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:

<table>
<thead>
<tr>
<th>experiment #</th>
<th>[NO] (M)</th>
<th>[Cl2] (M)</th>
<th>initial rate (M s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.0010</td>
<td>0.0020</td>
<td>3.55 \times 10^{-3}</td>
</tr>
<tr>
<td>(2)</td>
<td>0.0010</td>
<td>0.0040</td>
<td>1.42 \times 10^{-2}</td>
</tr>
<tr>
<td>(3)</td>
<td>0.0020</td>
<td>0.0040</td>
<td>2.84 \times 10^{-2}</td>
</tr>
</tbody>
</table>

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:

\[
\begin{align*}
\text{(step1)} & \quad A + B \xrightarrow{k_1} C \\
\text{(step2)} & \quad C \xrightarrow{k_2} D \\
\text{(step3)} & \quad D + E \xrightarrow{k_3} F \\
\text{(step4)} & \quad F \xrightarrow{k_4} G
\end{align*}
\]

(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 \(k_2 << k_3\),

(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: \( \ln C \)

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

Ans. (d)

IV. **(2 marks)** An opposing reaction of the type \( R \xrightleftharpoons{\text{f}}{\text{k}} P \) 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.

![Diagram](image)

V.

For the above reaction,

(i) \( k_2 = 3k_1 \)
(ii) $k_3 \gg k_2$

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

(A) \textbf{(1 mark)} Can steady state approximation be used for the concentration of C? \textbf{yes}

(B) \textbf{(2 marks)} What was the concentration of D after infinite time? \textbf{0.75 M}

VI. \textbf{(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 $\Delta H$ of the chemical reaction? Choose the correct option from below.

a) 16.7 kJ \hspace{1cm} b) −16.7 kJ \hspace{1cm} c) −150 kJ \hspace{1cm} d) 150 kJ

\textbf{Ans. (c)}

VII. \textbf{(2 marks)} Consider the reaction, \(2 \text{NO}_2(g) = \text{N}_2\text{O}_4(g)\) 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) Nonsentative at 50 °C, but can be made spontaneous at sufficiently high T.

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

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

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

e) Spontaneous under all temperature conditions.

Choose the correct option from above.

\textbf{Ans: (c)}

VIII. \textbf{(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 delta S is negative for crystallisation, $\Delta G$ is always negative since $\Delta H$ is highly negative.

\textbf{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:

(step1) \( N_2O_5 \xrightarrow{k_1} NO_2 + NO_3 \)

(step2) \( NO_2 + NO_3 \xrightarrow{k_2} N_2O_5 \)

(step3) \( NO_2 + NO_3 \xrightarrow{k_3} NO_2 + O_2 + NO \)

(step4) \( NO + N_2O_5 \xrightarrow{k_4} 3NO_2 \)

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

(B) If \( k_3 >> k_2 \), which of the above step(s) contribute(s) to the rate law?
answer:

(A)  
\[ \frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_2[NO_2][NO_3] - k_4[NO][N_2O_5] \]  
\[ \frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO_2][NO_3] = 0 \]  
\[ \frac{d[NO]}{dt} = k_1[NO_2][NO_3] - k_4[NO][N_2O_5] = 0 \]  
\[ \therefore \frac{d[N_2O_5]}{dt} = \frac{-2k_1k_3[N_2O_5]}{k_2 + k_3} \]  

(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,

\[ E + S \xrightarrow{k_1} ES \xrightarrow{k_2} P \]

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 \( \Delta A \), \( \Delta U \) and \( \Delta G \) 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 J mol\(^{-1}\).

Answer

\[ \Delta A = \Delta U - T \Delta S \]
\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta A = q_p + w_p - q_p = w_p \]
\[ \Delta G = q_p - q_p = 0 \quad \text{(1mark)} \]
\[ w_p \text{ (rev)} = -P \Delta V = -P(V_g - V_i) \approx V_g = \frac{RT}{P} \]
\[ w_p \text{ (rev)} = -RT = -8.314 \times 372.8 = -3099 \text{ J} \quad \text{(2marks)} \]
\[ \Delta A = -3099 \text{ J} \quad \text{(2marks)} \]
\[ \Delta U = q + w = 40893 - 3099 = 37794 \text{ J} \quad \text{(2marks)} \]

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5. (7 marks) The gas phase reaction, \( 2A \rightarrow \) 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 Å.

