[This question paper contains 04 printed pages]

Roll Number: ______________

HPAS Etc. Combined Competitive (Main) Examination, 2019

Chemistry-I

Time Allowed: 3 Hours | Maximum Marks: 100

Note:

1. This question paper contains total eight questions. *Attempt any five questions including compulsory question No.1.*
2. Each question carries equal marks. Marks are divided and indicated against each part of the question. Write answer in legible handwriting. Each part of the question must be answered in sequence and in the same continuation.
3. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of question shall be counted even if attempted partly. Any page or portion of the page left blank in answer book must be clearly struck off.
4. *Re-evaluation / Re-checking of answer book is not allowed.*
5. Some useful fundamental constants and conversion factors

$N_A = 6.022 \times 10^{23}$ mol^{-1}
Rydberg constant = 2.178×10^{-18} J
$c = 2.998 \times 10^{8}$ ms^{-1}
$k_B = 1.38 \times 10\text{-}23$ JK^{-1}
$m_e = 9.109 \times 10^{-31}$ kg
$F = 96485$ C mol^{-1}
$R = 8.314$ JK^{-1} mol^{-1}
$h = 6.626 \times 10^{-34}$ Js
$\pi = 3.142$
1 amu = 1.66×10^{-27} kg
1 cal = 4.184 J
1 J = 1 kg m^{2} s^{-2}
1 Å = 10^{-8} cm = 10^{-10} m = 0.1 nm = 100 pm
1 atm = 760 torr = 1.01325×10^{5} Pa
1 bar = 1×10^{5} Pa = 0.9869 atm
1 eV = 1.602×10^{-19} J
1 L atm = 101.34 J
1 L bar = 100 J

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1. (a) Using MO diagrams, explain NO is paramagnetic and CO is diamagnetic. (4)

(b) What is the probability density (expressed in terms of a_o) of a 1s-electron from the nucleus of a hydrogen atom? (5)

(c) The force constant of $^{1}H^{35}Cl$ molecule is 480 Nm^{-1}. Calculate the fundamental frequency and wave number. The atomic masses are $^{1}H = 1.673 \times 10^{-27}$ kg; $^{35}Cl = 58.06 \times 10^{-27}$ kg. (7)

(d) Why is the separation of lanthanides difficult? Name any two methods for their separation. (4)

2. (a) Sketch the normal modes of vibration of H_2O and CO_2 and explain which of them are Raman and which are IR-active. (4)

(b) For a particle in a one-dimensional box of length l ($0 \leq x \leq l$), calculate the values of the average position ($\langle x \rangle$). (5)

(c) Write the expression for energy for the particle in a one-dimensional box. How can you justify (i) quantization of energy? (ii) existence of zero point energy? (7)

(d) Write the Schrodinger wave equation for the hydrogen atom in spherical polar co - ordinates. (4)

3. (a) What are Rayleigh, Stokes and Anti-Stokes lines ? Is the intensity of Stokes lines different from that of the anti-Stokes lines? Explain. (5)

(b) Write down the wave functions for the H_2 molecule using

(i) Valence bond theory

(ii) Molecular orbital theory

Suggest modifications to the wave functions. (5)

(c) Calculate the change in entropy in an isothermal reversible expansion of 5 moles of an ideal gas from a volume of 10 dm^3 to 100 dm^3 at a temperature of 300 K. (5)

(d) Write the virial equation of state of a real gas. Express the van der Waals equation in the form of the virial equation of state. Discuss the physical significance of the virial coefficients. (5)

4. (a) An element exists in the bcc structure. Each edge of the structure is 2.88 Å. The density of this element is 7.20 g cm^{-3}. How many atoms there will be in 100 g of the element? (7)

(b) Using the Principle of equipartition of energy, estimate the energy of HCl molecule, assuming that all the degrees of freedom are excited and contribute towards the energy of the molecule. Give the statement of the law. (5)

(c) In the van der Waals gas equation, the pressure correction term is n^2a/V^2. Find the SI units of van der Waals constant 'a'. (4)

(d) Using the thermochemical data of the following reactions:

$H_2O\,(l) \rightarrow H^+\,(aq) + OH^-(aq)$; $\Delta H^o = 57$ kJ

$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l)$; $\Delta H^o = -286$ kJ

Estimate the enthalpy of formation (ΔH_f^o) of OH^- ions at 298 K.

(Given, $\Delta H_f^o[H^+(aq)] = 0$) (4)

5. (a) Determine the number of components and number of phases, and evaluate the degrees of freedom for the following equilibria: (6)

(i) $NaCl(s) – KCl(s) – H_2O(l) – H_2O(g)$ system

(ii) $KCl(s) – NaBr(s) - H_2O(l) – H_2O(g)$ system

(iii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(b) At 37 °C, the osmotic pressure of blood is 7.65 atm. How much glucose (M = 180 g cm^{-1}) should be used per L for an intravenous injection that is to be isotonic with osmotic pressure of blood. (5)

(c) Devise an electrochemical cell in which the following reaction takes place:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$ (5)

(d) Write electrode reaction for the $H_2 – O_2$ fuel cell with aqueous solution of NaOH. (4)

6. (a) Derive the expressions for half-life time of a first-order and second – order reaction. (5)

(b) The rate constant of a reaction is tripled by a 10 °C rise in temperature in the vicinity of 27 °C. Estimate the activation energy. (5)

(c) The quantum yield for the photochemical reaction between $H_2 – Cl_2$ is so high where as that of $H_2 – Br_2$ reaction is so slow, even though both are chain reactions. Account for the observations. (5)

(d) Distinguish between the following with one example of each: (5)

(i) Photochemical reactions and dark reactions

(ii) Fluorescence emission and Phosphorescence emission

7. (a) Derive an expression for Langmuir's absorption isotherm. Explain how it could be used for determination of the surface area of an absorbent. (8)

(b) Discuss the preparation, stability and applications of microemulsion. (6)

(c) Describe the co-operative effect of haemoglobin during oxygen transport in the blood. (6)

8. (a) Write the IUPAC names of following co-ordination compounds: (6)

(i) $[Cr(en)_3]Cl_3$

(ii) $(NH_4)_2[CuCl_4]$

(iii) $K_3[CoF_6]$

(b) What are the limitations of crystal field theory in explaining the bonding of coordination complexes? What modifications were suggested to overcome the limitations? (6)

(c) Transition metals and their compounds are frequently used as catalysts: (3)

(i) Name the catalyst in the Haber Process for the manufacture of ammonia.

(ii) Name the catalyst used in the hydrogenation of carbon-carbon double bonds.

(iii) Name the catalyst in the Contact Process for the manufacture of sulphuric acid.

(d) What is super acid? How is it prepared? Compare and contrast the reactivity of super acid and sulphuric acid. (5)

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