भू-विज्ञान परीक्षा
Geologist Examination 2014

A-FDN/RB-N-DIB

CHEMISTRY

Paper II

Time Allowed : Three Hours	Maximum Marks : 200

INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

There are THIRTEEN questions divided under THREE sections.

Candidate has to attempt TEN questions in all.

The ONLY question in Section A is compulsory.

Attempt any SIX questions from Section B.

Attempt any THREE questions from Section C.

The number of marks carried by a question/part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the answer book.

Attempts of questions shall be counted in chronological 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 answer book must be clearly struck off.

Answers must be written in ENGLISH only.

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.

Constants which may be needed :

Planck's constant (h)	$6{\cdot}626\times10^{-34}$ Js
Speed of light (c)	$2{\cdot}998\times10^{8}$ ms^{-1}
Mass of electron (m_e)	$9{\cdot}109\times10^{-31}$ kg
Avogadro constant (N_A)	$6{\cdot}022\times10^{23}$ mol^{-1}
Universal gas constant (R)	$8{\cdot}314$ JK^{-1} mol^{-1}

Section – A

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

   (a) Calculate most probable velocity of CO_2 molecule at 0°C.

   (b) Show that for van der Waals' gas $\frac{RT_c}{P_cV_c} = 8$

   (T_c, P_c and V_c represent critical constants).

   (c) Calculate the work done in blowing a soap bubble in air of radius 10 cm. Surface tension of soap solution is 30×10^{-3} Nm^{-1}.

   (d) State Le Chatelier's principle and apply it to discuss the optimum conditions for the manufacture of ammonia

   $$\left(N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92 \text{ KJ mol}^{-1}\right).$$

   (e) Show that work done in a reversible process is greater than the work done in an irreversible process.

   (f) A first order reaction is 40% complete in 10 minutes. What is the percentage of the reactant left after 1 hour ?

(g) 50 ml of 0·1 M acetic acid is mixed with 50 ml of 0·1 M sodium acetate. What is the pH of the resultant solution ? pK_a of acetic acid is 4·76.

(h) The osmotic pressure of human blood in the presence of various solutes is 7·65 atmospheres. What is the total concentration of various solutes in blood ?

(i) Enthalpy of adsorption is a function of surface coverage. Justify the statement.

(j) The molar conductance at infinite dilution of NaOH, NaCl and $BaCl_2$ are $248{\cdot}1\times10^{-4}$, $126{\cdot}5\times10^{-4}$ and $280{\cdot}0\times10^{-4}$ S m^2 mol^{-1}. Calculate the molar conductance at infinite dilution for $Ba(OH)_2$.

(k) The microwave spectrum of HF consists of a series of absorption bands, whereas its infrared spectrum has only a single band. Discuss the reasons for the difference in the features of a microwave spectrum compared to an infrared spectrum for a diatomic molecule using HF as an example.

(l) When light of 400 nm wavelength strikes the surface of calcium metal, electrons having a kinetic energy of $6{\cdot}3\times10^{-20}$ J are emitted. Calculate the binding energy of the electrons in calcium and the minimum frequency required to elicit this photoelectric effect.

(m) Calculate the de Broglie wavelength of

(i) an electron moving at 100 km s^{-1}

(ii) a 0·010 kg bird moving at 100 m s^{-1}

(n) The Bohr model for atomic hydrogen predicts that the energies of allowed orbits are given by

$$E_n = -2{\cdot}178 \times 10^{-18}/n^2 \text{ Joule,}$$

where $n = 1, 2, 3, \ldots\infty$

(i) The Paschen series involves transitions down to the $n = 3$ level. Calculate the expected wavelength in nanometer of a line in the spectrum of atomic hydrogen associated with a transition of this type from the $n = 10$ orbit to the $n = 3$ orbit.

(ii) Is this line in the UV, visible or infrared region of the electromagnetic spectrum ?

(o) The most probable electronic transition for a particular diatomic molecule is from $\upsilon'' = 0$ to $\upsilon' = 6$. The double prime indicates the molecule is in its ground electronic state, while the single prime indicates the molecule is in an electronic excited state.

