

(परीक्षार्थी द्वारा भरा जाए)

(To be filled by the Candidate)

First Periodical Test, July-December, 2021

परीक्षा का नाम (Name of Examination)..... First Periodical Test, July-December, 2021.....

अनुक्रमांक अंकों में (In figures)2141991

अनुक्रमांक(शब्दों में)(Roll No. in Words) Twenty one lakh forty one thousand nine hundred and ~~ninty~~ one

नामांकन संख्या (Enrollment No.).....

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विषय(Subject)..... CHEMISTRY.

प्रश्न पत्र कोड सहित (Paper with Code).....CHEM408- PHYSICAL CHEMISTRY

परीक्षा दिवस और दिनांक (Day and Date of Examination). 10th SEPTEMBER 2021

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Question	1	2	3	4	5	6
Write NA for questions not attempted			NA	NA		

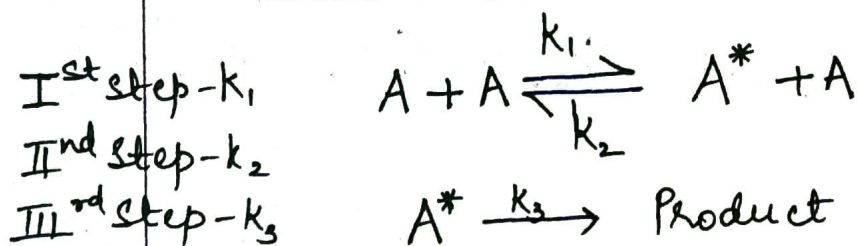
AAKRITI MEHROTRA

Signature of the Student

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Q.1a) "Unimolecular reactions are not always of first order — Justify the statement using Lindemann mechanism."

The above statement can be justified on the basis Lindemann Mechanism



Reactant molecule are activated by collision and form the activated complex (A^*)

Product formation is slow as compared to deactivation process (2)
 $[k_2 \gg k_3]$

At high pressure, k_2 is the rate constant of the backward reaction k_2 will depend on the concentration of A^* and $A \rightarrow [A^*]$ and $[A]$ so 1st Order of Reaction

At low pressure, k_3 is the rate constant of the forward reaction,

k_3 will depend only on $[A^*]$ and so k_1 is the forward reaction and will depend on $[A]$ and $[A]$ and so 2nd Order Reaction

When an intermediate species is formed
steady state treatment will be applied.

The concentration of activated complex
remains constant

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*]$$

$$0 = k_1[A]^2 - k_2[A^*][A] - k_3[A^*]$$

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$k_1[A]^2 = (k_2[A] + k_3)[A^*]$$

$$\frac{k_1[A]^2}{k_2[A] + k_3} = [A^*] \quad \text{--- (1)}$$

$$r = -\frac{d[A]}{dt} = k_3[A^*] \quad \text{--- (2)}$$

Substituting the value of
[A*] (1) in eq. (2).

$$r = \frac{-d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_2[A] + k_3} \quad \text{--- (3)}$$

At high pressure

$$k_2[A] \gg k_3$$

$$\frac{-d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_2[A]}$$

$$-\frac{d[A]}{dt} = \frac{k_3 k_1}{k_2} [A]$$

Rate of Reaction is dependent on the concentration $[A]$.

So, 1st Order of Reaction.

At low pressure $k_3 \gg k_2[A]$

$$-\frac{d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_3} = k_1 [A]^2$$

So, 2nd Order Reaction as rate of reaction - 2nd power of concentration $[A] \rightarrow [A]^2$

Thus, the statement that Unimolecular reactions are not always of first order is justified from this mechanism.



1 b)

In the Arrhenius equation,

$$k = A e^{-E_a/RT}$$

① — $e^{-E_a/RT} \rightarrow$ Represents the fraction of molecules (having effective collision)

$$E_a = 20000 \text{ cal/mol} \\ = 83680 \text{ J/mol}$$

$$T_1 = 27^\circ\text{C} = (27 + 273)\text{K} = 300\text{K}$$

$$T_2 = 227^\circ\text{C} = (227 + 273)\text{K} = 500\text{K}$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

Assuming ① $\rightarrow x = e^{-E_a/RT}$

let x be the fraction of molecules
for $T_1 \rightarrow x_1$ (fraction of molecules at T_1)
for $T_2 \rightarrow x_2$ (fraction of molecules at T_2)

