Part A. **Answer all twelve questions with a few sentences or equations (5 marks each).**

1. State the Pauli exclusion principle.

The Pauli exclusion principle states that no two electrons in an atom can have the same four quantum numbers.

2. Beginning with $NiS_{(s)}$, show the reactions leading to acid rain, i.e. $H_2SO_{4(aq)}$.

$NiS_{(s)} + 1.5\ O_{2(g)} \rightarrow NiO_{(s)} + SO_{2(g)}$

$SO_{2(g)} + ½\ O_{2(g)} \rightarrow SO_{3(g)}$

$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$

3. If a sample of gas is compressed and heated, is ΔE positive or negative? Why?

$\Delta E = q + w$. In this case, both q and w are positive, therefore ΔE is also positive.

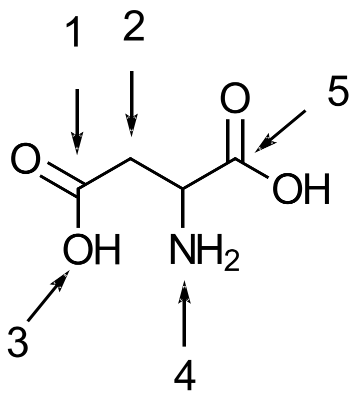
4. Which has the larger lattice energy: $RbBr_{(s)}$ or $CsBr_{(s)}$? Why

The lattice energy of RbBr is greater. The only difference is the size of the cation. The Rb^+ ion is smaller than the Cs^+ ion. Therefore the Rb^+ is closer to the Br^- than is the Cs^+, resulting in a larger force of attraction between Rb^+ and Br^-, thus the larger lattice energy of RbBr.

5. Why are metals not transparent?

In a metal, the bandgap is small. Thus, photons of almost any energy in the visible portion of the spectrum are easily absorbed, exciting electrons from the HOMO to the LUMO. These visible photons are therefore not transmitted by substance, causing it to be opaque (not transparent).

6. In the structure of aspartic acid shown below, what is the hybridization of each of the indicated atoms?



1. sp^2

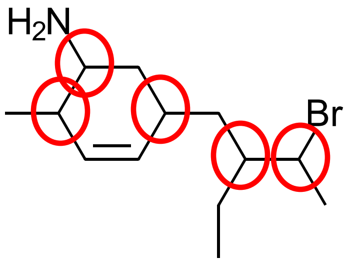
2. sp^3

3. sp^3

4. sp^3

5. sp^2

7. Circle each chirality centre in the molecule shown below (1 mark for each correct chirality centre, -1 for each one circled that is not chiral).



8. Is AsF_3 a polar molecule? Why or why not?

5 + 3(7) = 26 electrons. With 8 around each F atom, this leaves two as a lone pair on the central As atom. The structure is therefore trigonal pyramidal. Since each bond is polar, so is the molecule.

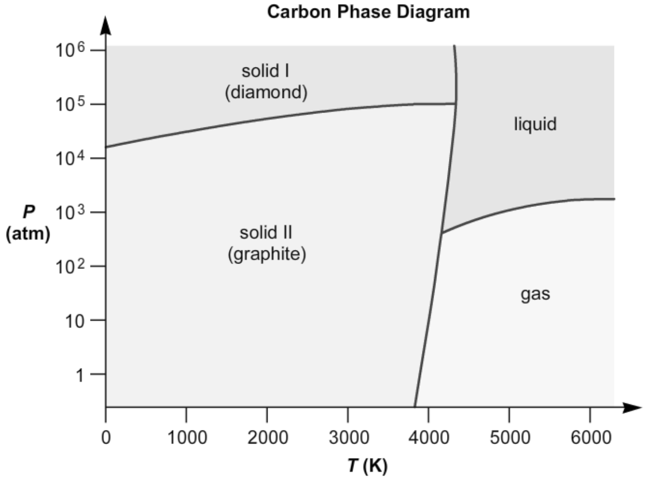
9. Which has the lowest freezing point: 1.0 m $NaCl_{(aq)}$, 1.0 m $Na_2SO_{4(aq)}$ or 0.5 m $AlCl_{3(aq)}$? Why?

