Use separate answer scripts for each Group

B.Sc. (Honours) Examination, 2019

Semester-II (CBCS)
Chemistry (Honours)
Core Course: CC-3
(Inorganic and Physical Chemistry)

Time: Three Hours **Full Marks: 60**

Questions are of value as indicated in the margin.

Group-A (Marks: 30)
(Inorganic Chemistry)

Answer ***any three*** questions.

1. a) A decimolar Daniell cell is working well at 25°C. Determine EMF of the cell. Calculate the value of equilibrium constant of the reaction occurring in the cell. Find out the free energy change and electrical work done by the cell. 2.5

   [Given: $E^{\circ}_{Zn^{2+}/Zn} = -0.76\,V;\ E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V$]

   b) Construct cells corresponding to the given reactions: 2.5

   i) $Hg_2^{2+}(aq) + 2C\bar{l}(aq) = Hg_2Cl_2(S)$

   ii) $2Ag(S) + Cl_2(g) = 2AgCl(S)$

   c) At neutral medium, dichromate cannot oxidize iodide to iodine. Justify the statement in the light of formal potential. 2.5

   (Given: $E^{o}_{Cr_2O_7^{2-}/Cr^{3+},\,H^+} = 1.33V,\ E^{o}_{\frac{1}{2}I_2/I^-} = 0.54V$)

   d) A solution of Fe^{3+} is titrated potentiometrically using Ce^{3+} solution at 25°C. Calculate the emf (in volt) of the redox system thus produced when (i) 50% of Fe^{3+}, (ii) 80% of Fe^{3+} and (iii) 100% of Fe^{3+} are titrated. 2.5

   (Given: $E^{o}_{Fe^{3+}/Fe^{2+}} = 0.77V,\ E^{o}_{Ce^{4+}/Ce^{3+}} = 1.28V$)

2. a) What is Latimer diagram? Mention its significance. Calculate E^{o} for $\overset{+}{M}O_2/M^{4+}$ system in 1M acid medium from the diagram: $MO_2^{2+} \xrightarrow{0.97V} MO_2^{+} \longrightarrow M^{4+} \xrightarrow{1.01V} M^{3+}$. 2.5

   b) Ferric ion normally oxidizes iodide to iodine in aqueous solution. But in presence of excess fluoride, it cannot. Justify. 2.5

   (Given: $E^{o}_{Fe^{3+}/Fe^{2+}} = 0.77V,\ E^{o}_{\frac{1}{2}I_2/I^-} = 0.54V,\ K_{eq} = 10^5$ for $Fe^{3+} + F = [FeF]^{2+}$)

   c) What are alpha and beta particle? How many alpha and beta particles are emitted during the following change: ${}^{b}_{a}X \rightarrow {}^{d}_{c}Y$. 2.5

   d) Which diagram is helpful in predicting the decay mode of radio nucleus? Draw the diagram and predict the decay modes of C-14 and O-14 with proper justification. 2.5

3. a) What do you mean by nuclear binding energy (NBE) and packing fraction (PF)? Show the NBE per nucleon is maximum when PF is minimum. 2.5

   b) What is magic number? Predict the end products of uranium, thorium and actinium series. Among the end products which one is the most stable? Justify your answer. 2.5

   c) Density of nucleus is independent of mass number and the nucleus is a tightly bound system of nucleon. Explain. 2.5

   d) What is nuclear force? Mention its characteristics. Comment on the origin of nuclear force. 2.5

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4. Among the chemical species: $Na_2[Fe(CN)_5NO]$, $Na_2[Fe(CN)_5]NO$ and $Na_2Fe[(CN)_5NO]$, select the correct position of the third bracket. Justify your answer in the light of Werner's theory for metal complexes. Mention the bonding nature of the constituents present within the third bracket. Compare the ligand activities of CN^- and NO. Find out the oxidation number of iron in the complex. (1+2)+2+4+1=10

5. Differentiate the given compounds in terms of their (i) physical properties, (ii) chemical properties and (iii) isomeric behavior. 4x2.5=10
$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_4)_5Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$

Group-B (Marks: 30)
(Physical Chemistry)

Unit-I
Answer ***any two*** questions.

