



தொண்டைமாளாறு வெளிக்கள நிலையம் நடாத்தும்
ஐந்தாம் தவணைப் பரீட்சை - 2022
Conducted by Field Work Centre, Thondaimanaru.
5th Term Examination - 2022

இரசாயனவியல் I
 Chemistry I

Two hours

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I

Gr -13 (2022)

Part - I

1) Consider the following statements I and II.

Statement I :- No two electrons in an atom can have all the four quantum numbers the same.

Statement II:- The positive charge on the nucleus of atoms increases by single electron units.

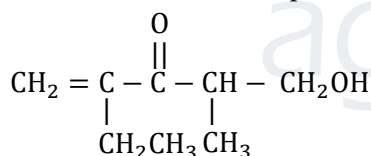
The scientists who put forward the principles relevant to the above statements are respectively.

- | | |
|--------------------------------------|--|
| (1) Niels Bohr and Max Planck | (2) Lewis de Broglie and Albert Einstein |
| (3) Ernest Rutherford and Max Planck | (4) Wolfgang Pauli, and Jeffrey Moseley |
| (5) Max Planck and Albert Einstein | |

2) The correct ascending order of the first ionization energies of the elements B, C, N, P, S and Cl is

- | | |
|----------------------------|----------------------------|
| (1) B < C < N < P < S < Cl | (2) B < N < C < P < S < Cl |
| (3) B < S < P < C < Cl < N | (4) N < P < S < C < Cl < B |
| (5) S < P < C < Cl < B < N | |

3) The IUPAC name of the compound



- (1) 4-ethyl-1-hydroxy-2-methylpent-4-en-3-one
- (2) 1-hydroxy-2-methyl-4-enylhexan-3-one
- (3) 2-ethyl-5-hydroxy-4-methyl-1-penten-3-one
- (4) 4-ethyl-2-methyl-3-oxopent-4-en-1-ol
- (5) 2-ethyl-5-hydroxy-4-methyl-3-oxopent-1-ene

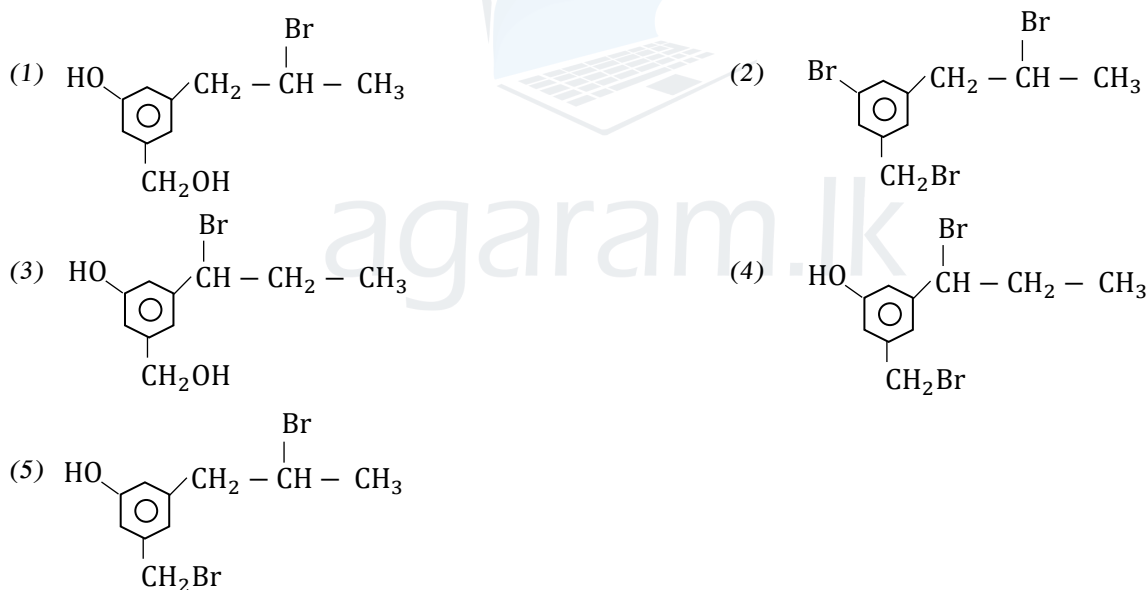
4) Which of the following statements regarding CH₄, NH₃ and H₂O, the hydrides of the elements C, N, O belonging to the second period, is correct?

- (1) The strength of their intermolecular forces follow the order CH₄ < H₂O < NH₃
- (2) All the three have tetrahedral electron pair geometry
- (3) Each of them has the highest boiling point among the hydrides in their respective groups.
- (4) Their bond angles are in the order CH₄ < NH₃ < H₂O
- (5) The central atoms in them are in different hybrid states.

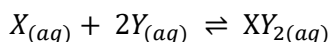
- 5) The correct statement regarding the S – block elements and their compounds.
- (1) All metals belonging to S – block liberate H_2 gas in their reaction with water.
 - (2) All metals belonging to S–block react with $NH_3(g)$ to produce amides with the liberation of H_2 gas
 - (3) All alkali metal carbonates are thermally stable.
 - (4) When heated, aqueous solutions of the bicarbonates of group 2 elements decompose without changing into solid state.
 - (5) All S – block metals form strongly alkaline hydrides with H_2 gas.

- 6) The incorrect statement regarding the 3d – elements.
- (1) The cations of Cr, Mn and Fe do not easily form ammine complexes with excess $NH_3(aq)$.
 - (2) Across the period, their atomic radii decrease from Sc to Ni and then increase.
 - (3) Their electronegativity values are greater than those of 4S elements.
 - (4) Their electronegativity values increase continuously from Sc to Zn.
 - (5) Their oxy anions in their highest oxidation states act as oxidizing agent.

- 7) The major product obtained when the compound $HO-C_6H_3(CH_2OH)-CH=CH-CH_3$ is reacted with excess HBr.



- 8) 1 dm^3 water sample containing 0.8 mol X and 0.5 mol Y was shaken well with 500 cm^3 of CCl_4 . During this, only the solute X gets distributed between the two solvents and, the following dynamic equilibrium is established between X and Y in aqueous layer.



The distribution coefficient of X between CCl_4 and water is 2 and $[X]_{CCl_4}$ is found to be 0.6 mol dm^{-3} . The equilibrium constant K_c (in $\text{mol}^{-2}\text{dm}^6$) for the above equilibrium is

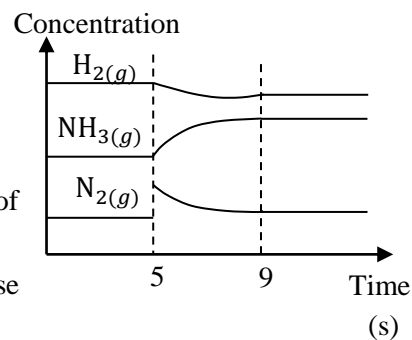
- (1) 333 (2) 100 (3) 4 (4) 66.7 (5) 125

