CHEM 3011: Chemical Kinetics

Reactants R transform to products P

$$\begin{array}{ccc} R & \longrightarrow & P \\ & \ddots & \\ R & \stackrel{\leftarrow}{\longrightarrow} & P \end{array}$$

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

$$R \leftrightarrows P$$

1. How fast are reactions?

 $t_{1/2}$: anywhere between 10^{-14} s and 10^{10} years!

2. How do reactants' concentrations change with time?

[R](t): sometimes simple (1st or 2nd 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

$$R \xrightarrow{years} P$$

to

$$R \xrightarrow{minutes} P$$

or from

$$P1 \stackrel{1 \ hour}{\leftarrow} R \stackrel{1 \ hour}{\rightarrow} P2$$

to

P1
$$\stackrel{1 \text{ min.}}{\longleftarrow} R \stackrel{1 \text{ hour}}{\rightarrow} P2$$

Kinetic control vs Thermodynamic control

 $P1 \leftarrow R \rightarrow P2$

Activation energies: $E_{a1} < E_{a2}$

Reaction energies: $\Delta G^{\circ}_{rxn,1} > \Delta G^{\circ}_{rxn,2}$ $(\Delta G^{\circ}_{rxn,1} \text{ and } \Delta G^{\circ}_{rxn,2} \text{ both negative})$ Near the start of reaction $([P_1] \text{ and } [P_2] \approx 0$, "small" t), we have <u>kinetic control</u>.

 $[P_1] \sim \exp(-E_{a1}/RT)$ $[P_2] \sim \exp(-E_{a2}/RT)$ $[P_2]/[P_1] \sim \exp((E_{a1} - E_{a2})/RT) < 1$

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

 $[P_2]/[P_1] \approx \exp((\Delta G_{rxn,1}^{\circ} - \Delta G_{rxn,2}^{\circ})/RT) > 1$

What is a "small" t? It depends on E_{a1}, E_{a2} and T. 1 min. could be "small" at T = 77 K but "large" at T = 373 K. So,

small t, low $T \Rightarrow$ kinetic control

long t, high $T \Rightarrow$ thermodynamic control

Either way, the *selectivity* $([P_2]/[P_1] \text{ or } [P_1]/[P_2],$ 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.,

$$A + 2B \rightarrow AB + B \rightarrow AB_2$$

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, λ)
- 7. sonication: bubbles form and collapse,
- hot spots with $T \approx 5000$ K and $P \approx 1000$ atm.

How to trigger or stop reactions

triggers:

flame (for ex., $H_2 + O_2$) light (photochemistry) spark (combustion engines) shock (for ex., nitroglycerin)

stops:

remove A(s) or catalyst quickly cool off the mixture, $T \searrow$ quickly add Q to quench reactant A: $A + Q \rightarrow inert$ sudden and large change of pH 9

Textbook

Physical Chemistry (PC)T Engel and P Reid (Pearson Prentice Hall) 3rdedition (2013), chapters 35, 36

or the second half of PC: Thermodynamics, Statistical thermodynamics, and Kinetics (TSK), chapters 18, 19 René Fournier

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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

$$aA + bB + \ldots \rightarrow cC + dD + \ldots$$

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

$$n_A(t) = n_A(0) - ax$$

then

$$n_B(t) = n_B(0) - bx$$

$$n_C(t) = n_C(0) + cx$$

etc.

x (ξ in PC): extent of the reaction

Reaction rate:

$$Rate = \frac{dx}{dt} = -\frac{1}{a}\frac{dn_A}{dt} = \dots = \frac{1}{c}\frac{dn_C}{dt} = \dots$$

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

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

$$R = -\frac{1}{aV}\frac{dn_A}{dt} = -\frac{1}{a}\frac{d[A]}{dt} = \dots$$

 $\frac{\text{homogeneous}}{\text{gases, or all in solution.}}$ rxn: reactants and products are all

 $\frac{\text{heterogeneous rxn: more than one phase (e.g., a solid + gases). The$ *interface*plays an essential role.

For now, we limit ourselves to homogeneous reactions.

Rate law

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

 α : rxn order w.r.t. A β : 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:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
$$R = k[NO]^2[O_2]$$

$$2SO_2(g) + O_2(g) \to 2SO_3(g)$$

 $R = k[SO_2][SO_3]^{1/2}$

$$H_2(g) + Br_2(g) \to 2HBr(g)$$
$$R = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[H_2]/[Br_2]}$$

R is in M s⁻¹; [A], [B], ... are in M; so

if
$$R = k[A]$$
, k is in s⁻¹
if $R = k[A][B]$, k is in M⁻¹s⁻¹
if $R = k[A][P]^{-1/2}$, k is in M^{1/2}s⁻¹

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

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

Consider a simple first-order reaction

$$A \to P$$

 $[A] = [A]_t$, and $R = k[A]_t$ varies with time.



Method of initial rates

$$A + B \xrightarrow{k} P$$
$$R = k[A]^{\alpha}[B]^{\beta}$$

We can get the 3 unknowns k, α , β , 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

$$\frac{R_2}{R_1} = \frac{k \left[A\right]_1^{\alpha} \left[B\right]_2^{\beta}}{k \left[A\right]_1^{\alpha} \left[B\right]_1^{\beta}}$$
$$= \left(\frac{\left[B\right]_2}{\left[B\right]_1}\right)^{\beta}$$
$$\beta = \ln(R_2/R_1) \div \ln(\left[B\right]_2/\left[B\right]_1)$$

Likewise

$$\alpha = \ln(R_3/R_1) \div \ln([A]_3/[A]_1)$$

Finally

$$k = R_1 \div ([A]_1^{\alpha} [B]_1^{\beta})$$

)

How do we measure R?

$$R = -\frac{1}{a} \lim_{\Delta t \to 0} \frac{[A](\Delta t) - [A](0)}{\Delta t}$$

- 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, pH, current, NMR signal, $I(\lambda), \ldots$

Photoabsorption is particularly useful because we can select a wavelength λ (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 ℓ : path length of light through the sample $\epsilon_A(\lambda)$: molar absorption coefficient

$$\ln(I_0(\lambda)/I(\lambda)) = \epsilon_A(\lambda) [A] \ell$$

This equation holds provided:

- 1. no other species absorbs at λ ;
- 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

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

Typical times "au"

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

 $\lambda \,=\, (1/3300)\,cm$

$$\tau = 1/\nu = \lambda/c = 1/(3300 \, cm^{-1} \times 2.998 \times 10^{10} \, cm/s) \approx 10^{-14} \, s$$

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

Molecules stay in an <u>excited electronic state</u> ...

fluorescence: $\sim 10^{-9}$ - 10^{-5} s phosphorescence: $\sim 10^{-4}$ s to several minutes Time for a molecule to rotate by 180° : water $\sim 5 \times 10^{-12}$ s small organic molecules $\sim 10^{-10}$ - 10^{-9} s proteins $\sim 10^{-8}$ to 4×10^{-8} s

Time interval between two successive <u>collisions</u> of a <u>gas molecule</u> with other gas molecules at rt and 1 atm: $\tau \sim 10^{-10}$ s

Time interval between two successive A-A <u>collisions</u> of a small molecule A <u>in solution</u> at rt, when $[A] = 1 \text{ M}: \tau \sim 10^{-11} \text{ s}$ If A is very big, $\tau \sim 10^{-9} \text{ s}.$

time resolution, Δt

chemical methods: $\Delta t \gtrsim 1 \min$

stopped-flow (biochemistry): A and B injected with syringes into a mixing chamber. $\Delta t \gtrsim$ 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 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 <u>elementary reactions</u> is directly related to their **molecularity**. For example:

$$I_2 \rightarrow 2I$$

$$R = k[I_2]$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$R = k[NO][O_3]$$

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

first mechanism.

