



---

## CHEMISTRY

---

# 2008 NATIONAL QUALIFYING EXAMINATION

*Time Allowed*

*Reading Time: 15 minutes*

*Examination Time: 120 minutes*

### INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.
  - Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.  
[This section is worth 30 marks.]
  - Section B: Apportion your time equally on the questions in this section.  
Answer **ANY THREE (3)** of Questions 16, 17, 18 or 19  
[This section is worth 90 marks.]
- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the spaces provided in the booklet.
- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable.
- Rough working must be done only on pages 23 and 24 of this booklet.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.

**DATA**

Avogadro constant (N)	$6.02 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c)	$2.998 \times 10^8 \text{ m s}^{-1}$
1 faraday	96,486 coulombs	Density of water at 25°C	$0.9971 \text{ g cm}^{-3}$
1 coulomb	$1 \text{ A s}^{-1}$	Acceleration due to gravity	$9.81 \text{ m s}^{-2}$
Universal gas constant (R)		1 newton (N)	$1 \text{ kg m s}^{-2}$
$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$			
$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$			
Planck's constant (h)	$6.626 \times 10^{-34} \text{ J s}$	1 pascal (Pa)	$1 \text{ N m}^{-2}$
Standard temperature and pressure (STP)		$\text{pH} = -\log_{10}[\text{H}^+]$	
273 K and 100 kPa		$\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$	
0°C and 100 kPa		$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$	
0°C and 1 bar		$\text{PV} = n\text{RT}$	
0°C and 750 mm Hg		$E = h\nu$	
Molar volume of ideal gas at STP	22.7 L	$c = \nu\lambda$	
1 bar = 100 kPa		Surface area of sphere $A = 4\pi r^2$	

**ATOMIC NUMBERS & RELATIVE ATOMIC MASSES\***

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98) <sup>†</sup>	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

\* The relative values given here are to four significant figures.

<sup>†</sup> A value given in parentheses denotes the mass of the longest-lived isotope.

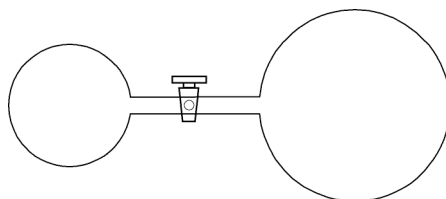
**SECTION A**

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section on the multiple choice answer sheet, using a 2B pencil. Only one choice is allowed per question. If you make a mistake **make sure that your incorrect answer is completely erased**.

**Please note the following:**

- It is recommended that you first record your answer on this question paper by circling **ONE** of the letters **A, B, C, D** or **E**.
- Then transfer these answers on to the computer sheet which will be computer marked for assessment.

- Q1** A 1 L vessel containing argon gas at a pressure of 100 kPa is attached via a tube and tap of negligible volume to a 2 L vessel containing neon gas at a pressure of 150 kPa.



When the tap is opened and the gases allowed to mix, what is the final pressure in the vessels?

- A** 100 kPa
- B** 125 kPa
- C** 133 kPa
- D** 150 kPa
- E** 250 kPa
- Q2** 1.000 mL of 0.1000 mol L<sup>-1</sup> hydrochloric acid was diluted to 100.0 mL with deionised water. 10.00 mL of this solution was diluted to 100.0 mL again using deionised water. What is the *pH* of the final solution?
- A** 1
- B** 2
- C** 3
- D** 4
- E** 5
- Q3** 0.5755 g of a compound, containing sulfur and fluorine only, has a volume of 255.0 mL at 288.0 K and 50.01 kPa. What is the molecular formula of this compound?
- A** S<sub>2</sub>F<sub>2</sub>
- B** SF<sub>2</sub>
- C** SF<sub>4</sub>
- D** SF<sub>6</sub>
- E** S<sub>4</sub>F<sub>10</sub>

- Q4** 50.0 mL of absolute ethanol and 50.0 mL of pure water, both at 10°C, are mixed. At 10°C the densities of water, absolute ethanol and the mixed solution are 1.00, 0.79 and 0.93 g mL<sup>-1</sup> respectively. What is the volume of the mixed solution at 10°C?
- A 79.0 mL
  - B 89.5 mL
  - C 93.0 mL
  - D 96.2 mL
  - E 100 mL
- Q5** The bond dissociation energies of a C-Cl bond and a C-F bond are 397 kJ mol<sup>-1</sup> and 552 kJ mol<sup>-1</sup> respectively. What is the minimum energy required to break any of the bonds in trichlorofluoromethane (CFCℓ<sub>3</sub>)?
- A 397 kJ
  - B 552 kJ
  - C 5.72 eV
  - D 9.17 x 10<sup>-22</sup> J
  - E 4.12 eV
- Q6** The second ionization energies for four consecutive elements of the periodic table W, X, Y and Z, (that is they have atomic numbers n, n+1, n+2 and n+3) are 2297.3 kJ mol<sup>-1</sup>, 2665.8 kJ mol<sup>-1</sup>, 3051.3 kJ mol<sup>-1</sup> and 1145.4 kJ mol<sup>-1</sup>, respectively. Which of the following pairs of oxides would be most stable?
- A WO, X<sub>2</sub>O
  - B X<sub>2</sub>O, YO<sub>2</sub>
  - C W<sub>2</sub>O, YO<sub>2</sub>
  - D XO<sub>3</sub>, Z<sub>2</sub>O
  - E Y<sub>2</sub>O, ZO
- Q7** An organic molecule of four carbons is shown to be 55.1% carbon, 0.40% hydrogen and 18.4% oxygen by mass. Which of the following functional groups is **NOT** present in this compound?
- A alcohol
  - B carboxylic acid
  - C amide
  - D alkene
  - E ketone

