

Lecture 23

We will continue to learn about “Chemical Kinetics”

Suggested book: Physical Chemistry by Ira Levine

Reversible first order reaction: (Also called Opposing reaction)

Let us assume the reversible reaction: $A \xrightleftharpoons[k_b]{k_f} B$

(with stoichiometric coefficients as 1 for both) be of first order in both forward and backward directions.

$$r_f = k_f [A] \quad , \quad r_b = k_b [B]$$

$$r_f = (-) \frac{d[A]}{dt} = k_f [A] \quad , \quad r_b = (+) \frac{d[A]}{dt} = k_b [B]$$

$$\frac{d[A]}{dt} = \left(\frac{d[A]}{dt}\right)_f + \left(\frac{d[A]}{dt}\right)_b = (-) k_f [A] + k_b [B] \quad \dots\dots\dots (i)$$

We know, $\Delta[B] = (-) \Delta[A]$, so $[B] - [B]_0 = - ([A] - [A]_0)$

Substituting $[B] = [B]_0 - [A] + [A]_0$ in equation (i) we get,

$$\frac{d[A]}{dt} = k_b [B]_0 + k_b [A]_0 - (k_f + k_b) [A] \quad \dots\dots\dots (ii)$$

To simplify the equation let us make some intuitive assumption. In the limit of $t = \infty$, the system reaches equilibrium which means rate of both forward and backward reactions becomes equal. At equilibrium concentration of both species remains constant i.e. $\frac{d[A]}{dt} = 0$

If concentration of A in equilibrium condition be $[A]_{eqm}$, then, equation (ii) becomes,

$$\text{As } \frac{d[A]}{dt} = 0, \quad k_b [B]_0 + k_b [A]_0 = (k_f + k_b) [A]_{eqm} \quad \dots\dots\dots (iii)$$

Using equation (iii), equation (ii) becomes,

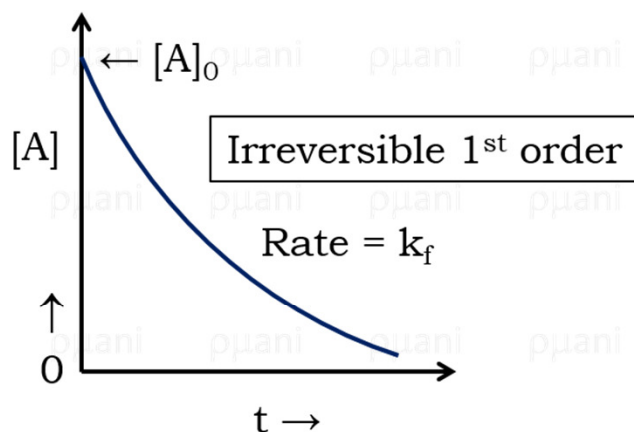
$$\frac{d[A]}{dt} = (k_f + k_b) ([A]_{eqm} - [A]) \quad \dots\dots\dots (iv)$$

Using the identity $\int \frac{dx}{x+s} = \ln(x+s)$ to integrate the equation (iv) we get,

$$\ln \left(\frac{[A] - [A]_{eqm}}{[A]_0 - [A]_{eqm}} \right) = -(k_f + k_b) t \quad \dots\dots\dots (v)$$

$$\Rightarrow [A] - [A]_{eqm} = ([A]_0 - [A]_{eqm}) \times e^{-(k_f + k_b) t} \quad \dots\dots\dots (vi)$$

