PG Odd Semester (CBCS) Exam., December—2018

CHEMISTRY

(1st Semester)

Course No. : CHMCC–103

(Physical Chemistry—I)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* What do you mean by 'exact differential'? Show that internal energy (U) is an exact differential. 2+2=4

(b) Calculate the work done, when one mole of a van der Waals' gas expands isothermally at 27 °C and reversibly from 2 litres to 20 litres. Given, a 1 42 10^{12} dynes cm^{4} per mole and b 30 c.c. per mole. 3

(c) State 'zeroth law of thermodynamics'. How was the concept of temperature introduced from zeroth law of thermodynamics? 1+6=7

2. *(a)* Assuming the mathematical form of the first law of thermodynamics, derive an expression for entropy change in terms of thermodynamically measurable quantities. 7

(b) Show that dq is not a perfect differential but $\frac{dq}{T}$ is a perfect differential. 4

(c) Find the expression for (C_p C_v) in case of van der Waals' gas. 3

UNIT—II

3. *(a)* Show that in a closed system consisting of several chemical species

$$\frac{G}{\quad}_{P,T} \qquad {}_{i} \; {}^{i \;\; i}$$

where the symbols have their usual significance. Explain the variation of G as a function of with a properly drawn diagram. 5+2=7

(b) Show that decrease in free energy at constant temperature and pressure is equivalent to maximum available work. 4

(c) For a reaction

$$G \quad 13 \;\; 850 \quad 16 \;\; 1\,\mathrm{T}\log T \quad 72 \;\; 59\;\mathrm{T}\;(\mathrm{cal})$$

calculate S at 327 °C. 3

4. (a) Derive Gibbs-Dühem relations for chemical potentials with the composition of the system. Hence, show that a reaction proceeds from higher potential to lower potential. 6+3=9

(b) Derive an expression for integrated form of van't Hoff equation and graphically explain the variation of equilibrium constant with temperature. 3+2=5

UNIT—III

5. (a) Obtain an expression for the entropy production per unit time in an open system containing two phases at different temperatures. 8

(b) Obtain an expression for entropy production in chemical reaction. 6

6. (a) Obtain the phenomenological relation for the electrokinetic phenomena. From this, derive the relation between different electrokinetic effects and show the interrelation between these effects. 6+2+2=10

(b) Considering non-equilibrium thermodynamic system, explain the concept of 'local formulation of entropy'. 4

UNIT—IV

7. (a) Obtain the rate constant of a bimolecular gas reaction using thermodynamic formulation of conventional transition state theory. 8

(b) The value of S for a reaction, (where, n 1) has been obtained as –80·5 J-k^{1} mol^{1} at 400 K. Find the value of Arrhenius factor, A for the reaction. 3

(c) Discuss the comparison of absolute reaction rate with those of collision theory. 3

8. (a) Obtain an expression relating to the rate constant in solution using transition state theory. 5

(b) Discuss the effect of salts on the rate of ionic reactions. 4

(c) *(i)* Write an expression of Arrhenius equation and explain the terms involved in it.

(ii) Draw the plot of $\ln K$ vs. $\frac{1}{T}$, $\ln K$ vs. $\ln T$ and $\ln K$ vs. T. 2+3=5

UNIT—V

9. *(a)* Discuss and obtain the rate expression of Christiansen, Herzfeld and Polanyi mechanism of the thermal formation of hydrogen bromide. 7

(b) How does the rate equation of the thermal formation of hydrogen bromide differ from that of the same reaction if it is initiated photochemically? 5

(c) The intercept and slope of Lineweaver-Burk plot were obtained as $5\ 0\quad 10^{\ 3}$ and $1\ 5\quad 10^{\ 5}$ respectively. Calculate the value of Michaelis-Menten constant (K_{m}). 2

10. *(a)* Discuss the general mechanism of acid-base catalysis. 4

(b) What is fast reaction? Explain why conventional techniques lead to difficulties for very rapid reactions. Discuss the relaxation method to study the fast reaction. 1+2+7=10

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