THE COPPERBELT UNIVERSITY

SCHOOL OF MATHEMATICS AND NATURAL SCIENCES

SESSIONAL EXAMINATION 2015/16 Marking guide

TITLE OF PAPER: GENERAL CHEMISTRY

COURSE NUMBER: CH110/CH120/FO130

Question 1 (20 marks)

a) **A 100.0ml aliquot of 0.200 M aqueous potassium hydroxide is mixed with 100.0 ml of 0.200 M aqueous magnesium nitrate** **[Total Marks – 6]**

i) **Write a balanced chemical, ionic and net ion equation for the reaction** **[3]**

Balanced chemical equation

$2KOH(aq) + Mg(NO_3)_2(aq) \longrightarrow Mg(OH)_2(s) + 2KNO_3(aq)$ *[1]*

Balanced ionic equation

$2K^+(aq) + 2OH^-(aq) + Mg^{2+}(aq) + 2NO_3^-(aq) \longrightarrow Mg(OH)_2(s) + 2K^+(aq) + 2NO_3^-(aq)$ *[1]*

Balanced net ionic equation

$2OH^-(aq) + Mg^{2+}(aq) \longrightarrow Mg(OH)_2(s)$ *[1]*

ii) **What precipitate is formed from this reaction?** **[1]**

$\mathrm{Mg(OH)_2(s)}$ [1]

iii) **Calculate the mass of the precipitate formed** **[3]**

Mole ratios: 2 moles of KOH produce a mole of 1 of $Mg(OH)_2$ [0.5]

Moles of KOH used up in this reaction is

$$\mathrm{M_{KOH} \times V_{KOH} = 0.1L \times 0.2M = 0.020\ mol} \quad [0.5]$$

Therefore 0.010 mol $Mg(OH)_2$ is formed [0.5]

The mass formed is given by the formula $\mathrm{m = n \times M_r}$ [0.5]

since

$\mathrm{M_r = M_{Mg} + 2 \times M_{OH} = 24.31 + 2 \times 17.008 = 58.33\ g/mol,}$ [0.5]

$$\mathrm{m = n \times M_r = 0.010\ mol \times 58.33 \frac{g}{mol} = 0.58\ g} \quad [0.5]$$

b) **Specify which of the following are Redox reactions. For the Redox reactions, identify the reducing agent, the oxidizing agent, the substance oxidized, and the substance reduced** **[3]**

i) **$2H^+(aq) + 2CrO_4^{2-}(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$**

Not a redox reaction! [0.5]

ii) **$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$**

Redox reaction [0.5]

Hydrogen in water is the oxidising agent [0.5], it oxidises carbon in methane [0.5]. Carbon is the reducing agent [0.5], it reduces hydrogen [0.5]

c) **Balance the following Redox reaction equations using oxidation numbers** **[2]**

i) **$Rh^{3+}(aq) + Ni(s) \rightarrow Rh^{2+}(aq) + Ni^{2+}(aq)$**

Step 1.Unbalanced equation is: $Rh^{3+}(aq) + Ni(s) \rightarrow Rh^{2+}(aq) + Ni^{2+}(aq)$

Step 2.We start by writing the oxidation numbers of each species in the equation

$Rh^{3+}(aq) + Ni(s) \rightarrow Rh^{2+}(aq) + Ni^{2+}(aq)$

+3 0 +2 +2 [0.5]

Step 3. We show how electrons are gained and lost

2 e⁻ lost

$Rh^{3+}(aq) + Ni(s) \rightarrow Rh^{2+}(aq) + Ni^{2+}(aq)$ [1]

1 e gained

Step 4. Show coefficients needed to equalize the electrons gained and lost

$$\overset{2\,e^-\text{ lost}}{\mathrm{Rh^{3+}(aq) + Ni(s) \longrightarrow Rh^{2+}(aq) + Ni^{2+}(aq)}}$$

1 e gained   MULTIPLY BY 2 to get equation below [0.5]

$$\mathbf{2Rh^{3+}(aq) + Ni(s) \longrightarrow 2Rh^{2+}(aq) + Ni^{2+}(aq)}$$

Step 5. All elements are balanced therefore the above equation is the required balanced equation

(d) **Consider the unbalanced chemical equation for the combustion of pentane (C_5H_{12}) given as $C_5H_{12}(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$. If 20.4 g of pentane are burned in excess oxygen, what mass of water can be produced, assuming 100% yield? [4]**