**Q8** 1 mole of nitrogen gas and 3 moles of hydrogen gas were added to a rigid 1 L container at 298 K and left to react. At equilibrium it was found that the concentrations of nitrogen, hydrogen and ammonia were  $0.116 \text{ mol L}^{-1}$ ,  $0.348 \text{ mol L}^{-1}$  and  $1.768 \text{ mol L}^{-1}$  and the pressure inside the container was 55 bar.

1 mole of hydrogen chloride gas was subsequently added to the container and the system was left to re-establish equilibrium (hydrogen chloride gas reacts with ammonia gas to produce solid ammonium chloride).

What are the concentrations (or range of concentrations) of nitrogen, hydrogen, ammonia and hydrogen chloride once equilibrium has been reached for the second time?

Final concentration ( $\text{mol L}^{-1}$ )				
	$[\text{N}_2]$	$[\text{H}_2]$	$[\text{NH}_3]$	$[\text{HCl}]$
<b>A</b>	0.116	0.348	1.768	1
<b>B</b>	$0 < [\text{N}_2] < 0.116$	$0 < [\text{H}_2] < 0.348$	$[\text{NH}_3] > 1.768$	1
<b>C</b>	0.116	0.348	0.768	0
<b>D</b>	$0 < [\text{N}_2] < 0.116$	$0 < [\text{H}_2] < 0.348$	$0 < [\text{NH}_3] < 1.768$	0
<b>E</b>	$0 < [\text{N}_2] < 0.116$	$0 < [\text{H}_2] < 0.348$	$0 < [\text{NH}_3] < 1.768$	$0 < [\text{HCl}] < 1$

**Q9** In a laboratory a small sheet of steel is submerged in a beaker containing 100 mL of  $1 \text{ mol L}^{-1} \text{Cr}_2(\text{SO}_4)_3$  and connected to an electrode of metal X submerged in 100 mL of a metal X salt solution. The two beakers were connected by a salt bridge for a certain amount of time. On removing the salt bridge it was found that a layer of chromium was deposited on the steel sheet. The mass of the deposited chromium was found to be 1.48 g and the other electrode was 1.04 g lighter. What is metal X?

- A** Al
- B** Mg
- C** Zn
- D** Ni
- E** Fe

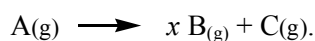
**Q10** Given that the average kinetic energy of a molecule at a temperature T is given by kinetic energy =  $kT$ , where  $k = 2.07 \times 10^{-23} \text{ J K}^{-1}$  and that kinetic energy is related to speed by kinetic energy =  $\frac{mv^2}{2}$ , what is the approximate speed of the average molecule of air at room temperature?

- A**  $5 \text{ m s}^{-1}$
- B**  $50 \text{ m s}^{-1}$
- C**  $500 \text{ m s}^{-1}$
- D**  $5\,000 \text{ m s}^{-1}$
- E**  $50\,000 \text{ m s}^{-1}$

**Q11** An aqueous solution of ammonia has of  $pH = x$ , and a solution of hydrochloric acid has  $pH = y$ ; it is also known that  $x + y = 14$ , and  $x > 11$ . If equal volumes of these two solutions are mixed together, what would be the concentration of the various ions in the resulting solution in **descending** order?

- A  $[\text{NH}_4^+] > [\text{Cl}^-] > [\text{OH}^-] > [\text{H}^+]$   
B  $[\text{Cl}^-] > [\text{NH}_4^+] > [\text{H}^+] > [\text{OH}^-]$   
C  $[\text{NH}_4^+] > [\text{Cl}^-] > [\text{H}^+] > [\text{OH}^-]$   
D  $[\text{Cl}^-] > [\text{NH}_4^+] > [\text{OH}^-] > [\text{H}^+]$   
E  $[\text{Cl}^-] = [\text{NH}_4^+] = [\text{OH}^-] = [\text{H}^+]$

**Q12** Substance **A** decomposes into **B** and **C** as indicated by the following reaction:



A certain amount of **A** is placed inside a closed vessel of fixed volume and the system comes to equilibrium. If we see a 20% increase in pressure inside the vessel and the amount of **A** present has decreased by 20%, what is the value of  $x$ ?

- A 1  
B 2  
C 3  
D 4  
E 5

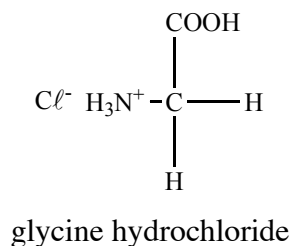
**Q13** Which of the following transformations can only be achieved with a reductant?

