Name _____ KEY _____ Rec. TA/time _____

1.   Recall the van der Waal's equation and the significance of the constants a and b.

Values of the van der Waal's constants are determined for two gases and given in the table below.

gas	a (atm·L/mol^2)	b (L/mol)
A	30.53	0.102
B	0.134	0.143

Which of the following statements is **FALSE**?

a) Ideal gases conform to the postulates of the Kinetic Molecular Theory and follow the Ideal Gas Law.
b) Deviations from ideal behavior of gases are most likely at high pressures and low temperatures.
c)* At high pressures gas A will exhibit larger positive deviations from ideality than gas B.
d) Gas A has stronger intermolecular forces than gas B.

$$\left(P + \frac{n^2 a}{V^2} \right)\left(V - nb \right) = nRT$$

or

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

causes **(+)**   causes **(−)**
deviation   deviation

$P_m > P_i$ $P_m < P_i$ P_m = measured (real) P; P_i = ideal P

due to vol   due to IAF
of molecules

b: corrects for finite molecular volume of real gases (b=0 for an ideal gas)

a: corrects for attractive forces between real molecules (a=0 for an ideal gas)

Thus,   larger molecule => larger molecular volume => larger b
               stronger AF => larger a

C: **This was false.** B has the bigger "b" value & should show biggest (+) dev. from ideality.

Real gases behave nearly ideally at high T (where KE is great enough to overcome IAF) and low P (larger container volume, in which case the molecular volume is less important). As the temp dec. and pressure inc. a gas behaves less ideally and approaches its liquefication point. A bigger molecule has larger volume (b value) & would exhibit larger (+) deviations. A molecule with larger "a" value has stronger AF and would exhibit larger (-) deviations.

2.   (3 pts) Which of the following compounds is **INCORRECTLY** paired with the intermolecular forces that exist between neighboring molecules?

a) PF_5 London forces only
b) $AsCl_3$ London forces, dipole-dipole forces
c) $SiCl_4$ London forces only
d) CH_3CH_2F London forces, dipole-dipole forces

e)* $CH_3\overset{\overset{O}{\|}}{C}CH_3$ London forces, dipole-dipole forces, hydrogen bonding

Determine if molecules are nonpolar or polar (Draw Lewis Structure and determine shape). Also, remember that in general if there is one or more lone pair of electrons (lpe–) on the "central" atom the molecule will be polar. The exceptions to this rule is a linear molecule resulting from 5 e– pairs (3 atoms and 2 lpe–) and a square planar molecule resulting from 6 e– pairs (4 atoms and 2 lpe–), which can be nonpolar.
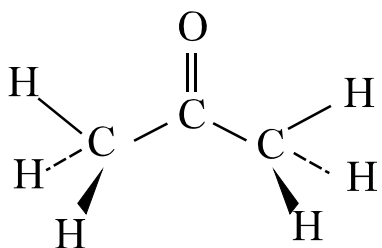
Tetrahedral around CH_3 C atoms & trigonal planar around C=O C atom.
POLAR (around C atoms, especially C=O group)
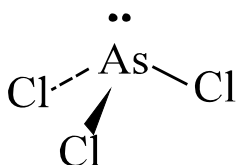**LF** & **DD** (NO H bonding - since no H on the O)
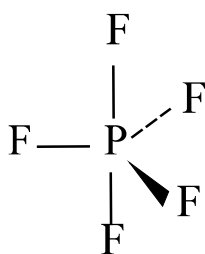
a) PF_5

Trigonal bipyramidal
Nonpolar (All 5 atoms around P are indentical.)
LF only
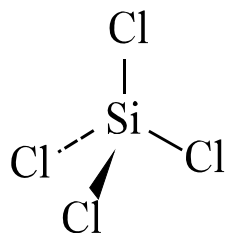
b) $AsCl_3$

Trigonal pyramidal (like $:NH_3,:NF_3,:PH_3,$ $:PF_3$, etc.)
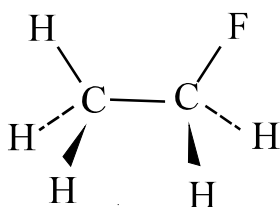**Polar** ; **LF** & **DD**
(Usually lpe– on central atom ⇒ polar)

c) $SiCl_4$

Tetrahedral (like CH_4, CF_4, SiH_4, etc.)
Nonpolar (all 4 atoms on Si are identical)
LF only

d) CH_3CH_2F

Tetrahedral around C atoms
POLAR (around the C atoms, atoms on C's are not identical)
LF & **DD** (No H bonding - since no H on the F)

3. (8 pts) Examine the following compounds and then answer the questions below which refer to these compounds, as pure substances. (**Give a short explanation for your choices**, i.e, types of **attractive forces**, whether **polar** or **nonpolar**, etc.)

