Eunice Sim

RAFFLES INSTITUTION
PRELIMINARY EXAMINATION 2010

H

Higher 2

CHEMISTRY   9647/01, 9746/01

Paper 1   Multiple Choice   27 September 2010

Additional Materials: OMR Answer Sheet   1 hour
                        Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, class and index number in the spaces provided on the Answer Sheet.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

This document consists of **17** printed pages.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

B   1   Which of the following stated particles contain an equal number of particles as 12 g of ^{12}C?

$N = 1 \text{ mol} \times 6.02 \times 10^{23}$ $= 1 \text{ mol}$

   A   aqueous chloride ions in a solution containing 0.25 mol of the complex, $[Pt(NH_3)_4Cl_2]Cl_2$ $n_{Cl^-} = (0.25/388) \times 2 = 1.28 \times 10^{-3} \text{ mol}$
   B   hydroxide ions in 2 dm^3 of 0.25 mol dm^{-3} aqueous calcium hydroxide $n_{OH^-} = (0.25 \times 2) \times 2 = 1 \text{ mol}$
   C   oxygen atoms in 100 g of allactite, $Mn_7(AsO_4)_2(OH)_8$, of molar mass 798 g mol^{-1} $n_O = (\frac{100}{798}) \times 16 = 2 \text{ mol}$
   D   oxygen atoms in 22.4 dm^3 of carbon dioxide gas at s.t.p. $n_O = \frac{22.4}{22.4} \times 2 = 2 \text{ mol}$

D   2   Which of the following statements is **correct**?

   A   The first ionisation energy of rubidium is higher than the first ionisation energy of calcium.
   B   The first ionisation energy increases from sodium to phosphorus as the number of protons increases but number of inner quantum shells remains the same.
   C   The second ionisation energy of chromium is lower than the second ionisation energy of manganese as manganese has one more proton than chromium.
   D   The second ionisation energy of any element is always higher than its first ionisation energy as more energy is required to remove an electron from an increasingly more positive species.

A   3   The boiling points (b.p.) of ammonia, carbon dioxide and hydrogen chloride are given below.

gas	formula	b.p. / °C
ammonia	NH_3	−33
carbon dioxide	CO_2	−78
hydrogen chloride	HCl	−85

Which of the following statements is **correct**?

   A NH_3 has a higher b.p. than HCl because the hydrogen bonding in NH_3 is stronger than the permanent dipole–permanent dipole interactions in HCl.
   B CO_2 has a higher b.p. than HCl because the permanent dipole–permanent dipole interactions in CO_2 are stronger than the permanent dipole–permanent dipole interactions in HCl.
   C   The strength of the instantaneous dipole–induced dipole interactions increases in the order $HCl < CO_2 < NH_3$.   (dep. on no. of e^- — infer fr Mr)
   D   The strength of the permanent dipole–permanent dipole interactions increases in the order $HCl < CO_2 < NH_3$.   (dep. on electronegativity of element + polarity of molecule)

2

At 298 K, $P_{total} = \left(\frac{2 \times 200}{10}\right) + \left(\frac{8 \times 400}{10}\right)$
$= 360$ kPa

$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{360}{298} = \frac{P_2}{348}$ $\therefore P_2 = 420$ kPa

A 4 At 298 K, two bulbs are connected by a stopcock. The 2 dm³ bulb is filled with oxygen at a pressure of 200 kPa and the 8 dm³ bulb is filled with nitrogen at 400 kPa. The stopcock is then opened to allow the gases to mix at 348 K.

The final total pressure, in kPa, of the system at 348 K is

A   420   B   400   C   360   D   310

D 5 A gaseous dimer, **J₂**, dissociates into its gaseous monomer, **J**, at 400 K and 1 atm pressure. Dissociation is complete at 450 K.

$J_2 \rightleftharpoons 2J$

Which of the following graphs shows the variation of volume with temperature when one mole of **J₂** is heated from 350 K to 500 K at a constant pressure of 1 atm? Assume that the gases behave ideally. (R = 0.082 dm³ atm K⁻¹)
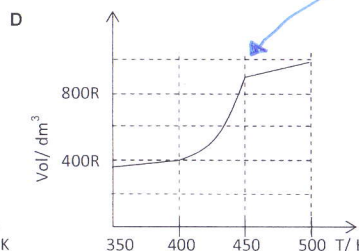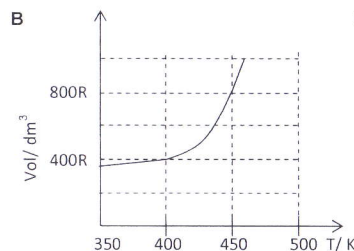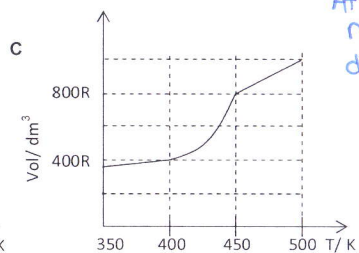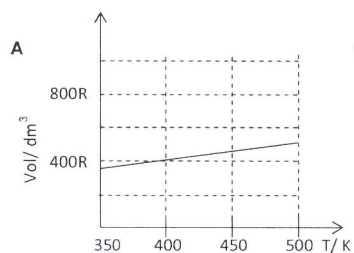
At 450K, n = 2 mol ∴ complete dissociation.
$PV = nRT$
$1 \times V = 2 \times R \times 450$
$V = 900R$

A

C

B

D

B 6 When 25 cm³ of 1.0 mol dm⁻³ sodium hydroxide is neutralised with an equal volume of 1.0 mol dm⁻³ hydrochloric acid, the temperature of the mixture rose by 6.8 °C.