1.
$$A \rightleftharpoons I$$
 (quasi equilibrium)
2. $I \rightarrow P$
 $K_1 \approx [I] \div [A]$
 $R = k'[I] = (k'K_1)[A]$
 $R = k[A]$

second mechanism.

1.
$$A \rightleftharpoons I$$
 (quasi equilibrium)
2. $I + A \rightarrow P + A$
 $R = k'[I][A] = (k'K_1)[A]^2$
 $R = k[A]^2$

third mechanism.

1.
$$A \to P$$

 $R = k[A]$

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 $R = \frac{-1}{a}d[A]/dt$ to concentrations $[A], [B] \dots$

An integrated rate law relates [A] (or [B], etc.) to initial concentration(s) and time: $[A](t) \equiv [A] = f(t, [A]_0, [B]_0, \ldots).$

$$\frac{-1}{a}\frac{d[A]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

$$\frac{-1}{a} \int_{[A]_0,[B]_0}^{[A]_t,[B]_t} \frac{d[A]}{[A]^{\alpha}[B]^{\beta}} = k \int_0^t dt$$

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

Integrated rate laws: 1. elementary reactions

1.1 elementary first-order reaction

$$A \to P$$

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

 $[A] = [A]_0$ 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

$$\ln[A] - \ln[A]_0 = -k(t - 0)$$
$$\ln([A] \div [A]_0) = -kt$$
$$[A] = [A]_0 e^{-kt}$$

1.1 (continued)

If $[P]_0 = 0$ then $[P] + [A] = [A]_0$ at all times:

$$[P] = [A]_0 - [A] = (1 - e^{-kt})[A]_0$$

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

$$\ln[A] = \ln[A]_0 - kt$$

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 $[A] = [A]_0/2$.

$$\ln(([A]_0/2)/[A]_0) = -k t_{1/2}$$
$$\ln 2 = k t_{1/2}$$
$$t_{1/2} = \ln 2/k$$

$$2A \rightarrow Products$$
$$R = -\frac{1}{2} \frac{d[A]}{d\tau} = k[A]^2$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = 2k \int_0^t d\tau$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$$

If we plot $\frac{1}{[A]}$ vs t, we get a straight line with slope equal to 2k and intercept $\frac{1}{[A]_0}$.

The half-life in this case:

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + 2kt_{1/2}$$
$$t_{1/2} = \frac{1}{2k[A]_0}$$

$A + B \rightarrow Products$

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

From the stochiometry we can write

$$[A] = [A]_0 - x$$
$$[B] = [B]_0 - x = [B]_0 - [A]_0 + [A]$$
$$[B] = \Delta + [A]$$

If
$$\Delta \neq 0$$
:

$$\begin{aligned} -\frac{d[A]}{d\tau} &= k[A](\Delta + [A]) \\ -\int_{[A]_0}^{[A]} \frac{d[A]}{[A](\Delta + [A])} &= k \int_0^t d\tau \end{aligned}$$

You can verify that

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

then,

$$\frac{1}{\Delta} \left[\ln \left(\frac{\Delta + [A]}{[A]} \right) - \ln \left(\frac{\Delta + [A]_{0}}{[A]_{0}} \right) \right] = kt$$

$$\ln\left(\frac{\left(\Delta + [A]\right)[A]_{0}}{\left(\Delta + [A]_{0}\right)[A]}\right) = \Delta kt$$

$$\ln\left(\frac{[B][A]_0}{[B]_0[A]}\right) = ([B]_0 - [A]_0) kt$$

If $\Delta = 0$, $[B]_0 = [A]_0$, and [B] = [A] at all times.

$A + B \rightarrow Products$

is just like the case

$$A + A \rightarrow Products$$

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

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

The most common case is the recombination reaction

$$2A + M \rightarrow A_2 + M^*$$

 A_2 is collisionally stabilized by M.

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

$$R = k'[M][A]^2 \approx k[A]^2$$

and we are back to case 1.2.

$3A \rightarrow Products$

It is a hypothetical case for which

$$\frac{1}{[A]^2} = \frac{1}{[A]_0^2} + 6kt$$

$A + B + C \rightarrow Products$

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

$$x = [A]_0 - [A] = [B]_0 - [B] = [C]_0 - [C]$$

$$\int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)([C]_0 - x)} = k \int_0^t d\tau$$

We evaluate the lhs by the method of partial fractions

• •

$$\Delta = [B]_0 [C]_0 ([B]_0 - [C]_0) + [C]_0 [A]_0 ([C]_0 - [A]_0) + [A]_0 [B]_0 ([A]_0 - [B]_0)$$

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

$$[B] = [A] + ([B]_0 - [A]_0)$$
$$[C] = [A] + ([C]_0 - [A]_0)$$

Numerical integration

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

$A \rightarrow P$

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

At t = 0, $[A] = [A]_0$. A short time Δt later

$$[A]_{\Delta t} = [A]_0 + [A]'_0 \cdot \Delta t + \frac{1}{2} [A]''_0 \cdot (\Delta t)^2 + \dots$$

$$[A]_{\Delta t} \approx [A]_0 - k[A]_0 \,\Delta t$$

Likewise,

$$[A]_{t+\Delta t} \approx [A]_t - k[A]_t \Delta t \qquad (*)$$

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

$$a_{1} = -k [A]_{t}$$

$$a_{2} = -k ([A]_{t} + a_{1}\Delta t/2)$$

$$a_{3} = -k ([A]_{t} + a_{2}\Delta t/2)$$

$$a_{4} = -k ([A]_{t} + a_{3}\Delta t)$$

$$[A]_{t+\Delta t} \approx [A]_t + \frac{1}{6}(a_1 + 2a_2 + 2a_3 + a_4)\,\Delta t$$

<u>Note</u>: a_1 approximates d[A]/dt at the beginning of the time interval; a_2 and a_3 approximate d[A]/dtat the middle of the interval; and a_4 approximates d[A]/dt at the end of the interval.

