KNU/18/BSc/3rdSem/CEMH/C7

2018

3rd Semester

CHEMISTRY

PAPER—C7

(Honours)

Full Marks : 40 *Time* : 2 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Physical Chemistry–II

1. Answer any *five* questions : 5×1

   (a) What is meant by an "Elementary reaction"?

   (b) Weiss indices of plane is (121), what will be the miller indices of this plane.

   (c) Explain why a mixture of aqueous solutions of NaH_2PO_4 and Na_2HPO_4 can act as a buffer, although both are salts.

   (d) Plot schematically $\log n_i$ versus c_i at a particular temperature as per Boltzmann distribution law. Symbols have their usual meanings.

(e) Show that $\mu_{JT} > 0$ implies cooling.

(f) What is clausius inequality ?

(g) What is the unit of entropy ?

(h) State the "bottle-neck" principle of chemical kinetics.

2. Answer any *five* questions : 5×2

(a) Which state function of the system is related to the maximum value of thermodynamic probability and how ?

(b) Write down the number of crystal system and Bravais lattice.

(c) Draw and explain the carnot cycle in *T–S* diagram.

(d) Write two use of buffer solution.

(e) A card is drawn from a pact of 52. What is the probability of its being an Ace or A King ?

(f) Establish a relation between heat change at constant pressure and that at constant volume.

(g) The rate of a reaction is given by : $\log k = A - (B/T) + C \log T$. Find the value of activation energy (as given by Arrhenius equation).

(h) The stirling's approximation is given by in $x! \approx x\ln x - x$, calculate the % error of using the approximation, when $x = 5$.

3. Answer any *three* questions : 3×5

(a) $\Delta G = a + bT + cT^2$. Show that $b = 0$, and $[\partial \Delta G / \partial T]_P$ and $[\partial \Delta H / \partial T]_P$ have values equal in magnitude and opposite in sign and both the values tend towards zero as $T \to 0$. 5

(b) (i) Prove that $\left(\frac{\partial G}{\partial ni}\right)_{T,P,n(j\neq i)} = \left(\frac{\partial u}{\partial ni}\right)_{S,V,nj(j\neq i)}$ for an open system.

(ii) Write the *SI* unit of chemical potential. 4+1

(c) Write down Arrhenius equation relating rate constant and activation energy (E) for a reaction. Calculate the percentage increase of rate constant for a 5% increase in temperature. Given $E = 20\ kJ\ mol^{-1}$ and $T = 300K$. 2+3

(d) Show that in a crystal lattice there cannot be five-fold rotational axis of symmetry. 5

(e) Deduce the expression of *pH* for a solution of salt of weak acid and weak base. 5

4. Answer any *one* question : 1×10

(a) (i) Aluminium (Al) crystallizes with a face centred cubic lattice. The inter-ionic distance in a unit cell of aluminium is $2.86\,\mathring{A}$. Calculate the density of Aluminium (Atomic weight of $Al = 27$).

(ii) Find a relation between the internal energy (U) and canonical partition function (Q).

(iii) A carnot engine works between $780k$ and $300k$. If the sink temperature is reduced by 10%, calculate the % charge in efficiency of the carnot engine. 4+4+2

(b) (i) Can there be two inversion temperatures for a real gas?

(ii) A gas reaction $AB_2X_2 \rightarrow AB_2 + X_2$ has rate constant $k_1 = 2 \cdot 28 \times 10^{-5} s^{-1}$. What percent of sample of AB_2X_2 would be decomposed by heating for two hours?

(iii) Calculate the dissociation constant of water, given that $k_w = 1 \cdot 0 \times 10^{-14}$ at 25°c. 4+4+2

(c) (i) What is buffer capacity? Show that buffer capacity of a half-neutralised weak acid is maximum.

(ii) Assuming U as a function of S and V write down the expression for dU. Using the expression for dU arrive at the Maxwell relation $(\partial P / \partial S)_v = -(\partial T / \partial V)_s$.

(iii) Write down the expression of chemical potential in terms of 'enthalpy' and 'internal energy'. 4+4+2