1. (4 marks)

(a) How many electrons are there in the **p orbitals** of the ***n* = 3** shell when all the orbitals are filled? (Clearly circle around the correct answer)

0	1	3	4	(6)	9	10	12

(b) How many electrons are there in the **d orbitals** of the ***n* = 3** shell when all the orbitals are filled? (Clearly circle around the correct answer)

0	1	3	4	6	9	(10)	12

(c) Name **TWO** elements that have completely filled d subshells in their lowest energy states and also have atomic numbers less than 36

Cu , Zn, Ga, Ge, As, Se, Br

2. (3 marks)

Chlorine is an element that has two stable isotopes in reasonable abundance. For the isotopic anion $^{37}Cl^{-}$, which has an atomic mass of 36.966, give the following:

(a) the number of protons per ion; 17

(b) the number of electrons per ion; 18

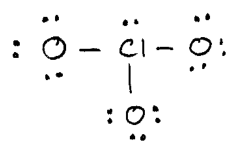
(c) the number of neutrons per ion. 20

3. (2 marks)

Draw the Lewis dot structure for the chlorate anion ClO_3^-, then select from the possibilities below for the number of **single bonds, double bonds** and **lone pairs**. (Clearly circle around the correct answer)

(a) 2,1,0 (b) 3,0,9 (c) 2,1,8 (d) 3,0,10 (e) 3,0,0

$n_e = 3\times6 + 7 + 1 = 26\bar{e}$



4. (6 marks)

An impure sample of calcium carbonate ($CaCO_3$) of mass 0.384 g was reacted with excess HCl and the CO_2 evolved was collected in a gas burette over water at 20 °C on a day when the barometric pressure was 749.70 Torr. The measured volume of gas was found to be 73.4 mL.

Data: At 20 °C, the vapour pressure of water is P_{H_2O} = 17.53 Torr; 1 atm = 760 Torr = 1.013×10^5 Pa; 20 °C = 293 K; R = 8.314 J mol^{-1} K^{-1}; $M(CaCO_3)$ = 100.9 g mol^{-1}. (1 Torr ≡ 1 mm of mercury).

(a) Write a balanced equation for the reaction of $CaCO_3$ and HCl.

$CaCO_3 + 2HCl \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

(b) Calculate the partial pressure of CO_2 in Pa.

$P_{CO_2} = 749.70 - 17.53 = 732.2$ Torr

$= \frac{732.2}{760}$ atmos $= \frac{732.2}{760} \times 1.013 \times 10^5 = 9.759 \times 10^4$ Pa

(c) Calculate the number of moles of CO_2 produced.

$PV = nRT$ $\therefore n = \frac{PV}{RT} = \frac{9.759 \times 10^4 \times 73.4 \times 10^{-6}}{293 \times 8.314}$

$V = 73.4 \times 10^{-6}$ m^3

$\therefore n = 2.941 \times 10^{-3}$ mol

(d) Calculate the mass of $CaCO_3$ present in the sample.

$m = nM_R = 2.941 \times 10^{-3} \times 100.9$ g

$= 0.297$ g

5. (5 marks)

The concentration of a hydrogen peroxide solution can be determined by titration against an acidified standard potassium permanganate solution.

(a) Use the ion-electron method to write balanced half equations for this redox reaction:

$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$ (×2)

$H_2O_2 - 2e \longrightarrow O_2 + 2H_3O^+$ (×5)

(b) Write a balanced equation for the full redox reaction.

$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

6. (16 marks)

Most packaged foodstuffs list 'nutritional information' about the food they contain. One such piece of information is the 'energy'. This is determined by combusting a sample of the food in a constant-volume (bomb) calorimeter.

(a) In a constant-volume calorimetry experiment, is the calorimeter taken to approximate an open, closed or isolated system? Explain your answer.

> It approximates an isolated system, because the sturdy, insulated walls ensure that there is very little mass and energy exchange between the calorimeter and surroundings.

(b) Briefly explain how the first law of thermodynamics applies when a combustion process is carried out in a constant-volume calorimeter.

> 1st law: $\Delta U = q + w$
> For an isolated system, $q = w = 0$ (see (a))
> So for the calorimeter as a whole, $\Delta U = 0$, i.e., wherever energy (heat) is evolved within the calorimeter, it is all absorbed somewhere else within the calorimeter.

(c) Does a constant-volume calorimeter measure the enthalpy change (ΔH) or the internal energy change (ΔU) for a process? Explain your answer.

> A calorimeter measures q for a process.
> Because it is constant volume, it measures q_v for the process.
> But $q_v = \Delta U$.
> So a constant-volume calorimeter measures ΔU for a process.
> [$w = 0$ for a constant-V process $\Rightarrow \Delta U = q + w = q$.]