LF ≡ London Forces   D-D ≡ Dipole-Dipole   IAF ≡ intermolecular attractive forces

C_3H_8 $CH_3CH_2 - \overset{..}{\underset{..}{O}} - H$ $CH_3 - \overset{..}{\underset{..}{O}} - CH_3$ CH_2F_2

MW ≈   nonpolar   polar   polar   polar
        44 amu   46 amu   46 amu   52 amu

a) Which compound(s) has(have) **only London forces**?
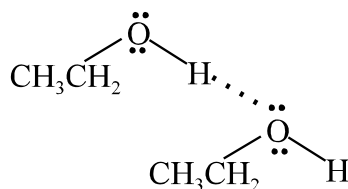
C_3H_8 nonpolar (only C and H in formula - nonpolar)

Nonpolar molecules have **ONLY LF**

b) Which compound(s) has(have) **Dipole-Dipole** forces?

CH₃CH₂   H   — bent
CH₃   CH₃ — bent
F---C with H and F — tetrahedral
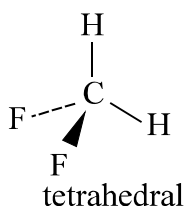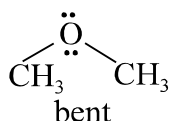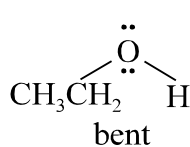
polar molec. have D-D forces
(In addition to LF)

c) Which compound(s) can form **H-bonds** between molecules (as a pure substance)?

This molec. can form H-bonds between two such molecules. There must be a H atom covalently bonded to an N, O or F atom and a lone pair e⁻ on one of those atoms (This is in addition to LF and DD att. forces.)

(CH_3OCH_3 and CH_2F_2 are polar but can **NOT** form H-bonds.)

d) Which compound should have the **highest** heat of vaporization, ΔH_{vap}?

CH_3CH_2OH has LF, D-D & H-bonding. The first 3 molecules are about the same size so the LF are about the same. CH_2F_2 isn't that much different in size than the other three so it's LF isn't that much different than first 3 (the CH_2F_2 LF may be slightly larger). The C_3H_8 is nonpolar and has only LF. CH_3CH_2OH, CH_3OCH_3 and CH_2F_2 are polar and have DD IAF in addition to LF (CH_3CH_2OH is more polar and has larger DD IAF). Most importantly, CH_3CH_2OH can form H-bonds between CH_3CH_2OH molecules (whereas CH_3OCH_3 and CH_2F_2 can't as pure substances since the H atoms are bonded to the C atoms and not an N, O or F atom).

∴ **CH_3CH_2OH** has **strongest IAF** & **highest** ΔH_{vap}

Remember (generally): **Stronger** Att. Forces   ⇒   **Lower** Vapor Pressure
Slower rater of **evaporation**

Higher b.p., m.p., sublimation pt.
ΔH_{vap}, ΔH_{fus}, ΔH_{sub},
critical temp., surface tension, viscosity

4. Which of the following statements is **FALSE**?

a) NF_3 has a permanent **dipole moment**.

b)* PCl_5 has a **lower surface tension** than CCl_4 at the same temperature.

c) CH_3F has **stronger** total **intermolecular forces** than BH_3.

d) O_2 has a **greater vapor pressure** at a specified temperature than CH_3F.

e) HF has a **higher boiling point** than PH_3.

a) T: NF_3 is **trigonal pyramidal** with a lone pair of electrons on the nitrogen. It looks like NH_3. The NF_3 molecule is **polar** (has a **permanent dipole** moment) and thus has London forces and Dipole-Dipole attractive forces.

b) F: surface tension (PCl_5) > surface tension (CCl_4) larger molecule ⇒ larger LF