Integrated rate laws 2. complex reactions

2.1 zeroth order reaction

This can happen with the generic mechanism

1. $A + S \rightleftharpoons A \cdot S$ (quasi equilibrium)

2.
$$A \cdot S \rightarrow S + Products$$

 $A \cdot S$ 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* θ :

$$\theta = n \div S_0$$

The quasi-equilibrium condition gives

$$k_f[A](1-\theta) = k_r\theta$$
$$K_{ads} = k_f/k_r = \frac{\theta}{[A](1-\theta)}$$

Rearranging,

$$\theta = \frac{K_{ads}[A]}{1 + K_{ads}[A]}$$

The rate is

$$R = k_2 S_0 \theta = \dots$$

$$R = k_2 S_0 \frac{K_{ads}[A]}{1 + K_{ads}[A]}$$

If [A] is very small: $R = k_2 S_0 K_{ads} [A]$

If [A] is very large:
$$K_{ads}[A] \gg 1$$
, $\theta \approx 1$ and
 $R = k_2 S_0$

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

$$[A] = [A]_0 - kt$$

$A \xrightarrow{k_A} I$

$I \xrightarrow{k_I} P$

The rate of change of the concentrations are

$$\frac{d[A]}{dt} = -k_A[A]$$
$$\frac{d[I]}{dt} = k_A[A] - k_I[I]$$
$$\frac{d[P]}{dt} = k_I[I]$$

Assume $[I]_0 = [P]_0 = 0$. For A we have as before

$$[A] = [A]_0 e^{-k_A t}$$

For I:

$$\frac{d[I]}{dt} = k_A[A]_0 e^{-k_A t} - k_I[I]$$

The solution to this differential equation is

$$[I] = \frac{k_A [A]_0}{k_I - k_A} (e^{-k_A t} - e^{-k_I t})$$

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)

$$\frac{d[P]}{dt} = R = \frac{k_A k_I}{k_I - k_A} \left(e^{-k_A t} - e^{-k_I t} \right) [A]_0$$

There are 2 limit cases.

(i)
$$k_I \gg k_A$$
:

$$R = k_A \exp(-k_A t) [A]_0$$

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)
$$k_A \gg k_I$$
:

$$R = k_I \exp(-k_I t) [A]_0$$

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]/dt = -d[A]/dt 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.





The concentrations of I_1 and I_2 vary rapidly at the beginning ($t \leq 20 s$) but slowly later on. We can get a simple analytical solution if we *assume*

$$\frac{d[I_1]}{dt} \approx 0$$
$$\frac{d[I_2]}{dt} \approx 0$$

Then

$$\frac{d[I_1]}{dt} = k_A[A] - k_1[I_1] \approx 0$$

$$[I_1] \approx k_A[A] \div k_1 = \frac{k_A}{k_1} [A]_0 \exp(-k_A t)$$

Likewise,

$$\frac{d[I_2]}{dt} = k_1[I_1] - k_2[I_2] \approx 0$$
$$[I_2] \approx k_1[I_1]/k_2 \approx \frac{k_A}{k_2} [A]_0 \exp(-k_A t)$$

and

$$\frac{d[P]}{dt} = k_2[I_2] \approx k_A [A]_0 \exp(-k_A t)$$

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

$$[P] \approx [A]_0(1 - \exp(-k_A t))$$

But is the SSA valid?

Look again at the numerical solution when $k_A = 0.02 \, s^{-1}, \, k_1 = 0.2 \, s^{-1}, \, k_2 = 0.2 \, s^{-1}.$

This time, we plot the *derivatives* of concentrations.









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

$$B \stackrel{k_B}{\leftarrow} A \stackrel{k_C}{\to} C$$

$$\frac{d[B]}{dt} = k_B[A]$$
$$\frac{d[C]}{dt} = k_C[A]$$

Suppose $[B]_0 = [C]_0 = 0$, and $k_B = 2k_C$. Then, at any time t, 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:

$$k = A \exp(-E_a/RT)$$

<u>A</u>, in s^{-1} , is related to the number of collisions per second between A and B (~ Z_{AB}), or the effective frequency of a vibrational mode, for example, ν (C–C) if a C–C bond is broken. E_a is the activation energy.

 $\exp(-E_a/RT) \sim$ fraction of molecules (unimolecular) or collisions (bimolecular) with sufficient energy for reaction to occur.

$$\ln k = \ln A - \frac{E_a}{RT}$$

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 + dv is F(v)dv.

$$F(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 \exp(-mv^2/2kT)$$
$$= \left(\frac{1}{2\pi kT}\right)^{3/2} 8\pi m^{1/2} \frac{mv^2}{2} e^{-mv^2/2kT}$$
$$= \left(\frac{1}{2\pi kT}\right)^{3/2} 8\pi m^{1/2} E_{trans} e^{-E_{trans}/kT}$$

What is a "big" activation energy?

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

At r.t. $RT = 0.026 \ eV = 0.59 \ kcal/mol = 2.5 \ kJ/mol$

Obviously RT is different at 77 K, 273.15 K, **298** K, 310 K, and 373.15 K.

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

$$k = a T^{m} \exp(-E'/RT)$$
$$\ln(k/T^{m}) = \ln a - \frac{E'}{RT}$$

where a and E' are independent of T.
Transition State Theory:

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

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E^{\ddagger}/k_B T}$$
$$= \frac{k_B T}{h} e^{-\Delta G_0^{\ddagger}/k_B T}$$

 $\frac{E^{\ddagger}, \text{ activation energy}}{Q_A, \text{ partition function}: \text{ number of microstates available to molecule A.}$ $\frac{\Delta G_0^{\ddagger}: \text{ free energy difference}}{\text{ state and reactants.}}$

$$\Delta G_0^{\ddagger} = \Delta H_0^{\ddagger} - T \Delta S_0^{\ddagger}$$

Reversible reactions

For every reaction with rate constant k_f there is a possible reverse reaction with rate constant k_r . Take

$$A \leftrightarrows B$$

$$\frac{d[A]}{dt} = -k_f[A] + k_r[B]$$

$$\frac{d[B]}{dt} = k_f[A] - k_r[B]$$

We must have

$$[A]_0 = [A] + [B]$$

solving the differential equation ...

With $k = k_f + k_r$, the integrated rate law is

$$[A] = [A]_0 \frac{k_r + k_f e^{-kt}}{k}$$

When $t \to \infty$, $[A] = [A]_{eq}$.

$$[A]_{eq} = [A]_0 k_r / k$$

 $[B]_{eq} = [A]_0 k_f / k$

[A] decreases exponentially from $[A]_0$ to $[A]_{eq}$ with rate constant k. So, at time $t_{1/2} = \ln 2/k$ we have $[A]_{1/2} = ([A]_0 + [A]_{eq})/2.$ From the measured $[A]_{eq}$, $[B]_{eq}$, and $t_{1/2}$ we get:

$$K_c = k_f / k_r = [B]_{eq} / [A]_{eq}$$

$$k = k_f + k_r = \ln 2/t_{1/2}$$

We can show that

$$[A] = [A]_{eq} + ([A]_0 - [A]_{eq})e^{-kt}$$

$$\ln([A] - [A]_{eq}) = \ln([A]_0 - [A]_{eq}) - kt$$

So we can get k by plotting $\ln([A] - [A]_{eq})$ vs time and taking the negative of the slope. Or we can plot [A] vs t: the slope at t = 0 is $-k_f[A]_0$.

<u>Note</u>: The graph in Fig. 18.16 is correct, but " $[A]_0 e^{-(k_A+k_B)t}$ " is a mistake.

