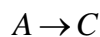


$$[C] = [A]_0 \left\{ 1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} \right\} \quad \dots (9)$$

Since  $k_1$  is much smaller than  $k_2$ , we may also ignore  $k_1$  in comparison to  $k_2$ . Thus, the above equation becomes

$$[C] = [A]_0 (1 - e^{-k_2 t})$$

Equation (9) can be obtained directly if we consider alone the reaction



Now, 
$$\frac{d[C]}{dt} = k_1 [A] = k_1 ([A]_0 - [C]) \quad \dots (10)$$

Or, 
$$\frac{d[C]}{[A]_0 - [C]} = k_1 dt; \quad \int_0^{[C]} \frac{d[C]}{[A]_0 - [C]} = k_1 \int_0^t dt$$

Or, 
$$\ln \frac{[A]_0 - [C]}{[A]_0} = -k_1 t$$

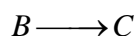
Or, 
$$\frac{[A]_0 - [C]}{[A]_0} = e^{-k_1 t}$$

Hence, 
$$[C] = [A]_0 (1 - e^{-k_1 t})$$

which is identical to equation (9). Thus, we may conclude that the reaction with the smaller rate constant is the rate-determining step. The same conclusion would be obtained if we consider that the first step is much faster than the second step, i.e.  $k_1 \gg k_2$ . In this case, we will ignore  $k_2$  in comparison to  $k_1$  and  $k_2 e^{-k_1 t}$  in comparison to  $k_1 e^{-k_2 t}$ . Hence, equation (9) in the present case will simplify to

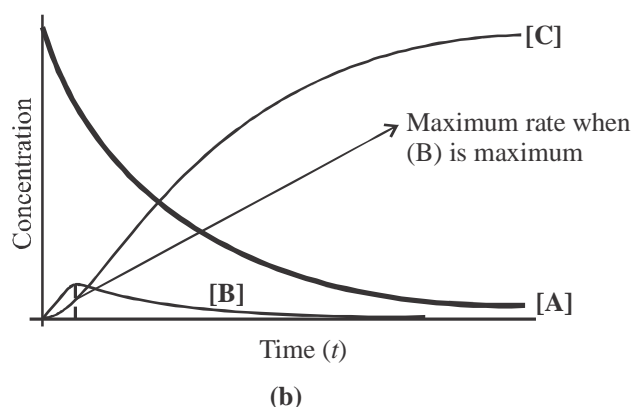
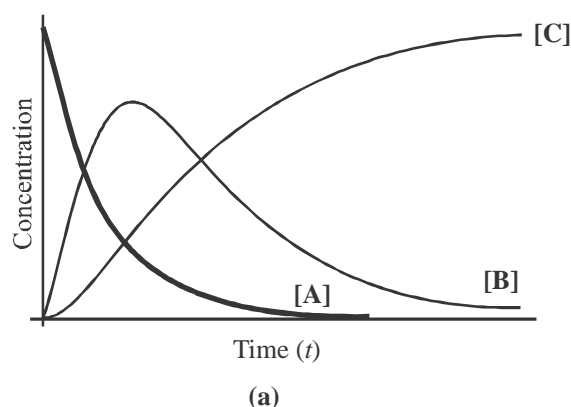
$$[C] = [A]_0 (1 - e^{-k_2 t})$$

The above equation can be obtained directly if we consider alone the reaction



with  $[B]_0 = [A]_0$  as the transformation A to B is very fast.

Figure (a) and (b) illustrate the typical variations in the concentration of A, B and C for the two consecutive first-order reactions with  $k_1 \gg k_2$  and  $k_1 \ll k_2$ .



In figure (a) and (b), a typical variation in concentration in a consecutive first-order reaction,  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$  with (a)  $k_1 \gg k_2$  and (b)  $k_1 \ll k_2$ .

In figure (a), the concentration of A disappears very rapidly as  $k_1 \gg k_2$  and since the rate at which B disappears is relatively slow, the concentration of B increases rapidly and after attaining the maximum in a small time interval, starts decreasing.

In figure (b), the concentration of A decreases slowly as the reaction rate constants  $k_1$  has a small value. The concentration of B practically remains constant for a reasonable length of time during the reaction, except at the very beginning and at the end. This constancy results from the fact that the intermediate B is very reactive as its transformation to C occurs at a very fast rate. In fact, the concentration of B at any instant will be much smaller than that of A. This follows from equation (5b) where on ignoring  $k_1$  in comparisons to  $k_2$  and  $\exp(-k_2 t)$  in comparison to  $\exp(-k_1 t)$ , we get

$$[B] \approx \frac{k_1}{k_2} e^{-k_1 t}$$

Since at any instant the concentration of A is given by equation (5a), we get

$$[B] \approx \frac{k_1}{k_2} [A]$$

that is, the concentration of B is smaller than the concentration of A by a factor of about  $\frac{k_1}{k_2}$ .