Taking \ln of eq 1.

$$\ln x = -\frac{E_a}{RT}$$

for $T_1 \rightarrow$

$$\ln x_1 = -\frac{E_a}{RT_1}$$

$$\ln x_1 = -\frac{83680}{8.314 \times 300} = -\frac{83680}{2494.2}$$

$$\ln x_1 = -33.54983562$$

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$$\log x_1 = \frac{-33.54983562}{2.303}$$

$$x_1 = \text{antilog} -14.5678347$$

$$x_1 = 2.704 \times 10^{-15} \text{ Ans.}$$

$x_1 \rightarrow$ fraction of the molecules having sufficient energy to decompose at T_1 (27°C or 300K).

for $T_2 \rightarrow$

$$\ln x_2 = \frac{-E_a}{RT_2}$$

$$\ln x_2 = \frac{-83680}{8.314 \times 500} = \frac{-83680}{4157}$$

$$\ln x_2 = -20.12990137$$

$$\log x_2 = \frac{-20.12990137}{2.303}$$

$$x_2 = \text{antilog} -8.740730079$$

$$x_2 = 1.81 \times 10^{-9} \text{ Ans.}$$

$x_2 \rightarrow$ fraction of the molecules having sufficient energy to decompose at T_2 (227°C or 500K)

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Q2a) Arrhenius factor "A" always have the same unit as the rate constant. Comment.

The Arrhenius factor "A" always have the same unit as the rate constant because in Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

$e^{-E_a/RT}$ is a mathematical constant and dimensionless.

So unit of A = Unit of k

b) The rate of reaction is given by

$$\log k = A - \frac{B}{T} + C \log T$$

Find the value of activation energy

$$\log k = A - \frac{B}{T} + C \log T$$

$$\ln k = A \times 2.303 - \frac{B \times 2.303}{T} + C \ln T$$

$$\frac{d}{dT} \ln k = \frac{d}{dT} \left[A \times 2.303 - \frac{(B \times 2.303)}{T} + C \ln T \right]$$

$$\left(\because \frac{d}{dT} \frac{1}{T} = -\frac{1}{T^2}; \frac{d}{dT} \ln T = \frac{1}{T} \right)$$

$$\frac{d}{dT} \ln k = 0 + \frac{B \times 2.303}{T^2} + \frac{C}{T}$$

$$\frac{d}{dT} \ln k = \frac{[2.303B + CT]}{T^2}$$

$$\therefore \frac{d}{dT} \ln k = \frac{E_a}{RT^2} \quad (\text{Arrhenius Equation})$$

$$\therefore \frac{E_a}{R} = (2.303B + CT)$$

$$\Rightarrow E_a = [R(2.303B + CT)] \rightarrow \text{This is the value of activation energy.}$$

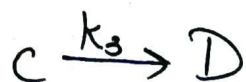
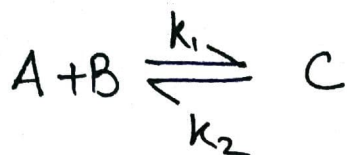
$$\text{Value of } R \text{ in cal mol}^{-1} \text{K}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\text{Value of } R \text{ in J mol}^{-1} \text{K}^{-1} = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$$

Arushi

Q5 a)

For the mechanism



(i)

According to the steady state treatment
The differential rate equations that apply to
this set of reactions are -

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_1[A][B] - k_2[C] \quad \text{--- (1)}$$

$$+\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C] \quad \text{--- (2)}$$

$$\frac{d[D]}{dt} = k_3[C] \quad \text{--- (3)}$$

The steady-state treatment, which is
valid provided that the concentration
of C is always small, involves
 $\frac{d[C]}{dt} = 0$

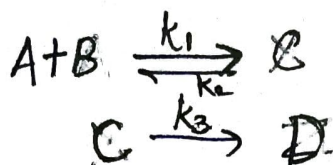
After the short induction
period the concentration
of C remains practically
constant, so that to a
good approximation.

$$\frac{d[C]}{dt} = 0$$

This is the basis of steady state
treatment.

The steady state treatment can be explained.

Suppose.



