Combined Geo-Scientist (Main) Examination-2025

BGSP–B–CMS

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 in **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.

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Some useful fundamental constants and conversion factors

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

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

$c = 2 \cdot 998 \times 10^{8}$ m s^{-1}

$k_B = 1 \cdot 38 \times 10^{-23}$ J K^{-1}

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

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

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

$R = 8 \cdot 314$ J K^{-1} mol^{-1}

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

$\pi = 3 \cdot 142$

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

1 cal $= 4 \cdot 184$ J

1 J $= 1$ kg m^2 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 mol^{-1}

$4\pi^2 c^2 = 3 \cdot 55 \times 10^{22}$ cm^2 s^{-2}

$\frac{h^2}{8m_e} = 6 \cdot 025 \times 10^{-38}$ J m^2

$hc = 1 \cdot 986 \times 10^{-25}$ J m

$\frac{h}{8\pi^2 c} = 2 \cdot 8 \times 10^{-44}$ kg m

SECTION—A

(Compulsory Section)

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

(a) Z (compressibility factor) versus P plots of H_2 and He gas are always above the plot of ideal gases. Explain why. 5

(b) Calculate the temperature and pressure of 1 mole of H_2S, which will correspond to the state of 1 mole of N_2 at 25 °C and 1·0 atm pressure.

Given :

	P_c (atm)	T_c (K)
N_2	33·5	126·3
H_2S	88·3	373·2

5

(c) Draw the qualitative band structure of *p*-type and *n*-type semiconductors. 5

(d) Mg_2SiO_4 crystallizes in an orthorhombic crystal system. What are the maximum and minimum symmetry elements it can possess? 5

(e) For closed system, at constant pressure, Gibbs' free energy (G) decreases with increase of temperature and vice versa. Justify with reasons. 5

(f) For a gas obeying the equation of state $P(V_m - b) = RT$, *(i)* Z (compressibility factor) > 1 and *(ii)* f (fugacity) > P. Justify with reasons. 5

(g) The mechanism of a chemical reaction is

$$A + B \rightarrow C + D$$
$$2C \rightarrow F$$
$$F + B \rightarrow 2A + G$$

Give the overall balanced equation and classify each species as reactant, product, intermediate or catalyst. Give reasons. 5

(h) For a specific H^+ ion catalyzed solution-phase reaction, draw the plot of log (rate constant) versus pH of the solution. State the values of slope and intercept. 5

(i) Can a salt bridge made from filter paper dipped in KCl solution be used to make a cell consisting of silver and lead half-cells? Justify your answer. 5

(j) Given that $E^{\circ}_{Cr^{3+}/Cr} = -0{\cdot}41$ V and $E^{\circ}_{Ce^{3+}/Ce} = -2{\cdot}33$ V, calculate the value of equilibrium constant for the following reaction at room temperature (25 °C) :

$$Ce(s) + Cr^{3+}(aq) \rightleftharpoons Ce^{3+}(aq) + Cr(s)$$ 5

(k) What are the conditions for an acceptable wave function? 5

(l) Prove that there is no acceptable solution to the time-independent Schrödinger equation for the particle in one-dimensional box with $E = 0$ (dimensions of the box are $x = 0$ and $x = a$). 5

(m) 'Discrete energy levels' and 'condition of resonance' are essential conditions for discontinuous line spectrum. Explain. 5

(n) Which one of the following molecules is rotational spectrum active and why?

CO_2 and CO 5

(o) Explain briefly about measuring the intensity of radiation using a chemical actinometer. 5

(p) How do watch hands glow in the dark? 5

SECTION—B

Attempt any *six* questions : 10×6=60

2. A gas at 350 K and 12 atm has a molar volume 12 percent larger than the calculated from the perfect gas law.

(a) Calculate the compressibility factor under these conditions. Which forces (attractive or repulsive) are dominating under these conditions?

(b) Calculate the molar volume of the gas. 10

3. Explain the limitations of powder X-ray diffraction to analyze samples with the following conditions :

(a) An alloy consisting of Co and Ni

(b) Powders with average crystallite size in sub-micron scale 10

4. Show that

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,\,P,\,n_j\,(j\neq i)}$$

$$= \left(\frac{\partial U}{\partial n_i}\right)_{S,\,V,\,n_j\,(j\neq i)}$$

10

5. The Debye-Hückel limiting equation is

$$\log_{10}(\gamma_i) = -AZ_i^2\sqrt{I}$$

(a) Write down the significance of each symbol with unit.

