Semester 1 (CC2): Chemical Kinetics

Consecutive Reactions or Sequential Reactions:

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Consecutive Reactions or Sequential Reactions:

The simplest consecutive is one which involves only one intermediate step. Let us consider the following consecutive reaction.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Let $[A]_0$ be the initial concentration of A and [A], [B], [C] be the concentrations of A, B and C respectively at time t.

Therefore, at any time, $[A]_0 = [A] + [B] + [C]$ (1)

Since the conversion of A to B is a first order process, the rate of disappearance of A,

$$-\frac{d[A]}{dt} = k_1[A] \qquad (2)$$

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Hence, on integrating eqn (2), we get

$$[A] = [A]_0 e^{-k_1 t} \qquad (3)$$

Now, the rate of accumulation of B = the rate formation of B – the rate of decomposition of B into C.

Thus,

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad (4)$$

Substituting [A] from eqn (3) into eqn (4), we get,

Or,

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B] \qquad (5)$$

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On rearranging the eqn (5) becomes,

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t} \qquad (6)$$

Multiplying both the sides of the eqn (6) by e^{k2t},

$$e^{k_2 t}\frac{d[B]}{dt} + e^{k_2 t} k_2[B] = k_1[A]_0\ e^{(k_2-k_1)t} \qquad (7)$$

On integrating eqn (7), we get

$$[B]e^{k_2 t} = \frac{k_1}{(k_2-k_1)}[A]_0\ e^{(k_2-k_1)t} + Z, where\ Z = constant$$

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When, t = 0, [B] = 0, $Z = -\frac{k_1}{(k_2-k_1)}[A]_0$

$$\therefore \ [B]e^{k_2 t} = \frac{k_1[A]_0}{(k_2-k_1)}\left[e^{(k_2-k_1)t} - 1\right]$$

$$\text{Or,} \quad [B] = [A]_0\left(\frac{k_1}{k_2-k_1}\right)\left[e^{-k_1 t} - e^{-k_2 t}\right] \qquad (8)$$

Substituting eqn (3) and (8) in eqn (1), we get

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0\left(\frac{k_1}{k_2-k_1}\right)\left[e^{-k_1 t} - e^{-k_2 t}\right] + [C] \qquad (9)$$

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Or,

$$[C] = [A]_0 - [A]_0 e^{-k_1 t} - [A]_0 (\frac{k_1}{k_2 - k_1}) [e^{-k_1 t} - e^{-k_2 t}] \quad (10)$$

Or,

$$[C] = [A]_0 \{ 1 - e^{-k_1 t} - \frac{k_1}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \} \quad (11)$$

Or,

$$[C] = [A]_0 \{ 1 - \frac{1}{(k_2 - k_1)} [k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \} \quad (12)$$

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Consecutive Reactions or Sequential Reactions:

Suppose in the above consecutive reactions the rate constant k_2 is greater than k_1 i.e., $k_2 >> k_1$. So in the above equation, $e^{-k1t} >> e^{-k2t}$ and hence $k_1 e^{-k2t}$ may be ignored in comparison to $k_2 e^{-k1t}$ and $(k_2 - k_1) \approx k_2$.

Thus, the equation (12) simplifies to

$$[C] \simeq [A]_0 \{1 - e^{-k_1 t}\} \qquad (13)$$