

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 $^{37}\text{Cl}^-$, 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

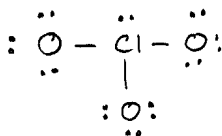
(b) 3,0,9

(c) 2,1,8

(d) 3,0,10

(e) 3,0,0

$$n_e = 3 \times 6 + 7 + 1 = 26e^-$$

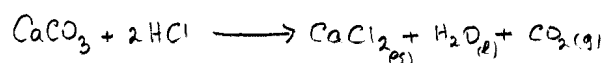


4. (6 marks)

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 $P_{\text{H}_2\text{O}} = 17.53$ Torr; $1 \text{ atm} = 760 \text{ Torr} = 1.013 \times 10^5 \text{ Pa}$; $20^\circ\text{C} = 293 \text{ K}$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $M(\text{CaCO}_3) = 100.9 \text{ g mol}^{-1}$. (1 Torr = 1 mm of mercury).

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



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

$$\begin{aligned} P_{\text{CO}_2} &= 749.70 - 17.53 = 732.2 \text{ Torr} \\ &= \frac{732.2}{760} \text{ atm} = \frac{732.2}{760} \times 1.013 \times 10^5 = \underline{9.759 \times 10^4 \text{ Pa}} \end{aligned}$$

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

$$\begin{aligned} PV &= nRT \quad \therefore n = \frac{PV}{RT} = \frac{9.759 \times 10^4 \times 73.4 \times 10^{-6}}{293 \times 8.314} \\ V &= 73.4 \times 10^{-6} \text{ m}^3 \\ \therefore n &= \underline{2.941 \times 10^{-3} \text{ mol}} \end{aligned}$$

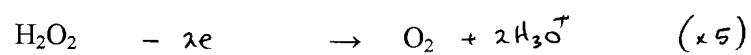
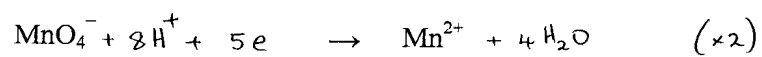
(d) Calculate the mass of CaCO_3 present in the sample.

$$\begin{aligned} m &= nM_r = 2.941 \times 10^{-3} \times 100.9 \text{ g} \\ &= \underline{0.297 \text{ g}} \end{aligned}$$

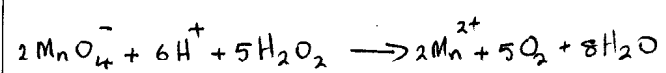
5. (5 marks)

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:



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



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.

$$\text{1st law: } \Delta U = q + w$$

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.

$$\text{But } q_v = \Delta U.$$

So a constant-volume calorimeter measures ΔU for a process.

$$[w = 0 \text{ for a constant-}V \text{ process} \Rightarrow \Delta U = q + w = q.]$$

- (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.

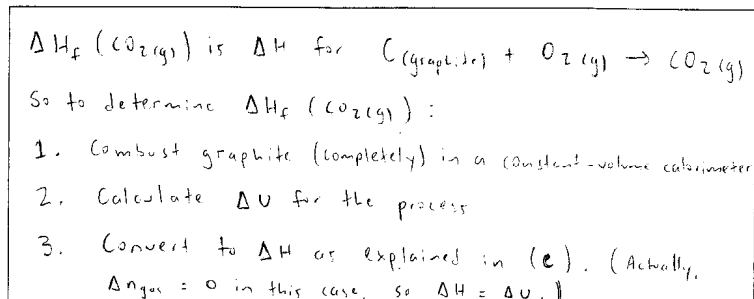
$$\begin{aligned}
 \text{From (b), } q_{\text{combustion}} + q_{\text{absorbed by calorimeter}} &= 0 \\
 \Rightarrow q_{\text{combustion}} &= -q_{\text{absorbed by calorimeter}} \\
 &= -C_{V, \text{calorimeter}} \Delta T_{\text{calorimeter}} \\
 &= -10.17 \text{ kJ K}^{-1} \times (22.45 - 19.28) \text{ K} \\
 &= -10.17 \text{ kJ K}^{-1} \times 3.17 \text{ K} \\
 &= -32.2 \text{ kJ for 2.86 g bread} \\
 \Rightarrow q_v &= -32.2 \text{ kJ} / 2.86 \text{ g} \\
 &= -11.3 \text{ kJ g}^{-1}
 \end{aligned}$$

↳ 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.

$$\begin{aligned}
 q_p &= \Delta H = \Delta U + RT \Delta n_{\text{gas}} \\
 \Delta U &: \text{measured by constant-volume calorimeter (see (c))} \\
 \Delta n_{\text{gas}} &: \text{from equation for combustion reaction} \\
 \Rightarrow & \text{calculate } q_p
 \end{aligned}$$

- (f) Explain how a constant-volume calorimeter could be used to determine $\Delta H_f(\text{CO}_2(\text{g}))$, the enthalpy of formation of $\text{CO}_2(\text{g})$. (Your answer should include a chemical equation.)



7. (10 marks)

For the reaction given below, the thermodynamic equilibrium constant at 25°C is $K = 0.49$.



