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# UPSC CGS Exam

Mains Chemistry Paper II

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**CHEMISTRY**  
**Paper – II**

Time Allowed : Three Hours

Maximum Marks : 200

**Question Paper Specific Instructions**

*Please read each of the following instructions carefully before attempting questions :*

*There are **FIFTEEN** questions divided under **THREE** sections.*

*Candidate has to attempt **TEN** questions in all.*

*The **ONLY** question in Section A is compulsory. In Section B, **SIX** out of **NINE** questions are to be attempted. In Section C, **THREE** out of **FIVE** questions are to be attempted.*

*The number of marks carried by a question / part is indicated against it.*

*Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.*

*Unless otherwise mentioned, symbols and notations have their usual standard meanings.*

*Assume suitable data, if necessary, and indicate the same clearly.*

*Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.*

*Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.*

*Answers must be written in **ENGLISH** only.*

## Some useful fundamental constants and conversion factors

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Rydberg constant} = 2.178 \times 10^{-18} \text{ J}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$F = 96485 \text{ C mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\pi = 3.142$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0.1 \text{ nm} = 100 \text{ pm}$$

$$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0.9869 \text{ atm}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ L atm} = 101.34 \text{ J}$$

## SECTION A

**Q1. Answer all of the following questions :**

**5×16=80**

- (a) At the critical point on P – V isothermal plot at critical temperature ( $T_c$ ) of real gas  $\left(\frac{\partial P}{\partial V}\right)_{n, T_c} = 0$  and  $\left(\frac{\partial^2 P}{\partial V^2}\right)_{n, T_c} = 0$ . What are the causes? 5
- (b) At Boyle temperature  $\left(T_B = \frac{a}{Rb}\right)$  and inversion temperature  $\left(T_i = \frac{2a}{Rb}\right)$  of van der Waals gas, it behaves ideally though values are not same. Explain with reasons. 5
- (c) Prove that greater the diffraction angle, greater is the accuracy in determining the lattice parameters. 5
- (d) Explain how thermodynamics relates non-expansion work to a change in composition of a system. 5
- (e) Discuss van't Hoff plots for endothermic and exothermic reactions. 5
- (f) Calculate ionic strength  $I$ , mean ionic activity coefficient  $r_{\pm}$ , and mean activity  $a_{\pm}$ , for a 0.0250 m solution of  $K_2SO_4$  at 298 K. Assume complete ionisation. 5
- (g) The rates of a reaction starting with initial concentration  $2 \times 10^{-3} \text{ mol L}^{-1}$  and  $1 \times 10^{-3} \text{ mol L}^{-1}$  are equal to  $2.40 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  and  $0.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ , respectively. Calculate the order of the reaction with respect to the reactant and the rate constant. 5
- (h) The activation energy of a reaction is  $75.2 \text{ kJ mol}^{-1}$  in the absence of a catalyst and  $50.14 \text{ kJ mol}^{-1}$  in the presence of a catalyst. How many times does the rate of reaction increase in the presence of a catalyst if the reaction proceeds at  $25^\circ\text{C}$ ? 5
- (i) Are chemical potential and electrochemical potential of  $Zn^{2+}(\text{aq})$  same? If not, write the expression for them. 5
- (j) By potentiometer, we measure equilibrium or zero-current potential ( $E$ ) of the galvanic cell. We know at equilibrium  $\Delta G_{P,T} = 0$ , but we write  $-\Delta G = nFE$ , where  $E > 0$ . How will you explain it? 5

