

DEPARTMENT OF CHEMISTRY, IIT MADRAS
CY 101: Equilibrium and Dynamics of Chemical Systems
I B. Tech. End Semester Examination; 28 November, 2005
Marks: 60(this part); Time: 3 hours (total)

This paper contains **7 questions** in **5 pages (8 pages with answers)**. Check the question paper.

$$R = (8.314 \text{ J} = 0.0821 \text{ atm dm}^3) \text{ K}^{-1} \text{ mol}^{-1}$$
$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.022 \times 10^{23}$$
$$h = 6.626 \times 10^{-34} \text{ Js}$$

1. (This question contains 10 short questions totaling 18 marks)

I. (2 marks) Data for the reaction, $2 \text{ NO} + \text{Cl}_2 \rightarrow 2 \text{ NOCl}_2$, are given:

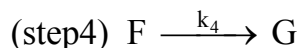
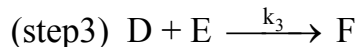
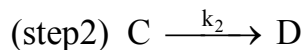
| experiment # | [NO] (M) | [Cl ₂] (M) | initial rate (M s ⁻¹) |
|--------------|----------|------------------------|-----------------------------------|
| (1) | 0.0010 | 0.0020 | 3.55×10^{-3} |
| (2) | 0.0010 | 0.0040 | 1.42×10^{-2} |
| (3) | 0.0020 | 0.0040 | 2.84×10^{-2} |

Choose the correct option from below:

- a) zero order in both [NO] and [Cl₂]
- b) 1st order in [NO], 1st order in [Cl₂], 2nd order overall
- c) 1st order in [NO], 2nd order in [Cl₂], 3rd order overall
- d) 2nd order in [NO], 1st order in [Cl₂], 3rd order overall
- e) 2nd order in [NO], 2nd order in [Cl₂], 2nd order overall

Ans. (c)

II. A reaction mechanism: (step1) $A + B \xrightarrow{k_1} C$ is believed to follow the following



- (a) **(1 mark)** List the intermediate(s) involved in the reaction, if any. **Ans: C,D,F**
- (b) **(1 mark)** Is/are catalyst(s) involved in the reaction? List if any. **Ans: None**
- (c) If the steps 1 and 4 are fast and the rate constant $k_2 \ll k_3$,
 - (i) **(1 mark)** What should be the order of the reaction and with respect to which species? **Ans: 1st order w. r. t. C**

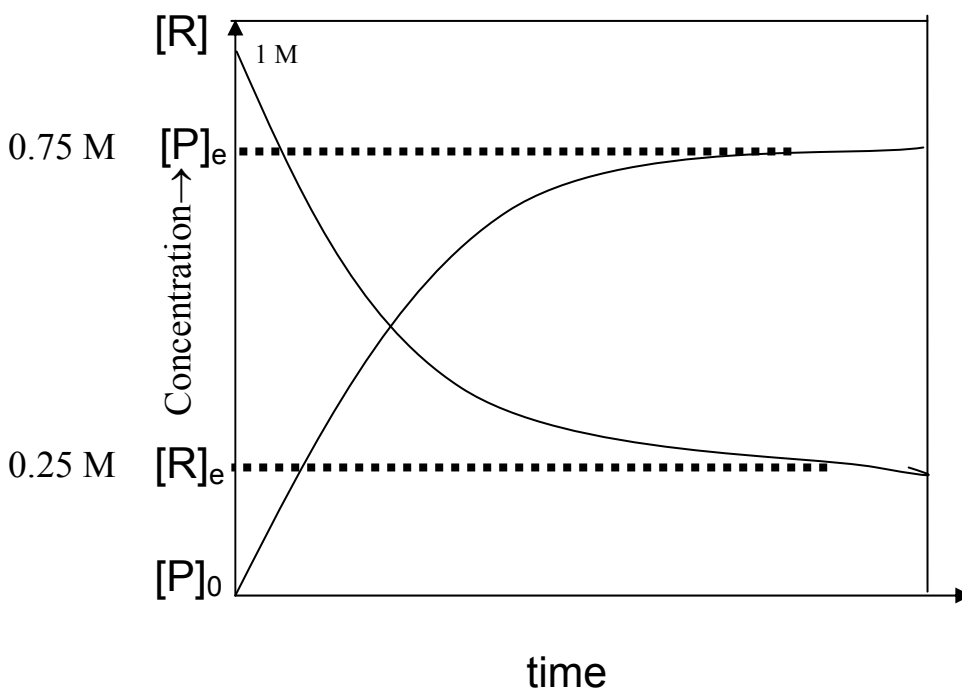
(ii) (1 mark) A plot of which parameter against time should be linear with a negative slope? Ans: **In C**

III. (1 mark) In Transition State Theory, which one of the following factors is related to the frequency of the activated complex crossing the activation barrier?