- (a) Write an expression for the thermodynamic equilibrium constant in terms of the **activities** of the reaction components.

$$K = \frac{(a_{\text{NH}_3(\text{g})})(a_{\text{H}_2\text{S}(\text{g})})}{(a_{\text{NH}_4\text{HS}(\text{s})})}$$

- (b) Indicate the working rules you would use for estimating the activities of **each** of the components in the reaction.

For the gases, $\text{NH}_3(\text{g})$ and $\text{H}_2\text{S}(\text{g})$: $a_{\text{X}(\text{g})} = \frac{P_{\text{X}}}{1 \text{ atm}}$

For the (pure) solid: $a_{\text{NH}_4\text{HS}(\text{s})} = 1$

- (c) 10.0 mol of $\text{NH}_4\text{HS}(s)$ are introduced into a closed, evacuated container of volume 2.0 L at 25 °C, and the system allowed to come to equilibrium at this temperature. What is the partial pressure of $\text{H}_2\text{S}(g)$? (You may assume that all gases are ideal.)

$$\text{From (a) and (b), } 0.49 = \left(\frac{P_{\text{NH}_3(g)}}{\text{atm}} \right) \left(\frac{P_{\text{H}_2\text{S}(g)}}{\text{atm}} \right)$$

Since $P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 0$ initially, it follows from reaction stoichiometry that $P_{\text{NH}_3} = P_{\text{H}_2\text{S}}$ at equilibrium.

$$\text{Hence } 0.49 = \left(\frac{P_{\text{H}_2\text{S}}}{\text{atm}} \right)^2 \Rightarrow P_{\text{H}_2\text{S}} = 0.70 \text{ atm}$$

- (d) If the volume of the system in (c) was doubled to 4.0 L, what would be the partial pressure of $\text{H}_2\text{S}(g)$ after re-establishment of equilibrium? **Explain.**

From (c) it follows that $P_{\text{H}_2\text{S}}$ is unaffected by volume change, i.e., $P_{\text{H}_2\text{S}} = 0.70 \text{ atm}$ still.

Although the volume increase results in more H_2S being produced (according to Le Chatelier's principle), this doesn't affect $P_{\text{H}_2\text{S}}$ because the larger amount is in a larger volume.

- (e) If 5.0 mol of $\text{NH}_4\text{HS}(s)$ were removed from the system in (c), what would be the partial pressure of $\text{H}_2\text{S}(g)$ after re-establishment of equilibrium? **Explain.**

$Q_{\text{NH}_4\text{HS}(s)} = 1$. This value is unaffected by removal of $\text{NH}_4\text{HS}(s)$. Thus the equilibrium is unaffected (see (c)), and so $P_{\text{H}_2\text{S}}$ is unchanged. (In other words, the reaction quotient Q is unchanged, so the equilibrium is unaffected.)

8. (14 marks)

The decomposition of an organic nitrile (substance X) in aqueous solution is described by the equation:



The following results were obtained in an experiment carried out at 45°C (318 K):

time/s	0	4000	8000	12000	∞
[X]/mol L ⁻¹	1.10	0.67	0.41	0.25	0

(a) Prove that the decomposition is a **first-order** process.

Given that no graph paper is provided, the easiest way to proceed is to test data numerically against the Integrated Rate Law for first-order (as given) $\Rightarrow [X] = [X]_0 \exp(-kt)$

Rearrange to $\ln\left(\frac{[X]_0}{[X]}\right) = kt$

or $k = \frac{1}{t} \ln\left(\frac{[X]_0}{[X]}\right)$ where $[X]_0 = 1.10$

(Should test at least two pairs of data points)

$$k = \frac{1}{4000} \ln\left(\frac{1.10}{0.67}\right) = 1.24 \times 10^{-4} \text{ s}^{-1}$$
$$k = \frac{1}{8000} \ln\left(\frac{1.10}{0.41}\right) = 1.23 \text{ " "}$$
$$k = \frac{1}{12000} \ln\left(\frac{1.10}{0.25}\right) = 1.24 \text{ " "}$$

Δ constant values therefore **FIRST-ORDER**

8 marks

(b) What is the **rate constant**, k , for the decomposition?

$$k = 1.24 \times 10^{-4} \text{ s}^{-1}$$

2 marks

(c) What are the units for k ?

$$s^{-1} \quad [(seconds)^{-1}]$$

1 mark

(d) If the temperature is raised from 45° to 55°C (328 K), the value of k is found to **increase** by a factor of 2.2. **Explain** how you would determine the activation energy (E_a) for the decomposition reaction.

[No calculation is required in this part.]

Use the form of Arrhenius expression (as given)

$$\ln_e \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\frac{k_2}{k_1} = 2.2 \quad T_1 = 318$$

$$T_2 = 328$$

Substitute these values and calculate E_a ...

$$E_a = \frac{R \ln_e \left(\frac{k_2}{k_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (= 68.4 \frac{kJ}{mol})$$

3 marks

END OF PAPER

Answer not required just an outline of method