G.C.E. (A/L) Support Seminar - 2016

Chemistry I

Two hours

Instructions :

- Answer **All** questions
- In each of the question 01 - 50, pick one of the altenatioves from (1), (2), (3), (4), (5) which is correct or most appropriate.

Universal gas constant	R	=	$8.314\ J\ K^{-1}\ mol^{-1}$
Avogadro constant	N_A	=	$6.022 \times 10^{23}\ mol^{-1}$
Planck's constant	h	=	$6.626 \times 10^{-34}\ J\ s$
Velocity of light	c	=	$3 \times 10^{8}\ m\ s^{-1}$

1. In which of the following elements does a gaseous atom in ground state contain **only** four unpaired electrons?

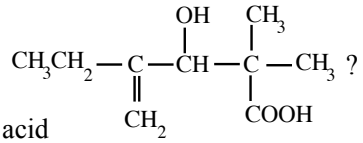
(1) Ti (2) Cr (3) Fe (4) Co (5) Sn

2. The correct variation of the first ionsation energy of the elements Li, K, N, O, Ne and Ar is

(1) K < Li < O < N < Ar < Ne.
(2) Ne < Ar < N < O < Li < K.
(3) K < Li < O < N < Ne < Ar.
(4) K < O < Li < N < Ar < Ne.
(5) Li < N < O < K < Ar < Ne.

3. In an atom, what is the number of atomic orbitals in which an electron with principal quantum number, n = 3 and magnetic quantum number, $m_l = 0$ can exist?

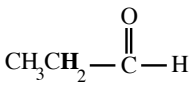
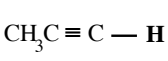
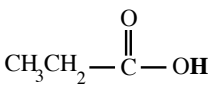
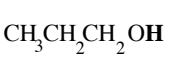
(1) 1 (2) 2 (3) 3 (4) 4 (5) 5

4. What is the correct IUPAC name of the organic compound  ?

(1) 2, 2 - dimethyl - 4 - ethyl - 3 - hydroxy - 4 - pentenoic acid
(2) 3 - hydroxy - 2, 2 - dimethyl- 4 - methylidene -4 - hexenoic acid
(3) 2 - ethyl - 3 - hydroxy - 4, 4 - dimethyl -1 - pentenoic acid
(4) 4 - ethyl - 3 - hydroxy - 2, 2 - dimethyl - 1-carboxy - 4 - pentene
(5) 4 - ethyl - 3 - hydroxy - 2, 2 - dimethyl - 4 - pentenoic acid

5. When a chlorohydrocarbon X converted to the gaseous state under a temperature 100 °C is subject to complete combustion in oxygen, steam and chlorine gas were formed in equal volumes and only carbon dioxide was the other product formed. The volume of oxygen required for complete combustion of 10 cm^3 of X was 60 cm^3 and the volume of carbon dioxide formed therein was 50 cm^3. If all the volume measurements were made under the same temperature and pressure, the molecular formula of X is,

(1) $C_5H_2Cl_2$. (2) $C_5H_4Cl_4$. (3) $C_5H_4Cl_2$. (4) $C_5H_8Cl_4$. (5) $C_3H_4Cl_2$.

6.    

A B C D

The correct order of variation of the acidity of bold faced hydrogen atoms in the above compounds is,

(1) C > A > D > B. (2) C > D > B > A. (3) D > C > B > A.
(4) A > C > D > B. (5) C > A > D > B.

[See page two

7. One mole of N_2H_4 forms the compound Y by removing 10 moles of electrons. If all the "N" atoms in the initial compound are present in compound Y, what is the oxidation number of a "N" atom in Y?

(1) -3 (2) -2 (3) +1 (4) +3 (5) +5

8. Which of the following gives the electron pair geometry and hybridisation around an oxygen atom in H_2O_2 respectively?

(1) angular, sp^3 (2) tetrahedral, sp^3 (3) tetrahedral, sp^2
(4) angular, sp (5) linear, sp

9. What is the molar ratio between ethanol (C_2H_5OH), and $KMnO_4$ when ethanol is oxidised to acetic acid (CH_3COOH) by $KMnO_4$ in acid medium?

(1) 3 : 2 (2) 1 : 5 (3) 4 : 5 (4) 2 : 5 (5) 5 : 4

10. When a sample of an alloy containing magnesium and aluminium in the molar ratio 1: 2 was reacted with excess hydrochloric acid, the volume of gas liberated under STP was 89.6 dm^3 . What is the mass of aluminium in the sample of the alloy? (The molar volume of a gas at STP is 22.4 dm^3mol^{-1}. Mg = 24 , Al = 27)

(1) 54.0 g (2) 72.0 g (3) 81.0 g (4) 105.0 g (5) 108.0 g

11. Which of the following does **not** show stereoisomerism?

(1) $CH_2=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (2) $CH_3CH=CH-CH_2OH$

(3) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$ (4) $CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(5) $CH_3-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle OH}{\overset{|}{C}}-CH_3$

12. The ascending order of the boiling point of the following compounds is,

(1) $SiH_4 < PH_3 < H_2S < HCl$ (2) $SiH_4 < PH_3 < HCl < H_2S$
(3) $HCl < H_2S < SiH_4 < PH_3$ (4) $HCl < H_2S < PH_3 < SiH_4$
(5) $H_2S < HCl < PH_3 < SiH_4$

13. Which of the following is the suitable expression for the solubility of solid Ag_2CrO_4 in a y mol dm^{-3} aqueous Na_2CrO_4 solution? (K_{sp} means the solubility product of Ag_2CrO_4).

(1) $(K_{sp})^{1/3}$ (2) $\left(\frac{K_{sp}}{4}\right)^{1/2}$ (3) $\left(\frac{K_{sp}}{4y}\right)^{1/2}$ (4) $\left(\frac{K_{sp}}{2y}\right)^{1/2}$ (5) $\left(\frac{K_{sp}}{y}\right)^{1/3}$

14. At room temperature, the vapour pressure of pure A is twice the vapour pressure of pure B. What is the mole fraction of A in the vapour in equilibrium with a binary solution in which the molar ratio of A : B is 3 : 2 (Assume that the solution behaves ideally.)

(1) 0.25 (2) 0.30 (3) 0.50 (4) 0.75 (5) 0.80

15. Which of the following is **not** oxidised by acidified $K_2Cr_2O_7$?

(1) CH_3CH_2OH (2) H_2S (3) Br_2 (4) NaBr (5) H_2O_2

16. A green coloured aqueous solution contains two sodium salts comprising two 'd' block elements. The solution, on addition of a solution of H_2O_2 gives a brown precipitate and a yellow solution. Which of the following would be the two 'd' block elements contained in the salts of the initial solution?

(1) Fe and Mn (2) Mn and Ni (3) Fe and Ni (4) Cr and Ni (5) Mn and Cr

[See page three

17. If the numerical value of the equilibrium constant of equilibrium $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at a certain temperature is 100 , what is the numerical value of the equilibrium constant of the equilibrium $NO_2(g) \rightleftharpoons 1/2N_2(g) + O_2(g)$?

