An Example of a Complex Mechanism

Consider the overall reaction

$$2NO + O_2 \rightarrow 2NO_2$$
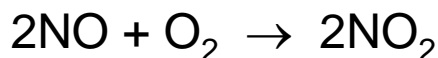
It is found experimentally to be third order overall, second order in NO, first order in O_2. It is much too fast to be a termolecular process

Test the mechanism:
$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$
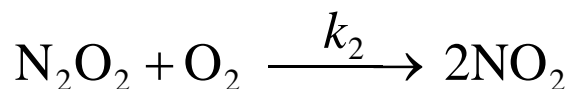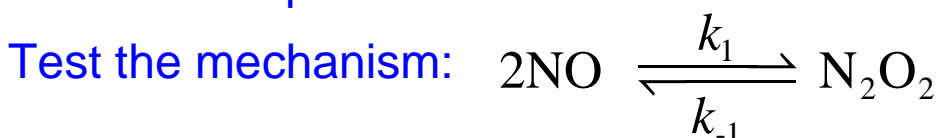
$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

Apply the steady-state approximation to [N_2O_2]

$$\frac{d}{dt}[N_2O_2] = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2] = 0$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]}$$

$$\text{rate} = \frac{1}{2}\frac{d}{dt}[NO_2] = k_2[N_2O_2][O_2] = \frac{k_1 k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]}$$

In the limit of $k_{-1} \gg k_2[O_2]$, $\quad \text{rate} = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]$

This is an example of a pre-equilibrium mechanism.

Atom/Radical Combination Reactions

In low pressure gases, atoms seem to react slower than expected because the combination product falls apart in the period of a molecular vibration ($\sim 10^{-14}$ s).

U

D_e

$$A + B \rightarrow (A\text{-}B)^* \rightarrow A + B$$

r(A-B)
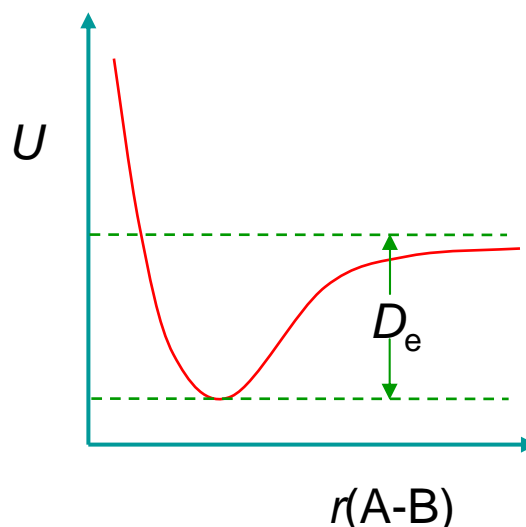
If A and B are polyatomic radicals, (A-B)* may live longer (e.g. 10^{-9} s), by distribution of D_e among different vibrational modes.
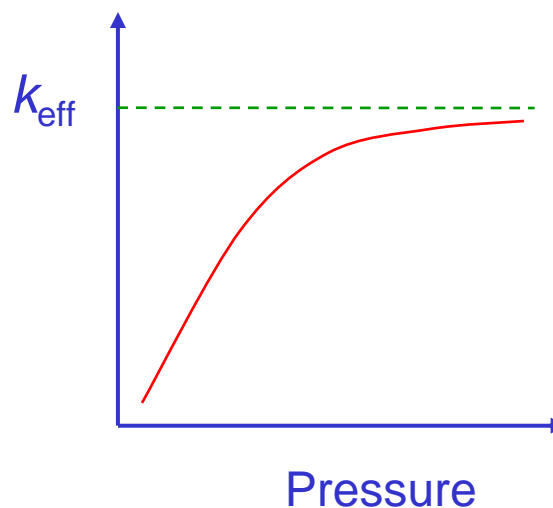
For efficient reaction a third body is needed:

1. $\quad A + B \rightleftharpoons AB^*$

2. $\quad AB^* + M \rightarrow AB + M$

k_{eff}
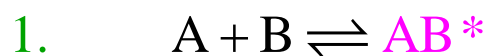
$$\rho = \frac{d[\text{AB}]}{dt} = k_2[\text{M}][\text{AB*}]$$

$$= k_2[\text{M}] \cdot \frac{k_1[\text{A}][\text{B}]}{k_{-1} + k_2[\text{M}]}$$

$$= \frac{k_1 k_2[\text{M}]}{k_{-1} + k_2[\text{M}]} \cdot [\text{A}][\text{B}]$$

Pressure

The effective rate constant depends on pressure ([M]).

