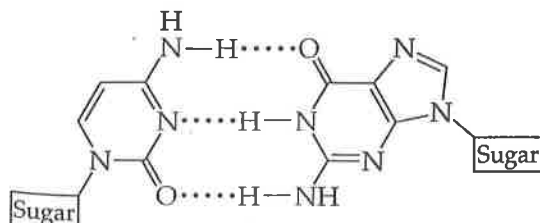
The DNA double helix (Figure 24.30) at the atomic level looks like a twisted ladder, where the "rungs" of the ladder consist of molecules that are hydrogen-bonded together. Sugar and phosphate groups make up the sides of the ladder. Shown are the structures of the adenine-thymine (AT) "base pair" and the guanine-cytosine (GC) base pair:



Thymine

Adenine

← A and T are held together by two hydrogen bonds



Cytosine

Guanine

← C and G are held together by three hydrogen bonds.

Since C and G are held together by an additional H-bond, I would expect C and G to be more stable to heating than A and T; C and G would require higher temperatures to be separated from each other, since they have stronger attractive forces holding them together.

Chapter 11

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80

	given	normal b.p.	Δbp	$\Delta \Delta bp$
Propane, C_3H_8	$-42.1^\circ C$		-	
butane, C_4H_{10}	$-0.5^\circ C$		41.6	> -5.0
pentane, C_5H_{12}	$36.1^\circ C$		36.6	> -4.0
hexane, C_6H_{14}	$68.7^\circ C$		32.6	> -2.9
heptane, C_7H_{16}	$98.4^\circ C$		29.7	
octane, C_8H_{18}	???		$\approx 27.8 ??$	$\approx -1.9 ??$

Question: (1) estimate bp
(2) explain trend.

$$29.7 - 1.9 = 27.8$$

$$98.4 + 27.8 = 126.2^\circ C$$

So I would estimate that the normal bp of octane is $\approx 126^\circ C$

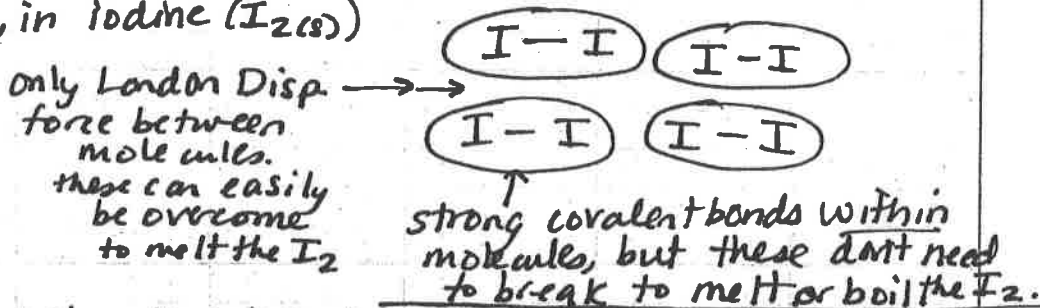
(acc to a few online sources, it is ≈ 125 to 126)

Explanation: As the hydrocarbons increase in length, the intermolecular force strength increases. Since hydrocarbons are essentially nonpolar, they have only London Dispersion Forces. As the chain length increases, the overall number of electrons, and therefore, polarizability, increases, causing stronger "temporary dipoles." Also, a longer chain means more surface area, so the chains can be attracted to neighboring chains along a larger surface. The higher polarizability and surface area both cause stronger IMF and therefore, higher boiling point.

7. Both molecular solids and covalent network solids contain covalent bonds. Why do they differ so much in terms of hardness and melting point?

In molecular solids, the crystal contains distinct molecules, which have covalent bonds within the molecule (so strong intra molecular forces) but relatively weak attractive forces between molecules, such as London Dispersion, dipole-dipole, or Hydrogen bonding. These intermolecular attractive forces are much weaker than covalent bonds, so the molecules can be separated from each other to melt or boil without a huge amount of kinetic energy (at relatively low temp)

For example, in iodine ($I_2(s)$)



In covalent network solids, however, (like Diamond, Si, SiO_2 ...) there are no distinct molecules; each atom is covalently bonded to all of its neighboring atoms. To melt or scratch the crystal, covalent bonds must be broken, for example, in Diamond, C-C covalent bonds would have to be broken. So covalent network solids have very high melting points and hardness.