What will be the temperature change, if **x** cm³ of 0.5 mol dm⁻³ sodium hydroxide is neutralised with an equal volume of 0.5 mol dm⁻³ hydrochloric acid?
(Assume heat losses to be negligible in each case.)

A   1.7   B   3.4   C   6.8   D   13.6

$\Delta H_{neut} = \frac{-(25+25) \times 4.2 \times 6.8}{\left(\frac{25}{100} \times 1.0\right)} = -57120 \text{ J mol}^{-1}$
$= -57.12 \text{ kJ mol}^{-1}$

$-57.12 = \frac{-2x \times 4.2 \times \Delta T}{\left(\frac{x}{1000} \times 0.5\right)} \div 1000$
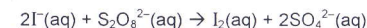
$\Delta T = 3.4$

---

rate $= k [I^-][S_2O_8^{2-}]$
rate $= k'[I^-] \because [S_2O_8^{2-}]$ in large excess.
$k' = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{6.9} = 0.100 \text{ s}^{-1}$ $k' = k[S_2O_8^{2-}]$
$k = \frac{0.100}{5.0}$
$= 0.02 \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$

B 7 Iodide ions react with peroxodisulfate ions to form iodine and sulfate ions:

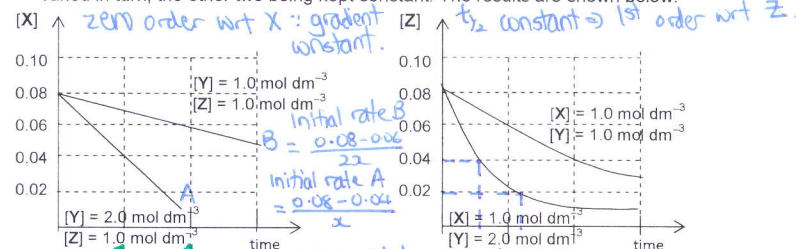$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

The above reaction is first order with respect to I⁻ and $S_2O_8^{2-}$ ions respectively. In an experiment, 5.0 mol dm⁻³ $Na_2S_2O_8$ was reacted with 0.025 mol dm⁻³ KI. The half-life for this reaction was found to be 6.9 s. What is the rate constant, in mol⁻¹ dm³ s⁻¹, of this reaction?

A   0.01   B   0.02   C   0.1   D   0.2

C 8 Substances **X**, **Y** and **Z** react according to the following equation:

$X(aq) + 2Y(aq) + Z(aq) \rightarrow 2W(aq) + U(aq)$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied in turn, the other two being kept constant. The results are shown below.

zero order wrt X ∴ gradient constant. $t_{1/2}$ constant ⟹ 1st order wrt Z.

Initial rate B
$B = \frac{0.08 - 0.06}{22}$
Initial rate A
$= \frac{0.08 - 0.04}{x}$
when [Y] doubled, initial rate increased by 4x.
⟹ 2nd order wrt Y.

If k is the rate constant, the rate equation is most likely to be

A   rate = k[Y]²   C   rate = k[Y]²[Z]
B   rate = k[Y][Z]   D   rate = k[X][Y][Z]

B 9 Under extreme conditions, gallium chloride, Ga_2Cl_6 can be formed via the dimerisation of $GaCl_3$

$2GaCl_3(g) \rightleftharpoons Ga_2Cl_6(g)$

In an experiment, a total pressure of 7.75 x 10³ Pa was measured when a 3.745 x 10⁻³ mol sample of $GaCl_3$ was allowed to dimerise in a 1.80 dm³ vessel at 200 °C.

Calculate α, the fraction of $GaCl_3$ that dimerised at 200 °C, assuming ideal gas behaviour.