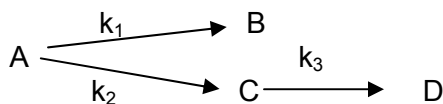
- (a) K^\ddagger / t (b) pZ_{AB} (c) r (rate of reaction) (d) $k_B T/h$

Ans. (d)

IV. (2 marks) An opposing reaction of the type $R \xrightleftharpoons[k_b]{k_f} P$ has an equilibrium constant value of 3. Starting at initial concentrations of R at 1 M and P at 0 M, sketch the plot of the variation of concentrations of R and P against time, in a time scale such that equilibrium concentrations of both R and P are indicated. Use the following format in your answer book.



V.



For the above reaction,

(i) $k_2 = 3k_1$

(ii) $k_3 \gg \gg k_2$

An experiment involving the above reaction was started with the initial concentration of A at 1M.

(A) (1 mark) Can steady state approximation be used for the concentration of C? **yes**

(B) (2 marks) What was the concentration of D after infinite time? **0.75 M**

VI. (1 mark) A chemical reaction taking place in a calorimeter causes the temperature to rise by 7.5°C . At the end of the reaction, an addition of 50 kJ of energy to the calorimeter by an electrical heater increases its temperature further by 2.5°C . What is ΔH of the chemical reaction? Choose the correct option from below.

a) 16.7 kJ

b) -16.7 kJ

c) -150 kJ

d) 150 kJ

Ans. (c)

VII. (2 marks) Consider the reaction, $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g})$ at 27°C , given $\Delta H^\circ = -57.2\text{ kJ mol}^{-1}$ and $\Delta S^\circ = -175.8\text{ J mol}^{-1}\text{K}^{-1}$. This reaction is

a) Nonspontaneous at 50°C , but can be made spontaneous at sufficiently high T.

b) Nonspontaneous at 50°C , but can be made spontaneous at sufficiently low T.

c) Spontaneous at 50°C , but can be made nonspontaneous by increasing T.

d) Spontaneous at 50°C , but can be made nonspontaneous by decreasing T.

e) Spontaneous under all temperature conditions.

Choose the correct option from above.

Ans: (c)

VIII. (1 mark) If the entropy of the universe is increasing in any spontaneous process, how can salts crystallize out of solution, a process which causes a greater ordering of the particles? Choose the correct option from below.

a) Although the entropy of a system, such as crystallization of dissolved salts in solution, may decrease during a spontaneous process, the entropy of the surroundings increases to a larger extent.

b) The crystallization process is a paradoxical violation of the Second Law of Thermodynamics.

c) Crystalline salts have higher entropy than their saturated solutions and therefore crystallization is spontaneous.

d) Although ΔS is negative for crystallisation, ΔG is always negative since ΔH is highly negative.

Ans. (a)

IX. (1 mark) Which of the following options represent the total number of independent variables that are needed to specify a system of 'C' components distributed in 'P' phases at equilibrium?

- (a) $P(C - 1) + 2$
- (b) $C(P - 1) + 2$
- (c) $C(P - 1)$
- (d) $C + P - 2$

Ans. (a)

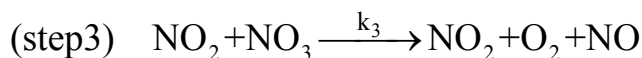
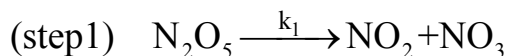
X. (1 mark) Which of the following is NOT a characteristic of a simple two-component eutectic system?

- (a) Liquid-A and liquid-B are miscible in all proportions.
- (b) Solid-A and solid-B form a solid solution at eutectic temperature.
- (c) Intimate mixture of solid-A and solid-B cause mutual lowering of melting points of each other.
- (d) At the eutectic temperature the system has the lowest degree of freedom.

Ans: (b)

2. (7 marks) For the decomposition of N_2O_5 as per the equation,

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, the following mechanism is suggested:



(A) Find the rate law, $\frac{d[N_2O_5]}{dt}$ consistent with this mechanism.

