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අධාායන පොදු සහතික පතු (උසස් පෙළ) විභාගය, 2023 (2024) கல்விப் பொதுத் தராதரப் பத்திர (உயர் தர)ப் பரீட்சை, 2023(2024) General Certificate of Education (Adv. Level) Examination, 2023 (2024)

රසායන විදහාව இரசாயனவியல் II Chemistry II



* Universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

PART B - ESSAY

Answer two questions only. (Each question carries 150 marks.)

5. (a) CaO(s) reacts with water as shown below.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \Delta H^o = -64 \text{ kJ mol}^{-1}$$

The following questions are based on the reaction given above.

(i) When 200 g of H₂O(l) was reacted with a certain mass of CaO(s), the temperature of water changed from 25 °C to 75 °C. Calculate the amount of heat (in kJ) absorbed by water. Specific heat capacity of water is 4.2 J g⁻¹ °C⁻¹.

(Note: Disregard the change in the mass of water due to the formation of Ca(OH)2.)

- (ii) What is the minimum mass of CaO(s) needed to make the temperature change that occurred in (i) above? (O = 16, Ca = 40)
- (iii) Standard entropy values of CaO(s), H₂O(l) and Ca(OH)₂(s) are 40, 70 and 80 J K⁻¹ mol⁻¹ respectively. Calculate the entropy change of the reaction.
- (iv) Predict the spontaneity of the reaction at 300 K. State any assumptions made.
- (v) Predict the spontaneity of the reaction at 400 K if steam (H2O(g)) is used instead of liquid

$$H_2O(g) \rightarrow H_2O(l) \Delta H^\circ = -44 \text{ kJ mol}^{-1}$$

 $S_{H_2O(g)}^\circ = 190 \text{ J K}^{-1} \text{ mol}^{-1}$

(80 marks)

(b) (i) At temperature 570 °C, the equilibrium given below exists in a closed rigid container. $Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$

The pressure of the container was found to be 7.0×10^5 Pa.

Calculate $K_{\rm P}$ and $K_{\rm C}$ for the reaction at the temperature 570 °C (at 570 °C, RT = 7000 J mol⁻¹).

- (ii) Giving reasons briefly explain the effect on the equilibrium in (b)(i) above when the following changes are done.
 - I. When Ca(OH)₂(s) is added.
 - II. When some amount of $H_2O(g)$ is removed.
- (iii) To determine the relationship between the pressure of the water vapour produced (PH2O) and the mass of Ca(OH)2(s) introduced into the container (MCa(OH)2), the pressure was measured introducing small quantities of Ca(OH)2(s) into an evacuated rigid container at 570 °C. Draw the expected graph for the variation of P_{H2O}with M_{Ca(OH)2} and briefly describe
- (i) Write the reversible reaction for the dissolution of Ca(OH)₂(s) in water at temperature 25 °C.
 - (ii) At temperature 25 °C the solubility product $(K_{\rm sp})$ of Ca(OH)₂(s) is $4.0 \times 10^{-6} \, {\rm mol}^3 \, {\rm dm}^{-9}$. Calculate the molar solubility of Ca(OH)₂(s) at this temperature.
 - (iii) State giving reasons whether the solubility of Ca(OH)2(s) will be higher, lower or the same in aqueous solutions of NaOH, NaCl and Ca(NO3)2 (concentrations of solutions 0.1 mol dm⁻³) when compared with the solubility of Ca(OH)₂(s) in water. (30 *marks*)

[see page ten

6. (a) At 25 °C the methanoate ion, HCOO-(aq) reacts with water to form methanoic acid, HCOOH(aq) and OH-(aq) as shown below.

$$HCOO^{-}(aq) + H_2O(1) \rightleftharpoons HCOOH(aq) + OH^{-}(aq)$$

- (i) Given that $[OH^{-}(aq)] = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$ in a solution prepared by dissolving 0.10 mol of HCO_2Na in 1.0 dm³ of water, calculate the following at 25 °C.
 - I. The value of K_b of methanoate ion.
 - II. The value of $K_{\rm a}$ of methanoic acid. $(K_{\rm w}=1.0\times10^{-14}~{\rm mol^2~dm^{-6}}$ at 25 °C)
- (ii) Calculate the pH of a methanoic acid solution of concentration 0.10 mol dm⁻³.
- (iii) When 3.40 g of HCO₂Na was dissolved in 50.00 cm³ of 0.10 mol dm⁻³ HCOOH(aq) solution, it was observed that there was no change in volume.

(H = 1, C = 12, O = 16, Na = 23)

- I. Determine the pH of this solution.
- II. Explain how this solution acts as a buffer solution.