Diffusion-limited Kinetics

For fast reactions in liquids, the rate-determining step can be diffusion of the reactants to form the encounter pair:

$$A + B \; \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} \; \{AB\} \; \xrightarrow{k_R} \; products$$
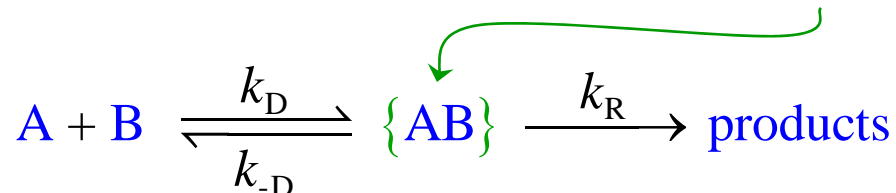
Apply the steady-state approximation to {AB}:

$$\frac{d}{dt}\big[\{AB\}\big] = k_D[A][B] - (k_{-D} + k_R)\big[\{AB\}\big] = 0$$

$$rate = k_R\big[\{AB\}\big] = \frac{k_D k_R}{k_{-D} + k_R}[A][B]$$

The effective rate constant has two limits:

Slow diffusion : $\quad k_{eff} = \dfrac{k_D k_R}{k_{-D} + k_R} \rightarrow k_D \quad$ if $\; k_R \gg k_{-D}$

Fast diffusion : $\quad k_{eff} \rightarrow \dfrac{k_D k_R}{k_{-D}} = K_{\{AB\}} k_R = k_{act} \quad$ if $\; k_{-D} \gg k_R$
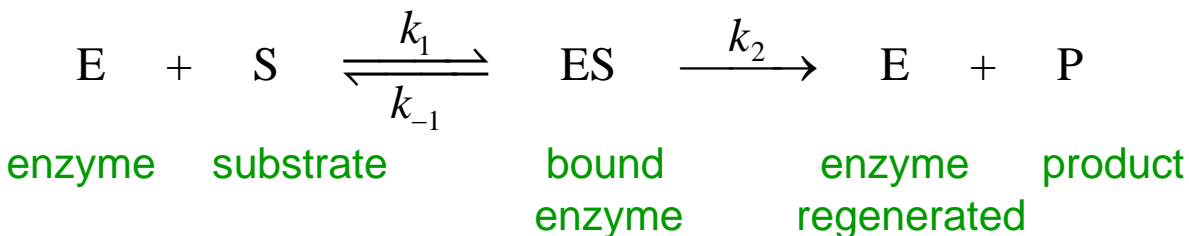
Intermediate situations can be described by:

$$k_{eff} = \frac{k_D k_R}{k_{-D} + k_R} = \frac{k_D (k_D k_R / k_{-D})}{k_D + (k_D k_R / k_{-D})} = \frac{k_D k_{act}}{k_D + k_{act}}$$

Take the inverse: $\qquad \dfrac{1}{k_{eff}} = \dfrac{1}{k_D} + \dfrac{1}{k_{act}}$

Enzyme Kinetics 1

Another example of a pre-equilibrium mechanism is one used to model the kinetics of enzyme action:

$$E \quad + \quad S \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad ES \quad \xrightarrow{k_2} \quad E \quad + \quad P$$

enzyme   substrate   bound   enzyme   product
                            enzyme   regenerated