- A chlorine molecules  $\longrightarrow$  chloride ions  
B hydrogen molecules  $\longrightarrow$  water molecules  
C iron atoms  $\longrightarrow$  iron(III) ions  
D iodine molecules  $\longrightarrow$  iodine monochloride molecules  
E iodide ions  $\longrightarrow$  iodine molecules

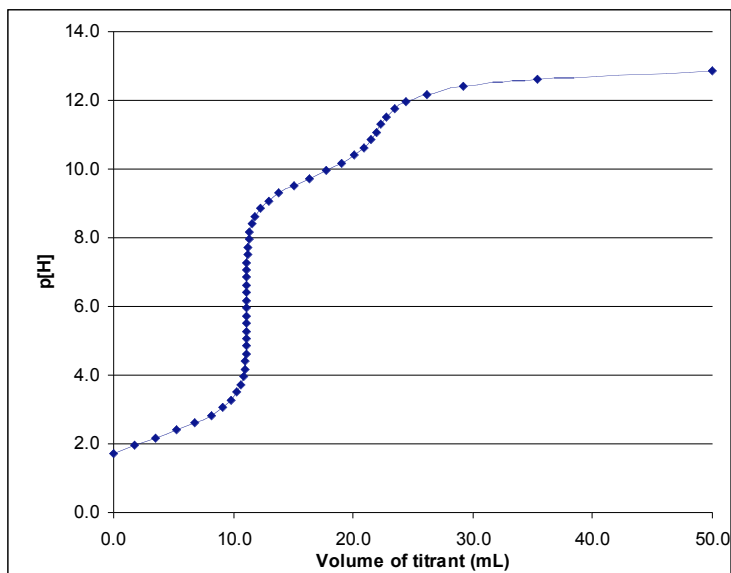
**Q14** If 42 g of Fe powder and 8 g of S powder are mixed and heated, what mass of FeS will be produced?

- A 22 g  
B 34 g  
C 44 g  
D 50 g  
E 66 g

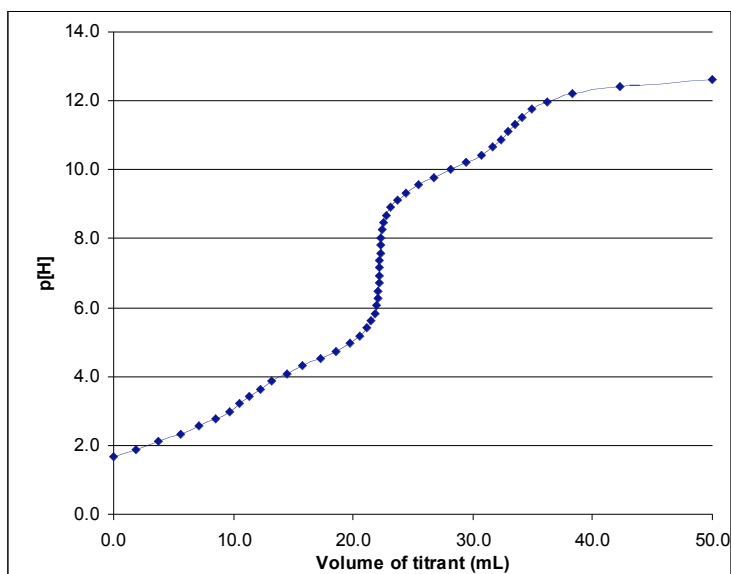
- Q15** When a  $0.1 \text{ mol L}^{-1}$  solution of glycine hydrochloride is titrated against  $0.18 \text{ mol L}^{-1}$  sodium hydroxide solution, titration curve I is obtained. When the experiment is repeated with a  $0.1 \text{ mol L}^{-1}$  solution of 'X' hydrochloride instead of glycine hydrochloride, curve II is obtained.



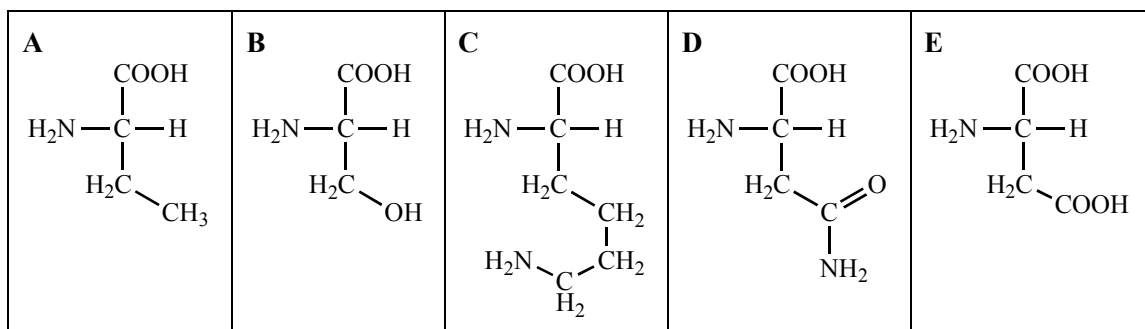
Curve I



Curve II



Which of the following molecules could be 'X'?



## SECTION B

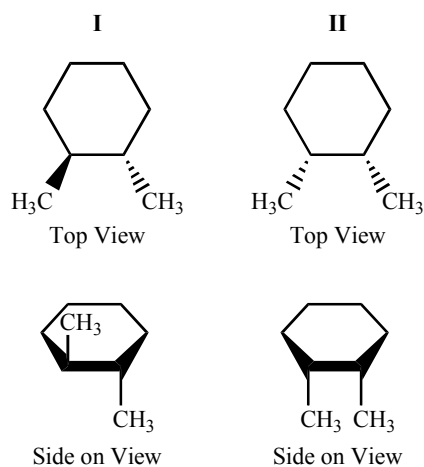
Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Answer any three of the four questions in this section.