(1) 0.01 (2) 0.10 (3) 10.0 (4) 25.0 (5) 50.0

18. Consider the following statements about NH_3.

A - The conjugate acid of NH_3 is NH_4^+.

B - NH_2^- is the conjugate base of NH_3.

C - NH_3 is formed by the reaction between NH_4NO_3 and $NaNH_2$.

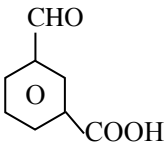
D - Ammonia cannot act as an oxidising agent as the N in NH_3 exists in the lowest oxidation state.

Of the above, the true statements are

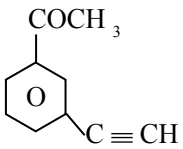
(1) only A and B. (2) only B and C. (3) only C and D.
(4) only A, B and C. (5) all A, B, C and D.

19. The organic compound X gives an orange coloured precipitate with Brady's reagent and reduces Tollen's reagent. Which of the following would be X?

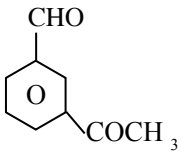
A



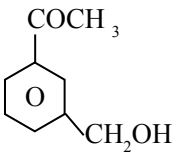
B



C



D



(1) only A (2) only A and C. (3) only B and D.
(4) only C and D. (5) only A, B and C.

20. What is the pH of the solution formed when 100 cm^3 of a 0.1 mol dm^{-3} H_2SO_4 solution were mixed with 100 cm^3 of a 0.4 mol dm^{-3} KOH solution at 25 °C? (K_w at 25 °C = 10^{-14} mol^2 dm^{-6})

(1) 10.0 (2) 11.0 (3) 12.0 (4) 12.5 (5) 13.0

21. The solid A introduced into a closed system comes to the following equilibrium when heated to a certain temperature.

$$2A(s) \rightleftharpoons B(g) + 2C(g)$$

Which of the following gives the equilibrium partial pressure of B(g) in this system?

(1) $\frac{Kp}{5}$ (2) $(Kp)^{1/2}$ (3) $\frac{Kp}{3}$ (4) $\left(\frac{Kp}{4}\right)^{1/3}$ (5) $\left(\frac{Kp}{2}\right)^{1/3}$

22. What is the temperature change occurring when 100 cm^3 of a 1.0 mol dm^{-3} NaOH solution were mixed with 100 cm^3 of a HCl solution of the same concentration in a thermally insulated container?

Standard enthalpy of neutralisation = -57 kJ mol^{-1}

Specific heat capacity of the solution = 4.2 J g^{-1} K^{-1}

Density of the solution = 1.0 g cm^{-3}

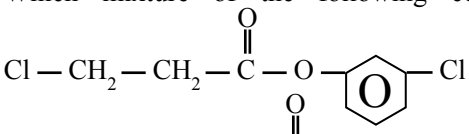
(1) 3.0 °C (2) 4.2 °C (3) 5.6 °C (4) 6.8 °C (5) 8.2 °C

23. A buffer solution of pH 4 is formed when 50.0 cm^3 of a 0.2 mol dm^{-3} solution of a weak monobasic acid HA are mixed with 50.0 cm^3 of a solution of its sodium salt NaA. If K_a of HA at the relevant temperature is 1.0×10^{-6} mol dm^{-3} ,what is the concentration in mol dm^{-3} of the NaA solution mixed?

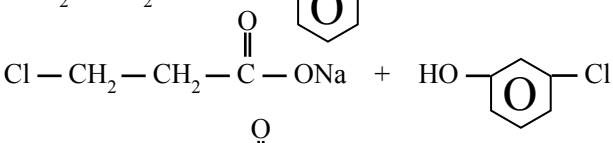
(1) 1.0×10^{-3} (2) 2.0×10^{-3} (3) 1.0×10^{-2} (4) 1.5×10^{-2} (5) 4.0×10^{-2}

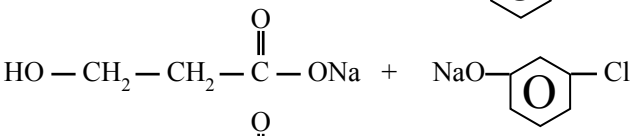
[See page four

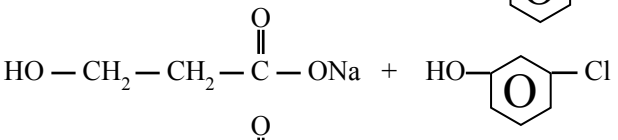
24. Which mixture of the following compounds is given by the reaction between the compound

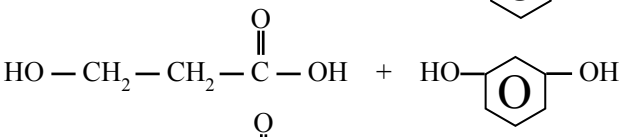


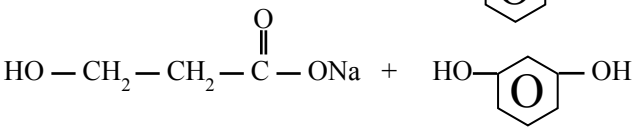
with excess aqueous NaOH?

(1) 

(2) 

(3) 

(4) 

(5) 

25. A is a coloured inorganic salt insoluble in water. When a few of solid A is dissolved in excess of hydrochloric acid a colourless gas G is liberated giving a yellow solution Q. When Q is diluted with water, first it turns green and finally blue. The gas G when passed into bromine water turns bromine water colourless giving the solution T. On addition of barium chloride solution, T gives a white precipitate P which is insoluble in nitric acid. Which of the following could be A?

(1) $CuBr_2$ (2) $CuCO_3$ (3) $NiSO_3$ (4) $CuSO_3$ (5) $CuSO_4$

26. Of the following, the pair of ions that **cannot** be distinguished by passing H_2S in an ammoniacal medium is

(1) Zn^{2+}, Ni^{2+} (2) Mg^{2+}, Cd^{2+} (3) Cu^{2+}, Bi^{3+}
(4) Cr^{3+}, Co^{2+} (5) Zn^{2+}, Co^{2+}

27. $A \xrightarrow{r_1} B + C$ ——(1)

$P \xrightarrow{r_2} Q + R$ ——(2)

The reaction 1 and 2 above are first order reactions. When t = 0, [A] = [P]. When t = 12 seconds, [A] = 2[P]. The half lives of A and P relevant to the reactions 1 and 2 respectively in seconds are

(1) 2 and 3. (2) 4 and 3. (3) 3 and 4.
(4) 6 and 8. (5) 3 and 2.

28. Contained in a vessel of volume 4.157 dm^3 are 0.01 moles of He, O_2 and Mg each at 300 K. What will be the total pressure of the vessel if all the magnesium is burnt completely and the vessel is brought to the initial condition?

