2015

CHEMISTRY

Paper : 101

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 $\langle \epsilon_v \rangle = KT$ 2
6. Deduce an expression for translational partition function in terms of thermal wave length (Λ) and show that the translational partition function is an extensive variable. 4+1=5
7. Calculate the rotational contribution for water molecules at

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

8. Prove that 3+3=6

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

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

9. What is mean activity coefficient? Why it is important for electrolytic solution? Deduce an expression for mean activity coefficient (λ) for the electrolyte A_xB_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 γ_- and $\gamma_\pm$ for 0.002 molal sodium chloride in water at 25° C. [Given $A = 0.509 \sqrt{\left(\frac{kg}{mol}\right)}$]. 3

17. Deduce an expression for change in Born□fs free energy when an ion is introduced from vacuum into a medium of dielectric constant, ϵ (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. Which one is a natural polymer? 1

a) Cellulose c) Dacron

b) Polypropylene d) Kevlar

21. Show the difference of different types of copolymer schematically. 2

22. What is the degree of polymerization? How molar mass can be calculated from the degree of polymerization? Explain with an example. 1+2=3

23. What is the functionality of a monomer? What is the functionality of ethylene, methyl methacrylate, vinyl chloride and ethylene glycol w.r.t. addition polymerization? 1+2=3

24. A sample of polystyrene has number average molecular weight of 100,000 and polydispersity five. What is its weight average molecular weight? 1

25. Discuss about the determination of molecular weight by light scattering method. 5

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