## Q16

Cyclic compounds are organic molecules which feature a series of atoms, most commonly all carbon, joined in a ring.

Because of the way the rings are connected, rotation around the carbon-carbon bonds is restricted allowing for compounds with the same formula and sequencing of groups to differ from each other in the spatial arrangement of atoms – a form of isomerism called *stereoisomerism*. For example 1,2-dimethylcyclohexane, the numbers in the name determine what carbon atom the methyl groups are bonded to:



Note that wedged lines () denote bonds pointing out of the page and dashed lines () denote bonds going into the page. Carbons and implicit hydrogens are not drawn, so that is

identical to .

For this compound two stereoisomers are possible, one when the two methyl groups are on opposite sides of the ring (**I**) and the other when they are on the same side of the ring (**II**).

- (a) Draw the two stereoisomers possible for 1,3-dichlorocyclohexane.



When the substituent groups are on the same side of the ring, the molecule is referred to as the *cis* isomer and when they are on opposite sides it is called the *trans* isomer.

- (b) Label the two stereoisomers drawn in part (a). Use the answer box for (a) above to answer this question.

Often reactions in organic chemistry yield only one stereoisomer, or form one stereoisomer in large excess compared to others. These reactions are termed stereoselective.

One method for predicting the outcome of a reaction is to investigate mechanisms, which show the step-by-step formation and breaking of bonds.

Mechanisms usually involve an electron-rich centre reacting with an electron-poor centre to form a new covalent bond. These electron-poor centres are termed 'electron-seeking' or electrophilic; the electron-rich centres are referred to as nucleophilic.

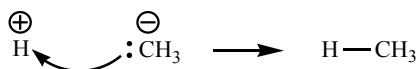
Nucleophilic centres generally involve an atom that has a negative charge or a neutral atom with one or more lone pairs of electrons. Electrophilic centres are those that have a positive charge or are connected to an electron-withdrawing group.

- (c) Identify the atoms (excluding hydrogens) in the following as nucleophilic, electrophilic or neither.

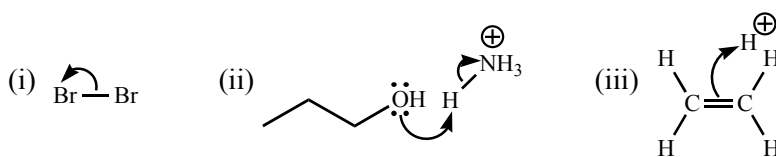
(i)  $\text{OH}^-$                       (ii)  $\text{NH}_3$                       (iii)  $\text{CH}_4$                       (iv)  $\text{H}_3\text{C}^+$

(i)	(ii)
(iii)	(iv)

When drawing a mechanism a curly arrow is used to represent the notional movement of a pair of electrons – usually breaking or making a bond – during the reaction. For example:



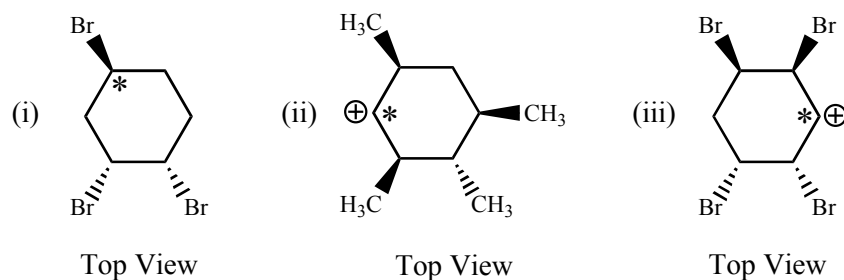
- (d) Draw the products that would result from the following movement of electrons.



(i)	(ii)	(iii)
-----	------	-------

The substituents which are already present on the molecule may influence how the reaction proceeds. The predominant cause of this is when large groups (for example bromine or a methyl group) prevent access of an electron pair to the reactive centre.

- (e) Which face (top, bottom or both equal) of the ring would be more likely to be approached by a nucleophilic centre for the carbon designated by \*?



(i)	(ii)	(iii)
-----	------	-------

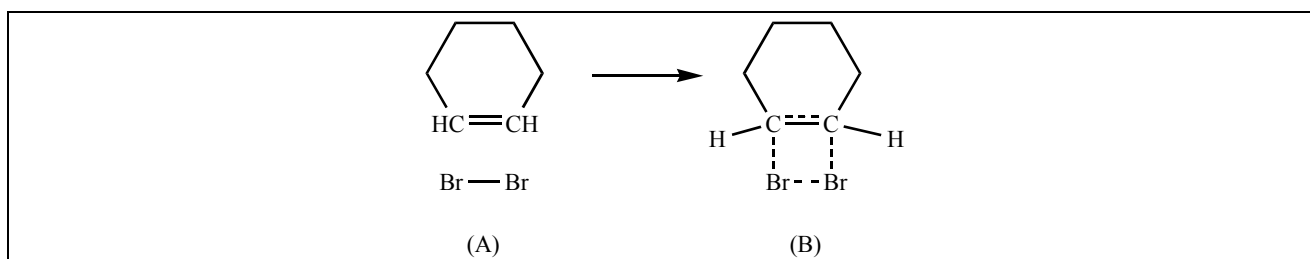
The mechanism cannot be determined conclusively by current techniques. All we can do is gather supporting and contradictory evidence for a proposed mechanism which is never more than a theory.