(1) 6.0×10^3 Pa
(2) 7.5×10^3 Pa
(3) 8.0×10^3 Pa
(4) 9.0×10^3 Pa
(5) 18×10^3 Pa

[See page five

29. In which of the following reaction is a compound with two asymmetric carbon atoms are formed?

(1) Addition of a dilute alkali to $CH_2 = CHCH_2CH_2Cl$

(2) Reacting $CH_3\overset{\overset{O}{\|}}{C}C(CH_3)_3$, with Zn/Hg and concentrated HCl

(3) Reacting $CH_3CH_2 - \overset{\overset{O}{\|}}{C} - H$ with HCN

(4) Addition of Br_2 to $CH_3CH_2CH = CH_2$

(5) Addition of dilute NaOH to CH_3CH_2CHO

30. You are provided with 100 cm^3 of ether to extract the insecticide X contained in 100 cm^3 of an aqueous solution. If the volume of ether was used in two successive equal extractions, what is the percentage of X left in the aqueous solution at the end? (Distribution coefficient of X between ether and water is 18).

(1) 1.0 % (2) 2.0 % (3) 5.0 % (4) 10.0 % (5) 20.0 %

- For each of the questions **31** to **40,** one or more responses out of the four responses (a), (b), (c) and (d) given is / are correct. Select the correct response / responses. In accordance with the instructions given on your answer sheet, mark

(1) if only (a) and (b) are correct.

(2) if only (b) and (c) are correct.

(3) if only (c) and (d) are correct.

(4) if only (d) and (a) are correct.

(5) if **any other** number of combinations or response is correct.

Summary of above instructions

1	2	3	4	5
only *(a)* and *(b)* are correct	only *(b)* and *(c)* are correct	only *(c)* and *(d)* are correct	only *(d)* and *(a)* are correct	**Any other** number of responses or combination is correct.

31. Consider the following system in dynamic equilibrium.

$$2A(g) + B(g) \rightleftharpoons 2C(g)$$

Which of the following statement(s) is / are correct about the probable changes in the above system when a little of A is removed at constant temperature?

(*a*) Rate of the forward reaction decreases. (*b*) Rate of the backward reaction increases.

(*c*) Value of K_p decreases. (*d*) Concentration of B increases.

32. Which of the following is correct about $[Co(NH_3)_4(NO)Cl]SO_4$?

(*a*) The co-ordination number of Co in it is 6.

(*b*) It is colourless in aqueous solution.

(*c*) The oxidation number of Co in it is +2.

(*d*) It gives a white precipitate with an aqueous solution of $BaCl_2$.

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33. Which of the following statement(s) is/ are true regarding polymers?

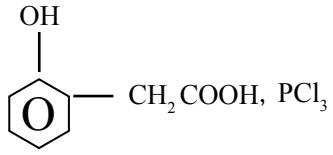
(*a*) Nylon-6,6 is a condensation polymer and is thermostable.

(*b*) The building unit of natural rubber is 2- methylbuta-1,3-diene.

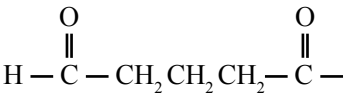
(*c*) Polyester is a linear polymer and is thermoplastic.

(*d*) Teflon is a condensation polymer and is thermostable.

34. In some carbon chains, when there are two functional groups which can react with one another, cyclic molecules are formed by the reaction between them. The reactions between which of the following would give rise to the formation of such cyclic molecules?

(*a*)  CH_2COOH, PCl_3

(*b*) $HOCH_2CH_2CH_2CH_2NH_2$, PCC

(*c*)  (i) $LiAlH_4$ (ii) H_2O

(*d*) $BrCH_2CH_2CH_2C \equiv C - H$, $NaNH_2$

35. Consider the electrochemical cell constructed by the electrodes of metals X and Y under standard conditions. If $E^\circ_{Y^{2+}/Y} = -0.14$ V and $E^\circ_{X^{2+}/X} = 2.57$ V, which of the following statement(s) is / are true?

(*a*) In this cell, electrons flow from X electrode to Y electrode.

(*b*) Oxidation takes place at Y.

(*c*) X electrode is the cathode.

(*d*) In this cell, $E^\circ_{cell} = 2.23$ V.

36. Consider the reaction $A(g) + B(g) \longrightarrow C(g) + D(g)$. For some concentrations of A and B, the initial rate of the reaction is r. When the concentration of A is doubled keeping the concetration of B constant, the rate becomes 2r while when the concentration of B is doubled keeping the concentration of A constant, the rate becomes 4r. Which of the following is / are true about this reaction?

(*a*) It is a first order reaction with respect to B.

(*b*) The rate of consumption of B is greater than the rate of consumption of A.

(*c*) It **cannot** be a one-step reaction.

(*d*) Its overall order is 3.

37. Which of the following statement(s) is /are true about the nitration of benzene and its derivatives?

(*a*) It is an electrophilic addition reaction.

(*b*) Toluene undergoes nitration faster than benzene.

(*c*) The intermediate carbocations formed in these reactions are stabilised by the delocalisation of their positive (+) charge.

(*d*) Chlorobenzene undergoes nitration faster than benzene.

38. Which of the following statement(s) is / are true about the chemistry of compounds containing nitrogen?

(*a*) NH_3 can act as a weak base as well as an acid.

(*b*) An acid and a base are formed by the hydrolysis of NCl_3 .

(*c*) N_2O can be prepared by heating a mixture of NH_4Cl and $NaNO_3$.

(*d*) HNO_2 and HNO_3 are two very strong oxoacids formed by nitrogen.

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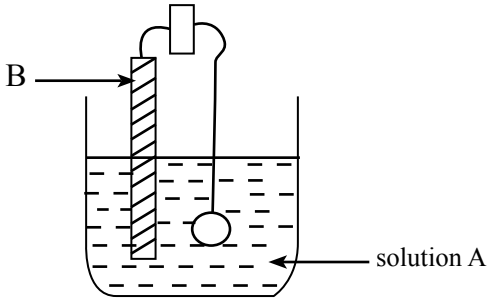
39. What is / are the product (s) formed when sulphur is reacted with aqueous NaOH?

(*a*) Na_2S (*b*) Na_2SO_4 (*c*) H_2O (*d*) $Na_2S_2O_3$

40. It is expected to deposit a very high quality silver plating on an iron ring using the following set up. Which of the following statement(s) is / are true with regard to that process?



(a) The ring should be connected to the positive terminal of the supply cell.

(b) $[Ag(NH_3)_2]NO_3$ solution is more suitable than a $AgNO_3$ solution for A.

(c) The ratio of the current used to the surface area of the ring should be small.

(d) Iron should be used in place of B.