Temperature-jump method

Start at equilibrium at T_1

$$A \leftrightarrows B$$

with k_{f1} and k_{r1} . Suddenly increase the temperature to T_2 : the rate constants change to k_{f2} and k_{r2} , $k_{f2}/k_{r2} \neq k_{f1}/k_{r1}$, and the system is no longer at equilibrium.

At equilibrium at T_2 , $[A] = [A]_2$ and $[B] = [B]_2$. Define

$$x = [A] - [A]_2 = [B]_2 - [B]$$

$$x_0 = [A]_1 - [A]_2$$

At equilibrium:

$$k_{f2}[A]_2 = k_{r2}[B]_2$$

After the T-jump

$$\frac{dx}{dt} = -k_{f2} [A] + k_{r2} [B]$$

= $-k_{f2} ([A]_2 + x) + k_{r2} ([B]_2 - x)$
 $\frac{dx}{dt} = -(k_{f2} + k_{r2})x$
so $x = e^{-(k_{f2} + k_{r2})t}$. Let $\tau = (k_{f2} + k_{r2})^{-1}$.

 $x = x_0 \exp(-t/\tau)$

Potential energy surfaces (PES) Example:

 $F + H_2 \rightarrow FH + H = -133.3 \, kJ/mol$

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

• initial positions \vec{R}_j and velocities $d\vec{R}_j/dt$ of the 3 atoms. If F is atom 1, $\vec{R}_1 = \vec{R}_F = (x_1, y_1, z_1)$.

- forces $\vec{f_j}$ acting on the 3 atoms
- time evolution of $\vec{R}_j, d\vec{R}_j/dt, \vec{f}_j$:

 $\vec{f_j} = m_j \, d^2 \vec{R_j} / dt^2 \Rightarrow$ 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 $d\vec{R}_j/dt$ 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

$$V \equiv V(x_1, y_1, z_1, x_2, \dots, z_3)$$

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 H—F distance d_1 , H—H' distance d_2 , and F—H' distance d_3 .

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

It is hard to visualize a function of more than 2 variables. So imagine that F, H and H' move on a line. Then

$$d_3 = d_1 + d_2$$

and the PES

$$V \equiv V(d_1, d_2)$$

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

- FH + H' is a valley
- F + HH' is another valley
- the separated atoms, F+H+H', 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 $E^{\ddagger} = V_{TS} - V_{reactants}$

Transition state theory

$$A + B \rightarrow P$$

Assume that

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

$$A + B \leftrightarrows AB^{\ddagger} \to P$$

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

$$\overline{K}_c^{\ddagger} = \frac{[AB^{\ddagger}]c^{\circ}}{[A][B]}$$

$$R = k'[AB^{\ddagger}] = k' \overline{K}_c^{\ddagger}[A][B] = k [A][B]$$

Key results of TS theory.

$$k = \kappa \frac{k_B T}{h c^{\circ}} \overline{K}_c^{\ddagger}$$

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

$$k = \kappa \frac{k_B T}{hc^{\circ}} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

That's the **Eyring equation**.

Comparing the Eyring equation to the Arrhenius relation, $k = A e^{-E_a/RT}$, one can get expressions for A and $E_a \dots$

For reactions in solution,

$$E_a = \Delta H^{\ddagger} + RT$$
$$A = \frac{ek_BT}{hz} e^{\Delta S^{\ddagger}/R}$$

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

For reactions in the gas phase,

$$E_a = \Delta H^{\ddagger} + mRT$$
$$A = \frac{e^m k_B T}{hz} e^{\Delta S^{\ddagger}/R}$$

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 $E_a > 3RT/2$

In solution:

- molecules move in a random walk
- when colliding, A and B stay close for some time
- in some cases $E_a < 3RT/2$
- 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

$$A + B \xrightarrow{k_d} AB$$

$$AB \xrightarrow{k_r} A + B$$

$$AB \xrightarrow{k_p} Products$$

$$R = k_p[AB]$$
Make the SSA:
$$\frac{d[AB]}{dt} \approx 0 = k_d[A][B] - (k_r + k_p)[AB]$$

$$[AB] = \frac{k_d[A][B]}{k_r + k_p}$$

and

 $\frac{d[AB]}{dt}$

$$R = \frac{k_p k_d[A][B]}{k_r + k_p}$$

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 (D_{AB}) and how big they are (r_A, r_B) :

$$k_d = 4\pi N_A \left(r_A + r_B \right) D_{AB}$$

 r_A : radius of A N_A : Avogadro's constant $D_{AB} = D_A + D_B$, and $D_A = \frac{k_B T}{6\pi\eta r_A}$

 η is the viscosity of the solvent.

$CH_3COO^- + H^+ \to CH_3COOH$

$$\begin{split} D_A &= 1.1 \times 10^{-5} \ {\rm cm}^2 \ {\rm s}^{-1} \\ D_B &= 9.3 \times 10^{-5} \ {\rm cm}^2 \ {\rm s}^{-1} \\ r_A + r_B &\approx 5 \ {\rm \AA}. \end{split}$$

$$k_d \approx 4\pi \times 6.02 \times 10^{23} \, mol^{-1}$$
$$\times 5 \times 10^{-8} \, cm$$
$$\times 10.4 \times 10^{-5} \, cm^2 \, s^{-1}$$

$$= 3.9 \times 10^{13} \, cm^3 \, s^{-1} \, mol^{-1}$$

$$= 3.9 \times 10^{10} L \, mol^{-1} \, s^{-1}$$

$$= 3.9 \times 10^{10} \, M^{-1} \, s^{-1}$$

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

$$2N_2O_5(g) \to 4NO_2(g) + O_2(g)$$

The observed rate law is $R = k[N_2O_5]$. A proposed mechanism:

1.
$$2 \times (N_2O_5 \rightleftharpoons NO_2 + NO_3)$$

2. $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$
3. $NO + NO_3 \rightarrow 2NO_2$

with rate constants k_1, k_{-1}, k_2 , and k_3 .

 $NO_3, NO:$ 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):

$$R = \frac{-1}{2} \frac{d[N_2 O_5]}{dt} = \frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt}$$

We can use any of the 3 expressions for R. The most convenient is $R = \frac{d[O_2]}{dt}$ because $[O_2]$ is affected by only one process, forward step 2.

$$R = \frac{d[O_2]}{dt} = k_2[NO_2][NO_3]$$

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

$$\frac{d[NO]}{dt} \approx 0 = k_2[NO_2][NO_3] - k_3[NO][NO_3]$$
$$[NO] = \frac{k_2[NO_2]}{k_3}$$

The second is

$$\frac{d[NO_3]}{dt} \approx 0 = k_1 [N_2 O_5] - k_{-1} [NO_2] [NO_3]$$
$$- k_2 [NO_2] [NO_3] - k_3 [NO] [NO_3]$$
$$= k_1 [N_2 O_5] - k_{-1} [NO_2] [NO_3]$$
$$- k_2 [NO_2] [NO_3] - k_3 \frac{k_2 [NO_2]}{k_3} [NO_3]$$

