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CHEMISTRY

TARGET : JEE Advanced - 2021

CAPS – 17

Chemical Kinetics

SCQ (Single Correct Type) :

1. For the system $A \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} B$, $A \underset{K_{-2}}{\overset{k_2}{\rightleftharpoons}} C$ which was started with only A, the equilibrium concentration $[A]_{eq}$ is correctly related to $[B]_{eq}$ and $[C]_{eq}$ as

(A) $\dfrac{k_{-1}[B]_{eq}+k_{-2}[C]_{eq}}{(k_1+k_2)}$

(B) $\dfrac{k_{-1}[B]_{eq}-k_{-2}[C]_{eq}}{(k_1-k_2)}$

(C) $\dfrac{k_{-1}[B]_{eq}+k_{-2}[C]_{eq}}{(k_1-k_2)}$

(D) $\dfrac{k_{-1}[B]_{eq}-k_{-2}[C]_{eq}}{(k_1-k_2)}$

Ans. (A)

2. For a hypothetical reaction,

$A + 3B \rightarrow P$ $\Delta H = -2x$ kJ/mole of A

& $M \rightarrow 2Q + R$ $\Delta H = +x$ kJ/mole of M

These reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is y M sec^{-1}, then the rate of formation (in M sec^{-1}) of Q is:

(A) $\frac{2}{3}y$ (B) $\frac{3}{2}y$ (C) $\frac{4}{3}y$ (D) $\frac{3}{4}y$

Ans. (C)

3. A(aq.) → B(aq.) + C(aq.) is a first order reaction.

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measured with the help of titration of reagent 'R'. If all A, B and C react with reagent and have 'n' factors [n factor; eq. mass = $\dfrac{\text{mol. mass}}{n}$] in the ratio of 1 : 2 : 3 with the reagent, the k in terms of t, n_1 and n_2 is:

(A) $k=\frac{1}{t}\ln\left(\frac{n_2}{n_2-n_1}\right)$ (B) $k=\frac{1}{t}\ln\left(\frac{2n_2}{n_2-n_1}\right)$ (C) $k=\frac{1}{t}\ln\left(\frac{4n_2}{n_2-n_1}\right)$ (D) $k=\frac{1}{t}\ln\left(\frac{4n_2}{5(n_2-n_1)}\right)$

Ans. (D)

4. 65.6 mg of Na_3PO_4 contains 20% P^{32} and 80% P^{31} atoms. Assuming only radio activity of P^{32}, if the half-life period for P^{32} = 14.3 days, the rate of decay of P^{32} is nearly (Take Mol. wt. of Na_3PO_4 = 164)

(A) 2.7×10^{15}dps (B) 8.4×10^{15} dps (C) 6.7×10^{15} dps (D) 27×10^{12} dps

Ans. (D)

MCQ (One or more than one correct) :

5. Select the correct statements(s):

(A) When T → ∞ or Ea → 0 then k = A.

(B) A positive catalyst can change ΔH of the reaction.

(C) A mixture of reactants may be thermodynamically unstable but kinetically stable.

(D) A negative catalyst increases the activation energy of the reaction.

Ans. **(ACD)**

6. A reaction takes place in three steps. The rate constant of the three steps are K_1, K_2 and K_3 respectively. The overall rate constant K = $\frac{K_1K_3}{K_2}$.

The energy of activation for the three steps are 40, 30 and 20 KJ respectively. Therefore :

(A) Overall energy of activation is 10 KJ

(B) Overall energy of activation is 30 KJ

(C) The reaction mechanism is $2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A; A^* \xrightarrow[\text{rds}]{K_3}$ product and overall order is one.