$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

$$-\frac{d[A]}{dt} = k_1[A] \quad \text{--- (a)}$$

Integration of above equation
Subject to the boundary condition that
[A] = [A]₀ when t = 0, gives.

$$[A] = [A]_0 e^{-k_1 t} \quad \text{--- (b)}$$

The net rate of the formation of
X is

$$\frac{d[C]}{dt} = k_1[A] - k_3[C] \quad \text{--- (c)}$$

Putting the value of [A] from eq (b) to (c)

$$\frac{d[C]}{dt} = k_1[A]_0 e^{-k_1 t} - k_3[C]$$

This contains only the variables
[C] and t, and integration
gives.

$$[C] = [A]_0 \frac{k_1}{k_3 - k_1} (e^{-k_1 t} - e^{-k_3 t})$$



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when k_1 is small and k_3 is large
the concentration of C is given by

$$[C] = [A]_0 \frac{k_1}{k_3} (e^{-k_1 t} - e^{-k_3 t})$$

At $t=0$

$$[C] = 0$$

but after a relative duration of
the reaction difference

$$e^{-k_1 t} - e^{-k_3 t}$$

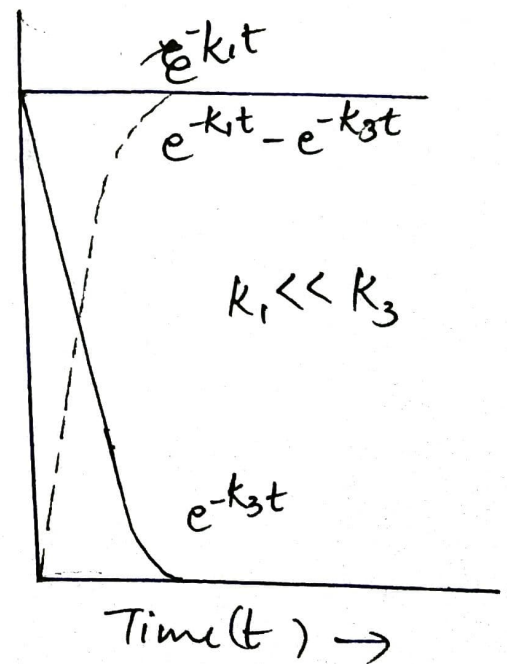
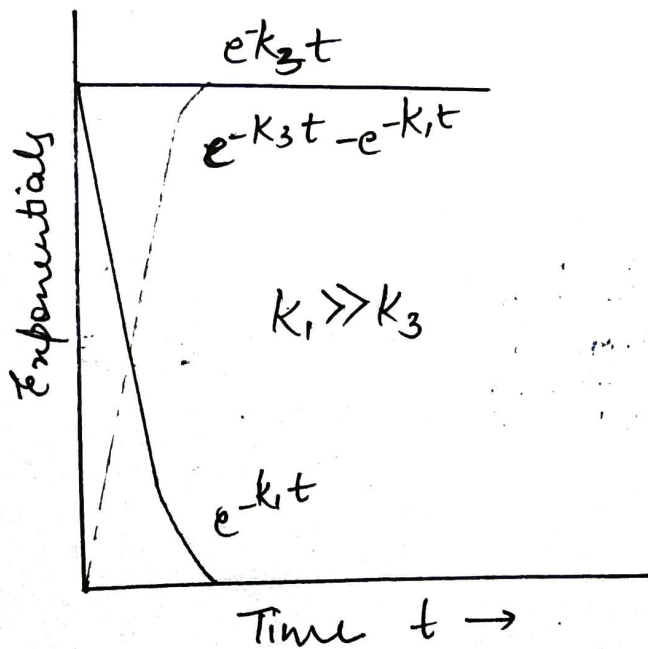
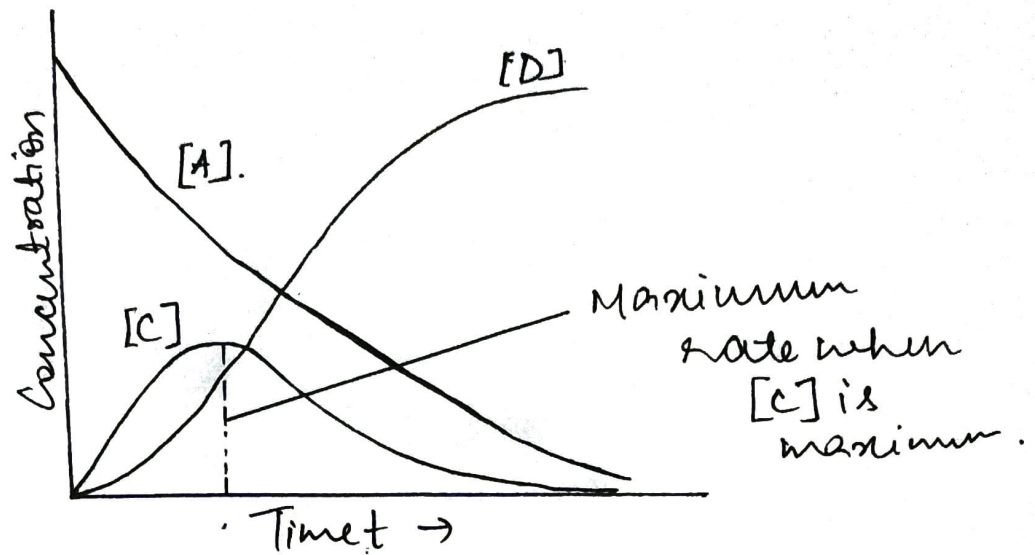
has attained the value of unity
and the concentration of C is
then $[A]_0 k_1/k_3$
which is much less than
 $[A]_0$.