- (k) Describe under what condition/s an operator is Hermitian. Prove that Hermitian operators have real eigenvalues. 5
- (l) Consider a system whose state is given by  $\psi = \frac{\sqrt{3}}{3}\phi_1 + \frac{2}{3}\phi_2 + \frac{\sqrt{2}}{3}\phi_3$ , where  $\phi_1, \phi_2$  and  $\phi_3$  are orthonormal.
- (i) Calculate the probability of finding the system in any of the states  $\phi_1, \phi_2$  and  $\phi_3$ .
- (ii) Consider an ensemble of 800 systems on which measurements are made. How many systems will be found in each one of the states  $\phi_1, \phi_2$  and  $\phi_3$ ? 5
- (m) Rigid  $H_2$  molecule is rotational spectrum inactive but rotational Raman spectrum active. Explain with reasons. 5
- (n) Does 'einstein' depend on wavelength of electromagnetic radiation? If yes, how? Give your answer with required expression. 5
- (o) For the reaction :
- $$UO_2^{2+}(\text{aq.}) + (\text{COOH})_2(\text{aq.}) \rightarrow UO_2^{2+}(\text{aq.}) + \text{CO}(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
- (i) What does the above reaction indicate?
- (ii) What is the role of  $UO_2^{2+}$  here? 5
- Give reasons in support of your answer.
- (p) Photodecomposition of HI (g) follows the following mechanism :
- $$\text{HI} + h\nu \rightarrow \text{H} + \text{I}$$
- $$\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$$
- $$\text{I} + \text{I} \rightarrow \text{I}_2$$
- Find its quantum yield,  $\phi$ . 5

## SECTION B

Attempt any six questions :

10×6=60

**Q2.** Gases A, B, C and D are van der Waals gases. Its van der Waals constants ('a' and 'b') values (in SI units) are :

	A	B	C	D
'a'	0.6	0.6	0.2	0.005
'10 <sup>3</sup> b'	0.025	0.15	0.10	0.02

- (i) Which gas has highest critical temperature ?
- (ii) Which gas molecule has highest molecular volume ?
- (iii) Which gas has highest  $\left(\frac{\theta}{\pi}\right)$  value at 273 K and 1.0 atm ? ( $\theta$  and  $\pi$  are the reduced temperature and pressure respectively)
- (iv) Which gas is most nearly ideal behaviour at 273 K and 1.0 atm ? Explain with reason.

10

**Q3.** Potassium chloride (rock salt structure) crystal has a density of 1.98 g cm<sup>-3</sup>. The first order (200) reflections were observed at 6.5° when X-rays of 70.8 pm (Mo source) were used. Calculate the number of KCl molecules in a unit cell.

10

**Q4.** BaSO<sub>4</sub> is not very soluble in water.

- (i) Calculate the solubility product equilibrium constant,  $K_{sp}$  for BaSO<sub>4</sub> from the following molar free energies of formation, expressed as  $\Delta_f G^\circ/RT$  at 298 K.

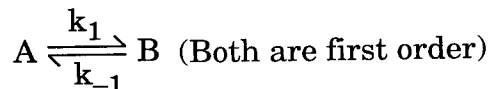
	BaSO <sub>4</sub> (s)	Ba <sup>2+</sup> (aq)	SO <sub>4</sub> <sup>2-</sup> (aq)
$\Delta_f G^\circ/RT$	- 549.53	- 226.21	- 300.34

- (ii) Experimentally, 0.246 mg of BaSO<sub>4</sub> (molar mass of BaSO<sub>4</sub> = 233.38 g mol<sup>-1</sup>) is dissolved in 0.1 L of water at 298 K. What  $K_{sp}$  does this fact predict, assuming that all activity coefficients are equal to 1 ?

- (iii) Why is there difference in the values of  $K_{sp}$  as calculated in (i) and (ii) ?

10

**Q5.** Consider the following opposing reaction :



$$\text{Derive : } (k + k_{-1}) t = \ln \left( \frac{x_e}{x_e - x} \right)$$

where  $x$  = concentration of B at time 't', and

$x_e$  = its equilibrium concentration.

