Advanced Level 2015 - Chemistry (Paper II)

Part A - Structured Essay

Answer all four questions on the paper itself (Each question caries 10 marks)

1. (a) Consider the following chemical species

XeF_2 NO_3^- SF_5^- Na_2SO_4 SO_3 HF

Which one of the above species.

(i) has both ionic bonds and covalent bonds? .....

(ii) is isoelectronic with BF_3 .....

(iii) has a square pyramidal shape? .....

(iv) has an equal number of bonding and non bonding electrons in its most stable structure? .....

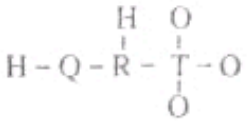
(v) has a σ - bond as a result of overlap of a 1s atomic orbital and a 2p atomic orbital?

.....

(vi) contains a bond angle of 180°? .....

(b) The compound. H_3O_3QRT shows acidic properties. It loses H^+ to form the anion $[H_2O_3QRT]$ When dissolved in water in the most acceptable Lewis structure for this anion, the negative charge is on an oxygen atom. There are no charges on the other atoms. The elements Q, R and T are non-metals with electrongativities greater than 2 (Pauling scale). The elements Q and R belong to the second period, whereas T belongs to the third period of the Periodic table

The following questions (i) to (v) are based on the anion (H_2O_3QRT) It's skeleton is given below



(i) Identify the elements Q R an T

Q = ... R = ... T = ...

(ii) Draw the most acceptable Lewis structure for this anion

(iii) Draw six resonance structures for this anion

(iv) State the following regarding Q R and T atoms in the table given below.

I. election pair geometry (arrangement of electron pairs around the atom

II. Shape around the atom

III. hybridization of the atom

IV. Approximate bond angic around be atom

	Q	R	T
I. Electron pair geometry			
II. Shpape			
III. Hybridization			
IV. Sound angle			

(v) Identify the atomic / hybrid orbitals involved in the formation of the following is bonds in the lewis structure drawn in part (ii) above

I. Q - R Q ..... R .....

II R - T R ..... T .....

III T - O T ..... O .....

(iv) I. State what information is directly provided by a Lewis structure of a covalent compound/ion

II. State what information is not directly provided by a Lewis structure of a covalent compound/ion

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(c) State whether the following statements are true or false. Give reasons for your choice

(i) The decreasing order of electronegativity of nitrogen in NH_3 NO_2F and NO_4^{3-} is

$NO_2F > NO_4^{3-} > NH_3$

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(ii) The increasing order of making points of lithium halides is Li < LiCl < LiBr < LiI

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2. (a) X is a p- block element in the periodic table with an atomic number less than 20. On burning X in air, the colourless gas X_1 is formed. X_1 has a pungent smell. X_1 is readily soluble in water. When a solution of $BaCl_2$ is added to this solution. a white precipitate X_2 is formed. X_2 dissolves in dil. HCl to give a weak acid X_3 as one of the products. X_1 decolorant an acidified solution of potassium permanganate. A gas X_4 is formed when X_1 is oxidized. X_4 is used in the industrial manufacture of the strong acid X_5

(i) Identify X and draw its structure in the crystalline state.

X .....

Structure of X

(ii) Write the ground state electronic configuration of X .....

(iii) What are the common positive oxidation states of X .....

(iv) Write the chemical formulae of the following compounds.

X_1 :.....

X_2 :.....

X_3 :.....

X_4 :.....

X_5 :.....

(v) Sketch the most stable structures of X_1 and X_4 indicate approximate bond angles, in each sketch.

(vi) Write the balance chemical equation for the reaction of X_1 with acidified potassium permanganate.

(b) Test tubes labelled A to E contain the following solids (not in order) $Mg(NO_3)_2$ $(NH_4)_2 CO_3$ $(HN_4)_2 SO_4$ NH_4NO_3 and $NaHCO_3$

A description of the products formed when each of these solids is heaied is given in the table below.

Solid	Description
A	1. A basic white powder 2. Water vapour, 3. A colourless, odourless gas that turns lime water creamy.
B	Three products which are in the gasous state.
C	1. A strong acid 2. A colourless gas that gives a brown precipitate / colouration with Nessler/s reagent.
D	1. A white oxide which reacts with water to form a weakly basic solution. 2. A colourless, diatomic gas at room temperature. 3. A red -brown gas.
E	1. Water vapour, 2. colourless, tasteless, non-toxic, triatomic gas with a linear structure.

