

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

1. Compare the average molecular kinetic energy of 1 mol of $\text{NH}_3(\text{g})$ in 1.00 L at 500°C with that of 3.35 mol of $\text{O}_2(\text{g})$ in 25.0 L at 500°C , and explain.

The average kinetic energies are the same because the two samples are at the same temperature.

2. Define the term “state function” and give three examples of a state function.

A state function is a function whose value does not depend on the path taken from reactants to products, nor on the reaction rate. Examples are enthalpy (H), internal energy (E), the distance between two cities, etc.

3. State the Pauli exclusion principle.

The Pauli exclusion principle states that no two electrons in an atom have identical quantum numbers.

4. Would you expect Zn^{2+} ions to be diamagnetic or paramagnetic? Answer with reference to the ion’s electronic configuration.

Zn’s electronic configuration is $\dots 4s^2 3d^{10}$. That of Zn^{2+} is therefore $\dots 3d^{10}$. Thus all 10 electrons are paired in the filled 3d and other subshells, so the ion is diamagnetic.

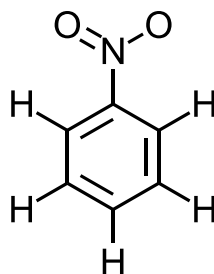
5. Oxygen has a greater electronegativity than carbon. Why is carbon dioxide not polar?

The Lewis structure is $\text{O}=\text{C}=\text{O}$, i.e. no lone pairs on the central carbon atom. The molecule is therefore linear. Although each $\text{O}=\text{C}$ bond is polar, these two dipoles point in opposite directions and cancel each other out, resulting in zero net dipole.

6. Name three physical properties of molecules predicted by molecular orbital theory, and not predicted by hybrid orbital theory.

Magnetic properties, bond length, bond energy

7. What is the strongest intermolecular force between two molecules of nitrobenzene, shown below?

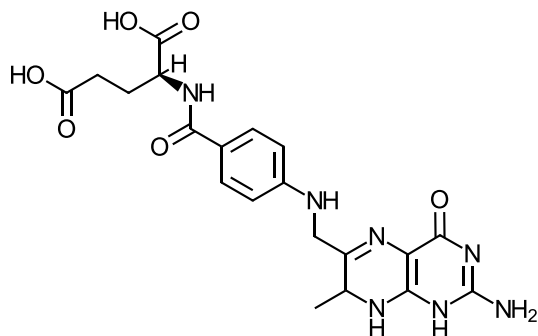


The C–C and C–H bonds are essentially non-polar. However, the C–N and N–O bonds are quite polar, resulting in a polar molecule. The dominant force between two of these molecules is thus a dipole–dipole force. (Note that it is not an H–bond because the H is not bound directly to the N.)

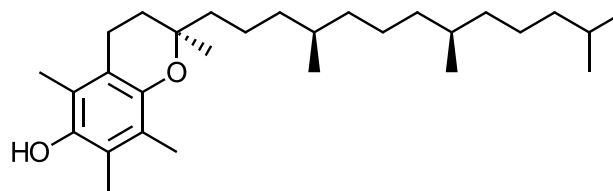
8. Diamond and graphite are both chemically just solid carbon. Why is diamond so much harder than graphite? Answer with respect to hybrid orbital theory.

The carbon atoms in diamond are each bound to three other carbon atoms via sp^3 hybrid orbitals. This results in a very strong three-dimensional lattice of carbon atoms. In graphite, the bonding is via sp^2 hybrids, with a p-orbital left over. Bonding between neighbouring p-orbitals in adjacent planes of graphite is weak.

9. Which of the vitamins folic acid or alpha-Tocopherol would you expect to be more soluble in water? Why?



Folic Acid



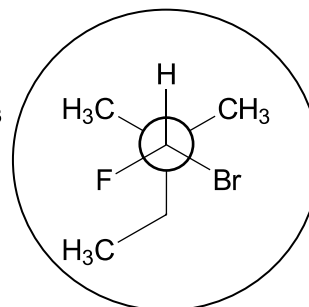
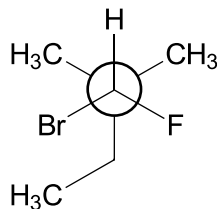
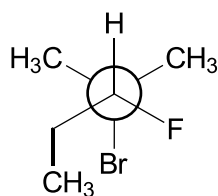
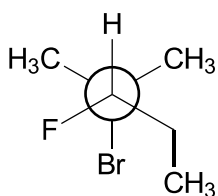
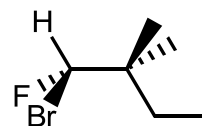
alpha-Tocopherol

Folic acid must have a higher solubility. The folic acid molecule contains more polar groups, especially O-H and N-H groups, which will hydrogen bond with water, increasing the solubility.

