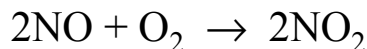
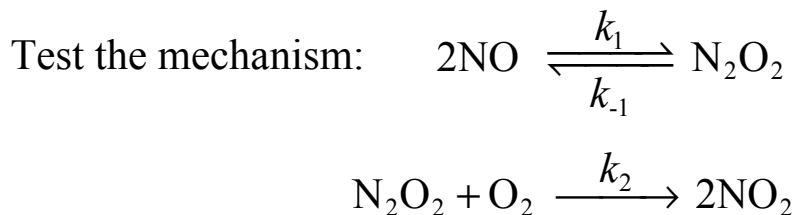


An Example of a Complex Mechanism

Consider the overall reaction



It is found experimentally to be third order overall, second order in NO, first order in O₂. It is much too fast to be a termolecular process



Apply the steady-state approximation to [N₂O₂]

$$\frac{d}{dt}[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2] = 0$$

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{O}_2]}$$

$$\text{rate: } \frac{1}{2} \frac{d}{dt}[\text{NO}_2] = k_2[\text{N}_2\text{O}_2][\text{O}_2] = \frac{k_1 k_2 [\text{NO}]^2 [\text{O}_2]}{k_{-1} + k_2 [\text{O}_2]}$$

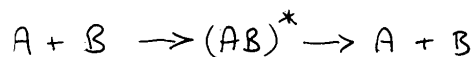
In the limit of $k_{-1} \gg k_2 [\text{O}_2]$,

$$\text{rate} = \frac{k_1 k_2}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$$

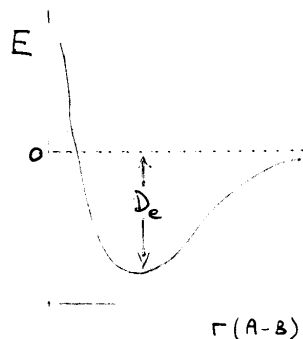
This is an example of a *pre-equilibrium* mechanism.

RADICAL COMBINATION REACTIONS

In low pressure gases, atoms



because $(AB)^*$ lives only $\sim 10^{-14}$ s, the period of a molecular vibration.



If A and/or B are polyatomic radicals $(AB)^*$ may live as much as 10^{-7} s, by distribution of D_e among several degrees of freedom.

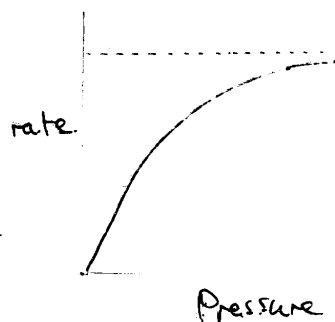
For efficient reaction a third body is needed:

1. $A + B \rightleftharpoons (AB)^*$
2. $(AB)^* + M \rightarrow AB + M$

$$\begin{aligned} \text{rate} &= \frac{d[AB]}{dt} = k_2[M][AB^*] \\ &= k_2[M] \cdot \frac{k_1[A][B]}{k_{-1} + k_2[M]} \\ &= k_1[A][B] \left(\frac{k_2[M]}{k_{-1} + k_2[M]} \right) \end{aligned}$$

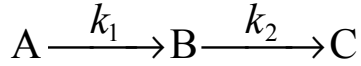
applying S-S Approx. to AB^*

The rate is pressure-dependent at low pressures, but constant in the "high-pressure limit", where $[M]$ is in excess.



Consecutive Reactions

Simplest case - two first-order steps



$$\frac{da}{dt} = -k_1 a$$

$$a = a_0 e^{-k_1 t}$$

$$\frac{db}{dt} = k_1 a - k_2 b$$

$$b = a_0 \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$\frac{dc}{dt} = k_2 b$$

