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**End Semester Examination of Semester–I, 2015**
**Subject : CHEMISTRY (PG)**
**Paper : CEM–103 (Theory)**
**Full Marks : 40**
**Time : 2 Hrs**

*The figures in the margin indicate the marks corresponding to the question*

*Candidates are requested to give their answers in their own word as far as practicable.*

*Illustrate the answers wherever necessar.*

Answer one question from each group

## Group A

1. a) Is '$PV^{\gamma}$ = constant' is a equation of state? 2

   b) Show that Gibb's energy of a pure substance always decreases with temparature at constant pressure. 2

   c) Draw that Carnot cycle in terms of V–T. 2

   d) Describe a reversible process which consists of more than one step if required by, which will change the state of a gas from ($P_1$, $T_1$) to ($P_2$, $T_2$) where $P_1 > P_2$ and $T_1 < T_2$. 2

   e) Write the Lewis and Randall statement describing the 'Third Law of Thermodynamics'. 2

2. a) Deduce a thermodynamic equation of state involving enthalpy. Calculate $\left(\frac{\partial H}{\partial P}\right)_T$ for a gas obeying [PV = RT + bTP]. 3

b) $C_p$ is independent of pressure for an ideal gas but it is depended on pressure for real gas–Justify. 3

c) A reversible Carnot refrigerator working between $0^0$C and $25^0$C is run for 1 min using a 0·25 HP electrical motor. [1 HP = 746 W]. 4

Find : i) The co-efficient of performance of the refrigerator.

ii) The amount of heat extracted from the water kept inside at $0^0$C.

iii) The mass of ice produced.

## Group–B

3. a) Consider two energy level. First energy level has a zero energy with degeneracy 1. Second energy level has an energy of 300 $cm^{-1}$ with degeneracy 2. At what temperature will the probability of occupying the second energy level be 0·15? 3

b) Which properties are held constant in micro-canonical, canonical and grand-canonical ensemble? 3

c) Determine the standard molar entropy of $N_2$ at P = 1 atm., T = 2500 K. [$\bar{\nu}$ = 2359 $cm^{-1}$, B = 2 $cm^{-1}$, $g_0$ =1] 4

4. a) What is the difference between 'configuration' and 'micro state'? Explain. 2

   b) Evaluate the translational partition function for 'Ar' confined in a volume of 100 $cm^3$ at T = 298 K. At what temperature will the translational partition function of 'Ne' be identical to that of 'Ar' at 298 K confined to the same volume? 4

   c) Why is the electronic portion function generally equals to the degeneracy of the ground state? 2

   d) What is the high temperature limit approximation of the rotational and vibrational partition function? 2

## Group–C

5. a) Define stokes and anti stokes line. Give a classical explanation of these lines. 2+3

   b) Write a short note on 'Doppler Broadening' in the spectra. 2

   c) Define symmetrical and asymmetrical top. Determine among the following molecule which one is fall into the above category – $C_6H_6$, $CH_4$. 2+1

6. a) 'With the increase in vibrational quantum number the difference between consecutive vibrational levels will decrease'. – Justify the statement considering appropiate model. 2

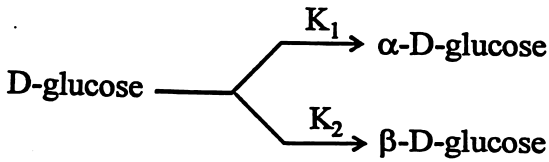
b) Derive the selection rules for the microwave active molecule. 4

c) Write the mechanism of interaction between the radiation and rotating molecule. 2

d) Derive a relation between maximum rotational quantum number and rotational constant using appropriate model. 2

## Group–D

7. a) If D-glucose anomerise as




Where $K_1$, $K_2$ is the specific rate constant. If the activation energy of the total reaction becomes 'E' then show that $E = \frac{K_1E_1+K_2E_2}{K_1+K_2}$; where $E_1$, $E_2$ is activation energy of the corresponding reaction. 3

b) What is the role of counter ion in stabilizing a micelle? How does it effect the CMC value. 2+1

c) Under what condition BET equation can be converted to Langmuir adsorption equation? 2

d) What is the basic difference in Vant-Hoff complex and Arrhenius complex? 2

8. a) The surface tension of solution of an acid in water is found to vary with $\nu = \nu^0 - bC^2$. Derive the relation between surface pressure ($\Pi$) and area occupied by 1mole of substance ($\sigma$). [b = constant and other terms has their usual meaning] 3

b) Prove that 'catalyst increases the rates of forward and backward reaction equally'. 3

c) What do you mean by 'water in oil' and 'oil in water' micro-emulsions? 2

d) 'In transition state theory, the transition state is Arrhenious complex, though steady state approximation is used'. – Justify the statement. 2