Unbalanced chemical equation is

$C_5H_{12}(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$

Balanced chemical equation is

$C_5H_{12}(g) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l)$ [1]

Stoichiometry requires that every mole of pentane burnt gives 6 moles of water [1]

20.4 g (or $m_{pentane}$) of pentane has $n_{pentane}$ moles given as

$n_{pentane} = \frac{m_{pentane}}{M_{pentane}}$ where $M_{pentane}$ is the molar mass of pentane

But $M_{pentane} = 12 \times M_H + 5 \times M_C$

where M_H and M_C are molar mass of hydrogen and carbon

$M_{pentane} = 12 \times 1.008 + 5 \times 12.01 = 12.096\text{g} + 60.05\text{g} = 72.146\text{ g}$

So that $n_{pentane} = \frac{20.4\text{ g}}{72.146\text{ g}} = 0.283$ moles [0.5]

The moles water produced (n_{water}) is $6 \times n_{pentane}$, that is

$n_{water} = 6 \times n_{pentane} = \frac{6\times 20.4\text{ g}}{72.146\text{ g}} = 1.697$ moles [0.5]

The mass of water produced (m_{water}) is

$m_{water} = M_{water} \times n_{water} = \frac{6\times 20.4\text{ g}}{72.146\text{ g}} \times 18.016\text{g} = \underline{30.6\text{ g}}$ [1]

(e) **The empirical formula of styrene is CH; the molar mass of styrene is 104.14 g/mol. What number of H atoms are present in a 2.00-g sample of styrene? [4]**

The empirical formula of styrene is given as, CH. This gives a molar empirical mass

$M_{em} = n_C \times M_C + n_H \times M_H$ that is $M_{em} = 12.01 + 1.008 = 13.018$ g [0.5]

The molecular mass of styrene (M_r) is given as 104.14 g.

The integer obtained from dividing molecular mass with empirical formula mass, $n_{integer}$, is

$n_{integer} = \frac{M_r}{M_{em}} = \frac{104.14}{13.018} = 8$ [1]

The number of moles of styrene, n is $n = \frac{m_s}{M_r} = \frac{2}{104.14} = 0.0192$ [0.5]

The number of molecules of styrene, $N_{molecules}$ is

$N_{molecules} = n \times N_{Avogadro} = 0.0192 \times 6.023 \times 10^{23} = 1.157 \times 10^{22}$ [1]

For each mole of styrene, there are 8 atoms of hydrogen, therefore, number of hydrogen atoms, N_H in 2 grams of styrene is

$N_H = n_{integer} \times N_{molecules} = 8 \times 1.157 \times 10^{22} = \underline{9.254 \times 10^{22}\text{ H atoms}}$ [1]

Question 2 (20 marks)

(a) **KClO$_3$ is decomposed by the following reaction:**

$$KClO_3\,(s) \longrightarrow KCl\,(s) \;+\; O_2\,(g)$$

The O$_2$ produced was collected by the displacement of water at 22 °C at a total pressure of 760 torr. The volume of gas collected was 1.20 liters, and the vapour pressure of water at 22°C is 21 torr.

(i) **Define the term partial pressure**

The portion of the total pressure that one gas in a mixture of gases contributes. Assuming ideal gas character, the partial pressure of any gas in a mixture is the pressure that the gas would yield if it were alone in the container [1 mark]

(ii) **Calculate the partial pressure of O$_2$ in the gas collected and the mass of KClO$_3$ in the sample that was decomposed** **[3]**

$P_{total} = P_{O2} + P_{H2O}$;

P_{O2} + 21 torr = 760 torr,

thus, P_{O2} = **739 torr** [1 mark]

Converting pressure in torr to pressure in atm,

$$P = \frac{739\text{ torr}}{760\text{ torr}}.\text{atm} = 0.9724\text{ atm}$$

$$n = \frac{PV}{RT} = \frac{(0.9724\ \text{x}\ 1.2\,)}{(0.08206\ \text{x}\ 295.15)} = 0.0482\text{ mol Oxygen gas}$$

No. mol (KClO$_3$) = 0.0482 mol O$_2$ x (2 mol KClO$_3$ ÷ 3 mol O$_2$) = 0.0321 mol according to the stoichiometry of the reaction equation. Student should be able to balance the reaction equation.

