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14 (CHM-1) CH 103

2019

CHEMISTRY

Paper : CH-103

(Physical Chemistry)

Full Marks : 60

Time : Three hours

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

(Symbols used signify their usual meaning)

1. Answer **any six** from the following :

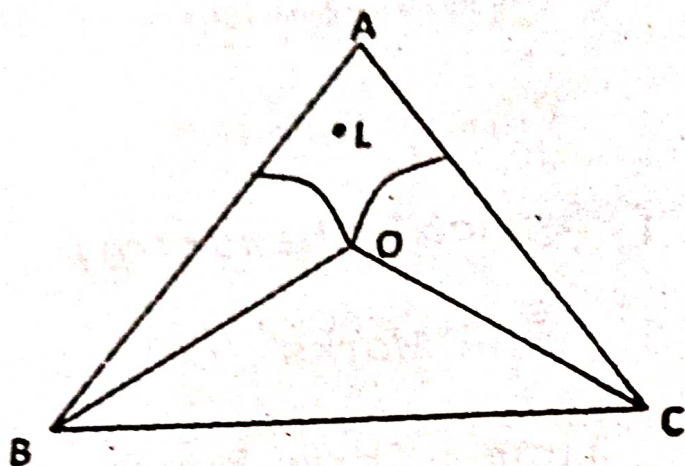
4×6=24

- (a) What is the phase rule for three component system? Draw the phase diagram for $\text{CHCl}_3 - \text{H}_2\text{O} - \text{CH}_3\text{COOH}$ system and explain.

1+3=4

Contd.

- (b) In the triangular plot of three component system (components A, B and C), illustrate the different phases if you start evaporating a dilute unsaturated solution at point L under isothermal isobaric conditions. 4



- (c) Prove that $\frac{f}{P} = e^{\frac{b}{RT} - \frac{aP}{(RT)^2}}$ for a real gas obeying van der Waals equation. 4

- (d) Calculate mean activity co-efficient (γ_+) of a 2+2=4

(i) NaCl at molality of 0.01m

(ii) Na₂SO₄ at molality of 0.01m in aqueous medium at 25°C

- (e) Explain the theory of minimum entropy production. 4

(f) Prove that $|L_{ij}| \leq \sqrt{L_{ii} L_{jj}}$
and L_{ii} and $L_{jj} > 0$. 4

(g) Define what Seebeck and Thomson effects are. 4

(h) Define fluxes and coupled forces with examples. Distinguish between equilibrium and steady state conditions. 2+2=4

2. Answer **any five** from the following : 4×5=20

(a) Express the following thermodynamic functions with respect to canonical partition function : 2+2=4

(i) The Helmholtz energy (A)

(ii) The Gibbs energy (G)

(b) A monatomic perfect gas expands from initial volume V_i to final volume V_f isothermally. Using Sackur-Tetrode

equation show that $\Delta S = nR \ln \frac{V_f}{V_i}$.

4

(c) Show that the internal energy of a perfect gas

$$U = U(0) + \frac{3N}{2\beta}$$

(d) Define characteristic rotational temperature (θ_R). Write the expressions of rotational partition functions for linear and non-linear molecules above the characteristic rotational temperature. 1+3=4

(e) What is residual entropy? Find the molar residual entropy for water. 1+3=4

(f) Derive the electronic partition function for NO molecule. 4

(g) Derive an expression for equilibrium constant in terms of partition function. 4

3. Answer **any two** from the following :

4×2=8

(a) Calculate the (a) mean, (b) median, and (c) standard deviation of the following sets of replicate measurements : 4

A	B
3.5	0.812
3.1	0.792
3.1	0.794
3.3	0.900
2.5	

(b) How will you obtain a best fitted straight line through a series of experimental points using least square method? Explain. 4

(c) Estimate the standard deviation and rewrite the complete result of the following : (**any two**) 2×2=4

(i) $y = \frac{157(\pm 6) - 59(\pm 3)}{1220(\pm 1) + 77(\pm 8)} = 7.5559 \times 10^{-2} (?)$

(ii) $y = 5.75(\pm 0.03) + 0.833(\pm 0.001) - 8.021(\pm 0.001)$
 $= -1.438(?)$

(iii) $y = \frac{4.10(\pm 0.02) \times 0.0050(\pm 0.0001)}{1.97(\pm 0.04)} = 0.010406 (?)$

4. Answer **any two** from the following :

4×2=8

(a) Discuss briefly how the calibration curve is obtained in size exclusion chromatography for determination of the molecular mass of a polymer. 4

(b) Define different types of molecular mass used for polymers. Give example of one method for each type of molecular mass determination. 4

(c) Define degree of polymerization. Derive an expression of 'degree of polymerization' for cationic polymerization. 1+3=4