- 9) A is a water soluble inorganic salt. When A is dissolved in dilute HCl, a coloured solution Q and a colourless gas G are obtained. Addition of concentrated HCl to the solution Q resulted in the formation of a yellow coloured solution. When gas G is passed into an aqueous solution of Br_2 , it was decolourized with the formation of a solution T. When $\text{Ba}(\text{NO}_3)_2(\text{aq})$ is added to solution T in the presence of dilute HNO_3 , a white precipitate is formed, Which of the following can possibly be A?
 (1) $\text{Ni}(\text{NO}_2)_2$ (2) NiSO_3 (3) CuCO_3 (4) CuCl_2 (5) CuSO_4
- 10) When 1.93mA current was passed through 500 cm^3 of 0.1 moldm^{-3} aqueous solution of NaCl at 25°C , the pH of the solution after a certain time was found to be 12. The time for which the current was passed is ($1\text{F} = 96,500 \text{ Cmol}^{-1}$)
 (1) $5 \times 10^5 \text{ s}$ (2) $4 \times 10^4 \text{ s}$ (3) $3 \times 10^4 \text{ s}$ (4) $2.5 \times 10^5 \text{ s}$ (5) $1 \times 10^4 \text{ s}$
- 11) At 25°C molar solubility of a sparingly soluble solid $\text{M}(\text{OH})_2$ is $s \text{ moldm}^{-3}$. By dissolving a soluble ionic solid MCl_2 into 1 dm^3 of a saturated solution of $\text{M}(\text{OH})_2(\text{s})$ if the OH^- ion concentration is to be halved its original concentration, the amount (in mole) of $\text{MCl}_2(\text{s})$ to be dissolved.
 (1) 1.5 s (2) 2 s (3) 3 s (4) 3.5 s (5) 4 s
- 12) The incorrect statement regarding $\text{C}_6\text{H}_5\text{NH}_2$ (aniline)
 (1) It is more basic than amides.
 (2) It can act as a nucleophile
 (3) Its basicity is greater than that of $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.
 (4) It reacts with CH_3CHO and gives the compound $\text{C}_6\text{H}_5 - \text{N} = \text{CH} - \text{CH}_3$.
 (5) It forms white precipitate with $\text{Br}_2(\text{aq})$.
- 13) Consider the following electrochemical cell
 $\text{Pt}_{(\text{s})} | \text{Y}_{(\text{aq})}^{3+}, \text{Y}_{(\text{aq})}^{2+} || \text{XO}_{4(\text{aq})}^-, \text{X}_{(\text{aq})}^{2+}, \text{H}_{(\text{aq})}^+ | \text{Pt}_{(\text{s})}$
 When electricity is generated from the above cell, which one of the following statements is correct?
 (1) XO_4^- gets reduced to $\text{X}_{(\text{aq})}^{2+}$.
 (2) Electric current flows from Pt immersed into aqueous solution containing $\text{Y}_{(\text{aq})}^{2+}$ and $\text{Y}_{(\text{aq})}^{3+}$ towards the Pt immersed into $\text{XO}_{4(\text{aq})}^-$ and $\text{X}_{(\text{aq})}^{2+}$.
 (3) Y^{3+} gets reduced to Y^{2+}
 (4) H^+ is oxidized to H_2 .
 (5) The standard reduction potential of $\text{XO}_{4(\text{aq})}^- / \text{X}_{(\text{aq})}^{2+}$ is less than that of $\text{Y}_{(\text{aq})}^{3+} / \text{Y}_{(\text{aq})}^{2+}$.
- 14) Which one of the following statements regarding the rate of a reaction and the catalyst is true?
 (1) The rate of reaction will always increase when the concentration of any of the reactants is increased.
 (2) Rate of a reaction having lower activation energy is always greater than that with higher activation energy.
 (3) The rate of a reaction with high activation energy can be increased only by use of a catalyst.
 (4) Overall rate of a reaction is given by the average of all the rates of individual steps involved in that reaction.
 (5) A catalyst changes the value of the rate constant and it may change the mechanism of the reaction as well.

- 15) The following graph shows the variation of the concentration of the species with time in the equilibrium system $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

The correct statement about the above equilibrium system

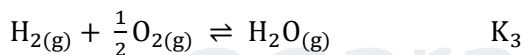
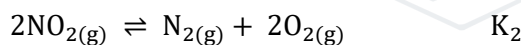
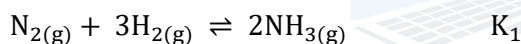
- (1) In the 5th second, some $H_{2(g)}$ is inserted into the system.
- (2) In the 5th second some $N_{2(g)}$ is removed from the system.
- (3) In the time interval 5 s – 9 s reaction quotient $Q_C < K_C$.
- (4) Before 5s, rate of forward reaction is greater than the rate of reverse reaction.
- (5) After 9s, the rate constants of both the forward and reverse reactions are equal.



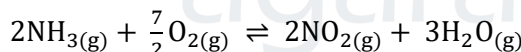
- 16) The incorrect statement regarding the chemistry of group 13 elements / their compounds.

- (1) None of the elements belonging to this group can be regarded as an absolute non – metal.
- (2) Stability of +3 oxidation state decreases down the group.
- (3) Some of the metallic oxides in the group are amphoteric.
- (4) When an aqueous solution of $AlCl_3$ is treated with $Na_2CO_{3(aq)}$, gas evolution is the only observation.
- (5) $AlCl_3$ may act as a Lewis acid.

- 17) Given below are three equilibrium reactions that exist at constant temperature. The equilibrium constants for the reactions at that temperature are indicated against them



What is the equilibrium constant in terms of K_1 , K_2 and K_3 for the following equilibrium reaction?



- (1) $K_1K_2K_3^3$ (2) $\frac{K_1K_2}{K_3^3}$ (3) $\frac{K_3^3K_2}{K_1}$ (4) $\frac{K_3^3}{K_1K_2}$ (5) $\frac{K_1K_2}{K_3}$

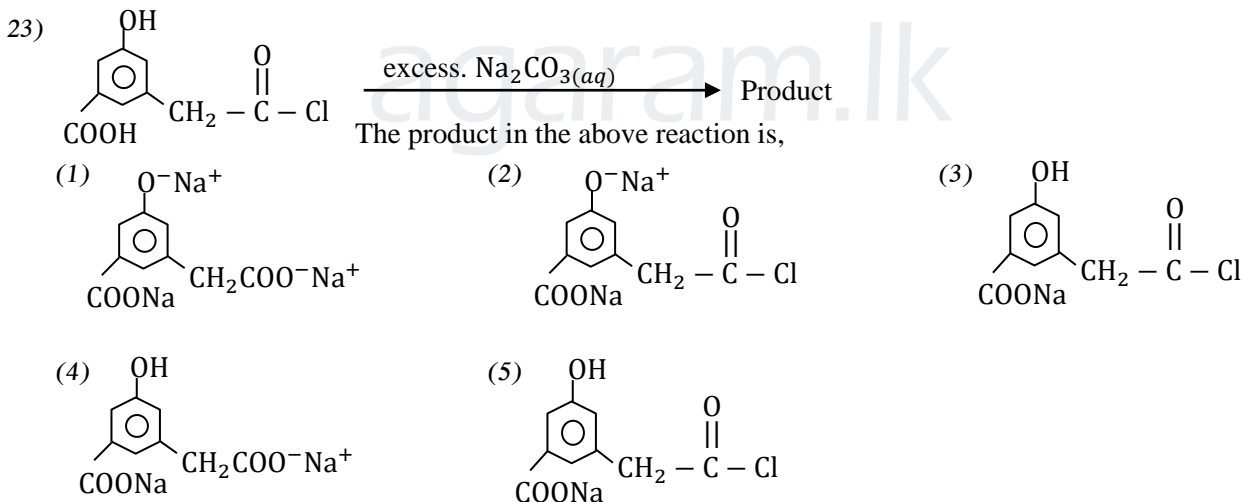
- 18) $AlCl_2$ is a sparingly soluble ionic solid. At a given temperature, its $K_{sp} = 4 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$. Which of the following statements regarding a saturated solution of $AlCl_2$ at that temperature is correct?

- (1) Concentration of Cl^- ions in the solution cannot be increased above $2 \times 10^{-4} \text{ mol dm}^{-3}$.
- (2) If $NaCl_{(s)}$ is added, the equilibrium shifts backward so that Cl^- ion concentration remains unchanged.
- (3) When water evaporates from the solution, the concentrations of A^{2+} and Cl^- ions in the solution will change.
- (4) Chloride ion concentration of the solution cannot be lowered by adding distilled water and maintaining the saturated condition.
- (5) A^{2+} ion concentration in the above solution is always $1 \times 10^{-4} \text{ mol dm}^{-3}$ in whatever temperature.

- 19) If the root mean square speed of $H_{2(g)}$ is $\sqrt{7}$ times the root mean square speed of $N_{2(g)}$ and T denotes the absolute temperature of the gas, which one of the following is the correct relationship?

