PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 54

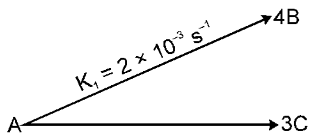
Total Marks : 38

Max. Time : 43 min.

Topic : Chemical Kinetics

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1	(3 marks 3 min.)	[3, 3]
Comprehension ('–1' negative marking) Q.2 to Q.6	(3 marks 3 min.)	[15, 15]
Subjective Questions ('–1' negative marking) Q.7 to Q.9	(4 marks 5 min.)	[12, 15]
Match the Following (no negative marking) Q.10	(8 marks 10 min.)	[8, 10]

1. For the following parallel chain reaction

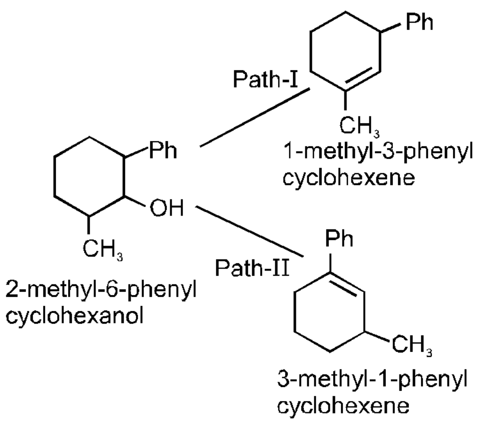


what will be that value of overall half-life of A in minutes? $\left[\text{Given that } \frac{[B]_t}{[C]_t} = \frac{16}{9}\right]$

(A) 3.3 (B) 6.3 (C) 3.6 (D) None

Comprehension # (Q.2 to Q.6)

Dehydration of 2-methyl-6-phenyl cyclohexanol is a first order kinetics. Dehydration of this cyclohexanol gives 3-methyl-1-phenyl cyclohexene and 1-methyl-3-phenyl cyclohexene. Yields of these products are different due to different rate constant of their respective parallel paths. 4 × 10^{-4}M sec^{-1} is the rate constant of first path in which 1-methy-3-phenyl-cyclohexene is formed. After 2303 seconds, 3M and 2M of 3-methyl-1-phenyl cyclohexene and 1-methyl-3-phenyl-cyclohexene are obtained respectively.



2. Which of the following is the value of rate constant of second path –

(A) 4 × 10^{-4} sec^{-1} (B) 6 × 10^{-4} sec^{-1} (C) 3 × 10^{-4} sec^{-1} (D) 2 × 10^{-4} sec^{-1}

3. The half life period of dehydration of 2-methyl-6-phenyl cyclohexanol is :

(A) 463 sec (B) 599 sec (C) 735 sec (D) 693 sec

4. The average life period of the above process is :

(A) 1000 sec (B) 1200 sec (C) 888.8 sec (D) 1271.92 sec

5. The initial concentration of 2-methyl-6-phenyl cyclohexanol taken is :

(A) 4.545 (B) 6.555 (C) 5.555 (D) 7.545

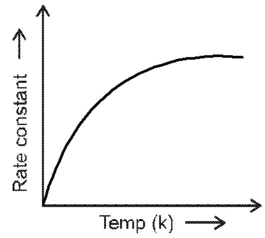
6. The rate of dehydration of alcohol at 2303 seconds is
(A) 5.55×10^{-4} mol/L-sec (B) 4×10^{-4} mol/L-sec
(C) 12×10^{-4} mol/L-sec (D) 6.55×10^{-4} mol/L-sec

7. For the reaction A $\longrightarrow$ products, the following data is given for a particular run.

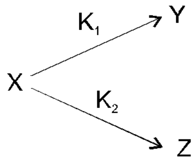
time (min.) :	0	5	15	35
$\frac{1}{[A]}$ (M^{-1}) :	1	2	4	8

Determine the order of the reaction.

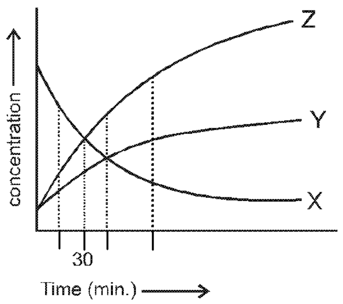
8. If for a first order reaction, rate constant varies with temperature according to the graph given below. At 27ºC, 1.5×10^{-4} percent of the reactant molecules are able to cross over the potential barrier.
At 52ºC, the slope of this graph is equal to 0.2 K^{-1} sec^{-1}, calculate the value of rate constant at 52ºC, assuming that activation energy does not change in this temperature range.



9. For a Parallel first order reaction



Concentration of reactant and product change according to the graph given below.



Calculate the value of k_1 and k_2. Given, $\frac{k_1}{k_2} = \frac{1}{2}$

10. For a general reaction A $\rightarrow$ B let α = Degree of dissociation. Other notations have their usual meaning

Column – I	**Column – II**
(A) α (if order = 1)	(p) $1-e^{-kt}$
(B) α (if order = 2)	(q) $\frac{kt}{C_{A_0}}$
(C) α (if order = 0)	(r) $\frac{C_{A_0}kt}{C_{A_0}kt+1}$
(D) α (if order = 0.5)	(s) $1-\frac{C_{A_t}}{C_{A_0}}$

Answer Key

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1. (A) 2. (B) 3. (D) 4. (A) 5. (C)

6. (A) 7. 2. 8. K = 5.25 sec^{-1}.