(80 marks)

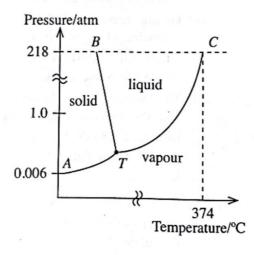
(b) (i) This question is in respect of a solution that could be made by mixing two completely miscible liquids A and B. Copy the following table on to your answer script and fill in the blanks. Different types of solutions (ideal, non-ideal/positive deviation, non-ideal/negative deviation) that could be made are given in the table.

While the mole fractions of **A** and **B** in the solution are X_A and X_B , and the vapour pressures of **A** and **B** at a given temperature are P_A and P_B respectively.

The saturated vapour pressures of **A** and **B** at this temperature are P_{A}^{o} and P_{B}^{o} respectively. Intermolecular forces between **A** and **A**, **B** and **B** and **A** and **B** are f_{A-A} , f_{B-B} and f_{A-B} respectively.

igil Salar e (no 6 Milledas Thi 200	Ideal solution	Non-ideal solution	
Property		Positive deviation from Raoults law	Negative deviation from Raoults law
ΔH of mixing	47	- 1 - 1 - 1) - 1) - 1	
relationship among $f_{\mathbf{A-A}}, f_{\mathbf{B-B}}$ and $f_{\mathbf{A-B}}$	N. Governor	agen	10 25 1 mg
relationship among $P_{\mathbf{A}}^{\circ}$, $P_{\mathbf{A}}$ and $X_{\mathbf{A}}$	2 · 1	E. Co. Ch. gill	

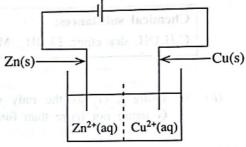
- (ii) The phase diagram of pure water is given below. Copy the diagram on to your answer script and answer the following questions.
 - I. Mark the normal boiling point (V) and melting point (L) of pure water.
 - II. What are represented by lines BT, TC and point T?
 - III. Assume that a small amount of salt (NaCl) is added to the pure water sample. After the addition of salt, positions of the lines BT and TC in the phase diagram were changed. Their new positions are B'T' and T'C' respectively. Draw their new positions on the phase diagram you have copied and label them as B'T' and T'C'. Mark the new boiling point (V') and the new melting point (L') on the phase diagram.



(70 *marks*)

[see page eleven

- (a) A Daniel cell consists of Zn and Cu rods immersed in ZnSO₄(aq, 1.0 mol dm⁻³) and CuSO₄(aq, 1.0 mol dm⁻³) respectively. The solutions are separated by a porous membrane. The overall cell reaction when the cell is operating is given below.
 - $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
 - (i) Identify the anode and the cathode.
 - (ii) Write the anodic half reaction of the cell.
 - (iii) Write the cathodic half reaction of the cell.
 - (iv) Give the cell notation of the cell above.
 - (v) Calculate the electromotive force $(E_{\rm cell}^{\rm o})$ of the Daniel cell given above at 25 °C. $E_{\rm Cu^{2+}(aq)/Cu(s)}^{\rm o} = 0.34 \text{ V}$ $E_{\rm Zn^{2+}(aq)/Zn(s)}^{\rm o} = -0.76 \text{ V}$
 - (vi) Calculate the time in seconds required to deposit 3.175 g of Cu(s) when a current of 5.0 A flows through the cell. (Cu = 63.5, 1 F = 96500 C mol^{-1})
 - (vii) How does the conductivity of the solution in the cell compartment containing the Zn-rod change when a current is drawn from the cell? Explain giving reasons.
 - (viii) It was observed that when a current is drawn from the cell, the intensity of the colour of the solution in the cell compartment containing the Cu-rod changes. Explain this observation.
 - (ix) As shown in the diagram, an external voltage higher than the calculated electromotive force in (v) above, was applied to the Daniel cell using another electrochemical cell. Write the overall cell reaction of the Daniel cell under this condition.



(75 marks)

(b) A, B, C and D are coordination compounds of iron with an octahedral geometry. The molecular formulae of the compounds are (not in order) FeH₁₄N₂O₄Br₃, FeH₁₅N₅Br₂, FeKH₄O₂Br₄ and FeH₁₅N₃O₃Br₂.

In each compound two types of ligands are coordinated to the metal ion.

Compound A: Gives three ions in aqueous solution. When AgNO₃(aq) is added to an aqueous solution of A, two moles of a yellow precipitate are formed per mole of A.

Compound B: Gives four ions in aqueous solution. When AgNO₃(aq) is added to an aqueous solution of B, three moles of a yellow precipitate are formed per mole of B.

Compound C: Gives two ions in aqueous solution. When AgNO₃(aq) is added to an aqueous solution of C one mole of a yellow precipitate is formed per mole of C.

