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# UPSC CGS Exam

Chemistry (Paper II)

Simplifying  
Government Exams

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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.*

*Diagrams / Figures, wherever required, shall be drawn in the space provided for answering the question itself.*

*Wherever any assumptions are made for answering a question, they must be clearly indicated.*

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

*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

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

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

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

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

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

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

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

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

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

$$\pi = 3.142$$

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

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

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

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

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

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

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

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

$$1 \text{ L bar} = 100 \text{ J}$$

## SECTION A

Q1. Answer all of the following questions :

5×16=80

- (a) The ratio of estimated molar heat capacities at constant volume (using Principle of Equipartition of Energy) of linear N-atomic molecules to its non-linear one is  $\frac{13}{12}$ . Find the value of N. 5
- (b) In the van der Waals gas equation, the pressure correction term is  $\frac{n^2 a}{V^2}$ . Find the SI unit of van der Waals constant, 'a'. 5
- (c) Show that surface energy of a cube-shaped liquid is 1.24 times of its sphere shape. 5
- (d) An element exists in the bcc structure where cell edge is 2.88 Å. The density of this element is 7.20 g cm<sup>-3</sup>. How many atoms does 104 g of the element contain ? 5
- (e) Show that  $\left(\frac{\partial C_V}{\partial V}\right)_{T,n} = 0$ ; for any ideal gas. 5
- (f) What will be the change in molar entropy (in SI) when volume of any ideal gas is doubled at constant temperature ? 5
- (g) Calculate the activity coefficient of Zn<sup>++</sup> ions and Cl<sup>-</sup> ions in 1.0 mM ZnCl<sub>2</sub>(aq) solution at 25°C. Given : A of water at 25°C = 0.51 M<sup>-1/2</sup>. 5
- (h) What is buffer solution ? Explain the buffer action in a buffer solution of (NH<sub>4</sub>OH + NH<sub>4</sub>Cl). 5
- (i) Liquids A and B form an ideal solution. At 50°C the total vapour pressure of solution containing 1 mol of A and 2 mol of B is 300 torr. When 1 mol more of A is added to the solution, total vapour pressure increases to 400 torr. Calculate the vapour pressures of pure liquids A and B at 50°C. 5
- (j) Define zero order reaction. Show that its half-life period is proportional to initial concentration of reactant. 5

- (k) Distinguish between Physisorption and Chemisorption. Which of these is responsible for the phenomenon of heterogeneous catalysis ? 5
- (l) Deduce Nernst equation for single electrode potential of electrode represented by  $(Pt) | Fe^{3+}, Fe^{2+}$  at T K. 5
- (m) Define one 'Einstein' of energy. Calculate its value for 350 nm of light. 5
- (n) Derive Bohr's quantum postulate, angular momentum ( $L \equiv m_e v r$ ) of rotating electron around the nucleus of H-atom in circular path is  $n \hbar$  (where  $n = 1, 2, 3, \dots$ ), using wave property of electron. (Symbols have their usual meanings) 5
- (o) Explain the terms 'bathochromic shift' and 'hypsochromic shift' with a suitable example of each. 5
- (p) The  $^1H$ -NMR spectrum of  $C_4H_9Br$  consists of single line. What could be its structure ? 5

## SECTION B

Attempt any six questions :

- Q2.** (a) The number of gas molecules of mass 'm' at T K within the speed range 'c' to 'c + dc' is given by

$$dN = Ac^2 e^{-mc^2/2k_B T} dc.$$

Find the expression of A.

Given :  $\int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4} \left( \frac{\pi}{\beta^3} \right)^{\frac{1}{2}}$  5

- (b) Dimethyl ether is more volatile than ethanol though both are of same molar masses. Explain with reason(s). 5

- Q3.** (a) Silver crystallizes in a fcc structure with a unit cell length of 408.6 pm. Use Bragg's equation to calculate first two diffraction angles from the 111 planes using X-ray radiation with wavelength of 154.43 pm. 5

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

- Q4.** Define compressibility factor (Z) of a gaseous state. Find the numerical value of a gas obeying equation of state :  $P(V - nb) = nRT$ , when its molar volume is 10 b at pressure P and temperature T K. 10

- Q5.** Define Carnot efficiency. You have to increase it either by increasing 10 K source temperature or decreasing same value of sink temperature. What will you do ? Give reason(s). 10

- Q6.** (a) For a gas phase reaction, pressure does not affect the value of equilibrium constant at constant temperature. Explain with reason. 5
- (b) Which of the function(s) is/are eigenfunction(s) of the operator  $\frac{d^2}{dx^2}$  ?  
Find its eigenvalue(s) also. 5
- (i)  $6 \cos(4x)$
- (ii)  $5x^2$
- (iii)  $3e^{-5x}$
- (iv)  $\ln(2x)$
- (v)  $\sin(3x)$
- Q7.** The activity product ( $\equiv a_{H^+} \times a_{OH^-}$ ) of pure water is  $1 \times 10^{-14}$  at  $25^\circ\text{C}$ . What will be the minimum and maximum possible values of pH for an aqueous solution at that temperature ? Give reasons in support of your answer. Finally give the pH-scale of aqueous solution at  $25^\circ\text{C}$ . 10
- Q8.** (a) Define adsorption isotherm. Write down the expression of Langmuir adsorption isotherm in terms of fraction of surface sites covered ( $\theta$ ) and equilibrium pressure (P). How can this expression be converted in terms of volume of gas adsorbed ? 5
- (b) Write down cell reaction and calculate emf of the following cell at  $25^\circ\text{C}$ .  