Mass (KClO$_3$) = No. mol x Molar mass

= 0.0321 mol x 122.5 gmol^{-1}

= **3.93 g KClO$_3$** [2 marks]

(b) **Incandescent light bulbs "burn out" because their tungsten filament evaporates, weakening the thin wire until it breaks. Argon gas is added inside the bulbs to reduce the rate of evaporation. (Argon is chosen because, as a noble gas, it will not react with the components of the bulb, and because it is easy to obtain in significant quantities. It is the third most abundant element in air).**

(i) **At what temperature would 0.0315 g of Ar in a 25.0-mL incandescent light bulb have a pressure of 952 mmHg?** **[3]**

$PV = \frac{gRT}{M}$ where g = mass, M = molar mass

$$T = \frac{PVM}{gR} = \frac{(952\text{ mmHg x }25.0\text{ mL x}\frac{39.948\text{g}}{\text{mol}}}{(0.0315\text{ g x }0.08206\text{ L atmK}^{-1}\text{mol}^{-1})} \text{ x } \frac{1\text{atm}}{760\text{mmHg}} \text{ x } \frac{1\text{L}}{1000\text{ mL}}$$

$= \mathbf{484\ K}$ [3 marks]

(ii) **What would be the density of argon gas in an incandescent bulb at 79.9 °C and 129.8 kPa?** **[3]**

P = 129.8 kPa, T = 79.9 + 273.15 = 353.05 K

$$\text{Density} = \frac{g}{V} = \frac{PM}{RT} = \frac{(129.8\text{ kPa} \times 39.948\times10^{-3}\text{kg/mol})}{(8.3145\text{JK}^{-1}\text{mol}^{-1} \times 353.05\text{K}} = \mathbf{1.77\ kg/m^3}$$

(= 1.77 g/L) L[3 marks]

(c) **In the study of gases in CH110, it is important that undergraduate students understand ideal and real gases with respect to the conditions surrounding these two types of gases.**

(i) **Define the term ideal gas and explain how it differs from a real gas.** **[3]**

An ideal gas is a hypothetical gas which obeys the equation PV = nRT.
How it differs from a real gas:

a. Particles in an ideal gas move randomly in straight line motion while real gases move in non-straight line motion (Brownian Motion)
b. An ideal gas does not experience any attractive forces due to the distance among molecules. Forces of attraction exist among molecules of a real gas (weak IMF)
c. Ideal gas particles do not lose energy during collisions (collisions are perfectly elastic). Real gas molecules lose energy during collisions.
d. Ideal gases are hypothetical; used in Science for easier calculations and analyses whereas real gases are real! [Any 3 of these, 1 mark each]

(ii) **Calculate the pressure exerted by 1.00 mol ammonia when it is confined at 25 °C in 500 cm^3 (a = 4.169 atm dm^6 mol^{-2}, b = 3.71 x 10^{-2} dm^3 mol^{-1}) behaving as:**

1) an ideal gas; **[2]**

PV = nRT

$$P = \frac{nRT}{V} = \frac{1.00 \times 0.08206 \times 298.15}{0.500} = \mathbf{48.9\ atm}$$ [2 marks]

2) a van der Waals gas. **[5]**

$$(p + \frac{an^2}{V^2})(v - nb) = nRT$$ [1 mark]

$$\left(p + \frac{4.169 \text{ x } 1.00^2}{0.500^2}\right)(0.500 - 1.00(3.71 \times 10^{-2})) = (1.00 \times 0.08206 \times 298.15)$$

$p = \mathbf{36.2\ atm}$ [4 marks]

Question 3 (20 marks - alternative)

(a) **Define a system and state the three types of systems** **[2]**

A system is ant part of the universe that we chose to focus our attention on (1)
The three types of system are: open system, closed system and isolated system. (1)

(b) **Write thermochemical equations corresponding to the following descriptions.**

(i) **The standard enthalpy of formation of iron(III) oxide at 298 K is -824.2 kJ/mol.**

(ii) **The standard enthalpy change at 298 K for the reaction between gaseous phosphorus trichloride and chlorine gas to give gaseous phosphorus pentachloride is -84.3 kJ.**

(iii) The standard enthalpy of combustion of liquid ethanol is -1368 kJ/mol. [6]

(i) $2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)$ -824.2 kJ

(ii) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ -84.3 kJ

(iii) $CH_3CH_2OH(l) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ -1368 kJ

(1 mark for correct eqn and 1 mark for enthalpy change)

(c) The reaction between a metal and an acid yields a salt and hydrogen gas. 50 g of iron is reacted with excess hydrochloric acid.

