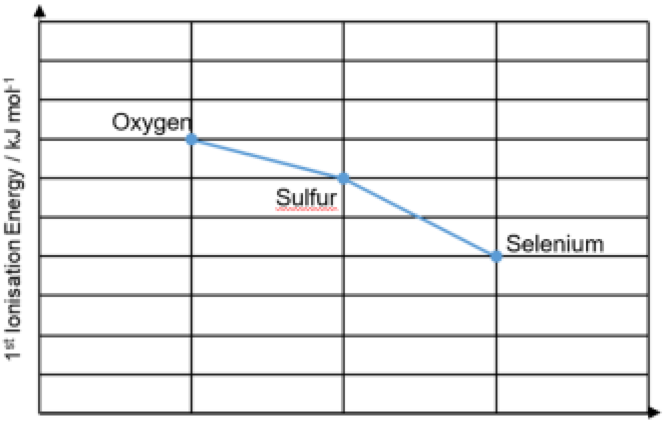
Victoria Junior College
2023 JC1 H2 Chemistry
December Self Practice Paper (Answers)
Recommended Questions For Consolidation of Concepts and Skills

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



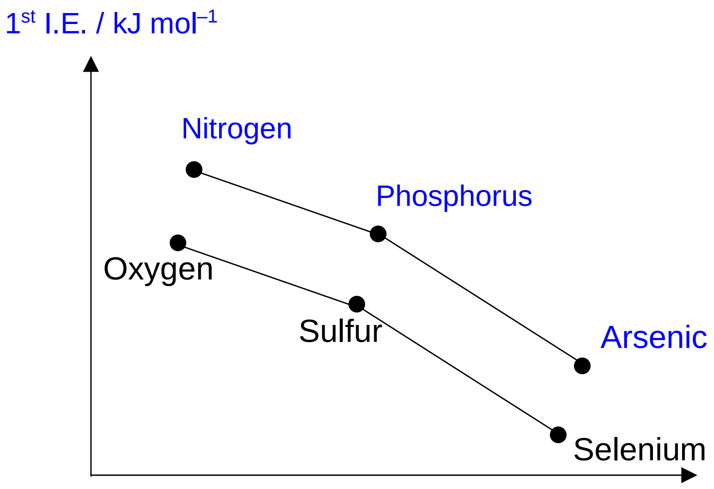
(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

The **first ionisation energy decreases** from oxygen to selenium. This is because down the group while the **nuclear charge increases**, **number of electronic shells increases** and **valence electrons are further away** from the nucleus.

Hence, the **valence electrons experience weaker electrostatic forces of attraction from the nucleus** and so a smaller amount of energy is required to remove this electron from the atom.

[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.



[1]

Note: Fewer electronic shells lead to higher ionisation energies.

(b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2. Hydrogen peroxide readily decomposes at room temperature.

Iodide ions, I^-, catalyse this decomposition, as shown below:

$$\text{Step I: } H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)}$$
$$\text{Step II: } H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

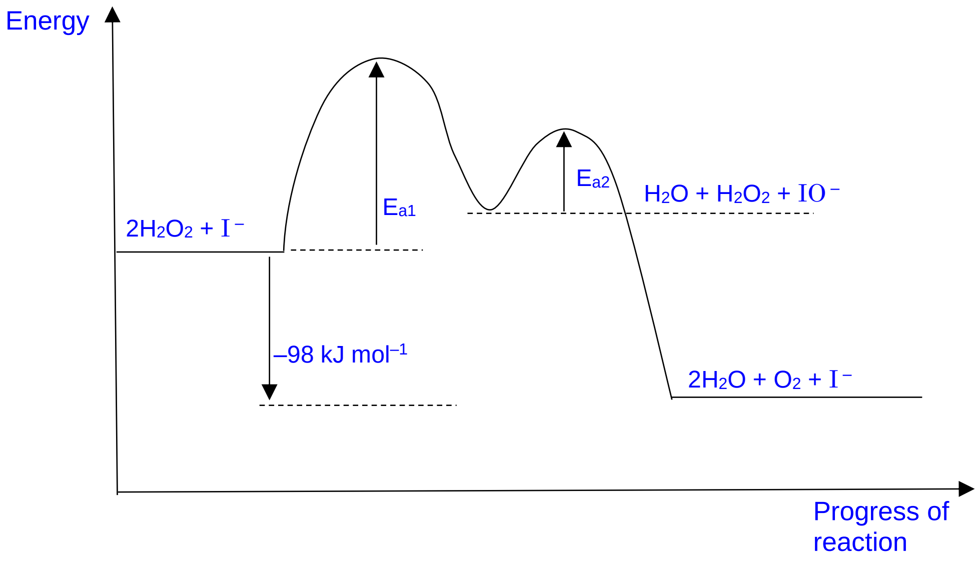
The overall equation for the decomposition of hydrogen peroxide is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	–98
Entropy change / J K^{-1} mol^{-1}	+71

(i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions labelling clearly the activation energies and enthalpy change of the reaction.



Note: Activation energy of slow step must be greater than that of fast step.

[2]

(ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at 120 °C. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel. (Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

$pV = nRT$

Total amount f gases (O_2 & H_2O) in vessel, $n = \frac{177000 \times 5 \times 10^{-3}}{8.31 \times (273+120)}$ = **0.27098 mol**

Hence, amount of hydrogen peroxide that decomposed
= 0.27098 ÷ 3 × 2
= **0.181 mol**

[2]

2 **(a)** Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

(i) Determine the molecular formula of ascorbic acid.

	C	O	H
Mass of atoms in 100 g	40.9	54.5	4.6
Divide by A_r	3.41	3.41	4.6
Simplest mole ratio	3	3	4

The empirical formula of ascorbic acid is $C_3O_3H_4$.
n x (empirical formula) = molecular formula
n[(3 x 12.0) + (3 x 16.0) + (4 x 1.0)] = 176.0
n = 2

- The molecular formula of ascorbic acid is $C_6O_6H_8$.

[2]

(b) Ascorbic acid is a monobasic acid, H**A**, and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water and titrated against 0.100 mol dm^{-3} sodium hydroxide.

(i) Calculate the volume of 0.100 mol dm^{-3} sodium hydroxide required for complete neutralisation.
Amount of moles of HA = Amount of NaOH = 0.500 ÷ 176.0 = $2.841\text{x}10^{-3}$ mol
Volume of NaOH needed = $2.841\text{x}10^{-3} \div 0.100 = 0.0284$ dm^3

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

$$[HA] = \frac{2.841\times10^{-3}}{(25.0)\div1000} = 0.1136 \text{ mol dm}^{-3}$$
$$K_a = 10^{-4.10}$$
$$[H^+] = \sqrt{K_a \times [HA]} = 3.00\times10^{-3} \text{ mol dm}^{-3}$$
$$pH = -\lg[3.00\times10^{-3}] = 2.52$$

[2]

(iii) Suggest a suitable indicator for the titration and describe the colour change at end-point.
Phenolphthalein, solution changes from **colourless to pink** at end point.
or **Thymolphthalein**, solution changes from **colourless to blue** at end point.

Note: These indicators are suitable for strong base titration. Methyl orange is suitable for strong acid titration.

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in **(iii)**.

$A^- + H_2O \rightleftharpoons HA + OH^-$
At end-point, the conjugate base or salt of ascorbic acid undergoes **hydrolysis** to form hydroxide ions causing the **$[OH^-]$ to be greater than $[H^+]$ and so pH > 7.**

The **rapid** **pH change at equivalence point coincides with the working range** of the indicator.

[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$10^{-4.10} = \frac{[10^{-2}][A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Let α represent the percentage ionisation.

$$\frac{\alpha}{100 - \alpha} = 7.93 \times 10^{-3}$$

$$\alpha = 0.788\%$$

Alternative method:
Since [HA]>>[A$^-$] or since K_a is small,
% ionisation = 0.793%

[2]

The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

When a little acid is present in blood, it will be removed by hydrogen carbonate.
$HCO_3^- + H^+ \rightarrow H_2CO_3$

When a little base is present in blood, it will be removed by carbonic acid.
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

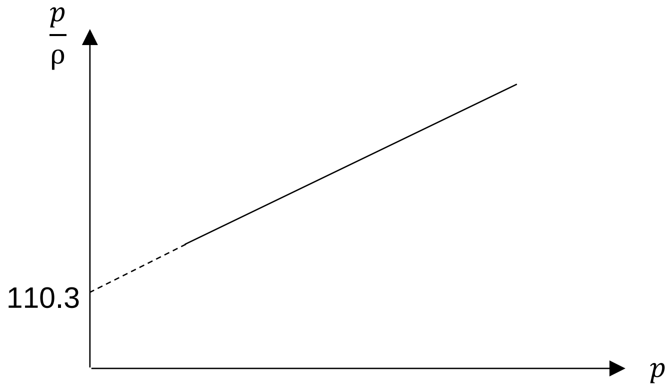
[2]

3 **(a)** Singapore has been affected by severe smoke haze due to forest fires in the region periodically. The National Environment Agency (NEA) is taking action to ensure that its population is better equipped to deal with haze.

