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FOR UPSC CGGE EXAM PREPARATION

UPSC CGGE 2024 Question Paper · Chemistry Paper II

EXAM	YEAR	TYPE	SUBJECT
UPSC CGGE	2024	Question Paper	Chemistry Paper II

DETAILS

Mains

Combined Geo-Scientist (Main) Examination, 2024

SGSE-M-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

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

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

$\pi = 3{\cdot}142$

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

1 cal = 4·184 J

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

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

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

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

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

1 L atm = 101·34 J

1 eV = 23060 cal/mol

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

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

$h_c = 1{\cdot}986 \times 10^{-25}$ Jm

$\frac{h}{8\pi^2 c} = 2{\cdot}8 \times 10^{-44}\ \text{kg m}^2\ \text{cm}^{-1}$

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SECTION A
(Compulsory Section)

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

(a) Gases A and B are van der Waals gases. If van der Waals constants ('a' and 'b') values (in SI units) are :

	A	B
a	21·764	3·457
'10^3b'	0·024	0·024

(i) Which of these would occupy greater volume under identical conditions ?

(ii) Which gas has the highest critical temperature ? *5*

(b) From virial equation of state for a real gas

$$pV_m = RT\,(1 + A_2\,(T)p + A_3\,(T)\,p^2 + ...)$$

where the symbols have their usual meanings,

Explain :

(i) The physical significance of the second virial coefficient 'A_2'.

(ii) The behaviour of the second virial coefficient (A_2) at low, moderate and high temperatures.

(iii) What happens when $A_2 = 0$? *5*

(c) Differentiate between conductors, semiconductors and insulators using band theory of solids. *5*

(d) Give an account of Bravais Lattices in cubic and tetragonal crystal system mentioning the minimum symmetry elements in them. *5*

(e) What do you understand by chemical potential ? Give an account of variation of chemical potential with temperature. *5*

(f) Obtain a relation between equilibrium constant, K_p, K_c and K_x. Under what conditions is $K_p = K_c = K_x$? *5*

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(g) The rate constant for the reaction $O(g) + O_3(g) \rightarrow 2O_2(g)$ is $8{\cdot}0 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Express this rate constant in dm^3 mol^{-1} s^{-1}. 5

(h) Write BET equation. Explain the terms involved in it. 5

(i) Given :

$$Cu^{2+} + 2e^- \rightarrow Cu; \quad E^o = +0{\cdot}350 \text{ V}$$

$$Zn^{2+} + 2e^- \rightarrow Zn; \quad E^o = -0{\cdot}763 \text{ V}$$

Construct the cell using these reactions.

(i) Write and balance the total cell reaction.

(ii) Find the E^o of the cell.

(iii) State whether the cell reaction will be spontaneous or not. 5

(j) What is the source of alkaline error in pH-measurements with the glass electrode ? 5

(k) Evaluate the commutator $\left[\hat{x}, \frac{\hat{d}}{dx}\right]$. 5

(l) Interpret the physical meaning of the square of the wave function $|\Psi(x)|^2$. What are the dimensions of $|\Psi(x)|^2$? 5

(m) What is the Raman effect and how does it differ from phosphorescence and fluorescence ? 5

(n) Hydrogen molecule gives neither vibrational nor rotational spectrum, but is Raman active. Explain. 5

(o) The fluorescence quantum yield and observed fluorescence lifetime of tryptophan in water are $\phi_{F,0} = 0{\cdot}20$ and $T_0 = 2{\cdot}6$ ns, respectively. Calculate the fluorescence rate constant, k_F. 5

(p) The first step in the photoinitiated reaction between hydrogen and bromine using 511 nm radiation is

$$Br_2 + h\upsilon \rightarrow 2Br$$

Why is hydrogen molecule not dissociated under these conditions ? 5

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SECTION B

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

Q2. Define Boyle temperature (T_B) of a non-ideal gas. Show that for a van der Waals gas, the Boyle temperature $T_B = \frac{a}{Rb}$, where 'a' and 'b' are van der Waals constants. *10*

Q3. (a) Obtain Miller indices of a crystal plane which cuts through the crystal axes at (2a, – 3b, – 3c). *3*

(b) A bcc element of density 10300 kg m^{-3} has a cell edge of 314 $\times 10^{-12}$ m. Calculate the atomic mass of the element. *7*

Q4. Obtain an expression for the equilibrium constant and standard free energy change using a general reversible reaction :

$$aA + bB \rightleftharpoons cC + dD$$ *10*

Q5. (a) The rate of decomposition of a gas A was 3·70 in some unit when 10% had reacted and it was 2·60 in the same unit when 25% had undergone decomposition. Calculate the order of the reaction. *5*

(b) Explain with reasons :

(i) Physical adsorption decreases with increase in temperature, but chemisorption increases. *3*

(ii) On adding detergent in water, surface tension decreases. *2*

Q6. The pH of a buffer solution containing 0·5 mol/m^3 of CH_3COOH and 0·5 mol/m^3 of CH_3COONa has been found to be 4·76. What would be the pH of this solution after 0·02 mol/m^3 NaOH has been added to the buffer ? Assume that the volume is unchanged. (Given $K_a = 1{\cdot}80 \times 10^{-5}$) *10*

