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[A-27]

No. of printed pages : 03

SARDAR PATEL UNIVERSITY

M. Sc. (Semester – IV) CBCS Examination

Tuesday, 28th April 2015

10.30 a.m. to 1.30 p.m.

PS04ECHE03 Selected Topics in Physical Chemistry – II

Total Marks : 70

Note : (i) Figures to the right indicate full marks.
(ii) Graph paper will be provided upon request.

(Useful constants are, $h = 6.63 \times 10^{-34}$ J.s , R = 1.987 cal. $K^{-1}.mol^{-1}$, $k = 1.38 \times 10^{-23}$ J. K^{-1}, $k = 0.695$ cm^{-1}, $k = 8.625 \times 10^{-5}$ eV.K^{-1}, $N_A = 6.023 \times 10^{23}$ $molecule^{-1}$)

Q . 1 Select the correct answer from the alternatives given below to the each question; [08]

[i] For athermal polymer solution,

(a) $\Delta H^E = 0, \Delta S^E = 0$ (b) $\Delta H^E \neq 0, \Delta S^E = 0$
(c) $\Delta H^E = 0, \Delta S^E \neq 0$ (d) $\Delta H^E \neq 0, \Delta S^E \neq 0$

[ii] The interaction parameter, χ_{cr} = ________ .

(a) $1 - \phi_{1c}$ (b) $BV_1\, m / R\, (1 + \sqrt{m})^2$
(c) $(\sqrt{m} + 1)^2 / 2\, m$ (d) $1 / (1 + \sqrt{m})$

[iii] According to Flory's original theory, $\alpha^5 - \alpha^3$ = ________ .

(a) 2.6 , (b) 1.4, (c) 1.35, (d) 3.6

[iv] For ideal polymer solution, the value of second virial coefficient, A_2 = ___.

(a) 3 (b) 2 (c) 1 (d) 0

[v] For perturbed state, the solubility parameter, δ have values _____.

(a) between 0 and 1 (b) between 1 and 1.33
(c) between 0 and 0.33 (d) between 0.75 and 1.25

[vi] According to geometric mean, E_{AB} = ____________.

(a) $\sqrt{E_{AA}} . E_{BB}$ (b) ½ $(E_{AA} + E_{BB})^2$
(c) $(E_{AA} + E_{BB})^2$ (d) $2\,(E_{AA} + E_{BB})$

[vii] In Zimm treatment, the excluded volume, u = ______________.

(a) $4/3\, \pi\, (2\, \mathbf{r})^3$ (b) $4/3\, \pi\, (\mathbf{r})^3$
(c) $\pi\, (\mathbf{r})^3$ (d) $\pi\, (2\, \mathbf{r})^3$

[viii] For a linear array of two dimensional polymer molecule, if the minimum value of coordination number (Z = 2) than, q = ______.

(a) 3 (b) 2 (c) 1 (d) 0

Cont..... 2........

Q . 2 Answer the following in short ; **(ANY SEVEN)** **[14]**

[a] What is mean by an unperturbed state?

[b] Define : Regular solution, Ideal solution

[c] Show that, $\langle r^2 \rangle = n\, l^2$.

[d] Enlist limitations of Guggenheim equation.

[e] According to Zimm approach, show a graph of variation in π/C as a function of concentration for an ideal and non-ideal solution.

[f] Give schematic representation of instantaneous chain configuration.

[g] Providing, $\alpha^2 - 1 = 4/3\ Z$, show that $\delta = 1.5$ for perturbed state.

[h] Justify "Change in potential of solvent and solute are same".

[i] Give expression $\Delta\mu_1^*/RT$.

Q . 3 **[a]** What do you mean by an ideal solution ? Formulate the free energy of mixing for an ideal solution considering a quasi crystalline model. **[06]**

[b] $\Delta G^* / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2$, due to Flory theory for athermal polymer solution. Deduce the expression for $\Delta\mu_1^*$ and $\Delta\mu_2^*$. **[06]**

OR

[b] [i] Give a brief discussion on the Guggenheim's treatment given to an athermal solution. **[03]**

[ii] Describe Zimm's approach to athermal solution. **[03]**

Q . 4 **[a]** What is solubility parameter? Discuss Hildebrand's theory of a regular solution to derive, $\Delta H = V\, \phi_A\ \phi_B\, (\delta_A - \delta_B)^2$. **[06]**

[b] Using free energy diagram, explain critical point, Binodal curve and spinodal curve. Also explain stable, meta stable and unstable regions of the solution. **[06]**

OR

[b] For general polymer solution, **[06]**
$\Delta\mu_1^* / RT = \ln \phi_1 + (1 - 1/m)\, \phi_1 + \chi\, \phi_2^2$
Obtained χ_{cr}, ϕ_{cr} and T_{cr}.

Q . 5 **[a]** [i] Prove that $\int_0^{\infty} \rho\,(\vec{s}\ /\ s)\, d\vec{s} = n$. **[03]**

[ii] For general polymer solution, **[03]**
$\Delta G^* = RT\ [\ n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi\, \phi_1\, \phi_2\, (n_1 + m n_2)\ ]$
Prove that the potential of mean force with fixed radius of gyration is,

$$V(s) = \left(\frac{3^{3/2}}{16\,\pi^{3/2}}\right) \frac{k\,T}{V_1} \left({}^1\!/_2 - \chi\right) \frac{M^2\, V^2}{N_A{}^2}\, S^{-3}$$

Cont..... 3........

[b] [i] As per Harmans and Overback, [03]

$1/x - x = 1/3\ KT\ dV(x)/dx$

Show that $\alpha^5 - \alpha^3 = C_1 Z$. (where C_1 = constant)

[ii] According to Fox-Flory theory of viscosity, Show that, [03]

$\upsilon = (3\varepsilon + 1)/2$.

OR

[b] For following values of **M** and η, Calculate the value of **($0.44\ \Phi\ B\ K^{-1/3}$)** and **$K^{2/3}$**, using appropriate graph, [06]

$M \times 10^{-4}$ (g.mol^{-1})	6	8	12	16	18
η (dl/gm)	4.782	6.378	9.564	12.75	14.32

Q . 6 [a] Using following equation, [06]
$1/x - x = 1/3\ k\ T\ dV(x)/dx$
Derive (i) Kurata-Stockmayer-ring equation,
(ii) Kurata equation.

[b] Using B-J equation, $\alpha^2 - 1 = 4/3\ \alpha\ Z$, Derive values of δ, ε, υ for perturbed and unperturbed state. Also deduced relation between ε & Z, and η & M. [06]

OR

[b] Using Fixman theory, $\alpha^3 - 1 = 2\ Z$, Derive values of δ, ε, υ for perturbed and unperturbed state. Also deduced relation between ε & Z, and η & M. [06]

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