During one of the sample analysis of air, the air sample was found to contain elevated amounts of NO_2 and gas **S**.

By careful measurements and extrapolation, the value of $\frac{p}{\rho}$ for gas **S** has been found to be approximately 110.3, at 100 °C and at very low pressure.

[p is the pressure of the gas in Pa and ρ is the density of the gas in g m^{-3}]



(i) State two main assumptions of the kinetic theory as applied to an ideal gas, and use these to explain why you might expect the behaviour of nitrogen dioxide to be less ideal compared to that of hydrogen.

[3]

- The gas particles have **zero or negligible volume compared to the volume of the container**.
- There are **no intermolecular forces of attraction** between gas particles.

NO_2 is less ideal than H_2 as it has a **larger size** since it has a **larger electron cloud.**

Both NO_2 and H_2 have **simple molecular structure** but NO_2 is a **polar molecule** while H_2 is a **non-polar molecule**. Hence there is **stronger permanent dipole-permanent dipole interactions** in NO_2 and **weaker instantaneous dipole-induced dipole interactions** in H_2.

(ii) Calculate an approximate value for the relative molecular mass of **S**. [1]

$pV = nRT = (m/M)RT$

$p = (m/V)(RT/M)$

$\frac{p}{\rho} = RT/M$

At 100 °C and very low pressure,

$RT/M = 110.3$

$M = (8.31 \times 373) / 110.3$

$= 28.1 \text{ g mol}^{-1}$

$M_r =$ **28.1**

(iii) Hence, identify gas **S**, where **S** is a diatomic neutral pollutant. [1]

Gas **S** is **CO**

(b) Atmospheric sulfur dioxide is a major air pollutant that forms acid rain. The pollution problem caused by sulfur dioxide is amplified in the presence of atmospheric oxides of nitrogen, which act as a homogeneous catalyst.

Explain, with the aid of equation(s), how atmospheric oxides of nitrogen act as a homogeneous catalyst to amplify the pollution problems of sulfur dioxide. [3]

$\mathbf{NO_2 + SO_2 \rightarrow SO_3 + NO}$

$\mathbf{NO + \tfrac{1}{2} O_2 \rightarrow NO_2}$

The NO_2 catalyst is a homogeneous catalyst as it is in **same physical state or phase** as the pollutant, SO_2. It **speeds up the rate of formation of SO_3 and itself remains unchanged at the end of reaction**.

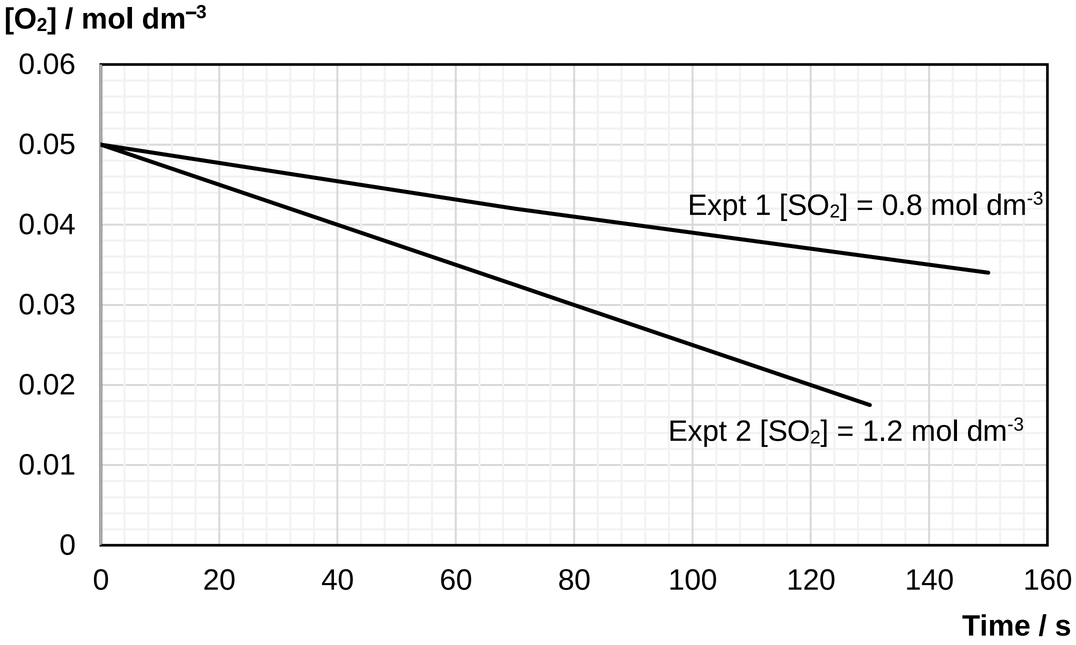
$\mathbf{SO_3 + H_2O \rightarrow H_2SO_4}$ *OR*

SO_3 **dissolves** in rain or water vapour in the atmosphere to form sulfuric acid, which causes acid rain.

(c) The Contact Process is an important industrial process that occurs at 450 °C. The key stage in this process is the reaction between sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Two laboratory experiments were conducted at 450 °C to investigate the kinetics of this reaction. The graph below shows the results obtained when concentrations of sulfur dioxide were varied.



(i) Use the graphs above to deduce the order of reaction with respect to sulfur dioxide and oxygen. [3]

Order of reaction w.r.t O_2 is zero as the graph of O_2 against time is a straight line with constant negative gradient, hence **rate of reaction is constant** with changing $[O_2]$.

When $[SO_2] = 0.8$ mol dm^{-3},

r_1, rate of reaction = $\left|\dfrac{0.04-0.05}{88}\right|$ = 1.13×10^{-4} mol dm^{-3} s^{-1}

When $[SO_2] = 1.2$ mol dm^{-3},

r_2, rate of reaction = $\left|\dfrac{0.030-0.05}{80}\right|$ = 2.50×10^{-4} mol dm^{-3} s^{-1}

$[SO_2]_{\text{expt 2}} / [SO_2]_{\text{expt 1}}$ = 1.2/0.8 = **1.5**

$r_2/r_1 = 2.21 \approx$ **2.25 = $(1.5)^2$**

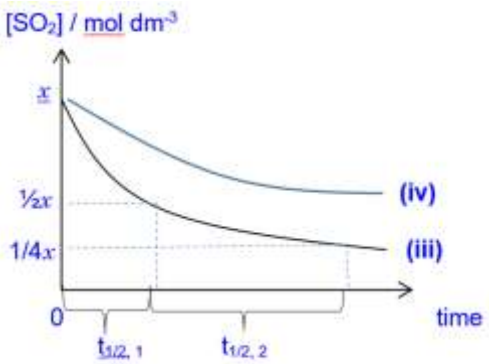
When $[SO_2]$ changed by a factor of 1.5, rate of reaction changed by a factor of 2.25, hence reaction is second order w.r.t. SO_2

(ii) Using one of the graphs above, calculate the value of rate constant, stating its units. [2]

rate = $k[SO_2]^2$
When $[SO_2] = 0.8$ mol dm^{-3},
$k = 1.77 \times 10^{-4}$ mol^{-1} dm^{3} s^{-1}
($k = 1.74 \times 10^{-4}$ mol^{-1} dm^{3} s^{-1}, if $[SO_2] = 1.2$ mol dm^{-3})

(iii) Using your answer in **(i)**, sketch the graph of concentration of sulfur dioxide against time for this reaction, while keeping $[O_2]$ constant. Use construction lines to label the first and second half-lives in your sketch. [1]

(iv) Sketch and label clearly, on the same axes as in **(iii)**, how the graph would look like if the experiment was conducted at 200 °C. [1]
[Lower temp => slower => more gentle gradient]



(d) Both phosphorous trichloride and phosphorous pentachloride can be used in the synthesis of tricresylphosphate, a common waterproofing agent.

