## CHEM 3011: Chemical Kinetics

## Reactants $R$ transform to products $P$

$$
R \longrightarrow P
$$

$$
R \stackrel{\leftrightarrows}{\leftrightarrows}
$$

- • •
$[R] \searrow$ and $[P] \nearrow$ until equilibrium is reached

$$
R \leftrightarrows P
$$

1. How fast are reactions?
$t_{1 / 2}$ : anywhere between $10^{-14} \mathrm{~s}$ and $10^{10}$ years!
2. How do reactants' concentrations change with time?
$[R](t)$ : sometimes simple (1st or 2 nd order, etc.), sometimes complicated.
3. What can we learn from $[R](t)$ ?
rxn mechanisms: sequence of molecular events
4. How can we control kinetics?

How do we go from

$$
R \xrightarrow{\text { years }} P
$$

to

$$
R \xrightarrow{\text { minutes }} P
$$

or from

$$
P 1 \stackrel{1}{\text { hour }} R^{1} \xrightarrow{\text { hour }} P 2
$$

to

$$
\mathbf{P} 1 \stackrel{1}{\stackrel{\text { min }}{\leftrightarrows}} R \xrightarrow{1 \stackrel{\text { hour }}{\leftrightarrows}} P 2
$$

## Kinetic control vs Thermodynamic control

$$
P 1 \leftarrow R \rightarrow P 2
$$

Activation energies: $E_{a 1}<E_{a 2}$

Reaction energies: $\Delta G_{r x n, 1}^{\circ}>\Delta G_{r x n, 2}^{\circ}$ ( $\Delta G_{r x n, 1}^{\circ}$ and $\Delta G_{r x n, 2}^{\circ}$ both negative)

Near the start of reaction $\left(\left[P_{1}\right]\right.$ and $\left[P_{2}\right] \approx 0$, "small" $t$ ), we have kinetic control.

$$
\begin{gathered}
{\left[P_{1}\right] \sim \exp \left(-E_{a 1} / R T\right)} \\
{\left[P_{2}\right] \sim \exp \left(-E_{a 2} / R T\right)} \\
{\left[P_{2}\right] /\left[P_{1}\right] \sim \exp \left(\left(E_{a 1}-E_{a 2}\right) / R T\right)<1}
\end{gathered}
$$

At "large" $t([R] \approx 0)$ equilibrium is reached and we have thermodynamic control.

$$
\left[P_{2}\right] /\left[P_{1}\right] \approx \exp \left(\left(\Delta G_{r x n, 1}^{\circ}-\Delta G_{r x n, 2}^{\circ}\right) / R T\right)>1
$$

What is a "small" $t$ ? It depends on $E_{a 1}, E_{a 2}$ and $T$. 1 min. could be "small" at $T=77 \mathrm{~K}$ but "large" at $T=373 \mathrm{~K}$. So,
small $t$, low $T \Rightarrow$ kinetic control
long $t$, high $T \Rightarrow$ thermodynamic control

Either way, the selectivity $\left(\left[P_{2}\right] /\left[P_{1}\right]\right.$ or $\left[P_{1}\right] /\left[P_{2}\right]$, whichever is $>1$ ) increases as $T$ decreases.

## How can we achieve control over chemical reactions?

1.1. mix reactants: $A+B \rightarrow P$
1.2. adjust stochiometric ratios, e.g.,

$$
A+2 B \rightarrow A B+B \rightarrow A B_{2}
$$

1.3. ... the order of reagents matters
2. vary $T, P$, solvent, concentrations or areas (for solids)
3. catalysts (affect kinetics only)
4. remove the products (keep $Q<K$ )
5. vary an electric current (electrochemistry)

6 . irradiate with light $(I, \lambda)$
7. sonication: bubbles form and collapse, hot spots with $T \approx 5000 \mathrm{~K}$ and $P \approx 1000$ atm.

How to trigger or stop reactions
triggers:
flame (for ex., $\mathrm{H}_{2}+\mathrm{O}_{2}$ )
light (photochemistry)
spark (combustion engines)
shock (for ex., nitroglycerin)
. .
stops:
remove $A(s)$ or catalyst quickly cool off the mixture, $T$ 】 quickly add Q to quench reactant A :

$$
A+Q \rightarrow \text { inert }
$$

sudden and large change of pH
. . .

## Textbook

Physical Chemistry (PC)
T Engel and P Reid (Pearson Prentice Hall) 3rd edition (2013), chapters 35, 36
or the second half of PC :
Thermodynamics, Statistical thermodynamics, and Kinetics (TSK), chapters 18, 19

René Fournier

Petrie 303, renef@yorku.ca

Office hours: MWF 13:00-14:00

## Grading

2 tests: $25 \%$ each

Exam: 50\%

## Important dates

Fri Oct 14: test \#1 (tentative)

Mon Oct 12: Thanksgiving Holiday

Fri Oct 30: reading day

Mon Nov 9: last day to drop without a grade

Fri Nov 13: test \#2 (tentative)

Mon Dec 7: last day of class

## Some applications of kinetics

1. maximize the yield of a desired product in competing reactions (selectivity, kinetic control)
2. slow down the corrosion of metals
3. speed up the decomposition of garbage
4. model complex systems to predict, and influence, rates of reactions, e.g.:
(a) in car exhaust
(b) in the atmosphere
(c) in the body (drugs, pharmacokinetics)

A chemical equation

$$
a A+b B+\ldots \rightarrow c C+d D+\ldots
$$

is a relation between number of moles.
If at time $t$

$$
n_{A}(t)=n_{A}(0)-a x
$$

then

$$
\begin{gathered}
n_{B}(t)=n_{B}(0)-b x \\
n_{C}(t)=n_{C}(0)+c x \\
\text { etc. }
\end{gathered}
$$

$x(\xi$ in PC$)$ : extent of the reaction

Reaction rate:

$$
\text { Rate }=\frac{d x}{d t}=-\frac{1}{a} \frac{d n_{A}}{d t}=\ldots=\frac{1}{c} \frac{d n_{C}}{d t}=\ldots
$$

Rate, in mole $s^{-1}$, is an extensive property.

We wish to have an intensive property " $R$ ", so we divide by the volume:

$$
R=-\frac{1}{a V} \frac{d n_{A}}{d t}=-\frac{1}{a} \frac{d[A]}{d t}=\ldots
$$

homogeneous rxn: reactants and products are all gases, or all in solution.
heterogeneous rxn: more than one phase (e.g., a solid + gases). The interface plays an essential role.

For now, we limit ourselves to homogeneous reactions.

## Rate law

$$
R=k[A]^{\alpha}[B]^{\beta} \ldots
$$

$\alpha$ : rxn order w.r.t. A
$\beta$ : rxn order w.r.t. B
$k$ is the rate constant. It does not depend on concentrations; but it does depend on $T, P$, solvent, and other things.

Rate laws are determined experimentally

A few examples:

$$
\begin{gathered}
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \\
R=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
\end{gathered}
$$

$$
\begin{gathered}
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{SO}_{3}(\mathrm{~g}) \\
R=k\left[\mathrm{SO}_{2}\right]\left[\mathrm{SO}_{3}\right]^{1 / 2}
\end{gathered}
$$

$$
\begin{gathered}
H_{2}(g)+B r_{2}(g) \rightarrow 2 H B r(g) \\
R=\frac{k\left[H_{2}\right]\left[B r_{2}\right]^{1 / 2}}{1+k^{\prime}\left[H_{2}\right] /\left[B r_{2}\right]}
\end{gathered}
$$

$R$ is in $\mathrm{Ms}^{-1} ;[A],[B], \ldots$ are in M ; so
if $R=k[A], \quad k$ is in $\mathrm{s}^{-1}$
if $\quad R=k[A][B], \quad k$ is in $\mathrm{M}^{-1} \mathrm{~s}^{-1}$
if $R=k[A][P]^{-1 / 2}, \quad k$ is in $\mathrm{M}^{1 / 2} \mathrm{~s}^{-1}$
etc.

To determine a rate of reaction, we need to monitor $[A]$, or $[B]$, or $\ldots$ as a function of time. We need to measure a property that depends on some concentration(s).

- pressure gauge $\left(P=P_{A}+P_{B}+\ldots\right)$
- electric current (in electrochemistry)
- pH meter $\left(\left[H^{+}\right]\right)$
- photoabsorption at wavelength $\lambda$. If no interference, absorbance is $\propto[M]$
- mass spectrometry (for reactions of gas-phase ions)
- a NMR signal

Consider a simple first-order reaction

$$
A \rightarrow P
$$

$[A]=[A]_{t}$, and $R=k[A]_{t}$ varies with time.


## Method of initial rates

$$
\begin{aligned}
A+B & \xrightarrow{k} P \\
\quad R & =k[A]^{\alpha}[B]^{\beta}
\end{aligned}
$$

We can get the 3 unknowns $k, \alpha, \beta$, from a set of 3 experiments ( 3 equations):

- mix A and B with known concentrations
- immediately measure the rate of reaction

| expt |  |  |  |
| :--- | :--- | :--- | :--- |
| $\# 1$ | $[A]_{1}$ | $[B]_{1}$ | $R_{1}$ |
| $\# 2$ | $[A]_{1}$ | $[B]_{2}$ | $R_{2}$ |
| $\# 3$ | $[A]_{3}$ | $[B]_{1}$ | $R_{3}$ |

$$
\begin{aligned}
\frac{R_{2}}{R_{1}} & =\frac{k[A]_{1}^{\alpha}[B]_{2}^{\beta}}{k[A]_{1}^{\alpha}[B]_{1}^{\beta}} \\
& =\left(\frac{[B]_{2}}{[B]_{1}}\right)^{\beta} \\
\beta & =\ln \left(R_{2} / R_{1}\right) \div \ln \left([B]_{2} /[B]_{1}\right)
\end{aligned}
$$

## Likewise

$$
\alpha=\ln \left(R_{3} / R_{1}\right) \div \ln \left([A]_{3} /[A]_{1}\right)
$$

Finally

$$
k=R_{1} \div\left([A]_{1}^{\alpha}[B]_{1}^{\beta}\right)
$$

How do we measure $R$ ?

$$
R=-\frac{1}{a} \lim _{\Delta t \rightarrow 0} \frac{[A](\Delta t)-[A](0)}{\Delta t}
$$

1. chemical methods - stop the reaction (by cooling or quenching) and analyze a sample of the reaction mixture.
2. physical methods - monitor a physical property that depends on $[A]: P, \mathrm{pH}$, current, NMR signal, $I(\lambda), \ldots$

Photoabsorption is particularly useful because we can select a wavelength $\lambda$ (UV, vis, or IR) specific to a molecular species.

## Beer-Lambert law:

$I_{0}$ : intensity of light incident on a sample $I$ : intensity transmitted through the sample $\ell$ : path length of light through the sample $\epsilon_{A}(\lambda)$ : molar absorption coefficient

$$
\ln \left(I_{0}(\lambda) / I(\lambda)\right)=\epsilon_{A}(\lambda)[A] \ell
$$

This equation holds provided:

1. no other species absorbs at $\lambda$;
2. there is no light scattering;
3. the light does not induce chemical reactions;
4. $I_{0}$ is small enough;
5. $[A]$ is small enough.

## time units

$10^{-3} \mathrm{~s}=1 \mathrm{~ms}$ : millisecond
$10^{-6} s=1 \mu s:$ microsecond
$10^{-9} s=1 \mathrm{~ns}$ : nanosecond
$10^{-12} s=1 \mathrm{ps}:$ picosecond
$10^{-15} s=1 \mathrm{fs}$ : femtosecond

## Typical times " $\tau$ "

The period of a vibrational mode at $3300 \mathrm{~cm}^{-1}$ :

$$
\begin{aligned}
\lambda & =(1 / 3300) \mathrm{cm} \\
\tau & =1 / \nu=\lambda / \mathrm{c} \\
& =1 /\left(3300 \mathrm{~cm}^{-1} \times 2.998 \times 10^{10} \mathrm{~cm} / \mathrm{s}\right) \\
& \approx 10^{-14} \mathrm{~s}
\end{aligned}
$$

for a $330 \mathrm{~cm}^{-1}$ mode, $\tau \approx 10^{-13} \mathrm{~s}$

Molecules stay in an excited electronic state ...
fluorescence: $\sim 10^{-9}-10^{-5} \mathrm{~S}$
phosphorescence: $\sim 10^{-4}$ s to several minutes

Time for a molecule to rotate by $180^{\circ}$ :
water $\sim 5 \times 10^{-12} \mathrm{~S}$
small organic molecules $\sim 10^{-10}-10^{-9} \mathrm{~s}$ proteins $\sim 10^{-8}$ to $4 \times 10^{-8} \mathrm{~S}$

Time interval between two successive collisions of a gas molecule with other gas molecules at rt and 1 atm: $\tau \sim 10^{-10} \mathrm{~S}$

Time interval between two successive A-A collisions of a small molecule A in solution at rt , when $[A]=1 \mathrm{M}: \tau \sim 10^{-11} \mathrm{~S}$
If A is very big, $\tau \sim 10^{-9} \mathrm{~s}$.
time resolution, $\Delta t$
chemical methods: $\Delta t \gtrsim 1$ min
stopped-flow (biochemistry): A and B injected with syringes into a mixing chamber.
$\Delta t \gtrsim \mathrm{a}$ few ms
NMR; IR and UV-vis absorption: $\Delta t \gtrsim 10^{-6} s$
flash photolysis (pump-probe): reaction triggered by a light pulse ("pump") and $[A]$ detected by laser spectroscopy ("probe").
$\Delta t \sim 10^{-8} s$ to $10^{-14} s$
for $\mathrm{IR}, \Delta t \gtrsim 10^{-13} s$

## How to initiate a reaction?

1. rapid mixing of reagents
2. addition of a radical initiator
3. pulse of light
4. arc discharge
5. sudden jump in $T$ (or $P, \ldots$ ) $\Rightarrow$ T-jump, perturbation-relaxation methods
reaction mechanism: sequence of elementary reaction steps (or "molecular events") that transform the reactants to products.