Bromination is a standard reaction that involves the addition of two Br substituent atoms across a double bond. A mechanism for this can be postulated where stereoisomerism in the products allows alternative proposed mechanisms to be compared. This can be done, for example, by brominating cyclohexene and looking at the stereochemistry of the product or products. Below are three possible mechanisms for the bromination reaction, however the product or products of only one is observed.

Proposed Mechanism 1:

In this notional mechanism the reaction occurs in a single step. We can draw a structure to represent the molecule part way through the reaction, when some bonds are partially formed and partially broken. This structure is called a transition state; the partial bonds are drawn with dashed lines (---).

- (f) (i) Insert the curly arrows onto (A) to show how the transition state (B) is obtained.



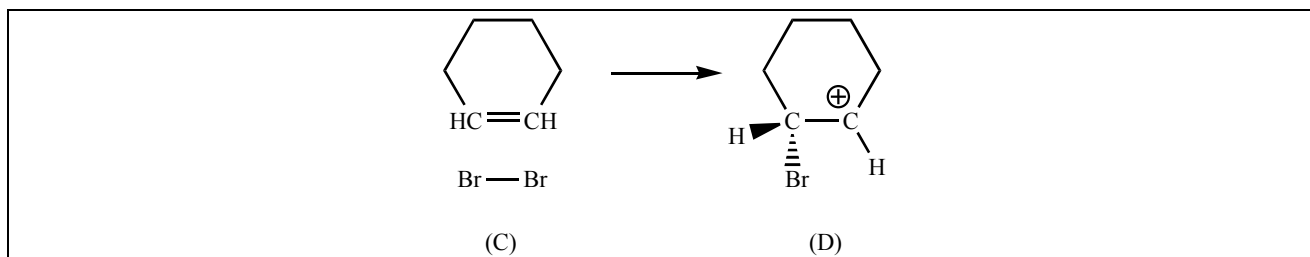
- (ii) Suggest the likely product or products, drawn and labelled with correct stereochemistry.

This question continues on the next page.

Proposed Mechanism 2:

Reactions may occur in a number of elementary steps. Below is the first step of the reaction, showing a planar carbocation intermediate (D).

- (g) (i) Insert the curly arrows onto (C) to show how intermediate (D) is obtained.

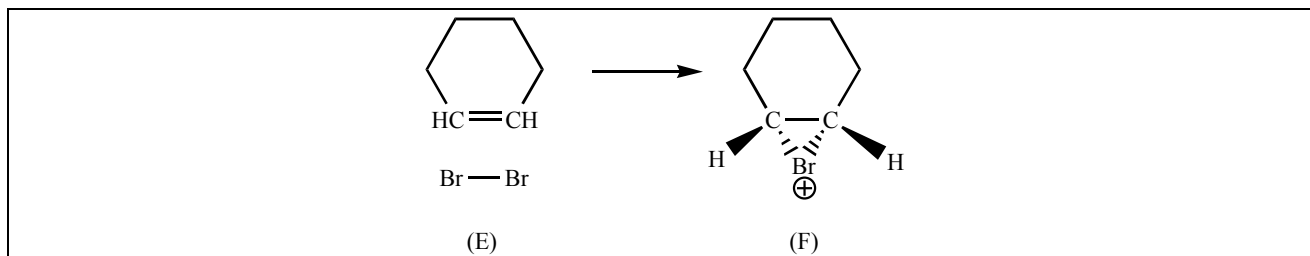


- (ii) Draw the curly arrows onto D for the second step of the mechanism and suggest the likely product or products, drawn and labelled with correct stereochemistry.

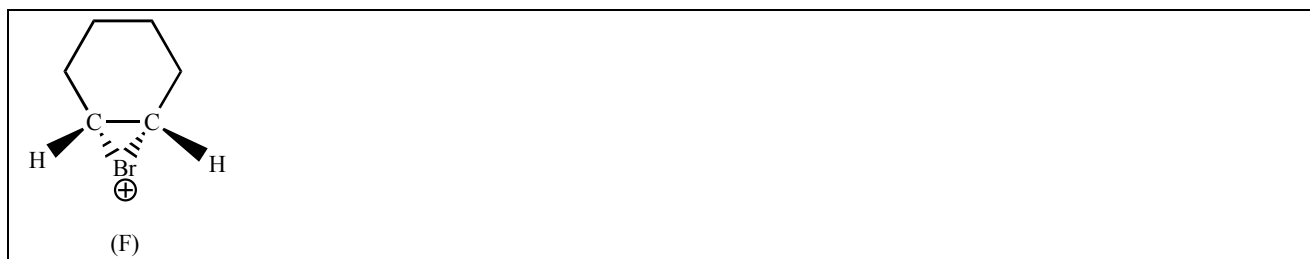
Proposed Mechanism 3:

A reactive ring could be the intermediate, as shown below.

- (h) (i) Insert the curly arrows onto (E) to show how intermediate (F) is obtained.

