

(II) Standard enthalpy changes of two reactions are given below.

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\theta} = -284 \text{kJmol}^{-1}$$

$$2NO_{(g)} + 2CO_{(g)} \longrightarrow N_{2(g)} + 2CO_{2(g)} \qquad \Delta H^{\theta} = -748 \text{kJmol}^{-1}$$
The following thermal charminal data are also given

The following thermo chemical data are also given

 $\Delta H^{\theta}_{f(H_2O_{(g)})} = -242 \text{ kJmol}^{-1}$ 

 $\Delta H^{\theta}_{f(NH_{3(g)})} = -46 \text{ kJmol}^{-1}$ 

 $S^{\theta}_{(H_2O_{(g)})} = 189 \, Jmol^{-1}K^{-1}$ 

 $S^{\theta}_{(NH_{3}(\sigma))} = 193 \, Jmol^{-1}K^{-1}$ 

 $S^{\theta}_{(NO_{(g)})} = 211 \, Jmol^{-1}K^{-1}$ 

 $S^{\theta}_{(O_{2(g)})} = 205 \text{ Jmol}^{-1} \text{K}^{-1}$ 

Using the above information calculate the following for the reaction

 $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$ 

I. Standard enthalpy of reaction  $(\Delta H_R^{\theta})$ 

II.  $\Delta S^{\theta}$ 

III.  $\Delta G^{\theta}$ 

Hence, predict whether the above reaction is spontaneous at 25°C.

6) (A) X + Y + 2Z  $\longrightarrow$  Products

To investigate the kinetics of the above reaction at  $25^{\circ}$ C, four experiments were carried out in which the initial concentrations of X, Y and Z were changed and in each circumstance, the change in concentration of reactant X and the time taken for it were measure. The results of the experiments were tabulated as below.

Experiment	[x]/moldm <sup>-3</sup>	[Y]/moldm <sup>-3</sup>	[Z]/moldm <sup>-3</sup>	$\Delta[\mathbf{x}]/\mathbf{moldm}^{-3}$	t/s	Initial rate R moldm <sup>-3</sup> s <sup>-1</sup>
1	0.2	0.1	0.1	0.040	25	
2	0.2	0.2	0.1	0.096	30	
3	0.1	0.1	0.2	0.012	30	
4	0.1	0.1	0.1	0.012	30	

- (i) Calculate the initial rates in each of the experiments and complete the relevant column in the table.
- (ii) Assuming the rate orders with respect to X, Y and Z to be a, b and c respectively and the rate constant as k, write a mathematical expression for the rate of the reaction (R)
- (iii) Using the data given in the table, calculate the volume of a, b, c and k

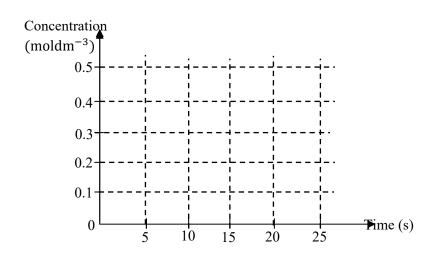
- (iv) Plot the variation of the concentration of Z with time while keeping the concentration of X and Y constant in a graph.
- (v) How would the rate change if the concentration of each of X and Y are doubled while keeping the concentration of Z constant?
- (B) Consider the reaction  $A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)}$ .

The above reaction tales place in a closed vessel of  $1 \text{ dm}^3$  volume at 400 K. Assume that the reaction was started at t = 0 and the concentration of  $A_{(g)}$ ,  $B_{(g)}$  and  $C_{(g)}$  at any time t = t s are 0.6 moldm<sup>-3</sup>, 0.3 moldm<sup>-3</sup>, 0.3 moldm<sup>-3</sup> respectively. The reaction attained equilibrium at t = 15 s and the equilibrium concentrations of  $A_{(g)}$ ,  $B_{(g)}$  and  $C_{(g)}$  were 0.4 moldm<sup>-3</sup>, 0.1 moldm<sup>-3</sup> and 0.3 moldm<sup>-3</sup>.

At t = 17 s, 0.2 moles of  $C_{(g)}$  was introduced to the system and at t = 25 s, the system attained a new equilibrium again.