The rate law of elementary reactions is directly related to their molecularity. For example:

$$
\begin{aligned}
I_{2} & \rightarrow 2 I \\
R & =k\left[I_{2}\right]
\end{aligned}
$$

$$
\begin{array}{r}
\mathrm{NO}+\mathrm{O}_{3} \rightarrow \mathrm{NO}_{2}+O_{2} \\
R=k[\mathrm{NO}]\left[O_{3}\right]
\end{array}
$$

Consider 3 possible mechanisms for a simple isomerization reaction, $A \rightarrow P$.
first mechanism.

1. $A \leftrightharpoons I \quad$ (quasi equilibrium)
2. $\quad I \rightarrow P$

$$
\begin{aligned}
K_{1} & \approx[I] \div[A] \\
R & =k^{\prime}[I]=\left(k^{\prime} K_{1}\right)[A] \\
R & =k[A]
\end{aligned}
$$

second mechanism.

1. $\quad A \leftrightharpoons I$ (quasi equilibrium)
2. $I+A \rightarrow P+A$

$$
\begin{aligned}
R & =k^{\prime}[I][A]=\left(k^{\prime} K_{1}\right)[A]^{2} \\
R & =k[A]^{2}
\end{aligned}
$$

third mechanism.

$$
\text { 1. } \begin{aligned}
\quad A & \rightarrow P \\
R & =k[A]
\end{aligned}
$$

Suppose that kinetics data shows $R=k[A]$. This proves that mechanism 2 is invalid.

Mechanism 1 and 3 are different but give the same rate law: one can not prove the validity of a mechanism from kinetics data alone.

Observing the presence of the intermediate $I$ would disprove mechanism 3., but it would still not prove that mechanism 1 is correct. Why?

## Integrated rate laws

A rate law relates the rate $R=\frac{-1}{a} d[A] / d t$ to concentrations $[A],[B] \ldots$

An integrated rate law relates $[A]$ (or $[B]$, etc.) to initial concentration(s) and time: $[A](t) \equiv[A]=$ $f\left(t,[A]_{0},[B]_{0}, \ldots\right)$.

$$
\begin{gathered}
\frac{-1}{a} \frac{d[A]}{d t}=k[A]^{\alpha}[B]^{\beta} \\
\frac{-1}{a} \int_{[A]_{0},[B]_{0}}^{[A]_{t}[B]_{t}} \frac{d[A]}{[A]^{\alpha}[B]^{\beta}}=k \int_{0}^{t} d t
\end{gathered}
$$

We solve this on a case-by-case basis.

Integrated rate laws: 1. elementary reactions
1.1 elementary first-order reaction

$$
\begin{aligned}
A & \rightarrow P \\
-R & =\frac{d[A]}{d \tau}=-k[A]
\end{aligned}
$$

$[A]=[A]_{0}$ when $\tau=0,[A]=[A]_{t}$ when $\tau=t$.
For simplicity, write $[A]$ instead of $[A]_{t}$.

$$
\int_{[A]_{0}}^{[A]} \frac{d[A]}{[A]}=-k \int_{0}^{t} d \tau
$$

The antiderivative of $1 / x$ is $\ln x$, so

$$
\begin{gathered}
\ln [A]-\ln [A]_{0}=-k(t-0) \\
\ln \left([A] \div[A]_{0}\right)=-k t \\
{[A]=[A]_{0} e^{-k t}}
\end{gathered}
$$

1.1 (continued)

If $[P]_{0}=0$ then $[P]+[A]=[A]_{0}$ at all times:

$$
[P]=[A]_{0}-[A]=\left(1-e^{-k t}\right)[A]_{0}
$$

It is convenient to plot $\ln [A]$ vs $t$ because

$$
\ln [A]=\ln [A]_{0}-k t
$$

The graph will show a straight line with slope equal to $-k$ and intercept equal to $\ln [A]_{0}$.
half-life $t_{1 / 2}$ : time at which $[A]=[A]_{0} / 2$.

$$
\begin{aligned}
\ln \left(\left([A]_{0} / 2\right) /[A]_{0}\right) & =-k t_{1 / 2} \\
\ln 2 & =k t_{1 / 2} \\
t_{1 / 2} & =\ln 2 / k
\end{aligned}
$$

## 1.2 elementary 2 nd order reaction, case $A+A$

$$
\begin{gathered}
2 A \rightarrow \text { Products } \\
R=-\frac{1}{2} \frac{d[A]}{d \tau}=k[A]^{2} \\
-\int_{[A]_{0}}^{[A]} \frac{d[A]}{[A]^{2}}=2 k \int_{0}^{t} d \tau \\
\frac{1}{[A]}=\frac{1}{[A]_{0}}+2 k t
\end{gathered}
$$

If we plot $\frac{1}{[A]}$ vs $t$, we get a straight line with slope equal to $2 k$ and intercept $\frac{1}{[A]_{0}}$.

The half-life in this case:

$$
\begin{gathered}
\frac{1}{[A]_{0} / 2}=\frac{1}{[A]_{0}}+2 k t_{1 / 2} \\
t_{1 / 2}=\frac{1}{2 k[A]_{0}}
\end{gathered}
$$

## 1.3 elementary 2 nd order reaction, case $A+B$

$$
A+B \rightarrow \text { Products }
$$

$$
R=-\frac{d[A]}{d \tau}=k[A][B]
$$

From the stochiometry we can write

$$
\begin{gathered}
{[A]=[A]_{0}-x} \\
{[B]=[B]_{0}-x=[B]_{0}-[A]_{0}+[A]} \\
{[B]=\Delta+[A]}
\end{gathered}
$$

If $\Delta \neq 0$ :

$$
\begin{gathered}
-\frac{d[A]}{d \tau}=k[A](\Delta+[A]) \\
-\int_{[A]_{0}}^{[A]} \frac{d[A]}{[A](\Delta+[A])}=k \int_{0}^{t} d \tau
\end{gathered}
$$

You can verify that

$$
\int \frac{d x}{x(c+x)}=\frac{-1}{c} \ln \left(\frac{c+x}{x}\right)
$$

then,

$$
\begin{gathered}
\frac{1}{\Delta}\left[\ln \left(\frac{\Delta+[A]}{[A]}\right)-\ln \left(\frac{\left.\Delta+[A]_{0}\right]}{[A]_{0}}\right)\right]=k t \\
\ln \left(\frac{(\Delta+[A])[A]_{0}}{\left(\Delta+[A]_{0}\right)[A]}\right)=\Delta k t \\
\ln \left(\frac{[B][A]_{0}}{[B]_{0}[A]}\right)=\left([B]_{0}-[A]_{0}\right) k t
\end{gathered}
$$

If $\Delta=0,[B]_{0}=[A]_{0}$, and $[B]=[A]$ at all times.

$$
A+B \rightarrow \text { Products }
$$

is just like the case

$$
A+A \rightarrow \text { Products }
$$

with the only difference that now $R=-\frac{d[A]}{d t}$, not $R=\frac{-1}{2} \frac{d[A]}{d t}$. So, with $[A]=[B]$, we end up with

$$
\frac{1}{[A]}=\frac{1}{[A]_{0}}+k t
$$

## 1.4 elementary 3 rd order reaction, case $2 A+M$

The most common case is the recombination reaction

$$
2 A+M \rightarrow A_{2}+M^{*}
$$

$A_{2}$ is collisionally stabilized by M .

Normally $[M] \gg[A]$, in which case

$$
R=k^{\prime}[M][A]^{2} \approx k[A]^{2}
$$

and we are back to case 1.2.

## 1.5 elementary 3rd order reaction, case 3A

$$
3 A \rightarrow \text { Products }
$$

It is a hypothetical case for which

$$
\frac{1}{[A]^{2}}=\frac{1}{[A]_{0}^{2}}+6 k t
$$

## 1.6 elementary 3rd order reaction, $A+B+C$

$$
A+B+C \rightarrow \text { Products }
$$

$$
R=\frac{-d[A]}{d t}=k[A][B][C]
$$

$$
x=[A]_{0}-[A]=[B]_{0}-[B]=[C]_{0}-[C]
$$

$$
\int_{0}^{x} \frac{d x}{\left([A]_{0}-x\right)\left([B]_{0}-x\right)\left([C]_{0}-x\right)}=k \int_{0}^{t} d \tau
$$

We evaluate the lhs by the method of partial fractions

$$
\begin{aligned}
\Delta & =[B]_{0}[C]_{0}\left([B]_{0}-[C]_{0}\right) \\
& +[C]_{0}[A]_{0}\left([C]_{0}-[A]_{0}\right) \\
& +[A]_{0}[B]_{0}\left([A]_{0}-[B]_{0}\right)
\end{aligned}
$$

$$
\begin{aligned}
& \left([B]_{0}-[C]_{0}\right) \ln \left(\frac{[A]_{0}}{[A]}\right)+ \\
& \left([C]_{0}-[A]_{0}\right) \ln \left(\frac{[B]_{0}}{[B]}\right)+ \\
& \left([A]_{0}-[B]_{0}\right) \ln \left(\frac{[C]_{0}}{[C]}\right)=\Delta k t
\end{aligned}
$$

$$
[B]=[A]+\left([B]_{0}-[A]_{0}\right)
$$

$$
[C]=[A]+\left([C]_{0}-[A]_{0}\right)
$$

## Numerical integration

Rate laws can not always be integrated analytically. But numerical methods can always be used. To show this, consider

$$
\begin{aligned}
A & \rightarrow P \\
\frac{d[A]}{d t} & =[A]^{\prime}=-k[A]
\end{aligned}
$$

At $t=0,[A]=[A]_{0}$. A short time $\Delta t$ later

$$
[A]_{\Delta t}=[A]_{0}+[A]_{0}^{\prime} \cdot \Delta t+\frac{1}{2}[A]_{0}^{\prime \prime} \cdot(\Delta t)^{2}+\ldots
$$

$$
[A]_{\Delta t} \approx[A]_{0}-k[A]_{0} \Delta t
$$

Likewise,

$$
[A]_{t+\Delta t} \approx[A]_{t}-k[A]_{t} \Delta t
$$

This particular numerical approach is called Euler's method. The errors in Euler's method are on the order of $(\Delta t)^{2}$ and get compounded when you iterate (*)

Much better numerical methods exist. In particular, the Runge-Kutta 4th order method (RK4) gives errors on the order of $(\Delta t)^{5}$.

RK4

Using the same example, $\frac{d[A]}{d t}=-k[A]$, we go from $t$ to $t+\Delta t$ with these equations.

$$
\begin{aligned}
& a_{1}=-k[A]_{t} \\
& a_{2}=-k\left([A]_{t}+a_{1} \Delta t / 2\right) \\
& a_{3}=-k\left([A]_{t}+a_{2} \Delta t / 2\right) \\
& a_{4}=-k\left([A]_{t}+a_{3} \Delta t\right) \\
& {[A]_{t+\Delta t} \approx[A]_{t}+\frac{1}{6}\left(a_{1}+2 a_{2}+2 a_{3}+a_{4}\right) \Delta t }
\end{aligned}
$$

Note: $a_{1}$ approximates $d[A] / d t$ at the beginning of the time interval; $a_{2}$ and $a_{3}$ approximate $d[A] / d t$ at the middle of the interval; and $a_{4}$ approximates $d[A] / d t$ at the end of the interval.