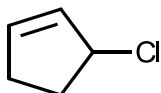
10. When you take a carbonated drink from the refrigerator, place it on the kitchen counter and open it, carbon dioxide evolves from the solution. Name two reasons why this happens.

First, opening the drink exposes the liquid to a lower pressure (atmospheric pressure instead of the 2–3 bar pressure in an unopened drink). Henry's law predicts that lower pressure means lower solubility of the gas. Second, as the solution warms, gases, including carbon dioxide, become less soluble.

11. Circle the Newman projection that correctly represents



12. Name this compound:



3-chlorocyclopentene

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

- B1. [20] Silver (Ag) crystallizes in a cubic unit cell. The edge length of the unit cell is 408 pm. The density of silver metal is 10.6 g cm^{-3} . What type of cubic unit cell does silver form?

$$\text{Volume of the unit cell} = V = (408 \times 10^{-10} \text{ cm})^3 = 6.79 \times 10^{-23} \text{ cm}^3$$

$$\text{Mass of unit cell} = m = \rho V = 10.6 \text{ g cm}^{-3} \times 6.67 \times 10^{-23} \text{ cm}^3 = 7.20 \times 10^{-22} \text{ g}$$

$$\text{Mass of one Ag atom} = \frac{107.9 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.79 \times 10^{-22} \text{ g}$$

$$\text{Number of atoms per unit cell} = \frac{7.20 \times 10^{-22} \text{ g / unit cell}}{1.79 \times 10^{-22} \text{ g / atom}} = 4 \text{ atoms / unit cell}$$

Only **FCC (face centered cubic)** has four atoms per unit cell.

(There are other ways to solve this problem...)

- B2. (a) [6] 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 18.6 Torr at 25°C. Calculate the molecular weight of the protein.

$$\Pi = MRT$$

$$\Pi = 18.6 \text{ Torr} = (18.6/760) = 0.0245 \text{ atm}$$

Thus,

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

$$= 0.0245 \text{ atm} / (0.002 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= 0.00100 \text{ mol L}^{-1}$$

In this 2.0 mL solution there would be $0.00100 \text{ mol L}^{-1} \times 0.002 \text{ L} = 2.00 \times 10^{-6} \text{ mol}$ of protein

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

- (b) A solution is made by adding 250 g $\text{Na}_2\text{SO}_4(\text{s})$ to 1.00 L $\text{H}_2\text{O}(\text{l})$ at 25.0°C.

- (i) [6] Calculate the vapor pressure of this solution at 30°C (in Pa). The vapor pressure of pure water at 30°C is 4242 Pa.

$$n_{\text{Na}_2\text{SO}_4} = \frac{250 \text{ g}}{(2(23.0) + 32.1 + 4(16.0)) \text{ g mol}^{-1}} = 1.76 \text{ mol Na}_2\text{SO}_4$$

$$n_{\text{solute}} = 3(1.76) = 5.28 \text{ mol (because Na}_2\text{SO}_4 \rightarrow 2\text{Na}_{(\text{aq})}^+ + \text{SO}_{4(\text{aq})}^{2-})$$

$$1.00 \text{ L H}_2\text{O} = 997 \text{ g H}_2\text{O}$$

$$n_{\text{H}_2\text{O}} = \frac{997 \text{ g}}{18.0 \text{ g mol}^{-1}} = 55.3 \text{ mol}$$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{solute}} + n_{\text{H}_2\text{O}}} = \frac{55.3}{5.28 + 55.3} = 0.913$$

$$\begin{aligned} p_{\text{H}_2\text{O}} &= p_{\text{H}_2\text{O}}^\circ X_{\text{H}_2\text{O}} \\ &= (4242 \text{ Pa})(0.913) \\ &= 3872 \text{ Pa} \end{aligned}$$