(B) If $k_3 \gg k_2$, which of the above step(s) contribute(s) to the rate law?

answer:

(A)

$$\frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_2[NO_2][NO_3] - k_4[NO][N_2O_5]$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO_2][NO_3] = 0$$

$$\frac{d[NO]}{dt} = k_1[NO_2][NO_3] - k_4[NO][N_2O_5] = 0$$

$$\therefore \frac{d[N_2O_5]}{dt} = \frac{-2k_1k_3[N_2O_5]}{k_2 + k_3}$$

(5marks)

(B) under the condition, only the first step contributes. (2 marks)

3. (7 marks) Michaelis-Menten Mechanism for an enzyme catalyzed reaction is given as,

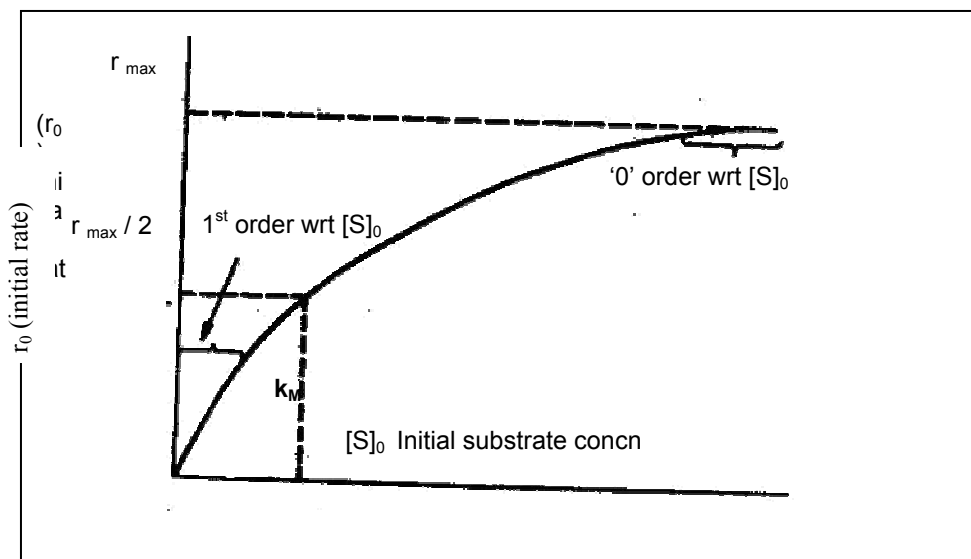


where the notations have their usual significance.

Sketch the plot of initial rate of the reaction (r_0) against initial substrate concentration ($[S]_0$) and indicate (in the plot) the following:

- (a) The range where the order of the reaction is '0' with respect to $[S]_0$.
- (b) The range where the order of the reaction is '1' with respect to $[S]_0$.
- (c) The position of ($r_0(\max)$), where r_0 is maximum.
- (d) The position of Michaelis-Menten constant (k_M).

Answer: (3 marks for the correct plot. 1 mark for each required indication)



4. (7 marks) Calculate ΔA , ΔU and ΔG for the vaporization of one mole of water at 372.8 K and one bar pressure. Assume water vapour to be an ideal gas. Heat of vapourisation of water is $40,893 \text{ J mol}^{-1}$.

Answer

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta A = q_p + w_p - q_p = w_p$$

$$\Delta G = q_p - q_p = 0 \quad (1\text{mark})$$

$$w_p(\text{rev}) = -P\Delta V = -P(V_g - V_l) \approx V_g = \frac{RT}{P}$$

$$w_p(\text{rev}) = -RT = -8.314 \times 372.8 = -3099\text{J} \quad (2\text{marks})$$

$$\Delta A = -3099\text{J} \quad (2\text{marks})$$

$$\Delta U = q + w = 40893 - 3099 = 37794\text{J} \quad (2\text{marks})$$

5. (7 marks) The gas phase reaction, $2A \rightarrow \text{Decomposition products}$ is bimolecular with an activation energy of 185 kJ mol^{-1} . 'A' has a molar mass of 0.128 kg and its radius is 1.75 \AA .

(a) Calculate from collision theory the specific rate constant for the decomposition reaction at 556 K.