## Integrated rate laws <br> 2. complex reactions

$\underline{2.1 \text { zeroth order reaction }}$

This can happen with the generic mechanism

1. $A+S \leftrightharpoons A \cdot S \quad$ (quasi equilibrium)
2. $\quad A \cdot S \rightarrow S+$ Products
$A \cdot S$ can be a molecule of A adsorbed on a surface; or it can be a small molecule bound to an enzyme. Suppose $A \cdot S$ is an adsorbate-surface complex.

The surface has $S_{0}$ binding sites, $n$ of which are occupied. Define the coverage $\theta$ :

$$
\theta=n \div S_{0}
$$

The quasi-equilibrium condition gives

$$
\begin{gathered}
k_{f}[A](1-\theta)=k_{r} \theta \\
K_{a d s}=k_{f} / k_{r}=\frac{\theta}{[A](1-\theta)}
\end{gathered}
$$

Rearranging,

$$
\theta=\frac{K_{a d s}[A]}{1+K_{a d s}[A]}
$$

The rate is

$$
R=k_{2} S_{0} \theta=\ldots
$$

$$
R=k_{2} S_{0} \frac{K_{a d s}[A]}{1+K_{a d s}[A]}
$$

If $[A]$ is very small: $R=k_{2} S_{0} K_{\text {ads }}[A]$

If $[A]$ is very large: $K_{a d s}[A] \gg 1, \theta \approx 1$ and

$$
R=k_{2} S_{0}
$$

In this case (zeroth order reaction) $R=k$ and

$$
[A]=[A]_{0}-k t
$$

## 2.2 sequential 1 st order reaction

$$
\begin{aligned}
& A \xrightarrow{k_{A}} I \\
& I \xrightarrow{k_{I}} P
\end{aligned}
$$

The rate of change of the concentrations are

$$
\begin{aligned}
\frac{d[A]}{d t} & =-k_{A}[A] \\
\frac{d[I]}{d t} & =k_{A}[A]-k_{I}[I] \\
\frac{d[P]}{d t} & =k_{I}[I]
\end{aligned}
$$

Assume $[I]_{0}=[P]_{0}=0$. For A we have as before

$$
[A]=[A]_{0} e^{-k_{A} t}
$$

For I:

$$
\frac{d[I]}{d t}=k_{A}[A]_{0} e^{-k_{A} t}-k_{I}[I]
$$

The solution to this differential equation is

$$
[I]=\frac{k_{A}[A]_{0}}{k_{I}-k_{A}}\left(e^{-k_{A} t}-e^{-k_{I} t}\right)
$$

We have $[P]=[A]_{0}-[A]-[I]$, so

$$
[P]=\left(1+\frac{k_{A} e^{-k_{I} t}-k_{I} e^{-k_{A} t}}{k_{I}-k_{A}}\right)[A]_{0}
$$

## Rate-determining step

Take the derivative of $[P]$ Eqn. (18.55)

$$
\frac{d[P]}{d t}=R=\frac{k_{A} k_{I}}{k_{I}-k_{A}}\left(e^{-k_{A} t}-e^{-k_{I} t}\right)[A]_{0}
$$

There are 2 limit cases.
(i) $k_{I} \gg k_{A}$ :

$$
R=k_{A} \exp \left(-k_{A} t\right)[A]_{0}
$$

Any I formed immediately converts to P . P is produced as fast as A is consumed. The first step is rate-determining. Increasing $k_{I}$ would have no effect on $R$. But if we can increase $k_{A}, R$ will increase.
(ii) $k_{A} \gg k_{I}$ :

$$
R=k_{I} \exp \left(-k_{I} t\right)[A]_{0}
$$

All A converts to I before any I has a chance to convert to P . The second step is rate-determining. Increasing $k_{A}$ would have no effect on $R$. But increasing $k_{I}$ would increase $R$.

Note: $d[P] / d t=-d[A] / d t$ at all times in case (i), but not in case (ii).

## Steady state approximation (SSA)

Consider

$$
A \xrightarrow{k_{A}} I_{1} \xrightarrow{k_{1}} I_{2} \xrightarrow{k_{2}} P
$$

Normally $k_{1} \gg k_{A}$ and $k_{2} \gg k_{A}$. The analytical treatment is complicated. If we take:
$k_{A}=0.02 s^{-1}, k_{1}=0.2 s^{-1}, k_{2}=0.2 s^{-1}$,
the numerical (RK4) solution is shown on the next page.

Concentrations vs time (s)


The concentrations of $I_{1}$ and $I_{2}$ vary rapidly at the beginning $(t \lesssim 20 s)$ but slowly later on. We can get a simple analytical solution if we assume

$$
\begin{aligned}
& \frac{d\left[I_{1}\right]}{d t} \approx 0 \\
& \frac{d\left[I_{2}\right]}{d t} \approx 0
\end{aligned}
$$

Then

$$
\begin{gathered}
\frac{d\left[I_{1}\right]}{d t}=k_{A}[A]-k_{1}\left[I_{1}\right] \approx 0 \\
{\left[I_{1}\right] \approx k_{A}[A] \div k_{1}=\frac{k_{A}}{k_{1}}[A]_{0} \exp \left(-k_{A} t\right)}
\end{gathered}
$$

## Likewise,

$$
\begin{gathered}
\frac{d\left[I_{2}\right]}{d t}=k_{1}\left[I_{1}\right]-k_{2}\left[I_{2}\right] \approx 0 \\
{\left[I_{2}\right] \approx k_{1}\left[I_{1}\right] / k_{2} \approx \frac{k_{A}}{k_{2}}[A]_{0} \exp \left(-k_{A} t\right)}
\end{gathered}
$$

and

$$
\frac{d[P]}{d t}=k_{2}\left[I_{2}\right] \approx k_{A}[A]_{0} \exp \left(-k_{A} t\right)
$$

In this case, the SSA leads to $\frac{d[P]}{d t}=-\frac{d[A]}{d t}$, and

$$
[P] \approx[A]_{0}\left(1-\exp \left(-k_{A} t\right)\right)
$$

But is the SSA valid?

Look again at the numerical solution when $k_{A}=0.02 \mathrm{~s}^{-1}, k_{1}=0.2 \mathrm{~s}^{-1}, k_{2}=0.2 \mathrm{~s}^{-1}$.

This time, we plot the derivatives of concentrations.


Next, take the case
$k_{A}=0.02 s^{-1}, k_{1}=2.0 s^{-1}, k_{2}=2.0 s^{-1}$.

Concentrations. The 2nd case has $\mathrm{k}_{\mathrm{A}}=0.02 \mathrm{~s}^{-1}, \mathrm{k}_{1}=\mathrm{k}_{2}=2.0 \mathrm{~s}^{-1}$



## Zoom on the first 10 seconds:



The rate constants for the decay of intermediate species is often orders of magnitude larger than the rate constant for the decay of the reagent. In those cases, the SSA is very good except a very short time after the start of the reaction.

## Parallel reactions

The simplest case is

$$
B \stackrel{k_{B}}{\leftrightarrows} A \xrightarrow{k_{C}} C
$$

$$
\begin{aligned}
& \frac{d[B]}{d t}=k_{B}[A] \\
& \frac{d[C]}{d t}=k_{C}[A]
\end{aligned}
$$

Suppose $[B]_{0}=[C]_{0}=0$, and $k_{B}=2 k_{C}$. Then, at any time $t, \mathrm{~B}$ is produced at twice the rate of C. So, at any time $t,[B]=2[C]$. In general, the selectivity toward B (or "branching ratio") is

$$
[B] \div[C]=k_{B} \div k_{C}
$$

The yield of B is defined as

$$
\Phi_{B}=\frac{k_{B}}{k_{B}+k_{C}}
$$

In general, if A can decay to $n$ different products $P_{1}, P_{2}, \ldots P_{n}$, the yield of species $j$ is

$$
\Phi_{j}=\frac{k_{j}}{\sum_{i=1}^{n} k_{i}}
$$

## Rate constants depend on temperature:

$$
k=A \exp \left(-E_{a} / R T\right)
$$

$A$, in $s^{-1}$, is related to the number of collisions per second between A and $\mathrm{B}\left(\sim Z_{A B}\right)$, or the effective frequency of a vibrational mode, for example, $\nu(\mathrm{C}-\mathrm{C})$ if a $\mathrm{C}-\mathrm{C}$ bond is broken.
$\underline{E_{a}}$ is the activation energy.
$\exp \left(-E_{a} / R T\right) \sim$ fraction of molecules (unimolecular) or collisions (bimolecular) with sufficient energy for reaction to occur.

$$
\ln k=\ln A-\frac{E_{a}}{R T}
$$

Plot $\ln k$ vs $1 / T$ : slope $\frac{-E_{a}}{R}$ and intercept $\ln A$.

In a gas, the fraction of molecules having speed between $v$ and $v+d v$ is $F(v) d v$.

$$
\begin{aligned}
F(v) & =\left(\frac{m}{2 \pi k T}\right)^{3 / 2} 4 \pi v^{2} \exp \left(-m v^{2} / 2 k T\right) \\
& =\left(\frac{1}{2 \pi k T}\right)^{3 / 2} 8 \pi m^{1 / 2} \frac{m v^{2}}{2} e^{-m v^{2} / 2 k T} \\
& =\left(\frac{1}{2 \pi k T}\right)^{3 / 2} 8 \pi m^{1 / 2} E_{\text {trans }} e^{-E_{\text {trans }} / k T}
\end{aligned}
$$

What is a "big" activation energy?

It depends on temperature and ... how long you can wait.

At r.t.
$R T=0.026 \mathrm{eV}=0.59 \mathrm{kcal} / \mathrm{mol}=2.5 \mathrm{~kJ} / \mathrm{mol}$

Obviously $R T$ is different at $77 \mathrm{~K}, 273.15 \mathrm{~K}, 298$ $\mathbf{K}, 310 \mathrm{~K}$, and 373.15 K .

Better theories of reaction rates give a slightly different form for $k(T)$.

$$
\begin{aligned}
k & =a T^{m} \exp \left(-E^{\prime} / R T\right) \\
\ln \left(k / T^{m}\right) & =\ln a-\frac{E^{\prime}}{R T}
\end{aligned}
$$

where $a$ and $E^{\prime}$ are independent of T .

## Transition State Theory:

$$
A+B \xrightarrow{k} \text { Products }
$$

$$
\begin{aligned}
k & =\frac{k_{B} T}{h} \frac{Q^{\ddagger}}{Q_{A} Q_{B}} e^{-E^{\ddagger} / k_{B} T} \\
& =\frac{k_{B} T}{h} e^{-\Delta G_{0}^{\ddagger} / k_{B} T}
\end{aligned}
$$

$E^{\ddagger}$, activation energy $\approx E_{a} \approx E^{\prime}$
$\underline{Q}_{A}$, partition function: number of microstates available to molecule A.
$\Delta G_{0}^{\ddagger}$ : free energy difference between the transition state and reactants.

$$
\Delta G_{0}^{\ddagger}=\Delta H_{0}^{\ddagger}-T \Delta S_{0}^{\ddagger}
$$

## Reversible reactions

For every reaction with rate constant $k_{f}$ there is a possible reverse reaction with rate constant $k_{r}$. Take

$$
\begin{aligned}
& \frac{d[A]}{d t}=-k_{f}[A]+k_{r}[B] \\
& \frac{d[B]}{d t}=k_{f}[A]-k_{r}[B]
\end{aligned}
$$

We must have

$$
[A]_{0}=[A]+[B]
$$

With $k=k_{f}+k_{r}$, the integrated rate law is

$$
[A]=[A]_{0} \frac{k_{r}+k_{f} e^{-k t}}{k}
$$

When $t \rightarrow \infty,[A]=[A]_{e q}$.

$$
\begin{aligned}
{[A]_{e q} } & =[A]_{0} k_{r} / k \\
{[B]_{e q} } & =[A]_{0} k_{f} / k
\end{aligned}
$$

$[A]$ decreases exponentially from $[A]_{0}$ to $[A]_{e q}$ with rate constant $k$. So, at time $t_{1 / 2}=\ln 2 / k$ we have $[A]_{1 / 2}=\left([A]_{0}+[A]_{e q}\right) / 2$.

From the measured $[A]_{e q},[B]_{e q}$, and $t_{1 / 2}$ we get:

$$
\begin{aligned}
K_{c} & =k_{f} / k_{r}=[B]_{e q} /[A]_{e q} \\
k & =k_{f}+k_{r}=\ln 2 / t_{1 / 2}
\end{aligned}
$$

We can show that

$$
[A]=[A]_{e q}+\left([A]_{0}-[A]_{e q}\right) e^{-k t}
$$

$$
\ln \left([A]-[A]_{e q}\right)=\ln \left([A]_{0}-[A]_{e q}\right)-k t
$$

So we can get $k$ by plotting $\ln \left([A]-[A]_{e q}\right)$ vs time and taking the negative of the slope. Or we can plot $[A]$ vs $t$ : the slope at $t=0$ is $-k_{f}[A]_{0}$.