Sketch potential energy curves, including vibrational energy levels, illustrating the fluorescence decay of the molecule from the electronic excited state down to the electronic ground state.

(p) Describe, in quantum mechanical terms, why electronic absorption and emission spectra consist of broad band peaks.

Section – B

(Answer any *six* questions.
Each question carries 10 marks) $6\times10=60$

2. Write Maxwell's distribution of molecular velocities of gases. What is the effect of temperature on the distribution ? Represent graphically. Discuss the important features.

3. The first order reflection from a crystal plane in a cubic crystal occurs at 13°41′. Find the miller indices of the plane.

   [$a = 5{\cdot}63$ A°, $\lambda = 1{\cdot}54$ A°, $\sin^2(13°41') = 0{\cdot}0561$]

4. (a) Explain what you mean by chemical potential. How would you represent chemical potential in terms of G, H, A & U ? 5

   (b) Deduce the equation of van't Hoff reaction isotherm for the reaction

   $aA + bB \rightleftharpoons cC + dD.$ 5

5. 0·01 M solution of aqueous NH_4Cl is prepared at 25°C. $K_b = 1{\cdot}81\times10^{-5}$, $K_w = 10^{-14}$. Calculate the pH of the solution.

6. The rate constant of a first order reaction is given by $K_1 = 5\times10^{13}e^{-\frac{(10,00,000)}{RT}}$. Find enthalpy and entropy of activation at 300 K. Energy is given in Joules.

7. The Schrödinger equation for a particle in a box is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

(a) Show that

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}; \quad n = 1, 2, 3, \ldots$$

are wavefunctions that satisfy the boundary conditions $\left(\psi(x) = 0 \text{ at } x = 0 \text{ and } x = L\right)$. 3

(b) Show that the energy levels are given by

$$E_n = \frac{n^2h^2}{8mL^2}$$ 3

(c) Derive an expression for minimum uncertainty in momentum Δp_x for an electron in a cubic box of length L. 4

8. The over all quantum yield for the photochemical decomposition of a dye is 0·5 at a wavelength of irradiation of 300 nm. Using a 100 W light source at 300 nm, how long (in min) will it take to photodecompose 1·0 mol of the dye under conditions of total light absorption ?

9. (a) What is the difference between the fluorescence lifetime and the radiative lifetime of a fluorescent compound ? 2

(b) Discuss the molecular orbitals and the various electronic transitions possible in formaldehyde, CH_2O. Draw an appropriate energy level diagram displaying these transitions. 8

Section – C

(Answer any ***three*** questions.
Each question carries 20 marks) 3×20=60

10. (a) State Carnot's theorem and deduce the expression for the efficiency of an ideal heat engine. State the criteria for spontaneity of a process and discuss the change of enthalpy and entropy for the feasibility of a spontaneous process. 10

(b) Deduce the relation

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$$ 5

(c) Calculate the minimum amount of work in Joules required to freeze 1 g of water at 0°C by means of a refrigerator which operates in a surrounding at 25°C. How much heat is given to the surroundings ? (Given that latent heat of fusion of water is $6{\cdot}03$ kJ mol^{-1}). 5

11. Derive an equation to show the effect of ionic strength of the medium on the rate of ionic reactions in solution.

12. Derive the BET adsorption isotherm. Show that it approximates to Langmuir adsorption isotherm under limiting condition.

13. For gaseous carbon monoxide, $^{12}C^{16}O$, the IR absorption spectrum consists of a single peak that occurs at a wavenumber of 2143 cm^{-1}. The energy of vibrational energy levels is given by

$$E_{vib} = \left(\upsilon + \frac{1}{2}\right)\hbar\omega, \quad \upsilon = 0, 1, 2, \ldots$$

(a) Calculate the energy difference, in Joule, of successive vibrational energy levels of CO(g), assuming it vibrates as a simple harmonic oscillator. 7

(b) Calculate the force constant of the C–O bond in carbon monoxide. 7

(c) Sketch the form of a *Morse* potential energy curve for the vibrational energy of a diatomic molecule. In your sketch, include the vibrational energy levels, illustrating their relative spacing. 6