	First Statement	Second Statement
41.	CH_3NH_2 reacts with CH_3MgCl.	CH_3NH_2 can act as a base.
42.	CH_3CH_2Cl is formed when CH_3COCl is reduced by $LiAlH_4$.	$LiAlH_4$ can be used to reduce carboxylic acid derivatives.
43.	In the Solvay process of producing Na_2CO_3, NH_3 gas is passed through brine saturated with CO_2.	The solubility of NH_3 in an aqueous solution saturated with CO_2 is greater than the solubility of NH_3 in water at that temperature.
44.	CH_2=$CHCH_2Br$ shows a greater tendency to undero single step nucleophilic substitution reactions.	CH_2=$CHCH_2Br$ is a primary alkyl halide.
45.	The solublity of an ionic compound in water depends on the hydration enthalpy and lattice enthelpy of its ions.	As the standard lattice enthalpy is greater than the sum of the standard hydration enthalpies of the relevant ions, the standard enthalpy of solution of an ionic compound in water is alway exothermic.
46.	When temperature increases, K_p of the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ increases.	When the temperature of the equilibrium system $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ in a constant volume container is increased, the pressure increases.
47.	The solubility of $Mg(OH)_2$ in a solution prepared by dissolving solid $Fe(OH)_2$ in water is much less than the solubility of $Mg(OH)_2$ in water at that temperature.	The solubility of an ionic compound in an aqueous solution containing a common ion is always less than the solubility of that ionic compound in water at that temperature.
48.	When a little of aqueous HBr acid is added to an excess of an aqueous solution of NaF, a buffer system is obtained.	In aqueous solution, HF is a weak acid and HBr is a strong acid.
49.	The critical temperature of NH_3 gas is greater than the critical temperature of CO_2 gas.	The attractive forces among NH_3 molecules are stronger than the attractive forces among the CO_2 molecules.
50.	A slurry of MgO can be used to scrub the acidic gases emitted by industries.	An aqueous solution of MgO shows strong basic properties.

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G.C.E (A/L) Support Seminar - 2016

Chemistry II

Three hours

Part A - Structured Essay

* Answer **all four** questions on this paper itself.
* Each question carries **10** marks.

Universal gas constant	R	=	$8.314\ J\ K^{-1}\ mol^{-1}$
Avogadro constant	N_A	=	$6.022 \times 10^{23}\ mol^{-1}$
Planck's constant	h	=	$6.626 \times 10^{-34}\ J\ s$
Velocity of light	c	=	$3 \times 10^{8}\ m\ s^{-1}$

1. (a) Q, R and T are three consecutive elements belonging to the p block of the Periodic Table while X, Y and Z are three consecutive elements belonging to the d block of the Periodic Table. The relative atomic mass of all these elements is below 60. The formulae of oxoanions corresponding to the highest oxidation states of elements T and Z are TO_4^- and ZO_4^- respectively. Fill in the blanks of the following sentences.

(i) The true symbol of element X is ..... .

(ii) The ions TO_4^- and ZO_4^- have..... shapes.

(iii) A solution of ..... ions can be used to determine the concentration of ZO_4^- ions in a solution volumetrically.

(iv) The highest oxidation state of R is..... .

(v) A solution of ..... ions can be used to determine the concentration of a solution containing oxoanions corresponding to the highest oxidation state of element R gravimetrically.

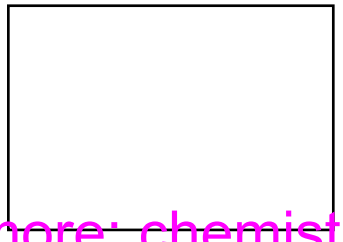
(vi) A solution of TO_4^- ions can be obtained by dissolving the oxide of formula ..... in water.

(vii) The first ionization energy of Q is ..... than the first ionization energy of R.

(viii) As regards the acidic, basic, amphoteric and neutral properties, the oxide corresponding to the highest oxidation state of X is .....

(2.4 marks)

(b) (i) Draw the Lewis structures of the oxalate ion ($C_2O_4^{2-}$) and the dinitrogen tetroxide molecule (N_2O_4).



$C_2O_4^{2-}$

N_2O_4

[See page two

(ii) Based on the above structures, explain why the oxalate ion stays stable whereas N_2O_4 easily dissociates into nitrogen dioxide (NO_2).

.....

.....

.....

.....

(1.9 marks)

(c) J and K are two non – metallic elements placed adjacently in the same group of the p block. J forms a triatomic molecule of molecular formula J_3 while J and K form a compound of molecular formula KJ_2. J_3 and KJ_2 molecules are similar in shape.

(i) Identify the elements J and K.

J - .....

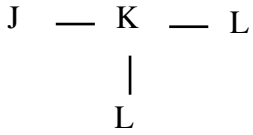
K - .....

(ii) What is the shape of the molecules J_3 and KJ_2 ?

.....

(iii) Draw the resonance (canonical) structures of the J_3 molecule.

(iv) The electronegativity of element L is greater than the electronegativity of J. The elements K, J and L form a molecule having the following skeleton.



Using true symbols,

(I) draw the most acceptable Lewis structure of the above molecule.

(II) state electron pair geometry around the K atom of the above molecule.

.....

(III) state the shape around the K atom of the above molecule.

.....

[See page three

(IV) draw **four** canonical structures for the molecule.

(4.5 marks)

(d) (i) Arrange the following compounds in the ascending order of their covalent character.

$MgBr_2$, $CaCl_2$, BaF_2, $BaCl_2$

.....

(ii) Arrange the following compounds in the ascending order of their solubility in water.

NaOH, $Al(OH)_3$, $Ca(OH)_2$, $Ba(OH)_2$

.....

(1.2 marks)

(Total 10.0 marks)

2. (a) The boiling point of the inorganic compound X which exists as a colourless liquid at room temperature is higher than that of water. When exposed to sunlight, X easily decomposes liberating a gas.

(i) Identify X and write its chemical formula.

.....

(ii) Write the balanced equation for the decomposition of X.

.....

(iii) In both acidic and basic media, X can behave as an oxidizing agent as well as a reducing agent. Write half ionic equations for the reduction of X in acidic medium and basic medium.

in acidic medium:

.....

in basic medium:

.....

(iv) Write balanced ionic equations for the reactions of X with the following compounds.

with Ag_2O in acidic medium:

.....

with $CrCl_3$ in basic medium:

.....

(3.4 marks)

(b) (i) Explain the following statements giving reasons.

(I) Descending the group, the reactivity of alkali metals increases but the reactivity of halogens decreases.

.....

.....

.....

.....

[See page four

(II) Though the first electron affinity of carbon is negative, the first electron affinity of nitrogen assumes a positive value.

.....

.....

.....

.....

(III) In aqueous solution, LiH is basic whereas H_2S is acidic.

.....

.....

.....

.....

(IV) The melting point of V is much greater relative to that of Na.

.....

.....

.....

.....

(ii) Fill in the blanks with suitable words taking into consideration the observations and chemical species relevant to each of the following situations.

(I) An acidic aqueous solution containing As^{3+} and Ni^{2+} ions was saturated with H_2S gas. Then a (A) ..... coloured precipitate could be seen at the bottom of a (B) ..... coloured solution. When this solution was made slightly alkaline a (C) ..... coloured precipitate was formed.