Phosphorous pentachloride can be formed by reacting phosphorous trichloride with chlorine gas.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 atm of PCl_3 and 1.5 atm of Cl_2 were left to equilibrate in a closed vessel at 600 K. At equilibrium, the total pressure in the vessel was determined to be 3.3 atm.

(i) Calculate the K_p of the above equlibrium. [2]

	$PCl_3(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$PCl_5(g)$
Initial partial pressure / atm	2	1.5	0
Change in partial pressure / atm	–x	–x	+x
Eqm Partial pressure/ atm	2 – x	1.5 – x	x

Hence, (2 – x) + (1.5 – x) + x = 3.3
Partial pressure of PCl_5 at eqm, x = 0.2 atm

$$K_p = \frac{(0.2)}{(2-0.2)(1.5-0.2)} = 0.0855 \text{ atm}^{-1}$$

(ii) Hence, comment on the position of the equilibrium and the sign for the Gibbs free energy change of the forward reaction at 600 K. [2]

Since **K_p is much less than 1**, the **position of the equilibrium lies to the left** (or to the reactant side). This means that the **forward reaction is not likely to be spontaneous** and hence, **ΔG is positive**.

(e) The table below shows common chlorides and oxides of other Group 15 elements.

	Nitrogen	Arsenic
Chlorides	NCl_3	$AsCl_3$ $AsCl_5$
Oxides	NO N_2O NO_2	As_2O_3 As_2O_5

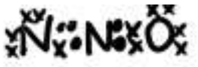
(i) Like PCl_5, arsenic pentachloride ($AsCl_5$) dissolves in water to give a solution with a very low pH. Explain the why this is so with the aid of an equation. [1]

$AsCl_5 + 4H_2O \rightarrow H_3AsO_4 + 5HCl$

$AsCl_5$ completely hydrolyses in water to produce a strong acid, HC*l*, which is responsible for the very low pH.

(ii) Draw the dot-and-cross diagram of N_2O and state its bond angle. [2]

OR



Bond angle: **180°**

4 **(a)** Atmospheric hydrogen and iodine, each 0.10 mol, are placed in a 2 dm^3 evacuated flask at 400 °C. After 30 minutes, the following equilibrium was established and the amount of HI was found to be 0.12 mol.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

(i) Write the expression for K_c and calculate its value at 400 °C. [2]

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial conc/ mol dm^{-3}	0.05		0.05		0
Change / mol dm^{-3}	- 0.03		- 0.03		+ 0.06
Eqm conc / mol dm^{-3}	0.02		0.02		0.06

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{(0.06)^2}{(0.02)^2} = 9$$

(ii) At 40 minutes, the temperature of the system was raised to 600 °C and equilibrium was re-established at 60 minutes.

Given that the K_c at 600 °C was 0.36, show that the equilibrium concentrations of H_2, I_2 and HI in the equilibrium mixture at 60 min are 0.0385 mol dm^{-3}, 0.0385 mol dm^{-3} and 0.0231 mol dm^{-3} respectively. [2]

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial conc/ mol dm^{-3}	0.02		0.02		0.06
Change / mol dm^{-3}	+x		+x		–2x
Eqm conc / mol dm^{-3}	0.02+x		0.02+x		0.06–2x

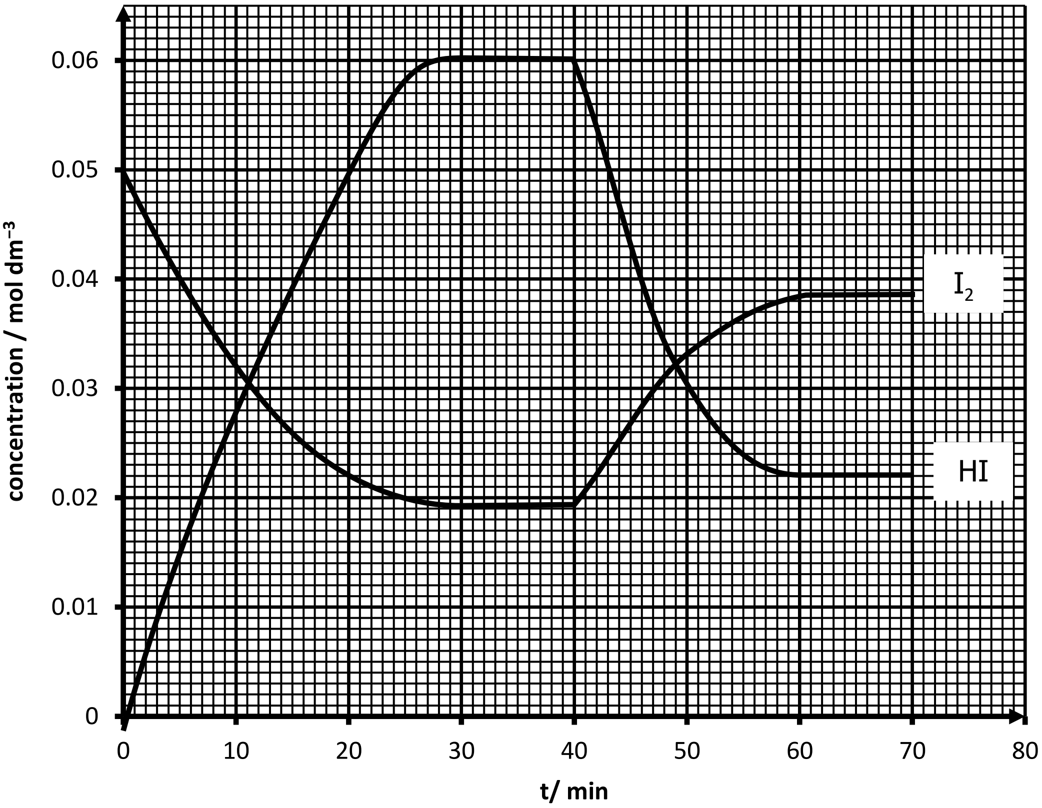
$$K_c = \frac{(0.06 - 2x)^2}{(0.02 + x)^2} = 0.36$$

$$\frac{(0.06 - 2x)}{(0.02 + x)} = 0.6$$

$x = 0.01846$

$[H_2] = [I_2] = 0.02 + x =$ **<u>0.0385 mol dm^{-3}</u>**
$[HI] = 0.06 - 2x =$ **<u>0.0231 mol dm^{-3}</u>**

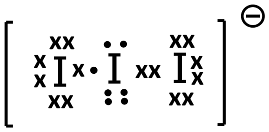
(iii) On the grid below, sketch the concentration versus time graphs for I_2 and HI respectively under the conditions as described in **(a)(i)** and **(a)(ii)** from 0 to 70 minutes. Label the graphs and indicate significant values on the axes. [4]



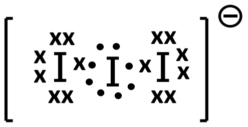
(iv) To find the amount of HI present at equilibrium at 30 minutes, the flask can be rapidly cooled and the HI is dissolved in water. The solution obtained can be titrated against NaOH(aq). Explain why the flask has to be rapidly cooled. [1]

- To <u>prevent the position of equilibrium from shifting</u> during the cooling process.

(b) When I_2 combines with I^-, it forms the I_3^- ion which is responsible for the characteristic brown colour of aqueous I_2.
Draw a dot-and-cross diagram to show the bonding in I_3^-. [1]



or



Note: central iodine has 10 electrons as iodine can expand its octet of electrons

(c) Explain, in terms of structure and bonding, why I_2 has a higher boiling point than HI. [2]

Both I_2 and HI have **simple molecular structure**. HI is polar with **permanent dipole-permanent dipole interactions (pd-pd)** while I_2 is non-polar with **instantaneous dipole-induced dipole interactions (id-id)**.
But I_2 has **more electrons**, and so its electron cloud is more polarisable, leading to **stronger** id-id than the pd-pd interactions.
So, a **larger amount of heat energy** is needed to separate the molecules, leading to a higher boiling point.