8. Silicon, like Diamond, is a covalent network solid. Each Si atom is sp^3 hybridized and single/sigma bonded to 4 other Si atoms, with 109.5° bond angles.

10. Which type(s) of crystalline solid have these characteristics:

(a) high mobility of e^- throughout the solid: Metallic Bonding

(b) softness, relatively low melting point: Molecular Solid

(c) high mp and poor electrical conductivity:

Covalent Network Solid or Ionic

↑ though graphite conducts..

could have London, Dipole-Dipole, or H-bonding holding molecules together. could also be metallic bonding depending on how soft / how low mp.

(d) A network of covalent bonds:

Covalent Network Solid (!)

38) classify as substitutional alloy, interstitial alloy, or intermetallic comp.



almost a 2:1 ratio, exactly, but not quite, so we won't call it a compound.

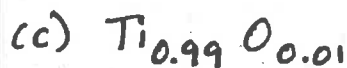
acc to page 255, atomic radii are
Cu: 1.38 Å, Zn: 1.31 Å.

Because the radii are similar, it is probably a substitutional alloy.

(since it is Cu and Zn, it is brass!)



has an exact 3:1 ratio (whole number ratio)
so it is an intermetallic compound.



not a compound since not shown as whole # ratio.

Ti radius = 1.36 Å
O radius = 0.73 Å

since the radii are pretty different and only a tiny amount of the smaller atom (oxygen) is present, it is probably an interstitial alloy.

39) True/False:

(a) substitutional alloys tend to be more ductile than interstitial alloys

True. The presence of the smaller atoms in the "gaps" in an interstitial alloy makes the metal less flexible.
for example, steel (an interstitial alloy w/ carbon in iron) is harder than pure iron / less flexible / ductile than pure Fe)

(b) interstitial alloys tend to form between atoms with similar radii.

False. In substitutional alloys, the radii are similar, but in interstitial alloys, one atom type must have a smaller radius than the others, so that it can fit in the empty spaces.

(c) nonmetallic elements are never found in alloys.

False. carbon (in steel) is a counterexample; carbon is a nonmetal.

- 67) Which element(s) would you pick, to replace Ga in GaAs Semiconductor, to make an n-type Semiconductor.
(The process of replacing a tiny fraction of atoms with another atom to increase conductivity is called "doping")

Ga has 3 valence electrons.

In an n-type semiconductor, you replace a tiny fraction of the atoms with an element with 1 more valence electron than the element you are replacing. The additional valence electron will be somewhat "mobile." Since e⁻ are negative, it is called an n-type semiconductor.

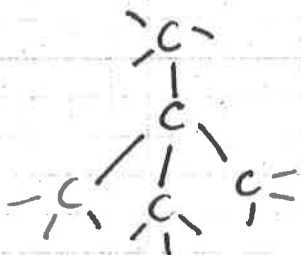
So we need something w/ 4 valence electrons, but probably similar in size to Gallium, so Si or Ge would be good choices.

- 68) Now we are replacing a few As in GaAs to make a p-type semiconductor, so we need something with one less valence e⁻ than As (As has 5 v.e.) to create a "hole" - a "missing" e⁻ from the crystal lattice, which can move around (since the hole is moving, and the hole represents the absence of an electron, it is called a positive type, or p-type, semiconductor.)

So, we need it to have 1 less than 5 valence e⁻, that is, we need it to have 4 v.e., but similar size to As. So again, we could "dope" it with Si or Ge!

- 112) What are C-C-C bond angles in diamond (a) and graphite (b)

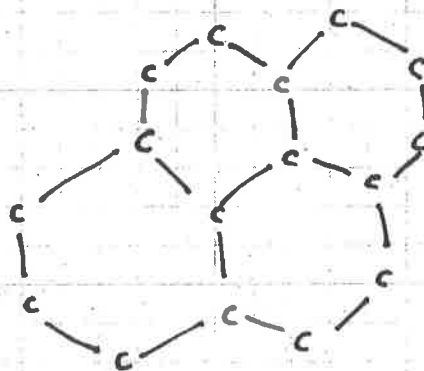
(a) Diamond



each C is sigma/single bonded to 4 other carbons;

each C is involved in 4 sigma bonds.
bond \angle 109.5°
hybridization: sp^3

(b) graphite (one sheet shown)



each C is involved in 3 sigma bonds
Bond \angle 120°
 sp^2 hybridization