In figure (b) the term steady state arises when the concentration of [B] is constant.

The term steady state is also used to describe a situation where some, but not all, of the state variables of a system are constant. For such a steady state to develop, the system does not have to be a flow system. Therefore, such a steady state can develop in a closed system where a series of chemical reactions take place. Literature in chemical kinetics usually refers to this case, calling it *steady state approximation*.

In simple systems the steady state is approached by state variables decreasing or increasing until they reach their steady state value. In more complex systems state variable might fluctuate around the theoretical steady state either forever (a limit cycle) or gradually coming closer and closer. It theoretically takes an infinite time to reach steady state, just as it takes an infinite time to reach chemical equilibrium.

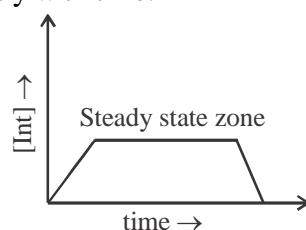
The steady state approximation, occasionally called the stationary state approximation, involves setting the rate of change of a reaction intermediate in a reaction mechanism equal to zero.

It is important to note that steady approximation does not assume the reaction intermediate concentration to be constant (and therefore its time derivative being zero), it assumes that the variation in the concentration of the intermediate is almost zero : the concentration of the intermediate is very low, so even a big relative variation in its concentration is small, if considered quantitatively.

If the steady state approximation is applied, then the derivative of the concentration of the intermediate is set of zero.

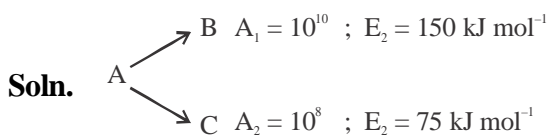
$$\frac{d[B]}{dt} = 0$$

The concentration of one of intermediate, [Int] varies with time as shown on the figure below. At the start and end of the reaction, [Int] does vary with time.



## SOLVED PROBLEMS

1. For a first order parallel reaction, the Arrhenius factor for formation of two products are  $10^{10}$  and  $10^8 \text{ sec}^{-1}$  and their energy of activation are  $150$  and  $75 \text{ kJ mol}^{-1}$ , respectively. At what temperature the two products will be formed at the same rate?



$$k_1 = A_1 e^{-E_1/RT} = 10^{10} e^{-\frac{150 \times 10^3}{8.314 \times T}}$$

$$k_2 = A_2 e^{-E_2/RT} = 10^8 e^{-\frac{75 \times 10^3}{8.314 \times T}}$$

$$k_1 = k_2$$

$$10^{10} e^{-\frac{150 \times 10^3}{8.314 \times T}} = 10^8 e^{-\frac{75 \times 10^3}{8.314 \times T}}$$

Taking log on both sides, we get

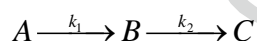
$$2.303 \times 10 - \frac{150 \times 10^3}{8.314T} = 2.303 \times 8 - \frac{75 \times 10^3}{8.314T}$$

$$2.303 \times (10 - 8) = \frac{(150 - 75) \times 10^3}{8.314 \times T}$$

$$2.303 \times 2 = \frac{75 \times 10^3}{8.314 \times T}$$

$$T = \frac{75 \times 10^3}{2.303 \times 2 \times 8.314} = 1958.5 \text{ K}$$

2. If the initial concentration of A is  $2.0 \text{ mol dm}^{-3}$  and  $k_1$  and  $k_2$  are  $0.30$  and  $0.15 \text{ min}^{-1}$ , respectively, at what time the concentration of B in the following reaction will maximum:

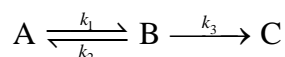


Also calculate the maximum concentration of B.

**Soln.** Time (max) =  $\frac{\ln k_1 - \ln k_2}{k_1 - k_2} = \frac{\ln(0.30) - \ln(0.15)}{(0.30) - (0.15)} = \frac{0.60}{0.15} = 4 \text{ min}$

$$[B]_{\text{max}} = [A]_0 \left( \frac{k_2}{k_1} \right)^{\frac{k_2}{k_1 - k_2}} = 2.0 \left( \frac{0.15}{0.30} \right)^{\frac{0.15}{0.30 - 0.15}} = 1.0 \text{ mol dm}^{-3}$$

3. In the following reaction scheme,



which of the following determines the rate of formation of C?

- (a) Only  $k_3$  (b) Only  $k_1$  and  $k_2$   
 (c) Only  $k_1$  and  $k_3$  (d)  $k_1, k_2$  and  $k_3$