Note: The graph in Fig. 18.16 is correct, but $"[A]_{0} e^{-\left(k_{A}+k_{B}\right) t "}$ is a mistake.

## Temperature-jump method

Start at equilibrium at $T_{1}$

$$
A \leftrightharpoons B
$$

with $k_{f 1}$ and $k_{r 1}$. Suddenly increase the temperature to $T_{2}$ : the rate constants change to $k_{f 2}$ and $k_{r 2}, k_{f 2} / k_{r 2} \neq k_{f 1} / k_{r 1}$, and the system is no longer at equilibrium.

At equilibrium at $T_{2},[A]=[A]_{2}$ and $[B]=[B]_{2}$. Define

$$
\begin{aligned}
x & =[A]-[A]_{2}=[B]_{2}-[B] \\
x_{0} & =[A]_{1}-[A]_{2}
\end{aligned}
$$

At equilibrium:

$$
k_{f 2}[A]_{2}=k_{r 2}[B]_{2}
$$

After the $T$-jump

$$
\begin{gathered}
\qquad \begin{array}{c}
\frac{d x}{d t}=-k_{f 2}[A]+k_{r 2}[B] \\
=-k_{f 2}\left([A]_{2}+x\right)+k_{r 2}\left([B]_{2}-x\right) \\
\frac{d x}{d t}=-\left(k_{f 2}+k_{r 2}\right) x \\
\text { so } x=e^{-\left(k_{f 2}+k_{r 2}\right) t} . \text { Let } \tau=\left(k_{f 2}+k_{r 2}\right)^{-1} \\
x=x_{0} \exp (-t / \tau)
\end{array} .
\end{gathered}
$$

## Potential energy surfaces (PES)

Example:

$$
F+\mathrm{H}_{2} \rightarrow F H+H \quad-133.3 \mathrm{~kJ} / \mathrm{mol}
$$

A microscopic description must include an atomic model of individual reaction events:

- initial positions $\vec{R}_{j}$ and velocities $d \vec{R}_{j} / d t$ of the

3 atoms. If F is atom $1, \vec{R}_{1}=\vec{R}_{F}=\left(x_{1}, y_{1}, z_{1}\right)$.

- forces $\vec{f}_{j}$ acting on the 3 atoms
- time evolution of $\vec{R}_{j}, d \vec{R}_{j} / d t, \vec{f}_{j}$ :

$$
\vec{f}_{j}=m_{j} d^{2} \vec{R}_{j} / d t^{2} \Rightarrow \text { Molecular dynamics }
$$

We can go from a microscopic description to a macroscopic description by averaging over all possible initial positions $\vec{R}_{j}$ and velocities $d \vec{R}_{j} / d t$ with appropriate Boltzmann factors.
complicated!

Forces are derivatives of the potential energy $V$.

$$
\vec{f}_{j, x}=\frac{-\partial V}{\partial x_{j}}
$$

$V$ appears to be a function of 9 coordinates

$$
V \equiv V\left(x_{1}, y_{1}, z_{1}, x_{2}, \ldots, z_{3}\right)
$$

But $V$ does not depend on overall translations (3 degrees of freedom, d.o.f.) or rotations (3 d.o.f.) of FHH. $V$ depends only on $3 \times 3-6=3$ d.o.f.: the $\mathrm{H}-\mathrm{F}$ distance $d_{1}, H-H^{\prime}$ distance $d_{2}$, and $F-H^{\prime}$ distance $d_{3}$.

The PES, $V$, of a $n$-atom system is a function of $(3 n-6)$ variables ( 1 variable when $n=2$ ).

It is hard to visualize a function of more than 2 variables. So imagine that $\mathrm{F}, \mathrm{H}$ and $\mathrm{H}^{\prime}$ move on a line. Then

$$
d_{3}=d_{1}+d_{2}
$$

and the PES

$$
V \equiv V\left(d_{1}, d_{2}\right)
$$

can be visualized.
see J.I. Steinfeld et al., Chemical kinetics and dynamics (Prentice Hall, 1989), page 228.

See also pages 222 and 223.

## On a contour plot

- $\mathrm{FH}+\mathrm{H}^{\prime}$ is a valley
- $\mathrm{F}+\mathrm{HH}^{\prime}$ is another valley
- the separated atoms, $\mathrm{F}+\mathrm{H}+\mathrm{H}^{\prime}$, is a plateau ( $V=0$ is conventional)
- small $d_{1}, d_{2}$, or $d_{3}$ : high $V$, repulsive
- a minimum energy path (MEP) connects the two valleys
- transition state (TS): the highest point along the MEP

The TS is a maximum along the MEP and a minimum perpendicular to it: it is a saddle point. The TS is short-lived (a few vibrational periods, $\sim 10^{-14} s$ ).

At moderate $T$, reactive collisions follow paths that are close to the MEP.

At high $T$, reactive collisions may occur for a wide variety of paths.

Barrier recrossing is possible.
The activation energy $E^{\ddagger}=V_{T S}-V_{\text {reactants }}$

## Transition state theory

$$
A+B \rightarrow P
$$

## Assume that

1. there is an equilibrium between the reactants and the TS:

$$
A+B \leftrightharpoons A B^{\ddagger} \rightarrow P
$$

2. decomposition of the TS to products is described by a single coordinate (reaction coordinate). Then:

$$
\bar{K}_{c}^{\ddagger}=\frac{\left[A B^{\ddagger}\right] c^{\circ}}{[A][B]}
$$

$$
R=k^{\prime}\left[A B^{\ddagger}\right]=k^{\prime} \bar{K}_{c}^{\ddagger}[A][B]=k[A][B]
$$

$\underline{\text { Key results of TS theory. }}$

$$
k=\kappa \frac{k_{B} T}{h c^{\circ}} \bar{K}_{c}^{\ddagger}
$$

$\kappa \leq 1$ : transmission coefficient, one minus the barrier recrossing probability.

$$
k=\kappa \frac{k_{B} T}{h c^{\circ}} e^{\Delta S^{\ddagger} / R} e^{-\Delta H^{\ddagger} / R T}
$$

That's the Eyring equation.

Comparing the Eyring equation to the Arrhenius relation, $k=A e^{-E_{a} / R T}$, one can get expressions for $A$ and $E_{a} \ldots$

For reactions in solution,

$$
\begin{aligned}
E_{a} & =\Delta H^{\ddagger}+R T \\
A & =\frac{e k_{B} T}{h z} e^{\Delta S^{\ddagger} / R}
\end{aligned}
$$

$z=1$ in the unimolecular case, and $z=c^{\circ}$ in the bimolecular case.

For reactions in the gas phase,

$$
\begin{aligned}
E_{a} & =\Delta H^{\ddagger}+m R T \\
A & =\frac{e^{m} k_{B} T}{h z} e^{\Delta S^{\ddagger} / R}
\end{aligned}
$$

$m=1$ for the unimolecular case, and $m=2$ for the bimolecular case. ( $z$ as before)

## In the gas phase:

- molecules move in straight lines
- collisions last a very short time
- usually $E_{a}>3 R T / 2$


## In solution:

- molecules move in a random walk
- when colliding, A and B stay close for some time
- in some cases $E_{a}<3 R T / 2$
- if $E_{a}$ is small, A and B react whenever they collide


Diffusion (random walk) of two molecules, starting at " 1 " and " 2 ", and ending at " 19 " and " 20 ".

## $A+B$ reaction in solution

$$
\begin{gathered}
A+B \xrightarrow{k_{d}} A B \\
A B \xrightarrow{k_{r}} A+B \\
A B \xrightarrow{k_{p}} \text { Products } \\
R=k_{p}[A B]
\end{gathered}
$$

Make the SSA:

$$
\begin{gathered}
\frac{d[A B]}{d t} \approx 0=k_{d}[A][B]-\left(k_{r}+k_{p}\right)[A B] \\
{[A B]=\frac{k_{d}[A][B]}{k_{r}+k_{p}}}
\end{gathered}
$$

and

$$
R=\frac{k_{p} k_{d}[A][B]}{k_{r}+k_{p}}
$$

## Diffusion controlled limit (DCL)

If $k_{p} \gg k_{r}$

$$
R=k_{d}[A][B]
$$

$k_{d}$ depends on how fast molecules diffuse relative to each other $\left(D_{A B}\right)$ and how big they are $\left(r_{A}, r_{B}\right)$ :

$$
k_{d}=4 \pi N_{A}\left(r_{A}+r_{B}\right) D_{A B}
$$

$r_{A}$ : radius of A
$N_{A}$ : Avogadro's constant
$D_{A B}=D_{A}+D_{B}$, and

$$
D_{A}=\frac{k_{B} T}{6 \pi \eta r_{A}}
$$

$\eta$ is the viscosity of the solvent.

$$
\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}
$$

$$
\begin{aligned}
& D_{A}=1.1 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1} \\
& D_{B}=9.3 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1} \\
& r_{A}+r_{B} \approx 5 \AA .
\end{aligned}
$$

$$
\begin{aligned}
k_{d} & \approx 4 \pi \times 6.02 \times 10^{23} \mathrm{~mol}^{-1} \\
& \times 5 \times 10^{-8} \mathrm{~cm} \\
& \times 10.4 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1} \\
& =3.9 \times 10^{13} \mathrm{~cm}^{3} \mathrm{~s}^{-1} \mathrm{~mol}^{-1} \\
& =3.9 \times 10^{10} \mathrm{Lmol}^{-1} \mathrm{~s}^{-1} \\
& =3.9 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

1. reactions between ions can be faster than the DCL because of long-range Coulombic attractions.
2. in the DCL:
rate $\propto$ inverse of solvent's viscosity
$R \propto T$

## Activation controlled limit

if $k_{p} \ll k_{r}$

$$
R=\frac{k_{p} k_{d}}{k_{r}}[A][B]
$$

## 19. Reaction mechanisms

A reaction mechanism is a series of molecular events (steps, elementary reactions) that describe how reactants transform to products.

- it is a hypothesis
- it can be disproved by experiments, but can not be proved
- the predicted rate law or intermediate(s) may be tested experimentally

$$
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \rightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)
$$

The observed rate law is $R=k\left[N_{2} O_{5}\right]$. A proposed mechanism:

$$
\begin{aligned}
& \text { 1. } 2 \times\left(\mathrm{N}_{2} \mathrm{O}_{5} \leftrightharpoons \mathrm{NO}_{2}+\mathrm{NO}_{3}\right) \\
& \text { 2. } \mathrm{NO}_{2}+\mathrm{NO}_{3} \rightarrow \mathrm{NO}_{2}+\mathrm{O}_{2}+\mathrm{NO} \\
& \text { 3. } \mathrm{NO}+\mathrm{NO}_{3} \rightarrow 2 \mathrm{NO}_{2}
\end{aligned}
$$

with rate constants $k_{1}, k_{-1}, k_{2}$, and $k_{3}$.
$\mathrm{NO}_{3}, \mathrm{NO}$ : intermediates

The stochiometric number of step 1 . is " 2 ".