The concentration of C remains
practically constant so,

$$\frac{d[C]}{dt} = 0$$

This is the basis of the
steady state treatment.

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so, from eq(3)]

$$k_1[A][B] - k_2[C] - k_3[C] = 0 \quad \text{--- (4)}$$

The concentration of [C] therefore is given by,

$$[C] = \frac{k_1[A][B]}{k_2 + k_3} \quad \text{--- (5)}$$

Substituting the value of [C] into eq(3), we get

$$r = \frac{d[D]}{dt} = \frac{k_1 k_3 [A][B]}{k_2 + k_3} = r \quad \text{--- (6)}$$

Thus, the rate law assuming the steady state approximation to eliminate the concentration of C is derived.

(ii) Assuming that $k_3 \ll k_2$

from eq(6), we get

$$r = \frac{k_1 k_3 [A][B]}{k_2}$$

Arrhenius Equation $\rightarrow k = A e^{-E_a/RT}$

$$k_1 = A_1 e^{-E_1/RT}$$

$$k_2 = A_2 e^{-E_2/RT}$$

$$k_3 = A_3 e^{-E_3/RT}$$



$$k_{\text{net}} = \frac{k_1 k_3}{k_2} \quad \text{so, } r = k_{\text{net}} [A][B]$$

$$k_{\text{net}} = \frac{A_1 e^{-E_1/RT} A_3 e^{-E_3/RT}}{A_2 e^{-E_2/RT}}$$

$$= \frac{A_1 A_3}{A_2} e^{-\frac{(E_1 + E_3 - E_2)}{RT}}$$

Thus, it can be deduced from the above equation that

$$A = \frac{A_1 A_3}{A_2}$$

$A \rightarrow$ pre-exponential factor

$E \rightarrow$ overall activation energy

$$E = (E_1 + E_3 - E_2)$$

5(b) The value of ΔS^\ddagger for a reaction has been obtained as $-80.5 \text{ JK}^{-1} \text{ mol}^{-1}$ at 400 K . Find the value of A for the reaction.

from Transition State Theory

$$k = \frac{k_b T}{h} e^{\Delta S^\ddagger / R} e^{-E_a / RT}$$

Arrhenius Equation,

$$k = A e^{-E_a / RT}$$

$$A = \frac{k_b T}{h} e^{\Delta S^\ddagger / R}$$

$$k_b \text{ (Boltzmann constant)} = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h \text{ (Planck's constant)} = 6.63 \times 10^{-34} \text{ Js}$$

$$\Delta S^\ddagger = -80.5 \text{ JK}^{-1} \text{ mol}^{-1} \text{ (given)}$$

$$T = 400 \text{ K (given)}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$A = \frac{k_b T}{h} e^{\Delta S^\ddagger / R} = \frac{1.38 \times 10^{-23} \text{ JK}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{6.63 \times 10^{-34} \text{ Js}} e^{-80.5 / 8.314}$$

$$A = 5.189 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$$

Ans.