Parvatibai Chowgule College of Arts and Science
Autonomous

B.Sc. Semester End Examination, January 2022

Semester: III

Subject: Chemistry

Course Title: Comprehensive Chemistry-I (Core)

Duration: 2 Hours   Maximum Marks: 45

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Instructions: 1. All Questions Are Compulsory.

2. Figures To The Right Indicate Full Marks.

3. Use Of Calculators Is Allowed.

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Q.1A) **Answer <u>ANY TWO</u> of the following:**

  i) Derive Clapeyron equation. **3**

  ii) Derive an expression for Variation of Free energy with Temperature and Pressure. **3**

  iii) Explain the determination of 'solubility product of a sparingly soluble salt' by conductometric method. **3**

B) Answer <u>**ANY ONE**</u> of the following:

  i) Name and draw the geometry exhibited by $[Ni(CN)_4]^{2-}$ and $[SbF_5]^{2-}$ complex. **3**

  ii) Write the structural formula of the following compounds and also calculate the effective atomic number of the central metal ion.

    x) Dicholorobisethylenediammine cobalt (III) chloride

    y) Tetraammine dichloroplatinum (IV) chloride **3**

Q.2 **Answer <u>ANY TWO</u> of the following:**

A)i) Compare the properties of lanthanides with actinides with respect to: (x) Oxidation state and (y) Complex formation. **3**

  ii) State the Lewis concept of acids and bases. Justify why ammonia is termed as base though it does not contain OH^- ions. **3**

B)i) Explain the following observations:

    (x) La^{3+}, Lu^{3+} and Ce^{4+} ions are diamagnetic, while Sm^{3+} shows paramagnetic behaviour.

    (y) La, Gd and Lu show only +3 oxidation state, whereas other lanthanides can exhibit +2 and +4 oxidation state. **3**

  ii) Giving reactions, explain what happens when;

(x) Ammonium chloride reacts with lithium nitrate in liquid NH_3.

(y) Barium nitrate reacts with ammonium sulphide in liquid NH_3. **3**

C) Explain the following observations:

i) (x) $La(OH)_3$ is more basic than $Lu(OH)_3$.

(y) Nd^{+3} and Er^{+3} have same color i.e red. **3**

ii) Giving suitable examples, explain the terms conjugate acid and conjugate base. Give reactions to show water can behave as an acid as well as base. **3**

Q.3) Answer <u>ANY TWO</u> of the following:

A) In an electrolysis experiment, the number of ion pairs in anodic and cathodic compartments are 8 each and 4 in the middle compartment. Predict the number of discharged species and fall or rise in concentration at anode and cathode based on following data:

x.   Anions and cations move at same speed and two anions leave the cathodic compartment during electrolysis of $AgNO_3$ with platinum electrodes.

y.   Cations move at thrice the speed of anions and two anions leave the cathodic compartment during electrolysis of $AgNO_3$ with platinum electrodes.

z.   Anions and cations move at same speed and three anions leave the cathodic compartment during electrolysis of $AgNO_3$ with silver electrodes. **6**

B) Derive expressions for entropy change of an ideal gas in isothermal, isochoric and isobaric process. **6**

C) i) Explain Lodge's moving boundary method. **3**

ii) Define cyclic process. Prove that work done by the system in a cyclic process is equal to the heat absorbed by the system. **3**

Q.4) Answer <u>ANY ONE</u> of the following:

A) i) Using Le Chatelier's principle, explain and justify the effect of following changes on a chemical reaction at equilibrium:

p.   Decrease in pressure for a reaction in which forward reaction proceeds with a decrease in number of moles.

q.   Decrease in temperature for a reaction in which forward reaction is exothermic.

r.   Increase in concentration of a reactant. **5**

ii) When aqueous solution of ammonia is added to green solution of a nickel compound A, the color changes to purple to give complex B.

x. Identify A and B and name them giving suitable reaction.

y. What is the primary and secondary valency in complex B?

z. State and draw the geometry exhibited by complex B. **4**

iii) Explain the extraction of lanthanides from monazite ore. **3**

B) i) x. Thermodynamic efficiency can never be equal to one. Justify the statement.

y. State Carnot Theorem.

z. Calculate the efficiency of a heat engine working reversibly between temperature range of 100 ^{o}C and 400 ^{o}C. **5**

ii) A compound with empirical formula $Co(NH_3)_5BrSO_4$ exists in two forms, red and violet. Solution of red gives a precipitate of AgBr on addition of $AgNO_3$. The violet form does not give precipitate with $AgNO_3$ but gives a white precipitate on addition of $BaCl_2$. Draw the structure of each compound and explain the observations. **4**

iii) Explain the extraction of thorium from monazite ore. **3**

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