- (1) $T_{(H_2)} = T_{(N_2)}$ (2) $T_{(H_2)} > T_{(N_2)}$ (3) $T_{(H_2)} < T_{(N_2)}$
 (4) $T_{(H_2)} = \sqrt{7} T_{(N_2)}$ (5) $T_{(H_2)} = 7 T_{(N_2)}$

- 20) The incorrect statement regarding H_2O_2
- (1) When heated, it undergoes disproportionation.
 - (2) Its boiling point is greater than that of $\text{OH} - \text{CH}_2 - \text{CH}_2 - \text{OH}$ (glycol).
 - (3) Ag_2O oxidizes H_2O_2 to O_2 .
 - (4) H_2O_2 can act as a bleaching agent as well as an antiseptic.
 - (5) $\text{O} - \text{O}$ bond length in H_2O_2 is longer than the same in O_2F_2 .
- 21) The correct statement regarding the reaction in which an ester is formed by the reaction between a carboxylic acid and an alcohol.
- (1) In this reaction, nucleophilic addition takes place first followed by nucleophilic substitution.
 - (2) $\text{O} - \text{H}$ bond in carboxylic acid is broken in the reaction.
 - (3) Overall reaction may be interpreted as a nucleophilic addition of a carbonyl compound.
 - (4) It is an acid - base reaction
 - (5) Nucleophilic addition followed by elimination takes place in this reaction in which alcohol acts as a nucleophile.
- 22) If 50cm^3 of a weak acid HA of concentration 0.2mol dm^{-3} is mixed with 50cm^3 of another weak acid HB of concentration 2mol dm^{-3} at 25°C , the concentration of H_3O^+ ions in the resulting solution (in mol dm^{-3}). (Give that K_a values of HA and HB at 25°C are $1 \times 10^{-5}\text{mol dm}^{-3}$ and $1 \times 10^{-6}\text{mol dm}^{-3}$ respectively)
- (1) 1×10^{-3}
 - (2) 1.41×10^{-3}
 - (3) 2×10^{-3}
 - (4) 1.5×10^{-3}
 - (5) 1.2×10^{-3}

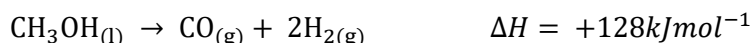


- 24) In which of the following reactions a compound with two asymmetric (Chiral) carbon atoms is formed?
- (1) Adding a dilute base to $\text{CH}_2 = \text{CH} - \text{CH}_2\text{CH}_2\text{Cl}$
 - (2) Allowing $\text{CH}_3\text{C}(=\text{O}) - \text{C}(\text{CH}_3)_3$ to react with Zn / Hg , conc. HCl
 - (3) Reacting $\text{CH}_3\text{CH}_2 - \text{CHO}$ with HCN .
 - (4) Reacting $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$ with Br_2
 - (5) Adding dilute NaOH to $\text{CH}_3\text{CH}_2\text{CHO}$

25) At 25°C , 25.00cm^3 of 0.2mol dm^{-3} NH_4OH solution is titrated against 0.05mol dm^{-3} HCl solution from (burette). Which of the following statements regarding this titration is not true? (at 25°C K_b of $\text{NH}_3 = 1 \times 10^{-5}\text{mol dm}^{-3}$, $\log 3 = 0.4770$)

- (1) The pH of the solution in the titration flask when 25cm^3 of HCl is added is 9.477.
- (2) At the stage when 25cm^3 of HCl is added, the resulting solution will act as a buffer.
- (3) In the above titration, the pH at the equivalence point will be less than 7.
- (4) If the resulting solution at the equivalence point of this titration is diluted with distilled water, pH will decrease.
- (5) To determine the end point of this titration, methyl orange is a suitable indicator.

26) $\text{CH}_3\text{OH}_{(l)}$ may undergo decomposition as CO and H_2 gases at high temperature according to the following equation.



Which of the following is not true regarding the above reaction? (H = 1, C = 12, O = 16)

- (1) When 64 g of $\text{CH}_3\text{OH}_{(g)}$ decomposes as above, the heat absorbed is less than 256 kJ.
- (2) The enthalpy of $\text{CH}_3\text{OH}_{(l)}$ is less than the total enthalpy of $\text{CO}_{(g)}$ and $2\text{H}_{2(g)}$.
- (3) The above reaction is spontaneous at any low temperature.
- (4) When 128 g of $\text{CH}_3\text{OH}_{(l)}$ dissociates as above, 512 kJ of heat is absorbed.
- (5) If the above reaction takes place in closed container, the enthalpy of the system will increase.

27) Consider the following solutions.

- A. Pure ethanol
- B. An aqueous solution of glucose in which the mole fractions of each of glucose and water are 0.5
- C. A solution of glucose and ethanol with mole fraction 0.5 each.
- D. Pure diethyl ether.

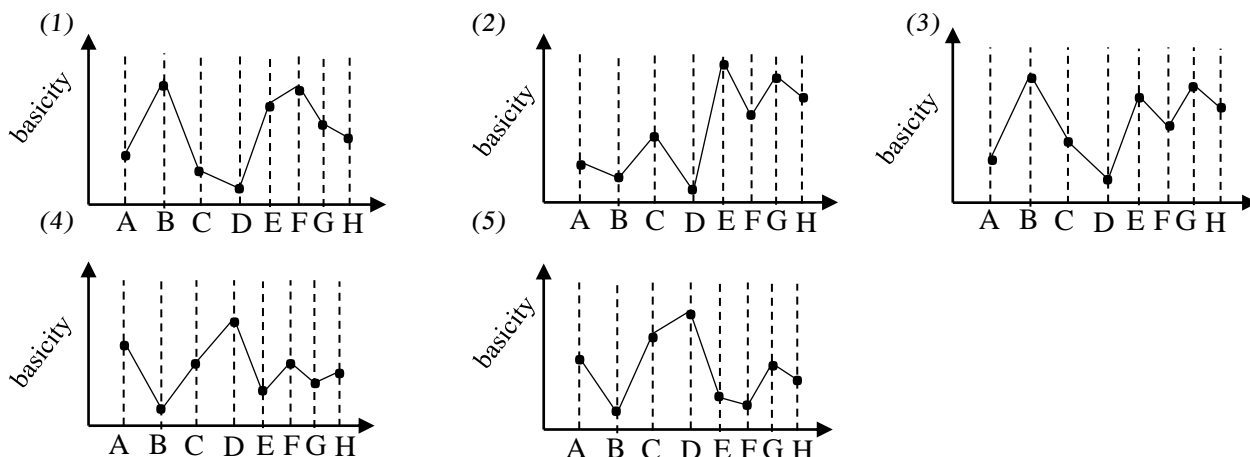
The increasing order of the boiling points of the above solutions is,

- (1) $A < B < C < D$
- (2) $D < A < B < C$
- (3) $C < D < B < A$
- (4) $B < C < D < A$
- (5) $D < A < C < B$

28) Consider the following compounds.

- | | | | |
|--|---|------------------------------|------------------------------|
| (A) H_2O | (B) $\text{CH}_3\text{CH}_2\text{MgBr}$ | (C) CH_3OH | (D) CH_3COOH |
| (E) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ | (F) $\text{CH}_3\text{NH}-\text{CH}_2\text{CH}_3$ | (G) CH_3NH_2 | (H) NH_3 |

Which of the following graphs best represents the variation of the basicity of the above compounds?



29) At a constant temperature, a buffer solution of $\text{pH} = 5$ was prepared by mixing equal volumes of a 0.1 mol dm^{-3} mono basic weak acid HA and a 0.1 mol dm^{-3} solution of its sodium salt NaA. When 20 cm^3 of this buffer solution was taken and a certain volume of 0.1 mol dm^{-3} HA was added into it, the pH of the resultant solution changed by one unit. The volume of the weak acid HA added and the pH of the solution after, addition of HA are respectively,

- (1) 100 cm^3 , 6 (2) 90 cm^3 , 4 (3) 90 cm^3 , 6
(4) 20 cm^3 , 4 (5) 20 cm^3 , 6

30) Two liquids A and B can form an ideal solution. In a mixture of A and B which is in equilibrium with its vapour, the mole percentage of A in liquid phase is 25 % and the mole percentage of it in gaseous phase is 50 %. The ratio of the saturated vapour pressures of pure A and pure B, $\frac{P_A^0}{P_B^0}$ is,

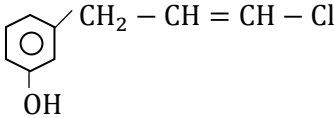
- (1) 3 (2) $\frac{1}{3}$ (3) $\frac{1}{2}$ (4) $\frac{1}{4}$ (5) $\frac{3}{4}$

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

1	2	3	4	5
Only (a) (b) are correct	Only (b) (c) are correct	Only (c) (d) are correct	Only (a) (d) are correct	The other numbers correct

31) The correct statement / statements regarding reaction kinetics is / are

- (a) A catalyst decreases the activation energy of a given reaction and thereby increases the rate of it
(b) Half life of a zeroth order reaction depends on the initial concentration of the reactant.
(c) When the concentration of one of the reactants is in large excess compared to the other, the rate of the reaction becomes independent of the concentration of that reactant.
(d) Rate order with respect to a particular reactant in a reaction may be zero and the molecularity of a reaction can also be equal to zero.