(i) Identify solids A to E.

A : ..... B : .....

C : ..... D : .....

E : .....

(ii) Write balanced chemical equations for the reactions that take place on heating each of the solids A to E

3. (a) The kinetics of the following reaction can he studied by measuring initial rates.

$$A(aq) + 5B(aq) + 6C(aq) \longrightarrow 3D(aq) + 3E(aq)$$

Four experiments carried out by changing initial concentration of A, B and C at a given temperature are described in the following table $[\Delta A]_0$. The change in concentration of A with time (t/s) was measured.

Expt.	$(A)_0$ / mol dm^{-3}	$(B)_0$ / mol dm^{-3}	$(C)_0$ / mol dm^{-3}	$[\Delta A]_0$ / mol dm^{-3}	t/s	initial Rate (R) / moldm^{-3} s^{-1}
1	0.2	0.2	0.2	0.040	50	R_1 = ...
2	0.4	0.2	0.2	0.096	60	R_2 = ...
3	0.4	0.4	0.2	0.128	40	R_3 = ...
4	0.2	0.2	0.4	0.080	25	R_4 = ...

(i) Calculate initial rates R_1, R_2, R_3 and R_4 and complete the table.

(ii) Taking a, b and c as orders with respect to each of the reactance A B and C respectively, and the rate constant as k, calculate a, b, c and write the rate expression for the reaction using the calculated values.

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(iii) State the overall order of the reaction

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(iv) Calculate the rate constant k of the reaction

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(b) (i) I In another experiment, if the concentrations are, $[A]_0$ = 1.0 x 10^{-1} moldm^{-3} $[B]_0$ = 1.0 mol dm^{-3}, and $[C]_0$ = 2.0 mol dm^{-3}, show that the rate expression for the reaction can be given by rate = $k'[A]^a$ (k' is the rate constant of the reaction under these conditions.)

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II State the assumption(s) made in deriving the expression in I above.

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(ii) In the above (b)(i) experiment, the concentration of A, [A], changes with time (t) according to the following equation. 2.303 log [A] = -k't + 2.303 log $[A]_0$ ($[A]_0$ is the initial concentration of A). Show that the half-life ($t_{1/2}$) of the reaction is given by 0.693/k' and calculate $t_{1/2}$ by using the data in (a) (iv) and (b) (i) above.

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(a) A B and C are structural isomers with the molecular formula $C_5H_{11}Br$. All three isomer exhibit optical isomerism. When reacted with alcoholic KOH, A. B and C give D E and F respectively. D exhibits geometric isomerism, while E and F do not exhibits geometric isomerism. When reacted with HBr, E and F both give the same compound G. G is structural isomer of A, B and C. G does not exhibit optical isomerism. Draw the structures of A , B, C, D, E, F and G in the box given below (It is not necessary to draw stereoisomeric forms)

A

B

C

D

E

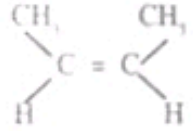
F

G

(b) Write the reagent(s) catalyst (s) H, I, J, K, L, M, N, O, P and Q (with suitable conditions, if any) of the following reactions in the boxes given on page 8

(i) $CH_2=CH_2 \xrightarrow{H} HOCH_2CH_2OH$

(ii) $C_6H_5N_2^{\oplus}Cl^{\ominus} \xrightarrow{I} C_6H_5I$

(iii) $CH_3-C\equiv C-CH3 \xrightarrow{J}$ 

(iv) $C_6H_5COCH_2CO_2H \xrightarrow{K} C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CO_2H$