If we ignore the kinetics at very short time and make the steady-state approximation (SSA):

$$
R=\frac{-1}{2} \frac{d\left[N_{2} O_{5}\right]}{d t}=\frac{d\left[O_{2}\right]}{d t}=\frac{1}{4} \frac{d\left[N O_{2}\right]}{d t}
$$

We can use any of the 3 expressions for $R$. The most convenient is $R=\frac{d\left[O_{2}\right]}{d t}$ because $\left[O_{2}\right]$ is affected by only one process, forward step 2 .

$$
R=\frac{d\left[O_{2}\right]}{d t}=k_{2}\left[N O_{2}\right]\left[N O_{3}\right]
$$

With 2 intermediates, and the SSA, we get 2 equations. The first is

$$
\begin{gathered}
\frac{d[N O]}{d t} \approx 0=k_{2}\left[N O_{2}\right]\left[N O_{3}\right]-k_{3}[N O]\left[N O_{3}\right] \\
{[N O]=\frac{k_{2}\left[N O_{2}\right]}{k_{3}}}
\end{gathered}
$$

The second is

$$
\begin{aligned}
\frac{d\left[N O_{3}\right]}{d t} \approx & 0=k_{1}\left[N_{2} O_{5}\right]-k_{-1}\left[N O_{2}\right]\left[N O_{3}\right] \\
& -k_{2}\left[N O_{2}\right]\left[N O_{3}\right]-k_{3}[N O]\left[N O_{3}\right] \\
= & k_{1}\left[N_{2} O_{5}\right]-k_{-1}\left[N O_{2}\right]\left[N O_{3}\right] \\
& -k_{2}\left[N O_{2}\right]\left[N O_{3}\right]-k_{3} \frac{k_{2}\left[N O_{2}\right]}{k_{3}}\left[N O_{3}\right]
\end{aligned}
$$

Rearranging:

$$
\left[N O_{2}\right]\left[N O_{3}\right]=\frac{k_{1}\left[N_{2} O_{5}\right]}{k_{-1}+2 k_{2}}
$$

Recall $R=k_{2}\left[\mathrm{NO}_{2}\right]\left[\mathrm{NO}_{3}\right]$, so

$$
R=\frac{k_{1} k_{2}}{k_{-1}+2 k_{2}}\left[N_{2} O_{5}\right]=k\left[N_{2} O_{5}\right]
$$

## Pre-equilibrium Approximation (PEA)

$$
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{NO}_{2}(g)
$$

mechanism:

$$
\begin{aligned}
& \text { 1. } 2 \mathrm{NO} \leftrightharpoons \mathrm{~N}_{2} \mathrm{O}_{2} \quad \text { (preequilibrium) } \\
& \text { 2. } \mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}
\end{aligned}
$$

The overall rate is $R=\frac{-d\left[O_{2}\right]}{d t}=k_{2}\left[N_{2} O_{2}\right]\left[O_{2}\right]$. $\mathrm{SSA}: \frac{d\left[\mathrm{~N}_{2} \mathrm{O}_{2}\right]}{d t} \approx 0$.

$$
\begin{gathered}
0=k_{1}[N O]^{2}-k_{-1}\left[N_{2} O_{2}\right]-k_{2}\left[N_{2} O_{2}\right]\left[O_{2}\right] \\
{\left[N_{2} O_{2}\right]=\frac{k_{1}[N O]^{2}}{k_{-1}+k_{2}\left[O_{2}\right]}}
\end{gathered}
$$

so

$$
R=k_{2}\left[O_{2}\right] \frac{k_{1}[N O]^{2}}{k_{-1}+k_{2}\left[O_{2}\right]}
$$

If $k_{2}\left[O_{2}\right] \ll k_{-1}$, this simplifies to

$$
\begin{aligned}
R & =k_{2}\left[O_{2}\right] \frac{k_{1}}{k_{-1}}[N O]^{2} \\
& =k_{2} K_{1}\left[O_{2}\right][N O]^{2}
\end{aligned}
$$

where $K_{1}$ is the equilibrium constant for step 1 ,

$$
K_{1} \equiv \frac{k_{1}}{k_{-1}}=\frac{N_{2} O_{2}}{[N O]^{2}}
$$

So, making the SSA and assuming $k_{2}\left[O_{2}\right] \ll k_{-1}$ is just like assuming that step 1 . reached equilibrium. That's the "PEA".

# Unimolecular dissociation and the 

## Lindemann mechanism

We look at the gas-phase dissociation of A $A \rightarrow$ fragments

How do molecules of "A" acquire enough energy to break? Normally through collisions with other molecules "M", where M may be A, or may be different. The assumed mechanism is:

1. $\quad A+M \leftrightharpoons A^{*}+M$
2. $\quad A^{*} \rightarrow P$
$A^{*}$ represents a molecule of A with sufficient internal energy to break.

$$
\begin{gathered}
\frac{d\left[A^{*}\right]}{d t}=k_{1}[A][M]-k_{-1}\left[A^{*}\right][M]-k_{2}\left[A^{*}\right]=0 \\
{\left[A^{*}\right]=\frac{k_{1}[A][M]}{k_{-1}[M]+k_{2}}}
\end{gathered}
$$

Then:

$$
\begin{aligned}
\frac{d[P]}{d t} & =k_{2}\left[A^{*}\right] \\
& =\frac{k_{2} k_{1}[A][M]}{k_{-1}[M]+k_{2}}
\end{aligned}
$$

Two limiting cases:
case 1. $k_{-1}[M] \gg k_{2}$

$$
\frac{d[P]}{d t}=\frac{k_{2} k_{1}}{k_{-1}}[A]
$$

case 2. $k_{-1}[M] \ll k_{2}$

$$
\frac{d[P]}{d t}=k_{1}[M][A]
$$

Back to the general case, we define

$$
k_{u n i}=\frac{k_{2} k_{1}[M]}{k_{-1}[M]+k_{2}}
$$

so that

$$
\frac{d[P]}{d t}=k_{u n i}[A]
$$

When $[M]$, or the pressure $P_{M}=R T\left(n_{M} / V\right)$, is high we are in case 1: $k_{\text {uni }}$ does not change if we increase $[M]$. If $[M]$ is low, $k_{\text {uni }}$ increases linearly with $[M]$. Take $1 / k_{u n i}$ :

$$
\frac{1}{k_{u n i}}=\frac{k_{-1}}{k_{1} k_{2}}+\left(\frac{1}{k_{1}}\right) \frac{1}{[M]}
$$

A plot of $1 / k_{\text {uni }}$ vs $1 /[M]$ is a straight line with slope $k_{1}$.

Catalyst. A substance that increases the rate of a reaction, but is not produced or consumed in the reaction.

Catalysts work by opening up alternative reaction paths that have lower activation energies $E_{a}$.

Some catalysts bind to, and stabilize, the transition state.

A simple catalytic mechanism, with $\mathrm{C}=$ catalyst, and $\mathrm{SC}=$ substrate-catalyst complex.

$$
\begin{aligned}
& \text { 1. } \quad S+C \leftrightharpoons S C \\
& \text { 2. } \quad S C \rightarrow P+C
\end{aligned}
$$

Applying the SSA to the intermediate "SC" we get

$$
\begin{gathered}
{[S C]=\frac{k_{1}}{k_{-1}+k_{2}}[S][C] \equiv \frac{[S][C]}{K_{m}}} \\
\frac{d[P]}{d t}=k_{2}[S C]=\frac{k_{2}[S][C]}{K_{m}}
\end{gathered}
$$

Often, we know only the initial concentrations $[S]_{0}$ and $[C]_{0}$.

$$
\begin{gathered}
{[C]=[C]_{0}-[S C]} \\
{[S]=[S]_{0}-[S C]-[P] \approx[S]_{0}-[S C]}
\end{gathered}
$$

We assume that $[P]$ is very small: one often removes P to drive the reaction forward.
$[S][C]=K_{m}[S C] \approx\left([S]_{0}-[S C]\right)\left([C]_{0}-[S C]\right)$
$[S C]$ is small compared to $[S]_{0}$ and $[C]_{0}$. So we neglect $[S C]^{2}$, and rearrange to

$$
\begin{gathered}
K_{m}[S C] \approx[S]_{0}[C]_{0}-[S C]\left([S]_{0}+[C]_{0}\right) \\
{[S C] \approx \frac{[S]_{0}[C]_{0}}{[S]_{0}+[C]_{0}+K_{m}}}
\end{gathered}
$$

The rate is

$$
R=\frac{d[P]}{d t} \approx R_{0}=\frac{k_{2}[S]_{0}[C]_{0}}{[S]_{0}+[C]_{0}+K_{m}}
$$

$R \approx R_{0}$ provided $[P]$ and $[S C]$ are small compared to $[S]_{0}$ and $[C]_{0}$. We have two limiting cases.

The most common case is $\mathbf{1}$ : $[C]_{0} \ll[S]_{0}$

$$
\begin{gathered}
R_{0}=\frac{k_{2}[S]_{0}[C]_{0}}{[S]_{0}+K_{m}} \\
\frac{1}{R_{0}}=\left(\frac{K_{m}}{k_{2}[C]_{0}}\right) \frac{1}{[S]_{0}}+\frac{1}{k_{2}[C]_{0}}
\end{gathered}
$$

If we know $[C]_{0}$, we find $k_{2}$ from the intercept of a plot of $1 / R_{0}$ vs $1 /[S]_{0}$. Then, from the slope, we get $K_{m}$.

If $[S]_{0}$ is very large, $R_{0}=k_{2}[C]_{0}$ : that's the upper limit for the rate of reaction.

The other case is 2: $[C]_{0} \gg[S]_{0}$

$$
R_{0}=\frac{k_{2}[S]_{0}[C]_{0}}{[C]_{0}+K_{m}}
$$

But catalysts are often expensive, so $[C]_{0} \gg[S]_{0}$ is uncommon.

Enzymes are proteins that catalyze chemical reactions in living organisms.

Through evolution, enzymes became extremely efficient.

The Michaelis-Menten mechanism can often describe enzymatic kinetics.

1. A substrate $S$ selectively binds to a site of the enzyme $E$ to form the complex $E S$. ("lock-and-key" model)
2. The complex $E S$ may go back to unreacted substrate, or give products.

$$
\begin{aligned}
& \text { 1. } \quad E+S \leftrightharpoons E S \\
& \text { 2. } \quad E S \rightarrow E+P
\end{aligned}
$$

It is the same mechanism we just saw, case 1 :

$$
R_{0}=\frac{k_{2}[S]_{0}[E]_{0}}{[S]_{0}+K_{m}}=\frac{R_{\max }[S]_{0}}{[S]_{0}+K_{m}}
$$

$K_{m}$ is called the Michaelis constant.

As before, the maximum rate is $k_{2}[E]_{0} \equiv R_{\max }$. Then,

$$
\frac{1}{R_{0}}=\left(\frac{K_{m}}{R_{\max }}\right) \frac{1}{[S]_{0}}+\frac{1}{R_{\max }}
$$

A plot of $1 / R_{0}$ vs $1 /[S]_{0}$ is called a LineweaverBurk plot.

The turnover number of an enzyme is $k_{2}=R_{\max } /[E]_{0}$, in $s^{-1}$.

It is the maximum number of product molecules generated by one enzyme per second.

Turnover numbers between 1 and $10^{5} \mathrm{~s}^{-1}$ are common.

# Let's see what happens when $[S]_{0}=K_{m}$. Then 

$$
R_{0}=\frac{R_{\max } K_{m}}{K_{m}+K_{m}}=R_{\max } / 2
$$

So $K_{m}$ has a simple meaning: it is the value of $[S]_{0}$ needed to achieve $50 \%$ of the maximum possible reaction rate.

If $[S]_{0}$ and $[C]_{0}$ are both very small compared to $K_{m}, \quad R_{0}=\left(k_{2} / K_{m}\right)[S]_{0}[C]_{0}$.
$k_{2} / K_{m}$ is called the catalytic efficiency.

|  | $k_{2}(1 / \mathrm{s})$ | $K_{m}(\mathrm{M})$ | $k_{2} / K_{m}$ |
| :---: | :--- | :--- | :--- |
| chymotrypsin | 0.14 | $1.5 \times 10^{-2}$ | 9.3 |
| firefly luciferase | 0.048 | $5.4 \times 10^{-4}$ | 89 |
| pepsin | 0.50 | $3.0 \times 10^{-4}$ | $1.7 \times 10^{3}$ |
| ribonuclease | 790 | $7.9 \times 10^{-3}$ | $1.0 \times 10^{5}$ |
| fumerase | 800 | $5.0 \times 10^{-6}$ | $1.6 \times 10^{8}$ |

The upper limit of $k_{2} / K_{m}$ is set by diffusion into the active site, it is around $10^{8}$ to $10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$.

A competitive inhibitor I:

- is structurally similar to S ,
- binds to the same enzyme active site,
- but does not react.

With inhibitor I:

$$
\begin{aligned}
& E+S \leftrightharpoons E S \\
& E S \rightarrow E+P \\
& E+I \leftrightharpoons E I
\end{aligned}
$$

Now $[E]_{0}=[E]+[E S]+[E I]$.
We use the PEA and assume that $k_{2}$ is small,

$$
\begin{aligned}
K_{s} & =\frac{k_{-1}}{k_{1}}=\frac{[E][S]}{[E S]} \approx \frac{k_{-1}+k_{2}}{k_{1}}=K_{m} \\
K_{i} & =\frac{k_{-3}}{k_{3}}=\frac{[E][I]}{[E I]}
\end{aligned}
$$

Rewrite $[E]$ and $[E I]$,
substitute in $[E]_{0}=[E]+[E S]+[E I]$,
and solve for $[E S] \ldots$

Assuming $[S] \approx[S]_{0}$, the rate, $R=k_{2}[E S]$, is

$$
R \approx \frac{k_{2}[S]_{0}[E]_{0}}{[S]_{0}+K_{m}\left(1+\frac{[I]}{K_{i}}\right)}
$$

as before with $K_{m}$ changed to $K_{m}^{*} \equiv K_{m}\left(1+\frac{[I]}{K_{i}}\right)$.
We also get the same equations for $R_{0}$ and $1 / R_{0}$, with $K_{m}$ replaced by $K_{m}^{*}$.
$K_{m}^{*}>K_{m}$, so $R_{0}$ decreases in the presence of an inhibitor.