5 A common magic demonstration where containers of "water" are mixed to obtain "milk" makes use of the following reaction between methanal and sulfite:

$$HCHO + SO_3^{2-} + H_2O \rightarrow CH_2(OH)(SO_3^-) + OH^-$$

As the reaction produces hydroxide ions, the pH of the solution rises. If a buffer solution is present, this rise is gradual at first. Eventually, when the buffer is exhausted, the pH rises quickly. If the cation Mg^{2+} is also present, the solution soon becomes saturated in magnesium hydroxide and a white precipitate appears.

The procedure of the demonstration is given below.

Procedure (steps 1 to 3 are prepared ahead of the demonstration whereas step 4 is performed in front of the audience)

To the same beaker, the following solutions are added according to the sequence below:

1. Add 100 cm^3 of 0.100 mol dm^{-3} Na_2SO_3 (solution A).
2. Add 100 cm^3 of 0.400 mol dm^{-3} $NaHSO_3$ (solution B).
3. Add 5 cm^3 of 2.00 mol dm^{-3} $MgCl_2$ (solution C).
4. Add 200 cm^3 of 0.300 mol dm^{-3} HCHO (solution D) and swirl.

20 s after step 4 is carried out, a white cloudy solution ("milk") suddenly appears in the beaker owing to the precipitation of magnesium hydroxide.

The following information is relevant.

K_a of HSO_3^-	1.02×10^{-7} mol dm^{-3}

(a) What do you understand by the term *buffer solution*? [1]

A buffer solution is a solution that resists changes in pH upon addition of small amounts of acid or base.

(b) Calculate the pH of the buffer solution in the beaker after Step 2. [1]

$[Na_2SO_3] = 0.100/2 = 0.050$ mol dm^{-3}

$[NaHSO_3] = 0.400/2 = 0.200$ mol dm^{-3}

$$K_a = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

$$1.02 \times 10^{-7} = \frac{[0.050][H^+]}{[0.200]}$$

$[H^+] = 4.08 \times 10^{-7}$ mol dm^{-3}

pH = **6.39**

(c) Write two equations to show how this buffer performs its function in **(a)**, in the process delaying the appearance of the white precipitate. [2]

$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$
$H^+ + SO_3^{2-} \rightarrow HSO_3^-$

(d) State and explain which solution (A, B, C or D) whose concentration you would **decrease** in order for the white precipitate to appear earlier. [2]

Solution B which is acidic will react with OH^- so lowering its concentration will increase concentration of OH^-, causing the precipitate to appear earlier.

(e) The procedure can be slightly amended as follows to produce “tea” instead of “milk”.

- Steps 1, 2 and 4 are unchanged.
- In step 3, instead of solution C, add 5 cm^3 of 3-nitrophenol indicator.

Indicator	**colour in acidic solution**	**colour in alkaline solution**	**working pH rang**
3-nitrophenol	colourless	yellow	6.7 – 8.7

In this way, a yellow solution suddenly appears at the end of the demonstration.

Previously, “milk” appeared 20 s after step 4 was carried out and the pH of the solution was found to be 9.2. Explain whether “tea” appears earlier, later or also at 20 s after step 4 was carried out. [1]

- **“Tea” appears earlier because the working pH range of 3-nitrophenol indicator (6.7-8.7) is lower than the pH at which white precipitate occurs (9.2).**

(g) Suggest another indicator you could use in place of 3-nitrophenol so that “red wine” may be obtained instead of “tea”. [1]

- **Phenolphthalein**

6 **(a)** *Azurite* is a deep blue copper-containing mineral. For many centuries, finely ground rock containing azurite has been used as a pigment in blue paints. Azurite is a mixture of copper(II) carbonate and copper(II) hydroxide. The formula of pure azurite is $Cu_3(CO_3)_2(OH)_2$, which has a relative formula mass of 344.5.

The percentage by mass of pure azurite in a sample of finely ground rock can be determined by back titration. 3.70 g of the sample is added to 100 cm^3 of 0.425 mol dm^{-3} sulfuric acid. The resulting solution was made up to 250 cm^3 with distilled water. 25.0 cm^3 of the diluted solution required 26.50 cm^3 of 0.100 mol dm^{-3} sodium hydroxide for neutralization.

Dilute sulfuric acid reacts with pure azurite as shown in the following equation.

$$Cu_3(CO_3)_2(OH)_2(s) + 3H_2SO_4(aq) \rightarrow 3CuSO_4(aq) + 4H_2O(\mathit{l}) + 2CO_2(g)$$

Calculate the percentage by mass of pure azurite in the sample. You may assume that azurite is the only substance in the rock that reacts with sulfuric acid. [3]

Amount of NaOH = 0.100 x 26.50/1000 = 2.65 x 10^{-3} mol
Amount of H_2SO_4 (in 25cm^3) = ½ x 2.65 x 10^{-3} = **1.325 x 10^{-3}** mol
Amount of H_2SO_4 (in 250cm^3) = 1.35 x 10^{-3} x **250/25.0** = 0.01325 mol
Amount of H_2SO_4 reacted = (0.425 x 100/1000) **–** 0.01325 = 0.02925 mol
Amount of $Cu_3(CO_3)_2(OH)_2$ = 0.02925 **x 1/3** = 9.75 x 10^{-3} mol
Mass of azurite = 9.75 x 10^{-3} **x 344.5** = 3.359 g
% by mass of pure azurite in the powdered rock = 3.359/3.70 x 100% = **90.8%**

(b) The brick-red precipitate, Cu_2O, dissolves in concentrated ammonia solution to form a colourless complex ion **P**, $[Cu(NH_3)_x]^{n+}$, which has a linear geometry about the central metal ion. When left exposed to air, the colourless complex ion **P** turns into a deep blue solution, containing the complex ion $[Cu(NH_3)_4]^{2+}$.

(i) State the value of x and write the formula of complex ion **P**. [2]

x = 2
$[Cu(NH_3)_2]^+$

(ii) With the help of the *Data Booklet*, write the two half equations, and hence the overall equation for the reaction of the colourless complex ion **P** to form $[Cu(NH_3)_4]^{2+}$. [2]

[O] $[Cu(NH_3)_2]^+ + 2NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + e^-$
[R] $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall: $4[Cu(NH_3)_2]^+ + O_2 + 8NH_3 + 2H_2O \rightarrow 4[Cu(NH_3)_4]^{2+} + 4OH^-$

(c) Iodine and chlorine react together to give iodine trichloride.

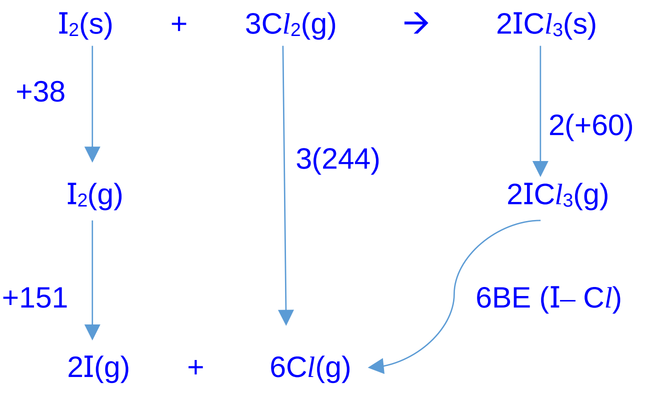
$$I_2(s) + 3Cl_2(g) \rightarrow 2ICl_3(s)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the average bond energy of the I–C*l* bond in IC*l*$_3$.

Your cycle should include relevant data from the *Data Booklet* together with the following data.

standard enthalpy change of formation ($\Delta H_f^\ominus$) of $ICl_3(s)$ = –81 kJmol^{-1}
enthalpy change of sublimation of $I_2(s) \rightarrow I_2(g)$ = +38 kJmol^{-1}
enthalpy change of sublimation of $ICl_3(s) \rightarrow ICl_3(g)$ = +60 kJmol^{-1}

[4]



-162 = +38 + 151 + 3(244) – 6BE(I– C*l*) – 120
BE(I– C*l*) = +160.5 kJmol^{-1}

(ii) The standard Gibbs free energy of formation, $\Delta G_f^\ominus$, of $ICl_3(s)$ is –40.4 kJmol^{-1}. Calculate $\Delta S_f^\ominus$ and comment on its sign with respect to the reaction. [2]

$$\begin{aligned}\Delta G_f^\ominus &= \Delta H_f^\ominus - T\Delta S_f^\ominus \\ -40.4 &= -81 - 298\Delta S_f^\ominus \\ \Delta S_f^\ominus &= -0.136 \text{ kJ mol}^{-1}\text{ K}^{-1} \\ &= -136 \text{ J mol}^{-1}\text{ K}^{-1}\end{aligned}$$

$\Delta S_f^\ominus$ is negative as there is a **decrease in the number of gaseous molecules**, resulting in **fewer number of ways** that the particles and the energy can be distributed.