(v) $C_2H_5CH_2OH \xrightarrow{L} C_2H_5CO_2H$

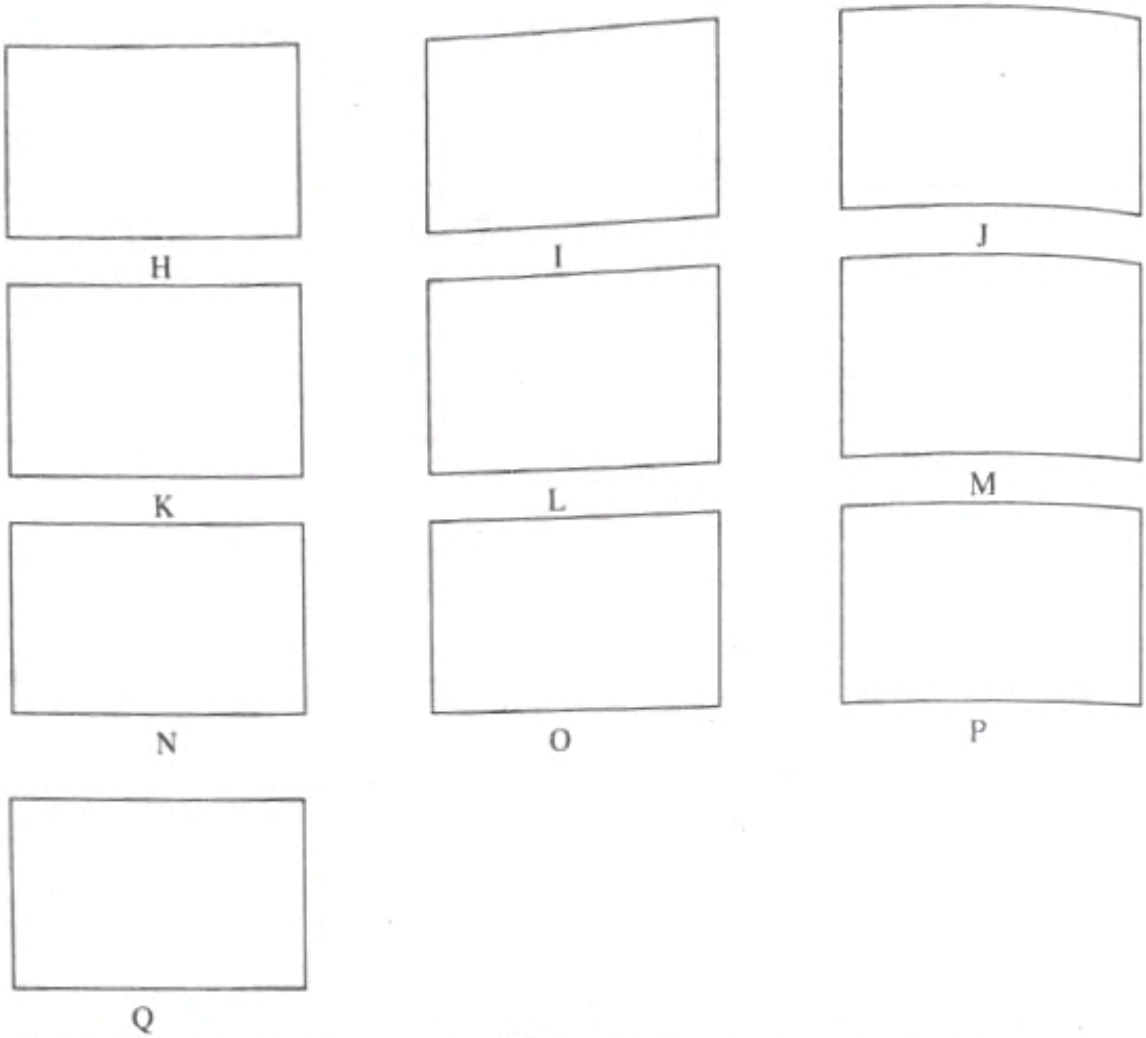
(vi) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3 \xrightarrow{M} CH_3CH=CH_2$

(vii) $CH_3C\equiv CH \xrightarrow{N} CH_3C\equiv CCu$

(viii) $C_6H_5CO_2H \xrightarrow{O} C_6H_5COCl$

(ix) $C_6H_5CONH_2 \xrightarrow{P} C_6H_5CH_2NH_2$

(x) $C_6H_6 \xrightarrow{Q} C_6H_5COCH_3$



(b) Write the mecchanism for the reaction of CH_3COCl with aqueous sodium hydroxde.