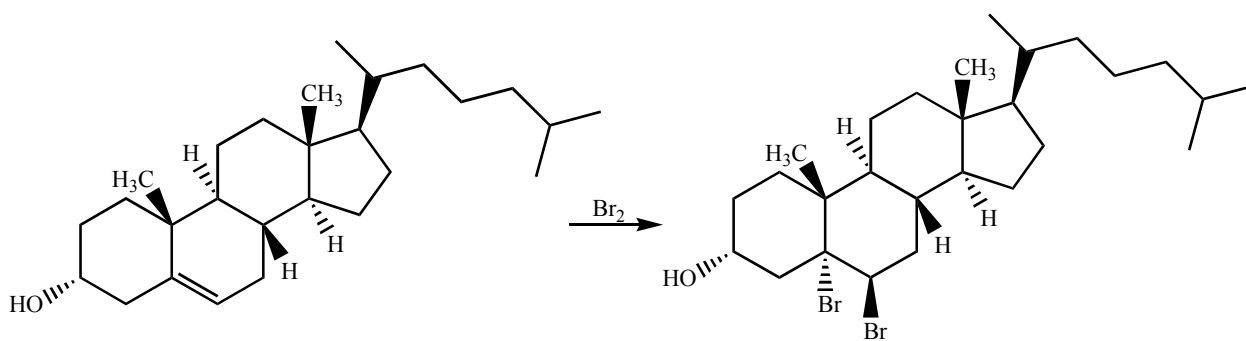


- (ii) Draw the curly arrows onto F for the second step of the mechanism and suggest the likely product or products, drawn and labelled with correct stereochemistry.



This question continues on the next page.

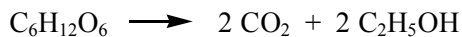
The product obtained from the experimental bromination of cholesterol is shown below.



- (i) Based on your work so far, deduce which of the above three possibilities is an acceptable mechanism for the bromination of alkenes.

## Q17

Chemistry has been used for analysis of food and drink for many years. The fermentation of grapes to produce wine is subject to strict quality control, in which analytical chemistry plays an important part. In the fermentation process, sugars are converted into carbon dioxide and ethanol according to the following equation.



Determining the alcohol (ethanol) content of wine is one of the most important analyses for wine and can be done a number of ways. One redox method involves the use of a permanganate solution, usually  $\text{KMnO}_4$ . The permanganate ion reacts with the ethanol to give  $\text{Mn}^{2+}$  ions and ethanoic acid,  $\text{CH}_3\text{COOH}$ .

- (a) From the following species;  $\text{CO}_2$ ,  $\text{MnO}_4^-$ ,  $\text{Mn}^{2+}$ ,  $\text{CH}_3\text{COOH}$ ;
- (i) Which one of the following elements, carbon, manganese, oxygen or hydrogen, in the above four species has the **highest** oxidation number?

Element: <hr/>	Oxidation number: <hr/>
Species: <hr/>	

- (ii) Which one of the following elements, carbon, manganese, oxygen or hydrogen, in the above four species has the **lowest** oxidation number?

Element: <hr/>	Oxidation number: <hr/>
Species: <hr/>	

- (b) Write balanced ionic half equations for the determination of ethanol in wine with permanganate ions. Indicate which is the oxidation half equation.

- (c) Using the half equations above write a full balanced ionic equation for the process.

In the analysis of a white wine a 10.00 mL sample is diluted up to 500.00 mL in a volumetric flask. From this diluted solution a 20.00 mL aliquot is titrated with a 0.0500 mol L<sup>-1</sup> solution of KMnO<sub>4</sub>. The average titre obtained was 14.40 mL.

- (d) What is the concentration in moles per litre of ethanol in the diluted white wine solution?

- (e) What is the percentage of ethanol with respect to volume in the white wine? (The densities of water and ethanol are 1.00 and 0.790 g mL<sup>-1</sup> respectively.)

One regulation with respect to wine is the content of volatile acid, mainly present as acetic acid, CH<sub>3</sub>COOH. It can be produced as a by-product of the fermentation of wine but can also be as a result of poor storage and handling. According to wine standards the content of volatile acid cannot be greater than 1.20 g L<sup>-1</sup> in non-red wines. A common way to determine amount of volatile acid is to distil a sample of the wine and then titrate the distillate with a solution of sodium hydroxide. It can be assumed that the only volatile acid present is acetic acid.

- (f) 20.00 mL of the same white wine is distilled and the distillate made up to 100.00 mL in a volumetric flask. 10.00 mL of this solution is then titrated with sodium hydroxide. Using calculations, which of the following concentrations of NaOH is the most appropriate to use for the titration;  $2.00 \times 10^{-2}$  mol L<sup>-1</sup>,  $2.00 \times 10^{-3}$  mol L<sup>-1</sup> or  $2.00 \times 10^{-4}$  mol L<sup>-1</sup>?

- (g) If a solution from a completed permanganate titration is used instead of wine for the analysis of volatile acid, which of the above NaOH solutions would be the most appropriate to use? Explain your answer using calculations.

- (h) Would the second method be appropriate for the determination of volatile acid? Explain.

## Q18

Glucagon is produced in the cells of the pancreas and helps maintain the blood glucose concentration within a normal range. It is often described as having the opposite effect to insulin. That is, glucagon has the effect of increasing blood glucose levels. Glucagon is a polypeptide hormone with 29 amino acids and has a molar mass of  $3485 \text{ g mol}^{-1}$ .

