## $T$ Dependence of Complex Reactions

Assume some complex reaction

$$
\mathrm{A}+\mathrm{B} \xrightarrow{k_{1}} \mathrm{C}+\mathrm{D} \xrightarrow{k_{2}} \cdots
$$

for which the overall reaction rate constant can be expressed in terms of the elementary steps:

$$
k_{\text {overall }}=\frac{k_{1}^{n_{1}} k_{2}^{n_{2}} \ldots}{k_{3}^{n_{3}} \ldots}
$$

If each rate constant obeys the Arrhenius expression,

$$
k_{i}=A_{i} \mathrm{e}^{-E_{i} / R T}
$$

$$
k_{\text {overall }}=\left(\frac{A_{1}^{n_{1}} A_{2}^{n_{2}} \ldots}{A_{3}^{n_{3}} \ldots}\right) \exp \left\{-\left(n_{1} E_{1}+n_{2} E_{2}-n_{3} E_{3}-\ldots\right) / R T\right\}
$$

i.e. The Arrhenius parameters are

$$
\begin{aligned}
& A_{\text {overall }}=\prod_{i} A_{i}^{n_{i}} \\
& E=\sum_{i} n_{i} E_{i}
\end{aligned}
$$

The overall "activation energy" may be negative, if $n_{i}$ is negative and the corresponding $E_{i}$ is large enough. Also, for a pre-equilibrium reaction where $k_{\text {overall }}=K_{1} k_{2}$

$$
E_{\mathrm{a}}=R T^{2} \frac{d \ln k_{\text {overall }}}{d T}=R T^{2} \frac{d \ln K_{1}}{d T}+E_{2}=\Delta H_{1}+E_{2}
$$

$E_{2}$ is positive but $\Delta H$ can be negative.

## Chain Reactions

$$
\begin{array}{rlr}
\mathrm{A} & \rightarrow \mathrm{R}_{1} & \\
\mathrm{R}_{1}+\mathrm{B} & \rightarrow \mathrm{R}_{2}+\mathrm{P}_{1} \\
\mathrm{R}_{2}+\mathrm{C} & \rightarrow \mathrm{R}_{1}+\mathrm{P}_{2} \\
2 \mathrm{R}_{1} & \rightarrow \mathrm{P}_{3}
\end{array} \quad \begin{aligned}
& \text { propagation } \\
&
\end{aligned} \quad \begin{aligned}
& \text { termination }
\end{aligned}
$$

$R$ is often, but not always, a free radical.
Initiation may be thermal, photochemical, radiolysis, ...
The overall reaction is determined by adding the propagation steps:

$$
\mathrm{B}+\mathrm{C} \rightarrow \mathrm{P}_{1}+\mathrm{P}_{2}
$$

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

$$
\begin{array}{rl}
\mathrm{CF}_{2} \mathrm{Cl}_{2} \xrightarrow{h \nu} \cdot \mathrm{CF}_{2} \mathrm{Cl}+\mathrm{Cl} \cdot \\
\mathrm{Cl} \cdot+\mathrm{O}_{3} & \mathrm{ClO} \cdot+\mathrm{O}_{2} \\
\mathrm{ClO} \cdot+\mathrm{O} \cdot & \mathrm{Cl} \cdot+\mathrm{O}_{2}
\end{array}
$$

The net effect is catalysis by the CFC of the reaction

$$
\mathrm{O} \cdot+\mathrm{O}_{3} \rightarrow 2 \mathrm{O}_{2}
$$

## Rice-Herzfeld Mechanism

e.g. for the thermal decomposition of acetaldehyde

$$
\begin{aligned}
\mathrm{CH}_{3} \mathrm{CHO} & \rightarrow \cdot \mathrm{CH}_{3}+\cdot \mathrm{CHO} \quad \text { initiation } \\
\cdot \mathrm{CHO} & \rightarrow \cdot \mathrm{H}+\mathrm{CO}
\end{aligned}
$$

$$
\cdot \mathrm{H}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{H}_{2}+\mathrm{CH}_{3} \dot{\mathrm{C} O}
$$

$\left.\begin{array}{lc}4 & \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{4}+\mathrm{CH}_{3} \dot{\mathrm{CO}} \\ 5 & \mathrm{CH}_{3} \dot{\mathrm{CO}} \rightarrow \cdot \mathrm{CH}_{3}+\mathrm{CO}\end{array}\right\}$ propagation

