Combined Geo-Scientist
(Main) Exam,2021

SDT-S-CHE

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

$N_A = 6{\cdot}022 \times 10^{23}\ \text{mol}^{-1}$

Rydberg constant $= 2{\cdot}178 \times 10^{-18}$ J

$c = 2{\cdot}998 \times 10^{8}\ \text{ms}^{-1}$

$k_B = 1{\cdot}38 \times 10^{-23}\ \text{JK}^{-1}$

$e = 1{\cdot}602 \times 10^{-19}$ C

$m_e = 9{\cdot}109 \times 10^{-31}$ kg

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

$R = 8{\cdot}314\ \text{JK}^{-1}\ \text{mol}^{-1}$

$h = 6{\cdot}626 \times 10^{-34}$ Js

$\pi = 3{\cdot}142$

1 amu $= 1{\cdot}66 \times 10^{-27}$ kg

1 cal $= 4{\cdot}184$ J

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

1 Å $= 10^{-8}$ cm $= 10^{-10}$ m $= 0{\cdot}1$ nm $= 100$ pm

1 atm $= 760$ torr $= 1{\cdot}01325 \times 10^{5}$ Pa

1 bar $= 1 \times 10^{5}$ Pa $= 0{\cdot}9869$ atm

1 eV $= 1{\cdot}602 \times 10^{-19}$ J

1 L atm $= 101{\cdot}34$ J

1 eV $= 23060$ cal

SECTION A

Q1. Answer all of the following questions : *5×16=80*

(a) Explain the conditions under which real gases show the ideal behaviour. *5*

(b) Define compressibility factor (Z). Describe Z vs. P plots with a suitable example. *5*

(c) A compound formed by elements X and Y crystallizes in the cubic structure. X atoms are situated at the corners and Y atoms are at the centre of faces. What is the formula of the compound ? *5*

(d) The data on the unit cell are given below. Identify the crystal system in each case. *5*

(i) $a = b \neq c$ $\alpha = \beta = \gamma = 90°$

(ii) $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$

(iii) $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$

(iv) $a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$

(v) $a = b = c$ $\alpha = \beta = \gamma = 90°$

(e) Explain the electrophoretic effect in Debye-Hückel-Onsager theory of strong electrolytes. *5*

(f) Explain the terms : activity and activity coefficient. Write their units and magnitudes. *5*

(g) Why is a finely powdered substance a more effective adsorbent ? *5*

(h) Show that the half-life period of a first order reaction is independent of initial concentration of the reactant. *5*

(i) What is the role of phosphoric acid in the volumetric titration of Fe^{2+} ions and $Cr_2O_7^{2-}$ ions when diphenylamine is used as internal indicator ? *5*

(j) Why can a voltmeter not be used for determining the EMF of a galvanic cell ? *5*

(k) What are well-behaved functions ? Which of the following functions are well-behaved ? 5

(i) $\phi(x) = e^{-\alpha x}$ $(\alpha > 0)$ $0 < x < \alpha$

(ii) $\phi(x) = \dfrac{1}{4 - x}$ $1 < x < 10$

(l) Suppose that the uncertainty in determining the position of an electron in an atom is 0·4 Å. What will be the uncertainty in its velocity ? 5

(m) Which of the following molecules are microwave active ? Why ? 5

C_2H_2, CH_3Cl, C_6H_6, CO_2

(n) Which of the following molecules has the highest fundamental frequency of vibration ? Explain. 5

H_2, D_2, HD

(o) What are photosensitized reactions ? Explain with examples. 5

(p) Calculate the energy in ergs, calories and electron volts in ultraviolet light of wavelength 2500 Å absorbed per mole. 5

SECTION B

Attempt any *six* questions : ***10×6=60***

Q2. What is the virial equation of state ? Derive the expression for the second virial coefficient from Van der Waals equation. *10*

Q3. The first order reflections from the 100, 110 and 111 planes of a given cubic crystal were found to occur at angles 5·9°, 8·4° and 5·2° respectively. Determine the type of crystal lattice to which the crystal belongs. *10*

Q4. For a component in a homogeneous mixture, the chemical potential is given as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_{js} \\ j\neq i}}$$

