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5 SEM TDC CHM M 1

2021

(March)

CHEMISTRY

(Major)

Course : 501

(Physical Chemistry—II)

Full Marks : 48
Pass Marks : 14

Time : 2 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer : 1×5=5

(a) Temperature dependence of reaction rate is given by

(i) Arrhenius equation

(ii) Eyring equation

(iii) both Arrhenius and Eyring equations

(iv) Kirchhoff's equation

(b) When benzoic acid is distributed between benzene and water, benzoic acid dimerises in organic layer. Correct form of Nernst distribution law for this distribution is

(i) $K_D = \frac{C_{org}}{C_{aq}}$

(ii) $K_D = \frac{\sqrt{C_{org}}}{C_{aq}}$

(iii) $K_D = \frac{C_{org}}{\sqrt{C_{aq}}}$

(iv) $K_D = \sqrt{\frac{C_{org}}{C_{aq}}}$

(c) Variation of equilibrium constant with temperature is given by

(i) Gibbs-Duhem equation

(ii) Duhem-Margules equation

(iii) van't Hoff equation

(iv) None of the above

(Continued)

(d) The adsorbent used in gas masks to adsorb all toxic gases and vapours is

(i) silica gel

(ii) alumina

(iii) finely divided nickel

(iv) activated charcoal

(e) Stability of lyophobic solution is due to

(i) the electrical charge present on the colloidal particles

(ii) solvation

(iii) both the electrical charge present on the colloidal particles and solvation

(iv) the size of the colloidal particles

2. Answer the following questions : 2×5=10

(a) Write two important characteristics of a first-order reaction.

(b) State and explain Raoult's law.

(c) On the basis of Le Chatelier's principle, discuss the effect of temperature and pressure on equilibrium.

(d) Discuss the application of adsorption on chemical analysis.

(e) Define the terms 'electrophoresis' and 'electroosmosis'. 1+1=2

3. Answer any *two* questions from the following : 6×2=12

(a) (i) Derive the integrated rate equation for a second-order reaction $A + B \rightarrow$ products. Under what condition, the reaction follows first-order kinetics? 3+1=4

(ii) Show that for a first-order reaction, the time required for 75% completion of the reaction is two times of its half-life period. 2

(b) (i) For an exothermic reaction, the activation energy for the forward reaction is always less than the activation energy for the backward reaction. Explain. 2

(ii) Derive Eyring equation on the basis of activated complex theory. 4

(Continued)

(c) (i) For a reversible first-order reaction, $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$, show that

$$(k_b + k_f) = -\frac{1}{t} \ln \frac{[A] - [A]_{eq}}{[A]_0 - [A]_{eq}}$$

where, $[A]_0$ and $[A]_{eq}$ are the initial and equilibrium concentration of A. 4

(ii) Half-life of a first-order reaction is 30 minutes at 27 °C and 10 minutes at 47 °C. Calculate the energy of activation. 2

4. Answer any *one* question from the following : 5

(a) (i) Derive a relationship between osmotic pressure and lowering of vapour pressure of an ideal solution thermodynamically. 4

(ii) 0·5% aqueous solution of KCl was found to freeze at –0·24 °C. Calculate the van't Hoff factor. ($K_f = 1 \cdot 86$ K kg mol^{-1}) 1

(b) Discuss the application of Nernst distribution law in solvent extraction. Show that multi-step solvent extraction is more efficient than single-step extraction. 2+3=5

5. Answer any *one* question from the following : 7

(a) *(i)* Derive Duhem-Margules equation. 3½

(ii) For a system of ideal gases, prove that $\mu = \mu^0 + RT \ln p_i$. 3½

(b) *(i)* Show that

$$\left(\frac{\partial G}{\partial T}\right)_{p, n_1, n_2, \ldots} = -S$$

2

(ii) Define chemical potential. What is its physical significance? 1+1=2

(iii) Discuss the variation of chemical potential with temperature. 3

6. Answer any *one* question from the following : 4

(a) *(i)* Heat of adsorption is greater for chemisorption than physisorption. Explain. 2

(ii) At 0°C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 $cm^3 g^{-1}$ of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0·162 $(nm)^2$. 2

(Continued)

(b) Explain Freundlich adsorption equation with the significance of the terms involved. What will be the form of this equation for adsorption from solution? What is the limitation of Freundlich adsorption isotherm? 2+1+1=4

7. Answer any *one* question from the following : 5

(a) (i) If a freshly formed stannic oxide is peptized by a small amount of hydrochloric acid, the solution carries a positive charge. But, if peptized by a small amount of sodium hydroxide, the solution carries a negative charge. Explain. 2

(ii) What do you mean by flocculation and flocculation value? Explain why $MgCl_2$ is better coagulant than NaCl for As_2S_3 solution. 2+1=3

(b) (i) Discuss the origin of charge on colloidal particles. 2

(ii) What is peptization? 1

(iii) Define the term 'critical micelle concentration' (CMC). Mention two properties of the ionic surfactant solution which undergoes abrupt change at CMC. 1+1=2

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