Applying the steady-state approximation to the bound state,

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$[ES] = \frac{k_1}{k_{-1} + k_2}[E][S] = \frac{k_1}{k_{-1} + k_2}([E]_0 - [ES])[S]$$

Rearranging: $$[ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$

Rate: $$\rho = \frac{d[P]}{dt} = k_2[ES] = \frac{k_1 k_2[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$

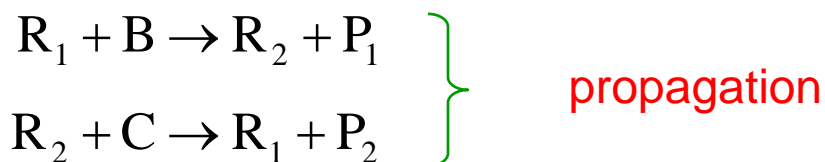$$\rho = \frac{k_2[E]_0[S]}{K_M + [S]} \qquad \text{with} \qquad K_M = \frac{k_{-1} + k_2}{k_1}$$

Michaelis-Menten   Michaelis constant

Chain Reactions

$$A \rightarrow R_1 \qquad \text{initiation}$$

$$R_1 + B \rightarrow R_2 + P_1$$
$$R_2 + C \rightarrow R_1 + P_2 \qquad \text{propagation}$$
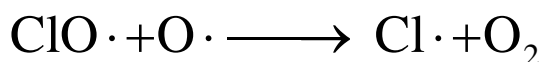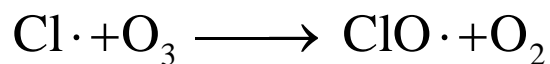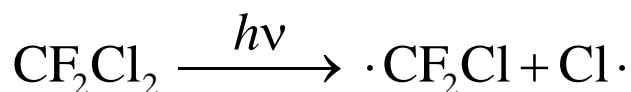
$$2R_1 \rightarrow P_3 \qquad \text{termination}$$

R is often, but not always, a free radical.

Initiation may be thermal, photochemical, radiolysis, …

The overall reaction is determined by adding the propagation steps:

$$B + C \rightarrow P_1 + P_2$$

Important examples include polymerization, combustion, photochemical smog production and the depletion of stratospheric ozone by CFCs.

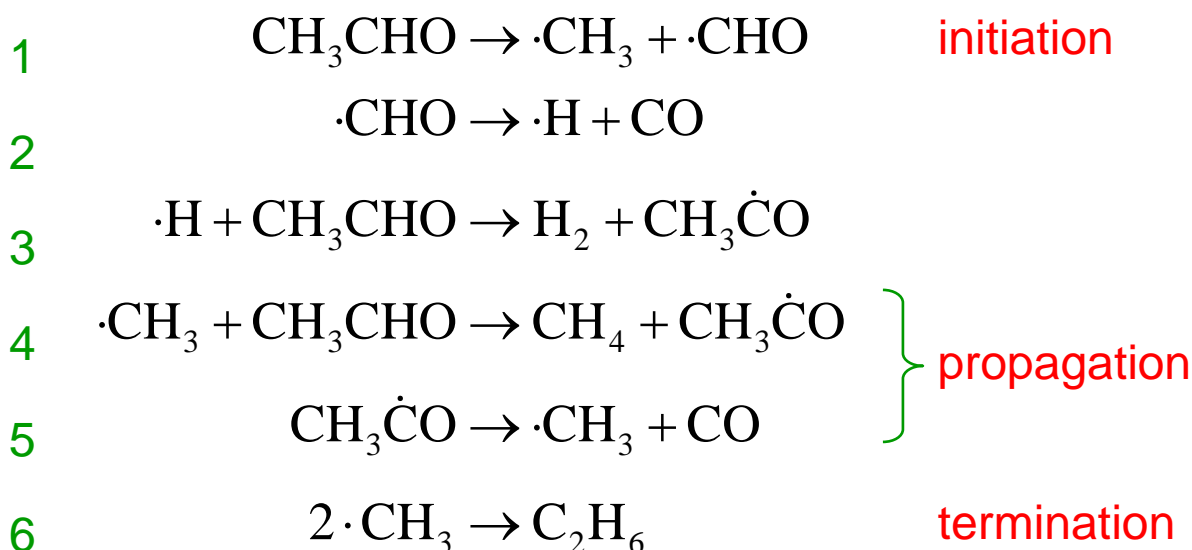$$CF_2Cl_2 \xrightarrow{\ h\nu\ } \cdot CF_2Cl + Cl \cdot$$