32) The correct statement / statements regarding the compound  is / are?

- (a) A Grignard reagent can be prepared by treating it with Mg / dry ether.
(b) A compound which shows enantiomers can be obtained by reacting it with HBr.
(c) It does not undergo nucleophilic substitution reaction with aqueous NaOH.
(d) It undergoes addition reactions only.

33) MX is a sparingly soluble ionic solid and HX is a weak acid of very low dissociation. The correct statement / statements regarding them is / are.

- (a) MX dissolves well in strong acids.
(b) Addition of $\text{HNO}_3(\text{aq})$ to a saturated solution of MX may sometimes decrease the H^+ ion concentration.
(c) If an aqueous solution of M^+ is added to $\text{HX}(\text{aq})$, the pH of it will increase.
(d) When $\text{HX}(\text{aq})$ is added into a saturated solution of MX, always a precipitation will occur.

- 34) Which of the following statements is / are true regarding an aqueous solution containing Sn^{2+} , Mg^{2+} and Zn^{2+} ions?
- Into a solution of it acidified with HCl, if H_2S gas is passed, a yellow precipitate will form.
 - Passing H_2S gas through the above solution in alkaline medium, results in the precipitation of ZnS only.
 - When a mixture of NH_4Cl and NH_4OH is added to it, Mg^{2+} ions will not be precipitated. However, if NH_4OH is only added first and then NH_4Cl added, the precipitate formed would dissolve in NH_4Cl .
 - A constant precipitate may be observed when adding excess $Ba(OH)_2(aq)$ into the solution.
- 35) The correct statement / statements regarding gases is / are
- Number of collisions with the container wall at a given time is proportional to the density of the gas.
 - At Boyle's temperature, for a large range of pressure, the compressibility factor will be equal to one.
 - Real gases can be liquefied at temperature greater than critical temperature by applying high pressure.
 - The constant a appearing in the correction factor for pressure in van – der Waals equation for real gases depends on the magnitude of the intermolecular forces and independent of the temperature or pressure.
- 36) At T K, the equilibrium $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ exists at constant pressure. At constant temperature, a certain amount of $He_{(g)}$ is inserted into the above constant pressure equilibrium system. Which of the following statements regarding the above system is incorrect?
- Initially, the partial pressures of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ will increase.
 - Until the new equilibrium is achieved $Q_p > K_p$.
 - The amounts of $N_{2(g)}$ and $H_{2(g)}$ would increase until the new equilibrium will be attachment
 - The equilibrium position will be unchanged as partial pressures of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ remain constant.
- 37) Which of the following compounds is / are more soluble in acidic aqueous solution than water?
- $PbSO_4$
 - CuS
 - PbC_2O_4
 - AgCl
- 38) The correct statement / statements regarding hybridization, shape and electron pair geometry of some species is / are
- The electron pair geometry around the central atom of the I_3^- ion is trigonal bipyramidal.
 - The central atom of N_2O is SP^2 hybridized.
 - The central atom of ClF_3 molecule has one lone pair electron.
 - $XeOF_4$ molecules has square pyramidal shape.
- 39) Which of the following statements regarding group 17 elements is incorrect/?
- Their bond dissociation enthalpies follow the order $F_2 > Cl_2 > Br_2$.
 - Except fluorine, all the other elements exhibit stable oxidation states from -1 to +7 in their compounds.
 - An aqueous solution of the compound formed in the reaction between $NH_{3(g)}$ and excess $Cl_{2(g)}$ shows bleaching properties.
 - Cl_2 , Br_2 and I_2 can be prepared by reacting concentrated H_2SO_4 with KCl, KBr, and KI respectively.

- 40) The correct statement / statements pertaining to a mixture of ethanol and water is / are.
- Heat is absorbed during the formation of the mixture,
 - The plot of boiling point against composition of the mixture has a minimum constant boiling point azeotropic mixture
 - The boiling point of the mixture is always between the boiling points of pure ethanol and pure water.
 - The total volume of the mixture is equal to the sum of the individual volumes of ethanol and water mixed.

❖ Instructions for questions 41 – 50.

Response	First statement	Second statement
1)	True	True and correctly explains the first statement.
2)	True	True, but does not explain the first statement correctly
3)	True	False
4)	False	True
5)	False	False

	First Statement	Second Statement
41)	In the reaction of $CH_3 - NH_2$ with Grignard's reagent in the presence of dry ether, alkane can be obtained.	The alkyl group in Grignard's reagent is a good nucleophile.
42)	Of the sparingly soluble compounds PbI_2 and PbC_2O_4 , although $PbSO_4$ dissolves in dilute HNO_3 , PbI_2 doesn't dissolve in it.	If the anion of a sparingly soluble salt is a conjugate base of a strong acid, the solubility of that salt never increases in acidic medium.
43)	The cation and anion of the electrolyte solution used in the salt bridge should have almost the same mobility.	Although a liquid junction potential arises when the cathodic and anodic compartments are separated by a membrane, its effect is minimized in salt bridge.
44)	The basicity of CH_3COO^- ion is greater than that of CH_3O^- ion.	CH_3COO^- ion is stabilized due to resonance.
45)	Addition of an aqueous solution of $NaHCO_3$ into an aqueous solution of $Al^{3+}_{(aq)}$ results in the formation of white gelatinous precipitate.	The concentration of OH^- ions formed due to partial hydrolysis of HCO_3^- ions is sufficient to precipitate Al^{3+} ions as $Al(OH)_3$.
46)	In the equilibrium system $2AO_{(g)} + Br_{2(g)} \rightleftharpoons 2AOB_{(g)}$, if the pressure is increased by decreasing the volume at constant temperature, rates of both forward and reverse reactions will increase	The equilibrium position of this equilibrium system, shifts to the right with the increase in pressure at constant temperature

47)	When $CH_3COOH_{(aq)}$ (dissociation constant K_c) is titrated against $NH_{3(aq)}$ (dissociation constant K_b), pH at the equivalence point can be given by $pH = 7 + \frac{1}{2}(pK_a - pK_b)$	n aqueous solution of a weak acid – weak base salt may be acidic or basic depending on the K_a and K_b values of the relevant acid or base.
48)	Ethylamine and ethanamide cannot be differentiated using $NaOH_{(aq)}$	The basicity of ethylamine is greater than that of ethanamide.
49)	When CH_3COONa is added into CH_3COOH aqueous, the acidity of the solution decreases.	When an aqueous solution of weak acid is diluted, at constant temperature, its pH and the extent of ionization will increase.
50)	Geometric isomers are a type of diastereo isomers.	All the non – superimposable stereo isomers, which are not mirror images of each other, are geometric isomers.



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தொண்டைமாளாறு வெளிக்கள நிலையம் நடாத்தும்

ஐந்தாம் தவணைப் பரீட்சை - 2022

Conducted by Field Work Centre, Thondaimanaru.

5th Term Examination - 2022

இரசாயனவியல் II A

Chemistry II A

Three Hours and
10 minutes

02

E

IIA

Gr -13 (2022)

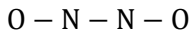
Part – II A

Structured Essay

1) (a) Write the correct answers for the following questions in the spaces provided against them.

- (i) Of the ions Li^+ , Na^+ , Be^{2+} and Mg^{2+} , the one which evolves the highest amount of energy during hydrolysis
- (ii) The element with the lowest melting point among Sc, Ti, Cr and Mn
- (iii) The molecule having smallest bond angle among H_2S , SO_2 , SF_2 and NO_2 is
- (iv) Which of the species O_3 , H_3O^+ , H_2O and OF_2 contains oxygen with the least electronegativity?
- (v) Among the four elements Si, P, S and Cl, which one has the highest second ionization energy?
- (vi) Of the species Cl_2 , concentrated H_2SO_4 , MnO_2/H^+ , and H_2O_2 , which one has the highest oxidizing ability?