Show that μ_i may be expressed in the following equivalent terms : *10*

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_{js} \\ j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{\substack{T,V,n_{js} \\ j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{\substack{S,P,n_{js} \\ j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{\substack{S,V,n_{js} \\ j\neq i}}$$

Q5. Outline the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

$$r = P\left\{\pi\,\sigma_{AB}^2\left(\frac{8KT}{\pi\mu}\right)^{\frac{1}{2}} N_A^*\, N_B^*\right\}\exp\left(\frac{-E_o}{RT}\right). \qquad 10$$

Q6. For the following cell

$$Pb\,|\,PbCl_2\,(s)\,|\,PbCl_2\,(soln)\,|\,AgCl\,(s)\,|\,Ag,$$

the potential at 298 K is 0·490 V and the variation of emf with temperature is given by

$$E = a - (1{\cdot}86 \times 10^{-4}\ V/K)\,(T - 25\ K)$$

Calculate ΔG, ΔH and ΔS for the reaction at 298 K. *10*

Q7. What is the probability of locating a particle in one-dimensional box between $\frac{L}{4}$ and $\frac{3L}{4}$ where L is the length of the box ? Assume the particle to be in the lowest energy state. *10*

Q8. (a) Sketch qualitatively the Raman spectrum showing Rayleigh, Stokes and anti-Stokes lines. Why are Stokes lines more intense than the anti-Stokes lines ? *7*

(b) State and illustrate the rule of mutual exclusion. Comment on the converse of this. *3*

Q9. Describe the changes observed in the vibrational quantum number in an electronic transition using Franck-Condon principle. *10*

Q10. (a) From the following reduction reactions and E° values :

$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq) \quad E_1^\circ = 0{\cdot}772\ V$$

$$Fe^{3+}(aq) + 3e \rightarrow Fe\ (s) \quad E_2^\circ = -0{\cdot}036\ V$$

Calculate E_3° for the half-cell reaction

$$Fe^{2+}(aq) + 2e \rightarrow Fe\ (s).$$ *5*

(b) Calculate the molecular diameter (d) of helium if its Van der Waals constant b is $23{\cdot}70\ cm^3\ mol^{-1}$. *5*

SECTION C

Attempt any *three* questions : ***20×3=60***

Q11. (a) What is Boyle temperature ? Give its significance for the gases H_2, He, N_2 and NH_3. *10*

(b) Classify the solid state of the following substances as ionic / covalent / molecular / metallic crystals and explain. *5*

SiC, S_4, KBr, LiCl, Mg

(c) How does the temperature dependence of electrical conduction in an aqueous solution compare with that in metal ? *5*

Q12. (a) Derive the Gibbs-Duhem equation in the term $\sum_i n_i(d\bar{Y}_i) = 0$ at constant temperature and pressure where $\bar{Y}_i$ is an extensive property of a solution. Describe the physical significance of the above equation. *10*

(b) For the first order reaction

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

A is $4{\cdot}3 \times 10^{13}\ s^{-1}$ and K is $4{\cdot}329 \times 10^{-5}\ s^{-1}$, calculate the energy of activation at 300 K. *10*

Q13. (a) How is the pH of a solution determined using hydrogen electrode ? *10*

(b) What are the steps involved in the mechanism of photochemical decomposition of hydrogen-iodide reaction ? *10*

Q14. (a) What is degeneracy ? Illustrate with the cubic box of length L. How many eigenstates are there with energy equal to $\frac{101\,h^2}{8\,mL^2}$? *10*

(b) Consider a particle moving in a three-dimensional box with sides a, b and c. Assuming n_1, n_2 and n_3 as quantum numbers for the motions along x, y and z directions, write down the wavefunction and energy for this system. State whether the pair of Laplacian operator and this wavefunction satisfy the eigenvalue equation. If yes, what is the eigenvalue ? *10*

Q15. (a) The $J = 3 \rightarrow 4$ transition for a diatomic molecule occurs at 0·50 cm^{-1}. What is the wave number for the $J = 6 \rightarrow 7$ transition for this molecule ? Assume the molecule is a rigid rotor. *10*

(b) Sketch the fundamental vibration modes of CS_2 and OCS. Which of these are IR active ? *5*

(c) Why is a saturated solution of KCl or NH_4NO_3 used in the salt bridge ? *5*