SH-I/CHEM/102/C-2/19

B.Sc. 1st Semester (Honours) Examination, 2019-20

CHEMISTRY

Course ID : 11412 **Course Code : SHCHEM/102/C-2**

Course Title: Physical Chemistry–I

Time: 1 Hour 15 Minutes **Full Marks: 25**

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* of the following: 1×5=5

(a) 'Pdv–Vdp' is not an exact differential— Justify.

(b) Show that $\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P\right] = -\frac{H}{T^2}$.

(c) A zero order reaction cannot be single step reaction — Explain.

(d) What is Clausius inequality?

(e) Plot logk vs. pH for acid-base catalysed reaction.

(f) Plot the Carnot cycle in a S–T diagram.

(g) What are the unit of rate constants for a first order and for a zero order reaction?

(h) State one difference between Joule–Thomson cooling and adiabatic cooling.

2. Answer *any two* of the following: 5×2=10

(a) (i) What is the importance of using the r.m.s. speed rather than the average speed for gas molecules?

(ii) Find out the fraction of molecule having kinetic energy in excess of $\in_0$ in a plane.

(iii) Why the factor '$\frac{1}{2}n$' is used for bimolecular collisions of the gas molecules? 2+2+1=5

(b) (i) What is Line-weaver Burke plot for the enzyme catalysis reaction? Plot it.

(ii) Obtain the integrated form of rate equation for a 2nd order reaction A + B $\rightarrow$ pdts, where the initial concentrations. of A and B are different. What would happen if conc. A and B are not different from each other [$b \rightarrow a$ and given ln $(1 + x) = x$ as $x \rightarrow 0$]. 2+3=5

(c) (i) A Carnot engine working between 0°C and 100°C has taken up 840 Joule from high temperature reservior. Calculate the work done and efficiency of the engine.

(ii) Prove that the thermodynamic equation of state $C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$ and also show that $\left(\frac{\partial P}{\partial T}\right)_P = \frac{\alpha}{\beta}$, where α and β have their usual meaning. 2+3=5

(d) (i) What do you mean by the turn over number of an enzyme?

(ii) Show that $-\Delta A_T = W_{Total}$, where A = Work function.

(iii) Show that at low pressure Dietrici equation leads to van der Waal's equation. 1+2+2=5

3. Answer *any one* of the following: 10×1=10

(a) (i) Show that for a first order reaction the time required for 99.9% completion is three times of that required for the completion of 90% of the reaction.

(ii) Transform the Maxwell's distribution of velocities into the distribution of kinetic energy for gaseous molecules.

(iii) Starting from $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$, where the symbols have their usual meanings, show that for ideal gas, $\mu_{JT} = 0$.

(iv) The critical temperature and pressure of CO_2 are 31°C and 73 atm respectively. Assuming that CO_2 obeys van der Waal's equation, estimate the diameter of CO_2 molecule.

2+2+3+3=10

(b) (i) Prove that, $W_{adia} = \frac{P_1V_1}{\nu-1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\nu-1}\right]$ where terms are their usual meanings.

(ii) Derive the Kinetics of Unimolecular reactions (Lindemann Scheme).

(iii) Comment upon the following:

Order of a reaction cannot be predicted from its equation.

(iv) Show that for an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

(v) Write down the value of Z_c for a van dar Wal's gas. 2+3+2+2+1=10

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