Rearranging:

$$[NO_2][NO_3] = \frac{k_1[N_2O_5]}{k_{-1} + 2k_2}$$

Recall $R = k_2[NO_2][NO_3]$, so

$$R = \frac{k_1 k_2}{k_{-1} + 2k_2} [N_2 O_5] = k [N_2 O_5]$$

Pre-equilibrium Approximation (PEA)

$$2NO(g) + O_2(g) \to 2NO_2(g)$$

mechanism:

1. $2NO \rightleftharpoons N_2O_2$ (preequilibrium)

$$2. \qquad N_2 O_2 + O_2 \to 2NO_2$$

The overall rate is $R = \frac{-d[O_2]}{dt} = k_2[N_2O_2][O_2].$ SSA: $\frac{d[N_2O_2]}{dt} \approx 0.$

$$0 = k_1 [NO]^2 - k_{-1} [N_2 O_2] - k_2 [N_2 O_2] [O_2]$$
$$[N_2 O_2] = \frac{k_1 [NO]^2}{k_{-1} + k_2 [O_2]}$$

SO

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

If $k_2[O_2] \ll k_{-1}$, this simplifies to

$$R = k_2[O_2] \frac{k_1}{k_{-1}} [NO]^2$$
$$= k_2 K_1 [O_2] [NO]^2$$

where K_1 is the equilibrium constant for step 1,

$$K_1 \equiv \frac{k_1}{k_{-1}} = \frac{N_2 O_2}{[NO]^2}$$

So, making the SSA <u>and</u> assuming $k_2[O_2] \ll k_{-1}$ 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:

$$1. \qquad A+M \leftrightarrows A^* + M$$

$$2. \qquad A^* \to P$$

 A^* represents a molecule of A with sufficient internal energy to break.

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0$$

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

Then:

$$\frac{d[P]}{dt} = k_2[A^*] \\ = \frac{k_2k_1[A][M]}{k_{-1}[M] + k_2}$$

Two limiting cases:

$$\frac{\text{case 1. } k_{-1}[M] \gg k_2}{\frac{d[P]}{dt}} = \frac{k_2 k_1}{k_{-1}}[A]$$

 $\frac{\text{case 2. } k_{-1}[M] \ll k_2}{\frac{d[P]}{dt}} = k_1[M][A]$

Back to the general case, we define

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2}$$

so that

$$\frac{d[P]}{dt} = k_{uni}[A]$$

When [M], or the pressure $P_M = RT(n_M/V)$, is high we are in case 1: k_{uni} does not change if we increase [M]. If [M] is low, k_{uni} increases linearly with [M]. Take $1/k_{uni}$:

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \left(\frac{1}{k_1}\right) \frac{1}{[M]}$$

A plot of $1/k_{uni}$ 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 C = catalyst, and SC = substrate-catalyst complex.

> 1. $S + C \leftrightarrows SC$ 2. $SC \rightarrow P + C$

Applying the SSA to the intermediate "SC" we get

$$[SC] = \frac{k_1}{k_{-1} + k_2} [S][C] \equiv \frac{[S][C]}{K_m}$$

$$\frac{d[P]}{dt} = k_2[SC] = \frac{k_2[S][C]}{K_m}$$

Often, we know only the initial concentrations $[S]_0$ and $[C]_0$.

$$[C] = [C]_0 - [SC]$$
$$[S] = [S]_0 - [SC] - [P] \approx [S]_0 - [SC]$$

We assume that [P] is very small: one often removes P to drive the reaction forward.

$$[S][C] = K_m[SC] \approx ([S]_0 - [SC]) ([C]_0 - [SC])$$

[SC] is small compared to $[S]_0$ and $[C]_0$. So we neglect $[SC]^2$, and rearrange to

 $K_m[SC] \approx [S]_0[C]_0 - [SC]([S]_0 + [C]_0)$

$$[SC] \approx \frac{[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

The rate is

$$R = \frac{d[P]}{dt} \approx R_0 = \frac{k_2[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

 $R \approx R_0$ provided [P] and [SC] are small compared to $[S]_0$ and $[C]_0$. We have two limiting cases.

The most common case is **1**: $[C]_0 \ll [S]_0$

$$R_0 = \frac{k_2[S]_0[C]_0}{[S]_0 + K_m}$$

$$\frac{1}{R_0} = \left(\frac{K_m}{k_2[C]_0}\right) \frac{1}{[S]_0} + \frac{1}{k_2[C]_0}$$

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 ES. ("lockand-key" model)

2. The complex ES may go back to unreacted substrate, or give products.

1.
$$E + S \leftrightarrows ES$$

$$2. \qquad ES \to E + P$$

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 **Lineweaver-Burk 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 $10^5 s^{-1}$ 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 , $R_0 = (k_2/K_m)[S]_0[C]_0$.

 k_2/K_m is called the catalytic efficiency.

	$k_2 (1/s)$	K_m (M)	k_2/K_m
chymotrypsin	0.14	1.5×10^{-2}	9.3
firefly luciferase	0.048	5.4×10^{-4}	89
pepsin	0.50	3.0×10^{-4}	1.7×10^{3}
ribonuclease	790	7.9×10^{-3}	1.0×10^{5}
fumerase	800	5.0×10^{-6}	1.6×10^{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} M⁻¹ 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:

$$E + S \leftrightarrows ES$$
$$ES \rightarrow E + P$$
$$E + I \leftrightarrows EI$$

Now $[E]_0 = [E] + [ES] + [EI]$. We use the PEA and assume that k_2 is small,

$$K_{S} = \frac{k_{-1}}{k_{1}} = \frac{[E][S]}{[ES]} \approx \frac{k_{-1} + k_{2}}{k_{1}} = K_{m}$$
$$K_{i} = \frac{k_{-3}}{k_{3}} = \frac{[E][I]}{[EI]}$$

Rewrite [E] and [EI], substitute in $[E]_0 = [E] + [ES] + [EI]$, and solve for $[ES] \dots$

Assuming $[S] \approx [S]_0$, the rate, $R = k_2[ES]$, 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*, pH, [*Na*⁺], [*K*⁺], ...).

 \star some CI drugs kill bacteria or viruses by binding to enzymes used in their replication.

 \star other CI drugs correct a metabolic imbalance by slowing down a reaction.

 \star protein kinase inhibitors are used in the treatment of cancers and inflammations.

 \star 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*.

 \star 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

1.
$$Cl + O_3 \rightarrow ClO + O_2$$

2. $ClO + O \rightarrow Cl + O_2$

net:

$$O_3 + O \rightarrow 2O_2$$

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 Cl, $R \equiv R_{nc} = k_{nc}[O][O_3]$, with $k_{nc} = 3.30 \times 10^5 \,\mathrm{M^{-1} \, s^{-1}}$.

With Cl,
$$k_1 = 1.56 \times 10^{10} \,\mathrm{M^{-1} \, s^{-1}}$$

and $k_2 = 2.44 \times 10^{10} \,\mathrm{M^{-1} \, s^{-1}}$.