MW:	208	154
# e– :	100	74

PCl_5 is trigonal bipyramidal with 5 identical atoms surrounding the central atom, P, and is thus nonpolar. CCl_4 is tetrahedral with 4 identical atoms surrounding the central atom, C, and is thus nonpolar. Since both molecules are nonpolar they only have London Forces. Larger molecules have larger LF. PCl_5 is bigger than CCl_4 and thus has larger LF and a greater surface tension.

c) T: $AF_{(CH_3F)}$ > $AF_{(BH_3)}$ CH_3F BH_3

MW:	34	14	LF	<<	LF
# e– :	18	8	DD		

The CH_3F molecule is polar (tetrahedral but the 4 atoms around C are not identical) and has LF and DD attractive forces (AF). The BH_3 molecule is nonpolar (trigonal planar and the 3 atoms around the B are identical) and has only LF. The CH_3F is also bigger than BH_3. Thus, CH_3F has larger LF and also DD forces.

d) T: $VP_{(O_2)}$ > $VP_{(CH_3F)}$ O_2 CH_3F

MW:	32	34	LF	≈	LF
# e– :	16	18			DD

CH_3F has stronger IAF than the nonpolar O_2 and thus a <u>lower</u> vapor pressure.

e) T: b.p. $_{(HF)}$ > b.p. $_{(PH_3)}$ HF PH_3

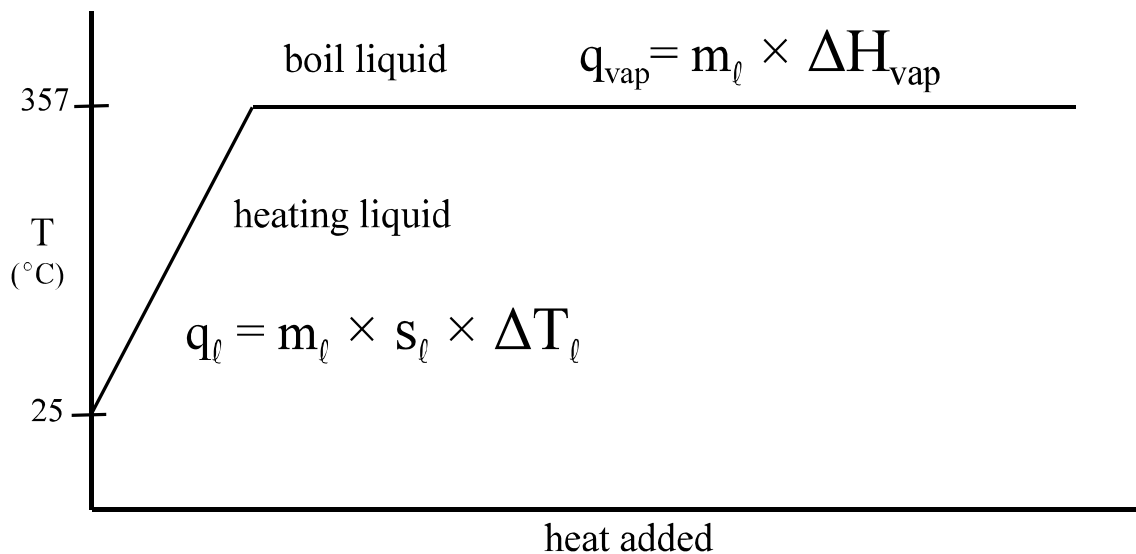|					
MW:	20	32	LF	<<	LF
# e– :	10	18	DD	>>	DD
			H-bonds		

The **H-bonding** that occurs between **HF** molecules is a **very strong IAF** compared to the other forces and is in addition to the other IAF and is what is the main reason for the higher IAF of HF compared to the other molecules of approximately same size.