Answer

(a)

$$\begin{aligned}Z_{AA} &= 2 \left(\frac{\pi RT}{M} \right)^{1/2} d_{AA}^2 N_A \\&= 2 \left(\frac{3.14 \times 8.314 \times 556}{0.128} \right)^{1/2} \times (3.5 \times 10^{-10})^2 \times (6.022 \times 10^{23}) \\&= 4.97 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 4.97 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\q &= \exp \left(\frac{185000}{8.314 \times 556} \right) = 4.25 \times 10^{-18}\end{aligned}$$

$$k_{\text{collision}} = 4.97 \times 10^{10} \times 4.25 \times 10^{-18} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.11 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

4 marks

(b) If the observed rate constant is $7.25 \times 10^{-8} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, find the steric factor.

Answer

(b)

$$\begin{aligned}k_{\text{experimental}} &= 7.25 \times 10^{-8} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\p &= \frac{7.25}{21.1} = 0.345\end{aligned}$$

The value of $k(\text{col})$ estimated by students may be slightly different from this. In such a case, their calculation of 'p' can be taken as correct, if the procedure is right.

1 mark

(c) If the temperature of the reaction is reduced by a factor of 4, the pre-exponential factor will decrease (increase / decrease) by a factor of 2. (Fill in the blanks)

2 marks

6. (7 marks) For the reaction, $\text{SnO}_2(\text{s}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{Sn}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

the equilibrium partial pressure of H_2 was found to be 0.45 atm at 900 K and 0.22 atm at 1100K. The total equilibrium pressure was maintained at 1 atm in a closed vessel.

Calculate the following:

(A) The standard molar free energy change for the reduction of SnO_2 at 1100 K.

At 1100 K, $p_{\text{H}_2} = 0.22 \text{ atm}$, $p_{\text{H}_2\text{O}} = (1 - .22) \text{ atm} = 0.78 \text{ atm}$

$$K_{1100} = (0.78 / 0.22)^2 = 12.57$$

$$\Delta G^\circ = -RT \ln K = -23150 \text{ J} \quad \text{(2 marks)}$$

(B) The standard molar enthalpy change for the reduction of SnO_2 , assuming it to be constant in the temperature range.

At 900 K, using a similar procedure, $K_{900} = 1.49$, $\Delta G^0 = -3002 \text{ J}$

$$\ln(K_{1100} / K_{900}) = (\Delta H^0/R)\{(1100-900)/(1100 \times 900)\}$$

$$\Delta H^0 = 87658 \text{ J} \quad (3 \text{ marks})$$

(C) The standard molar entropy change for the reduction of SnO_2 at 900 K.

At 900 K, $K_{900} = 1.49$, $\Delta G^0 = -3002 \text{ J}$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T = 100.7 \text{ J K}^{-1} \quad (2 \text{ marks})$$

7. (7 marks) For a chair-chair conformational inversion of cyclohexane, the specific

reaction rate is given by, $k = 1.76 \times 10^{13} e^{-46860/RT} \text{ s}^{-1}$ over the temperature range, -117°C to -24°C . Calculate the thermodynamic properties, $\Delta S^{0\ddagger}$, $\Delta H^{0\ddagger}$, $\Delta G^{0\ddagger}$ at -70°C .

Answer

$$k = \frac{k_B T}{h} e^{\Delta S^{0\ddagger}/R} \times e^{-E_a/RT} \times e^{\Delta n}$$

$$\frac{k_B T}{h} e^{\Delta S^{0\ddagger}/R} \times e^{\Delta n} = 1.76 \times 10^{13} \text{ s}^{-1} \text{ at } 203 \text{ K}$$

$$\frac{k_B T}{h} e^1 = e \times \frac{1.38 \times 10^{-23} \text{ JK}^{-1}}{6.626 \times 10^{-34} \text{ Js}} \times 203 \text{ K} = 1.33 \times 10^{13} \text{ s}^{-1}$$

$$e^{\Delta S^{0\ddagger}/R} = 1.323 \quad \text{and} \quad \Delta S^{0\ddagger} = 0.280 \times 8.314 = 2.33 \text{ JK}^{-1} \text{ mol}^{-1} \quad (3 \text{ marks})$$

$$\text{and } E_a = 46.86 \text{ kJ mol}^{-1}$$

$$\Delta H^{0\ddagger} = E_a - RT = 44.492 \text{ kJ mol}^{-1} \quad (2 \text{ marks})$$

$$\Delta G^{0\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = 44492 - (203 \times 2.33) = 44.02 \text{ kJ mol}^{-1} \quad (2 \text{ marks})$$