(b) What are the factors on which A depends?

(c) Derive the following equation :

$$\log_{10}(\gamma_\pm) = -A|Z_+ Z_-|\sqrt{I}$$

10

6. 5·0 kg of a catalyst adsorbs 400 m^3 of N_2 gas at 1 bar and 300 K to form a monolayer. What is the surface area of the catalyst if the area occupied per molecule of N_2 is 16×10^{-10} m^2?

10

7. *(a)* Derive the expressions to determine ΔG° and ΔS° of an electrochemical cell reaction by emf (E) measurements.

(b) Find the cell reaction and its ΔS° of the cell

$$(Pt)Fe\,|\,Fe^{2+}\,(aq)\,||\,Fe^{3+}\,(aq),\ Fe^{2+}\,(aq)\,|\,(Pt)$$

Given : $\left(\frac{\partial E^\circ}{\partial T}\right)_P = 1{\cdot}14\times10^{-3}\ V\,K^{-1}$ at 298 K

10

8. Explain how degeneracy can occur for a particle in a rectangular box with $a \neq b \neq c$. 10

9. Whether spectral lines of Balmer spectrum are equispaced? Give reason(s) with your answer. 10

10. For the reaction

$$H_2\,(g) + Br_2\,(g) \xrightarrow{h\nu} 2\,HBr\,(g)$$

show that the rate of the reaction varies as the square root of the intensity of the absorbed radiation. 10

SECTION—C

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

11. *(a)* The fugacity coefficient of a certain gas at 200 K and 50 bar is 0·72. Calculate the difference of its chemical potential from that of an ideal gas in the same state. 5

(b) The value of K_p for the reaction (at 298 K)

$$NH_3\,(g) \rightleftharpoons \frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g)$$

is $1{\cdot}36\times10^{-3}$. Determine the corresponding value of its K_c. 5

(c) Derive the expression $\frac{d\ln K_c}{dT} = \frac{\Delta U^\circ}{RT^2}$, clearly mentioning assumption(s) and approximation(s) used, and discuss the effect of temperature on the value of K_c (with graphical sketch also) for any solution-phase dimerization reaction. 10

12. *(a)* For a second-order reaction $A \rightarrow P$, show that the time required for 75% of the reaction ($t_{0\cdot75}$) is equal to $3\times t_{0\cdot5}$. 5

(b) Sucrose is hydrolyzed in presence of H^+ ion as catalyst. At any initial concentration of sucrose, the half-lives at pH = 5 and pH = 4 are 500 min and 50 min respectively. Find out the values of exponents a and b in the rate law

$$-\frac{d[\text{sucrose}]}{dt} = k[\text{sucrose}]^a\,[H^+]^b$$ 10

(c) The adsorption of a gas is described by the Langmuir isotherm with $\alpha = 0{\cdot}75\ \text{kPa}^{-1}$ at 298 K. Calculate the pressure at which the fractional surface coverage is *(i)* 0·15 and *(ii)* 0·95. 5

13. Given the reaction

$$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$$

for which $\Delta H^\circ_{298} = -3{\cdot}00$ kcal, the entropies are 6·5 cal/K for M, −22·2 cal/K for M^{3+}, 31·2 cal/K for H_2 and −10·0 cal/K for H^+; ΔG°_f for H^+ is 0·00. Calculate—

(a) the standard free energy of formation of M^{3+};

(b) E° for the half-reaction $M^{3+} + 3e^- \rightarrow M$. 20

14. Let $\hat{A}$ and $\hat{B}$ be Hermitian operators and c be the constant.

(a) Show that $c\hat{A}$ is Hermitian if c is a real number and $c\hat{A}$ is not Hermitian if c is not a real number.

(b) Show that $(\hat{A}+\hat{B})$ is a Hermitian. 20

15. *(a)* Symmetric stretching vibration of linear CO_2 molecule is vibrational spectrum inactive but vibrational Raman spectrum active. Give reason(s). 5

(b) Spectral lines of microwave spectrum of rigid diatomic molecules are equispaced. So energy levels are also equispaced. Justify or criticize with reasons. 5

(c) The microwave spectrum of $H^{35}Cl$ consists of equispaced spectral lines, separated by $6{\cdot}26\times10^{11}$ hertz. What is the—

(i) rotational constant $(\overline{B})$;

(ii) moment of inertia (I) in SI unit;

(iii) equilibrium bond length (r_0) in SI unit? 10

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