The amino acids that have an aromatic ring as part of their structure will absorb ultraviolet radiation. It is therefore the amino acids tryptophan (Trp), tyrosine (Tyr) and phenylalanine (Phe) that are primarily responsible for the fact that polypeptides such as glucagon absorb light at wavelengths between 240 nm and 300 nm.

**Beer-Lambert Law**

The greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. Furthermore, the more effectively a molecule absorbs light of a given wavelength, the greater the extent of light absorption. From these ideas, the following expression, known as the Beer-Lambert Law, can be formulated:

$$A = \log \frac{I_0}{I} = \epsilon \times c \times \ell \text{ for a given wavelength.}$$

- A is the absorbance.
- $I_0$  is the initial light intensity.
- $I$  is the light intensity after it passes through the sample.
- $c$  is the molar concentration of the solute ( $\text{mol L}^{-1}$ ).
- $\ell$  is the path length of the sample cell (cm).
- $\epsilon$  is the molar absorptivity ( $\text{L mol}^{-1} \text{ cm}^{-1}$ ).

If  $I$  is less than  $I_0$ , then the sample has absorbed some of the light. This is illustrated schematically in Figure 1.

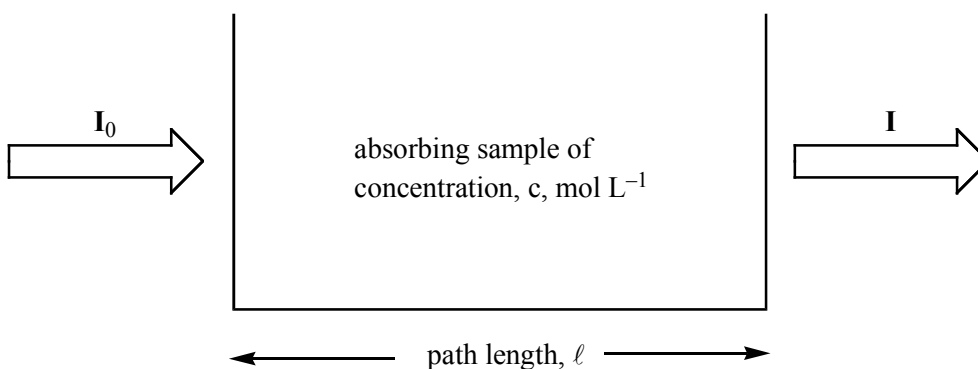


Figure 1: Absorption of light by a sample.

**The importance of concentration**

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose you have a strongly coloured organic dye. If it is in a reasonably concentrated solution, the solution will have a very high absorbance because there are lots of molecules to interact with the light.

However, in a very dilute solution, it may be very difficult to see that it is coloured at all. The absorbance is going to be very low.

**The importance of the container shape**



Suppose this time that you had a very dilute solution of the dye in a cube-shaped container so that the light travelled 1.0 cm through it. The absorbance isn't likely to be very high. On the other hand, suppose you passed the light through a tube 100 cm long containing the same solution. More light would be absorbed because it interacts with more molecules.

### Molar absorptivity

If you rearrange the Beer-Lambert Law, to give an expression for the molar absorptivity, you get:

$$\epsilon = \frac{A}{c \times \ell}$$

Remember that the absorbance of a solution will vary as the concentration and with the length of the path of the light through the solution. Molar absorptivity compensates for this by dividing by both the concentration and the path length. Molar absorptivity is a property unique to each species and is constant for all concentrations of solutions of the species.

If multiple species that absorb light at a given wavelength are present in a sample, the total absorbance at that wavelength is the sum due to all absorbers:

$$A = (\epsilon_1 \times c_1 \times \ell) + (\epsilon_2 \times c_2 \times \ell) + \dots \text{ for a given wavelength}$$

where the subscripts refer to the molar absorptivity and molar concentration of the different absorbing species that are present.

Figure 2 below shows the ultraviolet absorption spectrum for each of tryptophan, tyrosine and phenylalanine.

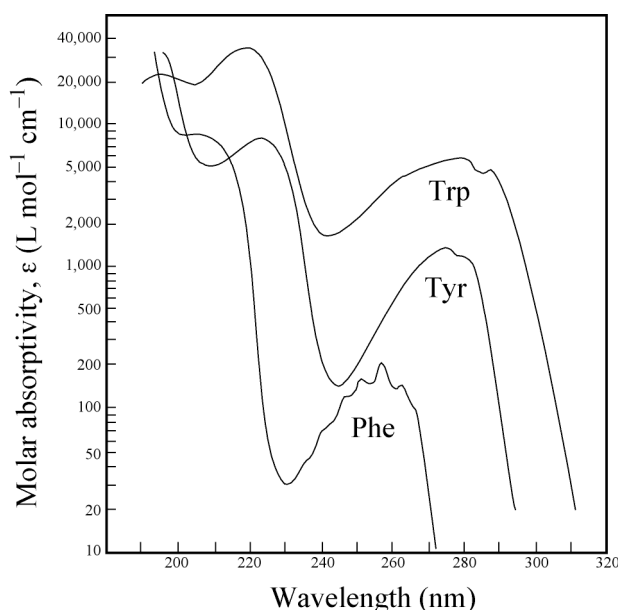


Figure 2: The ultraviolet absorption spectrum for each of tryptophan, tyrosine and phenylalanine.