Department of Examinations, Sri Lanka

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கல்விப் பொதுத் தராதர் பத்திர (உயர் தர)ப் பரீட்சை, 2015 ஓகஸ்ற்று
General Certificate of Education (Adv. Level) Examination, August 2015

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

02 E II

* Universal gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$
* Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$

PART B — ESSAY

*Answer **two** questions only. (Each question carries **15 marks**.)*

5. (*a*) Consider the following reaction at a temperature of 25 °C.

$$\mathbf{AB}(s) \longrightarrow \mathbf{C}(s) + \mathbf{D}(g)$$

The following data are given for ΔH_f° and S° at 25 °C.

	ΔH_f° /kJ mol^{-1}	S° /J K^{-1} mol^{-1}
AB(s)	−1208	100
C(s)	−600	50
D(g)	−500	170

(i) Show that the reaction is **non-spontaneous** at 25 °C.

(ii) This reaction is spontaneous when the temperature is greater than T °C. This reaction is non-spontaneous when the temperature is less than T °C. Calculate T.

(iii) State the assumptions you made in the calculation in (ii) above.

(5.0 marks)

(*b*) When the reaction described in (*a*) above is carried out in a closed container of volume 2.00 dm^3 at 930 °C, the system reaches an equilibrium as given below.

$$\mathbf{AB}(s) \rightleftharpoons \mathbf{C}(s) + \mathbf{D}(g)$$

(i) The pressure of the container was found to be 4.00×10^5 Pa. Calculate K_p and K_c at 930 °C. State the assumptions you made. (Consider that $8.314\ J\ K^{-1}\ mol^{-1} \times 1203\ K = 10\ 000\ J\ mol^{-1}$)

(ii) When the above reaction in (*b*)(i) is carried out in the presence of **X**(g) at 930 °C, the yield of **D**(g) can be enhanced. Then the system shows a new equilibrium as given below.

$$\mathbf{AB}(s) + \mathbf{X}(g) \rightleftharpoons \mathbf{C}(s) + 2\mathbf{D}(g)$$

When this reaction is carried out with 2.25×10^{-1} moles of **X**(g) at 930 °C in a closed container of volume 2.00 dm^3, the partial pressure of **D**(g) is found to be 7.50×10^5 Pa. Calculate K_p and K_c for the new equilibrium.

(iii) Explain qualitatively the changes that could take place in the equilibrium in part (*b*)(ii) in the following instances.

I. Some amount of solid **C** is removed from the system.

II. Some amount of gas **D** is removed from the system.

(10.0 marks)

6. (*a*) **XA**(s) and **YA**(s) are two sparingly water soluble salts.

(i) The solubility of salt **XA**(s) in water is 2.01 mg dm^{-3} at 25 °C. Calculate the solubility product K_{sp} of **XA**(s) at 25 °C. (**X** = 110 g mol^{-1}, **A** = 40 g mol^{-1})

(ii) A completely water soluble solid Na**A** is added slowly to a 1.00 dm^3 aqueous solution containing 0.100 moles of $\mathbf{X}^+(aq)$ and 0.100 moles of $\mathbf{Y}^+(aq)$.

I. Predict which of the salts precipitates first. (K_{sp}(**YA**) = 1.80×10^{-7} mol^2 dm^{-6}).

II. Calculate the cation concentration that remains in solution of the salt which precipitated first when the second salt begins to precipitate.

(5.0 marks)

(b) (i) When a weak acid HA(aq) is titrated with a solution of NaOH, considering the hydrolysis of $A^-(aq)$, show that the pH of the solution at the equivalence point is given by $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log[A^-(aq)]$.

(You are given that $pH + pOH = pK_w$, $pK_a + pK_b = pK_w$ and $K_b = \frac{[OH^-(aq)][HA(aq)]}{[A^-(aq)]}$)

(ii) Calculate the pH at the equivalence point when a solution of 1×10^{-3} mol dm^{-3} HA(aq), is titrated with a 1×10^{-3} mol dm^{-3} solution of NaOH. ($K_a = 1.8 \times 10^{-5}$ mol dm^{-3}).