Freezing point depression is a colligative property and therefore depends on the amount of solute in solution. 1.0 m $NaCl_{(aq)}$ is actually 2.0 m in ions, 1.0 m $Na_2SO_{4(aq)}$ is 3.0 m in ions and 0.5 m $AlCl_{3(aq)}$ is 2.0 m in ions. Thus 1.0 m $Na_2SO_{4(aq)}$ will have the lowest freezing point.

10. Why are unsaturated compounds often very reactive?

Unsaturated molecules have multiple C-C bonds. Some of these bonds are π-bonds. Electrons in π-bonds are delocalized and further from the C-C bond axis than the σ-electrons, and therefore are easier to remove (for instance by an oxidant).

11. The phase diagram for carbon is shown below. Which is more dense: diamond or graphite? How do you know?



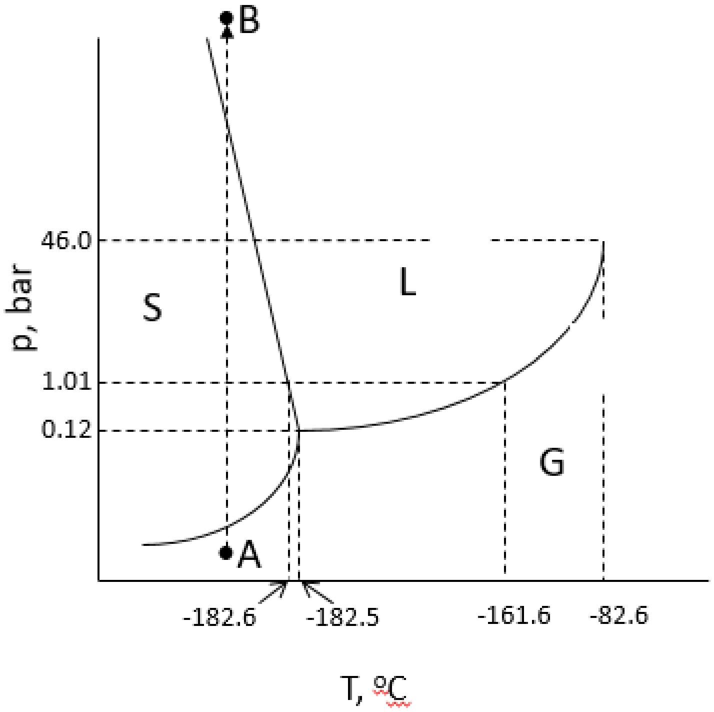
Diamond is more dense. We know this because it exists at higher pressure than graphite. Materials at higher pressure must have higher densities.

12. Name five functional groups containing the carbonyl group.

Aldehyde, ketone, carboxylic acid, ester, amide.

Part B. **Answer all three questions B1, B2 and B3 (20 marks each).**

B1. The phase diagram for methane (CH_4) is shown below.



(a) **[3]** Label the solid (S), liquid (L) and gas (G) regions on the phase diagram.

(b) **[2]** What are the critical pressure and temperature of methane?
46.0 bar and -82.6ºC

(c) **[2]** What is the normal boiling point of methane?
-161.6ºC

(d) **[2]** What is the normal melting point of methane?
-182.6ºC

(e) **[2]** At what temperature and pressure can all three phases coexist?
-182.5º C and 0.12 bar

(f) **[5]** Beginning at point A, describe what would be observed if the pressure was increased to 50 atm, keeping the temperature constant?

At point A, there is only methane gas. When the pressure reaches the S-G equilibrium line, solid methane appears. In the region labelled “S”, only solid exists. When the pressure reaches the S-L line, liquid appears. Above this line, only liquid exists.

(g) **[4]** Liquid methane exists in lakes on the surface of Saturn’s moon Titan. If some solid methane forms, will it sink or float in these lakes? How do you know?

According to the phase diagram, liquid methane is more dense than solid (note that the liquid phase is above the S-L equilibrium line, i.e. at higher pressure). The solid will therefore float in the liquid.