Write steady-state equations for [CHO], $[\mathrm{H}],\left[\mathrm{CH}_{3}\right],\left[\mathrm{CH}_{3} \mathrm{CO}\right]$ :
$\frac{d}{d t}[\mathrm{CHO}]=k_{1}\left[\mathrm{CH}_{3} \mathrm{CHO}\right]-k_{2}[\mathrm{CHO}]=0 \quad[\mathrm{CHO}]=\left(k_{1} / k_{2}\right)\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$

$$
\begin{array}{ll}
\frac{d}{d t}[\mathrm{H}]=k_{2}[\mathrm{CHO}]-k_{3}[\mathrm{H}]\left[\mathrm{CH}_{3} \mathrm{CHO}\right]=0 & {[\mathrm{H}]=\left(k_{1} / k_{3}\right)} \\
\frac{d}{d t}\left[\mathrm{CH}_{3} \mathrm{CO}\right]=k_{4}\left[\mathrm{CH}_{3}\right]\left[\mathrm{CH}_{3} \mathrm{CHO}\right]+k_{3}[\mathrm{H}]\left[\mathrm{CH}_{3} \mathrm{CHO}\right]-k_{5}\left[\mathrm{CH}_{3} \mathrm{CO}\right]=0
\end{array}
$$

$$
\frac{d}{d t}\left[\mathrm{CH}_{3}\right]=k_{1}\left[\mathrm{CH}_{3} \mathrm{CHO}\right]-k_{4}\left[\mathrm{CH}_{3}\right]\left[\mathrm{CH}_{3} \mathrm{CHO}\right]+k_{5}\left[\mathrm{CH}_{3} \mathrm{CO}\right]-2 k_{6}\left[\mathrm{CH}_{3}\right]^{2}=0
$$

$$
\left[\mathrm{CH}_{3}\right]^{2}=\left(k_{1} / k_{6}\right)\left[\mathrm{CH}_{3} \mathrm{CHO}\right]
$$

rate $=\frac{d}{d t}\left[\mathrm{CH}_{4}\right]=k_{4}\left[\mathrm{CH}_{3}\right]\left[\mathrm{CH}_{3} \mathrm{CHO}\right]=k_{4}\left(k_{1} / k_{6}\right)^{1 / 2}\left[\mathrm{CH}_{3} \mathrm{CHO}\right]^{3 / 2}$

## An Explosive Reaction

Overall: $2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{H}_{2} \rightarrow 2 \mathrm{H}$
$\mathrm{H}+\mathrm{O}_{2} \rightarrow \mathrm{O}+\mathrm{OH}$
$\mathrm{O}+\mathrm{H}_{2} \rightarrow \mathrm{OH}+\mathrm{H}$
$\mathrm{OH}+\mathrm{H}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{H}$
$\mathrm{H} \rightarrow$ wall

$$
\mathrm{H}+\mathrm{O}_{2}+\mathrm{M} \rightarrow \mathrm{HO}_{2}+\mathrm{M}
$$

$\mathrm{HO}_{2}+\mathrm{H}_{2} \rightarrow \mathrm{H}+\mathrm{H}_{2} \mathrm{O}_{2}$
$\mathrm{HO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{OH}+\mathrm{H}_{2} \mathrm{O}_{2}$
initiation
\}branching
propagation
$\}$ termination
$\}$ slow $\begin{aligned} & \text { propagation }\end{aligned}$

At 700 K and 0.1 bar $\mathrm{O}_{2}$,
each initial H atom $\rightarrow 10^{13} \mathrm{H}$ atoms in 0.3 s .

$$
\begin{aligned}
& 0^{N} I^{N} I^{N} \uparrow \quad I^{N} \left\lvert\, \begin{array}{c}
I^{N}
\end{array}\right. \\
& 0^{N} \uparrow I^{N} 0^{N} / \\
& \text { エ エ + エ } \\
& \stackrel{\top}{\mathrm{O}}+\mathrm{O} \\
& \text { エ I } \quad \text { +エ } \\
& \underbrace{2} \prod_{0}^{2} \prod_{0}^{2} \\
& 0^{\sim}{ }_{ \pm}^{\sim}
\end{aligned}
$$

$$
\begin{aligned}
& \overbrace{I}^{\circ} \\
& \text { C } \\
& { }^{\circ} \\
& +{ }_{+}^{T^{2}} \\
& 0^{\sim} \uparrow
\end{aligned}
$$

## Branching Chain Reactions

1 Initiation
2 Branching
3 Propagation
4 Termination (wall)
(combination)

A, B $\rightarrow \mathrm{R}_{1}$
$\mathrm{R}_{1}+\mathrm{A} \rightarrow \mathrm{R}_{2}+\mathrm{R}_{3}$
$[R]$ increases
$\mathrm{B}+\mathrm{R}_{i} \rightarrow \mathrm{R}_{i}+\ldots$
$\mathrm{R}_{i} \rightarrow \mathrm{P}_{1}$
$2 \mathrm{R}_{i} \rightarrow \mathrm{P}_{2}$
$[R]$ decreases

The steady-state approximation does not apply.
If $n$ is the number of radicals at time $t$,

$$
\left.\begin{array}{l}
\frac{d n}{d t}=\rho_{\mathrm{I}}+k_{\mathrm{b}} n-\left(k_{\mathrm{w}}+k_{\mathrm{g}}\right) n \\
\\
=\rho_{\mathrm{I}}+\phi n \\
n
\end{array}\right)=\frac{\rho_{\mathrm{I}}}{\phi}\left(\mathrm{e}^{\phi t}-1\right), \quad \phi=k_{\mathrm{b}}-\left(k_{\mathrm{w}}+k_{\mathrm{g}}\right)
$$