(d) A quantity of 2.86 g of wholemeal bread was burned in a constant-volume calorimeter. The temperature of the calorimeter rose from 19.28 °C to 22.45 °C. Given that the calorimeter and its contents had a heat capacity of 10.17 kJ K^{-1}, calculate the heat change for the combustion of the bread, expressing your answer in terms of kJ g^{-1}.

From (b), $q_{combustion} + q_{absorbed\ by\ calorimeter} = 0$

$\Rightarrow q_{combustion} = -q_{absorbed\ by\ calorimeter}$

$= -C_{V,\ calorimeter}\ \Delta T_{calorimeter}$

$= -10.17\ kJ\ K^{-1} \times (22.45 - 19.28)\ K$

$= -10.17\ kJ\ K^{-1} \times 3.17\ K$

$= -32.2\ kJ$ for 2.86 g bread

$\Rightarrow q = -32.2\ kJ / 2.86\ g$

$= -11.3\ kJ\ g^{-1}$.

↳ note the negative sign, signifying that heat is evolved (a positive answer is incorrect)

(e) The human body is not a constant-volume calorimeter. Rather, it burns food by metabolism carried out under approximately constant-pressure conditions. Explain how the heat change measured in a constant-volume calorimeter can be used to calculate the heat change for the same process carried out at constant pressure.

$q_P = \Delta H = \Delta U + RT\ \Delta n_{gas}$

ΔU : measured by constant-volume calorimeter (see (c))

Δn_{gas} : from equation for combustion reaction

$\Rightarrow$ calculate q_P

(f) Explain how a constant-volume calorimeter could be used to determine $\Delta H_f(CO_2(g))$, the enthalpy of formation of $CO_2(g)$. (Your answer should include a chemical equation.)

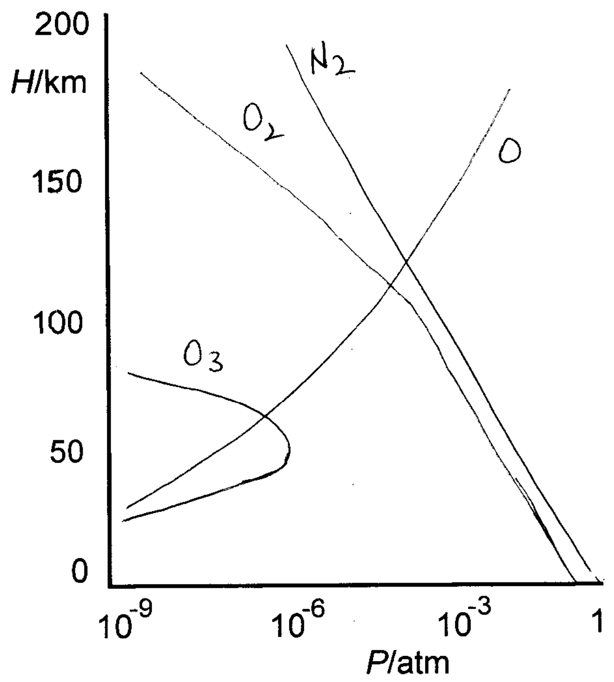
$\Delta H_f(CO_2(g))$ is ΔH for $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$

So to determine $\Delta H_f(CO_{2(g)})$:

1. Combust graphite (completely) in a constant-volume calorimeter
2. Calculate ΔU for the process
3. Convert to ΔH as explained in (e). (Actually, $\Delta n_{gas} = 0$ in this case, so $\Delta H = \Delta U$.)

7. (12 marks)

(a) Using the axes provided, sketch plots of composition *versus* altitude, *H*, for N_2, O_2, O and O_3 in the Earth's atmosphere.



(b) Explain the shape of the N_2 plot in one sentence.

Partical pressure of N_2 is determined by gravity and temperature since it is chemically unreactive.

(c) Write the Chapman equations for the formation and destruction of O_3 in the stratosphere and show that the overall outcome for steady-state conditions is the conversion of high energy ultraviolet light into heat.