With the catalyzed mechanism and SSA,

$$\frac{d[Cl]}{dt} = 0 = -k_1[Cl][O_3] + k_2[ClO][O]$$
$$[ClO] = \frac{k_1[Cl][O_3]}{k_2[O]}$$

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

$$[Cl] + [ClO] = [Cl]_{total}$$

where $[Cl]_{total}$ is a constant. Then

$$[Cl] = [Cl]_{total} - \frac{k_1[Cl][O_3]}{k_2[O]}$$
$$[Cl] = \frac{[Cl]_{total} k_2[O]}{k_1[O_3] + k_2[O]}$$

The rate is

$$R_{cat} = k_1[O_3][Cl] = \frac{k_1k_2 [Cl]_{total} [O] [O_3]}{k_1[O_3] + k_2[O]}$$

Ozone is reactive, but much less than O atoms, so $[O_3] \gg [O]$ and we can neglect $k_2[O]$ in the denominator:

$$R_{cat} = k_2[Cl]_{total}[O]$$

The ratio of rates $R_{cat}/R_{nc} = k_2[Cl]_{total}/k_{nc}[O_3].$

Using the numerical values of k_2 , k_{nc} , and $[Cl]_{total}/[O_3] \approx 10^{-3}$, we find $R_{cat}/R_{nc} \approx 74$.

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

Rowland and Molina hypothesized that photolysis of $CFCl_3$ and CF_2Cl_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

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

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 $\theta = V_{ads}/V_m$: fraction of sites occupied by A, and P = pressure of A(g).

 V_m : maximum volume of gas that can be adsorbed.

$$\frac{d\theta}{dt} = k_a P N (1 - \theta) - k_d N \theta$$

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

$$\theta = \frac{k_a P}{k_a P + k_d} = \frac{KP}{KP + 1}$$

 $K = k_a/k_d$. This is the **Langmuir isotherm**.

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

 $\ln K \text{ vs } 1/T \text{ is a line with slope } -\Delta H_{ads}/R$

(Recall
$$K = \exp(-\Delta G_{ads}^{\circ}/RT)$$

= $\exp(-\Delta H_{ads}^{\circ}/RT + \Delta S_{ads}^{\circ}/R)$)

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

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

In **dissociative chemisorption** a molecule " A_2 " breaks into two fragments A upon adsorption:

 $A_2(g) + 2M(\text{surface}) \rightarrow 2A \cdot M(\text{surface})$

and we get a somewhat different expression for θ ,

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

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 (CH₃·, Cl·, HO·, ...) are extremely reactive.

Small amounts of \mathbb{R} can trigger reactions that would not happen otherwise.

initiation steps: molecule(s) $\rightarrow R$.

propagation steps: the "main mechanism"

termination steps: $R \rightarrow molecule(s)$

The *propagation* steps add up to the net reaction.

initiation 1. $C_2H_6 \rightarrow 2CH_3 \cdot$ 2. $CH_3 \cdot + C_2H_6 \rightarrow CH_4 + C_2H_5 \cdot$

propagation 3. $C_2H_5 \rightarrow C_2H_4 + H \rightarrow 4$. $H \rightarrow C_2H_6 \rightarrow C_2H_5 \rightarrow H_2$

termination 5. $H \cdot + C_2 H_5 \cdot \rightarrow C_2 H_6$

 ΔH for each step:

1: +90 kcal/mol 2: -4.3 kcal/mol 3: +36 kcal/mol 4: -3.6 kcal/mol 5: -101 kcal/mol,

steps 1 and 5 are rare events; step 2 is "fed" CH_3 by step 1 only; steps 3 and 4 feed each other. The only step where C_2H_4 is produced is 3., so the rate for the overall reaction is

 $R = k_3 [C_2 H_5 \cdot]$

let $R \cdot = H \cdot, C H_3 \cdot$, or $C_2 H_5 \cdot$

$$0 \approx \frac{d[R \cdot]}{dt} = 2k_1 [C_2 H_6] - 2k_5 [H \cdot] [C_2 H_5 \cdot]$$
$$[H \cdot] = \frac{k_1 [C_2 H_6]}{k_5 [C_2 H_5 \cdot]}$$
$$0 \approx \frac{d[H \cdot]}{dt} = k_3 [C_2 H_5 \cdot]$$
$$-k_4 [C_2 H_6] \left(\frac{k_1 [C_2 H_6]}{k_5 [C_2 H_5 \cdot]}\right)$$
$$-k_5 [C_2 H_5 \cdot] \left(\frac{k_1 [C_2 H_6]}{k_5 [C_2 H_5 \cdot]}\right)$$

Let $x = [C_2H_5\cdot]$ and multiply by x/k_3 everywhere

$$0 = x^2 - \frac{k_1}{k_3} [C_2 H_6] x - \frac{k_1 k_4}{k_3 k_5} [C_2 H_6]^2$$

It is a quadratic equation for x with solutions

$$x = \frac{k_1}{2k_3} [C_2 H_6]$$

$$\pm \left(\left(\frac{k_1}{2k_3} [C_2 H_6] \right)^2 + \frac{k_1 k_4}{k_3 k_5} [C_2 H_6]^2 \right)^{1/2}$$

$$x = [C_2 H_6] \left[\frac{k_1}{2k_3} \pm \left(\left(\frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5} \right)^{1/2} \right]$$

• we keep the "+" sign, or else x < 0

• k_1 is very small, so we neglect $(k_1/2k_3)^2$, and

then neglect $(k_1/2k_3)$, so all that's left is

$$[C_2 H_5 \cdot] = x = \left(\frac{k_1 k_4}{k_3 k_5}\right)^{1/2} [C_2 H_6]$$

SO

$$R = k_3 [C_2 H_5 \cdot] = k_3 \left(\frac{k_1 k_4}{k_3 k_5}\right)^{1/2} [C_2 H_6]$$

$$R = \left(\frac{k_1 k_3 k_4}{k_5}\right)^{1/2} [C_2 H_6]$$

Radical-chain polymerization

We have radicals R formed by cleavage of an initiator I, and monomers M:

initiation $I \to 2 R \cdot$ (k_i) $R \cdot + M \to M_1 \cdot$ (k_1) propagation $M_1 \cdot + M \to M_2 \cdot$ $M_2 \cdot + M \to M_3 \cdot$ (k_p) \dots $M_{n-1} \cdot + M \to M_n \cdot$

termination $M_m \cdot + M_n \cdot \to M_{m+n} \cdot (k_t)$

Let $[M \cdot] = [M_1 \cdot] + [M_2 \cdot] + [M_3 \cdot] + \dots$ We apply the SSA to $[M \cdot]$.

$$\frac{d[M\cdot]}{dt} = 2\phi k_i[I] - 2k_t[M\cdot]^2 \approx 0$$

 ϕ is the probability that R reacts with M, and not with something else.

$$[M\cdot] = \left(\frac{\phi k_i}{k_t}\right)^{1/2} [I]^{1/2}$$

$$\frac{d[M]}{dt} = -k_p[M\cdot][M] - (k_1[R\cdot][M])$$
$$\approx -k_p \left(\frac{\phi k_i}{k_t}\right)^{1/2} [I]^{1/2} [M]$$

The kinetic chaing length ν is the ratio of (a) the rate of consumption of M, to (b) the rate of creation of M_1 .

$$\nu = \frac{k_p[M \cdot][M]}{2\phi k_i[I]}$$

$$\nu = \frac{k_p[M]}{2(\phi k_i k_t)^{1/2} [I]^{1/2}}$$

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

Explosions

Two types of explosions:

(1) If ΔH_{rxn} is large and negative, and heat does not dissipate quickly enough, $T \nearrow$, so $k \nearrow$, generating more heat, $T \nearrow$ and $k \nearrow$, ...