(i) Write a balanced equation for the above reaction [2]

(ii) State the equation employed in calculating the work done by the surrounding on a system. [1]

(iii) Calculate the work done if the reaction takes place in a closed vessel [2]

(iv) Calculate work done if the reaction takes place in an open beaker at 25°C. [3]

(i) $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$ (2)

(ii) $W = P\Delta V$ (1)

(iii) Since $\Delta V = 0$ (container is closed) $w = -P\,\Delta V = 0$ (2)

(iv) $w = -P\,\Delta V = -n_{H_2}RT$ (1)

number of mols of Fe in 50 g is $= 50\ g\ Fe\ x \frac{1\ mol\ Fe}{55.85\ g\ Fe} = 0.895\ mol\ Fe$ (½)

From balanced eqn $n_{Fe} = n_{H_2} = 0.895$ mol H_2. (½)

$W = -0.895$ mol x8.314 JK^{-1} mol^{-1} x 298 K = -2.2 kJ (1)

(d) Given the following thermochemical equations:

$4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(l)}$ $\Delta H_1 = -848KJ$

$N_2O_{(g)} + H_{2(g)} \rightarrow N_{2(g)} + H_2O_{(l)}$ $\Delta H_2 = -367KJ$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H_3 = -285.9KJ$

Calculate the value of ΔH for the reaction;

$2NH_{3(g)} + 3N_2O_{(g)} \rightarrow 4N_{2(g)} + 3H_2O_{(l)}$ $\Delta H = ?$ [4]

Number the equations as follows

(1) $4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(l)}$ $\Delta H_1 = -848$ kJ

(2) $N_2O_{(g)} + H_{2(g)} \rightarrow N_{2(g)} + H_2O_{(l)}$ $\Delta H_2 = -367$ kJ

(3) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H_3 = -285.9$ kJ

Target eqn is $2NH_{3(g)} + 3N_2O_{(g)} \rightarrow 4N_{2(g)} + 3H_2O_{(l)}$

Multiply eqn (1) by ½, eqn (2) by 3 and reverse eqn (3) and multiply it by 3

(4) $2\ NH_{3(g)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + 3H_2O_{(l)}$ $\Delta H_4 = -424$ kJ (1)

(5) $3\ N_2O_{(g)} + 3\ H_{2(g)} \rightarrow 3\ N_{2(g)} + 3H_2O_{(l)}$ $\Delta H_5 = -1101$kJ (1)

(1) $3\ H_2O_{(l)} \rightarrow 3\ H_{2(g)} + \frac{3}{2}O_{2(g)}$ $\Delta H_6 = +857.7$ kJ (1)

Adding these three gives the target eqn. Hence

$\Delta H = \Delta H_4 + \Delta H_5 + \Delta H_6 = (-424 + -1101 + 857.7)$kJ = - 667 kJ. (1)

Question 4 (20 marks)

(a) **In the quantum mechanical model of an atom**

(i) **When given the sublevels $E_{4_s}, E_{4_p}, E_{4_d}, E_{4_f}$ of a polyelectronic atom, state whether these are degenerate or not.** **[1]**

(ii) **If they are not degenerate, show how the quantum levels of the orbitals vary in energy. Zumdahl and Zumdahl, 9th Edition, pp. 345.** **[1]**

(iii) **For each Subshell above, copy the table below and fill the last column** **[4]**

Answer:

(i) The levels are different sublevels belonging to the same shell of a polyelectronic atom. Such levels are not degenerate. [1]

(ii) Their energy order is $E_{4_s} < E_{4_p} < E_{4_d} < E_{4_f}$ [1]

(iii) Elements in the table are

Subshell	Element with final Subshell electron configuration given as	Element name or symbol
E_{4_s}	$4s^2$	Calcium or Ca [1]
E_{4_p}	$4p^6$	Krypton or Kr [1]
E_{4_d}	$4d^{10}$	Cadmium or Cd [1]
E_{4_f}	$4f^{14}$	Lutetium or Lu [1]

(b) **Classify the elements in the last column of the table of (c) into following element groups (i) main group elements (ii) alkali metals (iii) alkaline earth metals (iv) transition metals (v) Actinides (vi) Noble gas** **[6]**