B2. **[7]** (a) A solution is prepared by dissolving 6.85 g of sucrose ($C_{12}H_{22}O_{11}$) in 34.0 g of water. Calculate the boiling point of this solution. For water, K_b = 0.52 °C kg mol^{-1}. Sucrose is non-volatile and does not dissociate in water.

$$\frac{6.85\,\text{g}}{12(12.011)+22(1.008)+11(16.00)\,\text{g mol}^{-1}} = 0.0200\,\text{mol}$$

$$\text{m} = \frac{0.0200\,\text{mol}}{0.034\,\text{kg}} = 0.589\,\text{mol kg}^{-1}$$

$$\Delta T_b = iK_b m = 1\times 0.52^{\circ}\text{C kg mol}^{-1}\times 0.589\,\text{mol kg}^{-1}$$

$$= 0.31^{\circ}\text{C}$$

$$\text{thus, } T_b = 100.00^{\circ}\text{C} + 0.31^{\circ}\text{C}$$

$$= 100.31^{\circ}\text{C}$$

(b) **[7]** A 0.15 g sample of a protein is dissolved in water to make 2.0 mL of solution. The osmotic pressure of this solution is found to be 2480 Pa at 25°C. Calculate the molecular weight of the protein.

$\Pi = MRT$

Thus, $M = \Pi/(RT)$

= 2480 Pa / (8.314 J K^{-1} mol^{-1} x 298 K)

= 1.00 mol m^{-3}

In this 2.0 mL solution there would be 1.00 mol m^{-3} (2 x 10^{-6} L) = 2.00 x 10^{-6} mol of protein.

The molecular weight is therefore 0.15 g / (2.00 x 10^{-6} mol) = 7.45 x 10^{4} g mol^{-1}

(c) **[6]** A solution is made by adding 3.0 mol $Na_2SO_{4(s)}$ to 2 kg $H_2O_{(l)}$. What is the vapor pressure (in Pa) of this solution at 30°C? The vapor pressure of pure water at 30°C is 4242 Pa.

3.0 mol $Na_2SO_4 \rightarrow$ 6.0 mol Na^+ + 3.0 mol SO_4^{-2}, or 9.0 moles of solute all together.

2 kg H_2O = 2,000 g = 2000 g / 18 g mol^{-1} = 111.1 mol H_2O

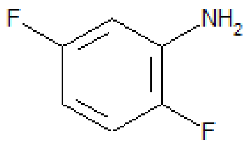
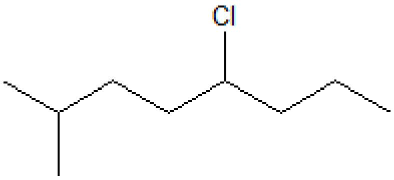
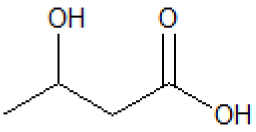
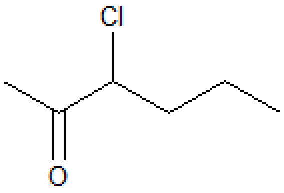
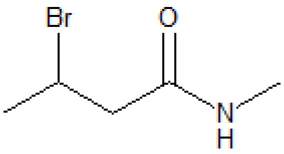
Thus, X_{H2O} = 111.1/(111.1 + 9.0) = 0.925

$$p_{H_2O} = p^{o}_{H_2O}X_{H_2O}$$

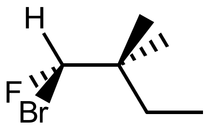
$$= 4242\,\text{Pa}(0.925)$$

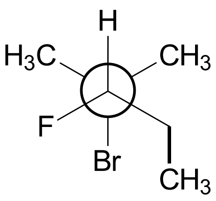
$$= 3924\,\text{Pa}$$

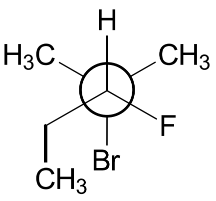
B3. (a) Name the following compounds **[2 each]**:

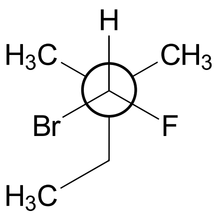
	2,5-difluoroaminobenzene (2-amino-1,4-difluorobenzene) (2,5-difluoroaniline)
	5-chloro-2-methyloctane
	3-hydroxybutanoic acid
	3-chloro-2-hexanone (3-chlorohexan-2-one) (1-chlorobutyl-methyl ketone)
	N-methyl-3-bromobutanamide

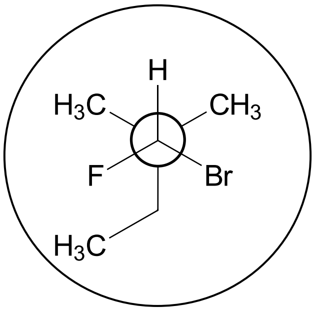
(b) **[5]** Circle the Newman projection that correctly represents