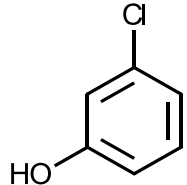
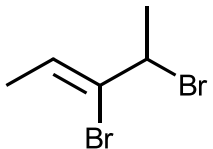
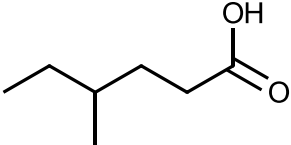
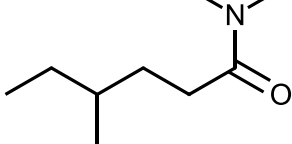
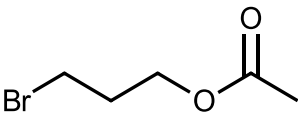
(ii) [4] Calculate the freezing point ($^{\circ}\text{C}$) of the solution. K_f for water is $1.86\text{ }^{\circ}\text{C kg mol}^{-1}$.

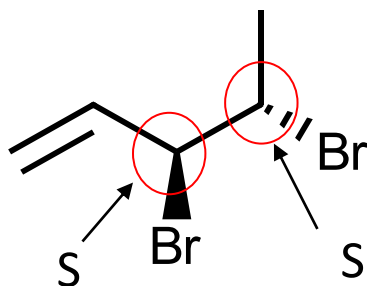
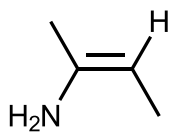
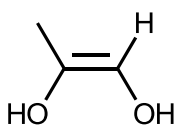
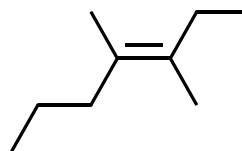
$$\begin{aligned}\Delta T_f &= iK_f m_{\text{solute}} \\ &= 3(1.86\text{ }^{\circ}\text{C kg mol}^{-1})\left(\frac{1.76\text{ mol}}{0.997\text{ kg}}\right) \\ &= 9.85\text{ }^{\circ}\text{C} \\ T_f &= 0.00\text{ }^{\circ}\text{C} - 9.86\text{ }^{\circ}\text{C} = -9.86\text{ }^{\circ}\text{C}\end{aligned}$$

(iii) [4] Calculate the boiling point ($^{\circ}\text{C}$) of the solution. K_b for water is $0.51\text{ }^{\circ}\text{C kg mol}^{-1}$.

$$\begin{aligned}\Delta T_b &= iK_b m_{\text{solute}} \\ &= 3(0.51\text{ }^{\circ}\text{C kg mol}^{-1})\left(\frac{1.76\text{ mol}}{0.997\text{ kg}}\right) \\ &= 2.70\text{ }^{\circ}\text{C} \\ T_b &= 100.00\text{ }^{\circ}\text{C} + 2.70\text{ }^{\circ}\text{C} = 102.70\text{ }^{\circ}\text{C}\end{aligned}$$

B3. (a) [10] Name the following compounds

	3-chlorophenol or 1-chloro-3-hydroxybenzene or 3-hydroxychlorobenzene
	3,4-dibromo-2-pentene or 3,4-dibromopent-2-ene
	4-methylhexanoic acid
	4-methyl-N,N-dimethylhexanamide
	3-bromopropylacetate or 3-bromopropylethanoate

(b) [4] Circle any chirality centres in the molecule shown below, and label each as *R* or *S*.(c) [6] Assign *E* or *Z* stereochemical descriptors to each of the following three compounds*Z**Z**E*

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. (a) [4] Calculate the density of $\text{CH}_3\text{F}_{(g)}$ (in g L^{-1}) at 2.00 bar and 50°C .

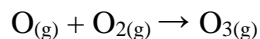
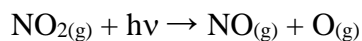
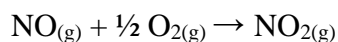
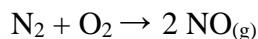
$$\rho = \frac{pM}{RT} = \frac{2.00 \text{ bar}(34.03 \text{ g mol}^{-1})}{0.08314 \text{ L bar K}^{-1}\text{mol}^{-1}(50 + 273.15) \text{ K}} = 2.53 \text{ g L}^{-1}$$

- (b) [6] It takes 85.0 s for 1.00 mol of $\text{CH}_3\text{F}_{(g)}$ to diffuse through a porous barrier. Under identical conditions, how long (in s) would it take for 1.00 mol of $\text{H}_{2(g)}$ to diffuse through the same barrier?