(II) Excess of acidified $FeCl_3$ solution and $CHCl_3$ were added to an aqueous KI solution and shaken well. After the separation of layers a (D) ..... colour could be seen in the $CHCl_3$ layer. Through this mixture SO_2 gas was bubbled for a long time and stirred well. After the separation of layers again, it could be observed that the $CHCl_3$ layer becoming (E) ..... while the aqueous layer turning (F) ..... .

(III) Write the chemical species relevant to the observations from A to F in parts I and II above.

(A) ..... (B) .....

(C) ..... (D) .....

(F) ..... **(4.6 marks)**

(c) Write balanced chemical equations for the reactions of the following compounds with water.

P_4O_{10}, $SiCl_4$, $SbCl_3$, AlN

.....

.....

.....

.....

(2.0 marks)

(Total 10.0 marks)

[See page five

3. One mole each of the gases carbon dioxide and hydrogen were mixed in a constant volume container and allowed to react as follows at the temperature 25 ºC.

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$

Some relevant thermochemical data at 25 ºC are given in the following table.

Substance	$\Delta G_f^{\emptyset}$ / kJ mol^{-1}	$S^{\emptyset}$/ J mol^{-1}K^{-1}
CO(g)	- 137	197.5
$CO_2(g)$	- 394	213.7
$H_2(g)$	0	130.6
$H_2O(g)$	- 229	188.7

(i) Calculate $\Delta G^{\ominus}$ of the above reaction at 25 °C.

.....

.....

.....

(1.2 marks)

(ii) Calculate $\Delta S^{\ominus}$ of the above reaction at 25 °C.

.....

.....

.....

(1.2 marks)

(iii) Thereby, calculate $\Delta H^{\emptyset}$ of the above reaction.

.....

.....

.....

(1.2 marks)

(iv) Does the above reaction occur spontaneously in the derection given?
If the system has to be heated above a certain temperature T(K) in order to make it spontaneously happen in the non spontaneous direction, calculate the value of T.

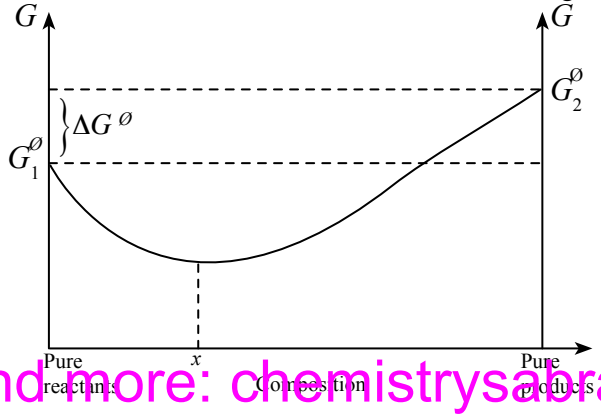
.....

.....

.....

(1.2 marks)

- The following graph illustrates how the Gibbs free energy varies with the composition of the reaction mixture when the above reversible reaction occurs in the given direction.



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(v) What are the values of $G_1^{\ominus}$ and $G_2^{\ominus}$?

.....

.....

(0.4 marks)

(vi) The change in Gibbs energy, ΔG_r relevant to any composition of the reaction is given by the following relationship.

$\Delta G_r = \Delta \overset{\ominus}{G} + 2.303\ RT\ log\ K$

K is the equilibrium constant.

When the system is in dynamic equilibrium deduce that,

$\Delta \overset{\ominus}{G} = -\ 2.303\ RT\ log\ K$

.....

.....

.....

(0.8 marks)

(vii) Calculate the equilibrium constant, K relevant to the above reaction at 25 °C.

.....

.....

.....

(1.0 marks)

(viii) Do you expect any relationship between the value of K and the spontaneity of the reaction at the relevant temperature? Explain.

.....

.....

.....

.....

.....

(1.0 marks)

(ix) Calculate the ratio $\frac{[CO(g)]}{[CO_2(g)]}$ at the composition indicated as x in the above graph.

.....

.....

.....

.....

.....

(2.0 marks)

(Total 10.0 marks)

[See page seven

4. (a) A, B and C are three structural isomers of molecular formula $C_5H_{13}N$. Only B shows optical isomerism. When reacted with $NaNO_2$/HCl A, B and C, gave three structural isomers D, E and F respectively of molecular formula $C_5H_{12}O$ of which E is optically active. When D, E and F were separately treated with the Lucas reagent ($ZnCl_2$ / conc. HCl) a turbidity could be observed instantly with D and after about 5 minutes with E. F gave a slight turbidity after a long time. When heated with concentrated sulphuric acid, F did not give a hydrocarbon but D gave a mixture of two hydocarbons G and H while E gave a mixture of two hydrocarbons G and I. G, H and I are structural isomers of molecular formula C_5H_{10}. G, H and I do not show geometrical isomerism. Draw the structures of A, B, C, D, E, F, G, H and I in the boxes given below. (Drawing stereoisomers is not required.)

A B C

D E F

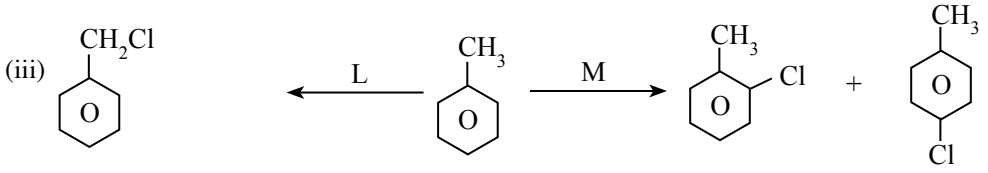
G H I

(3.6 marks)

(b) In the boxes given, write the suitable reagent(s) / catalyst(s) (along with suitable conditions if any) H, I, J, K, L and M in the reactions indicated below.

(i) $CH_3CH_2CH_3 \xleftarrow{H} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I} CH_3-CHOH-CH_3$

(ii) $CH_3CH_2OH \xleftarrow{J} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 \xrightarrow{K} CH_3-\overset{OH}{\overset{|}{\underset{CH_2CH_3}{\underset{|}{C}}}}-CH_2CH_3$

(iii) 

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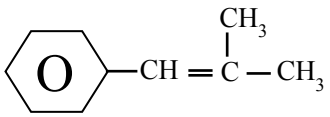
H I J

K L M

(2.4 marks)

(c) (i) Draw in the boxes A and B, the structures of the products of the reaction of the following compound with HBr.



A B

(ii) Draw in the following boxes X and Y, the structures of the intermediate ions which give rise to the above products.

X Y

(iii) Of the ions drawn by you in (ii) above, which is the more stable?

.....

(iv) Of the structures A and B drawn in (i) above, which is the major product?

.....

(v) Hence, write the mechanism of the reaction leading to the formation of the major product.

(4.0 marks)

(Total 10.0 marks)

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Part B - Essay

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

5. (a) A rigid vessel contains the gas A under 27 °C and 3.6×10^5 Pa pressure . Gas A partially dissociates as follows at temperatures above 200 °C.

$2A(g) \rightleftharpoons 2C(g) + P(g) + Q(g)$

This reaction occurs via the following two steps.