A   0.053   B   0.105   C   0.895   D   0.947

Amount/mol $2GaCl_3 \rightleftharpoons Ga_2Cl_6$
Initial 3.745×10^{-3} 0
Change $-2x$ $+x$
Eqm $3.745 \times 10^{-3} - 2x$ x

$n_{eqm} = 3.745 \times 10^{-3} - 2x + x$
$= 3.745 \times 10^{-3} - x$
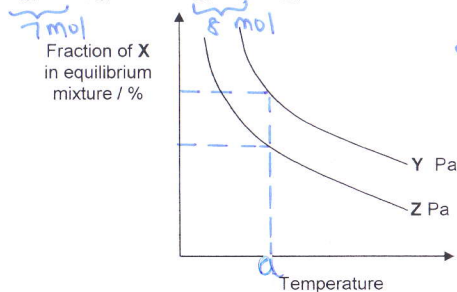$3.745 \times 10^{-3} - x = 3.549 \times 10^{-3}$
$x = 1.959 \times 10^{-4}$

$PV = nRT$
$7.75 \times 10^3 \times 1.80 \times 10^{-3} = n_{eqm} \times 8.31 \times 473$
$n_{eqm} = 3.549 \times 10^{-3}$ mol

$\alpha = \frac{2x}{3.745 \times 10^{-3}} = \frac{2(1.959 \times 10^{-4})}{3.745 \times 10^{-3}} = 0.1046$
≈ 0.105

A 10 The graph below shows how the fraction of a substance, **X** represented by one of the following compounds in the equilibrium mixture shown below varies with temperature at pressures of **Y** Pa and **Z** Pa.

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1267 \text{ kJ mol}^{-1}$$

7 mol   *8 mol*

Fraction of **X** in equilibrium mixture / %

Y Pa

Z Pa

a

Temperature

• When T↑, % X ↓
⇒ PoE shifts left (favour endothermic rxn)
∴ X must be N₂ or H₂O.
• At same T(a), % X is higher for Y Pa.
⇒ PoE shifts more to the left for Z Pa ∴ higher P (favours rxn that produces lesser amount of gas)

Identify **X** and the correct relative magnitudes of **Y** and **Z**.

	X	Pressure
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

B 11 Which of the following conjugate acid-base pairs can be used to prepare a buffer of approximately pH 6 that has maximum buffer capacity? *pH = pKa*

A	NH_4^+ / NH_3	K_b of NH_3 = 1.78 x 10^{-5} mol dm^{-3}
B	H_2CO_3 / HCO_3^-	K_b of HCO_3^- = 2.38 x 10^{-8} mol dm^{-3}
C	H_3PO_4 / $H_2PO_4^-$	K_b of $H_2PO_4^-$ = 1.33 x 10^{-12} mol dm^{-3}
D	CH_3COOH / CH_3COO^-	K_b of CH_3COO^- = 5.71 x 10^{-12} mol dm^{-3}

$pH = -lg\left(\frac{1\times10^{-14}}{1.78\times10^{-5}}\right) = 9.25$
$pH = -lg\left(\frac{1\times10^{-14}}{2.38\times10^{-8}}\right) = 6.38$
$pH = -lg\left(\frac{1\times10^{-14}}{1.33\times10^{-12}}\right) = 2.12$
$pH = -lg\left(\frac{1\times10^{-14}}{5.71\times10^{-12}}\right) = 2.76$

C 12 25 cm³ of 0.10 mol dm⁻³ of aqueous ammonia was added to 10 cm³ of 0.20 mol dm⁻³ hydrochloric acid. What is the pH of the resulting solution? The pK_b value for aqueous ammonia is 4.75.
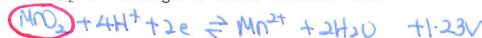
A	3.30	B	5.35	C	8.65	D	10.70

$pOH = pK_b + lg\frac{[salt]}{[base]} = 4.75 + lg\left(\frac{2\times10^{-3}}{35}\right) = 5.352$
$\left(\frac{5\times10^{-4}}{35}\right)$
$pOH = 14 - 5.352 = 8.647 \approx 8.65$

D 13 *Use of the Data Booklet is relevant to this question.*
Which of the following actions will allow MnO_2 to undergo a redox reaction with hydrochloric acid?

A   Add Mn^{2+} to the mixture.
B   Add more MnO_2 to the mixture. *(solid)*
C   Add MnO_4^- to the mixture.
D   Add Cl^- to the mixture.

$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \quad +1.23V$
$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad +1.36V$
$E^\ominus_{cell} = +1.23 - (+1.36) = -0.13V$
To ensure $E^\ominus_{cell} > 0$, $E^\ominus_R$ must be more +ve OR $E^\ominus_O$ must be more negative.
Addition of $Cl^- \Rightarrow \uparrow[Cl^-]$
*⇒ PoE shifts to the left*
⇒ $E^\ominus(Cl_2/Cl^-)$ becomes more -ve.

5

A 14 Aluminium and silicon are consecutive elements in Period 3 of the Periodic Table. Which statement concerning the compounds of aluminium and silicon is **incorrect**?

$AlCl_3 - pH 3$; $SiCl_4 - pH 2$

A   Both their chlorides give strongly acidic solutions when added to water.
B   Both their oxides give neutral solutions when added to water. *∴ both insoluble (pH=7)*
C   Both their oxides have high melting points. *Al_2O_3 - giant ionic; SiO_2 - giant molecular.*
D   Both their chlorides are covalent. *both have simple molecular structure.*

B 15 The diagram shows the first ionisation energy of eight consecutive elements, **P** to **W** in the Periodic Table. Their atomic numbers lie between 3 and 20.