$$Cl \cdot + O_3 \longrightarrow ClO \cdot + O_2$$

$$ClO \cdot + O \cdot \longrightarrow Cl \cdot + O_2$$

The net effect is catalysis by the CFC of the reaction

$$O \cdot + O_3 \rightarrow 2O_2$$
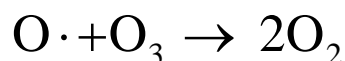
Rice-Herzfeld Mechanism

e.g. for the thermal decomposition of acetaldehyde

1. $$CH_3CHO \rightarrow \cdot CH_3 + \cdot CHO \qquad \text{initiation}$$

2. $$\cdot CHO \rightarrow \cdot H + CO$$

3. $$\cdot H + CH_3CHO \rightarrow H_2 + CH_3\dot{C}O$$

4. $$\cdot CH_3 + CH_3CHO \rightarrow CH_4 + CH_3\dot{C}O$$

5. $$CH_3\dot{C}O \rightarrow \cdot CH_3 + CO \qquad \text{propagation}$$

6. $$2 \cdot CH_3 \rightarrow C_2H_6 \qquad \text{termination}$$

Write steady-state equations for [CHO], [H], [CH$_3$], [CH$_3$CO]:

$$\frac{d}{dt}[CHO] = k_1[CH_3CHO] - k_2[CHO] = 0 \qquad [CHO] = (k_1/k_2)[CH_3CHO]$$

$$\frac{d}{dt}[H] = k_2[CHO] - k_3[H][CH_3CHO] = 0 \qquad [H] = (k_1/k_3)$$

$$\frac{d}{dt}[CH_3CO] = k_4[CH_3][CH_3CHO] + k_3[H][CH_3CHO] - k_5[CH_3CO] = 0$$

$$\frac{d}{dt}[CH_3] = k_1[CH_3CHO] - k_4[CH_3][CH_3CHO] + k_5[CH_3CO] - 2k_6[CH_3]^2 = 0$$

$$[CH_3]^2 = (k_1/k_6)[CH_3CHO]$$

$$\text{rate} = \frac{d}{dt}[CH_4] = k_4[CH_3][CH_3CHO] = k_4(k_1/k_6)^{1/2}[CH_3CHO]^{3/2}$$

An Explosive Reaction

Overall: $\qquad$ $2H_2 + O_2 \rightarrow 2H_2O$

$$H_2 \rightarrow 2H \qquad \text{initiation}$$

$$H + O_2 \rightarrow O + OH$$
$$O + H_2 \rightarrow OH + H \qquad \text{branching}$$

$$OH + H_2 \rightarrow H_2O + H \qquad \text{propagation}$$

$$H \rightarrow \text{wall}$$
$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{termination}$$