(D) The reaction mechanism is $A \xrightarrow{K_1} B; B \xrightarrow{K_2} C; C \xrightarrow{K_3}$ product and overall order is one

Ans. **(BC)**

Sol. $K = \frac{K_1K_3}{K_2}$

$$Ae\frac{-(E_a)_{overall}}{RT} = \frac{A_1e^{-\frac{E_1}{RT}} \times A_3e^{-\frac{E_3}{RT}}}{A_2e^{-\frac{E_2}{RT}}}$$

$$Ae\frac{-(E_a)_{overall}}{RT} = \left(\frac{A_1A_3}{A_2}\right)e^{-\frac{[E_1+E_3-E_2]}{RT}}$$

$(E_a)_{overall} = E_1 + E_3 - E_2 = 30$ KJ/mole

$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A$ [Fast]

$$\frac{K_1}{K_2} = \frac{[A^*][A]}{[A]^2} \text{or} [A^*] = \frac{K_1}{K_2}[A]$$

rate = $K_3[A^*] = \frac{K_1K_3}{K_2}$ [A]

7. The rate expression for the reaction :

$NH_4CNO \rightleftharpoons NH_2CONH_2$ can be derived from the mechanism :

i. $NH_4CNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4NCO$ (Fast)

ii. $NH_4NCO \xrightarrow{k_3} NH_3 + HNCO$ (Fast)

iii. $NH_3 + HNCO \xrightarrow{k_4} NH_2CONH_2$ (Slow)

Which of the following statement(s) is/are correct about the rate expression ?

(A) $\frac{d_{(urea)}}{dt} = \frac{k_1k_3}{k_2}[NH_4CNO]$

(B) $\frac{d_{(urea)}}{dt} = \frac{k_1k_3}{k_2k_4}[NH_4CNO]$

(C) $\frac{d_{(urea)}}{dt} = k[NH_4CNO]$

(D) $\frac{d_{(urea)}}{dt} = \frac{k_1 \times k_2}{k_3 \times k_4}[NH_4NCO]$

Ans. **(AC)**

Sol. $\frac{d}{dt}[NH_2CONH_2] = k_4[NH_3][HNCO]$ from (iii)

Applying steady state approximation to HNCO or NH_3

$$\frac{d[HNCO]}{dt} = O = k_3\,[NH_4NCO] - k_4[NH_3][HNCO]$$

$$\therefore \quad \frac{k_3}{k_4} = \frac{[NH_3][HNCO]}{[NH_4NCO]}$$

$$\frac{d[urea]}{dt} = k_4 \times [NH_3][HNCO] = k_4 \times \frac{k_3}{k_4}\,[NH_4NCO]$$

Also, $[NH_4NCO] = \frac{k_1}{k_2} \times [NH_4CNO]$

$$\therefore \quad \frac{d[urea]}{dt} = k_3 \times \frac{k_1}{k_2} \times [NH_4CNO] = k[NH_4CNO]$$

Comprehension Type Question:

Comprehension

Study the two photochemical reactions and answer the question at the end.

For the overall reaction between A and B to yield C and D, two mechanisms are proposed :

I. $A + B \longrightarrow AB^* \longrightarrow C + D$, $k_1' = 1 \times 10^{-5}\ M^{-1}\ s^{-1}$

II. $A \longrightarrow A^* \longrightarrow E$, $k_1 = 1 \times 10^{-4}\ s^{-1}$

$E + B \longrightarrow C + D$, $k_2 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$

(species with * are short-lived)

8. Rate according to mechanism I when concentration of each reactant is 0.1 M will be :

(A) $1 \times 10^{-7}\ Ms^{-1}$ (B) $1 \times 10^{-6}\ Ms^{-1}$ (C) $1 \times 10^{-5}\ Ms^{-1}$ (D) $1 \times 10^{-4}\ Ms^{-1}$

Ans. **(A)**

Sol. (I). Rate law for mechanism I

Rate = $k_1^1\,[A]\,[B]$

Rate = $1 \times 10^{-5}\,[.1]\,[.1] = 1 \times 10^{-7}$ m/sec .

9. Rate according to mechanism II when concentration of each reactant is 1 M will be:

(A) $1 \times 10^{-4}\ Ms^{-1}$ (B) $1 \times 10^{10}\ Ms^{-1}$ (C) $1 \times 10^{-6}\ Ms^{-1}$ (D) $1 \times 10^{-10}\ Ms^{-1}$

Ans. **(A)**

Sol. (II). Rate = $1 \times 10^{-4} \times [1] = 1 \times 10^{-4}$

10. At what concentration of B, rates of two mechanism are equal :

(A) 1 M (B) 5 M (C) 7 M (D) 10 M

Ans. **(D)**

Sol. (III). Rate I = Rate II

$k_1^1\,[A]\,[B] = k_1\,[A]$

$B = \frac{k_1}{k_1^1} = 10$ M

Numerical based Questions :

11. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M KMnO4 solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

Ans. **($k=0.022\ hr^{-1}$)**

Sol. $2H_2O_2 \rightarrow 2H_2O + O_2$

Meq. of H_2O_2 in 10 ml diluted solu. = Meq. of $KMnO_4$ titrated = 25 × 0.025 × 5 = 3.125

Meq. in 100 ml solu. = 31.25

but 22400 ml O_2 = 68 gm H_2O_2

$$1\text{ml} = \frac{68}{22400}$$

$$20\text{ ml} = \frac{68 \times 20}{22400}\text{in 1 ml } H_2O_2$$

$$= \frac{68 \times 20 \times 10}{22400}\text{in10 ml } H_2O_2$$

No. of Meq. in 10 ml of 20% kg ml H_2O_2

$$\text{Initially } = \frac{68 \times 20 \times 10 \times 1000}{17 \times 22400} = 35.71$$

$$k = \frac{2.303}{6}\log\left(\frac{35.71}{31.25}\right) = 0.022\text{ hr}^{-1}$$

12. Potassium having atomic mass = 39.1 u contains 93.10 atom % ^{39}K, having atomic mass 38.96371 u; 0.0118 atom % ^{40}K, which has mass of 40.0 u and is radioactive with t1/2 = 1.3 × 10^9 yr, and 6.88 atom % ^{41}K having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.

Ans. **(30.7242 dis $g^{-1}s^{-1}$)**

Sol. Let's take 1 gm sample of potassium.

$$\text{Thus, moles} = \frac{1}{39.1}$$

$$\text{Total, no. of K atoms} = \frac{6.023 \times 10^{23}}{39.1}$$

Since, K^{40} is 0.0118 %,

$$\text{No. of } K^{40} \text{ atoms} = \frac{0.0118}{100} \times \frac{6.023 \times 10^{23}}{39.1} = 1.818 \times 10^{18}$$

$$\text{Now, decay constant} = (\lambda) = \frac{0.693}{t_{1/2}}$$

$$\lambda = \frac{0.693}{1.3 \times 10^9 \times 365 \times 24 \times 60 \times 60}$$

$$\lambda = 1.69 \times 10^{-17}\text{s}^{-1}$$

Since specific activity is activity of 1 gm. sample, therefore,

S.A = $\lambda N = 1.69 \times 10^{-17} \times 1.818 \times 10^{18}$

$= 30.7242$ dis $g^{-1} s^{-1}$

13. A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At t = 0, the volume of the reagent consumed is 25 mL and at t = 10 min, the volume used up is 32 mL. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Ans. **(0.0207 $\mathbf{min^{-1}}$)**

Sol. $B^{n+} \rightarrow B^{(n+4)+}$

t = 0 a

t=10 min. a – x

v.f. of B^{n+} = 2

v.f. of $B^{(n+4)+}$ = 5

Let normality of reducing agent = N

so 2a = 25 N

2(a –x) + 5x = 32 N

2a + 3x = 32 N; $x = \frac{7}{3}N$

$$k \times 10 = \ln\frac{a}{a-x} = \ln\frac{12.5N}{12.5N - \frac{7}{3}N} = 0.0207 \text{ min}^{-1}$$

14. For a reversible first-order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mole L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s?

Ans. **(0.0025 M)**

Sol. $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\ s^{-1}$

$$\frac{[B]_{eq}}{[A]_{eq}} = 4 \Rightarrow k_{eq} = 4$$

$$\Rightarrow \frac{k_1}{k_2} = 4$$

$\Rightarrow$ $k_2 = 0.25 \times 10^{-2}$

$[A]_0 = 0.01$, $[B]_0 = 0$

$[B]_t = 30 = ?$

From mass conservation A + B = 0.01

A = 0.01 – B

$$\frac{dB}{dt} = k_1A - k_2B$$

$$\frac{dB}{dt} = k_1(0.01 - B) - k_2B$$

$$\frac{dB}{dt} = 0.01k_1 - B(k_1 + k_2)$$

$$\int_0^B \frac{dB}{0.01k_1 - B(k_1 + k_2)} = \int_0^t dt$$

$$\frac{-1}{(k_1 + k_2)} \ln\left(\frac{0.01k_1 - B(k_1 + k_2)}{0.01k_1}\right) = t$$