Many metabolic regulators, drug molecules, and poisons, are competitive inhibitors (CI).

* some CI are involved in negative feedback. They slow down an enzymatic reaction when products build up $\Rightarrow$ homeostasis, the ability of a cell (or an organism) to maintain stable conditions ( $T$, $\left.\mathrm{pH},\left[N a^{+}\right],\left[K^{+}\right], \ldots\right)$.
* some CI drugs kill bacteria or viruses by binding to enzymes used in their replication.
* other CI drugs correct a metabolic imbalance by slowing down a reaction.
* protein kinase inhibitors are used in the treatment of cancers and inflammations.
* snake venoms often contain powerful inhibitors. The king cobra's venom has alpha-neurotoxins that mimick the shape of acetylcholine, bind to its receptors on motor neurons, and cause paralysis.

Research on venoms may lead to new drugs!

* snakes evolved more powerful venoms while mongooses, opposums, and others evolved better resistance. That's the evolutionary arms race.
* humans evolved the phamaceutical industry ...


# A homogeneous catalyst is in the same phase as the reactants and products. 

A heterogeneous catalyst is in a different phase (usually solid).

## Gas-phase catalyzed ozone decomposition

$$
\begin{array}{ll}
\text { 1. } & \mathrm{Cl}+\mathrm{O}_{3} \rightarrow \mathrm{ClO}+\mathrm{O}_{2} \\
\text { 2. } & \mathrm{ClO}+\mathrm{O} \rightarrow \mathrm{Cl}+\mathrm{O}_{2}
\end{array}
$$

net:

$$
O_{3}+O \rightarrow 2 O_{2}
$$

Cl is an intermediate, but of a special kind: in the absence of Cl and ClO , this mechanism can not start.

In the absence of $\mathrm{Cl}, R \equiv R_{n c}=k_{n c}[O]\left[O_{3}\right]$, with $k_{n c}=3.30 \times 10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-1}$.

With $\mathrm{Cl}, k_{1}=1.56 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$
and $k_{2}=2.44 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$.

With the catalyzed mechanism and SSA,

$$
\begin{gathered}
\frac{d[\mathrm{Cl}]}{d t}=0=-k_{1}[\mathrm{Cl}]\left[\mathrm{O}_{3}\right]+k_{2}[\mathrm{ClO}][\mathrm{O}] \\
{[\mathrm{ClO}]=\frac{k_{1}[\mathrm{Cl}]\left[\mathrm{O}_{3}\right]}{k_{2}[\mathrm{O}]}}
\end{gathered}
$$

Then we make the SSA for the sum of intermediate concentrations:

$$
[\mathrm{Cl}]+[\mathrm{ClO}]=[\mathrm{Cl}]_{\text {total }}
$$

where $[C l]_{\text {total }}$ is a constant. Then

$$
\begin{gathered}
{[C l]=[C l]_{\text {total }}-\frac{k_{1}[C l]\left[O_{3}\right]}{k_{2}[O]}} \\
{[C l]=\frac{[C l]_{t o t a l} k_{2}[O]}{k_{1}\left[O_{3}\right]+k_{2}[O]}}
\end{gathered}
$$

The rate is

$$
R_{\text {cat }}=k_{1}\left[O_{3}\right][C l]=\frac{k_{1} k_{2}[C l]_{\text {total }}[O]\left[O_{3}\right]}{k_{1}\left[O_{3}\right]+k_{2}[O]}
$$

Ozone is reactive, but much less than O atoms, so $\left[O_{3}\right] \gg[O]$ and we can neglect $k_{2}[O]$ in the denominator:

$$
R_{c a t}=k_{2}[C l]_{t o t a l}[O]
$$

The ratio of rates $R_{\text {cat }} / R_{n c}=k_{2}[C l]_{\text {total }} / k_{n c}\left[O_{3}\right]$.

Using the numerical values of $k_{2}, k_{n c}$, and $[C l]_{\text {total }} /\left[O_{3}\right] \approx 10^{-3}$, we find $R_{\text {cat }} / R_{n c} \approx 74$.

Elimination of anthropogenic Cl in the atmosphere is crucial for preserving the ozone layer.

Rowland and Molina hypothesized that photolysis of $\mathrm{CFCl}_{3}$ and $\mathrm{CF}_{2} \mathrm{Cl}_{2}$ ("freon", used in old refrigerators and aerosols) was a major source of Cl . These compounds are being phased out.

## Solid catalysts

A key step is often the adsorption of gas molecules $A$ on a solid catalyst's surface

$$
A(g)+M(\text { surface }) \leftrightharpoons A \cdot M(\text { surface })
$$

M represents an adsorption site on the surface. Assume there are $N$ of them. The Langmuir model assumes that:

1. At most $N$ molecules can adsorb on the surface.
2. All the surface sites are equivalent.
3. Adsorption and desorption at a site happens independently of the other sites.

Define the coverage $\theta=V_{\text {ads }} / V_{m}$ : fraction of sites occupied by $A$, and $P=$ pressure of $A(g)$.
$V_{m}$ : maximum volume of gas that can be adsorbed.

$$
\frac{d \theta}{d t}=k_{a} P N(1-\theta)-k_{d} N \theta
$$

At equilibrium, $d \theta / d t=0$ and we get

$$
\theta=\frac{k_{a} P}{k_{a} P+k_{d}}=\frac{K P}{K P+1}
$$

$K=k_{a} / k_{d}$. This is the Langmuir isotherm.

$$
1 / \theta=1+(1 / K)(1 / P)
$$

$\ln K$ vs $1 / T$ is a line with slope $-\Delta H_{a d s} / R$
( Recall $K=\exp \left(-\Delta G_{a d s}^{\circ} / R T\right)$

$$
\left.=\exp \left(-\Delta H_{a d s}^{\circ} / R T+\Delta S_{a d s}^{\circ} / R\right)\right)
$$

As $P \nearrow, \theta \rightarrow 1$.

As $K \searrow, P$ needed to get $\theta \approx 1 \nearrow$

In dissociative chemisorption a molecule " $\mathrm{A}_{2}$ " breaks into two fragments A upon adsorption:

$$
A_{2}(g)+2 M(\text { surface }) \rightarrow 2 A \cdot M(\text { surface })
$$

and we get a somewhat different expression for $\theta$,

$$
\theta=\frac{(K P)^{1 / 2}}{1+(K P)^{1 / 2}}
$$

Surfaces " $M(s)$ " are often far from uniform, and the kinetics of reaction can be dominated by surface defects:

- M vacancy
- M adatom
- steps
- kinks


## Radical-chain reactions

Radicals $\left(\mathrm{CH}_{3} \cdot \mathrm{Cl} \cdot, \mathrm{HO} \cdot, \ldots\right)$ are extremely reactive.

Small amounts of $R$ - can trigger reactions that would not happen otherwise.
initiation steps: molecule $(s) \rightarrow R$.
propagation steps: the "main mechanism"
termination steps: $R \cdot \rightarrow$ molecule(s)

The propagation steps add up to the net reaction.
initiation 1. $\mathrm{C}_{2} \mathrm{H}_{6} \rightarrow 2 \mathrm{CH}_{3}$.

$$
\text { 2. } \mathrm{CH}_{3} \cdot+\mathrm{C}_{2} \mathrm{H}_{6} \rightarrow \mathrm{CH}_{4}+\mathrm{C}_{2} \mathrm{H}_{5} \text {. }
$$

propagation 3. $\mathrm{C}_{2} \mathrm{H}_{5} \cdot \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}+\mathrm{H}$.

$$
\text { 4. } H \cdot+C_{2} H_{6} \rightarrow C_{2} H_{5} \cdot+H_{2}
$$

termination $\quad$ 5. $\mathrm{H} \cdot+\mathrm{C}_{2} \mathrm{H}_{5} \cdot \rightarrow \mathrm{C}_{2} \mathrm{H}_{6}$
$\Delta H$ for each step:

$$
\begin{aligned}
& 1:+90 \mathrm{kcal} / \mathrm{mol} \\
& 2:-4.3 \mathrm{kcal} / \mathrm{mol} \\
& 3:+36 \mathrm{kcal} / \mathrm{mol} \\
& 4:-3.6 \mathrm{kcal} / \mathrm{mol} \\
& 5:-101 \mathrm{kcal} / \mathrm{mol},
\end{aligned}
$$

steps 1 and 5 are rare events; step 2 is "fed" $\mathrm{CH}_{3}$. by step 1 only; steps 3 and 4 feed each other.

The only step where $\mathrm{C}_{2} \mathrm{H}_{4}$ is produced is 3 ., so the rate for the overall reaction is

$$
R=k_{3}\left[C_{2} H_{5} \cdot\right]
$$

let $R \cdot=H \cdot, \mathrm{CH}_{3} \cdot$, or $\mathrm{C}_{2} \mathrm{H}_{5}$.

$$
\begin{aligned}
& 0 \approx \frac{d[R \cdot]}{d t}= 2 k_{1}\left[C_{2} H_{6}\right]-2 k_{5}[H \cdot]\left[C_{2} H_{5} \cdot\right] \\
& {[H \cdot]=\frac{k_{1}\left[C_{2} H_{6}\right]}{k_{5}\left[C_{2} H_{5} \cdot\right]} } \\
& 0 \approx \frac{d[H \cdot]}{d t}= k_{3}\left[C_{2} H_{5} \cdot\right] \\
&-k_{4}\left[C_{2} H_{6}\right]\left(\frac{k_{1}\left[C_{2} H_{6}\right]}{k_{5}\left[C_{2} H_{5} \cdot\right]}\right) \\
&-k_{5}\left[C_{2} H_{5} \cdot\right]\left(\frac{k_{1}\left[C_{2} H_{6}\right]}{k_{5}\left[C_{2} H_{5} \cdot\right]}\right)
\end{aligned}
$$

Let $x=\left[C_{2} H_{5} \cdot\right]$ and multiply by $x / k_{3}$ everywhere

$$
0=x^{2}-\frac{k_{1}}{k_{3}}\left[C_{2} H_{6}\right] x-\frac{k_{1} k_{4}}{k_{3} k_{5}}\left[C_{2} H_{6}\right]^{2}
$$

It is a quadratic equation for $x$ with solutions

$$
\begin{aligned}
x= & \frac{k_{1}}{2 k_{3}}\left[C_{2} H_{6}\right] \\
& \pm\left(\left(\frac{k_{1}}{2 k_{3}}\left[C_{2} H_{6}\right]\right)^{2}+\frac{k_{1} k_{4}}{k_{3} k_{5}}\left[C_{2} H_{6}\right]^{2}\right)^{1 / 2} \\
x= & {\left[C_{2} H_{6}\right]\left[\frac{k_{1}}{2 k_{3}} \pm\left(\left(\frac{k_{1}}{2 k_{3}}\right)^{2}+\frac{k_{1} k_{4}}{k_{3} k_{5}}\right)^{1 / 2}\right] }
\end{aligned}
$$

- we keep the "+" sign, or else $x<0$
- $k_{1}$ is very small, so we neglect $\left(k_{1} / 2 k_{3}\right)^{2}$, and
then neglect $\left(k_{1} / 2 k_{3}\right)$, so all that's left is

$$
\left[C_{2} H_{5} \cdot\right]=x=\left(\frac{k_{1} k_{4}}{k_{3} k_{5}}\right)^{1 / 2}\left[C_{2} H_{6}\right]
$$

SO

$$
\begin{aligned}
& R=k_{3}\left[C_{2} H_{5} \cdot\right]=k_{3}\left(\frac{k_{1} k_{4}}{k_{3} k_{5}}\right)^{1 / 2}\left[C_{2} H_{6}\right] \\
& R=\left(\frac{k_{1} k_{3} k_{4}}{k_{5}}\right)^{1 / 2}\left[C_{2} H_{6}\right]
\end{aligned}
$$

## Radical-chain polymerization

We have radicals $R$. formed by cleavage of an minitiator $I$, and monomers $M$ :
initiation

$$
\begin{equation*}
I \rightarrow 2 R \tag{i}
\end{equation*}
$$

$$
\begin{equation*}
R \cdot+M \rightarrow M_{1} \tag{1}
\end{equation*}
$$

propagation

$$
\begin{align*}
& M_{1} \cdot+M \rightarrow M_{2} . \\
& M_{2} \cdot+M \rightarrow M_{3} . \tag{p}
\end{align*}
$$

$$
M_{n-1} \cdot+M \rightarrow M_{n}
$$

$$
M_{m} \cdot+M_{n} \cdot \rightarrow M_{m+n}
$$

Let $[M \cdot]=\left[M_{1} \cdot\right]+\left[M_{2} \cdot\right]+\left[M_{3} \cdot\right]+\ldots$ We apply the SSA to $[M \cdot]$.

$$
\frac{d[M \cdot]}{d t}=2 \phi k_{i}[I]-2 k_{t}[M \cdot]^{2} \approx 0
$$

$\phi$ is the probability that $R$. reacts with M , and not with something else.

$$
\begin{gathered}
{[M \cdot]=\left(\frac{\phi k_{i}}{k_{t}}\right)^{1 / 2}[I]^{1 / 2}} \\
\frac{d[M]}{d t}=-k_{p}[M \cdot][M]-\left(k_{1}[R \cdot][M]\right) \\
\approx-k_{p}\left(\frac{\phi k_{i}}{k_{t}}\right)^{1 / 2}[I]^{1 / 2}[M]
\end{gathered}
$$

The kinetic chaing length $\nu$ is the ratio of (a) the rate of consumption of M , to (b) the rate of creation of $M_{1}$.

$$
\begin{aligned}
\nu & =\frac{k_{p}[M \cdot][M]}{2 \phi k_{i}[I]} \\
\nu & =\frac{k_{p}[M]}{2\left(\phi k_{i} k_{t}\right)^{1 / 2}[I]^{1 / 2}}
\end{aligned}
$$

The average length of polymers $\nu$ determines the properties of a material, and it can be controlled by the choice of $[I]$.