7 Phosphorus forms a wide range of compounds that are essential for life and have many applications in the industry and in the laboratory.

(a) Many detergents contain sodium dodecylbenzenesulfonate, $C_{18}H_{29}SO_3Na$ (M_r = 348), that can react with calcium ions in ‘hard’ water to give a precipitate, making the detergent ineffective. It was found that the concentration of calcium ions in water cannot exceed 4.80×10^{-11} mol dm^{-3} for the detergent to be effective.

In order for detergents to be used in ‘hard’ water, sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent. It ‘softens’ water by complexing with the calcium ions which can help to prevent the formation of precipitate.

$$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq) \qquad K_c = 7.70 \times 10^8 \text{ mol}^{-1}\text{ dm}^3$$

(i) Write an expression for the equilibrium constant of the above reaction. [1]

$$K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$$

(ii) Some solid sodium tripolyphosphate was added to ‘hard’ water containing the detergent. After forming the complex, the concentration of $P_3O_{10}^{5-}$ decreased to **one-tenth** of its original value at equilibrium.

Using the K_c value, calculate the concentration of Ca^{2+} in the equilibrium mixture. [1]

$$K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$$

$$7.70 \times 10^8 = \frac{0.90}{[Ca^{2+}] \times 0.10}$$

$[Ca^{2+}] = 1.17 \times 10^{-8}$ mol dm^{-3}

(vi) Hence, with reference to your answers in **(aii)**, comment on whether the amount of solid sodium tripolyphosphate added was sufficient to make the detergent effective. [1]

Since $[Ca^{2+}]$ is **more than 4.80×10^{-11}** mol dm^{-3}, the added solid sodium tripolyphopshate was **insufficient** to make the detergent effective.

(b) Phosphorus also forms a class of compounds with nitrogen known as phosphazenes.

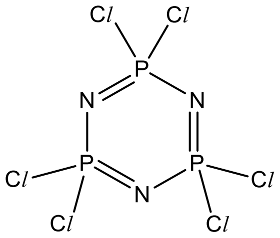
A commercially available phosphazene is $(Cl_2PN)_3$ which is the starting material for many biomedical polymers. It can be synthesized by reacting PCl_5 with NH_4Cl. HCl is formed as a by-product.

(i) Write an equation for the synthesis of $(Cl_2PN)_3$. [1]

$3PCl_5 + 3NH_4Cl \rightarrow (Cl_2PN)_3 + 12HCl$

(ii) $(Cl_2PN)_3$ has a cyclic backbone consisting of alternating phosphorus and nitrogen atoms. Each chlorine atom forms a single bond with a phosphorus atom.

Draw the structure of $(Cl_2PN)_3$. [1]



(iii) Like PCl_5, $(Cl_2PN)_3$ undergoes a similar reaction with water, forming $(PN(OH)_2)_3$.

Suggest the type of reaction undergone by $(Cl_2PN)_3$ and predict what would be observed when a few drops of water was added to $(Cl_2PN)_3$. [2]

- **$(Cl_2PN)_3$ undergoes hydrolysis.**
- **White fumes of HCl is observed.**

(iv) The atomic radii of P, N and C*l* are listed in the *Data Booklet*.

State and explain the differences between the atomic radii of these three atoms. [2]

From the Data Booklet, atomic radius of P = 0.110 nm, atomic radius of N = 0.074 nm and atomic radius of C*l* = 0.099 nm

Atomic radius of N is the smallest as it has **one less electronic shell** than P and C*l* and hence their **valence electrons are closer to the nucleus**.

Atomic radius of C*l* is smaller than P.
C*l* has **higher nuclear charge or higher proton number** but **similar shielding effect** as P. Hence, C*l* **has higher effective nuclear charge** and so the valence electrons are held closer to the nucleus.

Note: atomic radius of N must be compared to C*l*.
Explaining atomic radius of N < P and atomic radius of C*l* < P does not fully explain the trend atomic radius of N < C*l* < P.

(c) PH_3 is part of a series of Group 15 compounds with the formula **X**H_3. The boiling points of some **X**H_3 compounds are given below.

	NH_3	PH_3	AsH_3	SbH_3
Boiling point / °C	–34.5	–87.5	–62.4	–18.4

Describe and explain the trend in their boiling points. [3]

Boiling points generally increase from PH_3 to SbH_3 due to an **increase in the number of electrons** OR the electron cloud size for each molecule and hence an **increase in strength of instantaneous dipole-induced dipole interactions** between the molecules.
NH_3 has an exceptionally high boiling point or a boiling point higher than PH_3 due to **stronger** inter-molecular **hydrogen bondings** which needed **more energy to be overcome.**

(d) Describe the reactions, if any, of the oxides P_4O_{10} and Al_2O_3 with water.
Include the approximate pH value of any resulting solutions, and write equations, with state symbols, for any reactions that occur. [3]

P_4O_{10} reacts with water to form an acidic solution with **pH 2 (or 3)**.
Al_2O_3 **does not react with water / not soluble in water**.
$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

8 Butanoic acid undergoes esterification with methanol to produce methyl butanoate which gives the distinct aroma of apples in certain perfumes.

$$CH_3CH_2CH_2COOH(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2CH_2COOCH_3(l) + H_2O(l)$$

(a) Write an expression for the equilibrium constant for the above reaction, K_c. [1]

$$K_c = \frac{[CH_3CH_2CH_2COOCH_3][H_2O]}{[CH_3CH_2CH_2COOH][CH_3OH]}$$

(b) Given that $K_c = 4.15$ at 298 K, calculate the amount of ester present at equilibrium, when two moles of butanoic acid are reacted with two moles of methanol. [1]

	acid	+	alcohol	⇌	ester	+	water
Initial amount / mol	2.00		2.00				
Change / mol	–x		–x		+x		+x
Eqm amount / mol	2.00 – x		2.00 – x		x		x

$$\frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{2-x}{V}\right)} = 4.15$$

$$\left(\frac{x}{2-x}\right)^2 = 4.15$$

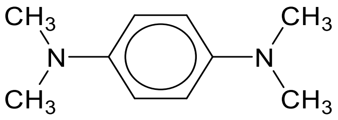
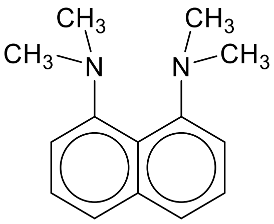
Amount of ester, $x = 1.34$ mol

(c) State Le Chatelier's Principle and use it to predict the effect on the yield of the ester when water is removed. [2]

When **a system at equilibrium** is subjected to a **change** (or stress), the system will react **to counteract the change** (or stress) imposed so as to **re–establish the equilibrium**.

When water is removed, **equilibrium position shifts to the right**, i.e. forward reaction is favoured, to produce more water, hence the **yield of the ester also increases**.

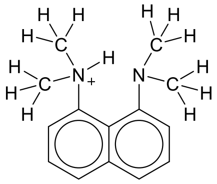
9 TMPD and DMAN are *Lewis bases*. The following table compares their pK_b values.

Base	Structure	pK_{b1}	pK_{b2}
TMPD		7.7	11.7
DMAN		1.7	23.0

(a) Explain what is meant by *Lewis base*. [1]

A Lewis base is an electron-pair donor.

(b) Draw the displayed formula for the conjugate acid of DMAN and use it to explain why the pK_{b1} of DMAN is *so much less* than the pK_{b1} of TMPD. [2]



Conjugate acid of DMAN is **stabilised** through **intramolecular hydrogen bond formed between the 2 nitrogen groups which are near to each other.** This makes it easier for it to be formed and so DMAN is stronger base. Such stabilising effect is absent in the conjugate acid of TMPD.

10 **(a)** Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are eroded by acid rain containing sulfuric acid. The carbonate stone is converted into sulfate by acid rain.