$$HO_2 + H_2 \rightarrow H + H_2O_2$$
$$HO_2 + H_2O \rightarrow OH + H_2O_2 \qquad \text{slow propagation}$$
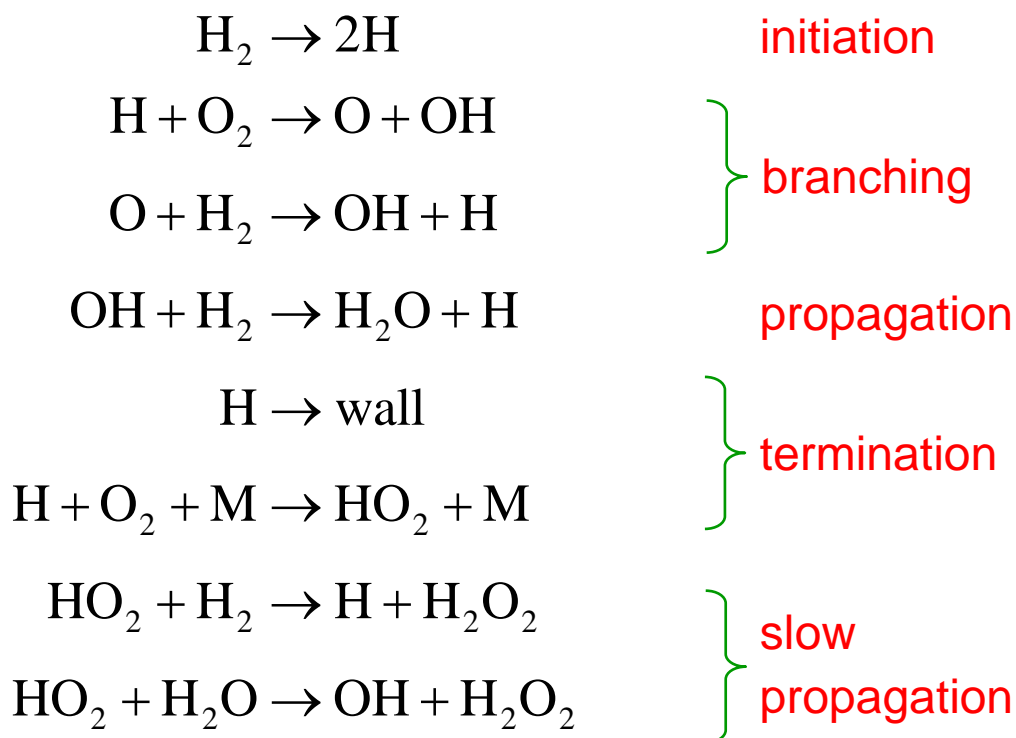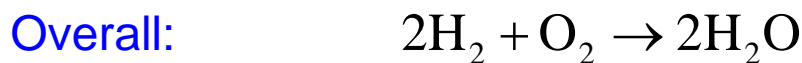
At 700 K and 0.1 bar O_2,