Compound D: Gives two ions in aqueous solution. A yellow precipitate is not formed when AgNO₃(aq) is added to an aqueous solution of D.

- (i) What are the common oxidation states of iron (Fe)?
- (ii) Identify the yellow precipitate. (Give chemical formula.) Name a chemical reagent that can dissolve this precipitate.
- (iii) Identify the ligands coordinated to the metal ion in each compound A, B, C and D.
- (iv) In each of the compounds A, B, C and D,
 - I. write the oxidation state of iron.
 - II. write the electronic configuration of iron.
- (v) Give the structures of A, B, C and D.

(75 marks)

[see page twelve

PART C - ESSAY

Answer two questions only. (Each question carries 150 marks.)

8/(a) (CH₃)₂CHCO₂H has been converted to compound F by using the reaction scheme given below.

$$(CH_3)_2CHCO_2H \xrightarrow{Reaction 1} A \xrightarrow{Reaction 2} B \xrightarrow{Reaction 3} C$$

$$\downarrow \text{Reaction 4} \qquad OH$$

$$D \xrightarrow{C} E \xrightarrow{Reaction 5} (CH_3)_2CH - C - CH_2CH(CH_3)_2$$

$$CH_2CH(CH_3)_2$$

$$E$$

Complete the above reaction scheme by giving the structures of compounds A, B, C, D and E and the reagents required for the reactions 1 - 5. Only the chemical substances given below should be used (either singly or as combinations) as reagents.

Chemical substances:

C₂H₅OH, dry ether, LiAlH₄, Mg, PBr₃, conc. H₂SO₄, dil. H₂SO₄

(45 marks)

(b) (i) Using C₂H₂ as the only starting compound, show how you would prepare compound G using not more than four (04) steps.

G

(ii) Give the structure of the compound **H** which is formed when compound **G** is reacted with excess Cl₂.

(30 marks)

- (c) Write the product and the mechanism of the reaction of benzene with conc. HNO₃/conc. H₂SO₄.

 (25 marks)
- (d) Show how you would carry out each of the following conversions in not more than three (03) steps.

(i)
$$\longrightarrow$$
 CH_2CH_3

(ii)
$$CH_3CHCH_3$$
 \longrightarrow $CH_3CH_2CH_2OH$ OH

(50 marks)

[see page thirteen

9. (a) (i) Aqueous solutions of compounds MgSO₄, NaOH, BaCl₂, Na₂SO₄ and Zn(NO₃)₂ are contained in five 100 cm³ beakers labelled A, B, C, D and E (not in order). Identify A, B, C, D and E based on the observations given below. (Reasons not required.)

Note: Small portions of the solutions are mixed in test tubes.

On mixing D and E a white precipitate is formed. When excess E is added to the precipitate, the precipitate dissolves giving a colourless solution. A white precipitate is formed when E is added to C. Precipitates are not formed when E is added to A and when E is added to B. On mixing A and B a white precipitate is formed. When C is added to A, a white precipitate is formed. However, a precipitate is not formed when C is added to B.

(25 marks)

(ii) An aqueous solution M contains three cations. The following tests (1-5) were carried out to identify these cations.

Test No.	Test	Observation
vo es 1 colum	Dilute HCl was added to solution M.	A white precipitate (P ₁)
2	P ₁ was separated by filtration and H ₂ S was bubbled through the solution.	No precipitate
3	The solution was boiled until all the H ₂ S was removed and then cooled. NH ₄ Cl/NH ₄ OH was added.	
4	H ₂ S was bubbled through this solution.	A pale pink precipitate (P ₂)
P ₂ was separated by filtration and the solution was boiled until all the H ₂ S was removed. (NH ₄) ₂ CO ₃ solution was added.		A white precipitate (P ₃)

The following tests were carried out for the precipitates P1, P2 and P2.

Precipitate	Test Test	Observation
P ₁	Dilute ammonia solution was added to P1.	P ₁ dissolved.
P ₂	P ₂ was dissolved in dil. HNO ₃ and excess dilute NaOH was added to the solution.	A white precipitate which turns brown on standing
P ₃	P ₃ was dissolved in conc. HCl and the solution was subjected to the flame test.	A green colour flame

- I. Identify the three cations in solution M. (Reasons not required.)
- II. Write the chemical formulae of the precipitates P₁, P₂ and P₃.

(24 marks)

(iii) X, Y and Z are ionic solids. Sodium is the cation in all three compounds. The following tests were carried out to identify the anions in X, Y and Z.