$$\begin{aligned} \frac{\text{rate}_{\text{H}_2}}{\text{rate}_{\text{CH}_3\text{F}}} &= \sqrt{\frac{M_{\text{CH}_3\text{F}}}{M_{\text{H}_2}}} \\ \text{rate}_{\text{H}_2} &= \text{rate}_{\text{CH}_3\text{F}} \sqrt{\frac{M_{\text{CH}_3\text{F}}}{M_{\text{H}_2}}} \\ &= \frac{1 \text{ mol}}{85 \text{ s}} \sqrt{\frac{34.03 \text{ g mol}^{-1}}{2.02 \text{ g mol}^{-1}}} = 0.0483 \text{ mol s}^{-1} \end{aligned}$$

$$\text{Time required} = \frac{1}{0.0483 \text{ mol s}^{-1}} = 20.7 \text{ s mol}^{-1}$$

- (c) [4] Beginning with $\text{N}_{2(g)}$ and $\text{O}_{2(g)}$, show the reactions responsible for producing ozone in a smoggy city.



- (d) [6] Calculate the pressure exerted by 25.0 g $\text{CH}_3\text{F}_{(g)}$ in 2.50 L at 100°C . For this gas, $a = 5.009 \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 0.05617 \text{ L mol}^{-1}$.

$$\frac{25.0 \text{ g}}{34.03 \text{ g mol}^{-1}} = 0.735 \text{ mol}$$

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

$$= \frac{0.735 \text{ mol}(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})(100 + 273.15)\text{K}}{2.50 - 0.735 \text{ mol}(0.05617 \text{ L mol}^{-1})} - 5.009 \text{ bar L}^2\text{mol}^{-2} \left(\frac{0.735 \text{ mol}}{2.50 \text{ L}} \right)^2$$

$$= 9.27 \text{ bar} - 0.43 \text{ bar}$$

$$= 8.84 \text{ bar}$$

- C2. (a) [8] Use data in the table to calculate the amount of heat released (in MJ) when 100 mol of $C_2H_2(g)$ is burned in excess oxygen according to the reaction $C_2H_2(g) + 2.5 O_2(g) \rightarrow 2 CO_2(g) + H_2O(g)$.

	$C_2H_2(g)$	$CO_2(g)$	$H_2O(g)$
ΔH_f° , kJ/mol	227.4	-393.5	-241.83

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(CO_2(g)) + \Delta H_f^\circ(H_2O(g)) - \Delta H_f^\circ(C_2H_2(g)) - 2.5\Delta H_f^\circ(O_2(g)) \\ &= 2(-393.5) + (-241.8) - 227.4 - 2.5(0) \\ &= -1256.2 \text{ kJ mol}^{-1}\end{aligned}$$

$$\times 100 \text{ mol} = -125620 \text{ kJ} = -1.26 \text{ MJ}$$

- (b) [6] Calculate the work done (in J) when a balloon is inflated to a volume of 2.50 L if the atmospheric pressure is 0.98 bar.

$$\begin{aligned}w &= -p\Delta V \\ &= -0.98 \text{ bar}(2.50 \text{ L}) \\ &= -2.45 \text{ L bar}\end{aligned}$$

$$\times \frac{1 \text{ m}^3}{1000 \text{ L}} \times \frac{10^5 \text{ Pa}}{1 \text{ bar}} = 245 \text{ Pa m}^3 = 245 \text{ J}$$

- (c) [6] A 2.70 g sample of caffeine ($C_8H_{10}N_4O_2$) is burned in a constant volume calorimeter that has a heat capacity of $7.85 \text{ kJ } ^\circ\text{C}^{-1}$. The temperature increases from 19.27°C to 28.05°C . Calculate the energy of combustion of caffeine (in kJ mol^{-1}).

$$\begin{aligned}q &= C\Delta T \\ &= 7.85 \text{ kJ } ^\circ\text{C}^{-1}(28.05 - 19.27)^\circ\text{C} \\ &= 68.9 \text{ kJ}\end{aligned}$$

$$\Delta E = \frac{q}{n} = \frac{68.9 \text{ kJ}}{\left(\frac{2.70 \text{ g}}{194.2 \text{ g mol}^{-1}}\right)} = 4960 \text{ kJ mol}^{-1}$$

- C3. (a) [5] Calculate the frequency (in s^{-1}) of the light emitted by hydrogen atoms when electrons fall from level $m = 5$ to level $n = 2$.