 \Rightarrow thermal explosion

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

 \Rightarrow chain-branching explosion

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

$$1. \quad H_2 + O_2 \to 2 OH \cdot \tag{+2}$$

- $2. H_2 + OH \cdot \to H \cdot + H_2O (0)$
- 3. $H \cdot + O_2 \to OH \cdot + \cdot O \cdot$ (+1)
- 4. $\cdot O \cdot + H_2 \rightarrow OH \cdot + H \cdot$ (+1)
- 5. $H \cdot + O_2 + M \to HO_2 \cdot + M^*$ (0)

. . .

1. <u>initiation</u>: stable molecules give radicals.

2. and 5. <u>propagation</u>: no net change in number of radicals.

3. 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: any radical

A, B: reactants ; P_1, P_2 : products

 ϕ : mean number of radicals produced in branching reactions (branching efficiency)

initiation	$A + B \to R \cdot$	k_i
branching	$R \cdot \to \phi R \cdot + P_1$	k_b
termination	$R \cdot \to P_2$	k_t

$$\frac{d[R\cdot]}{dt} = k_i[A][B] + (-k_b + \phi k_b - k_t)[R\cdot]$$

Define $\Gamma \equiv k_i[A][B] \approx \text{a constant},$ and $a \equiv k_b(\phi - 1) - k_t$. Then

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

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

$$\frac{d[R\cdot]}{dt} = \frac{dy}{dt} = ay$$

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

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

or

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

If $k_t < k_b(\phi - 1)$, then a > 0, and as $t \to \infty$, $[R \cdot] \to \infty$: explosion

If $k_t > k_b(\phi - 1)$, then a < 0. Let $a' \equiv -a$ (a' > 0), then

$$[R\cdot] = \frac{\Gamma}{a'} \left(1 - e^{-a't}\right)$$

As $t \to \infty$, $[R \cdot] \to \Gamma/a'$. $[R \cdot]$ goes to a finite limiting value: no explosion.

Photochemistry

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

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

energy of a photon

$$E_{photon} = h\nu = hc/\lambda$$

Beer-Lambert law:

$$I_{abs} = 2.303 \times I_0 \,\epsilon \,\ell \,[A]$$

 I_0, I_{abs} : incident/absorbed light intensity, in "mole of photon $cm^{-2}s^{-1}$ " ℓ : optical path length, in cm ϵ : molar absorptivity, in $M^{-1}cm^{-1}$ $2.303 = \ln 10$

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 ℓ and exits with intensity $I < I_0$. We want to calculate I or $I_{abs} = I_0 - I$.

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: ℓ 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 = dx is $\operatorname{Prob} (A) dx$ or $\operatorname{Prob} (\epsilon A) dx$, where ϵ is the proportionality factor which depends on the molecule "A" absorbing light and the wavelength λ . The attenuation factor between x = 0 and x = dx is $(1 - \epsilon A) dx$, and the intensity of light at x = dxis

$$I(dx) = I_0(1 - \epsilon[A]dx)$$

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

$$I(2dx) = I_0(1 - \epsilon[A]dx)^2$$

$$I(3dx) = I_0(1 - \epsilon[A]dx)^3$$

. . .

Then, $I(\ell) \equiv I = I_0(1 - \epsilon[A]dx)^n$, or $I_0/I = (1 - \epsilon[A]dx)^{-n}$

$$\ln(I_0/I) = -n\ln(1-\epsilon[A]dx)$$

 $= -n(-\epsilon[A]dx - (\epsilon[A]dx)^2 - \dots)$
In the limit $dx \to 0$ we have

$$\ln(I_0/I) = n\epsilon[A]dx$$

Since $n = \ell/dx$,

$$\ln(I_0/I) = \epsilon \ell[A]$$

Instead of I_0/I or $I_{abs} = I_0 - I$, 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 ϵ that is 2.303 times smaller:

$$T = 10^{-\epsilon\ell[A]} \equiv 10^{-A}$$
$$A = \epsilon\ell[A]$$

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:

$$I_0/I = e^{\epsilon \ell[A]}$$

= $1 + \epsilon \ell[A] + \frac{1}{2} (\epsilon \ell[A])^2 + \dots$

Keeping only the first two terms,

$$I_0/I \approx I/I + \epsilon \ell [A]$$
$$I_0 - I \approx I \epsilon \ell [A]$$

When [A] is very small, we normally have $I/I_0 \approx 1$ and we can write $I_{abs} = I_0 - I$ like this

$$I_0 - I \equiv I_{abs} \approx I_0 \epsilon \ell[A]$$

or, if we use the \log_{10} convention instead,

$$I_{abs} \approx 2.303 \times I_0 \epsilon \ell[A]$$

with ϵ smaller by a factor 2.303.

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

$$R = \frac{I_{abs}}{\ell} \times 1000 \, cm^3 / L$$

SO

$$-\frac{d[A]}{dt} = 2303 I_0 \epsilon [A]$$

After integration,

$$[A] = [A]_0 e^{-2303I_0\epsilon t}$$

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

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

$$-\frac{dA}{dt} = \frac{2303I_0\epsilon}{N_A}A$$
$$A = A_0 e^{-I_0(2303\epsilon/N_A)t}$$
$$A = A_0 e^{-I_0\sigma_A t}$$

NOTE: now
$$I_0$$
 is in "photon $cm^{-2}s^{-1}$ "

 σ_A has units $\frac{cm^3}{L} \times \frac{M^{-1}cm^{-1}}{mol^{-1}} = cm^2$ and is called the *absorption cross section*.

$$k_a = I_0 \sigma_A$$
 is in $cm^{-2} s^{-1} cm^2$, or 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.

$$\alpha(s_1)\beta(s_2) \equiv \alpha\beta, \ \beta(s_1)\alpha(s_2) \equiv \beta\alpha, \alpha(s_1)\alpha(s_2) \equiv \alpha\alpha, \text{ and } \beta(s_1)\beta(s_2) \equiv \beta\beta.$$

The 4 *correct* spin functions are:

$$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha): \text{ one state } S_1$$

$$\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha), \ \alpha\alpha, \text{ and } \beta\beta: \text{ a triplet of states } T_1$$

Each process has an associated rate constant.