(iii) A 500.00 cm^3 solution of 2×10^{-3} mol dm^{-3} $Y^+(aq)$ is added to a 500.00 cm^3 of 2×10^{-3} mol dm^{-3} solution of HA(aq). Solid NaA was slowly added to this solution in order to precipitate YA(s). Calculate the pH of the solution when YA(s) begins to precipitate. ($K_{sp}(YA) = 1.80 \times 10^{-7}$ mol^2 dm^{-6}).

(7.0 marks)

(c) Benzene and toluene mix completely with each other to form a binary mixture. Boiling points of benzene and toluene are 80 °C and 110 °C respectively.

(i) Draw an appropriate temperature - composition phase diagram for the above system.

(ii) Consider the distillation of a liquid mixture (P) with 30% of benzene.

I. Mark the boiling point T_1 of liquid mixture P on the phase diagram above.

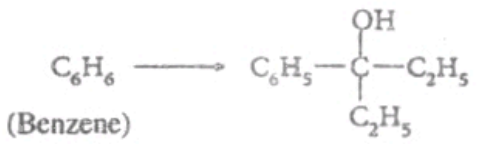
II. Mark the composition (Q) of the vapour phase at temperature T_1 on the phase diagram above.

III. Explain qualitatively, the difference in composition between the liquid and vapour phases at temperature T_1. Name the technique which is used to separate benzene from the above binary mixture based on this difference.

(iii) Draw the temperature - composition phase diagram for a binary mixture formed by two fully miscible liquids with equal boiling points.

(3.0 marks)

7. (a) Show how the conversion given below could be carried out using **only** the chemicals given in the list.



List of chemicals
$KMnO_4$, PBr_3, Mg, dry ether, CH_3Cl, C_2H_5OH, Anhydrous $AlCl_3$, conc. H_2SO_4

(5.0 marks)

(b) Show how compound B could be synthesized in less than 7 steps, using compound A as the **only** organic starting material.

$C_6H_5CH_2CONHC_6H_5$ A

$C_6H_5CH_2CH{=}N{-}C_6H_5$ B

(7.0 marks)

(c) Methyl iodide reacts with ethylamine as shown below.

$$CH_3I + CH_3CH_2NH_2 \longrightarrow CH_3{-}CH_2{-}\overset{\overset{H}{|}}{N}{-}CH_3 + HI$$

(i) State whether ethylamine reacts as a nucleophile or an electrophile in this reaction.

(ii) Indicate the mechanism of the reaction by the use of curved arrows.

(iii) Taking into account that amides are less basic than amines, explain why the methyl iodide does not react with propionamide according to the reaction given below.

$$CH_3I + CH_3CH_2CONH_2 \longrightarrow CH_3CH_2CONHCH_3 + HI$$

(3.0 marks)

PART C — ESSAY

Answer two questions only. (Each question carries 15 marks.)

8. (*a*) A metal M belongs to the *s*-block of the Periodic Table. It burns with a yellow flame in the presence of excess oxygen gas to give a solid, M_1. On treatment with cold water M_1 gives a clear basic solution, M_2 and a covalent compound, M_3. M_3 reacts with acidified Ag_2O to give a colourless diatomic gas, M_4. Excess of M_2 reacts with metal T to give a colourless diatomic gas M_5, and a water soluble compound, M_6. The addition of dilute HCl dropwise to an aqueous solution of M_6 gives a white gelatinous precipitate, M_7 which dissolves in excess acid. M_7 does not dissolve in dilute NH_4OH.

(i) Identify M, M_1, M_2, M_3, M_4, M_5, M_6, M_7 and T.

(ii) Predict the products of the reaction of M_1 with hot water.

(5.0 marks)

(*b*) A crystalline ionic inorganic compound Q (molar mass = 248 g mol^{-1}) when heated gently releases a substance which turns anhydrous $CuSO_4$ blue.

Three tests (1), (2) and (3) were carried out with an aqueous solution of Q. Tests and observations are given below.

Test	Observation
(1) Added dilute HCl.	Solution turned turbid with the evolution of a colourless gas. Burning a Mg ribbon in this gas gave two solids white and yellow in colour.
(2) Added $AgNO_3$ solution dropwise.	White precipitate. It turns black on heating.
(3) Added $Pb(NO_3)_2$ solution dropwise.	White precipitate. It turns black on heating.

(i) Identify Q and draw the most acceptable Lewis structure for its anion.