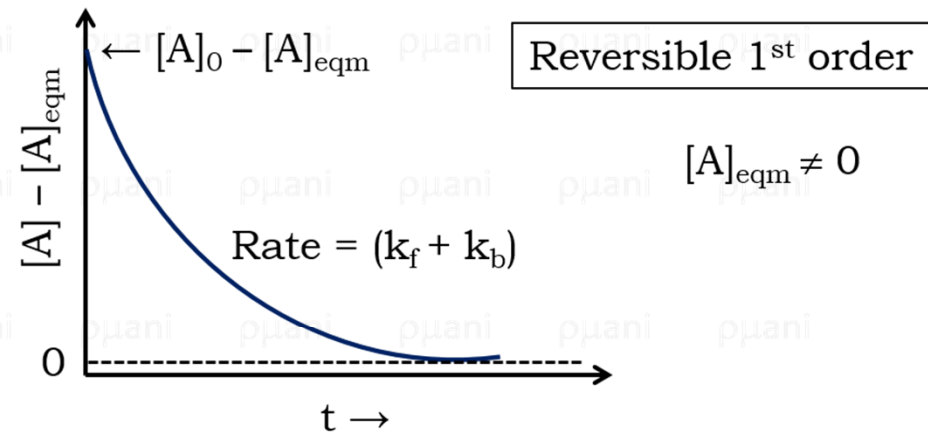
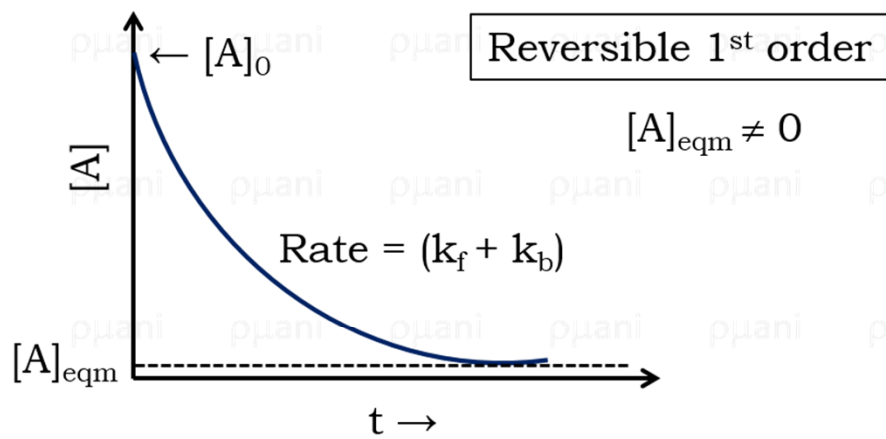
$[A]_{eqm}$ can be obtained from equation (iii). Equation (vi) is similar to 1st order rate equation.



For $k_b = 0$, $[A]_{eqm} = 0$, equation (vi) gets the form for 1st order reaction

$$[A] = [A]_0 \times e^{-k_f \times t} \quad \dots\dots\dots (vii)$$

Necessary plots:



Consecutive first order reaction:

Let us consider a consecutive, irreversible, first order reaction: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

We also assume that the stoichiometry for both reaction is 1.

Rate of first reaction $r_1 = k_1 [A]$

Rate of second reaction $r_2 = k_2 [B]$

We consider here the ratio of change of [B] due to first and second reactions

$$\left(\frac{d[B]}{dt}\right)_1 = k_1 [A] \quad , \quad \left(\frac{d[B]}{dt}\right)_2 = (-) k_2 [B]$$

$$\text{Thus, } \frac{d[B]}{dt} = \left(\frac{d[B]}{dt}\right)_1 + \left(\frac{d[B]}{dt}\right)_2$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B]$$

$$\frac{d[A]}{dt} = -k_1 [A]$$

$$\frac{d[C]}{dt} = k_2 [B]$$

} (i)

At $t = 0$, only A is present, i.e. $[B] = [C] = 0$, $[A] \neq 0$

For A, $[A] = [A]_0 \times e^{-k_1 \times t}$ (From 1st order rate equation) (ii)

Substituting [A] in equation (i) we get,

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

Integrating equation (iii) we get,

$$[B] = \frac{k_1 \times [A]_0}{k_2 - k_1} (e^{-k_1 \times t} - e^{-k_2 \times t}) \quad \text{..... (iv)}$$

To find [C] we simply use conservation of matter principle

$$\text{i.e. } [A]_0 = [A] + [B] + [C] \quad \text{..... (v)}$$

Using equation (ii) and (iv) we get,

$$[C] = [A]_0 \left(1 - \frac{k_2}{k_2 - k_1} \times e^{-k_1 \times t} + \frac{k_1}{k_2 - k_1} \times e^{-k_2 \times t} \right) \quad \text{..... (vi)}$$

