Universal gas constant R = 8.314 J K^{-1} mol^{-1} Avogadro's constant N_A = 6.022 × 10^{23} mol^{-1}

PART B - ESSAY (*Answer **two** questions only*)

5. a) At 27 ℃ , N_2O_3 gas dissociates in a closed system to give NO_2 and NO gases.

	ΔH^0_f (kJ mol^{-1})	S^0(J mol^{-1} K^{-1})
NO (g)	90	210
NO_2 (g)	33	240
N_2O_3 (g)	81	316

(i) Write the balanced chemical equation for the above dissociation.

(ii) Calculate the standard enthalpy change for this reaction. State with reasons whether its sign (+ / -) is suitable or unsuitable for the reaction.

(iii) Calculate the standard entropy change for this reaction. State with reasons whether its sign (+ / -) is suitable or unsuitable for the reaction.

(iv) Show by an appropriate calculation that this reaction occurs spontaneously in both forward and backward directions at 27 ℃ . State an assumption you made in this calculation.

(v) Predict the effect of temperature on the reaction between NO_2 (g) and NO (g) using the thermodynamic data of the reaction. ***(marks : 50)***

b) Pure N_2O gas of mass 6.6 g was allowed to dissociate and reach equilibrium in a closed vessel of volume 5 dm^3 at 328 ℃ as follows. At 328 ℃ , assume the RT product equals 5 × 10^3 J mol^{-1} .

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$

The pressure of this equilibrium system is 2 × 10^5 Pa .

(i) What are the concentrations of each gas in the equilibrium system?

(ii) Obtain the K_C of the above equilibrium. Hence calculate its K_P

(iii) 1 g of He gas was introduced to the above system while keeping the temperature constant. State with reasons how the mole fractions and partial pressures of the above gases change during this process.

(iv) When 0.5 mol of each of the above gases is introduced at this temperature into the above equilibrium system and allowed to reach equilibrium, determine using an appropriate calculation whether the forward or backward reaction occurred faster for that.

(marks : 60)

c) Controlling the rate of reactions is an important aspect of a chemical industry. The rate of a given reaction can be presented in three main ways, and the average rate is one of them.

The following shows the reaction between peroxydisulfate ($S_2O_8^{2-}$) and iodide (I^-)

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(i) Write an expression for the rate of the reaction in terms of the rate of consumption of I^- (aq)

(ii) If the concentration of I^-(aq) decreased from 0.4 mol dm^{-3} to 0.04 mol dm^{-3} within a time period of two minutes after mixing the reactants, express the rate of the reaction in mol dm^{-3} s^{-1}

(iii) The following shows the results of an experiment conducted to determine the order of the reaction with respect to I^- (aq) for the above reaction. In each experiment, the trials were carried out by keeping the concentration of $S_2O_8^{2-}$ (aq) at a relatively very high, constant value.

Exp. NO	**Initial [$S_2O_8^{2-}$ (aq)] (mol dm^{-3})**	**Initial [I^- (aq)] (mol dm^{-3})**	**Rate (r) (mol $dm^{-3}s^{-1}$)**
1	2.5	3.2×10^{-2}	1.0×10^{-4}
2	2.5	1.0×10^{-2}	1.0×10^{-5}
3	2.5	3.2×10^{-3}	1.0×10^{-6}

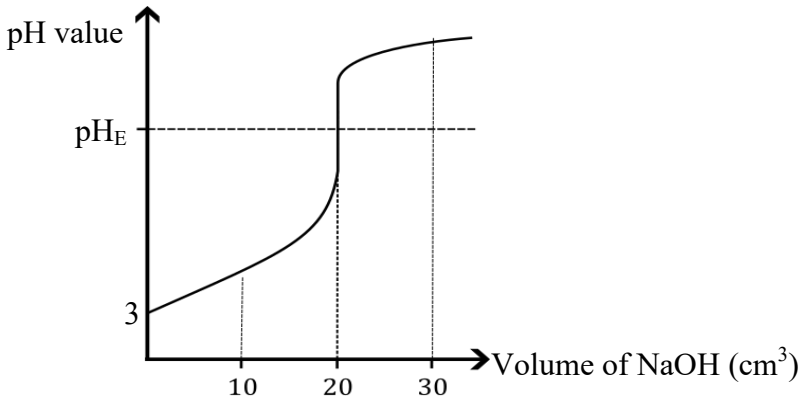
I. Using the data given in the above table, calculate the order of the reaction with respect to I^- (aq)

II. If the order of the reaction with respect to $S_2O_8^{2-}$(aq) is 1, write the rate equation for the reaction.

(marks : 40)

6. a) BH^+ is the conjugate acid of the base B. At 25 °C, a titration was carried out by placing 30 cm^3 of 0.05 mol dm^{-3} aqueous solution of BH^+ in a titration flask and adding an aqueous solution of NaOH from a burette and the corresponding pH curve is shown below.