First I.E.

Period 2
Period 3
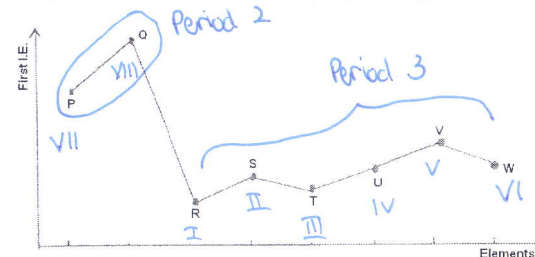
Elements

Which of the following statements is **incorrect**?

A   **P** forms an acidic oxide.
B   **R** is strongly oxidising. *strongly reducing ∴ lose valence e⁻ readily (Group I)*
C   **U** does not dissolve in water.
D   **W** forms a hydride of general formula H_2W.

C 16 Which one of the following statements concerning the thermal decompositions of anhydrous magnesium nitrate and anhydrous barium nitrate is **incorrect**?

A   Lattice energy of magnesium nitrate is more exothermic than that of barium nitrate. *$|\Delta H lattice| \propto \frac{|z+ \times z-|}{r+ + r-}$*
B   Nitrogen dioxide is evolved at a lower temperature from magnesium nitrate than from barium nitrate.
C   The oxide from the barium nitrate is formed more readily than that from magnesium nitrate. *∴ thermal stability $Ba(NO_3)_2$ > $Mg(NO_3)_2$*
D   The volume of acidic gas evolved from the decomposition of 1 mole of barium nitrate is four times that of the neutral gas evolved from that 1 mole of magnesium nitrate.
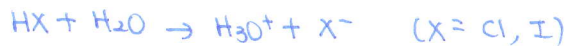
Acidic   Neutral
$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2}O_2$
$Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$
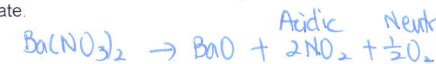
Acidic gas : Neutral gas
$NO_2 : O_2$
$2 : \frac{1}{2}$
⇒ 4 : 1

6

HX + H₂O → H₃O⁺ + X⁻   (X = Cl, I)
Acidic strength dep on H-X bond strength. More easily broken ⇒ more acidic.

C 17 Why is hydrogen iodide a stronger acid than hydrogen chloride?

A   A molecule of hydrogen chloride is more polar than a molecule of hydrogen iodide.

B   The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C   The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

D   The dissociation of hydrogen chloride molecules is suppressed by the stronger permanent dipole–permanent dipole interactions.

D 18 The table shows the possible oxidation states of four d-block elements in the Periodic Table. (The elements are represented by letters which are **not** their symbols.)

element	possible oxidation numbers					
W	–	2	3	4	–	–	–
X	1	2	3	4	5	–	–
Y	–	–	3	4	5	6	–
Z	–	–	–	4	5	6	7

Which of the following ions is likely to exist? *(must correspond to table given above)*

A WO_3^- B XO_4^{2-} C YO_4^- D ZO_4^{3-}
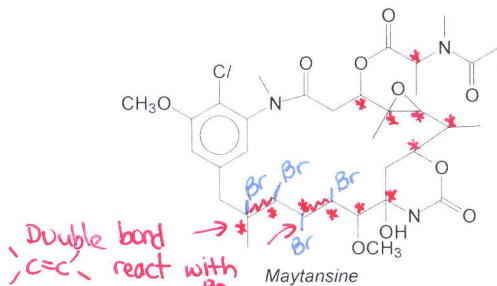
*oxidation no:* +5   +6   +7   +5

C 19 *Maytansine* is a potent antitumour agent. How many chiral centres are present in the product of the reaction between *Maytansine* and Br_2 in CCl_4 in the dark?

Double bond 'C=C' react with Br₂.

Maytansine

A   8   B   10   C   12   D   14

B 20 *(Not in syllabus)* How many H atoms are in the same plane as H_a in the following molecule?

A   0   B   1   C   2   D   3

Ha Ha
Hb and Ha are not on the same plane
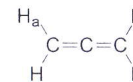
A 21 In which of the following pairs does reaction I take place more rapidly than reaction II?