(a) Calculate from collision theory the specific rate constant for the decomposition reaction at 556 K.
Answer
(a)
\[ Z_{AA} = 2 \left( \frac{\pi RT}{M} \right)^{1/2} d_{AA}^2 N_A \]
\[ = 2 \left( \frac{3.14 \times 8.314 \times 556}{0.128} \right)^{1/2} \times (3.5 \times 10^{-10})^2 \times (6.022 \times 10^{23}) \]
\[ = 4.97 \times 10^7 \text{m}^3\text{mol}^{-1}\text{s}^{-1} = 4.97 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \]
\[ q = \exp \left( \frac{185000}{8.314 \times 556} \right) = 4.25 \times 10^{-18} \]

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

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)
\[ k_{\text{experimental}} = 7.25 \times 10^{-8} \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \]
\[ p = \frac{7.25}{21.1} = 0.345 \]

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, \( \text{SnO}_2 (s) + 2\text{H}_2 (g) \rightleftharpoons \text{Sn} (s) + 2\text{H}_2\text{O} (g) \)
the equilibrium partial pressure of \(\text{H}_2\) 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 \(\text{SnO}_2\) at 1100 K.
At 1100 K, \(p_{\text{H}_2} = 0.22\) atm, \(p_{\text{H}_2\text{O}} = (1 - .22)\) atm = 0.78 atm
\[ K_{1100} = (0.78 / 0.22)^2 = 12.57 \]
\[ \Delta G^0 = -RT\ln K = -23150 \text{ J} \] (2 marks)
(B) The standard molar enthalpy change for the reduction of \(\text{SnO}_2\), assuming it to be constant in the temperature range.
At 900 K, using a similar procedure, \( K_{900} = 1.49 \), \( \Delta G^0 = -3002 \text{ J} \)

\[
\ln(K_{1100} / K_{900}) = (\Delta H^0/R)((1100-900)/(1100\times900))
\]

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

(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, \( k = 1.76\times10^{13} e^{-46860/RT} \text{ s}^{-1} \) over the temperature range, \(-117 ^\circ\text{C} \text{ to } -24 ^\circ\text{C}\). Calculate the thermodynamic properties, \( \Delta S^0^\ddag \), \( \Delta H^0^\ddag \), \( \Delta G^0^\ddag \) at \(-70 ^\circ\text{C}\).

Answer

\[
\begin{align*}
\frac{k_B T}{h} e^{\Delta S^0^\ddag / R} &\times e^{-E_a / RT} \times e^{\Delta S^0} \text{ at } 203 \text{ K} \\
\frac{k_B T}{h} e^{\Delta S^0^\ddag / R} &\times e^{\Delta S^0} = 1.76\times10^{13} \text{ s}^{-1} \text{ at } 203 \text{ K} \\
\frac{k_B T}{h} &e^{1} = e \times \frac{1.38\times10^{-23} \text{ JK}^{-1}}{6.626\times10^{-34} \text{ Js}} \times 203\text{K} = 1.33\times10^{13} \text{ s}^{-1} \\
e^{\Delta S^0^\ddag / R} & = 1.323 \text{ and } \Delta S^0^\ddag = 0.280 \times 8.314 = 2.33 \text{ JK}^{-1}\text{mol}^{-1} \quad (3 \text{ marks})
\end{align*}
\]

and \( E_a = 46.86 \text{ kJmol}^{-1} \)

\[\Delta H^0^\ddag = E_a - RT = 44.492\text{kJmol}^{-1} \quad (2 \text{ marks})\]

\[\Delta G^0^\ddag = \Delta H^\ddag - T\Delta S^\ddag = 44492 - (203\times2.33) = 44.02\text{kJmol}^{-1} \quad (2 \text{ marks})\]