The ionic product of water (K_w) at 25 °C = 1×10^{-14} mol^2 dm^{-6}



(i) Calculate the initial concentration of the NaOH in the burette.

(ii) Calculate the K_b value of base B.

(iii) Obtain the pH value of the solution in the flask at the equivalence point.

(iv) Qualitatively explain the changes occur in the pH of the solution in the flask at 10 cm^3 of the burette reading , when adding a small volume of a strong acid, strong base and distilled water separately into the solution at this point. ***(marks : 60)***

b) In order to prepare a ideal binary solution, at 47 °C , 60 g of pure propanol (CH_3-CH_2-CH_2-OH) and 90 g of acetic acid (CH_3COOH) respectively were mixed in a closed vessel and allowed to equilibrate with their vapor phase. The volume and the pressure of its vapor phase were 415.7 dm^3 and 3.2 $\times 10^3$ Pa respectively and it contained CH_3-CH_2-CH_2-OH and CH_3COOH in a 3 : 2 molar ratio.

The saturated vapor pressure of propanol at 47 °C is 6.4×10^3 Pa.

(i) Obtain the total number of gaseous moles in the vapor phase.

(ii) What are the mole fractions of A and B in the liquid phase?

(iii) Calculate the saturated vapor pressure of acetic acid at this temperature. ***(marks : 50)***

c) At 25 °C, a mixture containing 50.00 cm^3 of a 0.1 mol dm^{-3} NH_3 solution and 50.00 cm^3 of a CCl_4 solution was shaken well and allowed to stand. The system reached equilibrium as a mole percentage of 20 % of the NH_3 that was in the aqueous solution diffused into the organic layer.

(i) Obtain the distribution coefficient (K_D) corresponding to the distribution of NH_3 between the aqueous and organic phases in the mixture At 25 °C.

(ii) When 50.00 cm^3 of 0.02 mol dm^{-3} aqueous $AgNO_3$ is mixed with 50.00 cm^3 of 0.04 mol dm^{-3} aqueous NH_3 , following equilibrium is established in the solution mixture (A).

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

Above solution is then shaken vigorously with 50.00 cm^3 of CCl_4 and allowed to stand to reach the equilibrium. The organic layer of the equilibrium system required 5.0 cm^3 of 0.01 mol dm^{-3} HCl solution for the titration.

I. What are the initial concentrations of $AgNO_3$ (aq) and NH_3 (aq) in the aqueous solution A?

II. What is the concentration of NH_3 in the organic layer in equilibrium with solution A?

III. Calculate the equilibrium constant for the above equilibrium. ***(marks : 60)***

7. a) During rusting of iron, the formation of $Fe(OH)_2$ occurs first as the oxygen and water in contact with Fe react with each other. Later, it is converted to hydrous ferric oxide due to the further oxidation.

In order to construct an electro chemical cell required for the study of the electro chemical process of the above first step, you are provided with an Fe (s) electrode immersed in a 1 mol dm^{-3} $Fe(NO_3)_2$ (aq) and a standard Oxygen electrode in which O_2 gas at 1 atm interacting with 1 mol dm^{-3} KOH in the presence of Pt.

To connect these components together, facilities such as connecting wires, a voltmeter, and a salt bridge containing $NaNO_3$ (aq) are also provided. (O = 16, Fe = 56, H = 1)

At 25 °C $E^0_{\left(O_2(g)\middle|OH^-(aq)\right)} = +0.40\ V$ and $E^0_{\left(Fe^{2+}(aq)\middle|Fe(s)\right)} = -0.44\ V$

(i) Draw a rough diagram of this electrochemical cell, indicating the standard conditions.

(ii) For this cell, write down :

I. Anode and cathode

II. Positive and negative terminals

III. Half-ionic reactions occurring at the electrodes

IV. Overall cell reaction

(iii) Calculate the electromotive force of the cell (E^0_{cell}) at 25 °C .

(iv) Write down the IUPAC notation of this cell.

(v) Describe how the charge equilibrium in the half-cells is maintained by the salt bridge here.

(vi) The change in mass that occurred at the anode over a period of 5 hours was 112 mg. What is the volume of gas that should be supplied to / removed from the system during that time under standard temperature and pressure conditions (1 atm \ 0 °C)

(marks : 70)

b) A, B, C, D, and E are complex compounds formed by stable cations of the element iron (Fe).