Assuming that the temperature of the system remains unchanged throughout all the above processes, answer the following

- (i) Calculate the equilibrium constant  $k_c$  for the above reaction at 400 K.
- (ii) If there was no  $C_{(g)}$  in the system initially, what would be the amounts of A and B in the system at t = 0?
- (iii) By calculating the value of  $Q_c$  at time t = t s after the reaction has started, predict the direction in which the reaction has proceeded so as to attain equilibrium.
- (iv) Indicate the changes in concentrations of the reactants and products in the above process at times t = 0, 15 s, 20 s and 25 s in a graph indicated as below.



- 7) (A) A transition metal M forms a coloured complex ion P in aqueous medium. It has the general formula [M(H<sub>2</sub>O)<sub>n</sub>]<sup>m+</sup>
  - When a limited amount of concentrated NH<sub>3(aq)</sub> is added to P, initially a pink coloured precipitate (Q) is formed.
  - On further addition of conc. NH<sub>3(aq)</sub>, the above precipitate dissolves to give a yellow coloured solution (R).
  - The above yellow coloured solution turned brown after some times.
  - When concentrated HCl is added to P, the blue coloured (S) is formed.
  - (i) Identify the metal M and mention the oxidation state of M in the complex ion P.
  - (ii) Give the electronic configuration of M in the complex ion P.
  - (iii) Give the values of m and n.
  - (iv) Give the structure of Q, R and S
  - (v) Write the IUPAC names of the complex ions P, R and S
  - (vi) Explain the reason for the change in colour from yellow to brown
  - (B) A and B are two coordination compound with molecular formula  $CoN_5H_{12}I_2O_2$ . H atom exist only as NH<sub>3</sub> in both compounds and cobalt is in he same oxidation state. Only compound B gives a yellow precipitate with AgNO<sub>3(aq)</sub> which is insoluble even in concentrated NH<sub>3</sub>
    - (i) In the above compounds, what is the oxidation state of Co?
    - (ii) Write the complete electronic configuration of Co ion given in above?
    - (iii) Identify common ligands coordinated in compounds A and B.
    - (iv) Deduce the structural formulae of compounds A and B (Reasons are required)
    - (v) Give a chemical test to identify the anion in compound A.

#### Part – II C

8) (A) Using  $CH_2 = CH_2$  as the only organic starting material and as reagents only those given in the list, show how would you synthesis the following compound in not more than eight (8) steps.

$$CH_3CH = CHCH_2 - \langle \circ \rangle$$

# List of Reagents

 $Cl_2$ ,dilH<sub>2</sub>SO<sub>4</sub>, anhydrous *Alcl*<sub>3</sub>conH<sub>2</sub>SO<sub>4</sub>, *H*<sub>2</sub>O, *PCl*<sub>5</sub>, *Mg*, dry ether, Pyridinium Chlorochromate PCC. (B) Show how you would carry out the following conversion not more than eight (8) steps

$$CH \equiv CH \longrightarrow CH_3 - CH = N - CH_2 CH_2 CH_2 CH_3$$

(C) Give the major product of the following reaction

$$CH_3 - CH_2 CH = CH_2 \xrightarrow{conc. H_2SO_4}$$

- (i) Write the structure of the major product
- (ii) Write the mechanism for the formation of the product in part (i).
- 9) a) Solution P contains two cations and two anions. Following tests were carried out to identify these cations and anions.

#### Test for cations

	Test	Observation		
(i)	Dilute KOH solution was added drop	A grey precipitate $(X_1)$		
	wise into a small portion of P	A brown precipitate $(X_2)$		
(ii)	Dilute NH <sub>3</sub> solution was added into the	A part of precipitate dissolves.		
	above obtained precipitates.	The brown precipitate remains.		
(iii)	Solution was separated from (ii) by	White precipitate $(X_3)$		
	filtration and dilute HNO3 was added then	It turns black $(X_4)$ when heated.		
	excess $Na_2S_2O_3$ was added to the solution			
(iv)	Dilute HNO <sub>3</sub> was added to the precipitate	Red colour complex compound		
	$(X_2)$ then NH <sub>4</sub> SCN added	(X <sub>5</sub> )		