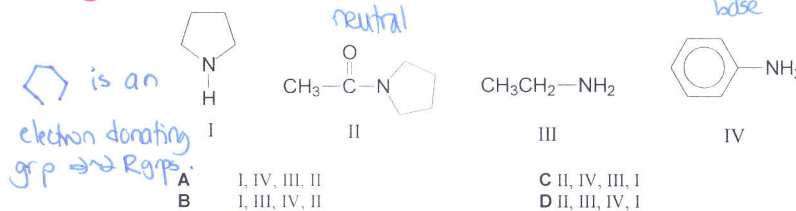|	
A	$CH_3CH_2CH_2Br + CH_3S^- \xrightarrow{I} CH_3CH_2CH_2SCH_3 + Br^-$
	$CH_3CH_2CH_2Br + CH_3SH \xrightarrow{II} CH_3CH_2CH_2SCH_3 + HBr$
B	$(CH_3)_3CCl + H_2O \xrightarrow{I} (CH_3)_3COH + HCl$
	$(CH_3)_3CBr + H_2O \xrightarrow{II} (CH_3)_3COH + HBr$
C	$(CH_3)_3CCl \ (1 \ mol \ dm^{-3})$
	$+$ $\xrightarrow{I}$ $(CH_3)_3COCH_2CH_3 + Cl^-$
	$CH_3CH_2O^- \ (2 \ mol \ dm^{-3})$
	$(CH_3)_3CCl \ (1 \ mol \ dm^{-3})$
	$+$ $\xrightarrow{II}$ $(CH_3)_3COCH_2CH_3 + Cl^-$
	$CH_3CH_2O^- \ (1 \ mol \ dm^{-3})$
D	$C_6H_5Cl + H_2O \xrightarrow{I} C_6H_5OH + HCl$
	$(CH_3)_3CCl + H_2O \xrightarrow{II} (CH_3)_3COH + HCl$

steric hindrance due to 3 CH₃- group (rate determining step)
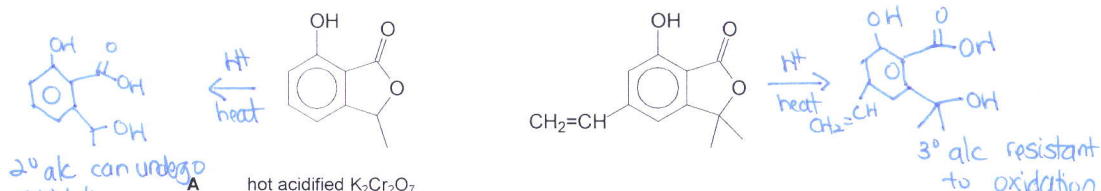
○-Cl (C-Cl bond v. strong)

B 22 Arrange the following compounds in order of decreasing K_b. *strongest base → weakest base*

neutral

○ is an electron donating grp ⇒ Rgps.

A   I, IV, III, II   C   II, IV, III, I

B   I, III, IV, II   D   II, III, IV, I

A 23 Which of the following can be used to distinguish between the following two compounds?

[handwritten: OH, O, structures drawn left; ← H+ / heat]

[structures of two compounds shown]

[handwritten: OH O, H+ → heat CH₂=CH]

[handwritten annotations: 2° alc can undergo oxidation; 3° alc resistant to oxidation.]

A hot acidified $K_2Cr_2O_7$
B hot acidified $KMnO_4$ [handwritten: (both alkene + 2° alc undergo oxidation)]
C neutral $FeCl_3(aq)$
D $Br_2(aq)$

A 24 An organic compound has the following properties:

(i)   It gives a yellow precipitate with alkaline aqueous iodine solution. [handwritten: CH₃–C–OH / CH₃–C– structure]
(ii) It gives an orange precipitate with 2,4-dinitrophenylhydrazine. [handwritten: carbonyl]
(iii) It forms a brick-red precipitate with Fehling's solution. [handwritten: aldehyde. H]

Which compound could give these results?

A $CH_3COCH_2C(OH)(CH_3)CH_2CHO$
B $CH_3COCH=CHCH(CH_3)CO_2H$
C $CH_3COCH_2COCH_2CH_3$
D $CH_3COCH_2C_6H_4CHO$

[handwritten: benzaldehyde.]

C 25 A chloroalkane **W** with molecular formula of $C_5H_{11}Cl$ exhibits optical activity. On warming **W** with alcoholic NaOH, two alkenes **X** and **Y** are formed, **X** being the major product. One of the products of the reaction between **X** and hot acidified potassium manganate(VII) gives a yellow precipitate with alkaline aqueous iodine. Which of the following could be **W**?
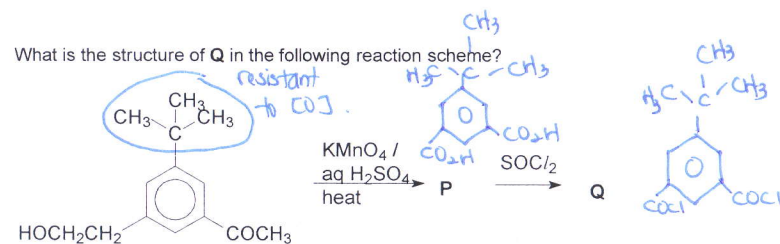
[handwritten left margin: – Cl cannot be terminal ∴ more than 1 pdt formed.]
[handwritten: X=C< (contains more R grps) ⇒ W should not be straight-chained.]
[handwritten: CH₃–C–R]

A $CH_3CHClCH_2CH_2CH_3$
B $CH_3CH_2CHClCH_2CH_3$
C $CH_3CH(CH_3)CHClCH_3$
D $CH_3CCl(CH_3)CH_2CH_3$

[handwritten: X → CH₃ ,H C=C ,CH₃ CH₃ + CHCCH₃)₂ , H C=C H H]

D 26 Consider the reaction between butanone and hydrogen cyanide in which the enthalpy change of the reaction is near zero. Which one of the following statements is **incorrect**?