Each of these compounds contains two common types of ligands, which are neutral and anionic ligands. The composition of the ligands consists only of C, H, O, and N. The coordination number of all the above central metal cations is 6, and there are K^+ or halide ions outside the coordination sphere.

Specifications for each compound are given below

	Charge of the cation	**Charge of the coordination sphere**	**Number of ions given to water by a formula unit**	**Observation with aqueous $AgNO_3$**
A	**+3**	**0**	**-**	**-**
B	**+2**	**-3**	**4**	**-**
C	**+2**	**-2**	**3**	**-**
D	**+3**	**+1**	**2**	**A precipitate soluble in diluted NH_3**
E	**+3**	**+2**	**3**	**A precipitate soluble only in concentrated NH_3**

(i) Identify the ligands found in these compounds and write their corresponding formulas.

(ii) Draw the structural formulas of compounds A, B, C, D, and E.

(iii) Write the IUPAC names of compounds A, D, and E.

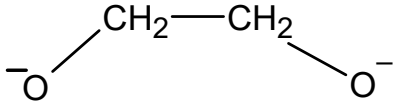
(iv) Identify the compounds from A to E that react with the following reagents. Also, state the observations obtained.

(a) $KMnO_4 / H^+$

(b) $K_3[Fe(CN)_6]$

(c) CCl_4 / Cl_2

(v) The diol given by C_2H_4 with $KMnO_4$ in alkaline medium forms the following bidentate ligand with K.

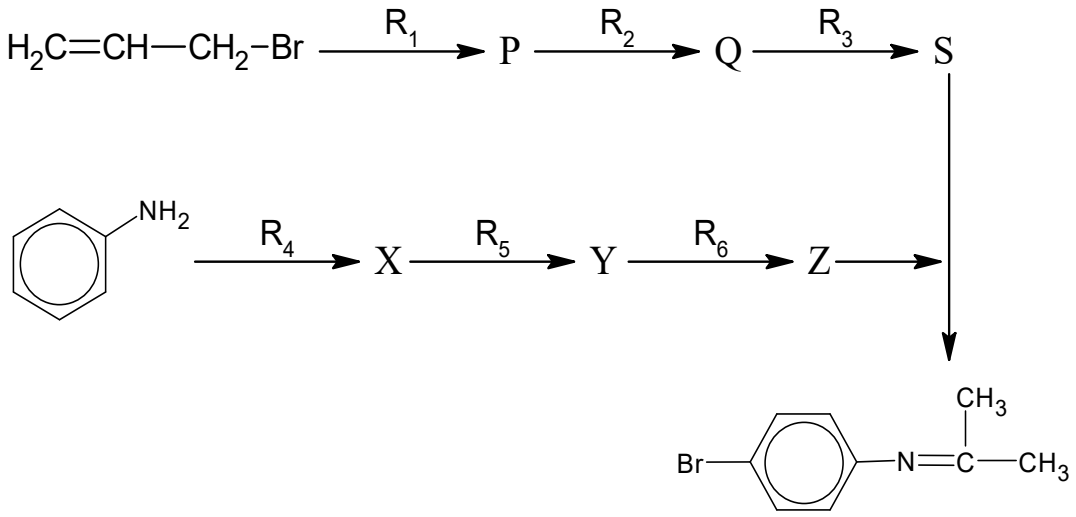


State the formula or structure of the octahedral complex ion formed by this with the ion having the highest oxidation state among the above central metal cations. Above ligand can be indicated as ‘do’ in the formula or structure.

(marks : 80)

PART C - ESSAY (*Answer **two** questions only*)

8. a) Answer using the reaction scheme and reagent list given below.



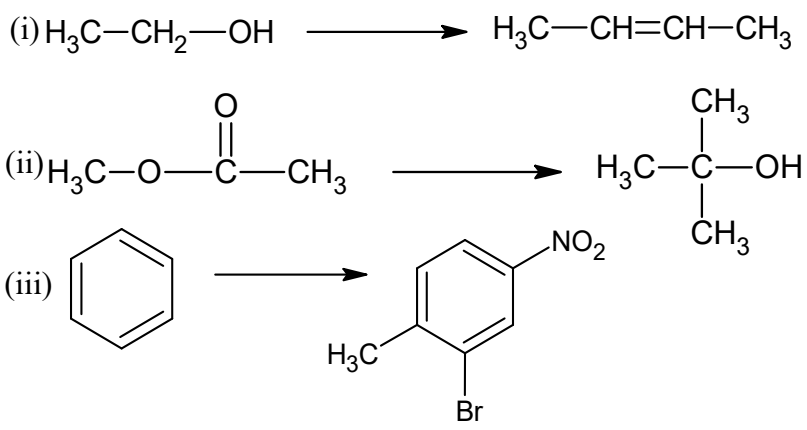
List of reagents :