(b) I. NO is a gas that contributes to depletion of ozone layer and the formation of photochemical smog. At low temperatures, two NO molecules associate to form N_2O_2 . The skeleton of N_2O_2 molecule is given below.



i) Draw the most acceptable Lewis structure for the above molecule

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ii) Draw five other resonance structures for the molecule drawn in Part (i) above.

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iii) The reaction $2\text{NO}_{(g)} \rightarrow \text{N}_2\text{O}_{2(g)}$ is spontaneous at low temperatures but as the temperature is increased, it is not so. Explain this with the help of thermo dynamic principles

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II. Draw the most acceptable Lewis structure for SF_2NO^- ion

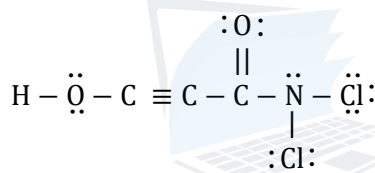
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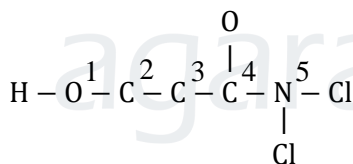
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III. Complete the following table based on the Lewis structure given below



The atoms in the above molecule are numbered as follows



		O ¹	C ²	C ³	C ⁴	N ⁵
(i)	VSEPR pairs around the atom					
(ii)	Electron pair geometry around the atom					
(iii)	Shape					
(iv)	Hybridization of the atom					
(v)	Oxidation state of the atom					

- (c) The energy of a particular energy level in Hydrogen atom is defined as the energy required to bring an electron from infinity to the energy level concerned and it is given by the equation

$$E = -hcR_H\left(\frac{1}{n^2}\right)$$

Where h = Planck's constant

c = Speed of light

R_H = Rydberg constant

n = Principal quantum number for the energy level

- i) What is the energy of a mole of electrons in the first main energy level of H atom? (Given that $hcR_H = 2.18 \times 10^{-18} \text{ J}$)

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- ii) Hence, calculate the first ionization energy of hydrogen.

(Hint : The energy emitted / absorbed when electron jumps from one energy level to another is given the equation

$$E_f - E_i = \Delta E = -hcR_H\left[\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\right]. \text{ Where } n_f = \text{ final energy level, } n_i = \text{ initial energy level}$$

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- iii) Using the equation given in part (ii) above, find the energy change associated with the line corresponding to the highest wave length among the lines in Balmer series and calculate its frequency. What is the colour of this line?

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- 2) (a) The element A belongs to S- block of the periodic table. The nitride of A is red in colour. In the thermal decomposition of the nitrate of A, a brown coloured gas P was liberated. Another element B is in the same group of A and is immediately below A in the periodic table and its nitrate does not give such a brown coloured gas during thermal decomposition. The element C,D and E also belong to S- block but they are not in the group to which B belongs. All these three elements impart colours in flame test. The solubility of the oxalates of C,D and E follows the order $C < E < D$.

- i) Identify the elements A to E

A B C D E

ii) Mention the colours imparted by the elements C,D and E in the flame test

C = D = E =

iii) State the chemical name of the gas P and write balanced chemical equations for the thermal decomposition of the nitrates of A and B

Gas P :

Nitrate of A :

Nitrate of B :

iv) Write balanced equation for the reaction of the nitride of A with water

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v) Mention a test and its observation to identify the gas evolved in part (iv) above

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vi) The above mentioned gas reacts with Cl_2 gas under certain conditions and the aqueous solution of the product formed shows bleaching property.

Explain this with suitable equations.

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vii) Write the ascending order of the following properties concerned with the element C,D and E

I. Thermal stability of carbonates < <

II. Solubility of sulphates in water < <

III. Solubility of Oxalates in CH_3COOH < <

(b) Aqueous solutions of the following compounds are labelled as A to E (not in that order)

$Pb(NO_3)_2$, $MnCl_2$, $Zn(NO_3)_2$, $NaOH$, $Na_2S_2O_3$

Some experiments to identify the above compounds and the relevant observations are given below.

	Experiment	Observation
(1)	Addition of C slowly into B.	A white precipitate formed and it dissolved in excess C.
(2)	Mixing the solutions B and E	A white precipitate formed which turned black on standing for some time.
(3)	Adding C into D.	Formation of a white precipitate which turned (blackish) brown.
(4)	Mixing A and D.	A clear solution

i) Identify A, B, C, D and E

A = B = C =

D = E =

ii) If the compound A is heated in solid state and the residue is allowed to cool, mention an observation other than the evolution of gas.

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iii) Write balanced equations for the reactions involved with the formation of precipitates in the above table.

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iv) Write the chemical equation for the reaction responsible for the colour change of the precipitates in experiment (2)

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v) Mention 2 observations when $HCl_{(aq)}$ is added to solution E.

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(c) State whether the following statements are true or false. (Reasons are not required)

i) Although the reactivity of alkaline metals increases down the group, reactivity of halogens shows the opposite trend down the group. ()

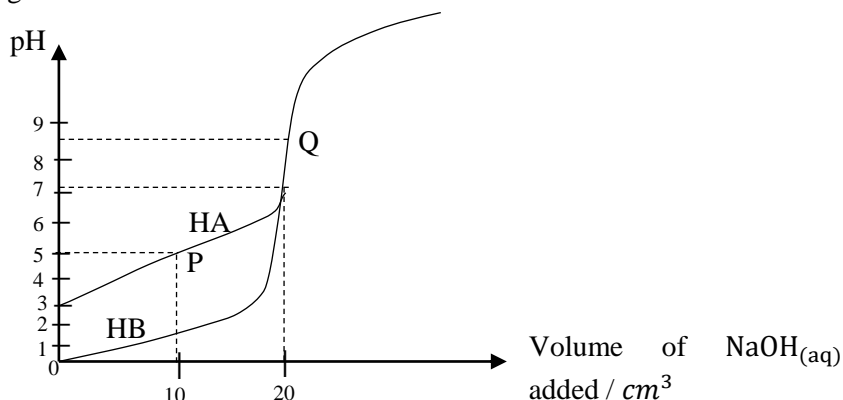
ii) When a common ion is present, the solubility of a sparingly soluble ionic compound in such solution is always less than the solubility of it in water. ()

iii) The critical temperature of NH_3 gas is less than that of CO_2 gas. ()

iv) Of the ionic compounds NaI, KF and KBr, the one which has the least solubility in water is NaI ()

v) The bond dissociation energy of halogens follows the order $F_2 > Cl_2 > Br_2$ ()

- 3) (a) At 25°C , two mono – basic acids HA and HB of volumes V_1 and V_2 were taken separately in two titration flasks and were titrated against a $0.5 \text{ mol dm}^{-3} \text{ NaOH}_{(\text{aq})}$ using a suitable indicator. When the pH change during this titration was plotted against the volume of $\text{NaOH}_{(\text{aq})}$ added, the following curves were obtained.



In the above two titrations, volume of NaOH at the equivalence point was 20 cm^3 . In the above graph, the point P represents the pH on addition of 10 cm^3 of the given $\text{NaOH}_{(\text{aq})}$ to the acid $\text{HA}_{(\text{aq})}$ and the point Q denotes the pH corresponding to the equivalence point of the titration of HA.

Answer the questions below based on the given graph.

- i) Of the two acids HA and HB, which one can possibly be a strong acid? Give reasons.

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- ii) What is the value of V_2 ?

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- iii) What is the value of the dissociation constant K_a of the weak acid?

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- iv) Find the value of V_1 ?

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- v) Given that V_1 volume of another weak acid HC having $K_a = 1.6 \times 10^{-6} \text{mol dm}^{-3}$ and the same concentration as that of HA is titrated against the same (0.5mol dm^{-3}) $\text{NaOH}_{(\text{aq})}$. Mention whether the pH at the present equivalence point is greater than the point Q. Briefly explain your answer.

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- (b) Metal – Metal ion solution, metal – its insoluble salt and gas electrode are some of the electrode types.

- i) Standard calomel electrode is a type of electrode belonging to metal – insoluble salt electrode. Write the equilibrium electrode reaction for this electrode.

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- ii) Draw the labelled diagram of the standard electrochemical cell constructed by connecting standard calomel electrode with standard chlorine electrode and write its IUPAC notation

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When the cell mentioned in part (ii) above produces current, it is given that chlorine electrode functions as positive terminal and std. Electrode potentials of the two electrodes (not in the order) are 0.24 V and 1.36 V.