Remember: <u>Stronger</u> Att. Forces ⇒   <u>Lower</u> **Vapor Pressure**
                (Generally)   <u>Slower</u> rater of **evaporation**

                          Higher b.p., m.p., sublimation pt.
                              ΔH_{vap}, ΔH_{fus}, ΔH_{sub},
                              critical temp., surface tension, viscosity

5.   (5 pts) Calculate the amount of heat (kJ) required to heat 125 g of mercury (Hg) from 25.0 °C to its boiling point (357 °C) and then vaporize it? (specific heat of liquid Hg = 0.138 J/g•°C, ΔH_{vap} = 292 J/g)

a) 42.2 kJ   b) 47.4 kJ   c) 30.8 kJ   d) 36.5 kJ   e) 5.73 kJ

Draw a heating curve and label it (makes it easier)

boil liquid $q_{vap} = m_\ell \times \Delta H_{vap}$

357 —

heating liquid

T
(°C)

$q_\ell = m_\ell \times s_\ell \times \Delta T_\ell$

25 —

heat added

$$q = q_{heat\ liquid} \quad + \quad q_{boiling}$$

$$= (m_\ell \bullet s_\ell \bullet \Delta T_\ell) \quad + \quad (m_\ell \bullet \Delta H_{vap})$$

$$= [125\ g \bullet 0.138\ J/g\text{-}°C \bullet (357 - 25.0)°C] \quad + \quad (125\ g \bullet 292\ J/g)$$

$$= 57\underline{2}7\ J \quad + \quad 36\underline{5}00\ J \quad = \quad 42\underline{2}27\ J \quad = \quad 42.2\ kJ$$

6. (6 pts) A substance has a $\Delta H_v = 20.0$ kJ/mol. It has a vapor pressure of 0.800 atm at -2.00 °C. What is it's **normal boiling point**?

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$P_1 = 0.800$ atm $P_2 = 1.00$ atm   (normal b.p. occurs at 1 atm)

$T_1 = -2.00°C + 273.15 = 271.15$K $T_2 = ?$ (the normal b.p.)

## T **MUST** be in kelvin (K)

$$\ln\left(\frac{1.00}{0.800}\right) = \frac{20.0 \times 10^3\ \text{J/mol}}{8.314\ \text{J/mol}\bullet\text{K}}\left(\frac{1}{271.15\ \text{K}} - \frac{1}{T_2}\right)$$

$0.22\underline{3}14 = 2.4\underline{0}558 \times 10^3\ \text{K}\left(3.687\underline{9}9 \times 10^{-3}\ \text{K} - T_2^{-1}\right)$

$T_2^{-1} = 3.592\underline{3}4 \times 10^{-3}\ \text{K}^{-1}$ $T_2 = 278.1\underline{4}5\ \text{K} = 4.9\underline{9}59°C = 5.00°C$

higher T $\longrightarrow$ higher VP   (and vice versa)

7.   (5 pts) The following is a phase diagram for an unknown substance. **Label** the regions (**phases**) <u>**AND**</u> write what points **A-D** represent (1 or 2 sentences next to the letters listed below). For letter **E** answer the question given there and give a brief explanation.
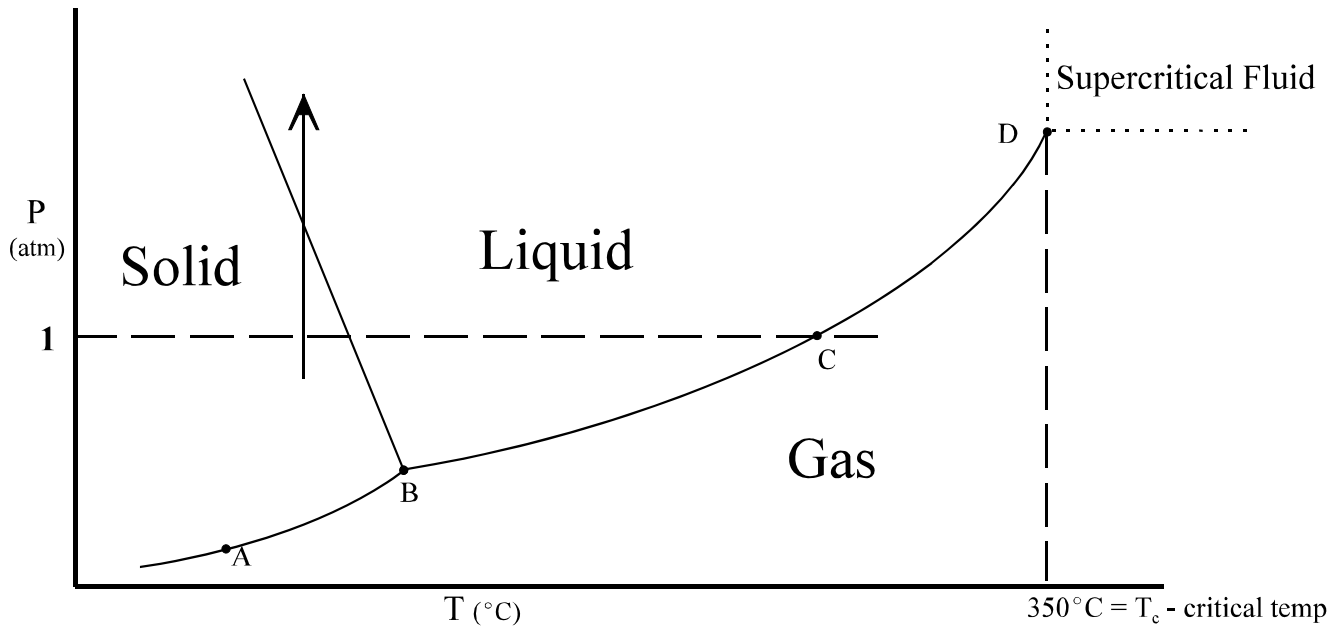
A. Sublimation point or P & T at which solid and gas are in equilibrium