(ii) Write balanced chemical equations for the reactions taking place in tests (1), (2) and (3). Indicate the precipitates with an arrow (↓) in the equations.

(iii) Give two uses of Q.

(H = 1, O = 16, Na = 23, S = 32)

(5.0 marks)

(*c*) The following procedure was used to determine the percentage by mass of $KClO_3$ and KCl in a mixture X. Mixture X contains $KClO_3$, KCl and a water soluble inert material.

A mass of 1.100 g of X was dissolved in 50 cm^3 of distilled water in a 250 cm^3 volumetric flask and diluted with distilled water to give a final volume of 250.0 cm^3. (Solution Y).

A 25.00 cm^3 portion of this solution was treated with $SO_2(g)$ to reduce the ClO_3^- to Cl^-. The excess $SO_2(g)$ was removed by boiling the solution. Aqueous $AgNO_3$ was added to this solution to precipitate the total Cl^- as AgCl. The precipitate was then filtered, washed with distilled water, and dried at 105°C until a constant weight was obtained. The mass of the AgCl precipitate formed was 0.135 g.

Another 25.00 cm^3 portion of Solution Y was heated with 30.00 cm^3 of 0.20 mol dm^{-3} Fe(II) solution, in acidic medium. The volume of 0.02 mol dm^{-3} $KMnO_4$ required to oxidize the unreacted Fe(II) was 20.00 cm^3.

Fe(II) reacts with ClO_3^- as given below.

$$H^+ + ClO_3^- + Fe^{2+} \longrightarrow Cl^- + Fe^{3+} + H_2O \quad \text{(unbalanced)}$$

Calculate separately the percentage by mass of $KClO_3$ and KCl in X.

(O = 16, Cl = 35.5, K = 39, Ag = 108)

(5.0 marks)

9. (a) The following questions are based on the properties of nitric acid and the Ostwald's process used in its manufacture.

(i) State the raw materials used in this process.

(ii) Write balanced chemical equations with appropriate conditions, for the reactions taking place in this process.

(iii) Calculate the maximum amount of nitric acid that can be produced from 1000 moles of the diatomic gas present in one of the raw materials identified in (i) above.

(iv) Give **three** uses of nitric acid.

(v) Pure concentrated nitric acid is a colourless liquid. It turns yellow when exposed to light. Explain this observation with the aid of a balanced chemical equation.

(vi) Give balanced chemical equations for the following reactions.

I. $S(s) + \text{conc. } HNO_3 \xrightarrow{\Delta}$

II. $Cu(s) + \text{conc. } HNO_3 \xrightarrow{\Delta}$

III. $Cu(s) + \text{dil. } HNO_3 \xrightarrow{\Delta}$

(7.5 marks)

(b) The following questions are based on N_2 (the major component in the earth's atmosphere) and nitrogen containing compounds which contribute to a variety of environmental problems.

(i) Special conditions are required to fix N_2 due to its inert nature. Explain why N_2 is inert.

(ii) State the **two** natural N_2 fixing processes.

(iii) State the name of the main industrial process used to fix N_2.

(iv) Identify the **two** nitrogen compounds that contribute to photochemical smog.

(v) Explain how the compounds you mentioned in (iv) above contribute to photochemical smog.

(vi) Identify **two** nitrogen containing organic compounds that contribute to photochemical smog.

(vii) Name **two** detrimental effects that photochemical smog has on the environment.

(viii) Identify the main nitrogen compound that contributes to the greenhouse effect.

(ix) Identify the **two** gaseous nitrogen compounds that contribute to acid rain.

(x) N_2 gas can be prepared in the laboratory by thermal decomposition of compounds. Give balanced chemical equations for two such reactions.

(7.5 marks)

10. (*a*) A, B, C and D are coordination compounds (complex compounds) of chromium. They have an octahedral geometry. All the compounds consist of a single chromium ion, three chlorine atoms which could be either covalent and/or ionic and molecules of water. The number of molecules of water in the compounds vary. The chromium ion in all the compounds has the same oxidation state. The complex ion part (metal ion and ligands coordinated to it) of A, B, C and D have charges of +3, +2, +1 and zero respectively.
Note: Disregard geometric isomers.