$$\begin{aligned}\frac{1}{\lambda} &= R \left[\frac{1}{n^2} - \frac{1}{m^2} \right] \\ &= 0.01097 \text{ nm}^{-1} \left[\frac{1}{2^2} - \frac{1}{5^2} \right] \\ &= 0.002304 \text{ nm}^{-1} \\ \lambda &= \frac{1}{0.002304 \text{ nm}^{-1}} = 434.0 \text{ nm} = 434.0 \times 10^{-9} \text{ m} \\ \nu &= \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{434.0 \times 10^{-9} \text{ m}} = 6.91 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

- (b) [5] Do a calculation to show whether or not 500 nm light can dissociate O_2 molecules, which have a bond dissociation energy of 498 kJ mol^{-1} .

$$\begin{aligned}E &= \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J s} (3.00 \times 10^8 \text{ m s}^{-1})}{500 \times 10^{-9} \text{ m}} = 3.98 \times 10^{-19} \text{ J} \\ &\times 6.02 \times 10^{23} \text{ mol}^{-1} = 239,000 \text{ J mol}^{-1} = 239 \text{ kJ mol}^{-1}\end{aligned}$$

These photons are therefore not energetic enough to break the bond in the O_2 molecule.

- (c) [5] Place the following ions in increasing order of radius:



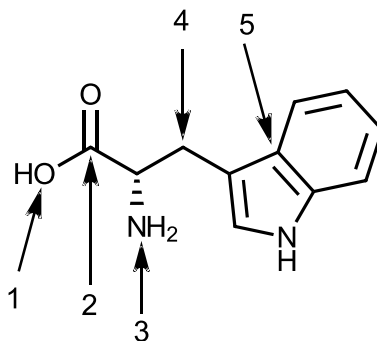
(All of these have the same number of electrons. Thus the lower the atomic number (i.e. the number of protons), the larger the radius.)

From smallest to largest are therefore $\text{Sr}^{2+} < \text{Rb}^+ < \text{Br}^- < \text{Se}^{2-} < \text{As}^{3-}$

- (d) [5] Indicate with a check mark whether or not each of the following sets of quantum numbers are valid in an Mn atom:

n	l	m_l	m_s	Valid	Not Valid
1	0	0	$+\frac{1}{2}$	✓	
4	2	2	$-\frac{1}{2}$	(3d in Mn, not 4d)	✓
4	1	-1	$+\frac{1}{2}$	✓	
4	0	0	$-\frac{1}{2}$	✓	
3	2	1	$-\frac{1}{2}$	✓	

- C4. (a) [5] What type of hybrid orbitals are used by each of the five indicated central atoms shown in the structure of tryptophan below?



1: sp^3 2: sp^2 3: sp^3 4: sp^3 5: sp^2

- (b) [10] Predict the shapes of the following four molecules:



$$5 + (5 \times 7) = 40 e^-$$

$$5 + (4 \times 7) = 33 e^-$$

$$6 + (2 \times 6) = 18 e^-$$

$$5 + (3 \times 7) = 26 e^-$$

Thus, AX_5

Thus, AX_4E

Thus, AX_2E

Thus, AX_3E

Thus, trigonal bipyramidal

Thus, seesaw

Thus, bent

Thus, Trigonal pyramidal

- (c) [5] The highest energy electron in a molecule of NO is in a π^*_{2p} molecular orbital. Is the bond energy of NO^+ higher or lower than that of NO? Why?

Making the NO^+ ion requires removing the electron from NO that is in the highest energy MO. Since this is an antibonding MO, removing it will result in an increased bond order. This in turn will make the bond energy in NO^+ higher than that in NO.

C5. (a) Answer the following question about the phase diagram of CO₂ shown below.

(i) [12] Name all phases present at points:

A	Solid	D	Solid, Gas	G	Solid, Liquid, Gas
B	Liquid	E	Solid, Liquid		
C	Gas	F	Gas, Liquid		

(ii) [1] What is the vapour pressure of CO₂ at room temperature, approximately?

73 bar

(iii) [1] What is the name of the point at G?

The triple point

(iv) [1] What is the name of the point at H?

The critical point

(v) [2] Why can we not observe liquid CO₂ at STP?

The lowest pressure at which the liquid can exist is 5.1 bar, which is higher than standard pressure.

(vi) [3] A block of dry ice is taken from the freezer and placed on the lab bench. What temperature is the block at? How do you know?

Dry ice is solid CO₂. Under 1 bar pressure (like the pressure in a lab), the temperature of the solid-gas equilibrium is -78°C .