$A(g) \rightleftharpoons B(g) + C(g)$ _____ I

$2B(g) \rightleftharpoons P(g) + Q(g)$ _____ II

Though reaction I above occurs at temperatures above 100 °C, reaction II occurs only at temperatures above 200 °C.

The vessel containing the gas A above was heated to 227 °C and the system was allowed to attain equilibrium. The total equilibrium pressure was found to be 1.0×10^6 Pa and at 227 °C the equilibrium constant relating to reaction II is 0.25.

(i) Calculate the initial pressure of A at 227 °C before dissociation.

(ii) Calculate the equilibrium partial pressures of A, B, C and P at 227 °C.

(iii) When the temperature of the system was instantly decreased to127 °C, the amounts of moles of P and Q remained unchanged and the total pressure became 7.4×10^5 Pa. Calculate the partial pressure of P at 127 °C.

(iv) Calculate the partial pressures of A, B and C at 127 °C before coming to the equilibrium.

(v) Calculate the equilibrium partial pressures of A, B and C at 127 °C.

(vi) Calculate K_p relating to equilibrium I at 127 °C.

(vii) If K_p relating to equilibrium I at 227 °C is 4×10^5 Pa, deduce the sign of ΔH for the forward reaction.

(7.5 marks)

(b) (i) Write Faraday's laws of electrolysis.

(ii) State **three** main differences in the chemical process taking place in an electrochemical cell and an electrolytic cell.

(iii) An electrolysis experiment was conduted by passing an electric current of 10 A for 1.0 h through 1.0 dm^3 of a solution of 0.5 mol dm^{-3} HCl solution using inert electrodes.

I. Write anodic reaction, cathodic reaction and overall reaction.

II. Draw a labeled sketch of the apparatus used for this experiment.

III. Write **two** observations you would make during the above experiment.

(iv) Calculate the change in pH resulted at the end of the experiment. State the assumptions you made in your calculation if any.

(v) If the above experiment was conducted in a closed system, comment on the change of entropy occurred in the system.

(vi) At the end of the above experiment, 1.0 dm^3 of a 0.40 mol dm^{-3} NaOH solution was added to the solution and electrolysis was repeated. Write the anodic reaction, cathodic reaction and the overall reaction that would take place at the outset of this experiment.

(Faraday constant = 96 500 C mol^{-1})

(7.5 marks)

(Total 15.0 marks)

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6. (a) $2\ FeCl_3(aq) + 3\ KI(aq) \longrightarrow KI_3(aq) + 2\ FeCl_2(aq) + 2\ KCl(aq)$

In order to find the order of the above reaction with respect to $FeCl_3$ and KI, an experiment was designed using the solutions of following concentrations. Its results are given in the table below.

$FeCl_3$ concentration / mol dm^{-3}	**KI concentration / mol dm^{-3}**	**Rate of the reaction in relation to the formation of KI_3 (R) / mol $dm^{-3}s^{-1}$**
(1) 0.01	0.02	0.08
(2) 0.01	0.04	0.16
(3) 0.02	0.02	0.16

(i) If R is the rate of formation of KI_3 and $R^{/}$ is the rate of consumption of $FeCl_3$, write the relationship between R and $R^{/}$.

(ii) Calculate $R^{/}$ for (1) above.

(iii) Calculate total order for the reaction.

(iv) Calculate the rate constant at the relevant temperature.

(v) Explain briefly the method used to measure the time taken for the formation of a constant amount of KI_3 when designing the above experiment.

(5.4 marks)

(b) $S_2 + B \longrightarrow P$

The above reaction is exothermic and its steps are as follows.

$S_2 \rightleftharpoons 2S$ (fast) _____ (I)

$B + 2S \longrightarrow P$ (slow) _____ (II)

(i) Write the rate equation for the above reaction using the concentration terms of reactants.

(ii) What is the rate determining step of the above multistep reaction?

(iii) Find the order of the reaction with respect to the reactant S_2.

(iv) Draw an energy profile for the mechanism of the above reaction.

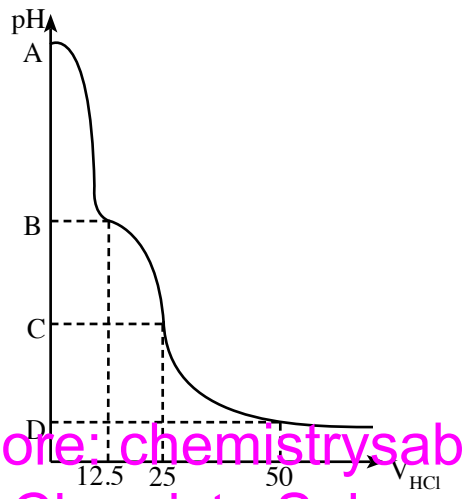
(2.1 marks)

(c) (i) Considering the dissociation of a monobasic weak acid HA in aqueous solution, derive an expression for its dissociation constant, K_a.

(ii) Considering the hydrolysis reaction of the ion A^-, write an expression for the dissociation constant K_b of the base A^-.

(iii) Obtain the relationship among K_a, K_b and the ionic product of water K_w.

(iv) 50.00 cm^3 of a 0.18 mol dm^{-3} HCl solution were gradually added to 25.00 cm^3 of a 0.18 mol dm^{-3} CH_3COONa solution. The following graph sketches the variation of the pH of the medium during this addition.



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Calculate the pH values corresponding to the points A, B, C and D in the graph.

K_a of CH_3COOH = 1.8×10^{-5} mol dm^{-3}

K_w at 25° C = 1.0×10^{-14} mol^2 dm^{-6}

(v) Consider the following aqueous solutions.

P ⟶ 0.1 mol dm^{-3} CH_3COONa

Q ⟶ A solution containing equal volumes of 0.1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} CH_3COONa

R ⟶ A solution containing equal volumes of 0.1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} NaCl

S ⟶ A solution containing equal volumes of 0.1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} HCl

Equal volumes of the above solutions are taken and to each of them 1 cm^3 of a 0.1 mol dm^{-3} HCl solution is added. Arrange the above solutions in the ascending order of the change in pH caused. Considering only the solutions Q and R, explain your answer referring to the graph.

(7.5 marks)

(Total 15.0 marks)

7. (a) i. Though ethanol forms chloroethane with PCl_5 , phenol does not form chlorobenzene with PCl_5.

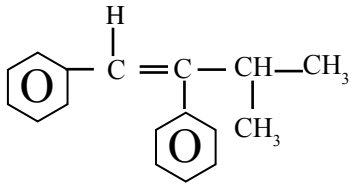
(I) To which category does the reaction of ethanol with PCl_5 belong?

(II) Explain the reasons why phenol does not show the above reaction.

ii. Write the compounds $CH_3CH_2NH_2$, $CH_3CH_2NHCH_2CH_3$, NH_3 and $C_6H_5NH_2$ in the ascending order of their basicity. Give reasons for the proposed variation.