Br_2 , NaOH, $HgSO_4$, dill: H_2SO_4, HBr, $FeBr_3$, CH_3-COCl, H_2O, KOH / C_2H_5OH

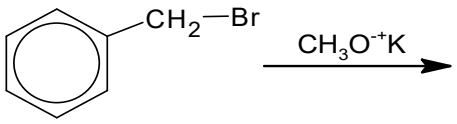
(i) Identify the compounds P, Q, S, X, Y and Z

(ii) Write down the reagents from R_1 to R_6. ***(marks : 60)***

b) Carry out the following conversions using a reaction sequence not exceeding 4 steps.



(marks : 45)

c) (i) Consider the following reaction 

I. State the major product of this reaction

II. Identify the type of this reaction which the mechanism belong to and the number of steps stating reasons.

(ii) Write down the mechanism of the above reaction.

(iii) Show by presenting appropriate structures that this organic mechanism occurs under the number of steps you mentioned.

(iv) State another pair of reactants that can be used to produce the above organic product via this same mechanism. ***(marks : 45)***

9. a) The following steps are proposed to separate and identify 4 metal/non-metal cations in an aqueous solution A.

Step	Observation
1.Acidifying a portion of solution **A** and passing H_2S gas.	No change occurs in the solution.
2.Heating the solution from **1**. above and boiling with conc. HNO_3 and adding a mixture of NH_4Cl / NH_4OH.	A mixture of precipitates $\mathbf{P_1}$ and $\mathbf{P_2}$.
3.Filtering the mixture of precipitate from **2** above and bubbling H_2S gas through the filtrate.	Light colored precipitate $\mathbf{P_3}$
4.Adding conc. NaOH to an initial portion of solution **A**.	Gas $\mathbf{G_1}$ evolved.

The products obtained above were further tested under the following steps.

Step	Observation
1. Adding an aqueous solution of NaOH to the mixture of $\mathbf{P_1}$ and $\mathbf{P_2}$.	Precipitate $\mathbf{P_1}$ dissolves to give colorless solution $\mathbf{S_1}$.
2. I.Filtering and separating precipitate $\mathbf{P_2}$ and adding dil. HCl to it. II.Adding NH_4SCN to the solution $\mathbf{S_2}$.	A colored solution $\mathbf{S_2}$ is obtained. A deeply colored solution $\mathbf{S_3}$ is obtained.
3. I.Adding dill: H_2SO_4 to precipitate $\mathbf{P_3}$. II.Add NaOH to solution $\mathbf{S_4}$.	Gas $\mathbf{G_2}$ and solution $\mathbf{S_4}$ are obtained. A pale colored precipitate $\mathbf{P_4}$ is initially obtained and later turns into a deep colored precipitate $\mathbf{P_5}$.
4. Inserting moist litmus paper into gas $\mathbf{G_1}$	Changes the color of litmus.

(i) Identify the gases $\mathbf{G_1}$ and $\mathbf{G_2}$. State a suitable chemical reaction to identify each, along with observations.

(ii) Identify precipitates $\mathbf{P_1}$ to $\mathbf{P_5}$.

Write the formulas of the chemical compounds contained in the solutions S_1 to S_2.

(iii) Write down the types of metal/non-metal cations identified during the above procedures.

(iv) Represent the following reactions by balanced equations.

I.Dissolution of precipitate P_1 in NaOH.

II.Conversion of precipitate P_4 into P_5. ***(marks : 100)***

b) A chemical mixture (A) used for fireworks is prepared by mixing $NaNO_3$, $Cu(NO_3)_2$ and another inert ingredient

The results of an experimental procedure carried out by a group of students to determine its composition are given below .

step I :

- Accurately measuring 10.00 g of the solid mixture A, dissolving it in distilled water, and diluting it to 250 cm^3 to prepare solution B.

Step II

- Accurately weighing 4.28 g of solid KIO_3, dissolving it in distilled water, and preparing 250 cm^3 of aqueous solution C.
- Adding excess KI and only the required amount of dil. H_2SO_4 to a 25 cm^3 of solution C and allowing the necessary time to react. .
- The volume of aqueous $Na_2S_2O_3$ consumed during the titration of that reaction mixture for the standardization was 30.00 cm^3.

step III :

- The gas X evolved upon heating 25.00 cm^3 of the above mixture B with Devarda's alloy (an alloy containing Al) and excess NaOH crystals was absorbed into 100 cm^3 of an HCl acid solution of concentration 0.1 mol dm^{-3}. Subsequently when that solution was titrated against a 0.1 mol dm^{-3} NaOH solution, the endpoint was 10.00 cm^3.

step IV :

- Upon mixing 25.00 cm^3 of solution B with excess KI and heating, a precipitate and a colored solution were obtained .
- When that precipitate was filtered and the filtrate was titrated with the $Na_2S_2O_3$ standardized under step II above, the burette reading consumed was 7.50 cm^3.