Sub $k_1 = 10^{-2}$, $k_2 = 0.25 \times 10^{-2}$

t = 30

B = 0.0025

15. A small quantity of solution containing ^{24}Na radionuclide (half-life 15 hours) of activity 1.0 microcurie is injected into the blood of a person. A sample of the blood of volume 1 cm^3 taken after 5 hours shows an activity of 296 disintegrations per minute. Determine the total volume of blood in the body of the person. Assume that the radioactive solution mixes uniformly in the blood of the person. (1 Curie = 3.7 × 10^{10} disintegrations per second)

Ans. **(6 litre)**

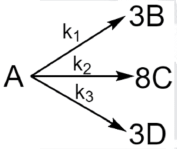
Sol. If N_0' is the initial no of radioactive nuclei in 1 cm^3 of sample, then

$$\frac{N'}{N_0'} = \left(\frac{1}{2}\right)^{\frac{t}{T}} \Rightarrow N_0' = 2^{t/T}N' = 2^{5/15} \times 3.844 \times 10^5$$

$$N_0' = 4.843 \times 10^5$$

Volume of blood = $\frac{N_0}{N_0'} = \frac{2.883 \times 10^9}{4.843 \times 10^5} = 0.595 \times 10^4 cm^3 \simeq 5.95L \simeq 6L$

16.



At time t = 0, initial mole of A is 1.

Overall half-life of the reaction is 15 days. Then calculate the number of mole of C after 45 days if the ratio of $k_1 : k_2 : k_3$ is 4 : 2 : 1

Ans. **(2.00)**

Sol. $[At] = [A]_0e^{-kt}$

$$\frac{1}{8}\frac{d[C]}{dt} = k_2[A_t]$$

$d[C] = 8k_2[A_0]e^{-kt}$

$$[C]_t - 0 = 8k_2[A_0]\left(\frac{-1}{k_T}\right)(e^{-kt}-1)$$

$$[C]_t = 8 \times \frac{2}{7} \times 1(1 - e^{-3in2})$$

$$= 8 \times \frac{2}{7}\left(1 - \frac{1}{8}\right)$$

$$= \frac{2}{7} \times \frac{7}{8} \times 8$$

= 2

17. $3A + B \longrightarrow C + D$

Mechanism of given reaction is :

Step 1 $A + B \xrightarrow{k_1} E$

Step 2 $E + 2A \xrightarrow{k_2} C + D$

What is the total order of reaction considering steady state approximation.

Ans. **(2)**

Sol. From steady state approximation

$$\frac{dE}{dt} = K_1[A][B] - K_2[E][A]^2 = 0$$

$$[E] = \frac{K_1[A][B]}{K_2[A]^2} = \frac{k_1}{k_2}\frac{[B]}{[A]}$$

So $-\frac{dB}{dt} = k_1[A][B]$

or $-\frac{dA}{dt} = k_1[A][B] + 2k_2[E][A]^2 = k_1[A][B] + 2k_2 \times \frac{k_1}{k_2}\frac{[B]}{[A]}[A]^2 = 3k_1[A][B]$

$$-\frac{1}{3}\frac{dA}{dt} = k_1[A][B]$$

18. A reaction take place at 300K. When catalyst is added rate of reaction increases. Calculate the change in temp (in ºC) which would have same effect on rate of reaction as that of catalyst. (Assume catalyst change the activation energy by 20%).

Ans. **(75)**

Sol. $\ell n\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ ....(i)

$\ell n\frac{K_C}{K_1} = \frac{E_a - E_{ac}}{RT_1}$ for effect of catalyst new $K_C = K_2$

$\ell n\frac{K_2}{K_1} = \frac{E_a - E_{ac}}{RT_1}$ ....(ii)

from (i) and (ii) $\frac{E_a - E_{ac}}{RT_1} = \frac{E_a}{R}.\left(\frac{1}{T_1}, \frac{1}{T_2}\right)$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{E_a - E_{ac}}{E_a.T_1}$$