A The reaction is catalysed by a small amount of base.
B The slow step involves the formation of a C–C bond.
C The Gibbs free energy of the reaction is positive at high temperatures.
D The reaction between butanal and hydrogen cyanide is slower than the reaction between butanone and hydrogen cyanide.
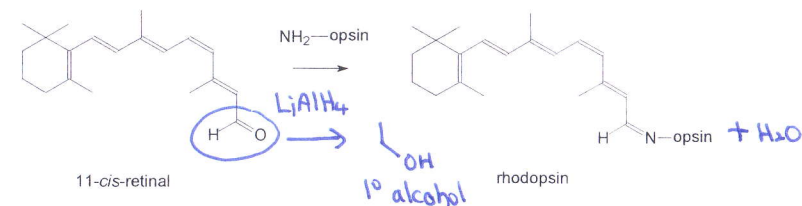
[handwritten: (butanone has 1 more R grp ⇒ steric hindrance ⇒ rxn is slower)]

C 27 What is the structure of **Q** in the following reaction scheme?

[handwritten: CH₃ resistant to CO] ; structures]

[reaction scheme: HOCH₂CH₂ ... COCH₃ → KMnO₄ / aq H_2SO_4 heat → **P** → SOCl₂ → **Q**]

A [structure]
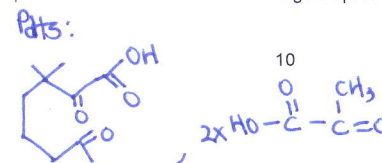B [structure]
C [structure] [handwritten CH₃ drawn]
D [structure]

B 28 A key molecule in the chemistry of vision is the highly conjugated rhodopsin, which is synthesised in the rod cells of the eye from 11-*cis*-retinal and a primary amine in the protein opsin.
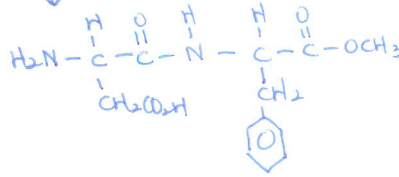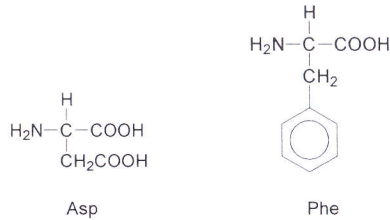
[reaction scheme diagram: 11-*cis*-retinal → NH₂—opsin → rhodopsin]

[handwritten: LiAlH₄ → OH 1° alcohol ; + H₂O]

11-*cis*-retinal   rhodopsin

Which of the following statements is **correct**?

A 1 mole of 11-*cis*-retinal reacts with 5 moles of hydrogen gas. [handwritten: (6 mol)]
B The reaction between 11-*cis*-retinal and NH₂-opsin is a condensation reaction.
C The reaction of 11-*cis*-retinal with $LiAlH_4$ produces a product that is optically active.
D The reaction between 11-*cis*-retinal with hot acidified potassium manganate(VII) produces a total of five different organic products.

[handwritten: Pdts: OH ... O ; 10 ; 2x HO–C–C=O CH₃]

D 29 *Aspartame*, a non-nutritive sweetener marketed under the trade name *NutraSweet*, is the methyl ester of a simple dipeptide, Asp–Phe–OCH$_3$.

The structures of Asp and Phe are shown as follows:

(handwritten: H$_2$N–C–C–N–C–C–OCH$_3$ with CH$_2$CO$_2$H and CH$_2$ and phenyl ring)

Phe:
H$_2$N–C–COOH
       |
       CH$_2$
(with phenyl ring)

Asp:
H$_2$N–C–COOH
       |
       CH$_2$COOH

Asp   Phe

The isoelectric point of *aspartame* is 5.9. Which of the following is the predominant species present in an aqueous solution at physiological pH 7.3? *(handwritten: ⇒ alkaline)*

(handwritten: –COOH becomes –COO⁻.)

A   H$_3$N⁺–C–C(O)–NH–C–COOCH$_3$
     with CH$_2$–COO⁻ and CH$_2$–phenyl

B   H$_2$N–C–C(O)–NH–C–COO⁻
     with CH$_2$–COOCH$_3$ and CH$_2$–phenyl

C   H$_3$N⁺–C–C(O)–NH–C–COO⁻
     with CH$_2$–COOCH$_3$ and CH$_2$–phenyl

D   H$_2$N–C–C(O)–NH–C–COOCH$_3$
     with CH$_2$–COO⁻ and CH$_2$–phenyl

11

A 30 The structures of some amino acids are shown below:

glutamic acid	H$_2$N–C(H)–COOH, (CH$_2$)$_2$, COOH
lysine	H$_2$N–C(H)–COOH, (CH$_2$)$_4$, NH$_2$
phenylalanine	H$_2$N–C(H)–COOH, CH$_2$, (phenyl ring)
serine	H$_2$N–C(H)–COOH, CH$_2$OH
valine	H$_2$N–C(H)–COOH, CH, CH$_3$ CH$_3$

