COMBINED GEO-SCIENTIST (MAIN) EXAM-2022 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.

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Some useful fundamental constants and conversion factors

$N_A = 6\cdot022 \times 10^{23} \text{ mol}^{-1}$

Rydberg constant $= 2\cdot178 \times 10^{-18}$ J

$c = 2\cdot998 \times 10^8 \text{ ms}^{-1}$

$k_B = 1\cdot38 \times 10^{-23} \text{ JK}^{-1}$

$e = 1\cdot602 \times 10^{-19}$ C

$m_e = 9\cdot109 \times 10^{-31}$ kg

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

$R = 8\cdot314 \text{ JK}^{-1} \text{ mol}^{-1}$

$h = 6\cdot626 \times 10^{-34}$ Js

$\pi = 3\cdot142$

1 amu $= 1\cdot66 \times 10^{-27}$ kg

1 cal $= 4\cdot184$ J

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

1 Å $= 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0\cdot1 \text{ nm} = 100 \text{ pm}$

1 atm $= 760 \text{ torr} = 1\cdot01325 \times 10^5$ Pa

1 bar $= 1 \times 10^5 \text{ Pa} = 0\cdot9869 \text{ atm}$

1 eV $= 1\cdot602 \times 10^{-19}$ J

1 L atm $= 101\cdot34$ J

1 eV $= 23060$ cal

SECTION 'A'

1.(a)   What are the postulates of kinetic theory of gases ? Out of these which ones are not valid for real gases ?   3+2

1.(b)   What is Boyle temperature (T_B). Assuming oxygen as a van der Waals gas, calculate the Boyle temperature of it. The values of van der Waals constants a and b for oxygen respectively are $a = 1·36 \, dm^6 \, atm \, mol^{-2}$ and $b = 0·0318 \, dm^3 \, mol^{-1}$. Given : $R = 0·08206 \, dm^3 \, atm \, K^{-1} \, mol^{-1}$.   5

1.(c)   A temperature variation study of conductivity can distinguish between a metallic conductor and a semiconductor — Explain.   5

1.(d)   Both NaCl and KCl crystallize in the same cubic pattern. However, X-ray diffraction study reveals that NaCl has FCC while KCl has SCC pattern — Explain.   5

1.(e) $HCl \, (g) + NH_3 \, (g) \rightleftharpoons NH_4Cl \, (s)$

At lower temperatures the forward reaction is spontaneous while at higher temperatures the reverse reaction is spontaneous. Explain the reversal of the above reaction at different ranges of temperature in the light of thermodynamics (Given : ΔH for the reverse reaction is positive).   5

1.(f)   Calculate the Gibbs free energy change accompanying the compression of one mole of a gas at 25°C from 20 to 200 atm. The fugacities of the gas be taken as 18 and 120 atm respectively at pressure of 20 and 200 atm.   5

1.(g)   Through derivation of the relevant relation, show whether $t_{1/2}$ for a second order reaction depends on the initial concentration of the reactant or not.   5

1.(h)   Why are Brownian movement and Tyndal effect shown by colloidal solutions only ?   5

1.(i)   Derive Nernst equation for single electrode potential of an electrode of type, Pt/Cr^{6+}, Cr^{3+}.   5

1.(j)   A given electrode can act as positive as well as negative — Justify or criticize. 5

1.(k)   From the "uncertainty relation" how would you justify that the uncertainty in measuring the energy of a photoexcited state is greater than that of the ground state.   5

1.(l)   Show that the eigenvalues of a Hermitian operator are real.   5

1.(m)   If the rotational constants for $^{14}N^{16}O$ and $^{15}N^{16}O$ respectively are B and B', then which of the following is correct and why ?

    (i) $B > B'$ (ii) $B = B'$

    (iii) $B < B'$ (iv)   none of these   5

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1.(n) Citing the case of rotation of HCl molecule, explain how the photon-molecule interaction takes place. You may draw pictures or scheme to establish yourself. 5

1.(o) Radiative transitions (both absorption and emission) are displayed by vertical lines in Jablonski diagram. Explain why these lines are kept vertical. 5

1.(p) Calculate the relative energies of one einstein of photon of wavelength 600 nm to that of wavelength 300 nm. 5

SECTION 'B'

2.(a) Derive the reduced equation of state from van der Waals equation. 5

2.(b) Show that the excluded volume is four times the actual volume of the gas molecule. 5

