

# Semester 1 (CC2): Chemical Kinetics

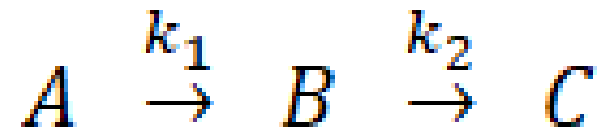
## Consecutive Reactions or Sequential Reactions:

**Dr. Biswajit Pal**

*Department of Chemistry,  
St. Paul's C. M. College, Kolkata, India*

# Consecutive Reactions or Sequential Reactions:

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



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,

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

## Consecutive Reactions or Sequential Reactions:

Hence, on integrating eqn (2), we get

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

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

Thus,

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

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

Or,

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

# Consecutive Reactions or Sequential Reactions:

On rearranging the eqn (5) becomes,

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

Multiplying both the sides of the eqn (6) by  $e^{k_2 t}$ ,

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

On integrating eqn (7), we get

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

# Consecutive Reactions or Sequential Reactions:

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

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

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

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

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

## Consecutive Reactions or Sequential Reactions:

Or,

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

Or,

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

Or,

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

## Consecutive Reactions or Sequential Reactions:

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

Thus, the equation (12) simplifies to

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