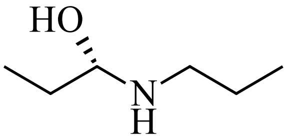




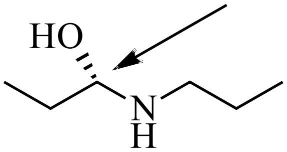




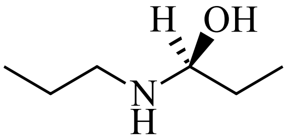
(c) **[5]** Determine whether the molecule of 1-(propylamino)-1-propanol shown below is the *R* or *S* enantiomer and show clearly step by step how you arrived at your answer.



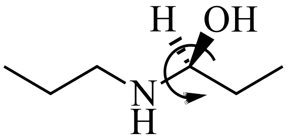
First, find the chiral carbon, which is the one one with four different groups bound to it (remember the implicit H atom on this carbon):



Then prioritize the four groups, with the highest priority having the highest atomic weight, and rotate the molecule until the lowest priority (the H atom) in this case) is at the back:



And reading the other three groups from highest (-OH) to (-NH) to lowest (-C_2H_5) is in a counterclockwise direction, hence this is the *S* enantiomer:



Part C. Answer any three of the five questions C1 – C5. If you answer more than three, the best three will be used to calculate your mark (20 marks each).

C1. [2] Chlorine gas, $Cl_{2(g)}$, is produced from seawater via the "chlor-alkali" process. The gas is stored in containers to prevent unwanted and explosive reactions. If a 10.0 L container holds 8.17 mol $Cl_{2(g)}$ at 200°C:

(a) Calculate the pressure (in bar) assuming ideal behaviour.

$$p = \frac{nRT}{V} = \frac{8.17\,\text{mol} \times 0.08314\,\text{L bar K}^{-1}\text{mol}^{-1} \times (200+273)\text{K}}{10.0\,\text{L}}$$
$$= 32.1\,\text{bar}$$

(b) [5] Calculate the pressure (in bar) using the van der Waals equation. For $Cl_{2(g)}$, a = 6.58 bar L^2 mol^{-2} and b = 0.0562 L mol^{-1}.

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$
$$= \frac{8.17\text{ mol} \times 0.08314\text{ L bar K}^{-1}\text{mol}^{-1} \times (200+273)\text{K}}{10.0\text{ L} - 8.17\text{mol} \times 0.0562\text{ L mol}^{-1}} - 6.58\text{ bar L}^2\text{mol}^{-2}\left(\frac{8.17\text{ mol}}{10.0\text{ L}}\right)^2$$
$$= 33.67\text{ bar} - 4.39\,\text{bar}$$
$$= 29.3\,\text{bar}$$

(c) [4] Why is the van der Waals pressure lower than the ideal gas pressure for chlorine under these conditions?

The van der Waals equation takes account of the fact that the chlorine molecules have volume and interact. In this case, the intermolecular forces are reducing the pressure below what the ideal gas law predicts.

(d) [5] Repeat the calculation in part (b) using the same number of moles of ethane in the same volume at the same temperature. For ethane, a = 5.56 bar L^2 mol^{-2} and b = 0.0638 L mol^{-1}.

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$
$$= \frac{8.17\text{ mol} \times 0.08314\text{ L bar K}^{-1}\text{mol}^{-1} \times (200+273)\text{K}}{10.0\text{ L} - 8.17\text{mol} \times 0.0638\text{ L mol}^{-1}} - 5.56\text{ bar L}^2\text{mol}^{-2}\left(\frac{8.17\text{ mol}}{10.0\text{ L}}\right)^2$$
$$= 33.90\text{ bar} - 3.71\,\text{bar}$$
$$= 30.19\,\text{bar}$$

(e) [4] Why is the calculated pressure for ethane higher than that for chlorine?

The 'b' term for ethane is higher than that of Cl_2. Also, the 'a' term for ethane is lower than that of Cl_2. Both of these tend to make the pressure higher.