$$\text{Fe} | \text{Fe}^{2+} (0.01 \text{ M}) || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$$
 Given :  $E_{\text{Ag}^+/\text{Ag}}^0 = 0.8 \text{ V}$  and  $E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44 \text{ V}$  at  $25^\circ\text{C}$ . 5
- Q9.** (a) For the reaction  

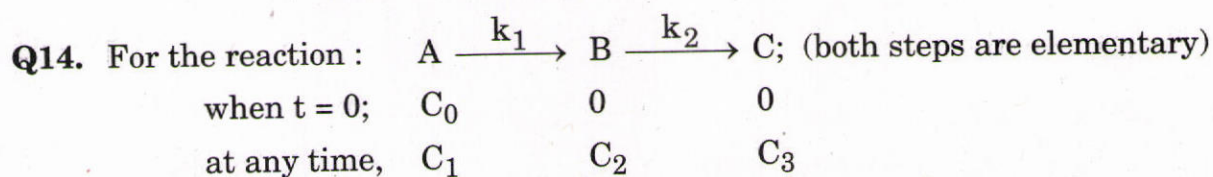
$$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g}),$$
 the quantum yield was found to be  $1.0 \times 10^6$  with wavelength of 480 nm. What amount of HCl(g) would be produced under these conditions per calorie of radiant energy absorbed ? 5
- (b) How can we distinguish between p-xylene and ethyl benzene by using NMR spectra ? 5
- Q10.** (a)  $^1\text{H} \ ^{35}\text{Cl}$  has a force constant value of  $480 \text{ Nm}^{-1}$ . Calculate the fundamental frequency and wave number. 5
- (b) 'Electronic spectrum of molecules is more complex.' Justify this statement. 5

## SECTION C

Attempt any *three* questions :

- Q11.** (a) Suppose initially all the gas molecules (in a rigid and adiabatic container) have the same translational kinetic energy of  $6.0 \times 10^{-21}$  J. As time passes, the motion becomes random, chaotic and energies get finally distributed in a Maxwellian way. Compute the final temperature and average translational kinetic energy per mol. 10
- (b) With the help of Jablonski diagram, explain the possible decay routes for an electronically excited molecule. 5
- (c) Find the number of degeneracy of the energy level  $\frac{14 h^2}{8 mL^2}$  for a free particle of mass 'm' in a cubical box of edge length L. 5
- Q12.** (a) The working substance used in an engine is 1 mol diatomic ideal gas ( $\gamma = 1.4$ ). The engine completes its cycle with the following three steps :
- (i) An adiabatic expansion against a constant pressure of 1 bar from volume 10 to 20 L.
- (ii) Cooling and contraction at constant pressure of 1 bar to its initial volume of 10 L.
- (iii) Heating at constant volume to its initial pressure.
- Calculate the work involved in each step in SI system and efficiency of the engine. Mention the redundant data also. 15
- (b) Symmetric stretching vibration of  $\text{CO}_2$  molecule is IR inactive but Raman active. Explain why. 5
- Q13.** (a) For the reaction :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ; change of pressure does not affect the  $K_p$ -value but affects the  $K_x$ -value at constant temperature. Explain, by deriving a relation between  $K_p$  and  $K_x$ . Assume all component gases in the reaction mixture behave ideally. 15

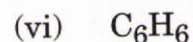
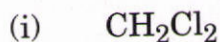
- (b) A dilute solution of KCl was placed between two Pt electrodes 10 cm apart, across which a potential difference of 6.0 V was applied. What will be the velocity of  $K^+$  ion? Given: Molar ionic conductivity of  $K^+$  ion at this dilution and at experimental temperature is  $73.52 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ . 5



Derive the expressions of  $C_1$ ,  $C_2$  and  $C_3$  in terms of rate constants and time of reaction and draw the plot of concentration of each A, B and C against time. 20

**Q15.** (a) KCl but not NaCl has been used in construction of salt-bridge. Justify. 5

(b) In connection to the  $^1\text{H-NMR}$  spectrum, arrange the following compounds in increasing order of chemical shift, with reason. 5



(c) (i) Define rotational constant of a rigid rotor molecule. Does it depend on temperature?

(ii) Spacing between two spectral lines in MW spectra of  $^1\text{H} \ ^{127}\text{I}$  is  $13.2 \text{ cm}^{-1}$ . Calculate its equilibrium bond length in pm. 4+6=10



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