   Line AB is the vapor pressure curve for the solid. Every point on this line represents an equilibrium between solid and gas.

B. Triple point - 3 phases in equilibrium

   In this case, all 3 states (solid, liquid and gas) exist in equilibrium (at the same time).

C. <u>Normal</u> **boiling** point - b.p. at 1 atm

   The temperature at which the liquid and gas are in equilibrium at 1 atm

   Line BD is the b.p. curve - each point on this line is a b.p. at a particular atmospheric pressure.

D. Critical point: temperature and pressure above which only 1 fluid phase (supercritical fluid) exists.

   Can <u>**NOT**</u> liquefy the gas by applying pressure when $T > T_c$. Last point where both the liquid and gas exist in equilibrium (can still liquefy the gas at this temp by applying pressure, Pc)

E. Which phase is <u>**MORE**</u> dense (circle answer and explain)?   solid   or   (liquid)

   When you apply pressure to the solid at a constant temp you will eventually get a liquid (see arrow on diagram). This means the liquid has a smaller volume and larger density than the solid $(V_s > V_\ell, D_s < D_\ell)$. (When you apply pressure to anything you go to a smaller volume.)

   The s $\rightleftharpoons$ ℓ (m.p.) line has a negative slope (leans to the left like H_2O)

   m.p. dec w. inc $P_{atmospheric}$

8.　(5 pts) It would be helpful to sketch a phase diagram for an imaginary compound (the points are already plotted for you):

Which of the following statements is **INCORRECT** about the compound?

a) **Increasing** the **temperature** from 0°C to 60°C at 0.7 atm will cause **fusion** to occur.

b) The solid is **less** dense than the liquid.

c) The solid **can** melt at temperatures below 49°C when the **pressure** is **increased**.

d)* **Condensation** occurs if the pressure is increased from 0.1 atm to 0.5 atm at 0°C.

e) The solid will **sublime** rather than melt when the temperature is **raised** if the **pressure** is **0.3** atm.