Test No.	Test Test Test	Observation
1	(i) A portion of X was dissolved in water in a test tube.	A colourless solution
	(ii) Pb(CH ₃ COO) ₂ solution was added to the colourless solution.	A yellow precipitate
	(iii) The resulting mixture (yellow precipitate and solution) was heated.	The precipitate dissolved giving a colourless solution.
	(iv) This colourless solution was cooled.	A yellow precipitate (as golden yellow plates)

[see page fourteen

2	(i) A portion of Y was dissolved in water in a test tube.	A colourless solution
	(ii) A BaCl ₂ solution was added to the colourless solution.	A white precipitate
	(iii) Dilute HCl was added to the resulting mixture (white precipitate and solution).	A clear colourless solution with the evolution of a gas
	(iv) The gas evolved was tested by holding a filter paper moistened with acidified K ₂ Cr ₂ O ₇ over the mouth of the test tube.	Orange filter paper turned green.
3	(i) A portion of Z was dissolved in water in a test tube.	A colourless solution
	(ii) AgNO ₃ solution was added to the colourless solution.	A black precipitate
	(iii) Dilute HCl was added to a portion of Z in a test tube.	A colourless gas evolved.
	(iv) The gas evolved was tested by holding a filter paper moistened with Pb(CH ₃ COO) ₂ solution over the mouth of the test tube.	Filter paper turned black

- I. Identify the anions in X, Y and Z. (Reasons not required.)
- II. Write balanced chemical equations for the reactions taking place in the above tests.

 (26 marks)
- (b) A solid sample X contains the compounds P, Q and an inert substance. Here $P = Fe_2O_3$ and $Q = Fe_3O_4$. Q is a single compound and contains iron in Fe^{2+} and Fe^{3+} oxidation states. It reacts with I^- in an acidic medium as follows.

$$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + I_2$$

The following experimental procedure was used to determine the mass percentages of P and Q in X.

When 3.2 g of sample X was treated with excess KI solution in the presence of dilute H_2SO_4 , all the Fe^{3+} in it was converted to Fe^{2+} with the liberation of iodine. The resulting solution was diluted to $100.00~\rm cm^3$ (labelled as S). To convert the iodine to iodide in a 25.00 cm³ volume of this diluted solution (S), $15.00~\rm cm^3$ of $0.50~\rm mol~dm^{-3}~Na_2S_2O_3$ was required.

After complete removal of iodine from another 50.00 cm³ volume of the diluted solution (S), in dil. H₂SO₄ medium, 14.00 cm³ of 0.25 mol dm⁻³ KMnO₄ was required to oxidize all the Fe²⁺ contained in it.

- (i) Write balanced chemical equations for the reactions taking place in the above procedure.
- (ii) Calculate the mass percentages of P and Q in X.(O = 16, Fe = 56)

(75 marks)

- 10.(a) The following questions are based on the extraction of magnesium by the Dow process.
 - (i) State the raw materials used.
 - (ii) Give balanced chemical equations/half reactions in the sequence they occur in the Dow process. Appropriate conditions must be stated as required.
 - (iii) Give two industrial uses of magnesium.
 - (iv) Give two ways in which the Dow process has a negative impact on the environment.

 (50 marks)
 - (b) Given below are some pollutants that exist in the atmosphere.

Pollutant List

where n is an integer.

CH₄, CO₂, NO, NO₂, N₂O, SO₂, SO₃, CH₃CH₂CH₂CH₂CH₃,

The following questions are based on the pollutant list given above.

- (i) Identify the pollutant that directly contributes towards increasing the level of ozone in the atmosphere.
- (ii) Explain using balanced chemical equations how the pollutant you identified in (i) above increases the ozone level in the atmosphere.
- (iii) Identify two pollutants that contribute to the reduction of ozone level in the upper atmosphere.
- (iv) Briefly explain using balanced chemical equations how one of the pollutants you identified in (iii) above contributes to the reduction of ozone level in the upper atmosphere.
- (v) Identify two pollutants that cause photochemical smog.
- (vi) Identify four pollutants that can absorb infrared radiation in the atmosphere and remain stable in the atmosphere for a long period of time.
- (vii) What is the commonly used name that describes the behaviour of the pollutants you identified in (vi) above?
- (viii) Identify two pollutants that contribute to make a significant change in some water quality parameters when dissolved in water. State the water quality parameter(s) that will be affected by the pollutants you identified.
 (50 marks)
- (c) Consider the polymerization reactions between one monomer from group A and one monomer from group B given below.

- (i) Write the pair/pairs of monomers that would release an acidic molecule during the polymerization reaction.
- (ii) Write the pair/pairs of monomers that would release a neutral molecule during the polymerization reaction.
- (iii) The molar mass of the repeating unit $\begin{bmatrix} O & O & H & H \\ C (CH_2)_n C N (CH_2)_n N \end{bmatrix}$ is 226 g mol⁻¹. Calculate the number of $-CH_2$ units in a repeating unit.

[see page sixteen

(50 marks)