(handwritten: hydrophyllic grps (R) ⟸ (soluble) ⇒ outside; hydrophobic grps (R) ⇒ inside)

Which of the following pairs of amino acids are likely to be found on the outside of a globular protein, and which on the inside?

	on the outside	on the inside
A	glutamic acid and lysine *(ionic bds)*	valine and phenylalanine *(vdWs')*
B	valine and phenylalanine *(vdWs')*	glutamic acid and lysine *(ionic)*
C	serine and lysine *(H-bd)*	valine and glutamic acid *(vdWs')*
D	glutamic acid and valine *(vdWs')*	phenylalanine and serine *(vdWs')*

12

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	**1 and 2** only are correct	**2 and 3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

B *(Not in syllabus)*

31 For which of the following pairs does the first species have a smaller bond angle?

1   OCl_2, $SnCl_2$ OCl_2 – 2 b.p, 2 l.p (107°); $SnCl_2$ – 2 bp, 1 l.p (<120°)
2   NF_3, NCl_3 F is more electronegative. ∴ NF_3 has smaller bd ∠.
3   I_3^-, N_3^-
       (180° for both)

B

32 Given only the standard enthalpy changes of combustion of carbon, hydrogen and methane, which of the following can be calculated?

1   The enthalpy change for the hypothetical reaction: $\Delta H_r = \Delta H_c(rxt) - \Delta H_c(pdt)$
      $2CO_2(g) + 4H_2O(l) \rightarrow 2CH_4(g) + 4O_2(g)$. $= [2\Delta H_c(C) + 4\Delta H_c(H_2)] - 2\Delta H_c(CH_4)$
2   The enthalpy change of formation of water. $= \Delta H_c(H_2)$
3   The enthalpy change of formation of liquid methane.
       (CH4 is (g) at std conditions)

B

33 A $20\ cm^3$ solution contains $1 \times 10^{-3}\ mol\ dm^{-3}$ X^+ and $1 \times 10^{-3}\ mol\ dm^{-3}$ Y^{2+} metal ions. 7×10^{-4} mol of solid sodium sulfate is added to the solution. The numerical values of the solubility product of **X** and **Y** sulfates are 7.4×10^{-7} and 9.1×10^{-6} respectively. What can be deduced from this information?

1   The metal **Y** sulfate will precipitate out selectively.
2   There are more X^+ ions than Y^{2+} ions remaining in the solution.
3   The solubility products of metal **X** and **Y** sulfates will change when 2 g of solid sodium sulfate is added to the solution. K_{sp} only affected by temp.

D

34 A sample of copper which contains silver and zinc impurities can be purified by electrolysis. Which of the following statements are true?

1   The impure copper is made the anode. So that $Cu \rightarrow Cu^{2+} + 2e$
2   Both zinc and silver are preferentially oxidised to its ions. Zn preferentially [ox]: more –ve E^θ.
3   The concentration of the copper(II) ions in the electrolyte remains constant.
       $[Cu^{2+}] \downarrow$.

13

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	**1 and 2** only are correct	**2 and 3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

A

35 (Take I_2 as reference)

Astatine is an element in Group VII. Which of the following statements are **correct**?

1   Silver astatide is insoluble in aqueous ammonia. AgI insol. in $NH_3(aq)$
2   Sodium astatide and hot concentrated sulfuric acid react to form astatine.
3   Hydrogen astatide is less stable to heat than hydrogen iodide.
       ∴ H–At bond is longer + weaker.

B

36 A stability constant is an equilibrium constant for the formation of a complex in solution.

Consider the formation of $[Ni(NH_3)_6]^{2+}(aq)$ in solution:

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$
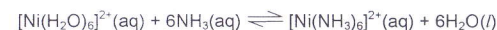
The equilibrium constant, K_{stab}, of the above reaction, taking the concentration of water as being constant, is

$$K_{stab} = \frac{[Ni(NH_3)_6^{2+}]}{[Ni(H_2O)_6^{2+}][NH_3]^6}$$

The following table lists some iron complexes together with their colours and the values of their stability constants. Larger K_{stab} ⟹ complex more stable.

complex	colour	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}(aq)$	deep red	1×10^2
$[FeF_6]^{3-}(aq)$	colourless	2×10^{15}
$[Fe(CN)_6]^{3-}(aq)$	orange-yellow	1×10^{31}
$[Fe(edta)]^{2-}(aq)$	colourless	2×10^{14}
$[Fe(edta)]^-(aq)$	yellow	1×10^{25}

$[edta = (^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2]$
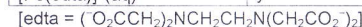
Which of the following statements are **incorrect**?