(4.0 marks)

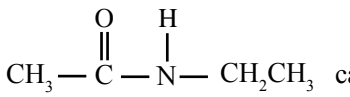
(b) Indicate how the following conversion can be effected using only the given chemicals.

benzaldehyde ⟶ 

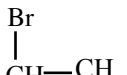
List of chemicals :

dilute NaOH, Al_2O_3, Zn/Hg and HCl, H_2O, CH_3CH_2CHO, Mg, dry ether, PBr_3

(5.5 marks)

(c) Indicate how the compound  can be synthesised through not more than six steps using ethyne as the only organic compound.

(3.5 marks)

(d) Write the structures of all the products that would be formed when the compound  is reacted with CH_3ONa.

(2.0 marks)

(Total 15.0 marks)

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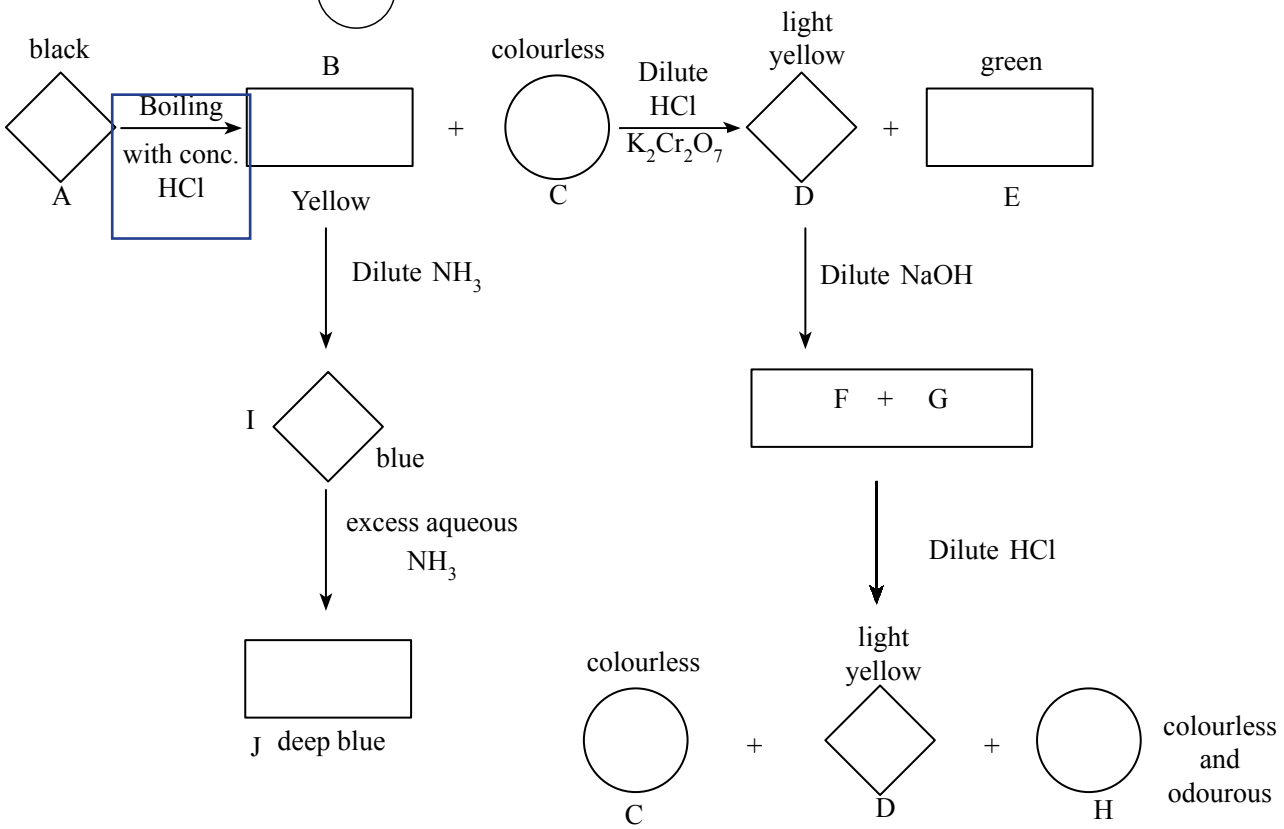
Part C - Essay

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

8. (a) Consider the following reaction scheme. In it, the figures ◇ represent sloid substances, ▭ solutions and ○ gases.



(i) Identify the species A, B, C, D, E, F, G, H, I, J and write their chemical formulae.

(ii) Write the balanced chemical equation for the reaction between D and a dilute NaOH solution.

(iii) Write the balanced ionic equation for the reaction between C and $K_2Cr_2O_7$ in the presence of dilute HCl.

(5.0 marks)

(b) When a solid salt Q giving lilac colour to the Bunsen Flame was thermally decomposed, a mixture of two dark coloured solid substances and a gas X were obtained. Addition of the above solid mixture to an alkaline aqueous solution gave a green solution (R) and a precipitate (W).

(i) Identify the salt Q.

(ii) Write the balanced chemical equation for the thermal decomposition of Q.

(iii) When the basicity of the solution R was reduced by adding an acid to it, the above precipitate W and the anion of Q were formed again. Write the balanced ionic equation relevant to this process. Also write the observations which you expect here.

(iv) The precipitate W was mixed with solid NaBr and acidified with dilute H_2SO_4 . Stating what you expect to see here, write the balanced chemical equation for this reaction.

(3.0 marks)

(c) S is an aqueous solution containing $FeSO_3$ and $FeSO_4$. Solution T was prepared by mixing 50.0 cm^3 of solution S with 50.0 cm^3 of 0.20 mol dm^{-3} H_2O_2 solution.

- Excess of aqueous $BaCl_2$ solution was added to exactly half of the solution T and the mass of the dried precipitate formed on this addition was 0.5825 g.
- To the remainder of the solution T, excess KI solution was added and the volume of the 0.40 mol dm^{-3} $Na_2S_2O_3$ solution needed to react with the I_2 released during this addition was 20.00 cm^3. (Ba = 137, S = 32, O = 16)

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(i) Write balanced ionic equations relating to all the reactions taking place in this experiment.

(ii) Calculate the amount of moles of $BaSO_4$ formed taking the amount of moles of $FeSO_3$ as x and the amount of moles of $FeSO_4$ as y in the solution S, and obtain a relationship for it in terms of x and y.