# Test for anions

Test	Observation
I. Acidified KMnO <sub>4</sub> solution was added into P.	KMnO <sub>4</sub> colour decolourized gas evolved.
II. BaCl <sub>2</sub> solution was added into the solution from (I)	White precipitate $(X_6)$ which is insoluble in dil HNO <sub>3</sub> was obtained.
III. Gas from (I) was passed through clear lime water.	First white precipitate formed $(X_7)$ then a clear solution $(X_8)$ was obtained.
IV. $Ca(NO_3)_2$ was added into solution of P.	A white precipitate $(X_9)$
V. Dilute HCl was added into P solution	A brown colour gas $(X_{10})$ evolved.
(i) Identify cations and anions	
(ii) Identify $X_1 - X_{10}$ .	

B) Solution G contains Hg<sup>2+</sup>, Br<sup>-</sup> and H<sup>+</sup>. The following procedures were used to determine their concentrations.

#### Procedure - I

Excess AgNO<sub>3</sub> solution was added to  $25.00 \text{ cm}^3$  of the solution G forming a precipitate. Dried mass of the precipitate is 3.761 g

### Procedure - II

 $H_2S$  was bubbled through 25.00 cm<sup>3</sup> of solution G to precipitate  $Hg^{2+}$  as HgS. The precipitate was filtered and the filtrate was kept to be used in procedure III. The precipitate was transferred into 30.00 cm<sup>3</sup> of 0.2 moldm<sup>-3</sup> acidic KMnO<sub>4</sub> to produce  $Hg^{2+}$ , Mn<sup>2+</sup> and SO<sub>2</sub>. (Assume there's no reaction between SO<sub>2</sub> and KMnO<sub>4</sub>) The solution was boiled to remove SO<sub>2</sub>, and the excess KMnO<sub>4</sub> was titrated with 0.3 moldm<sup>-3</sup> Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The needed volume of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to completely react with KMnO<sub>4</sub> is 20.00 cm<sup>3</sup>

# Procedure III

The filtrate from II above was boiled to remove  $H_2S$  and cooled to room temperature. The solution was neutralized by 0.4 moldm<sup>-3</sup> Ba(OH)<sub>2</sub>. The needed volume of Ba(OH)<sub>2</sub> for complete neutralization is 25.00 cm<sup>3</sup>

According to the procedures above, find the concentrations of  $Hg^{2+}$ ,  $Br^-$  and  $H^+$ 

- 10) a) X is a P block element. In room temperature, it found as a diatomic molecule.  $X_1$ . It has a boiling point of  $34.7^{\circ}$ C and melting point of  $101^{\circ}$ C. It has high electron affinity. X can take both positive and negative oxidation numbers.
  - I. Identify X,  $X_1$
  - II. Write the electronic configuration of X as  $1S^2$ ,  $2S^2$  ... ... ...
  - III. Give the oxidation numbers of X
  - IV. Give four oxyacids of X
  - V. Give the hydrides of the elements (HX) in the group to which X belongs and sketch the variation in boiling points of these hydrides. Explain the variation
  - VI. In each of the following instances, give balanced chemical equation
    - i. With excess NH<sub>3</sub>
    - ii. With excess NaOH
  - VII. Give one use of X.

b) Give the highest oxidation number oxides of third period elements and give their,

I. Oxidation number

- II. Bond type.
- III. Acidic or basic behaviour

c) Acidic strength of carboxylic acid is greater than acidic strength of phenol . Explain this.

d) Write balanced chemical equation for the following chemical reactions.

- I. Thermal decomposition Of LiNO<sub>3</sub>
- II. Hydrolysis of SCl<sub>2</sub>
- III. Reaction of Br<sub>2</sub> with NaOH
- IV.  $KMnO_4 + H_2SO_4 + H_2S \longrightarrow$
- V.  $\operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{H}_2 \operatorname{O}_2 + \operatorname{H}^+ \longrightarrow$
- e) Excess KI was added into 2.568 g of KIO<sub>3</sub> solution. Find the minimum volume of 3 moldm<sup>-3</sup> HCl to completely convert KIO<sub>3</sub> to I<sub>3</sub><sup>-</sup>. [K-39, I-127, O-16]