 $k_{vr} \approx 10^{13} \, s^{-1}$ 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: $k_f[S_1]$

 T_1 to $S_0 + h\nu$, phosporescence: $k_p[T_1]$

$$S_1$$
 to T_1 , isc: $k_{isc,S}[S_1]$

 S_1 to S_0 , ic: $k_{ic}[S_1]$

 T_1 to S_0 , isc: $k_{isc,T}[T_1]$

Excited molecules in state S_1 can return to the ground state by **collisional quenching**:

 $S_1 + Q \to S_0 + Q$

with rate

$$R_q = k_q [S_1][Q]$$

Accounting for all processes involving S_1 and making the SSA,

$$0 \approx k_a[S_0] - [S_1](k_f + k_{ic} + k_{isc,S} + k_q[Q])$$

The *fluorescence lifetime* is

$$\frac{1}{\tau_f} = k_f + k_{ic} + k_{isc,S} + k_q[Q]$$

Then

$$[S_1] = k_a[S_0] \tau_f$$

The fluorescence intensity is

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

 $\Phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc,S} + k_q[Q]}$ 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 $k_f \gg k_{ic}$ and $k_f \gg k_{isc,S}$. Then

$$\frac{1}{I_f} \approx \frac{1}{k_a[S_0]} + \frac{k_q}{k_a k_f[S_0]}[Q]$$
$$\frac{I_0}{I_f} = 1 + \frac{k_q}{k_f}[Q]$$

 $\frac{I_0}{I_f}$ vs [Q] is a Stern-Volmer (SV) plot.

 O_2 and acrylamide (CH₂CHCONH₂) are common quenchers.

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

W Qiu et al., Chemical Physics 350 (2008) 154– 164. 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.).

1.
$$D \xrightarrow{h\nu,k_a} D^*$$

$$2. \quad D^* \xrightarrow{k_f} D$$

3.
$$D^* \xrightarrow{k_{nr}} D$$

4.
$$D^* + A \xrightarrow{k'_{fret}} D + A^*$$

5.
$$A^* \xrightarrow{k_{f'}} A$$

 $k_{fret} = k'_{fret}[A]$ ([A] is not always relevant)

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

$$\Phi_f = \frac{k_f}{k_f + k_{nr}}$$
$$k_{nr} = k_{ic} + k_{ics,S} + k_q[Q]$$

becomes

$$\Phi_{f,fret} = \frac{k_f}{k_f + k_{nr} + k_{fret}}$$

The quantum yield for FRET is

$$\Phi_{fret} = \frac{k_{fret}}{k_f + k_{nr} + k_{fret}}$$

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

In practice Φ_{fret} is measured by the difference in the fluorescence of D in the presence of A

$$\Phi_{fret} = 1 - \frac{\Phi_{f,fret}}{\Phi_f}$$

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

$$\Phi_{fret} = \frac{1}{1 + (r/r_0)^6}$$

 r_0 depends on the D/A pair and is normally between 10 and 60 Å.

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 Φ_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

$$R_{photochem.} = k_{photo,S1}[S_1]$$

Quantum yield

$$\phi = \frac{k_{photo,S1}}{k_f + k_{nr} + k_{photo,S1}}$$

 ϕ : fraction of excited molecules that react

Number of absorbed photons, N_{abs}

$$N_{abs} = \frac{E_{abs}}{E_{photon}} = \frac{P\Delta t}{h\nu} = \frac{P\Delta t}{hc/\lambda}$$

P: power (in Watts, W)

Electron transfer

 $D + A \leftrightarrows D^+ + A^-$

essential in photovoltaics & photosynthesis

 $6CO_2(g) + 6H_2O(\ell) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$

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

- light absorption
- FRET (energy migration to rxn center)
- e⁻ transfer reactions
- many other reactions

e^- transfer kinetics

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

$$D + A \rightleftharpoons DA \qquad (k_d, k'_d)$$
$$DA \leftrightarrows D^+ A^- \qquad (k_e, k'_e)$$
$$D^+ A^- \to D^+ + A^- \qquad (k_{sep})$$
SSA for $[D^+ A^-]$:

$$[D^+A^-] = \frac{k_e[DA]}{k'_e + k_{sep}}$$

SSA for [DA]:

$$[DA] = \frac{k_d[D][A] + k'_e[D^+A^-]}{k'_d + k_e}$$

Substituting:

$$[D^{+}A^{-}] = \frac{k_{e}k_{d}}{k'_{e}k'_{d} + k_{sep}k'_{d} + k_{sep}k_{e}} [D][A]$$

the rate is

$$R = k_{sep}[D^+A^-] = k[D][A]$$

We assume $k_{sep} \gg k'_e$, so

$$R = \frac{k_e k_d}{k_e + k'_d} [D][A]$$

Two limiting cases:

1) $k_e \gg k'_d$: $R = k_d[D][A]$ (diffusion controlled)

2)
$$k_e \ll k'_d$$
: $R = k_e K_d[D][A] \quad (K_d = k_d/k'_d)$

case 2. applies when D and A are bonded, or held together by a surrounding protein(s).

A microscopic view of e⁻ transfer:

Marcus theory (~ 1956)

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: $k \propto e^{-\Delta G^{\ddagger}/k_B T}$

 ΔG° : free energy change for the charge transfer

 $\lambda > 0$: reorganization energy, free energy of DA at the equilibrium geometry of D⁺A⁻, including the solvent.

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

x: reaction coordinate

x = 0, equilibrium geometry of DA; x = a, equilibrium geometry of D⁺A⁻

Assume the free energies of DA (G_n) and D⁺A⁻ (G_t) are quadratic wrt displacement from equilibrium, with force constant k, and set $\Delta G = 0$ at x = 0.

$$G_n = \frac{1}{2}kx^2$$

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

The two energy curves cross at x_c :

$$\frac{1}{2}kx_{c}^{2} = \frac{1}{2}k(x_{c}^{2} - 2ax_{c} + a^{2}) + \Delta G^{\circ}$$
$$kax_{c} = \frac{1}{2}ka^{2} + \Delta G^{\circ}$$

$$\lambda = \frac{1}{2} k a^2$$
, so
 $kax_c = \Delta G^\circ + \lambda$

$$x_c = \frac{\Delta G^\circ + \lambda}{ka}$$

Energy at x_c :

$$\Delta G^{\ddagger} = \frac{1}{2} k x_c^2 = \frac{k}{2} \left(\frac{\Delta G^{\circ} + \lambda}{ka} \right)^2$$
$$= \frac{(\Delta G^{\circ} + \lambda)^2}{2ka^2}$$
$$\Delta G^{\ddagger} = \frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda}$$

- $k \propto e^{-\beta r} e^{-\Delta G^{\ddagger}/k_B T} \propto A e^{-\Delta G^{\ddagger}/k_B T}$ same form as Eyring's formula
- the rate is maximum at $\Delta G^{\circ} = -\lambda$
- $\Delta G^{\circ} < -\lambda$: "inverted regime" (expt in 1984)

• e⁻ transfer can be accompanied by an important solvent reorganization, and large λ

• "outer sphere" reactions: only the solvent reorganizes. The e⁻ transfers when the solvation shell is optimal for stabilizing a fictitious $D^{+q}A^{-q}$.

- ΔG° generally more negative in polar solvents
- applications: photosynthesis, corrosion, chemiluminescence, solar cells

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