Answer: (i) Ca [1] (ii) None [1] (iii) Ca [1] (iv) Cd [1] (v) Lu [1] (vi) Kr [1]

(c) **Wave particle duality: Neutron diffraction is used in determining the structures of molecules. Calculate the de Broglie wavelength of a neutron moving at 1.00% of the speed of light. Zumdahl and Zumdahl, 9th Edition, Question 7.54 pp. 369** **[5]**

Answer:

Using the de Broglie equation, $\lambda = \frac{h}{mv}$ [1]

where Planck's constant is $h = 6.63 \times 10^{-34} J \cdot s$,

mass of a neutron is $m = 1.675 \times 10^{-27} kg$ and

velocity of the neutron is $v = 0.01c = 0.01 \times 3.00 \times 10^{8} ms^{-1}$ [1]

Thus, $\lambda = \frac{6.63 \times 10^{-34}}{1.675 \times 10^{-27} \times 3.0 \times 10^{6}} m$ [1]

$= 1.32 \times 10^{-15} m$ [2;1 mark for correct answer & 1 mark for correct units]

(d) **Photoelectric Effect: At the conclusion of the study of the photoelectric effect, the phenomenon of the dual *nature of light* was demonstrated. Explain what is meant by this phenomenon. What was the name of the scientist who demonstrated the dual nature of light using the photoelectric effect. Zumdahl and Zumdahl, 9th Edition, pp. 328.** **[3]**

Answer:

Light exhibits both wave properties [1] and shows certain characteristics of particulate matter as well [1].

Albert Einstein demonstrated the dual nature of light using the photoelectric effect. [1]

Question 5 (20 marks)

(a) Predict the order of increasing electronegativity in each of the following groups of elements: [2]

(i) Si, Ge, Sn

$Sn < Ge < Si$

(ii) **Tl, Cl, Ge**

$Tl < Ge < Cl$

(iii) **B, O, Ga**

$Ga < B < O$

(iv) **S, O, F**

$S < O < F$

(b) Identify the noble gas that has the same electron configuration as each of the ions in the following compounds: [3]

(i) **Strontium fluoride**

Strontium ion (Sr^{2+}) – Krypton
Fluoride ion (F^-) – Neon

(ii) **Calcium nitride**

Calcium ion (Ca^{2+}) – Argon
Nitride ion (N^{3-}) - Neon

(iii) **Cesium bromide**

Cesium ion (Cs^+) – Xenon
Bromide ion (Br^-) – Krypton

(c) Arrange the following atoms/ions in order of increasing size: [2]

(i) **Ni^{2+}, Pd^{2+}, Pt^{2+}**

$Pt^{2+} > Pd^{2+} > Ni^{2+}$

(ii) **Cu, Cu^+, Cu^{2+}**

$Cu > Cu^+ > Cu^{2+}$

(iii) **O, O^-, O^{2-}**

$O^{2-} > O^- > O$

(iv) **Cs^+, K^+, Rb^+**

$Cs^+ > Rb^+ > K^+$

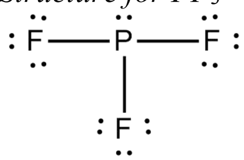
(d) Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3. [1]

$N_2 < SO_2 < ClF_3 < LiF < K_2O$

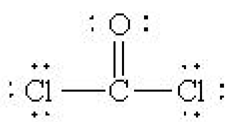
(e) For each of the following molecules: PF_3 and $COCl_2$: [2]

i) **Draw the Lewis Structure.**

Structure for PF_3



Structure of $COCl_2$



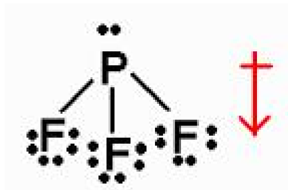
ii) **Determine the geometry of the molecule. [2]**

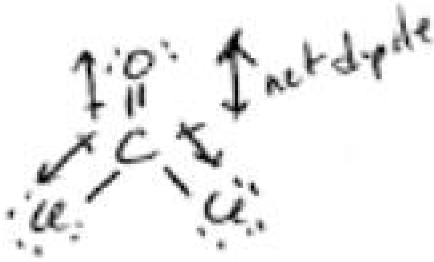
PF_3: Trigonal pyramidal
$COCl_2$: Trigonal planar

iii) **Sketch the molecule to show the dipoles. [2]**

For PF_3

For $COCl_2$





iv) **Indicate if the molecule is polar or non polar. [1]**

PF_3: Polar
$COCl_2$: Polar

v) **What intermolecular force exists in each of them? [1]**

Dispersion and dipole-dipole attraction forces in both molecules.