## Explosions

Two types of explosions:
(1) If $\Delta H_{r x n}$ is large and negative, and heat does not dissipate quickly enough, $T \nearrow$, so $k \nearrow$, generating more heat, $T \nearrow$ and $k \nearrow, \ldots$

## $\Rightarrow$ thermal explosion

(2) If radicals are produced faster than they are consumed, their concentration increases exponentially, reaction rates increase exponentially, ...

$$
\Rightarrow \text { chain-branching explosion }
$$

$$
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

1. $\mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{OH}$.
2. $\mathrm{H}_{2}+\mathrm{OH} \cdot \rightarrow \mathrm{H} \cdot+\mathrm{H}_{2} \mathrm{O}$
3. $\mathrm{H} \cdot+\mathrm{O}_{2} \rightarrow \mathrm{OH} \cdot+\cdot \mathrm{O}$.
(+1)
4. $\cdot \mathrm{O} \cdot+\mathrm{H}_{2} \rightarrow \mathrm{OH} \cdot+\mathrm{H}$.
5. $\mathrm{H} \cdot+\mathrm{O}_{2}+\mathrm{M} \rightarrow \mathrm{HO}_{2} \cdot+\mathrm{M}^{*}$
6. initiation: stable molecules give radicals.
7. and 5. propagation: no net change in number of radicals.
8. and 4. branching reactions: one radical in reactants, two radicals in products.
termination steps are omitted for simplicity

Radicals produced in 3. and 4. may diffuse out of the reaction mixture: at low $P$, diffusion prevents explosion.

At high $P$, radical-radical recombination may prevent explosion.

At intermediate $P$, the reaction is explosive.

## A generic chain-branching mechanism

$R \cdot$ : any radical

A, B: reactants $\quad ; \quad P_{1}, P_{2}$ : products
$\phi$ : mean number of radicals produced in branching reactions (branching efficiency)

$$
A+B \rightarrow R
$$

$k_{i}$
branching
$R \cdot \rightarrow \phi R \cdot+P_{1}$
$k_{b}$
termination

$$
R \cdot \rightarrow P_{2}
$$

$$
k_{t}
$$

$$
\frac{d[R \cdot]}{d t}=k_{i}[A][B]+\left(-k_{b}+\phi k_{b}-k_{t}\right)[R \cdot]
$$

Define $\Gamma \equiv k_{i}[A][B] \approx \mathrm{a}$ constant, and $\quad a \equiv k_{b}(\phi-1)-k_{t}$. Then

$$
\frac{d[R \cdot]}{d t}=\Gamma+a[R \cdot]
$$

let $y=\Gamma / a+[R \cdot]$, then

$$
\frac{d[R \cdot]}{d t}=\frac{d y}{d t}=a y
$$

The solution is $y=C e^{a t}=\Gamma / a+[R \cdot]$.
At $t=0,[R \cdot]=0$, so $C=\Gamma / a$ and

$$
(\Gamma / a) e^{a t}=\Gamma / a+[R \cdot]
$$

or

$$
[R \cdot]=\frac{\Gamma}{a}\left(e^{a t}-1\right)
$$

If $k_{t}<k_{b}(\phi-1)$, then $a>0$, and as $t \rightarrow \infty$, $[R \cdot] \rightarrow \infty$ : explosion

If $k_{t}>k_{b}(\phi-1)$, then $a<0$. Let $a^{\prime} \equiv-a$ ( $a^{\prime}>0$ ), then

$$
[R \cdot]=\frac{\Gamma}{a^{\prime}}\left(1-e^{-a^{\prime} t}\right)
$$

As $t \rightarrow \infty,[R \cdot] \rightarrow \Gamma / a^{\prime} .[R \cdot]$ goes to a finite limiting value: no explosion.

## Photochemistry

Many reactions are driven by absorption of light. One of the simplest scheme is

$$
A \xrightarrow{h \nu} A^{*} \rightarrow \text { Products }
$$

energy of a photon

$$
E_{\text {photon }}=h \nu=h c / \lambda
$$

Beer-Lambert law:

$$
I_{a b s}=2.303 \times I_{0} \epsilon \ell[A]
$$

$I_{0}, I_{a b s}$ : incident/absorbed light intensity, in "mole of photon $\mathrm{cm}^{-2} \mathrm{~s}^{-1 \text { " }}$
$\ell$ : optical path length, in cm
$\epsilon$ : molar absorptivity, in $M^{-1} \mathrm{~cm}^{-1}$
$2.303=\ln 10$

Beer's law
A beam of light of intensity $I_{0}$ goes through a homogeneous dilute solution of absorbers "A" with concentration $[A]$. The light gets attenuated as it goes through the cell of length $\ell$ and exits with intensity $I<I_{0}$. We want to calculate $I$ or $I_{a b s}=I_{0}-I$.

Let's say the light travels along $x$, with $x=0$ at the entry point into the solution, and $x=\ell$ at the exit point: $\ell$ is the path length. At $x=0, I=I_{0}$. The probability that a photon of the beam gets absorbed between $x=0$ and $x=d x$ is $\operatorname{Prob} \propto[A] d x$ or Prob $=\epsilon[A] d x$, where $\epsilon$ is the proportionality factor which depends on the molecule "A" absorbing light and the wavelength $\lambda$. The attenuation factor between $x=0$ and $x=d x$ is $(1-\epsilon[A] d x)$, and the intensity of light at $x=d x$ is

$$
I(d x)=I_{0}(1-\epsilon[A] d x)
$$

The attenuation factor is also $(1-\epsilon[A] d x)$ for $x=d x$ to $x=2 d x$, and for $x=2 d x$ to $x=3 d x$, and so on. So

$$
\begin{aligned}
I(2 d x) & =I_{0}(1-\epsilon[A] d x)^{2} \\
I(3 d x) & =I_{0}(1-\epsilon[A] d x)^{3}
\end{aligned}
$$

. . .

Then, $I(\ell) \equiv I=I_{0}(1-\epsilon[A] d x)^{n}$, or

$$
\begin{aligned}
I_{0} / I & =(1-\epsilon[A] d x)^{-n} \\
\ln \left(I_{0} / I\right) & =-n \ln (1-\epsilon[A] d x) \\
& =-n\left(-\epsilon[A] d x-(\epsilon[A] d x)^{2}-\ldots\right)
\end{aligned}
$$

In the limit $d x \rightarrow 0$ we have

$$
\ln \left(I_{0} / I\right)=n \epsilon[A] d x
$$

Since $n=\ell / d x$,

$$
\ln \left(I_{0} / I\right)=\epsilon \ell[A]
$$

Instead of $I_{0} / I$ or $I_{a b s}=I_{0}-I$, people sometimes write Beer's law in term of the transmittance $T=I / I_{0}$ :

$$
I / I_{0} \equiv T=e^{-\epsilon \ell[A]}
$$

Instead of natural logarithms, people sometimes use base-10 log, and a $\epsilon$ that is 2.303 times smaller:

$$
\begin{aligned}
& T=10^{-\epsilon \ell[A]} \equiv 10^{-A} \\
& A=\epsilon \ell[A]
\end{aligned}
$$

$A$ is called the absorbance. The derivation of Beer's law depends on the assumption that $[A]$ is sufficiently small (dilute solution). If $[A]$ is large, we could have A-A interactions and cooperative effects. If $[A]$ is small enough, we can further simplify Beer's law:

$$
\begin{aligned}
I_{0} / I & =e^{\epsilon \ell[A]} \\
& =1+\epsilon \ell[A]+\frac{1}{2}(\epsilon \ell[A])^{2}+\ldots
\end{aligned}
$$

Keeping only the first two terms,

$$
\begin{aligned}
I_{0} / I & \approx I / I+\epsilon \ell[A] \\
I_{0}-I & \approx I \epsilon \ell[A]
\end{aligned}
$$

When $[A]$ is very small, we normally have $I / I_{0} \approx 1$ and we can write $I_{a b s}=I_{0}-I$ like this

$$
I_{0}-I \equiv I_{a b s} \approx I_{0} \epsilon \ell[A]
$$

or, if we use the $\log _{10}$ convention instead,

$$
I_{a b s} \approx 2.303 \times I_{0} \epsilon[A]
$$

with $\epsilon$ smaller by a factor 2.303 .

The rate of photoexcitation $R=\frac{d\left[A^{*}\right]}{d t}=-\frac{d[A]}{d t}$, in $M s^{-1}$, is

$$
R=\frac{I_{a b s}}{\ell} \times 1000 \mathrm{~cm}^{3} / L
$$

so

$$
-\frac{d[A]}{d t}=2303 I_{0} \epsilon[A]
$$

After integration,

$$
[A]=[A]_{0} e^{-2303 I_{0} \epsilon t}
$$

This describes the kinetics of many first-order photochemical reactions.

Working with number of molecules " $A$ " and $N_{A}=$ $6.022 \times 10^{23} \mathrm{~mol}^{-1}$ instead of concentration $[A]$, we have ...

$$
\begin{aligned}
-\frac{d A}{d t} & =\frac{2303 I_{0} \epsilon}{N_{A}} A \\
A & =A_{0} e^{-I_{0}\left(2303 \epsilon / N_{A}\right) t} \\
A & =A_{0} e^{-I_{0} \sigma_{A} t}
\end{aligned}
$$

NOTE: now $I_{0}$ is in "photon $\mathrm{cm}^{-2} \mathrm{~s}^{-1 \text { ". }}$
$\sigma_{A}$ has units $\frac{\mathrm{cm}^{3}}{L} \times \frac{M^{-1} \mathrm{~cm}^{-1}}{\mathrm{~mol}^{-1}}=\mathrm{cm}^{2}$ and is called the absorption cross section.

$$
k_{a}=I_{0} \sigma_{A} \text { is in } \mathrm{cm}^{-2} \mathrm{~s}^{-1} \mathrm{~cm}^{2} \text {, or } \mathrm{s}^{-1} .
$$

$$
A=A_{0} e^{-k_{a} t}
$$

## Jablonski diagram

# wiggly lines: vibrational relaxation (vr) 

horizontal lines:
$S_{1}$ to $S_{0}$ : internal conversion (ic)
$S_{1}$ to $T_{1}$ : intersystem crossing (isc) " S "
$T_{1}$ to $S_{0}$ : isc "T"
vertical lines:
$S_{0}$ to $S_{1}$ : photon absorption
$S_{1}$ to $S_{0}$ : fluorescence (photon emission)
$T_{1}$ to $S_{0}$ : phosphorescence (photon emission)

Most molecules have a closed-shell electronic ground state, and most electronic excitations can be viewed as promoting a single electron. This leads to 4 spin configurations for the excited states.

$$
\begin{aligned}
& \alpha\left(s_{1}\right) \beta\left(s_{2}\right) \equiv \alpha \beta, \quad \beta\left(s_{1}\right) \alpha\left(s_{2}\right) \equiv \beta \alpha, \\
& \alpha\left(s_{1}\right) \alpha\left(s_{2}\right) \equiv \alpha \alpha, \quad \text { and } \beta\left(s_{1}\right) \beta\left(s_{2}\right) \equiv \beta \beta .
\end{aligned}
$$

The 4 correct spin functions are:
$\frac{1}{\sqrt{2}}(\alpha \beta-\beta \alpha):$ one state $S_{1}$
$\frac{1}{\sqrt{2}}(\alpha \beta+\beta \alpha), \alpha \alpha$, and $\beta \beta$ : a triplet of states $T_{1}$

Each process has an associated rate constant. $k_{v r} \approx 10^{13} s^{-1}$ is very big. We assume that vibrational relaxation is instantaneous.