- (a) Using the information in Figure 2, determine the molar absorptivity (at 280 nm) for each of phenylalanine (Phe), tyrosine (Tyr) and tryptophan (Trp).

Molar absorptivity (Phe)	Molar absorptivity (Tyr)	Molar absorptivity (Trp)

- (b) In a polypeptide containing several aromatic amino acids, the sum of the molar absorptivities **per** amino acid  $\Sigma \epsilon_{\text{amino acid}}$ , is approximately equal to the molar absorptivity,  $\epsilon_{\text{polypeptide}}$ , for the polypeptide. Use this information and the information provided in Figure 2 to calculate the molar absorptivity for glucagon,  $\epsilon_{\text{glucagon}}$  at 280 nm.

**Glucagon contains two phenylalanine units, two tyrosine units and one tryptophan unit.**

The absorption of a solution of glucagon is measured using a container with a 1.0 cm light path. The absorbance,  $A$ , is measured as being 0.95.

- (c) Calculate the molar concentration ( $\text{mol L}^{-1}$ ) of glucagon in the sample.

- (d) Calculate the mass concentration ( $\text{g L}^{-1}$ ) of glucagon in the sample.

- (e)(i) Calculate the absorbance (at 280 nm with a 1.0 cm path length) of a  $1.0 \text{ g L}^{-1}$  solution of **glucagon**.

**This question continues on the next page.**

The frequency (expressed as a percentage) of the aromatic amino acids in an **average** polypeptide is calculated from known amino acids sequences using a large number of polypeptides:

Amino Acid	Frequency
Phenylalanine	3.9%
Tryptophan	1.3%
Tyrosine	3.4%

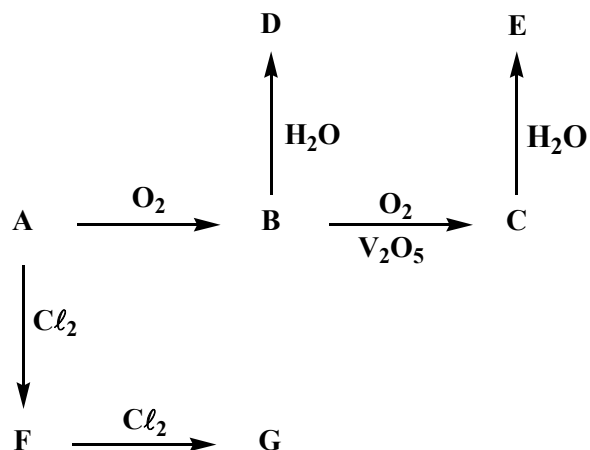
- (ii) Calculate the absorbance (at 280 nm with a 1.0 cm path length) of a  $1.0 \text{ g L}^{-1}$  solution of an **average** polypeptide. [Assume that the average mass of the amino acids in glucagon is the same as in an average polypeptide.]

A solution of a mixture of glucagon and an unknown protein is provided. The unknown protein consists of 129 amino acids, of which 3 are phenylalanine, 3 are tyrosine and 6 are tryptophan. Using a glucagon-specific analysis the mass concentration of glucagon is calculated to be  $0.24 \text{ g L}^{-1}$ .

- (f) Calculate the concentration ( $\text{mol L}^{-1}$ ) of the unknown protein when the absorbance of the mixture is measured to be 1.85 at 280 nm and a light path of 1.0 cm is used.

## Q19

The element **A** burns in oxygen to produce **B**, which can be catalytically oxidised further (using  $V_2O_5/K_2O$ ) to **C**. **B** reacts with water to produce a weak acid **D**, while **C** reacts with water to produce a strong acid **E**. In 2001, 165 tons of **E** were produced worldwide (more than any other chemical). Element **A** reacts with chlorine gas to form a toxic golden-yellow liquid **F**. **F** has two structural isomers. **F** can be further chlorinated to form a cherry red liquid **G**, which boils at  $59^\circ\text{C}$ , with molecular formula  $ACl_2$ . Both **F** and **G** react with water to form a mixture of products, including **B**, **D** and **E**. The above information is summarised in the following diagram.



- (a) Based on the information above, do you think **A** is a metal or a non-metal?

- (b) A 0.29 g sample of the element was exhaustively oxidised and the product (compound **C**) absorbed in water and titrated with  $1.00 \text{ mol L}^{-1}$  sodium hydroxide. The volume of hydroxide required was 18.0 mL. Use this information to deduce the identity of **A**.

- (c) Identify all of the unknown compounds and write balanced chemical equations for all the reactions shown in the diagram above.

<b>A</b>
<b>B</b>
<b>C</b>
<b>D</b>
<b>E</b>
<b>F</b>

- (d) **C** reacts with **G** to produce **H** and **B**. **H** reacts with water to produce **D** and a strong acid **I**. Identify **H** and **I** and write a balanced equation for each of these reactions.

<b>H</b>
<b>I</b>

- (e) Draw an electron dot diagram for each of **B** and **C** then draw **two** possible isomers of **F**. Hence predict the shape of the molecules **B**, **C** and **F** (linear, bent, planar, pyramidal etc.).

<b>B</b>	<b>C</b>	<b>F</b>	<b>F</b>

*This page is intentionally left blank.*

*This page is intentionally left blank.*