(i) Give the oxidation state of chromium in the coordination compounds.

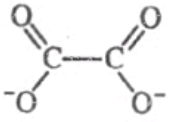
(ii) Write the electronic configuration of chromium in these compounds.

(iii) Write the structural formulae of A, B, C and D.
Note: Disregard geometric isomers.

(iv) Give the IUPAC name of A.

(v) Give a chemical test that could be used to distinguish between A and D.
Note: State the test as well as the observation.

(vi) Given below is the structure of the oxalate ion.



oxalate ion (ox)

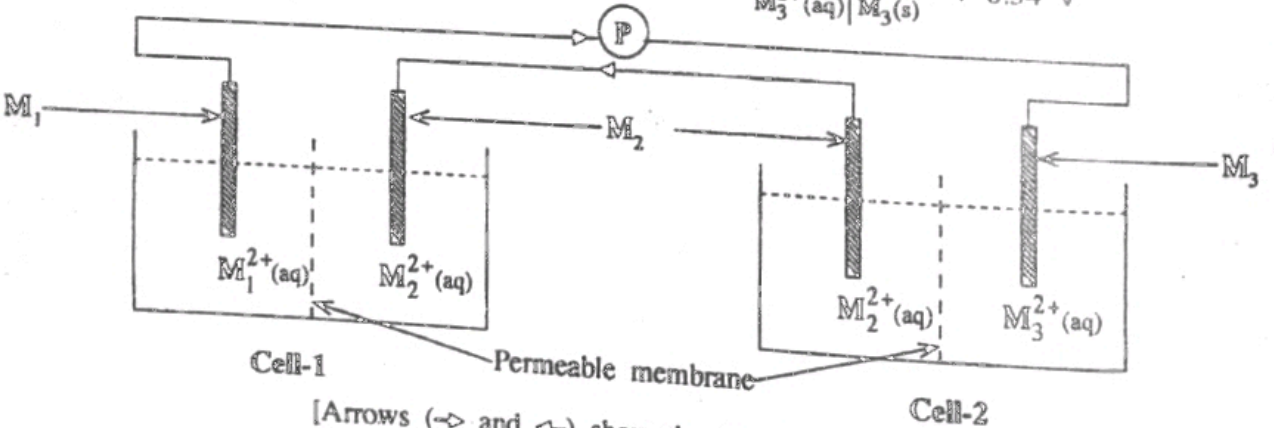
The oxalate ion coordinates the chromium ion through the two negatively charged oxygens to give a complex ion part, E, which has an octahedral geometry. Write the structural formula of E. (The chromium ion in E has the same oxidation state as the chromium in compounds A - D.)
Note: Use the abbreviation 'ox' to denote the oxalate ion in your structural formula.

(7.5 marks)

(*b*) The diagram given below shows two electrochemical cells connected in series at 25 °C. M_1, M_2 and M_3 metals are dipped in aqueous solutions of their own ions $M_1^{2+}(aq)$, $M_2^{2+}(aq)$ and $M_3^{2+}(aq)$, respectively. The concentrations of all solutions are 1.0 mol dm^{-3}. The standard electrode potentials for the metals M_1 and M_3 are given below.

$E^\circ_{M_1^{2+}(aq)|M_1(s)} = -2.36\ V$

$E^\circ_{M_3^{2+}(aq)|M_3(s)} = +0.34\ V$



[Arrows (⇨ and ⇦) show the direction of electron flow]

(i) Giving reasons, identify the anode and the cathode of each cell.

(ii) Write the reactions taking place at the anode and the cathode in each cell.

(iii) Calculate the reading of the digital voltmeter, P.

(iv) The electromotive force of cell–1 $\left(E^\circ_{\text{cell-1}}\right)$ was found to be +1.60 V. Calculate the standard electrode potential $\left(E^\circ_{M_2^{2+}(aq)|M_2(s)}\right)$ of the $M_2^{2+}(aq)/M_2(s)$ electrode.

(v) Calculate the electromotive force of cell–2 $\left(E^\circ_{\text{cell-2}}\right)$

(vi) If you are provided only a metal M_4 and a solution of M_4^{2+} (aq, 1.0 mol dm^{-3}) in addition to the above set up, suggest an experimental method in brief to determine the value of E°