**2015**

## CHEMISTRY

Paper : 101 (Old Course)

## PHYSICAL CHEMISTRY

Full Marks : 80

Time : 3 hours

*The figures in the margin indicate full marks for the questions*

1.  Partition function can be used to calculate all the ..............................................(electrical/ physical/ thermal/ thermodynamic) properties. 1

2.  How internal energy is related to the canonical partition function? 1

3.  Write down the rotational partition function for a nonlinear polyatomic molecule. 1

4.  For a diatomic molecule, if temperature is increased by two fold, how its rotational partition function value will change? 1

5.  Show that the mean vibrational energy is $\langle \in_v \rangle = KT$  2

6.  Deduce an expression for translational partition function in terms of thermal wave length ( $\Lambda$ ) and show that the translational partition function is an extensive variable.  4+1=5

7.  Calculate the rotational contribution for water molecules at

( 1 )   *P.T.O.*

3000 K, if $I_a I_b I_c$ for water is 5.76 x 10$^{-141}$ Kg$^3$m$^6$.  3

8. Prove that  3+3=6

a) $P = NKT \left( \dfrac{d\ln q}{dv} \right)_T$

b) $\mu = -KT \ln \left( \dfrac{q}{n} \right)$

9. What is mean activity coefficient? Why it is important for electrolytic solution? Deduce an expression for mean activity coefficient ($\lambda$) for the electrolyte $A_x B_y$.  1+1+2=4

10. Write down the thermodynamic criteria for a three phase-three component system  2

11. How a three component phase is presented on paper? Explain with an example.  4

12. Prove that proper phenomenological coefficients are positive.  2

13. Discuss about the thermoelectric effects; Peltier, Seebeck and Thomson.  9

14. Show that the Gibbs energy of mixing of perfect gases is always spontaneous.  4

15. How Clapeyron equation helps to describe precise locations of phase boundaries?  5

16. Calculate $\gamma$ - and $\gamma \pm$ for 0.002 molal sodium chloride in water at 25$^0$ C. [Given $A = 0.509 \sqrt{\left( \dfrac{kg}{mol} \right)}$].  3

17. Deduce an expression for change in Born's free energy when an ion is introduced from vacuum into a medium of dielectric constant, $\in$ (say). How determines the spontaneity of the process?  4+1=5

18. What is Debye length ($L_D$)? How does it vary with ionic strength (I) ?  2

19. Derive the Einstein-Smoluchowski equation.  5

20. What is Born-Oppenheimer approximation?  2

21. What is radial distribution function? Draw radial distribution functions for 1s and 2s orbitals.  1+2 = 3

22. Write down the wave function for a particle in a one dimensional box and evaluate the expectation value of kinetic energy for that particle.  1+3 = 4

23. Derive the expression for wave function for a particle in a ring.  6

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