vi) **Determine the number of lone pairs of electrons on each atom.[1]**

PF_3: one pair
$COCl_2$: zero pair

(f) **Given the following molecules: C_2H_2, H_2, $C(CH_3)_4$, N_2.**

i) **Identify the type of intermolecular force present in the compounds. [1]**

Dispersion forces/London forces/instantaneous dipole forces

ii) **Are the compounds polar or non polar? [1]**

All the molecules are non polar

iii) **Arrange the molecules in order of increasing intermolecular force. [1]**

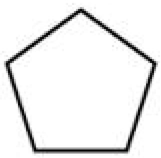
$H_2 < N_2 < C_2H_2 < C(CH_3)_4$

Question 6 (20 marks)

(a) Give the condensed structural formula and name of a hydrocarbon containing five carbon atoms that is
(i) an alkane (ii) a cycloalkane (iii) an alkene (iv) an alkyne [4]

(i) $CH_3CH_2CH_2CH_2CH_3$ pentane (or any of its isomer 2-methylbutane, 2,2-dimethypropane)

(ii)


cyclopentane

(iii) $CH_3CH_2CH_2CH = CH_2$ 1-pentene or $CH_3CH_2CH = CHCH_3$ 2-pentene or an alkene derived from isomers of pentane see (i)

(iv) $CH_3CH_2CH_2C \equiv CH$ 1-pentyne or $CH_3CH_2C \equiv CCH_3$ 2-pentyne or an alkene derived from isomers of pentane see (i)

½ mark for structural formula and ½ for correct name

(b) Using condensed structural formulas, write a balanced chemical equations for each of the following reactions. In each case name the products.

(i) hydrogenation of 2-butene

(ii) addition of H_2O to 2-pentene using H_2SO_4 as a catalyst (two products)

(i) $CH_3CH = CHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$ (1)

Butane (1)

(ii) $CH_3CH_2CH{=}CHCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2CH(OH)CH_2CH_3 + CH_3CH_2CH_2CH(OH)CH_3$ (2)

3-pentanol(1) 2-pentanol (1)

(c) Give the condensed structural formula of

(i) an aldehyde that is an isomer of acetone

(ii) an ether that is an isomer of 1-propanol

(iii) 2-choro-pentanoic acid [3]

(i) CH_3CH_2CHO (1)

(ii) $CH_3CH_2OCH_3$ (1)

(iii) $CH_3CH_2CH_2\underset{\substack{|\\ Cl}}{C}HCOOH$ (1)

(d) Draw the structural formula of the compound formed by the condensation reactions between

(i) ethanoic acid and methylamine

(ii) ethanoic acid and phenol [3]

(i) $CH_3\underset{\substack{\|\\ O}}{C}\text{-}OH + H\text{-}\overset{\substack{H\\ |}}{N}\text{-}CH_3 \rightarrow CH_3\underset{\substack{\|\\ O}}{C}\text{-}\overset{\substack{H\\ |}}{N}\text{-}CH_3 + H_2O$ (1½)

(ii) $CH_3\underset{\substack{\|\\ O}}{C}\text{-}OH + HO\text{-}C_6H_5 \rightarrow CH_3\underset{\substack{\|\\ O}}{C}\text{-}O\text{-}C_6H_5$ (1½)

Question 7 (20 marks)

(a) **Given the following general reaction,**

3 A + 2 B → 4 C

Write down the instantaneous rate for each of the reactants and products. [2]

$$-\frac{1}{3}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{1}{4}\frac{\Delta[C]}{\Delta t}$$

(b) **Study the following experimental data for the reaction below which was conducted at 25 °C and answer the questions below:**

$NO\ (g) + NO_2\ (g) + O_2\ (g) \rightarrow N_2O_5\ (g)$

Run	$[NO]_o$	$[NO_2]_o$	$[O_2]_o$	Initial Rate, Ms^{-1}
1	0.10 M	0.10 M	0.10 M	2.1×10^{-2}
2	0.20 M	0.10 M	0.10 M	4.2×10^{-2}
3	0.20 M	0.30 M	0.20 M	1.26×10^{-1}
4	0.10 M	0.10 M	0.20 M	2.1×10^{-2}