C2. Some data are given for the reaction $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

	$CaCO_{3(s)}$	**$CaO_{(s)}$**	**$CO_{2(g)}$**
ΔH^o_f , kJ mol^{-1}	-1,207.6	-634.9	-393.5

Assuming 1000 kg of $CaCO_{3(s)}$ reacts at 1000°C and 1.00 bar:

(a) **[5]** Calculate the total enthalpy change (in kJ, not just kJ/mol)

$$\Delta H^o = \Delta H^o_f(CaO_{(s)}) + \Delta H^o_f(CO_{2(g)}) - \Delta H^o_f(CaCO_{3(s)})$$

$$= -634.9 + (-393.5) - (-1207.6)$$

$$= 179.2 \text{ kJ mol}^{-1}$$

$$1000 \text{ kg } CaCO_3 \times \left(\frac{1000 \text{ g}}{1 \text{ g}}\right) \times \left(\frac{1 \text{ mol } CaCO_3}{100.1 \text{ g } CaCO_3}\right) = 9.99 \times 10^3 \text{ mol}$$

$$179.2 \text{ kJ mol}^{-1}(9.99 \times 10^3 \text{ mol}) = 1.79 \times 10^6 \text{kJ}$$

(b) **[10]** Calculate the total work (in kJ, not just kJ/mol)

$$w = -RT\Delta n$$

$$= -8.314 \text{ J K}^{-1}\text{mol}^{-1}(1000 + 273)\text{K}(+1)$$

$$= -1.06 \times 10^4 \text{J mol}^{-1}$$

$$\times\, 9.99 \times 10^3 \text{mol} = -1.06 \times 10^8 \text{J}$$

$$= -1.06 \times 10^5 \text{kJ}$$

(c) **[5]** Calculate the total ΔE (in kJ, not just kJ/mol). Has the system gained or lost energy?

$\Delta E = q + w$

$= 1.79 \times 10^6$ kJ – 1.06×10^5 kJ

$= 1.68 \times 10^6$ kJ

The system has gained this much energy (i.e. $\Delta E > 0$).

C3. (a) **[10]** The Balmer-Rydberg equation can also be used for He^+ because it has one electron (the same as an H atom). The lines in the spectrum of He^+ from stars include transitions to the n = 4 level. Calculate the energy (in kJ mol^{-1}) of the lowest energy transition in this series.

The "lowest energy transition" must begin at m = 5:

$$\frac{1}{\lambda} = R\left[\frac{1}{n^2} - \frac{1}{m^2}\right]$$

$$= 0.01097\ nm^{-1}\left[\frac{1}{4^2} - \frac{1}{5^2}\right]$$

$$= 2.47 \times 10^{-4}\ nm^{-1}$$

$$\lambda = \frac{1}{2.47 \times 10^{-4}\ nm^{-1}} = 4051\ nm$$

$$E = h\nu$$

$$= h\left(\frac{c}{\lambda}\right)$$

$$= 6.63 \times 10^{-34}\ J\ s\left(\frac{3.00 \times 10^{8}\ m\ s^{-1}}{4051 \times 10^{-9}\ m}\right)$$

$$= 4.91 \times 10^{-20}\ J$$

$$\times 6.02 \times 10^{23}\ mol^{-1} = 2.96 \times 10^{4}\ J\ mol^{-1}$$

$$= 29.6\ kJ\ mol^{-1}$$

(b) **[10]** The binding energy of electrons to a chromium metal surface is 7.20×10^{-19} J. Calculate the maximum wavelength (in nm) of light required to give ejected electrons a kinetic energy of 2.50×10^{-19} J.

The incoming photon must supply the binding energy plus the energy of the ejected electron. In this case this sum is $7.20 \times 10^{-19} + 2.50 \times 10^{-19} = 9.70 \times 10^{-19}$ J.

$$E = h\nu = h\left(\frac{c}{\lambda}\right)$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.63 \times 10^{-34}\ J\ s\ (3.00 \times 10^{8}\ m\ s^{-1})}{9.70 \times 10^{-19}\ J}$$

$$= 2.05 \times 10^{-7}\ m$$

$$= 205\ nm$$

C4. (a) Use VSEPR to predict the shapes of the following two species. Wrong name = zero marks.