$\qquad$ *each* initial H atom $\rightarrow$ 10^{13} H atoms in 0.3 s.
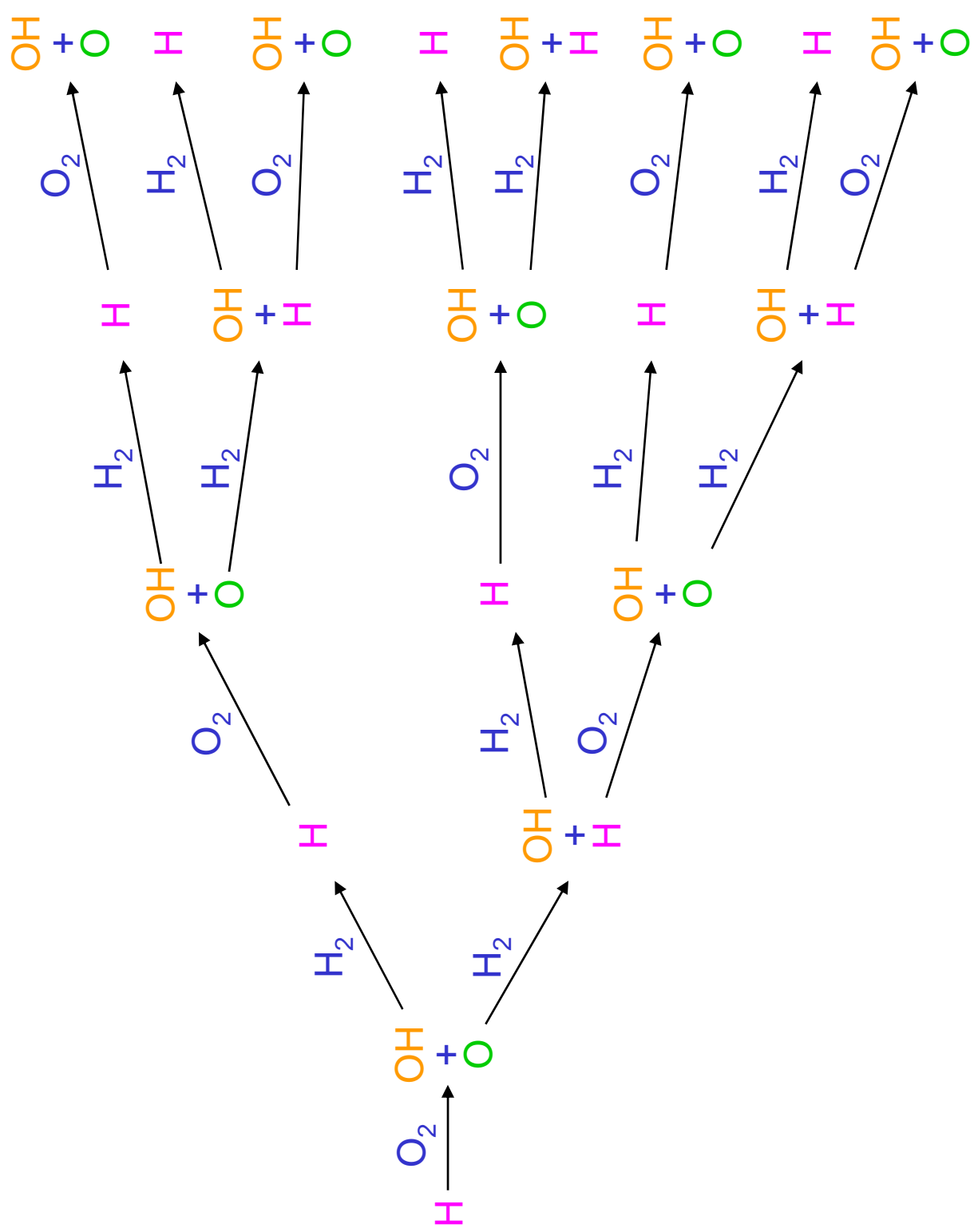
Branching Chain Reactions

1   Initiation $\text{A, B} \rightarrow \text{R}_1$

2   Branching $\text{R}_1 + \text{A} \rightarrow \text{R}_2 + \text{R}_3$ [R] increases

3   Propagation $\text{B} + \text{R}_i \rightarrow \text{R}_i + \dots$

4   Termination (wall) $\text{R}_i \rightarrow \text{P}_1$

             (combination) $2\text{R}_i \rightarrow \text{P}_2$ [R] decreases

The steady-state approximation does not apply.

If *n* is the number of radicals at time *t*,

$$\frac{dn}{dt} = \rho_{\text{I}} + k_{\text{b}}n - \left(k_{\text{w}} + k_{\text{g}}\right)n$$

$$= \rho_{\text{I}} + \phi n \qquad\qquad \phi = k_{\text{b}} - \left(k_{\text{w}} + k_{\text{g}}\right)$$

$$n = \frac{\rho_{\text{I}}}{\phi}\left(e^{\phi t} - 1\right)$$

The exponential increase in *n* for $\phi > 0$ leads to explosion.