(i) **Deduce the order of reaction with respect to each reactant and determine the overall order of reaction. [6]**

Using the initial rate method;
Comparing (dividing) run 1 and run 4, the order of reaction (a) with respect to (w.r.t) O_2 can be calculated as follows:

$$(0.1/0.2)^a = (2.1\ x\ 10^{-2})/(2.1\ x\ 10^{-2})$$
$$(0.5)^a = (1)^0$$
$$Thus, a = 0$$

The order of reaction w.r.t O_2 is 0. *[1.5 marks]*

For NO, compare run 1 and run 2 as follows,

$$(0.1/0.2)^b = (2.1\ x\ 10^{-2})/(4.2\ x\ 10^{-2})$$
$$(0.5)^b = (0.5)^1$$
$$Thus, b = 1$$

The order of reaction w.r.t NO is 1. *[1.5 marks]*

For NO_2, compare run 2 and run 3 as follows,

$$(0.1/0.3)^c.\ (0.1/0.2)^a = (4.2\ x\ 10^{-2})/(1.26\ x\ 10^{-1})$$

Since a = 0,

$$(0.33)^c = (0.33)^1$$
$$Thus, c = 1$$

The order of reaction w.r.t NO_2 is 1. *[1.5 marks]*

The overall reaction order = 1 + 1 + 0 = 2 *[1.5 marks]*

(ii) **Write down an expression for the rate law for the above reaction and calculate the value of the rate constant for the reaction. [3]**

Rate = k[NO] [NO_2] ***[2 marks]***

To calculate the value of the rate constant k, plug in the values of [NO] and [NO_2] with their corresponding reaction rate for any run in the table above. Thus,

$$k(0.1)(0.1) = \; 2.1\; x\; 10^{-2}$$

$$\boldsymbol{k = 2.1\; M^{-1}s^{-1}}$$ *[1 mark]*

(c) **Derive an expression for the half life for a first order reaction and use this result to show that in a first order reaction the time taken for the reactant concentration to drop by three quarters of its initial value is double that for the initial concentration to drop by one half. [5]**

$$In\left(\frac{[A)]_o}{[A]_t}\right) = \; kt$$

$$\text{At}\; t = \; t_{1/2}, \quad [A]_t = \frac{[A]_o}{2}$$

The integrated rate law for $t = \; t_{1/2}$ *becomes,*

$$In\left(\frac{[A)]_o}{[A]_o/2}\right) = \; kt_{1/2}$$

Therefore,

$$In(2) = \; kt_{1/2}$$

Replacing the value of $In(2)$ *and then solving for* $t_{1/2}$ *gives the required equation for half life,*

$$\boldsymbol{t_{1/2} = \frac{0.693}{k}}$$ *[3 marks]*

If the reactant concentration drops by three quarters, the remainder is 25 % (0.25). Thus,

$$In\;(0.25) = \; -kt$$

$$t_1 = 1.386/k$$

If the reactant concentration drops by one half, the remainder is 50 % (0.5). Thus,

$$In\;(0.5) = \; -kt$$

$$t_2 = 0.693/k$$

Since the rate constant remains the same throughout,

$$t_1 = 2t_2 \; \textit{(Hence shown)}$$ *[2 marks]*

(d) Consider the reaction: 2B → C + 3D. In one experiment it was found that at 300 K the rate constant was 0.134 L/ (mol.s). A second experiment showed that at 450 K, the rate constant was 0.569 L/ (mol.s). Determine the activation energy for the reaction. [4]

At 300 K: $k_{300} = Ae^{\frac{-E_a}{RT}}$

At 450 K: $k_{450} = Ae^{\frac{-E_a}{RT}}$

$In\left(\frac{k_{450}}{A}\right) = \frac{-E_a}{RT}$ $where\ In(A) = In(K_{300}) - \frac{-E_a}{RT}$

So that,

$In(k_{450}) - \left[In(k_{300}) - \frac{-E_a}{RT}\right] = \frac{-E_a}{RT}$

$In\left(\frac{k_{450}}{k_{300}}\right) = \frac{E_a}{R}\left(\frac{1}{T_{300}} - \frac{1}{T_{450}}\right)$

Plugging and solving for E_a,

$\boldsymbol{E_a = 10.8\ kJ}$ *[4 marks]*