[4] OF_4

Electrons = 6 + 4(7) = 34. Connecting the F atoms to the O atom using single bonds uses 8 of these. Completing the octets around the F atoms uses another 24, for a total of 32. The two extra electrons go on the O atom as a lone pair. The molecule is therefore of the form AX_4E, which has the shape of a **SEESAW.**

[4] $SeCl_5$

Electrons = 6 + 5(7) = 41. Connecting the Cl atoms to the Se atom using single bonds uses 10 of these. Completing the octets around the Cl atoms uses another 30, for a total of 40. The remaining electron goes on the Se atom alone. The molecule is therefore of the form AX_5E which has the shape **SQUARE PYRAMIDAL.**

(b) What hybridization would you expect for the central atom in each of the following two species?

[3] OF_4

As shown in (a) above, the central O atom has a steric number of 5. It is therefore using sp^3d hybrid orbitals.

[3] $SeCl_5$

As shown in (a) above, the central Se atom has a steric number of 6. It is therefore using sp^3d^2 hybrid orbitals.

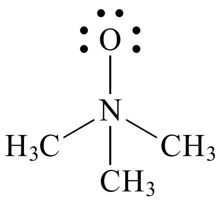
(c) Referring to the structure shown below,

[2] Calculate the formal charge on the N atom: 5 – 4 = 1

[2] Calculate the formal charge on the O atom: 6 – 7 = –1

[2] The formal charges on the C and H atoms are all zero. Calculate the overall charge on the molecule.

Formal charges must sum to the charge on the molecule. –1 + 1 = 0.



C5. **[20]** Iron metal crystallizes in a body-centred cubic structure and has a density of 7.87 g cm^{-3}. Calculate the radius of an iron atom (in pm). You may use geometry to solve this problem, or the fact that the atoms in a BCC structure occupy 68% of the volume of the unit cell.

Method A: In a BCC unit cell, there are the equivalent of two whole atoms (1/8 atom at each corner plus a whole atom in the centre). The mass of the unit cell is therefore:

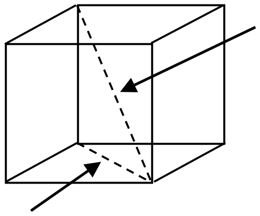
$$m_{\text{unit cell}} = 2\text{ atoms}\left(\frac{55.85\text{ g}}{6.02\times10^{23}\text{atoms}}\right) = 1.86\times10^{-22}\text{ g}$$

And the volume of the unit cell is therefore:

$$V_{\text{unit cell}} = \frac{\text{mass}_{\text{unit cell}}}{\rho} = \frac{1.86\times10^{-22}\text{ g}}{7.87\text{ g cm}^{-3}} = 2.36\times10^{-23}\text{cm}^3$$

And so the edge length of the unit cell is:

$$l = \sqrt[3]{V_{\text{unit cell}}} = \sqrt[3]{2.36\times10^{-23}\text{cm}^3} = 2.86\times10^{-8}\text{cm}$$



In the diagram above, note that the diagonal through the centre of a BCC unit cell passes through three atoms, and has a length of 4r:

$d^2 = l^2 + l^2$

but, $(4r)^2 = l^2 + d^2 = 3l^2$

Thus, $16r^2 = 3l^2$, or $r = \frac{l\sqrt{3}}{4} = \frac{2.86\times10^{-8}\text{cm}(\sqrt{3})}{4} = 1.24\times10^{-8}\text{cm} = 124\text{ pm}$

Method B: Density of the metal is 7.87 g cm^{-3}.

The volume occupied by one gram of iron is therefore $V = \dfrac{1}{7.87\ \text{g cm}^{-3}} = 0.1271\,\text{cm}^3\text{g}^{-1}$

and per mole, it is $0.1271\,\text{cm}^3\text{g}^{-1} \times 55.85\ \text{g mol}^{-1} = 7.098\,\text{cm}^3\text{mol}^{-1}$

but the atoms occupy only 68% of this space, thus the volume occupied by one mole of the atoms themselves is 0.68(7.098 cm^3 mol^{-1}) = 4.827 cm^3 mol^{-1}

and per atom, it is $\dfrac{4.827\ \text{cm}^3\text{mol}^{-1}}{6.02\times10^{23}\,\text{mol}^{-1}} = 8.02\times10^{-24}\,\text{cm}^3$

Each atom is a sphere of radius r, and volume = (4/3)πr^3

Thus, $r = \sqrt[3]{\dfrac{3V}{4\pi}} = \sqrt[3]{\dfrac{3(8.02\times10^{-24})\text{cm}^3}{4\pi}} = 1.24\times10^{-8}\,\text{cm} = 124\ \text{pm}$