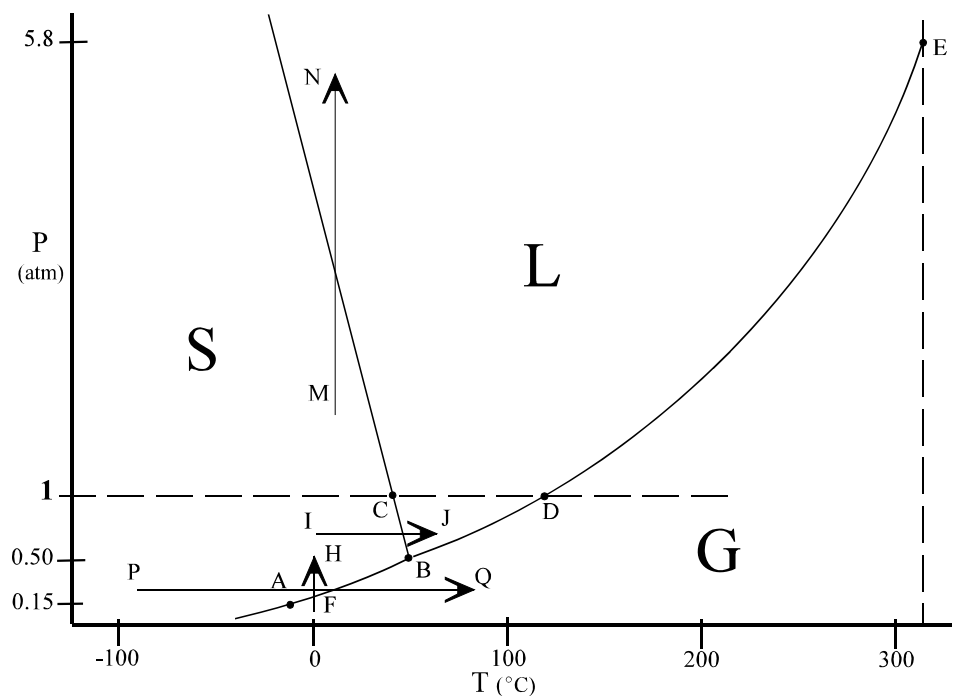triple point = 52 °C, 0.5 atm

vapor pressure of solid at -15 °C
　　= 0.15 atm

normal melting point = 49 °C

normal boiling point = 118 °C

critical point = 329 °C, 5.8 atm

line AB: VP curve for solid (s ⇌ g)
　　　-sublimation curve
line BE: VP curve for liq (ℓ ⇌ g)
　　　-boiling pt. curve
line BC: m.p. curve for solid
　　　(s ⇌ ℓ)

a) T: Line IJ. A phase change occurs going from a solid to a liquid. This is fusion (melting).

b) T: The m.p. curve (line BC, s-ℓ equil.) slopes to the left (has a negative slope) - **m.p. dec.** as **Pressure inc.** (like H_2O, exception to that of most substances).
　　　- when pressure is supplied you go to the state with a smaller volume.
　　　　- Apply P to solid and get a liquid so the **liquid** has smaller vol., **greater density** (solid is less dense than the liquid)

c) T: The normal melting point is 49 °C. The s-ℓ equil. line has a negative slope (T dec. as P inc.). The **m.p. dec.** as **P inc.** Thus, the solid **can** be liquefied at temp. less than that of the melting point by applying pressure (inc. P). (See line MN.)

d) F: Line FH. A phase change occurs going from a gas to a solid, **deposition**.

e) T: Line PQ is represents the phase transition of s → g, sublimation.

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9. (7 pts) A metal crystalizes in a body-centered-cubic unit cell with an atomic radius of 2.20 Å and a density of 3.48 g/cm³. (1 Å = 1 x 10⁻⁸ cm, N_A = 6.02 x 10²³)

(a) What is the atomic weight of the metal?

$D = 3.48$ g/cm³   1 mol = 6.02 x 10²³ atoms

bcc ⇒ 2 atoms/uc   r = 2.20 Å = 2.20 x 10⁻⁸ cm

a) <u>atomic weight</u> - find g/mol

　Need to find volume - need edge length

$$V = \ell^3 \quad \ell = V^{1/3} \qquad \ell = \frac{4r}{\sqrt{3}} \quad \text{(for bcc)}$$

$$\ell = \frac{4r}{\sqrt{3}} = \frac{4\,(2.20\ \text{Å})}{\sqrt{3}} = 5.0\underline{8}06\ \text{Å} = 5.0\underline{8}06 \times 10^{-8}\ \text{cm}$$

$$V = \ell^3 = (5.0\underline{8}06 \times 10^{-8}\ \text{cm})^3/\text{uc}$$

$$?\ \frac{\text{g}}{1\ \text{mol}} = \frac{3.48\ \text{g}}{\text{cm}^3} \times \frac{(5.0\underline{8}06 \times 10^{-8}\ \text{cm})^3}{1\ \text{uc}} \times \frac{1\ \text{uc}}{2\ \text{atoms}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}}$$

$$= 13\underline{7}.36\ \text{g/mol}$$
$$= 137\ \text{g/mol}$$

(b) What is the coordination number of the metal atom in this structure?