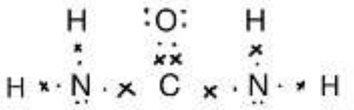
$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

The life of such monuments is now being extended by treating them with a mixture of urea, $(NH_2)_2CO$, and barium hydroxide solutions.

reaction 1: After soaking in the pores of the carbonate stone containing water, urea reacts gradually to give ammonia and carbon dioxide.

reaction 2: Carbon dioxide produced then reacts with barium hydroxide to form barium carbonate.

(i) Draw dot-cross diagram of $(NH_2)_2CO$ and state the shape and bond angle around the C atom. [2]



Shape: **trigonal planar**
Bond angle: **120 °**

(ii) Write balanced equations for **reactions 1** and **2**. [2]

Reaction 1: $\mathbf{(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2}$
Reaction 2: $\mathbf{Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O}$

(b) When carbon dioxide gas dissolves in water, carbonic acid, H_2CO_3, is formed.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

In a school laboratory, a student was instructed to titrate 25.0 cm^3 of 0.100 mol dm^{-3} carbonic acid with 0.125 mol dm^{-3} NaOH using phenolphthalein indicator. (K_{a1} of H_2CO_3 = 4.3×10^{-7} mol dm^{-3})

(i) Calculate the pH of 0.100 mol dm^{-3} H_2CO_3. [1]

$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$

$K_a = \frac{(x)^2}{0.100-x} = 4.3 \times 10^{-7}$ mol dm^{-3}

$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.074 \times 10^{-4}$ mol dm^{-3}

pH = **3.68**

(ii) Calculate the volume of NaOH needed to completely react with 25.0 cm^3 of 0.100 mol dm^{-3} H_2CO_3. [1]

$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$

Amount of $H_2CO_3 = \frac{25}{1000} \times 0.1 = 0.0025$ mol

Amount of NaOH required = 0.005 mol

Volume of NaOH required $= \frac{0.005}{0.125} = 0.04 dm^3 = 40.0 cm^3$

(iii) Calculate the pH of the solution when H_2CO_3 and HCO_3^- are in equal concentrations. [1]

At maximum buffering capacity,

pH = pK_{a1} = **6.37**

(iv) Calculate the pH of the resulting solution when 20.0 cm^3 of NaOH is added to 25.0 cm^3 of H_2CO_3. [2]

From part (ii), 40 cm^3 of NaOH is required to completely neutralise the 2 H^+ from H_2CO_3.

When 20 cm^3 of NaOH is added, only 1 H^+ from H_2CO_3 will react with NaOH

	OH^-	$+ H_2CO_3$	$\rightarrow$	HCO_3^-	$+ H_2O$
Initial / mol	0.0025	0.0025		0	-
Change / mol	–0.0025	–0.0025		+0.0025	-
Final / mol	0	0		0.0025	-

$[HCO_3^-] = 2.50 \times 10^{-3} / (0.02 + 0.025) = 0.05556$ mol dm^{-3}

HCO_3^- acts as a weak base that hydrolyses partially.

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$

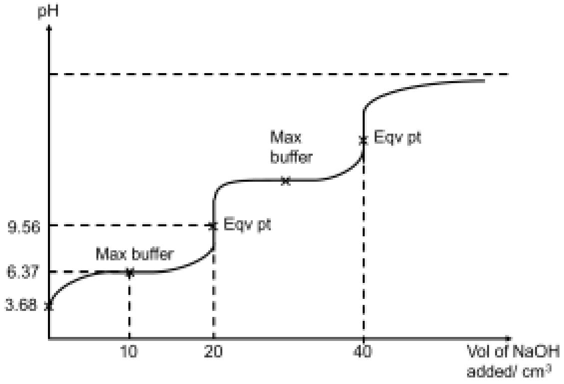
$K_b = \frac{(x)^2}{0.05556-x} = \frac{1\times10^{-14}}{4.3\times10^{-7}} = 2.325 \times 10^{-8}$ mol dm^{-3}

$x = [OH^-] = 3.595 \times 10^{-5}$

$pOH = -\lg[OH^-] = 4.44$

pH = **9.56**

(v) Using your answers in **(i)** to **(iv)**, sketch the shape of the pH curve during the titration. [2]



(c) Barium compounds also have other uses and soluble barium salts are highly poisonous. For example, barium sulfate is used as a ‘barium meal’ in X-ray diagnostic work for patients with digestive tract problems. On the other hand, barium carbonate is used in rat poison.

When the concentration of Ba^{2+} ions exceeds 0.100 mol dm^{-3}, it is lethal. Suggest a reason why barium carbonate is poisonous when ingested by mouth whereas barium sulfate is safe. [2]

$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ --- eqm (1)

When ingested by mouth, the **H^+ in stomach will react with CO_3^{2-}** to form H_2CO_3 or CO_2. **[CO_3^{2-}] will decrease and equilibrium (1) will shift right**. $BaCO_3$ will be more soluble in presence of H^+ and **produces more Ba^{2+}**, resulting in concentration of Ba^{2+} to exceed 0.100 mol dm^{-3}.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ --- eqm (2)

[SO_4^{2-}] remains unchanged as SO_4^{2-} does not react with H^+. Hence, there is no shift in the position of equilibrium in (2). **Concentration of Ba^{2+} is not affected** and will not exceed the lethal level of 0.100 mol dm^{-3}

(d) The values of lattice energy of $CaSO_4$ and $BaSO_4$ are −2374 kJ mol^{-1} and −2480 kJ mol^{-1} respectively.

Some standard enthalpy changes of hydration are listed below.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	−1577
Ba^{2+}	−1305
SO_4^{2-}	−1099

Determine the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for these two salts. Hence, comment on the difference in the solubilities of the two salts. [3]

$\Delta H_{sol}^{\ominus} = \Sigma\Delta H_{hyd}^{\ominus} - LE$
$\Delta H_{sol}^{\ominus}$ of $CaSO_4 = -1577 - 1099 + 2374$
$= -302$ kJ mol^{-1} [1]
$\Delta H_{sol}^{\ominus}$ of $BaSO_4 = -1305 - 1099 + 2480$
$= +76$ kJ mol^{-1} [1]

The **$\Delta H_{sol}^{\ominus}$ of $CaSO_4$ is more negative compared to $BaSO_4$. $CaSO_4$ is more soluble than $BaSO_4$**.

11 (a) Calcium chloride, $CaCl_2$, is commonly used as a desiccant to reduce humidity level of an enclosed space to allow the storage of articles that are prone to damage in high humidity. The lattice energy of $CaCl_2$ can be calculated from a Born–Haber cycle using the relevant data in the *Data Booklet* and the following data.

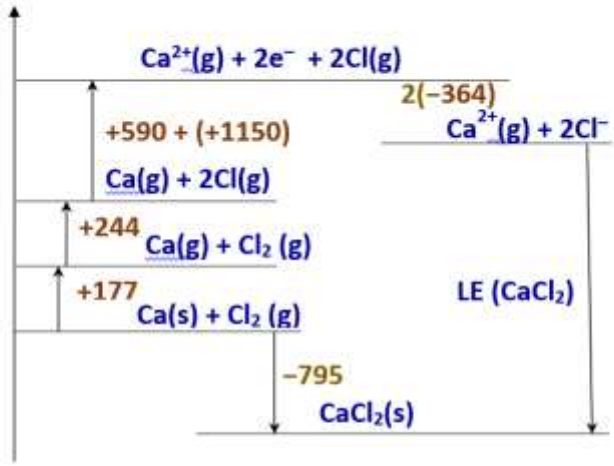
Enthalpy change of atomisation of calcium	= +177 kJ mol^{-1}
Enthalpy change of formation of calcium chloride, $CaCl_2$(s)	= −795 kJ mol^{-1}
First electron affinity of chlorine	= −364 kJ mol^{-1}

(i) Explain, with the aid of an equation, what is meant by *lattice energy* of $CaCl_2$. [1]

Lattice energy of $CaCl_2$ is the **heat evolved** when **one mole** of **solid** $CaCl_2$ is formed from its **gaseous Ca^{2+} and Cl^- ions**.

$Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$ L.E < 0 (negative)

(ii) Construct a Born-Haber cycle for the formation of $CaCl_2$ and use it to calculate the lattice energy of $CaCl_2$. [4]



L.E. = −795 − 177 − 244 − 590 − 1150 − 2(−364)
= −2228 kJ mol^{-1} ≈ **−2230 kJ mol^{-1}**

(iii) Explain how you would expect the magnitude of the lattice energy of aluminium oxide, Al_2O_3 (s) might compare to that of $CaCl_2$(s). [2]

$$|\text{L.E.}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

<u>Cationic and anionic charges</u> of Al_2O_3 are **<u>larger</u>** than those of $CaCl_2$.
<u>Cationic and anionic radii</u> of Al_2O_3 are **<u>smaller</u>** than those of $CaCl_2$.
Hence, lattice energy of Al_2O_3 will be **<u>larger in magnitude</u>** than that of $CaCl_2$.

(iv) Calcium chloride can be prepared by the reaction of calcium oxide and chlorine gas.

$$2CaO(s) + 2Cl_2(g) \rightarrow 2CaCl_2(s) + O_2(g)$$

Using the data above and given that the enthalpy change of formation of calcium oxide is −635 kJ mol^{-1}, construct an energy cycle and use it to calculate the enthalpy change of reaction for the equation above. [2]

$$\begin{tikzcd}
2CaO\,(s) + 2Cl_2\,(g) \arrow[rr, "\Delta H_r"] & & 2CaCl_2\,(s) + O_2\,(g) \\
& 2Ca\,(s) + O_2\,(g) + Cl_2\,(g) \arrow[ul, "2 \times (-635)"'] \arrow[ur, "2 \times (-795)"] &
\end{tikzcd}$$

$2 \times (-635) + \Delta H_r = 2 \times (-795)$
$\Delta H_r = 2 \times (-795) - 2 \times (-635) =$ **−320 kJ mol^{-1}**

(b) Calcium chloride, $CaCl_2$ is a solid with a high melting point (775 °C) whereas aluminium bromide, $AlBr_3$, melts at 97.5°C.

(i) Explain the difference in melting points between these two chlorides in terms of their structure and bonding. [3]

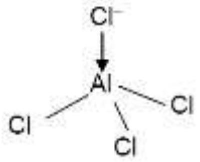
$CaCl_2$ has **giant ionic structure**. A larger amount of energy required to overcome strong **ionic bonds** between Ca^{2+} and Cl^- ions.
$AlBr_3$ has **simple molecular structure**. A smaller amount of energy is required to overcome weak **instantaneous dipole-induced dipole** interactions between the molecules
Hence melting point of $CaCl_2$ is higher than $AlCl_3$.

(ii) Aluminium chloride is a halogen carrier where it reacts with chloromethane gas to generate the electrophile in the electrophilic substitution of hydrogen atoms in benzene:

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$$

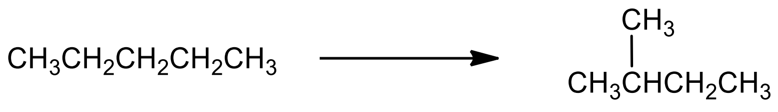
Explain why aluminium chloride can react with chlorine gas. Draw a diagram to illustrate the bonding in $AlCl_4^-$. [2]

Al in $AlCl_3$ is **electron deficient** so it is able to accept a pair of electrons from Cl^-.



12 (a) Industrially, straight chain alkanes often undergo the isomerisation process to be rearranged into more useful branched isomers.

For example:



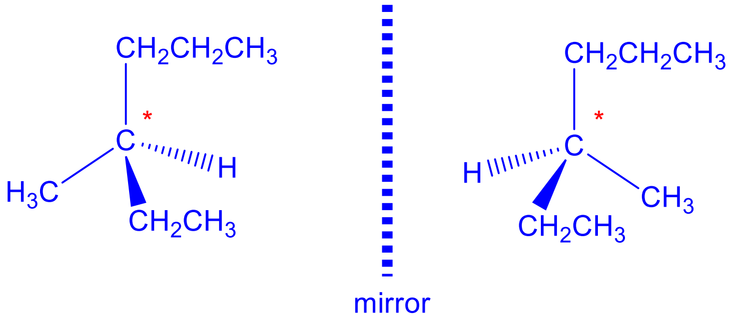
$$CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

pentane

When heptane undergoes isomerisation, several branched isomers of C_7H_{16} can be formed.

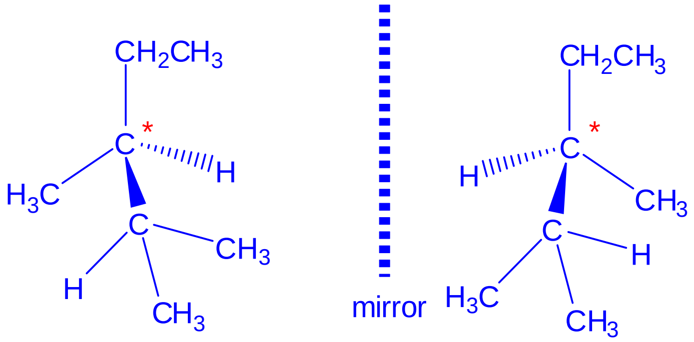
Name and draw one isomer of C_7H_{16} that can exhibit stereoisomerism, showing clearly the pair of stereoisomers. [2]

Name: 3−methylhexane

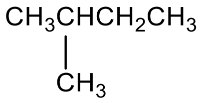


OR

Name: 2,3−dimethylpentane



2–methylbutane is an extremely volatile and flammable liquid at room temperature. It is used in conjunction with liquid nitrogen in cryosectioning in histology.



$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

2–methylbutane

(b) Alkanes are generally unreactive. Suggest a possible reason why this is so. [1]

Due to the similar electronegativities of C and H, alkanes are non–polar and hence there is a lack of electron-poor and electron-rich regions to be attacked by polar reagents and ions.

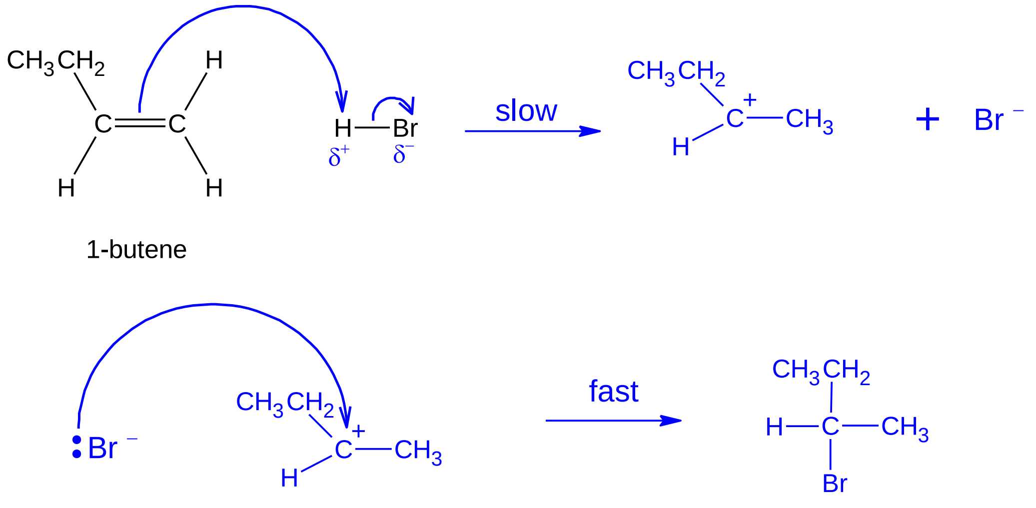
OR

The C–C and the C–H bond are very strong and requires a large amount of energy to be broken.

(c) Pentadecane, $C_{15}H_{32}$ can undergo cracking to produce propene, but–1–ene and octane.

(i) Name and outline the mechanism of the reaction between but–1–ene and hydrogen bromide to obtain 2–bromobutane. The mechanism should show curly arrows, charges, dipoles and any relevant lone pairs. [2]

Name of mechanism: Electrophilic Addition



(ii) Explain why this reaction produces an equimolar mixture of the two stereoisomers of 2–bromobutane. [1]

In the 2nd step, Br^- can attack the trigonal planar carbocation from either the top or bottom of the plane with equal probability. A racemic mixture is formed, containing equal amounts of both enantiomers.