(Na = 23, N = 14, O = 16, Cu = 63.5)

(i) State a suitable indicator for the titrations carried out in steps II and III, along with the color change at the endpoint

(ii) Represent the reactions that occurred under step II by balanced equations and determine the concentration of $Na_2S_2O_3$.

(iii) Present balanced equations for the reactions that occurred under step IV and obtain the mass percentage of $Cu(NO_3)_2$

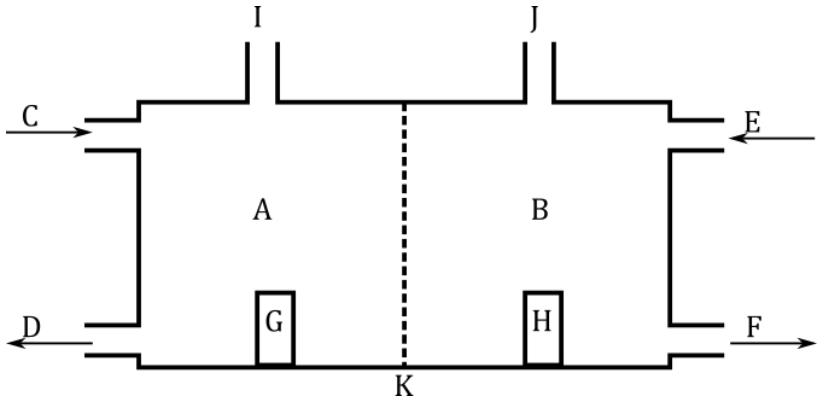
(iv) Give the balanced equations for the reactions that occurred under step III and calculate the mass percentage of $NaNO_3$.

(marks : 50)

10. a) The "sea" is the main natural resource possessed by Sri Lanka.

(i) It has been proposed to build a chemical industrial park using seawater as the starting source. Name five chemical industries for that industrial park.

(ii) A rough diagram of a cell related to the main industry found in the industrial park using seawater is provided.



I. In the above diagram:

(A) Identify chambers A and B.

(B) What are the species entering / exiting through C, D, E, F?.

(C) Identify the electrodes G and H.

(D) Identify the products exiting through I and J.

(E) State what K is and its function.

II. Describe this production process, mentioning the relevant equations and conditions.

III. Explain how above method of this production process is more efficient than other methods that are carrying out in this production process.

IV. Identify the chemical substance produced using the main product of this industry as a starting material along with plant oils, and briefly describe the main steps of that industry.

V. Name the chemical industry carried out by reacting gas J, which is obtained as a byproduct in this chemical industry, with the most abundant atmospheric gas, and describe that production process.

(marks : 100)

b) The Iran-Israel war in the Middle East region caused a massive environmental destruction

(i) State two points for the effect occurred there to each of

I. The lithosphere

II. The hydrosphere

III. The atmosphere

(ii) Name five major air pollutants added to the atmosphere due to this warfare and state a harfmful effect of each pollutant.

c) Clean water is an essential factor for living beings. Studying water quality parameters is essential to determine the purity/impurity of water.

(i) Name five water quality parameters that should be studied in this manner.

(ii) I. Name four major metal ions that cause water hardness.

II. It has been found that the only species causing hardness in a certain water sample is the presence of $CaCl_2$. in order to determine the Ca^{2+} concentration of the hard water, a sample of 5000 cm^3 was treated with excess soap and allowed the precipitate to settle. The mass of the scum deposited as a precipitate was weighed and found to be 1.212 g.

(i) By considering the soap as $C_{17}H_{35}COO^-Na^+$, write the balanced chemical equation for the reaction between soap and Ca^{2+}

(ii) Calculate the concentration of Ca^{2+} in the sample.
(Ca = 40, C = 12, H = 1, Na = 23)

(marks : 50)

The periodic table

	1																2
1	H																He
	3	4											5	6	7	8	9	10
2	Li	Be											B	C	N	O	F	Ne
	11	12											13	14	15	16	17	18
3	Na	Mg											Al	Si	P	S	Cl	Ar
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	55	56	La-	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	87	88	Ac-	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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