Combined Geo-Scientist (Main)
Examination, 2026

वियोज्य *DETACHABLE*

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

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

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

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

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

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

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

$h = 6{\cdot}626 \times 10^{-34}$ 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 $= 23060\ \text{cal mol}^{-1}$

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

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

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

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

SECTION 'A'

(Compulsory Section)

(Answer **all** of the following questions) 5×16=80

1.(a) Define compressibility factor (Z). What is its significance : when its value is either (i) 1 or (ii) <1 or (iii) >1 ? 5

1.(b) Draw Andrew's plot of P *vs.* V isotherms of a real gas at different temperatures.

At the critical point why (i) $\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0$ and (ii) $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$? 5

1.(c) What is the angle of first order X-ray diffraction for 110-planes of a simple cubic lattice of edge length 800 pm when X-ray wavelength is 0·4 nm. 5

1.(d) Which one of the following is an intrinsic semiconductor and how do you convert it into an extrinsic semiconductor ?

(i) diamond

(ii) α-tin

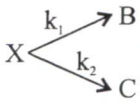
(iii) silicon

(iv) $YBa_2Cu_3O_7$ 5

1.(e) With the help of the relation between fugacity (f) and pressure (P) of a non-ideal gas, mention the conditions when (i) $f > P$, (ii) $f = P$ and (iii) $f < 1$. 5

1.(f) Write down the relation between K_p and K_c of the reaction : $A(g) + B(g) \rightleftharpoons C(g)$. (Assuming all gases in the reaction mixture behave ideally) Under what conditions K_p will be equal to the K_c ? 5

1.(g) A radioactive nuclide X has two decay modes (both first order)



; k_1 and k_2 are decay constants

Express $t_{1/2}$ (half-life period) of X in terms of k_1 and k_2. 5

1.(h) What are the basic differences of soap and detergent though both are used for cleaning purpose of clothes ? 5

1.(i) Construct a galvanic cell in which the following spontaneous reaction will happen. $2\,Cu^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + Cu(s)$. 5

1.(j) Calculate the pH of an aqueous solution of a weak monoacidic base at 298 K which has been neutralised by a strong monobasic acid to the extent of 65%. Given K_b and K_w are $2{\cdot}0\times10^{-5}$ and $1{\cdot}0\times10^{-14}$ respectively at 298 K. 5

1.(k) A student says "If a particle is in an energy eigenstate, its energy is fixed, so there is no uncertainty in any quantity".

Is this statement correct ? Explain your answer with a suitable example. 5

1.(l) Define the expectation value of an operator. How does it differ from an eigenvalue ? Explain with reference to energy measurements. 5

1.(m) How many normal modes of vibrations are possible for the following molecules ?

(i) C_6H_6

(ii) C_4H_2

(iii) $Os(CO)_5$

(iv) $SiCl_4$

(v) CS_2 5

1.(n) (i) What is the condition for a molecular vibration to be Raman active ?

(ii) Draw the polarizability ellipsoids for symmetric stretching mode of vibration of CO_2. 5

1.(o) Identify the INCORRECT statement and correct it briefly :

(i) Electronic transitions occur much faster than vibrational motion.

(ii) Franck-Condon principle explains the intensity distribution of vibrational structure of electronic spectra.

(iii) Fluorescence always originates from the lowest vibrational level of the excited singlet state.

(iv) Phosphorescence involves a spin-forbidden transition. 5

1.(p) An excited molecule can lose energy without emitting light. Name *two* non-radiative decay processes and explain *one* reason why these processes compete with fluorescence. 5

SECTION 'B'

(Attempt any **six** questions) 10×6=60

2. A non-ideal gas has three characteristic temperatures; Critical temperature (T_C), Boyle temperature (T_B) and Inversion temperature (T_i). Write expressions of T_C and T_B when the gas is van der Waals. What are the significances of T_C and T_B ? 10

3. The elements Ne, Ar, Kr and Xe of group 18 form cubic close-packed crystalline solids at very low temperatures. Answer the following :

(i) What type of bonding forces are involved in these solids ?

(ii) What crystal structure do they adopt ?

(iii) How many atoms are present in the unit cells of these solids ?

(iv) What is the coordination number of each atom in these structures ?

(v) How many tetrahedral and octahedral holes per atom are present in these crystal structures ? 10

4. The Gibbs-Duhem relations are :

(i) $dG = \sum_i \mu_i \, dn_i$

(ii) $G = \sum_i n_i \mu_i$ } For closed systems and at constant P and T

(iii) $O = \sum_i n_i \, d\mu_i$

(I) Mention the nature of the system

(II) Derive the expression of μ_i using eqn. (i)

(III) Which one is an intensive property and why; μ_i or G ?