- iii) Find the emf of the cell mentioned in is about

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- iv) Mention the cathode and the anode of the cell.

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v) Write the half-cell reactions occurring in cathode and anode.

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vi) Write the cell reaction.

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vii) The notation of another electrode of the type metal – its insoluble salt is $Ag_{(s)} | AgCl_{(s)} | Cl^-_{(aq)}$. Presently, instead of standard hydrogen electrode, the above electrode is used as a reference electrode. Mention 3 advantages of it when compared to standard H – electrode.

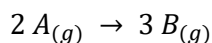
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(c) Consider the elementary reaction



At a particular temperature, at time $t = 0$, a known amount of $A_{(g)}$ was placed in a closed, rigid vessel and the initial pressure was found to be P_0 and initial rate of reaction was R_0 . After time t , when the pressure of the system was P_t , rate of reaction became half its initial value. Deduce an expression for $\frac{P_t}{P_0}$.

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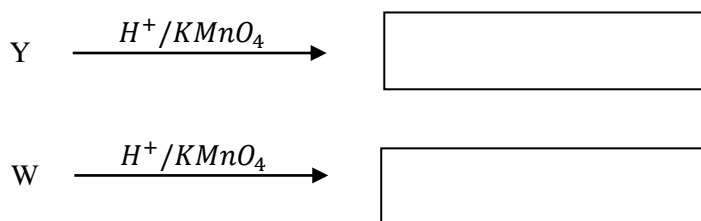
4) (a) P, Q, R and S are four compounds with the molecular formula $C_4H_8O_2$. None of the above compounds evolves H_2 gas with Na. However, all the compounds react with NaOH. In the reaction with NaOH, each of the above four compounds gives two products.

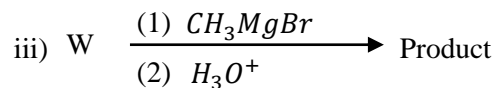
- In the reaction of R with NaOH the products X and Y are obtained. whereas X and W are obtained in the reaction of S with NaOH.
- The product W gives turbidity with Lucas reagent after a short time (5 minutes) but Y gives turbidity after a very long time.
- In the reaction with NaOH, P gives the products M and L while Q gives N and Z.
- When P and Q are treated separately with $LiAlH_4$ followed by hydrolysis, P gives the same product L while Q gives two products Y and Z.

i) Identify the compounds P, Q, R, S, X, Y, Z, W, L, M and N and write the structures in the relevant boxes.

P	Q	R
S	X	Y
Z	W	L
M	N	

ii) Write the structures of the organic products when $H^+/KMnO_4$ is added to the compounds Y and W





Write the structure of the product and write the suitable mechanism for this reaction.

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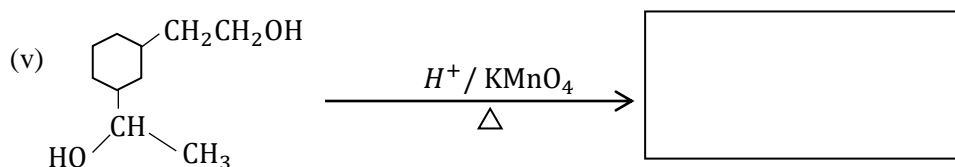
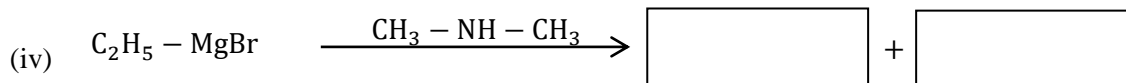
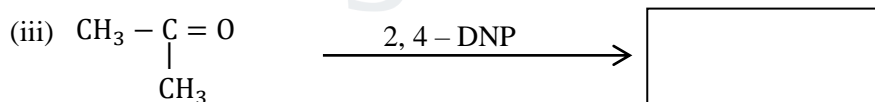
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(b) In the following reaction schemes, write the structures of the reagents / products, catalysts if any, with appropriate reaction conditions wherever needed in the relevant cages.





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5th Term Examination - 2022

இரசாயனவியல் II B
Chemistry II B

Gr -13 (2022)

02

E

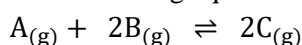
IIB

Part – II B

❖ Answer any two questions from this part.

5) (a)

i) Consider the following equilibrium reaction.



When 1 mol of $A_{(g)}$ and 2 moles of $B_{(g)}$ were placed initially in a closed, rigid container and the temperature was raised to 600 K, the above equilibrium was attained. It was found that 0.4 moles of $C_{(g)}$ was formed at the equilibrium.

If the total pressure of the equilibrium mixture was 2.8×10^5 Pa, calculate the equilibrium constant K_p at 600 K for the above equilibrium reaction.

ii) When the temperature of the equilibrium system was suddenly decreased to 300 K, a small amount of $A_{(g)}$ and $B_{(g)}$ condensed to their liquid states. This liquid mixture of A and B formed an ideal solution which is in equilibrium with its vapour phase and $C_{(g)}$ does not dissolve in this liquid mixture. It was found that 0.2 moles of $C_{(g)}$ was present in the vapour / (gaseous) phase and the total pressure of the gaseous phase was 9×10^4 Pa.

In gaseous phase, the mole ratio A : B was 3 : 5 respectively

- I. Find the partial pressures of $A_{(g)}$, $B_{(g)}$ and $C_{(g)}$ at 300 K at the gaseous phase
- II. Find the saturated vapour pressure of $A_{(g)}$ and $B_{(g)}$ at 300 K.
- III. State the assumption, if any, you made in the above calculations.

(b) $Ag_2CrO_4(s)$ is a sparingly soluble ionic solid which is considered as a strong electrolyte

i) Give the reason as to why $Ag_2CrO_4(s)$ is considered as a strong electrolyte.

ii) In a saturated solution of $Ag_2CrO_4(s)$ solid Ag_2CrO_4 is in equilibrium with its ions At $25^\circ C$, $Ag^+_{(aq)}$ concentration of such a solution is 54 ppm Calculate the solubility product (K_{sp}) of Ag_2CrO_4 at $25^\circ C$.

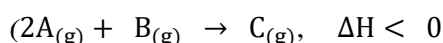
(Ag = 108, Cr = 52, O = 16, 1ppm = $1mgdm^{-3}$)

iii) At $25^\circ C$, the above solution was filtered and to $500 cm^3$ of the filtrate, $500 cm^3$ of $0.1 moldm^{-3} Ba(NO_3)_2(aq)$ was added Using a suitable calculation, show that a precipitate will form in the above solution (K_{sp} of $BaCrO_4(s) = 1 \times 10^{-10} mol^2 dm^{-6}$)

iv) $100 cm^3$ of the filtrate solution mentioned in part (ii) above was diluted to $1 dm^3$ by adding distilled water and it was planned to precipitate $AgCl(s)$ by adding NaCl solid into it. Calculate the minimum mass of $NaCl(s)$ required for this purpose. (Na = 23, Cl = 35.5, K_{sp} of $AgCl = 1 \times 10^{-10} mol^2 dm^{-6}$)

- (c) i) Concentration of an aqueous solution of NH_4Cl is $c \text{ mol dm}^{-3}$. Given that the dissociation constant of $\text{NH}_4\text{OH}_{(\text{aq})}$ is K_b and the ionic product of water is K_w . Show that the pH of the above NH_4Cl solution is given by $\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$.
- ii) If 0.33 g of $(\text{NH}_4)_2\text{SO}_{(\text{s})}$ is dissolved in water and 250 cm^3 of a solution is prepared, deduce the pH of the solution.
- [$K_b(\text{NH}_3) = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $N = 14$, $O = 16$, $S = 32$, $H = 1$, $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$]
- iii) If 0.33 g $(\text{NH}_4)_2\text{SO}_{(\text{s})}$ is dissolved in 500 cm^3 of 0.1 mol dm^{-3} $\text{NH}_4\text{OH}_{(\text{aq})}$ at the same temperature, what would be the pH of the resulting solution?

