

2016

CHEMISTRY

( Major )

Paper : 5.2

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following in brief : 1×7=7

(a) Write whether the values of enthalpy of adsorption and entropy of adsorption are negative or positive. -ve

(b) Write the difference between chemical reaction and photochemical reaction in terms of Gibbs free energy change.

(c) In photosynthesis,  $\text{CO}_2$  reacts with water in presence of chlorophyll and other plant pigments to produce starch. State the role of chlorophyll and the other pigments in the reaction.

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*See time*  
 (d) The standard Gibbs energies of formation of  $\text{HN}_3$  at 298 K are  $+327 \text{ kJ mol}^{-1}$  and  $+328 \text{ kJ mol}^{-1}$  for the liquid and gas phases respectively. Which phase of hydrogen azide is the more stable at that temperature and 1 bar?

(e) In case of many reaction, the entropy of activation is negative. State the reason.

(f) Why are powdered substances more effective absorbents than their crystalline forms?

(g) An iceberg is floating in the lake. If one considers the lake, iceberg and atmosphere as a one system, what are the number of phases?

2. Answer the following questions :  $2 \times 4 = 8$

(a) Express Eyring equation regarding activated complex theory in terms of entropy and enthalpy of activation.

*See to the*  
 The fluorescence quantum yield and observed fluorescence lifetime of tryptophan in water are  $\phi_{F,0} = 0.20$  and  $\tau_0 = 2.6 \text{ ns}$  respectively. Determine the fluorescence rate constant of this substance.

The standard molar entropy of liquid water at  $0^\circ\text{C}$  is  $65 \text{ JK}^{-1} \text{ mol}^{-1}$  and that

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$du_i = SdT$   
 $2 - 5(20)$

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$x_i = P_i/P$   
 $P_i = \frac{\gamma_i P_i^0}{\gamma}$   
 of ice at that temperature is  $43 \text{ JK}^{-1} \text{ mol}^{-1}$ . Calculate  $du(l)$  and  $du(s)$  for water by rise of  $1.0 \text{ K}$  temperature. What is the effect of increasing the temperature by  $1.0 \text{ K}$ ?

(d) Write the Clapeyron equation on the solid-liquid boundary of the phase diagram. How does pressure vary with temperature on this boundary?

3. Answer any three of the following :  $5 \times 3 = 15$

(a) (i) Show that when a diatomic gas adsorbs as atoms on the surface of a solid, the Langmuir adsorption isotherms becomes

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

where the symbols have their usual meanings. 3

(ii) Calculate the surface excess of 1-aminobutanoic acid in a  $0.10 \text{ mol dm}^{-3}$  aqueous solution at  $20^\circ\text{C}$ . Given that

*Affairs*

$$-\frac{1}{RT} \left( \frac{d\gamma}{d \ln C} \right)_T = -40 \mu\text{Nm}^{-1}$$

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( Turn Over )



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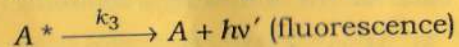
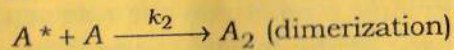
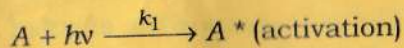
Using steady state approximation for  $[ES]$ , show that the reaction rate is given by

$$r = \frac{K_2[E]_0[S]}{K_m + [S]}$$

where the symbols have their usual meanings. Discuss the rate when  $K_m \gg [S]$ . 3+1=4

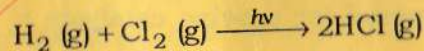
5. Answer either (a) and (b) or (c) and (d) :

(a) What is the role of photosensitizer in the photochemical reaction? The mechanism of photochemical dimerization of an anthracene is given below :



Show that quantum yield for dimerization of anthracene is independence of intensity of light absorbed. 1+4=5

(b) What is quenching? The quantum efficiency for the photochemical reaction



is  $1.0 \times 10^6$  with a wavelength of 480 nm. Calculate the number of moles of HCl (g) produced per joules of radiant energy absorbed. 1+4=5

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( Continued )

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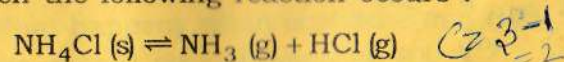
(c) Write the mechanism of the  $H_2-Cl_2$  photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. 2+3=5

(d) In a certain photochemical reaction using 464 nm radiation, the incident light power was 16.0 W and the system absorbed 75% of the incident light. The quantum yield of the reaction was found to be 0.15. How many moles of the product were formed in the reaction in 100 S? 5

6. Answer either (a), (b) and (c) or (d) and (e) :

(a) What do you mean by solid compound with congruent melting point? Draw the phase diagram of a such system forming two such compounds. Explain the diagram. 2+4=6

(b)  $NH_4Cl(s)$  is heated in a closed vessel when the following reaction occurs :



Find the number of components, phase and degrees of freedom. p=3, 2, h.c.p.p.1

(c) What is the maximum possible number of phases that can coexist for a two-component system? Explain. 2

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(d) Draw the phase diagram of water and explain what the different curves signify. Using Clapeyron equation, predict the slope of each curve. 3+3=6

(e) Show that the free energy of mixing of three gases has a minimum value with respect to each gas only when the mole fraction of the components are equal. Consider ideal behaviour. 4

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$n_1, n_2, n_3$

$n_1, n_2, n_3$   
 $n_1, n_2, n_3$

$n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln n_3$