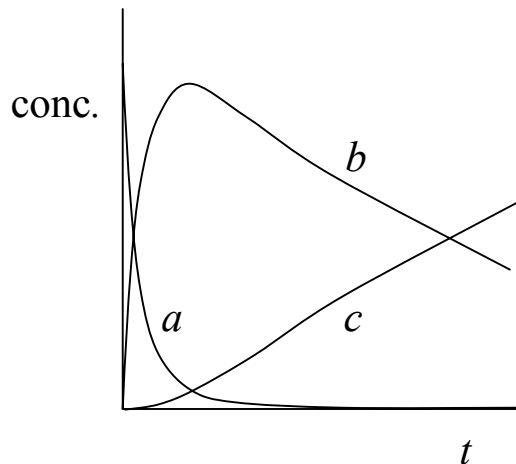
$$c = a_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

$$\frac{da}{dt} + \frac{db}{dt} + \frac{dc}{dt} = 0$$

$$a + b + c = a_0$$

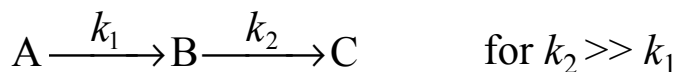
For $k_1 \gg k_2$ the reaction mechanism can be considered as two distinct steps:

1. At short times b increases as a falls. $b \rightarrow a_0 e^{-k_2 t}$
2. At longer times ($k_1 t \gg 0$), c increases as b falls.

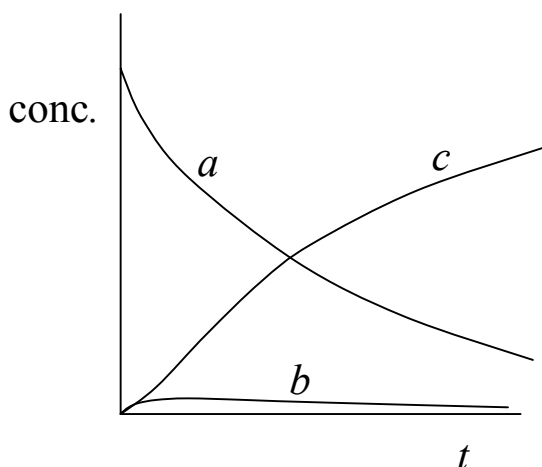


$$c \rightarrow a_0 (1 - e^{-k_2 t})$$

The Steady-State Approximation



$$\frac{db}{dt} = k_1 a - k_2 b = k_1 a_0 e^{-k_1 t} \left[\frac{k_1}{k_2 - k_1} + \frac{k_2}{k_2 - k_1} e^{-(k_2 - k_1)t} \right]$$



After the induction period, i.e. for $k_2 t \gg 0$,

$$\frac{da}{dt} = -k_1 a_0 e^{-k_1 t}, \quad \frac{dc}{dt} \approx k_1 a_0 e^{-k_1 t}, \quad \frac{db}{dt} \approx -k_1 a_0 e^{-k_1 t} \left[\frac{k_1}{k_2 - k_1} \right]$$

$$\frac{db}{dt} \ll \frac{da}{dt}, \left| \frac{dc}{dt} \right|$$

Although b is not constant...

it changes at a much smaller rate than a or c .

This is the essence of the steady-state approximation.

Numerical Integration of Differential Rate Expressions

Use second-order decay as example.

Simple integration:

$$\frac{dx}{dt} = -kx^2$$

$$\delta x = -kx^2 \delta t$$

$$x(t + \delta t) = x(t) - kx(t)^2 \cdot \delta t$$

Error is introduced by using a fixed value of x for the interval δt .

Runge-Kutta

e.g Take the equation $\frac{dx}{dt} = f(x)$ with initial value $x = x_0$

$$\text{Define } \left. \begin{array}{l} a = f(x_0) \cdot \delta t \\ b = f(x_0 + \frac{1}{2}a) \cdot \delta t \\ c = f(x_0 + \frac{1}{2}b) \cdot \delta t \\ d = f(x_0 + c) \cdot \delta t \end{array} \right\} \text{ then } x_1 = x_0 + \frac{1}{6}(a + 2b + 2c + d)$$

More generally, for $\frac{dx}{dt} = f(t, x)$

$$\left. \begin{array}{l} a = f(t_0, x_0) \cdot \delta t \\ b = f(t_0 + \frac{1}{2}\delta t, x_0 + \frac{1}{2}a) \cdot \delta t \\ c = f(t_0 + \frac{1}{2}\delta t, x_0 + \frac{1}{2}b) \cdot \delta t \\ d = f(t_0 + \delta t, x_0 + c) \cdot \delta t \end{array} \right\}$$