　Body-centered cubic

　　Coord. no. = # nearest neighbors = **8**

bcc has 1/8 particle in each corner and 1 particle in the center of the unit cell. In the **bcc** structure each particle is surrounded by 8 other particles and has a coordination number of 8. Think of the particle in the center of the unit cell. It is surrounded by the 8 particles in the corners.

10.   Choose the member of each of the following pairs that are expected to have the **HIGHER** normal melting point.

SiC or NaCl   HF or Na   W or Bi Al_2O_3 or NaCl

a) NaCl	HF	Bi	Al_2O_3
b) NaCl	Na	W	NaCl
c) SiC	HF	W	NaCl
d) SiC	Na	Bi	Al_2O_3
e)* **SiC**	**Na**	**W**	**Al_2O_3**

SiC   Na   W Al_2O_3

SiC(s)   or   NaCl
covalent   ionic
network

SiC is a covalent network solid, with a diamond-like structure - hard and high m.p. (solid at room temp., mp = 2830°C) Must break covalent bonds to melt this type of solid.
          (Group 4A elements form covalent network solids as pure solids and compounds of these elements - C(diamond), C(graphite), Si, Ge, gray Sn & elements close to group 4A - BN (s), SiO_2 (quartz))

NaCl is an ionic solid and these also tend to have high m.p. (801°C) However, one would not expect the m.p. to be as high as that of a covalent network, especially since the charges are small (+1 and -1). See the explanation below.

HF   or   **Na**
molecular   **metallic**

Na is a metallic solid. **Metallic solids** in general have **higher m.p.** (up to about 3000°C) than the majority of molecular compounds. All metals except Hg are solids at room temperature.
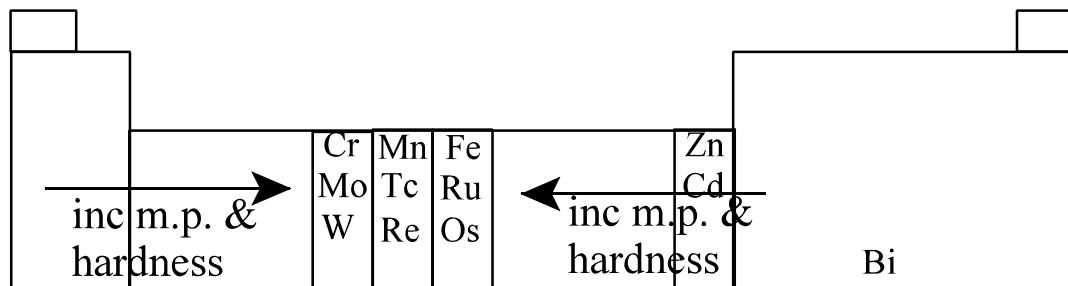
HF is a molecular solid and has LF, DD & H-bonding. Even though HF can form H-bonds these IAF are **NOT** as strong as metallic bonds. HF is a gas at room temp.

***** continued on the next page *****

10.   (cont.)

W   or   Bi
metallic   metallic

Both are metallic & m.p. inc from both the left and right in the PT toward the middle of the transition elements (has to do with # "valence" e⁻ in the metal).

Al₂O₃   or   NaCl   Ionic Solids - m.p. & hardness (and solubility)
 ionic   ionic   depends on Lattice Energy

$$LE \propto \frac{Q^+ Q^-}{d}$$

Q: charge on ion
d: distance between centers of ions & usually determined by adding ionic radii.

The Al^{3+} has a +3 charge while Na^+ has a +1 charge & Al^{3+} is smaller than Na^+

The O^{2-} has a a −2 charge while Cl^- has a −1 charge & O^{2-} is smaller than Cl^-.

∴ Numerator for $Al_2O_3 \propto |(+3)(-2)| = 6$ &   for NaCl $\propto |(+1)(-1)| = 1$

so numerator for Al_2O_3 is 6 times larger than that for NaCl

Also, $r_{(Al^{3+})} < r_{(Na^+)}$ & $r_{(O^{2-})} < r_{(Cl^-)}$ so $d_{(Al_2O_3)} < d_{(NaCl)}$

∴ $LE_{(Al_2O_3)} > LE_{(NaCl)}$ (mostly based on the charges)

& Al_2O_3 has higher m.p. (greater LE => higher m.p.   Also, generally less soluble.)