k_{eff} vs pressure: explosion limits; curves labelled k_{b}, $k_{\text{g+w}}$, k_{g}, k_{w}
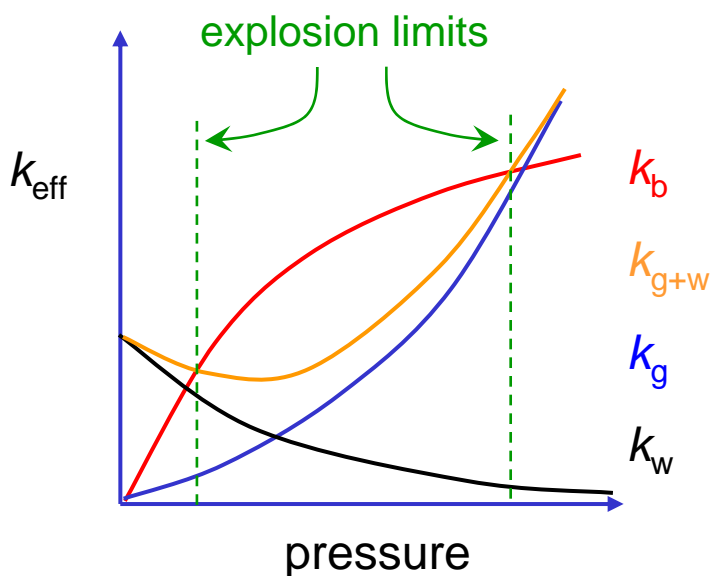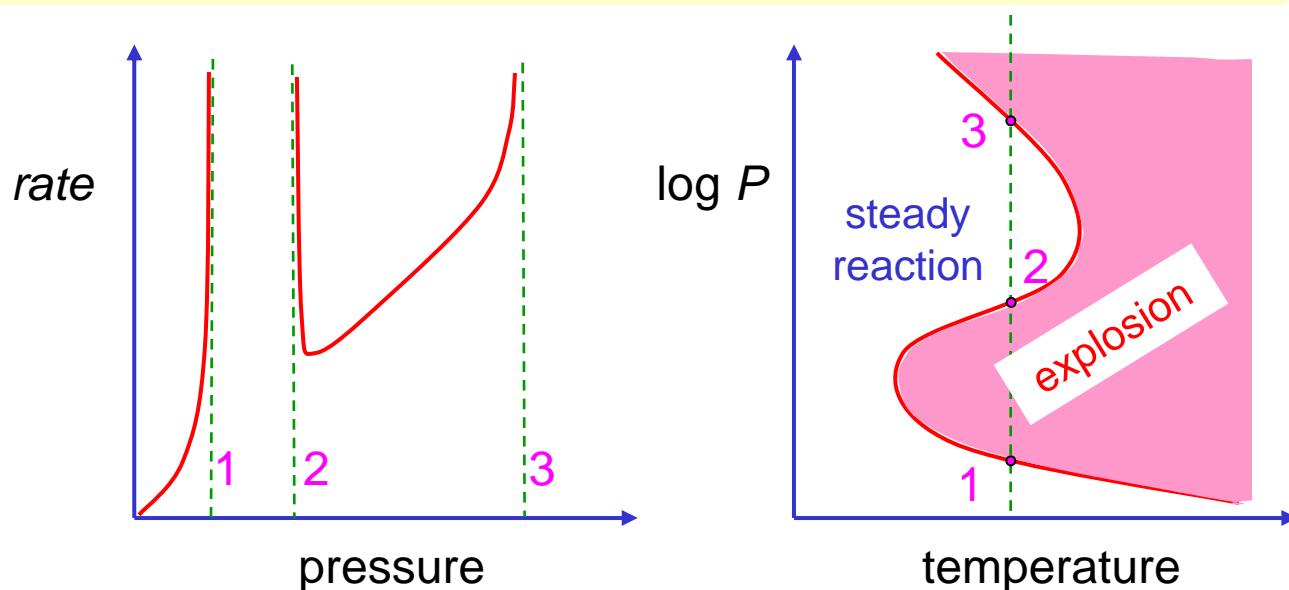
Explosion Limits

At pressures below 1,
- ➤ wall termination is dominant
- ➤ the limit depends on surface composition and area
- ➤ the limit is altered by the size of the reaction vessel

Between 1 and 2,
- ➤ is the explosion peninsula
- ➤ the limits change with temperature because branching reactions are T dependent, diffusion less so

Between 2 and 3,
- ➤ gas phase termination reactions are dominant

At pressures above 3,
- ➤ reaction products are important
- ➤ heat from exothermic reactions → thermal explosion