3. Establish the relative order of compactness between simple cubic, body centered cubic and face centered cubic crystals. Draw diagrams, if needed. 10

4. How does chemical potential vary with temperature and pressure ? Derive the relevant equations. 10

5. Derive an equation relating the effect of ionic strength on the rate constant of an ionic reaction. Discuss the effect of ionic product on rate constants. 6+4

6.(a) In lead acid storage cell write down the electrode reactions and the total cell reaction during discharging. 6

6.(b) Specific gravity of the sulfuric acid used in a lead acid storage cell gives an assessment about the performance of the cell — justify or criticise. 4

7. Solution of a two-dimensional box problem gives the following for wave function and energy :

$$\psi_{n_1,n_2}(x, y) = \frac{2}{L} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \text{ for } 0 \leq x \leq L \text{ and } 0 \leq y \leq L$$

$$\psi_{n_1,n_2}(x, y) = 0 \text{ outside the box and } E_{n_1,n_2} = \left(n_1^2 + n_2^2\right) \frac{h^2}{8mL^2}.$$

Show that if the 2D box becomes a square there arises the case of degeneracy. 10

8.(a) Homonuclear diatomic molecules like H_2, N_2, O_2 are insensitive to microwave spectroscopy. Hence their bond lengths cannot be determined from microwave spectroscopy. How are their bond lengths determined ? — Logically explain your answer. 5

8.(b) We have the following spectral data for N_2O molecule.

$\bar{v}(cm^{-1})$	Infra-red	Raman
589	Strong; PQR Contour	—
1285	Very strong; PR Contour	Very strong; polarized
2224	Very strong; PR Contour	Strong; depolarized

From this data logically comment on the structure of the linear N_2O molecule.   5

9.(a) Using the relative method how can you determine the fluorescence quantum yield of a fluorophore in solution ?   5

9.(b) On which factors does fluorescence quantum yield of a fluorophore in a solution depend ?   5

10. CO_2 is a linear triatomic molecule. How many lines do you expect to have in its vibrational spectrum ?

Compare this with the observed IR spectrum of CO_2.   6+4

SECTION 'C'

11.(a) From the concept of "particle in a box", how would you predict the relative positions of the absorption bands of linear conjugated alkenes as the chain length increases.   10

11.(b) A metallic element exists as a cubic lattice. Each edge of the unit cell is 2·88 Å. The density of the metal is 7·20 g cm^{-3}. How many unit cells will be there in 100 g of the metal ?   10

12.(a) A buffer solution contains 0·2 mole of acetic acid and 0·25 mole of potassium acetate per litre. Calculate the change in pH of the solution if 0·5 mL of 1 M HCl is added to it. The dissociation constant of acetic acid at room temperature is $1·75 \times 10^{-5}$. (The volume change on the addition of HCl may be neglected).   10

12.(b) An aqueous solution at 25°C is 0·005 molal in sodium chloride and 0·001 molal in potassium sulphate. Calculate activities of Na^+ and SO_4^{2-} ions. At 25°C the Debye–Huckel constant A is equal to 0·509.   10

13.(a) Derive the rate equation for the overall reaction of type,

$$A \overset{k_1}{\underset{k_2}{<}} \begin{matrix} L \\ M \end{matrix}$$
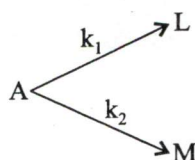
How can we evaluate individual rate constants k_1 and k_2 ?   10

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13.(b) The equilibrium constant of the reaction $X \longrightarrow Y$ is doubled when temperature is raised from 25°C to 35°C. Calculate the enthalpy of the reaction.   10

14.(a) Without derivation, write down the BET equation giving the meanings of the terms.

Using BET equation how can one measure the total surface area of a solid catalyst in powder state. Given : cross sectional area of each adsorbed gas molecule is A and m g of solid adsorbent is present.   3+7

14.(b) Using the law of corresponding state for a van der Waals gas, calculate pressure exerted by one mole of carbon dioxide at 40°C confined to a volume of 0.107 dm³. (For carbon dioxide $P_c = 73.0$ atm; $V_c = 0.0957$ dm³; $T_c = 304$ K)   10

15.(a) On irradiation of propionaldehyde at 30°C with light of 302 nm, the quantum yield of formation of CO is found to be 0.54. The intensity of incident light is 15000 erg s⁻¹. Find out the rate of formation of CO.   10

15.(b) What are 1st overtone and hot band in IR spectroscopy ? How can these two be differentiated experimentally ?   6+4

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