9. $k_1 = \frac{1}{90}\ln(2.5)min^{-1}$; $k_2 = \frac{1}{45}\ln(2.5)min^{-1}$. 10. (A – p,s) ; (B – r, s) ; (C – q, s) ; (D – s)

Hints & Solutions

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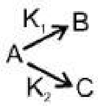
1. We have,

$$\frac{[B]_t}{[C]_t} = \frac{4k_1}{3k_2} = \frac{16}{9} \quad \text{so,} \quad \frac{k_1}{k_2} = \frac{4}{3}$$

Now, $k = k_1 + k_2 = [2 \times 10^{-3} + \frac{3}{4} \times 2 \times 10^{-3}]\ sec^{-1}$

$$= \frac{7}{2} \times 10^{-3}\ sec^{-1} = \frac{7 \times 10^{-3} \times 60}{2}\ min^{-1} \qquad \text{so, } T_{1/2} = \frac{\ell n\ 2}{7 \times 30 \times 10^{-3}}\ min = \frac{693}{7 \times 30} = 3.3\ min.$$

2. 

$$\frac{[B]}{[C]} = \frac{K_1}{K_2} = \frac{2}{3}$$

$K_1 = 4 \times 10^{-4}$

$K_2 = \frac{3}{2} \times 4 \times 10^{-4} = 6 \times 10^{-4}\ sec^{-1}$.

3. $t_{1/2} = \frac{0.693}{K_1 + K_2} = \frac{0.693}{10^{-3}} = 693$ sec.

4. $t = \frac{1}{K_1 + K_2} = 10^3$

5. $t = \frac{2.303}{K}\log\left(\frac{C_0}{C_0 - X}\right) \Rightarrow 2303 = \left(\frac{2.303}{10^{-3}}\right)\log\left(\frac{C_0}{C_0 - 5}\right)$

$\log\frac{C_0}{C_0 - 5} = 1 \Rightarrow \frac{C_0}{C_0 - 5} = 10 \Rightarrow 9C_0 = 50,\ C_0 = 50/9$.

6. Rate $= K\,[C]$
$= 10^{-3} \times [C_0 - x]$
$= 10^{-3} \times [50/9 - 5]$
$= 10^{-3} \times \frac{5}{9} = 5.55 \times 10^{-4}$

7. $K = \left(\frac{1}{C_t} - \frac{1}{C_0}\right) \times \frac{1}{t} = \frac{2-1}{5} = \frac{4-1}{15} = \frac{8-1}{35} = \frac{1}{5}$ = constant

8. % of reaction molecules which are $= e^{-Ea/RT} \times 100$
able to cross potential barriee

$\Rightarrow e^{-Ea/RT} \times 100 = 1.5 \times 10^{-4}$

$\Rightarrow e^{-Ea/RT} \times 100 = 1.5 \times 10^{-6}$

$\Rightarrow e^{-Ea/2\times 300} = 1.5 \times 10^{-6} \Rightarrow E_a\text{ (cal)} = 8014.5 \text{ cal.}$

$K = Ae^{-Eq/RT}$

$$\frac{dK}{dT} = Ae^{-Eq/RT}\left(\frac{-Ea}{R} \times \frac{-1}{T^2}\right)$$

$$\frac{dK}{dT} = K\frac{Ea}{RT^2} \Rightarrow 0.2 = K\frac{Ea}{2 \times (325)^2}$$

$$\Rightarrow K = \frac{0.2 \times 2 \times (325)^2}{Ea\,(cal)} = 5.25\ S^{-1}$$

9. $X \xrightarrow{K_1} Y$, $X \xrightarrow{K_2} Z$ & $\frac{k_1}{k_2} = \frac{1}{2}$

$[X]_t = a e^{-(k_1+k_2)t}$

$$[Y]_t = \frac{k_1 a}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \ \& \ [Z]_t = \frac{k_2 a}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

At $t = 30$ min.,

$[X]_t = [Z]_t$

$$a e^{-(k_1+k_2)\times 30} = \frac{k_2 a}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)\times 30}\right)$$

$\Rightarrow$ on solving, $(k_1 + k_2) = \frac{1}{30} \text{ In } \frac{5}{2}$ .... (i)

10. (A) $\alpha = \frac{x}{a} = \frac{C_{A_0} - C_{A_t}}{C_{A_0}} = 1 - \frac{C_{A_t}}{C_{A_0}}$

$$\therefore C_{A_t} = C_{A_0}e^{-Kt} \Rightarrow \alpha = 1 - \frac{C_{A_0}e^{-Kt}}{C_{A_0}} = 1 - e^{-Kt}$$

(B) $$\frac{1}{C_{A_t}} - \frac{1}{C_{A_0}} = Kt \Rightarrow C_{A_t} = \frac{C_{A_0}}{C_{A_0}Kt + 1} \Rightarrow \alpha = \frac{\frac{C_{A_0}}{C_{A_0}Kt+1}}{C_{A_0}} = \frac{C_{A_0}Kt}{C_{A_0}Kt + 1}$$

(C) $\alpha = 1 - \frac{C_{A_t}}{C_{A_0}}$ $\therefore C_{A_t} = C_{A_0} - Kt$

$$\alpha = 1 - \frac{C_{A_0} - Kt}{C_{A_0}} = \frac{Kt}{C_{A_0}}$$

C_{A_t}