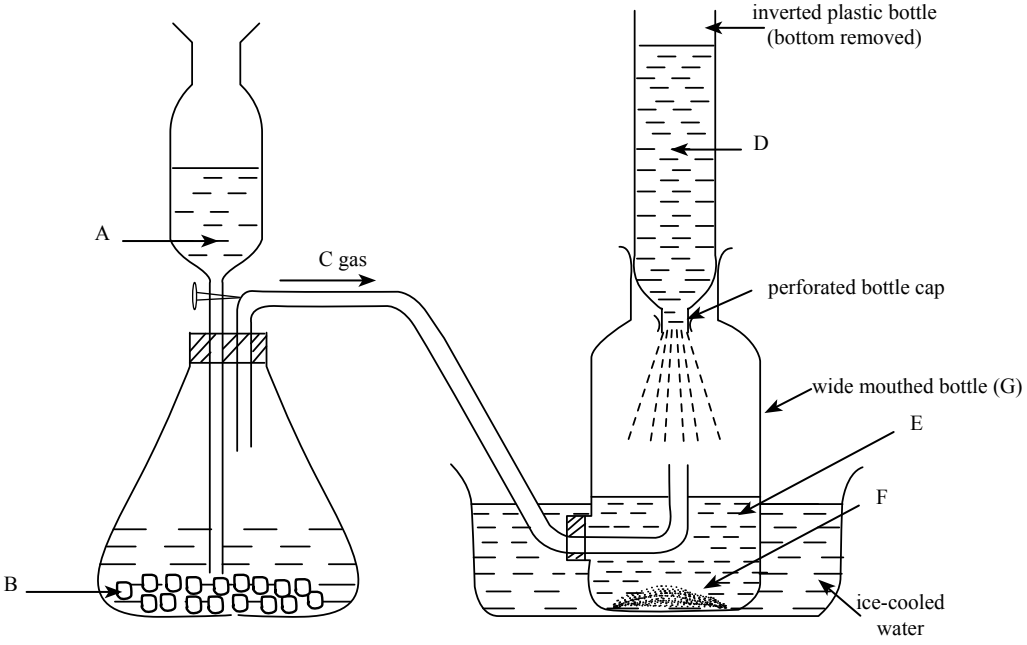
(iii) Obtain an expression for the amount of moles of H_2O_2 left in solution T in terms of x and y.

(iv) Calculate the values of x and y.

(v) Calculate separately the concentrations of $FeSO_3$ and $FeSO_4$ in solution S.

(7.0 marks)
(Total 15.0 marks)

9. (a) A kit of apparatus set up to demonstrate the process of the production of sodium carbonate by the Solvay process in the school laboratory is given below.



(i) Name **two** substances which can be used as *A* and *B*.

(ii) Name the **two** substances, excepting water, that can be used to prepare the solution labeled *D*.

(iii) How does the method used in the Slovay process to produce the gas *C* using limestone as the raw material differ from that adopted in the above set up?

(iv) Name the compound *F*.

(v) Write balanced equations for the reactions happening inside the bottle *D*.

(vi) Explain how each of the following contributes to increase the efficiency of the process.

I. Allowing solution *D* to percolate through tiny pores

II. Making solution *D* and gas *C* to flow in opposite directions as counter currents

III. Cooling the solution in the bottle *G*

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(vii) Write the balanced equation relevant to the production of the final product from the solid *F*.

(viii) Give **two** uses of sodium carbonate.

(ix) The following overall reaction indicates the initial reactants and the final products of the Solvay process.

$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$

According to this equation, calculate the atom economy of the Solvay process.
The atom economy of a process is defined by the following equation.

$$\text{Atom economy} = \frac{\text{Mass of the useful product}}{\text{Total mass of the reactants}} \times 100$$

(C = 12, O = 16, Na = 23, Cl = 35.5, Ca = 40)

(x) As a parameter, what is the importance of atom economy in chemical industry?

(xi) State a solid pollutant, a gaseous pollutant and a non – material pollutant that would be released to the environment during the Solvay process. Give one unfavourable effect that would be caused by each of them on the environment.

(7.5 marks)

(b) The optimum composition of the atmosphere is important to maintain the balance in the environment for the sustainability of earth.

(i) Name the **four** main components of dry air in the atmosphere and state their approximate percentage by volume.

(ii) Name and inorganic gaseous substances that change the composition of dry air in the atmosphere and state one way of releasing each of them to the atmosphere.

(iii) Name the environmental problems brought about by the inorganic gaseous substances you stated in part (ii) above.

(iv) Explain in which way one environmental problem in (iii) above causes damage to marble constructions and metal structures.

(v) State **two** impacts caused by the damages stated in (iv) above on environmental balance.

(vi) State one gaseous substance that would be released to the atmosphere leading to environmental pollution by each of the following chemical industries and briefly explain a chemical course of action that would be taken to minimize their impact on environmental balance.

I. Production of sulphuric acid by the contact process.

II. Production of nitric acid by the Ostwald method.

(7.5 marks)
(Total 15.0 marks)

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10. (a) M is an element belonging to 3d series. The common salts of M show a pink colour in aqueous solutions but turns blue on addition of concentrated hydrochloric acid.

(i) Identify M.

(ii) Write the electron configuration of an atom of M in the ground state using the common notation $1s^2$, $2s^2$ .....

(iii) What are the main oxidation states of M in the compounds it forms?

(iv) Using the formulae of the complex ions responsible for the respective colours, write the ionic equation relevant to the aforesaid colour change taking place on addition of concentrated hydrochloric acid to a solution of a salt of M.

(v) Formulae of two compounds with a complex cation formed by M are as follows.

$[M(NH_3)_2(OH_2)_4]Cl_2$ (A) $\qquad$ $[MCl_2(NH_3)_2(OH_2)_2]Cl$ (B)

I. Write the IUPAC names of compounds A and B.

II. What is the shape around the metal atom in the cations of A and B?

III. If you are provided with two equimolar, dilute soluitons of A and B and a 0.1 mol dm^{-3} silver nitrate solution, explain briefly how you distinguish A and B.

(vi) Draw the structure of the cation formed by the replacement of all the water moleules in cation A by 1, 2 - diaminoethane. You should also show the charge of the ion.

H_2N — CH_2 — CH_2 — NH_2

1, 2 - diaminoethane.

(vii) Suggest a method to obtain a pure sample of metal M from an alloy consisting of M and copper.

(7.5 marks)

(b) A solution has been prepared by dissolving 1.42 g of Na_2SO_4 and 1.50 g of NaI in water and diluting to 2.50 dm^3.

(Na = 23, S=32, O=16, Pb=207, N=14, I = 127)

K_{sp} $[PbI_2]$ $= 1.6 \times 10^{-9}$ mol^3 dm^{-9}

K_{sp} $[PbSO_4]$ $= 1.6 \times 10^{-8}$ mol^2 dm^{-6}

(i) Calculate the concentration of Na^+, I^-, and SO_4^{2-} ions in the above solution.

(ii) By calculation show which compound precipitates first when a $Pb(NO_3)_2$ solution is gradually added to the above solution.

(iii) What is the minimum mass of $Pb(NO_3)_2$ that should be added to the above solution in order to observe the precipitation of the above compound?

(iv) Show that any other compound does not precipitate even when $Pb(NO_3)_2$ is added to the solution till the Pb^{2+} ion concentration is double the valve of that in (iii) above and calculate the mass of the initial compound that has precipitated at this instant?

(v) Calculate the minimum mass of $Pb(NO_3)_2$ that should be added to precipitate all the ions in the solution which can be pecipitated.

(vi) State two assumptions you made in the above calculations.

(7.5 marks)

(15.0 marks)