(IV) What factors can influence the value of μ_i ? 10

5.(a) A sample of milk kept at 25°C is found to sour 40 times rapidly as when it is kept at 4°C. Determine the Arrhenius activation energy for this souring process in SI unit. 5

5.(b) At constant P and T, for a spontaneous chemical reaction, $\Delta_r G$ must be negative but $\Delta_r^{\#} G$ must not be necessarily negative. Explain. 5

6. Discuss a method to determine the partial orders and total order of the following reaction : A(aq.) + 2B(aq.) = P(aq.) 10

7. The T-dependence of E° of a galvanic cell is given by $E° = A + BT + CT^2$. Find the expression of $\Delta_r H°$ for the cell reaction. Show that when $T \to \infty$ the $\Delta_r G°$ and $\Delta_r H°$ are the same. 10

8. For a particle in a one-dimensional box :

(i) Why is the ground state energy not zero, even though the potential inside the box is zero ?

(ii) Why does the energy increase as n^2 and not linearly with n ? 5+5

9. Calculate the energy in joules of the rotational level (with $J = 1$) of the rigid H_2 molecule.

Given : $r_{H_2} = 74{\cdot}1\,\text{pm}$

Relative mass of H atom is 1·0080 amu. 10

10. Using a Jablonski diagram, explain the following :

(i) Why fluorescence lifetimes are typically much shorter than phosphorescence lifetimes.

(ii) Why phosphorescence is usually observed at longer wavelengths.

(iii) Why fluorescence intensity decreases in the presence of heavy atoms.

3+3+4=10

SECTION 'C'

(Attempt any **three** questions) 20×3=60

11.(a) For a solution phase reaction : A(aq.) + B(aq.) $\rightleftharpoons$ D(aq.); derive the expression for K_c in terms of the standard free energy change.

(i) What would be the standard state value ?

(ii) What would be the unit of K_c ?

(iii) What factors can influence the value of K_c ? 15

11.(b) Are the values of $\Delta_r G°(P)$ and $\Delta_r G°(C)$ the same, in general ? If not, under what conditions will they be the same ? 5

12.(a) Show with the help of the Hard-sphere collision theory, that a unimolecular elementary gas phase reaction behaves kinetically as a second order reaction at very low pressure of the reactant. 10

12.(b) In a photochemical reaction, the following data were obtained using an actinometer :

* Number of photons absorbed per second = $2{\cdot}0\times10^{16}$
* Rate of formation of product molecules = $3{\cdot}6\times10^{16}$ molecules s^{-1}

(i) Calculate the quantum yield of the reaction.

(ii) What does the obtained value indicate about the nature of the mechanism ?

(iii) Name one reaction from the syllabus where such behaviour is observed. Explain your choice. 3+4+3=10

13.(a) At 298 K, the galvanic cell :

(Pt) H_2(g, 1 atm) |HCl(aq, 0·1 M)|AgCl|Ag, has the EMF(E) = 0·35 V and

$\left(\frac{dE}{dT}\right)_P = -18\times10^{-4}$ V K^{-1}. Determine $\Delta_r G$, $\Delta_r H$ and $\Delta_r S$ of the cell reaction for the production of 1 faraday electricity. 10

13.(b) Define buffer capacity (β) of a buffer solution. Show that β of an acetic acid-acetate buffer solution is maximum when [salt]/[acid] is one. 10

14. A particle is confined to a three-dimensional cubical box of side a.

(i) Derive the expression for the energy eigenvalues of the particle.

(ii) Define degeneracy and determine the degeneracy of the energy levels corresponding to $E = \frac{3h^2}{4ma^2}$ and $\frac{7h^2}{4ma^2}$.

(iii) Explain how degeneracy reflects the underlying symmetry of the system. 8+8+4=20

15.(a) The rotational constant of $^{12}C^{14}N$ (rigid rotor) is $1{\cdot}91\ cm^{-1}$. Calculate the equilibrium bond length (in pm) of CN. 10

15.(b) A diatomic molecule shows an intense absorption ($v = 0 \rightarrow v = 1$) at $2886\ cm^{-1}$. The anharmonicity constant of this molecule (x_e) is 0·0174. Calculate the equilibrium vibrational frequency of this molecule. 10