The rates of the other processes are:
$S_{1}$ to $S_{0}+h \nu$, fluorescence: $k_{f}\left[S_{1}\right]$
$T_{1}$ to $S_{0}+h \nu$, phosporescence: $k_{p}\left[T_{1}\right]$
$S_{1}$ to $T_{1}$, isc: $k_{i s c, S}\left[S_{1}\right]$
$S_{1}$ to $S_{0}$, ic: $k_{i c}\left[S_{1}\right]$
$T_{1}$ to $S_{0}$, isc: $k_{i s c, T}\left[T_{1}\right]$

Excited molecules in state $S_{1}$ can return to the ground state by collisional quenching:

$$
S_{1}+Q \rightarrow S_{0}+Q
$$

with rate

$$
R_{q}=k_{q}\left[S_{1}\right][Q]
$$

Accounting for all processes involving $S_{1}$ and making the SSA,

$$
0 \approx k_{a}\left[S_{0}\right]-\left[S_{1}\right]\left(k_{f}+k_{i c}+k_{i s c, S}+k_{q}[Q]\right)
$$

The fluorescence lifetime is

$$
\frac{1}{\tau_{f}}=k_{f}+k_{i c}+k_{i s c, S}+k_{q}[Q]
$$

Then

$$
\left[S_{1}\right]=k_{a}\left[S_{0}\right] \tau_{f}
$$

The fluorescence intensity is

$$
I_{f}=k_{f}\left[S_{1}\right]=k_{a} k_{f} \tau_{f}\left[S_{0}\right]=k_{a} \Phi_{f}\left[S_{0}\right]
$$

$\Phi_{f}=\frac{k_{f}}{k_{f}+k_{i c}+k_{i s c, S}+k_{q}[Q]} \quad$ is the quantum yield for fluorescence - the fraction of molecules in $S_{1}$ that return to the ground state by fluorescing.

Molecules that emit strongly often have $k_{f} \gg k_{i c}$ and $k_{f} \gg k_{i s c, S}$. Then

$$
\begin{aligned}
& \frac{1}{I_{f}} \approx \frac{1}{k_{a}\left[S_{0}\right]}+\frac{k_{q}}{k_{a} k_{f}\left[S_{0}\right]}[Q] \\
& \frac{I_{0}}{I_{f}}=1+\frac{k_{q}}{k_{f}}[Q]
\end{aligned}
$$

$\frac{I_{0}}{I_{f}}$ vs $[Q]$ is a Stern-Volmer (SV) plot.

## $\mathrm{O}_{2}$ and acrylamide $\left(\mathrm{CH}_{2} \mathrm{CHCONH}_{2}\right)$ are common quenchers.

SV plots have been used to measure the accessibility of tryptophan residues in proteins $\Rightarrow$ conformation, $\sim 10^{-10} \mathrm{~s}$ dynamics

W Qiu et al., Chemical Physics 350 (2008) 154164.

Fluorescence resonance energy transfer (FRET): an excited donor molecule D gives its excess energy to an acceptor molecule A which becomes excited (4.). "A" returns to its ground-state by fluorescence (5.).

$$
\begin{array}{ll}
\text { 1. } & D \xrightarrow{h \nu, k_{a}} D^{*} \\
\text { 2. } & D^{*} \xrightarrow{k_{f}} D \\
\text { 3. } & D^{*} \xrightarrow{k_{n r}} D \\
\text { 4. } & D^{*}+A \xrightarrow{k_{f r e t}^{\prime}} D+A^{*} \\
\text { 5. } & A^{*} \xrightarrow{k_{f^{\prime}}} A
\end{array}
$$

$k_{\text {fret }}=k_{\text {fret }}^{\prime}[A] \quad([A]$ is not always relevant $)$

From the viewpoint of $\mathrm{D}^{*}$, FRET is one more nonradiative ( nr ) process for returning to the ground state, in addition to ic, ics, and quenching, so

$$
\begin{aligned}
\Phi_{f} & =\frac{k_{f}}{k_{f}+k_{n r}} \\
k_{n r} & =k_{i c}+k_{i c s, S}+k_{q}[Q]
\end{aligned}
$$

becomes

$$
\Phi_{f, f r e t}=\frac{k_{f}}{k_{f}+k_{n r}+k_{f r e t}}
$$

The quantum yield for FRET is

$$
\Phi_{f r e t}=\frac{k_{f r e t}}{k_{f}+k_{n r}+k_{f r e t}}
$$

( $\Phi_{\text {fret }}$ is "Eff" in the book, equation (19.179))

In practice $\Phi_{\text {fret }}$ is measured by the difference in the fluorescence of D in the presence of A

$$
\Phi_{f r e t}=1-\frac{\Phi_{f, f r e t}}{\Phi_{f}}
$$

The probability of energy transfer, $\Phi_{\text {fret }}$, is very sensitive to the D-A separation " $r$ ".

$$
\Phi_{\text {fret }}=\frac{1}{1+\left(r / r_{0}\right)^{6}}
$$

$r_{0}$ depends on the $\mathrm{D} / \mathrm{A}$ pair and is normally between 10 and $60 \AA$.

A FRET signal tells us that D and A are close.

Ex. 1: we label a membrane receptor with D, and a ligand with A. We see a FRET signal and conclude that the ligand binds to the receptor.

Ex. 2: we label two sites of a biomolecule with D and A. At pH 7.4, we see a FRET signal; at pH 5.0 we see no FRET. We conclude that the biomolecule underwent a conformational change.

For FRET to occur, $r / r_{0}$ must be small enough. In order to have a sizeable $r_{0}$,

- D should have a large $\Phi_{f}$,
- the absorption band of A and fluorescence band of D should overlap,
- and the transition dipoles of D and A should be aligned, at least some of the time.

FRET is essential for photosynthesis

A FRET-based heterojunction has been proposed for use in solar cells, see Nature Photonics 7 (2013) 479-485.

Photochemical reactions: a photoexcited molecule, usually in $S_{1}$ reacts at a rate

$$
R_{\text {photochem. }}=k_{\text {photo }, S 1}\left[S_{1}\right]
$$

Quantum yield

$$
\phi=\frac{k_{\text {photo }, S 1}}{k_{f}+k_{n r}+k_{p h o t o, S 1}}
$$

$\phi$ : fraction of excited molecules that react

Number of absorbed photons, $N_{a b s}$

$$
N_{a b s}=\frac{E_{a b s}}{E_{\text {photon }}}=\frac{P \Delta t}{h \nu}=\frac{P \Delta t}{h c / \lambda}
$$

$P$ : power (in Watts, W)

## Electron transfer

$$
D+A \leftrightharpoons D^{+}+A^{-}
$$

essential in photovoltaics $\mathcal{E}$ photosynthesis

$$
6 \mathrm{CO}_{2}(g)+6 \mathrm{H}_{2} \mathrm{O}(\ell) \rightarrow \mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(s)+6 \mathrm{O}_{2}(g)
$$

$\Delta G^{\circ}=2870 \mathrm{~kJ}$ : reaction driven by light.

- light absorption
- FRET (energy migration to rxn center)
- $\mathrm{e}^{-}$transfer reactions
- many other reactions


## $\mathrm{e}^{-}$transfer kinetics

The donor D and acceptor A diffuse and form a complex, transfer an e-, and separate.

$$
\begin{array}{ll}
D+A \leftrightharpoons D A & \left(k_{d}, k_{d}^{\prime}\right) \\
D A \leftrightharpoons D^{+} A^{-} & \left(k_{e}, k_{e}^{\prime}\right) \\
D^{+} A^{-} \rightarrow D^{+}+A^{-} & \left(k_{\text {sep }}\right)
\end{array}
$$

SSA for $\left[D^{+} A^{-}\right]$:

$$
\left[D^{+} A^{-}\right]=\frac{k_{e}[D A]}{k_{e}^{\prime}+k_{s e p}}
$$

SSA for $[D A]$ :

$$
[D A]=\frac{k_{d}[D][A]+k_{e}^{\prime}\left[D^{+} A^{-}\right]}{k_{d}^{\prime}+k_{e}}
$$

Substituting:

$$
\left[D^{+} A^{-}\right]=\frac{k_{e} k_{d}}{k_{e}^{\prime} k_{d}^{\prime}+k_{s e p} k_{d}^{\prime}+k_{s e p} k_{e}}[D][A]
$$

the rate is

$$
R=k_{s e p}\left[D^{+} A^{-}\right]=k[D][A]
$$

We assume $k_{s e p} \gg k_{e}^{\prime}$, so

$$
R=\frac{k_{e} k_{d}}{k_{e}+k_{d}^{\prime}}[D][A]
$$

Two limiting cases:

1) $k_{e} \gg k_{d}^{\prime}: R=k_{d}[D][A] \quad$ (diffusion controlled)
2) $k_{e} \ll k_{d}^{\prime}: R=k_{e} K_{d}[D][A] \quad\left(K_{d}=k_{d} / k_{d}^{\prime}\right)$
case 2. applies when D and A are bonded, or held together by a surrounding protein(s).

## A microscopic view of $\mathrm{e}^{-}$transfer:

## Marcus theory ( $\sim 1956$ )

$\mathrm{e}^{-}$transfer between D and A occurs if ...
orbitals overlap: $k \propto e^{-\beta r}$

D and A have sufficient energy to overcome an activation barrier: $k \propto e^{-\Delta G^{\ddagger} / k_{B} T}$
$\Delta G^{\circ}$ : free energy change for the charge transfer $\lambda>0$ : reorganization energy, free energy of DA at the equilibrium geometry of $\mathrm{D}^{+} \mathrm{A}^{-}$, including the solvent.

$$
\Delta G^{\ddagger}=\frac{\left(\Delta G^{\circ}+\lambda\right)^{2}}{4 \lambda}
$$

$x$ : reaction coordinate
$x=0$, equilibrium geometry of DA ; $x=a$, equilibrium geometry of $\mathrm{D}^{+} \mathrm{A}^{-}$

Assume the free energies of $\mathrm{DA}\left(G_{n}\right)$ and $\mathrm{D}^{+} \mathrm{A}^{-}$ $\left(G_{t}\right)$ are quadratic wrt displacement from equilibrium, with force constant $k$, and set $\Delta G=0$ at $x=0$.

$$
G_{n}=\frac{1}{2} k x^{2}
$$

$$
G_{t}=\frac{1}{2} k(x-a)^{2}+\Delta G^{\circ}
$$

$$
=\frac{1}{2} k\left(x^{2}-2 a x+a^{2}\right)+\Delta G^{\circ}
$$

The two energy curves cross at $x_{c}$ :

$$
\begin{aligned}
\frac{1}{2} k x_{c}^{2} & =\frac{1}{2} k\left(x_{c}^{2}-2 a x_{c}+a^{2}\right)+\Delta G^{\circ} \\
k a x_{c} & =\frac{1}{2} k a^{2}+\Delta G^{\circ}
\end{aligned}
$$

$\lambda=\frac{1}{2} k a^{2}$, so

$$
\operatorname{kax}_{c}=\Delta G^{\circ}+\lambda
$$

$$
x_{c}=\frac{\Delta G^{\circ}+\lambda}{k a}
$$

Energy at $x_{C}$ :

$$
\begin{aligned}
\Delta G^{\ddagger} & =\frac{1}{2} k x_{c}^{2}=\frac{k}{2}\left(\frac{\Delta G^{\circ}+\lambda}{k a}\right)^{2} \\
& =\frac{\left(\Delta G^{\circ}+\lambda\right)^{2}}{2 k a^{2}} \\
\Delta G^{\ddagger} & =\frac{\left(\Delta G^{\circ}+\lambda\right)^{2}}{4 \lambda}
\end{aligned}
$$

- $k \propto e^{-\beta r} e^{-\Delta G^{\ddagger} / k_{B} T} \propto A e^{-\Delta G^{\ddagger} / k_{B} T}$ same form as Eyring's formula
- the rate is maximum at $\Delta G^{\circ}=-\lambda$
- $\Delta G^{\circ}<-\lambda$ : "inverted regime" (expt in 1984)
- $\mathrm{e}^{-}$transfer can be accompanied by an important solvent reorganization, and large $\lambda$
- "outer sphere" reactions: only the solvent reorganizes. The $\mathrm{e}^{-}$transfers when the solvation shell is optimal for stabilizing a fictitious $D^{+q} A^{-q}$.
- $\Delta G^{\circ}$ generally more negative in polar solvents
- applications: photosynthesis, corrosion, chemiluminescence, solar cells


## Rudolph Marcus:

## PhD McGill 1946

postdoc at NRC, Ottawa 1946-49
UNC Chapel Hill, 1949-51
prof at Brooklyn Polytechnic, U Illinois Urbana-Champaign, Caltech