1. a) What is the rate law? Mention its importance. 1+1
   b) Molecularity of a reaction can only be integers – explain. 1
   c) First order reaction occurs more rapidly than the second order reaction when both the reactions have same value of rate constant and start from same initial concentration – explain. 2.5
   d) The half life of a reaction having order n > 1 is inversely proportional to the initial concentration of the reactant – explain. 2

2. a) Explain why in the differential method of order determination the order n_c is regarded as true order but the order n_t is not? (symbols have usual meaning) 2.5
   b) For the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ $(\text{when } k_2 >> k_1)$ show that the rate of formation of C is totally governed by the rate of the slower step. (Apply the steady state approximation for the derivation). 2
   c) Show that the order of the following multi step reaction is 3/2 with respect to CH_3CHO. 3

$$Ch_3CHO \xrightarrow{k_1} {}^{\bullet}CH_3 + {}^{\bullet}CH_3$$
$${}^{\bullet}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CHO$$
$${}^{\bullet}CH_2CHO \xrightarrow{k_3} {}^{\bullet}CH_3 + CO$$
$${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \xrightarrow{k_4} CH_3 - CH_3$$

3. a) What is actually done in the relaxation method for studying fast reactions? 1
   b) Find out the expression for the following fast reaction using the concept of relaxation method.
   $$H^+ + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O(l)$$ 5
   c) Define relaxation time of the fast reaction. 1
   d) Calculate the relaxation time using $[H^+]_{eq} = 10^{-7}\,\text{mole/lit}$, $[H_2O]_{eq} = 55.5\,\text{mole/lit}$ and $k_1 = 1.4\times10^{11}\,\text{lit.mol}^{-1}\,\text{sec}^{-1}$. 0.5

4. a) What are the main features of the collision theory of reaction rate? 1.5
   b) Calculate k_{obs} for the reaction, $2HI \rightarrow I_2 + H_2$ using the collision theory. 3
   c) What is the reaction co-ordinate? 2
   d) Define the activation energy of a reaction and show the activation energy plot for an exothermic reaction. 1

Unit-II
Answer ***any two*** questions.

5. a) Discuss the limitation of the first law of thermodynamics with two examples. 3
   b) Prove that the efficiency of all the reversible engines which are working between the same two reservoirs is same. Do you believe such a result? Answer with reason. 3.5+1

6. a) Based on the second law of the thermodynamics prove that (i) $\oint \frac{đQ_{rev}}{T} = 0$ and $\oint \frac{đQ_{irev}}{T} < 0$.
   b) A refrigerator is operated by a $\frac{1}{4}$-hp motor. If the interior of the box is to be maintained at –20°C against a maximum exterior temperature of 35°C, what is the maximum heat leak (in watts) into the box that can be tolerated if the motor runs continuously? Assume that the coefficient of performance is 75% of the value for a reversible engine. (1hp = 746watt). 4

7. a) Comment on the following statements:
      i) 1^{st} and 2^{nd} laws of thermodynamics are independent law of nature. 1.5
      ii) The second law of thermodynamics disregards the first law. 1.5
   b) One mole of carbon monoxide is transformed from 25°C and 5 atm. pressure to 125°C and 2 atm. pressure. If $C_p/R = 3.1916 + 10^{-3}\,T - 1.41 \times 10^{-7}\,T^2$. Calculate ΔS and interpret the result. 3+1.5

8. a) What is the thermometric equation corresponding to the centigrade scale of temperature. Is there any approximation to have this scale? Is it absolute scale of temperature? Answer with reason. 1+1+0.5
   b) Prove that the scale of temperature in the kinetic theory corresponds to the ideal gas scale of temperature. 1
   c) Show that temperature in the ideal gas scale is proportional to that in the thermodynamics scale. What is the value of the proportionality constant? Is there any justification? 2+0.5+1.5

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