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Q7. (a) State the different assumptions involved in the derivation of Langmuir adsorption isotherm. *5*

(b) What Raman shifts (in cm^{-1}) are expected for the first four Stokes lines for CO_2 ($B = 0{\cdot}3906\ cm^{-1}$) ? *5*

Q8. Prove that the operator $i\frac{d}{dx}$ is Hermitian, but $\frac{d}{dx}$ is not. *10*

Q9. The vibrational wave numbers of H_2^+, D_2 and H_2 are approximately 2322, 3118, and 4400 cm^{-1}, respectively. Calculate the force constants for these molecules and comment on the relative magnitudes of the values you obtain. (H = 1, D = 2) *10*

Q10. (a) Describe the Franck-Condon principle and its significance in photochemistry. *5*

(b) The continuum limit for the dissociation of Br_2 gas

Br_2 (ground) = Br (ground) + Br (excited) occurs at 19,750 cm^{-1}.

The transition of a ground bromine atom to an excited one corresponds to a wave number of 3865 cm^{-1}.

Calculate the energy for the process

Br_2 (ground) = 2Br (ground) in cm^{-1}. *5*

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SECTION C

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

Q11. (a) Show that in a first order reaction, the time required for completion of 99% reaction is 10 times of the half-life ($t_{1/2}$) of the reaction. *10*

(b) The values of the rate constant (k) for the reaction *5*

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

were determined at several temperatures. A plot of *ln* K vs 1/T gave a straight line of which the slope was found to be $-1{\cdot}2 \times 10^4$ K. What is the activation energy of the reaction ?

(c) For the following cell

$$Cd\,|\,CdCl_2\,(sat.)\,||\,AgCl\,|\,Ag,$$

$$E = 0{\cdot}675\ V \text{ and } \frac{dE}{dT} = -6{\cdot}5 \times 10^{-4}\ VK^{-1} \text{ at } 298\ K.$$

What is the reaction taking place in the cell ? What are the values of ΔG, ΔH and ΔS at 298 K ? *5*

Q12. (a) A flask of 4 dm^3 capacity contains O_2 at 101·325 kPa and 298 K. The gas pressure is reduced to 0·10 Pa by attaching the flask to a pump. Assuming ideal behavior, answer the following :

(i) What will be the volume of the gas which is left behind ?

(ii) What amount of O_2 and the corresponding number of molecules are left behind in the flask ?

(iii) If now, 2 g of N_2 is introduced, what will be the pressure of the flask ? *10*

(b) Evaluate the potential of a silver electrode in a solution that is saturated with silver iodide.

(Given $a_{I^-} = 1{\cdot}00$, K_{sp} for $AgI = 8{\cdot}3 \times 10^{-17}$) *10*

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Q13. (a) $HgCl_2$ crystallizes in orthorhombic system. Using radiation with $\lambda = 154$ pm, for the (100), (010) and (001) planes, first order reflections in an X-ray diffractometer occur at $7° 25'$, $3° 28'$ and $10° 23'$ respectively. Calculate the dimensions of the unit cell and the number of $HgCl_2$ molecules in the unit cell. The density of the crystal is 5·42 g cm^{-3} and $M(HgCl_2) = 271·5$ g mol^{-1}. *10*

(b) Show that the activity is the thermodynamic counterpart of gas pressure. *10*

Q14. (a) For a particle confined at constant potential within a cubic box, determine the quantum numbers of

(i) the lowest excited state that is not degenerate. *2*

(ii) the lowest energy level with a degeneracy of 6. *3*

(b) Calculate the corresponding energies (in J) if the side length of the box is 0·5 nm. *5*

(c) What will be the wavelength of the radiation absorbed/emitted when an electron makes a transition between these two energy levels ? In what region of the electromagnetic spectrum does this transition lie ? *5*

(d) In the uranyl oxalate actinometer, $5·1875 \times 10^{18}$ molecules were decomposed when exposed to a radiation of $\lambda = 365·5$ nm. During this time, the number of photons absorbed were $10·5875 \times 10^{18}$. Calculate the quantum efficiency. *5*

Q15. (a) $^1H^{35}Cl$ has a rotational constant of 10·26 cm^{-1}.

(i) Explain how the rotational constant is determined from the microwave spectrum. *3*

(ii) Calculate the moment of inertia of $^1H^{35}Cl$. *4*

(iii) Calculate the bond length of the HCl molecule using the above data. *3*

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(b) The photolysis of hydrogen iodide follows the mechanism :

$$HI + h\upsilon \xrightarrow{I_a} H^{\bullet} + I^{\bullet}$$

$$H^{\bullet} + HI \xrightarrow{k_2} H_2 + I^{\bullet}$$

$$I^{\bullet} + I^{\bullet} \xrightarrow{k_3} I_2$$

$$H^{\bullet} + I_2 \xrightarrow{k_4} HI + I^{\bullet}$$

Use the steady-state approximation to $H^{\bullet}$ to construct the rate law. What is the overall quantum yield of the process ? *10*

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