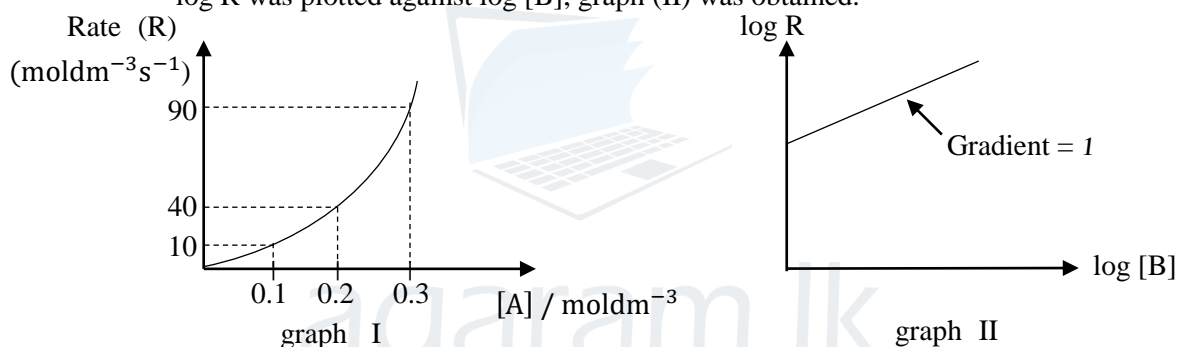
6) (a) Consider the following reaction



Two experiments were carried out to determine the order with respect to A and B in the above reaction.

Expt - I : - When the rates of the reaction (R) were measured with varying concentrations of A while keeping the concentration of B a constant, graph (I) was obtained.

Expt - II : - When the concentration of B was changed keeping the concentration of A constant, and $\log R$ was plotted against $\log [B]$, graph (II) was obtained.



- Deduce the orders with respect to A and B.
- Taking the rate constant for this reaction as k , write the rate law expression.
- According to the statement of a student, the above reaction should be a fundamental one (single step reaction) Do you agree with this? Explain your answer briefly.
- Under the conditions of experiment (II), the initial concentration of B was 1 mol dm^{-3} and after 132 s, it became $0.0625 \text{ mol dm}^{-3}$. What is the half - life?
- The mechanism suggested by a student for the above reaction is given below.

Step I :- $\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \xrightleftharpoons[\text{Slow}]{\text{Fast}} \text{AB}_{(\text{g})} \quad \Delta H > 0 \quad \text{Equilibrium constant } K_c$

Step II :- $\text{AB}_{(\text{g})} + \text{A}_{(\text{g})} \xrightarrow{\text{Slow}} \text{C}_{(\text{g})} \quad \Delta H < 0$
- Which one of the above steps is the RDS (Rate determining step) of the reaction? Write the equation for the rate of that step.
- Hence, deduce the rate law expression for the reaction that you wrote in part (ii) of the question.
- Draw the energy profile diagram (reaction coordinate against energy) for the above reaction. Indicate the transition states in intermediate and activation energies of each step.

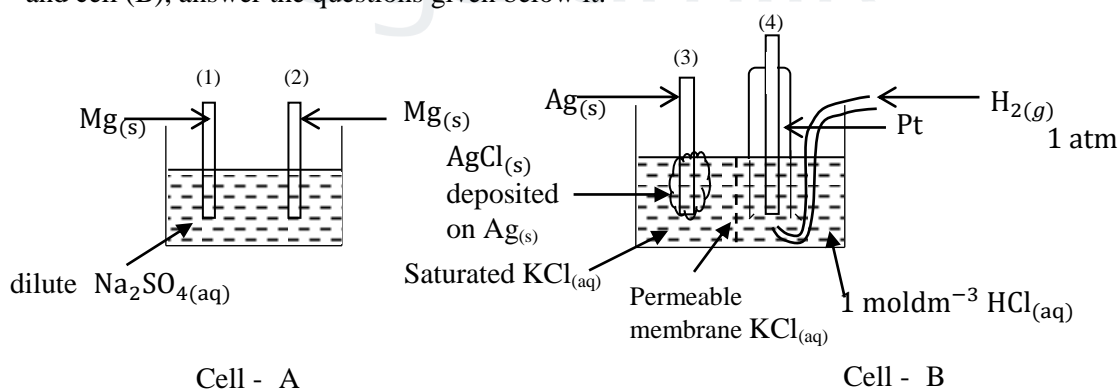
- (b) Two completely miscible, volatile liquids A and B form ideal solution in all compositions. At a particular temperature, a mixture of liquids A and B is in equilibrium with its vapour. At the given temperature, saturated vapour pressures of pure liquids A and B are P_A^0 and P_B^0 respectively. The mole fractions of A and B in liquid phase are X_A and X_B respectively. The mole fractions of A and B in the vapour phase which is in equilibrium with the liquid phase are X'_A and X'_B respectively.
- Explain the ideal behavior of the solution AB on the basis of intermolecular attractions.
 - State Raoult's law pertaining to the solution and write a mathematical expression for it.
 - Prove that $\frac{1}{P} = \frac{1-X'_A}{P_B^0} + \frac{X'_A}{P_A^0}$, where P is the total vapour pressure of the equilibrium mixture.
 - Given that $P_A^0 = 3 \times 10^4$ Pa and $P_B^0 = 2 \times 10^4$ Pa. If the mole fraction of B in vapour phase which is in equilibrium with a given mixture of A and B is 0.6, deduce the total vapour pressure P.
 - Calculate the partial pressures of A and B and the mole fractions of A and B in the liquid phase (X_A, X_B)
 - Plot separately the variation of the vapour pressure and boiling points against the composition of the mixture.

- (c) An aqueous solution contains Zn^{2+} and Fe^{2+} ions each with concentration 0.1 mol dm^{-3} . The above cations can be separated by passing H_2S gas through the solution and saturating it with H_2S . What should be the pH range if they are to be separated by passing H_2S gas through the solution?

$$K_{sp}(ZnS) = 2 \times 10^{-25} \text{ mol}^2 \text{ dm}^{-6}, \quad K_{sp}(FeS) = 4.9 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$$

$$\text{In a saturated solution of } H_2S, [H_3O^+_{(aq)}]^2 [S^{2-}_{(aq)}] = 9.1 \times 10^{-28} \text{ mol}^3 \text{ dm}^{-9}$$

- 7) (a) Based on the diagram given below, which represents two electro chemical cells denoted by cell (A) and cell (B), answer the questions given below it.

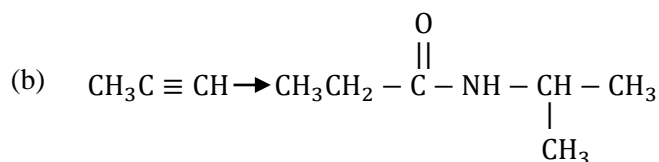


Each electrode of the cells are denoted by the numbers (1), (2), (3), (4)

$$E_{AgCl(s) / Ag(s) / Cl^-_{(aq)}}^\theta = 0.22 \text{ V}$$

Based on cell (B) answer the questions from (i) to (iv)

- What is the emf of the cell?
- Identify the anode and the cathode and write the half – cell reactions if the cell operates to produce current.
- Write the cell reaction.



Using the starting material as the only organic compound, mention a reaction scheme to carry out the above conversion in not more than eight steps.

- (c) i) Reaction of PCl_5 with ethanol gives chloroethane but phenol does not react with PCl_5 to give chlorobenzene. Explain.
 ii) Basicity of alcohols is less when compared to the basicity of amines. Explain this briefly with necessary reactions and on the basis of the electro negativities of the atoms concerned

- 9) (a) In a coloured solution X, two cations and two anions are present. The experiments carried out to identify the ions and the relevant observations are given below.

	Experiment	Observation
(1)	Into a portion of X, H_2S gas is bubbled after the addition of dil HCl	No special observation
(2)	Addition of conc. HNO_3 solution to another portion of X and heating the mixture after which of NH_4Cl and NH_4OH . were added	No precipitate.
(3)	Bubbling H_2S gas through the resulting solution in (2)	Black precipitate.
(4)	To a portion of X, addition of $\text{BaCl}_2(\text{aq})$ followed by the addition of dil. HCl to acidify the mixture.	A white precipitate and a coloured solution
(5)	To a portion of X, addition of conc. $\text{NaOH}(\text{aq})$	A green precipitate and a green solution with the evolution of at gas.
(6)	To the precipitate formed in (5) above, addition of conc. $\text{NH}_3(\text{aq})$ in excess.	The precipitate dissolves forming a deep blue solution.
(7)	The solution formed in (5) is diluted with water (or with acid)	Violet (purple) coloured solution and blackish brown propitiate formed.
(8)	Addition of dilute HCl drop – wise into the solution formed in (7) above	A white precipitate 25 formed which dissolves upon the addition of HCl in excess.
(9)	Addition of $\text{NH}_3(\text{aq})$ slowly to the resulting solution in (8)	A white precipitate is formed which dissolves upon the addition of excess. $\text{NH}_3(\text{aq})$.