10

**Q6.** (a) Discuss the variation of molar conductivity of an aqueous solution of surfactant with the increase in concentration of surfactant solution. 5

(b) Why does critical micelle concentration of sodium dodecyl sulphate decrease as the concentration of added sodium chloride salt increases? Explain this effect. 5

**Q7.** (a) For a galvanic cell reaction, how will you determine its thermodynamic parameters ( $\Delta_r G$ ,  $\Delta_r S$  and  $\Delta_r H$ )? Derive the required expressions. 5

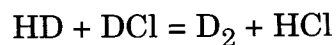
(b) The emf (E) of the cell :



25°C and 0.260 V at 35°C. Calculate the  $\Delta_r H$  of the cell reaction at 25°C. 5

**Q8.** Evaluate the expectation values of  $p$  and  $p^2$  for a particle confined in the region  $-a/2 < x < +a/2$  of a one-dimensional box. 10

**Q9.** The energy equivalent wave numbers, obtained from vibrational spectra of HD, D<sub>2</sub>, HCl and DCl in their ground level are 3627, 2990, 2885 and 1990 cm<sup>-1</sup> respectively. Calculate the energy change (in J mol<sup>-1</sup>) of the following reaction in the ground level. 10



**Q10.** (a) Fluorescence and phosphorescence are photophysical phenomena, not photochemical ones. Explain with reason. 5

(b) Glowing of fireflies is a result of combination of chemical and physical processes. Explain with reasons. 5

## SECTION C

Attempt any *three* questions :

20×3=60

- Q11.** (a) Express van der Waals equation in virial form (in terms of molar volume,  $V_m$ ). From this, derive the expression of Boyle temperature ( $T_B$ ). 10
- (b) Show that the average position of a particle confined to the 3-dimensional box of length (a, b, c) is  $(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$ . 10
- Q12.** The dissociation vapour pressure of  $\text{NH}_4\text{Cl}$  (s) at  $427^\circ\text{C}$  is 608 kPa but at  $459^\circ\text{C}$  it has risen to 1115 kPa. Calculate (i) equilibrium constant, (ii) the standard reaction free energy, (iii) the standard enthalpy, and (iv) the standard entropy of dissociation, all at  $427^\circ\text{C}$ . Assume that the vapours behave as a perfect gas and that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature in the range given. 20
- Q13.** (a) For the reaction :  $\text{A} + \text{B} \rightarrow \text{P}$ ;  
derive the expression of rate constant (k) where reaction is first order with respect to each A and B and initial concentrations of A and B are 'a' and 'b' respectively. 10
- (b) Calculate the rate constant of above reaction, when 'a' =  $0.075 \text{ mol L}^{-1}$ ; 'b' =  $0.050 \text{ mol L}^{-1}$  and concentration of B =  $0.020 \text{ mol L}^{-1}$  after 1 h. 10
- Q14.** (a) For the following galvanic cell :
- $$\text{Zn (s)} | \text{ZnCl}_2 \text{ (aq)} | \text{AgCl (s)} | \text{Ag (s)}$$
- (i) Write down electrode reactions and cell reaction.
- (ii) Is it a cell with transference ? Give reason in support of your answer.
- (iii) Find the  $E^\circ$  of cell and equilibrium constant ( $K^\circ$ ) of cell reaction at  $25^\circ\text{C}$ .
- Given :  $E^\circ_{\text{Zn}^{++}/\text{Zn}} = -0.76 \text{ V}$  and  $E^\circ_{\text{AgCl}/\text{Ag}, \text{Cl}^-} = +0.22 \text{ V}$  at  $25^\circ\text{C}$ . 10
- (b) The emf of the cell :
- $$\text{Ag} | \text{AgI} | (0.05 \text{ M KI}) || 0.05 \text{ M AgNO}_3 | \text{Ag}$$
- is  $0.788 \text{ V}$ . Calculate the concentration solubility product ( $K_{sp}$ ) of AgI. 10

- Q15.** (a) Define rotational constant of a molecule. How will its value change with the equilibrium bond length and reduced mass ? 5
- (b) Bending vibration of linear carbon dioxide molecule is IR active but Raman inactive though both electric dipole moment and electrical polarisability changes with vibration. Explain with reason. 5
- (c) Dimerisation of anthracene (A) in benzene happens by absorption of electromagnetic radiation. The concentration of its dimer at equilibrium,  $[A_2]_{eq}$  is independent of initial monomer concentration,  $[A]_0$  at higher concentration region. Explain with reason. 10



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