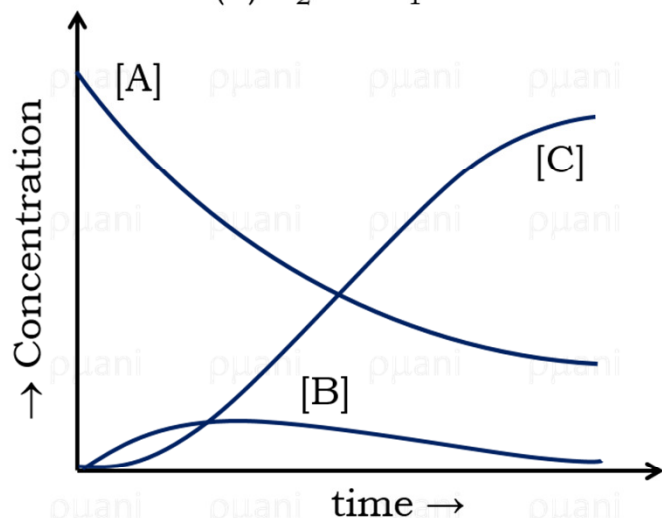
Rearranging equation (vi) we get,

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

$$= [A]_0 \left(1 - \left(1 + \frac{k_1}{k_2 - k_1} \right) \times e^{-k_1 \times t} + \frac{k_1}{k_2 - k_1} \times e^{-k_2 \times t} \right) \quad \text{..... (vii)}$$

Considering equation (vi), there can be two cases:

(a) $k_2 \gg k_1$



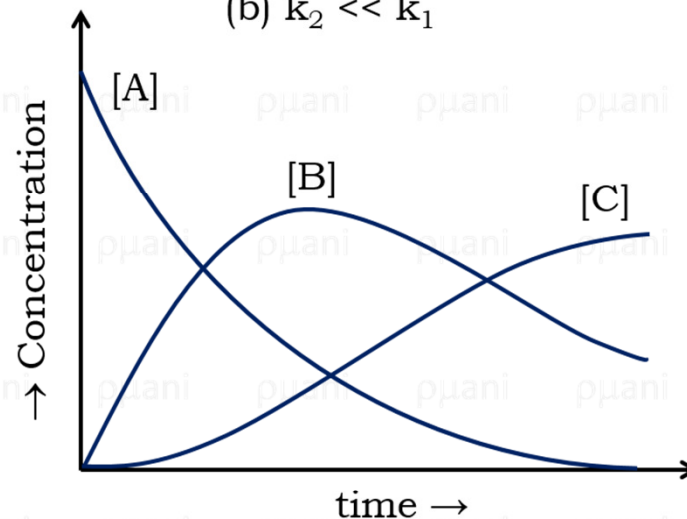
When $k_2 \gg k_1$

Equation (vi) becomes

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

At any point of time $[A] + [B] + [C] = [A]_0$

(b) $k_2 \ll k_1$



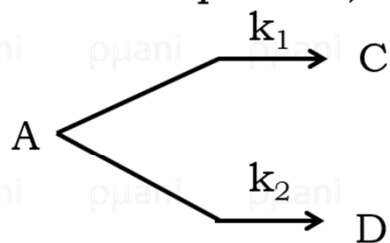
When $k_2 \ll k_1$

Equation (vi) becomes

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

Parallel/Competing first order reaction:

Let us assume a parallel, irreversible, first order reaction



We assume the stoichiometries are 1 in both cases.

The rate law is

$$\frac{d[A]}{dt} = -k_1 [A] - k_2 [A] = -(k_1 + k_2) [A] \quad \text{..... (i)}$$

$$\text{Integrating, } [A] = [A]_0 \times e^{-(k_1 + k_2) \times t} \quad \text{..... (ii)}$$

(Same as first order reaction with total rate constant, $k = k_1 + k_2$)

$$\text{For C, } \frac{d[C]}{dt} = (+) k_1 \times [A] = k_1 \times [A]_0 \times e^{-(k_1 + k_2) \times t} \quad [\text{using equation (ii)}] \quad \text{..... (iii)}$$

At time $t = 0$, $[C] = 0$, at time $t = t$, concentration of C = $[C]$

Integrating equation (iii) we get,

$$[C] = \frac{k_1 \times [A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2) \times t}) \quad \text{..... (iv)}$$

Similarly for D,

$$\frac{d[D]}{dt} = k_2 \times [A] = k_2 \times [A]_0 \times e^{-(k_1 + k_2) \times t} \dots\dots\dots (v)$$

At time $t = 0$, $[D] = 0$

Integrating we get,

$$[D] = \frac{k_2 \times [A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2) \times t}) \dots\dots\dots (vi)$$

Note that the sum of both k_1 and k_2 appears in exponential for both $[C]$ and $[D]$

Dividing equation (iv) with equation (vi) we get,

$$\frac{[C]}{[D]} = \frac{k_1}{k_2}$$

Thus, amount of $[C]$ and $[D]$ depends on the relative values of k_1 and k_2 .

Thus, the relative values of k_1 and k_2 will determine kinetically controlled product.

However, thermodynamically the product with most negative G^0 will be favoured. The favoured product is called thermodynamically controlled product.