भू-विज्ञान परीक्षा
GEOLOGIST EXAM-2017

ZLX–D–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.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Any page or portion of the page left blank in the QCA Booklet must be clearly struck off.

Answers must be written in ENGLISH only.

Some useful fundamental constants and conversion factors

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

SECTION—A

1. Answer **all** of the following : 80

(a) Write down the equation of state for van der Waals gases with symbolic significances and find the dimension of van der Waals constants. 8

(b) Helium gas at 500 K expands adiabatically and reversibly to double its volume. Find the final temperature of the gas in degree Celsius. (Assume that He gas behaves ideally.) 6

(c) Explain the Arrhenius theory of acids and bases with examples. 6

(d) List the factors which influence the efficiency of Carnot engine. How? 6

(e) The effect of temperature on the value of dimerization constant is negative. Justify with the help of van't Hoff equation isobar. 6

(f) Derive the integrated rate equation for a zero-order reaction. Give one example of zero-order reaction. 6

(g) What is van't Hoff factor (i) of a solution? Derive its relation with degree of ionization of solute in a solution. 6

(h) Define 'molar extinction coefficient (ε)'. What is its unit? What factor(s) can influence its value? 6

(i) Show that the unit of magnetic dipole moment is A m^2 which is also equivalent to J T^{-1}. Here T stands for tesla, the unit of magnetic field strength. 6

(j) Why is surface tension of liquid ethanol greater than liquid dimethyl ether though both have same molecular mass? 5

(k) Explain why H_2O is a liquid while H_2S is a gas at room temperature. 5

(l) Show that $y = e^{ikx}$ is an eigenfunction of the operator, $\hat{A} = -i\hbar \frac{d}{dx}$. What is the eigenvalue? 6

(m) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom? Give reason(s) : 8

(i) $2s \rightarrow 1s$

(ii) $2p \rightarrow 1s$

(iii) $3d \rightarrow 2p$

(iv) $3d \rightarrow 4s$

(v) $5p \rightarrow 3s$

SECTION—B

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

2. Derive $(C_P - C_V) = \left[\left(\frac{\partial U}{\partial V}\right)_{T,n} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n}$ (symbols have their usual meanings). Find the expression of $(C_P - C_V)$ for a gas obeying equation of state, $P(V - nb) = nRT$. 10

3. 18·0 g of liquid water vaporizes at 1 bar and 373 K. Calculate q, w, ΔU, ΔH, ΔS, ΔA and ΔG (in SI units) for this process. Given, latent heat of vaporization of liquid water at 1 bar and 373 K is 540 cal g^{-1}. 10

4. Derive Gibbs-Duhem equations for a mixture system at constant pressure and temperature. 10

5. $0{\cdot}1$ kg mol^{-1} aqueous solutions of two 1-1 electrolytes A and B freeze at $-0{\cdot}360$ °C and $-0{\cdot}208$ °C, respectively. Calculate *(a)* van't Hoff factor of each solution and *(b)* the degrees of ionization of A and B in their solution. Suggest the nature of electrolytes. Given, K_f of water = $1{\cdot}86$ K kg mol^{-1}. 10

6. *(a)* What will be the value of absorbance of transparent liquid water with respect to visible light? Give reason.

(b) Write a note on 'photosensitized reaction' with example of photosynthesis.

2+8=10

7. *(a)* Define 'most probable speed' of a molecule in gaseous system. Derive its expression using the following speed distribution equation :

$$dN_c = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} c^2 e^{-\frac{mc^2}{2k_B T}}\, dc$$

(Symbols have their usual meanings.)

(b) Find the pH of 10^{-4} (M) aqueous caustic soda solution. 8+2=10

8. *(a)* Show that for a first-order reaction, the time required for completion of 99·9% reaction is ten times of its half-life period.

(b) The standard reduction potential value of Zn^{++}/Zn electrode is negative and of Cu^{++}/Cu electrode is positive. What will be the cell reaction, if we couple two electrodes to form a galvanic cell? Give reason(s) in support of your answer.

5+5=10

9. A spherical water drop of radius $1{\cdot}0$ mm is sprayed into a million of droplets of same size. Find the work done in this process. Given that γ (surface tension) of water at the experimental temperature is $72{\cdot}0$ dyne cm^{-1}. 10

10. *(a)* Silver crystallizes in an f.c.c. structure with a unit cell length of 408·6 pm. Using Bragg equation, calculate the first-order diffraction angle for {1 1 1} plane using X-ray of wavelength 154·433 pm.

(b) The force constant of a harmonic oscillator of reduced mass $1 \cdot 5 \times 10^{-27}$ kg is 10 N m^{-1}. Calculate its zero-point energy. 5+5=10

SECTION—C

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

11. *(a)* Derive $\Delta T_f = K_f \, m_2$ (symbols have their usual meanings) using thermodynamic concept of chemical potential. Mention all assumptions and approximations at proper places.

(b) The temperature of a hot cup of tea decreases spontaneously in a closed system at constant pressure without loosing its mass. So for this change $\Delta H < 0$, $\Delta S_{\text{univ}} > 0$ and $\Delta G > 0$. Justify with reasons. 10+10=20

12. *(a)* Discuss hypochromic effect in connetion to UV spectra.

(b) The quantum yield (ϕ) for the reaction, $2HI \rightarrow H_2 + I_2$, at $\lambda = 250$ nm is 2·0. If 3070 J of light is absorbed, find the number of moles of HI decomposed.

(c) What is indicated by peak area in PMR spectrum? How many peaks will be observed in PMR spectrum of pure ethanol? What will be their peak area ratio? Explain with diagram, if possible. 5+5+10=20

13. *(a)* Write down Debye-Hückel limiting equation with symbolic significances and units. Find the ionic strength of 0·01 mol L^{-1} aqueous solution of potassium ferrocyanide.

(b) The average lifetime of phosphorescence is higher than fluorescence. Explain with Jablonsky diagram.

(c) Hydrogen nucleus is NMR active but the nuclei of ^{16}O and ^{12}C are inactive. Explain why. 10+5+5=20

14. *(a)* Derive Langmuir adsorption isotherm expression for the process

$$O_3(g) \rightarrow 3O(ads)$$

Calculate the equilibrium constant, K for this process when the coverage of O (ads) is 0·50 at $P_{O_3} = 1$ atm.

(b) The wave number of $J = 0$ to $J = 1$ transition for pure rotational spectrum of $^{1}H^{81}Br$ is $16{\cdot}93\ \text{cm}^{-1}$. Assuming the molecule as a rigid rotor, calculate its moment of inertia in kg m^2 and equilibrium bond length in m. 10+10=20

15. *(a)* Derive the expressions of critical constants (P_c, V_c and T_c) for van der Waals gases.

(b) In an aqueous solution of HCl, the transport number of H^+ ion is abnormally higher than Cl^- ion. Explain why.

(c) Find the units of A and E_a (in SI units) using the equation, $k = Ae^{-E_a/RT}$. k is the zero-order rate constant. 8+8+4=20

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