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

## 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 $\rightarrow$ thermal explosion

## Autocatalysis

$$
\mathrm{A}+\mathrm{P} \xrightarrow{k} 2 \mathrm{P}
$$

$$
\begin{aligned}
\text { rate } & =-\frac{d a}{d t}=\frac{d x}{d t} \quad[\mathrm{~A}]=a_{0}-x, \quad[\mathrm{P}]=p_{0}+x \\
\frac{d x}{d t} & =k\left(a_{0}-x\right)\left(p_{0}+x\right) \\
k t & =\int_{0}^{x}\left\{\frac{d x}{\left(a_{0}-x\right)\left(p_{0}+x\right)}\right\} \\
& =\frac{1}{\left(a_{0}+p_{0}\right)} \int_{0}^{x}\left\{\frac{1}{\left(a_{0}-x\right)}+\frac{1}{\left(p_{0}+x\right)}\right\} d x \\
& =\frac{1}{\left(a_{0}+p_{0}\right)}\left[-\ln \left(a_{0}-x\right)+\ln \left(p_{0}+x\right)\right]_{0}^{x} \\
& =\frac{1}{\left(a_{0}+p_{0}\right)} \ln \left\{\frac{a_{0}}{\left(a_{0}-x\right)} \frac{\left(p_{0}+x\right)}{p_{0}}\right\}
\end{aligned}
$$

Substitute $\alpha=\left(a_{0}+p_{0}\right) k, \quad \beta=p_{0} / a_{0}$

$$
\begin{aligned}
& \alpha t=\ln \frac{\left(1+x / p_{0}\right)}{\left(1-\beta x / p_{0}\right)} \\
& x / p_{0}=\frac{\mathrm{e}^{\alpha t}-1}{1+\beta \mathrm{e}^{\alpha t}}
\end{aligned}
$$



## Oscillations in Gas Phase Kinetics

Consider the concentration profile of an intermediate in the $\mathrm{H}_{2}+\mathrm{O}_{2}$ reaction.


What if more reactant is supplied?


## Examples:

Flaring of phosphorus in a loosely stoppered flask (Robert Boyle, 17th century)
Cool flames =limited combustion of hydrocarbons due to "long-lived" intermediates which damp the explosion.

Pre-ignition (autoignition) producing "knock" in auto engines.

## Cool Flame Oscillations

Hydrocarbon fuels spontaneously ignite in the presence of $\mathrm{O}_{2}$ at T > 400-500 K.
"True" ignition gives $\mathrm{CO}, \mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}$ and T increases $\sim 1000 \mathrm{~K}$.
"Cool" flames produce ROH, RCHO, RCOOH and $\Delta \mathrm{T} \sim 100 \mathrm{~K}$


temperature

Oscillations occur because of both chemical and thermal feedback.

chain termination thermal damping

$\longrightarrow ~$| low $T$ |
| :--- |
| chain branching |
| thermal acceleration |

## Oscillating Reactions

The Lotka-Volterra Mechanism

$$
\begin{aligned}
\mathrm{A}+\mathrm{X} & \rightarrow 2 \mathrm{X} \\
\mathrm{X}+\mathrm{Y} & \rightarrow 2 \mathrm{Y} \\
\mathrm{Y} & \rightarrow \mathrm{~B}
\end{aligned}
$$

[A] is held constant (replenished). [X] and [Y] oscillate.
conc.



## Oscillating Reaction Models

Brusselator

$$
\mathrm{A} \rightarrow \mathrm{X}
$$

Prigogine et al

$$
\begin{aligned}
2 \mathrm{X}+\mathrm{Y} & \rightarrow 3 \mathrm{X} \\
\mathrm{~B}+\mathrm{X} & \rightarrow \mathrm{Y}+\mathrm{C} \\
\mathrm{X} & \rightarrow \mathrm{D}
\end{aligned}
$$

[A] and [B] are held constant. [X] and [Y] settle down to a limit cycle:


Oregonator Noyes et al

$$
\begin{aligned}
\mathrm{A}+\mathrm{Y} & \rightarrow \mathrm{X} \\
\mathrm{X}+\mathrm{Y} & \rightarrow \mathrm{C} \\
\mathrm{~B}+\mathrm{X} & \rightarrow 2 \mathrm{X}+\mathrm{Z} \\
2 \mathrm{X} & \rightarrow \mathrm{D} \\
\mathrm{Z} & \rightarrow \mathrm{Y}
\end{aligned}
$$

The $B-Z$ reaction is of this general form, with
$\mathrm{X}=\mathrm{HBrO}_{2}$
$Y=\mathrm{Br}$
$Z=2 \mathrm{Ce}^{4+}$
18 steps, 21 species!