1   Addition of $KSCN(aq)$ to a solution of $Fe^{3+}(aq)$ produces a deep red solution which remains red when $KF(aq)$ is added. F^- is stronger ligand than $SCN^- + H_2O$.
2   Addition of edta to a solution containing $[FeF_6]^{3-}(aq)$ does not produce any colour change. edta is a stronger ligand than F^-.
3   Addition of $KCN(aq)$ to a solution containing $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ produces an orange-yellow solution. CN^- is a stronger ligand than $SCN^- + H_2O$.

14

The responses **A** to **D** should be selected on the basis of
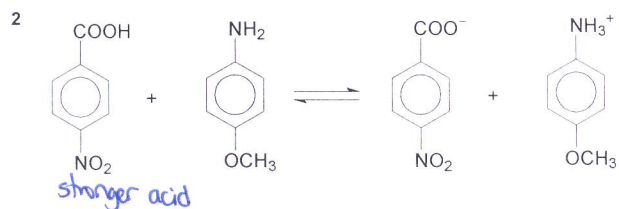
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

C 37   The pK_a values of the following compounds are given below. *lower pka ⟹ higher Ka ⟹ stronger acid.*

Conjugate base	Compound	pK_a
HCO_3^-	H_2CO_3	6.4
CF_3COO^-	CF_3COOH	0.2
$CH_3CH_2O^-$	CH_3CH_2OH	16.0
⟨⟩-O^-	⟨⟩—OH	10.0
O_2N-⟨⟩-COO^-	O_2N—⟨⟩—COOH	3.4
CH_3O-⟨⟩-NH_2	CH_3O—⟨⟩—NH_3^+	5.3

In which of the following acid-base reactions will the equilibrium favour the products over the reactants? *stronger acids displace weaker acids.*

1   ⟨⟩—OH + HCO_3^- ⇌ ⟨⟩—O^- + H_2CO_3 *stronger acid*

2   COOH (with NO₂) + NH₂ (with OCH₃) ⇌ COO⁻ (with NO₂) + NH₃⁺ (with OCH₃)   *stronger acid*

3   CF_3C(=O)OH + $CH_3CH_2O^-$ ⇌ CF_3C(=O)O⁻ + CH_3CH_2OH *stronger acid*

The responses **A** to **D** should be selected on the basis of

D 38   Which products are formed when phenyl propanoate undergoes acidic hydrolysis in the presence of water labeled with the ^{18}O isotope?

$CH_3CH_2C(=O)-O-⟨⟩ + H-^{18}O-H$

1    $CH_3CH_2CO^{18}OH$
2    $C_6H_5{}^{18}OH$
3    $C_6H_5CO^{18}OH$

⇌ $CH_3CH_2C(=O)-^{18}O-H + HO-⟨⟩$
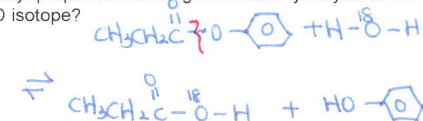
B 39   The structures and pK_a values of fumaric acid and maleic acid are given below:

	pK_{a1}	pK_{a2}
HOOC—H / H—COOH (fumaric acid)	3.0	4.5
HOOC—COOH / H—H (maleic acid)	1.9	?

Which of the following statements are **correct**?

1   Maleic acid has a lower boiling point than fumaric acid as it can form intra-molecular hydrogen bonding. *(extent of intermolecular H-bd ↓)*
2   pK_{a2} of maleic acid is larger than that of fumaric acid because the acidic hydrogen atom in maleic acid can be stabilised by intra-molecular hydrogen bonding, hence making it more difficult to remove.
3   For each acid, pK_{a2} is larger than pK_{a1} because it is easier to remove a second proton from the conjugate base formed in the first ionisation. *↘ more difficult to remove 2nd H+ from negatively charged conjugate base.*
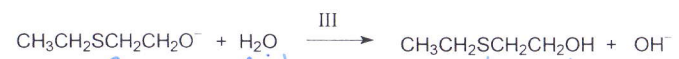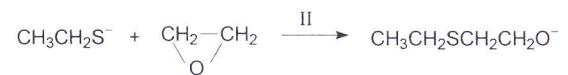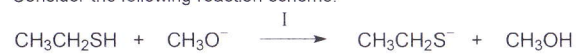
The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

40   Consider the following reaction scheme.

$$CH_3CH_2SH + CH_3O^- \xrightarrow{\text{I}} CH_3CH_2S^- + CH_3OH$$

$$CH_3CH_2S^- + CH_2\!-\!CH_2 \overset{O}{\diagdown\diagup} \xrightarrow{\text{II}} CH_3CH_2SCH_2CH_2O^-$$

$$CH_3CH_2SCH_2CH_2O^- + H_2O \xrightarrow{\text{III}} CH_3CH_2SCH_2CH_2OH + OH^-$$

Base   *Acid*   *conjugate acid*   *conjugate base*

Which of the following types of reactions are shown in reactions I, II and III?

1   oxidation
2   nucleophilic substitution   *(Reaction I)*
3   neutralisation   *(Reaction III)*

END OF PAPER

17