- i) Identify the two cations and the two anions present in the solution explaining the observations wherever necessary.
 ii) Write balanced equations for the reactions involved in the observations in steps 3, 4, 5, 7, 8 and 9.

- (b) An aqueous solution contains CuSO_4 , NiSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ When excess $\text{BaCl}_2(\text{aq})$ was added to 100 cm^3 portion of this solution, the dry mass of the precipitate (X) obtained was 9.32 g. When the precipitate was filtered and excess $\text{KI}(\text{aq})$ was added to the filtrate, the dry mass of the

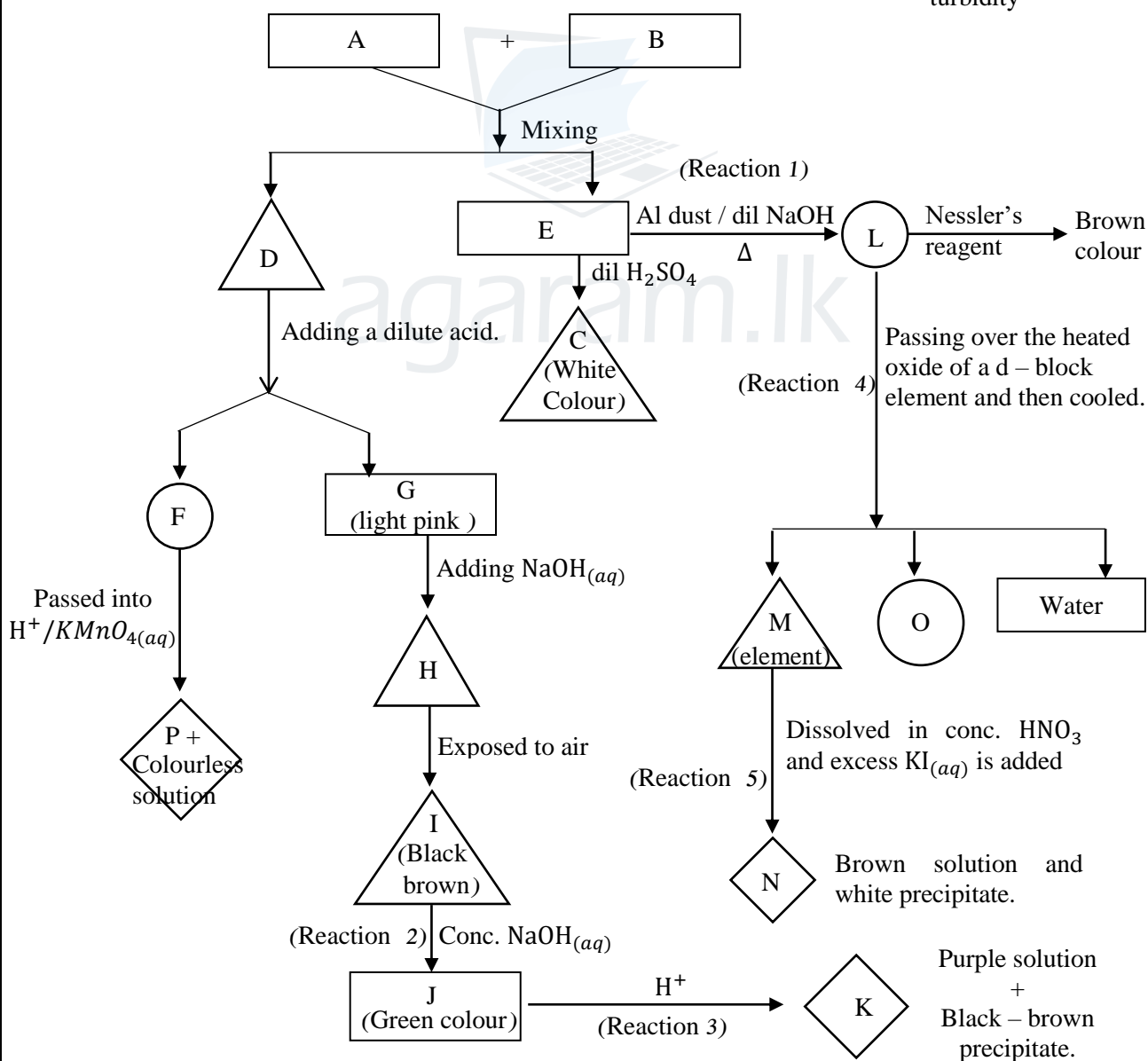
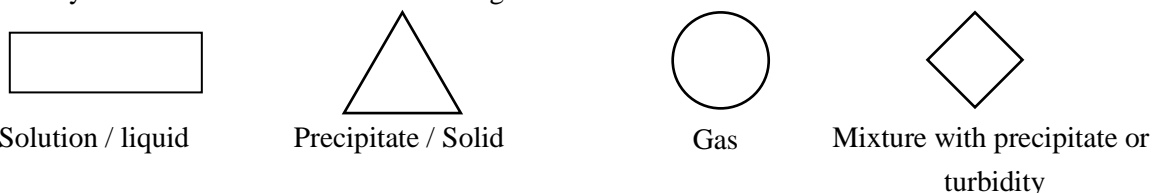
precipitate (Y) thus obtained was 1.905 g. After the precipitate was removed, the resulting solution was then titrated with a $1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$, The volume of $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ required at the end point was found to be 20 cm^3 .

(Fe = 56 , Cu = 63.5 , N = 58.6 , Ba = 137 , S = 32 , I = 127)

- Identify X, Y and Z.
- Write balanced equations for the reactions taking place upon the addition of $\text{KI}(\text{aq})$.
- Calculate the concentrations of Cu^{2+} , Ni^{2+} , Fe^{3+} and SO_4^{2-} ions in the solution.
- Mention the indicator used in the above titration with $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ and explain briefly how the end point is found.

10) (a) The following flow chart is based on the aqueous solutions of the compounds A and B and some reactions involving them.

The symbols used in the flow – chart are given below.



- Solid B imparted yellow green colour when subjected to flame test.
 - P is a pale yellow coloured turbid substance.
- i) Identify the compounds denoted by the letters from A to P and write their chemical symbols.
 - ii) Write balanced chemical equations for the reactions denoted by 1 to 5.

(b) M is a 3d – transition element with atomic number Z. It can form acidic, basic and amphoteric oxides. M exhibits a wide range of oxidation numbers in its compounds.

The aqueous solution of the cation in the least oxidation state of M is pale pink coloured.

The elements P and Q have atomic numbers (Z – 1) and (Z + 1) respectively.

The element P forms two different oxy anions X and Y with the same oxidation number of which Y is stable in acidic medium.

- i) Identify M.
- ii) Write the electronic configuration of M in its ground state in the usual manner.
- iii) Mention the two oxy anions formed by M and Write their names and colours.
- iv) Mention the observation when a small amount of $\text{NaOH}_{(aq)}$ is added into $\text{P}_{(aq)}^{3+}$ and colour of the species responsible for it.
- v) Write balanced equation for the reaction that takes place when excess $\text{NaOH}_{(aq)}$ and $\text{H}_2\text{O}_{2(aq)}$ are added into $\text{P}_{(aq)}^{3+}$.
- vi) Write balanced equation for the reaction that the aqueous solution of the cation of M in its lowest oxidation state in neutral medium undergoes with $\text{S}_2\text{O}_8^{2-}_{(aq)}$.
- vii) Identify X and Y and write the relevant equation for the reaction by which X may be converted to Y. What is the colour change.
- viii) Arrange the elements M, P and Q in the ascending order of melting points.
- ix) Identify X and Y and write balanced equation for the reaction by which X may be converted to Y. What is the colour change in it?