OZONE FORMATION

$$O_2 + UV(<242nm) \rightarrow 2O$$

$$\times 2 \quad O_2 + O + M \rightarrow 2O_3 + M^* + heat$$

$$3O_2 + UV \rightarrow 2O_3 + heat$$

OZONE DESTRUCTION

$$O_3 + UV(<310nm) \rightarrow O_2 + O$$

$$O_3 + O \rightarrow 2O_2 + heat$$

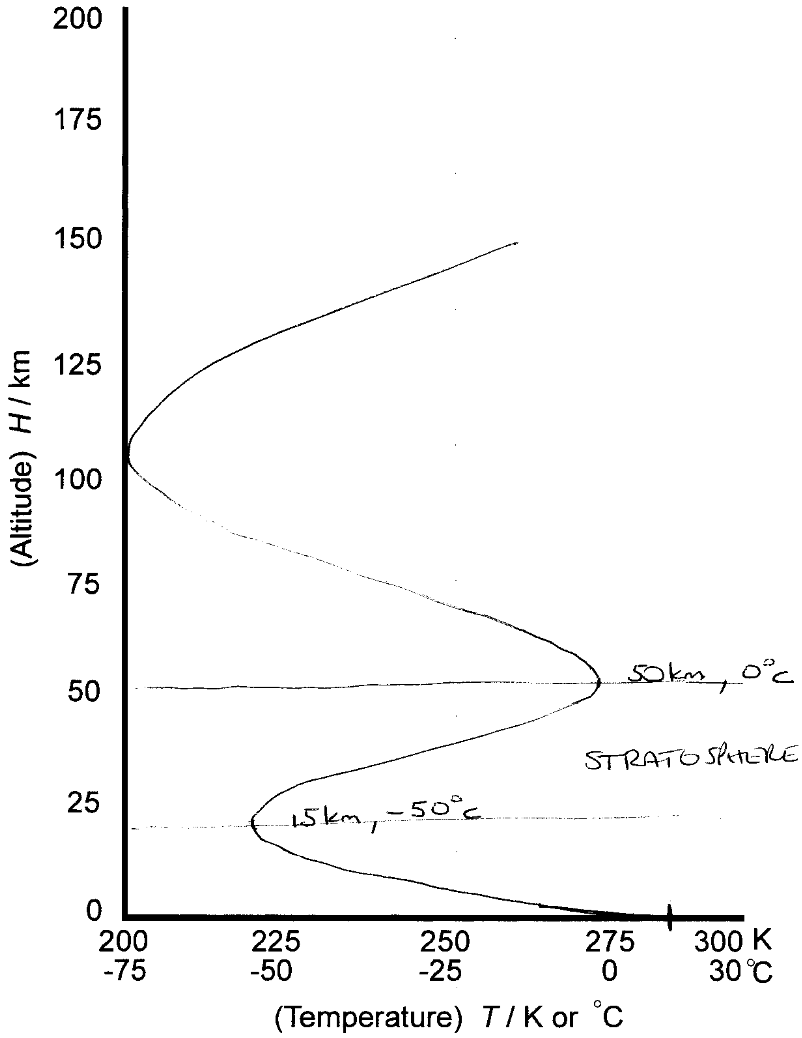
$$2O_3 + UV \rightarrow 3O_2$$

OVERALL $UV \rightarrow heat$.

(d) Using the axes provided:

(i) sketch the temperature versus altitude profile of the Earth's atmosphere;

(ii) draw horizontal lines to show the stratosphere and write the altitudes and temperatures for the lower and upper turning points of this region.



8. (6 marks)

(a) Name **TWO** examples of global anthropogenic atmospheric pollutants **and their sources**.

1) CO_2 from combustion of fossil fuels

2) CFCs industrial synthesis

SO_2 burning of coal, oil, industry

N_2O bacterial action on fertilizers in soil

(b) Write equations to show how O_3 is produced close to ground level under photochemical smog conditions.

$$N_2 + O_2 + \text{heat (engine)} \rightarrow 2NO$$

$$2NO + O_2 \text{ (air)} \rightarrow 2NO_2$$

$$NO_2 + \text{sunlight} \rightarrow NO_2^* \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M^*$$

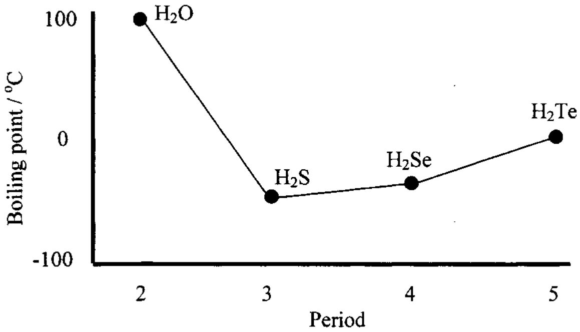
$$M = N_2, O_2, \ldots$$

(c) Write equations to show how powdered $CaCO_3$ can be used to reduce SO_2 emissions from high temperature coal powered furnaces.

$$CaCO_3(s) + \underset{(\text{furnace})}{\text{heat}} \rightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + SO_2(g) \xrightarrow[\text{tower}]{\text{water}} CaSO_3(s)\downarrow$$

9. (4 marks)



Answer the following questions in relation to the figure above.

(a) Why does water have the highest boiling point?

Extensive 3-D H-bonding in water must be disrupted before temperature can rise (molecular velocity can increase). H_2S has smaller dipole moment and very weak H-bonds

(b) Why do the boiling points of H_2S to H_2Te increase?

Atomic dimensions increase with period giving rise to molecules with increasing molecular polarisability and stronger van der Waals interactions.

10. (2 marks)

Which of the salts Na_2SO_4, $MgSO_4$, $CaSO_4$, $BaSO_4$

(a) is likely to be most **insoluble** in water? $BaSO_4$

(b) is likely to be most **soluble** in water? Na_2SO_4

END OF PAPER