(iii) Compound **Z,** a structural isomer of 2–bromobutane**,** could also be formed via the same reaction. Identify **Z**, and with reference to the mechanism drawn in **(a)(i),** explain why compound 2–bromobutane was formed as the major product. [3]

Z is $CH_3CH_2CH_2CH_2Br$

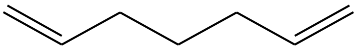
2-bromobutane is formed via $CH_3CH_2\overset{+}{C}HCH_3$, a secondary carbocation,

while Z is formed via $CH_3CH_2CH_2\overset{+}{C}H_2$, a primary carbocation.

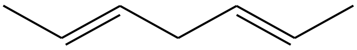
The secondary carbocation has more alkyl groups which exert greater electron-donating inducting effect.

Hence, this disperses the positive charge on the secondary carbocation to a greater extent, making the carbocation more stable and so leading to the formation of 2–bromobutane as the major product.

(d) This part question is about two isomeric compounds, **C** and **D**, as shown below.



C



D

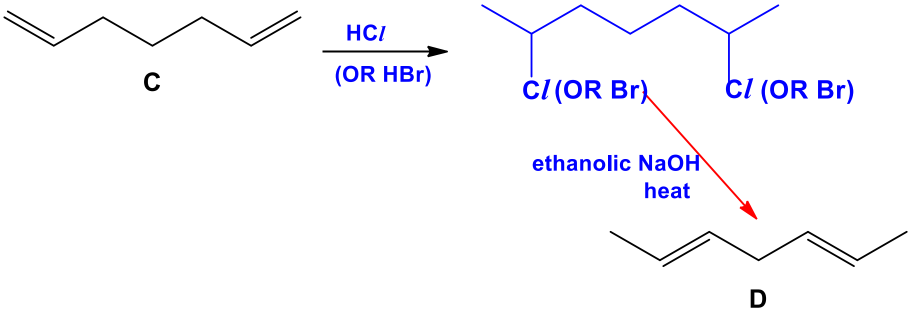
(i) Suggest a simple chemical test to distinguish **C** from **D**. [2]

Reagents and conditions:

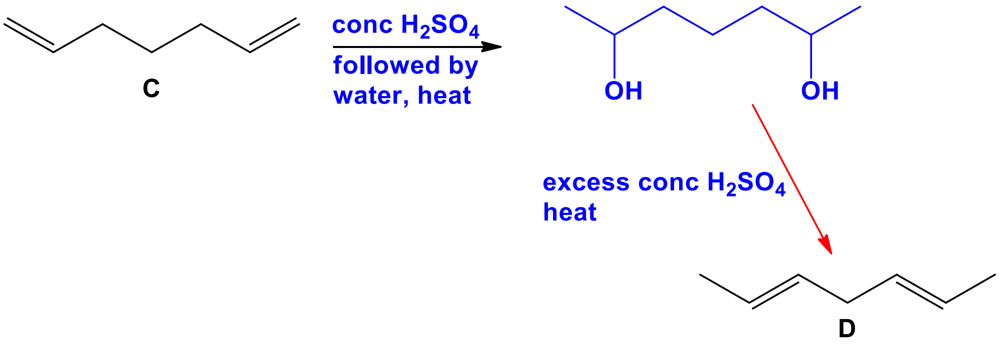
- **Heat with $KMnO_4$(aq) acidified with H_2SO_4(aq)**

Observations:
C: purple solution is decolourised with effervescence of CO_2 gas
D: purple solution is decolourised without effervescence

(ii) Suggest a **two-step** synthetic route to convert **C** to **D**. State clearly all reagents and conditions and any intermediate compound(s) formed. [2]



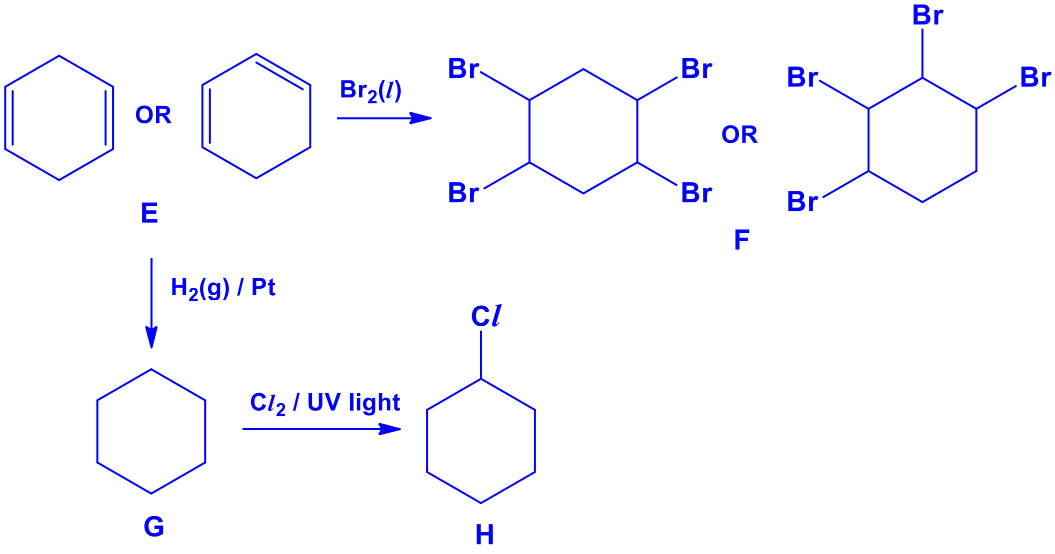
OR



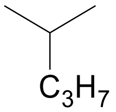
(e) 1 mol of compound **E**, C_6H_8, reacts with 2 mol of bromine in an inert solvent to form compound **F**. Compound **E** also reacts with hydrogen gas in the presence of Pt to form compound **G**. Compound **G** reacts with chlorine gas in UV light to give only one monochlorinated product **H**.

Deduce the identities of **E** to **H**. [6]

Tests	**Deductions** **(include reaction types and functional groups or class)**
E has a formula of C_6H_8	**E has either 3 C=C bonds or 2 C=C bonds and a ring structure**
1 mol of **E** + 2 mol of Br_2 → **F**	**E undergoes electrophilic addition.** **E has 2 C=C bonds per molecule, hence E is cyclic.** **F is halogenoalkane**
E + hydrogen / Pt → **G**.	**E is reduced by hydrogen.** **G is an alkane.**
G + Cl_2 / uv → only one monochlorinated **H.**	**G undergoes free radical substitution.** **H is a halogenoalkane.** **G is a symmetrical alkane.**



(f) Compound **K** has the following structure.



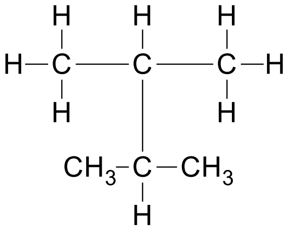
Compound **K**

When compound **K** is reacted with chlorine under sunlight, only **two** monochlorinated products **L** and **M** are produced.

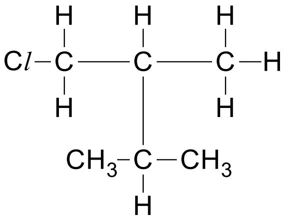
- Compound **K** and **M** does not rotate plane polarised.
- Product **L** rotate plane polarised light.

Suggest the structure of products **L** and **M**. [2]

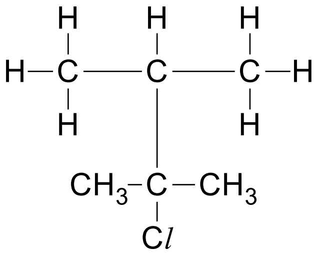
Since K produces only 2 monochlorinated products, its structure is:



L has a chiral centre. Hence it is:



M does not have a chiral centre. Hence it is:



(g) Compounds **A** and **B** have the same molecular formula C_8H_8. Both compounds possess a six-membered ring each.

When both compounds undergo oxidative cleavage separately, only one organic compound is formed in each case, as shown in Table 1.1.

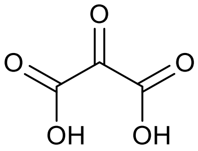
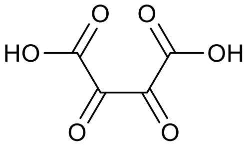
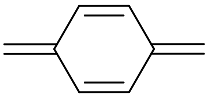
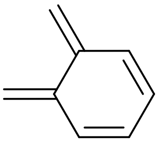
compound	**A**	**B**
product		

Table 1.1

Suggest the structures of **A** and **B**. [2]



A



B