Complex Reaction Mechanisms
Chapter 36

Reaction Mechanisms:

Reaction mechanism is a *collection of elementary (one step) reactions* that would add up to result in the overall reaction. Generally elementary (simple) reactions are bimolecular and unimolecular, rarely are termolecular.

Experimentally determined rate law does not conform with the stoichiometric coefficients of reactions, in general; unless the mechanism itself is simple. Therein lies the need to propose a mechanism for the reaction.

A valid reaction mechanism must be consistent with the experimental rate law.

For example; $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$

Rate Law is of the 'form'; $R = k[N_2O_5]$

The form of the rate law signals that the reaction involves multiple steps (a 'complex' mechanism).

Mechanisms involve many single step reactions (sum of them is the overall reaction), creation of intermediates (allowing use of steady state approximation) and equilibria.

Proposed mechanism: $2\left\{N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \cancel{NO_2} + \underline{\cancel{NO_3}}\right\}$

$$\cancel{NO_2} + \cancel{NO_3} \xrightarrow{k_2} NO_2 + O_2 + \underline{\cancel{NO}}$$

$$\cancel{NO} + \cancel{NO_3} \xrightarrow{k_3} 2\,NO_2$$

Reaction rate law can be written as;

$$-\frac{d[N_2O_5]}{dt} = (k_1[N_2O_5] - k_{-1}[NO_2]\underline{[NO_3]})$$ ★

$$R = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}(k_1[N_2O_5] - k_{-1}[NO_2]\underline{[NO_3]})$$

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + \underline{NO}$$

$$\underline{NO} + NO_3 \xrightarrow{k_3} 2\,NO_2$$

Invoking SSA for NO and NO_3.

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

$$\frac{d[NO_3]}{dt} = 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3]$$

$$\Rightarrow \quad [NO] = \frac{k_2[NO_2]}{k_3}$$

$$\Downarrow$$

$$0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - \cancel{k_3}\left(\frac{k_2[NO_2]}{\cancel{k_3}}\right)[NO_3]$$

$$0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - 2k_2[NO_2][NO_3]$$

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

$$R = \frac{1}{2}(k_1[N_2O_5] - k_{-1}[NO_2][NO_3]) \qquad ★$$

$$= \frac{1}{2}\left(k_1[N_2O_5] - k_{-1}\left(\frac{k_1[N_2O_5]}{k_{-1} + 2k_2}\right)\right)$$

$$= \frac{k_1k_2}{k_{-1} + 2k_2}[N_2O_5] = k_{eff}\,[N_2O_5] \qquad ★★$$

Viola!!

Pre-equilibrium Approximation:

A useful concept for reactions that can proceed via an equilibrium involving an intermediate I.

$$\overbrace{A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}}}^{(1)} \underbrace{I \xrightarrow{k_p} P}_{(2)} \qquad \text{and rate=} \frac{d[P]}{dt} = k_p[I]$$

$$\Updownarrow$$

$$\frac{[I]}{[A][B]} = \frac{k_f}{k_r} = K_c$$

Upon rearrangement $[I] = K_c[A][B]$

Substituting for [I] in rate expression $\frac{d[P]}{dt} = k_p[I] = \underbrace{k_pK_c}[A][B] = k_{eff}\,[A][B]$

Reaction

$$2\mathrm{NO}(g) + \mathrm{O}_2(g) \rightarrow 2\mathrm{NO}_2(g)$$

Experiment

$$R = k_{eff}[\mathrm{NO}]^2[\mathrm{O}_2]$$

Mechanism: Pre-equilibrium

$$2\mathrm{NO} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{N}_2\mathrm{O}_2 \Longrightarrow [\mathrm{N}_2\mathrm{O}_2] = \frac{k_f}{k_r}[\mathrm{NO}]^2 = K_c[\mathrm{NO}]^2$$

Decay of intermediate

$$\mathrm{N}_2\mathrm{O}_2 + \mathrm{O}_2 \xrightarrow{k_p} 2\mathrm{NO}_2 \qquad R = \frac{1}{2}\frac{d[\mathrm{NO}_2]}{dt} = k_p[\mathrm{N}_2\mathrm{O}_2][\mathrm{O}_2]$$

$$R = k_p[\mathrm{N}_2\mathrm{O}_2][\mathrm{O}_2] = k_pK_c[\mathrm{NO}]^2[\mathrm{O}_2] = k_{eff}[\mathrm{NO}]^2[\mathrm{O}_2]$$

Lindeman Theory – Unimolecular Reactions:

$$\mathrm{A} \rightarrow fragments$$

The energy necessary to overcome the activation energy is achieved by collisions with any molecule (M) and M can very well be A itself. Two steps involved.

In gas phase the reaction constants are concentration, (i.e. pressure (total)) dependent.

In solution it is not concentration dependent, due to the fact that the particle concentration is nearly constant in solution phase.

Lindeman Theory – Unimolecular Reactions:

$$\mathrm{A} \rightarrow fragments$$

The energy necessary to overcome the activation energy is achieved by collisions with *any* molecule M and M can very well be an A. Two steps are involved, formation of A^* (activated reactant *not* an activated complex) and decomposition of A^* to form products.

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + M$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{P}$$

Lindeman Theory – Uni-molecular Reactions:

$$\mathrm{A} \rightarrow fragments$$

In general (solutions/ gases);

$$\left\{\begin{array}{l} \mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + M \\ \mathrm{A}^* \xrightarrow{k_2} \mathrm{P} \end{array}\right.$$

For M=A

The pre-equilibrium step.

$$\left\{\begin{array}{l} \mathrm{A} + \mathrm{A} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{A} \\ \mathrm{A}^* + \mathrm{A} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{A} \end{array}\right.$$

Reaction rate = $\dfrac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}^*]$

Applying SSA to A*.

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{A}][\mathrm{A}^*] - k_2[\mathrm{A}^*] = 0$$

$$\Rightarrow \quad [\mathrm{A}^*] = \frac{k_1[\mathrm{A}]^2}{(k_{-1}[\mathrm{A}] + k_2)}$$

Reaction rate = $\dfrac{d[\mathrm{P}]}{dt} = \dfrac{k_1 k_2[\mathrm{A}]^2}{k_{-1}[\mathrm{A}] + k_2}$

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2[\mathrm{A}]^2}{k_{-1}[\mathrm{A}] + k_2}$$

For k_{-1}[A]>>k_2

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}]$$

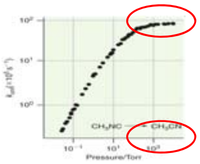
uni

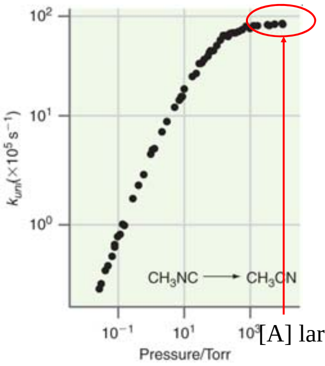
For k_{-1}[A]<<k_2

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{A}]^2$$

bi

True for [A] large.





[A] large

For the general case - Lindeman Theory :

Reactions in *solutions* or gases at high pressure - k_{-1}[A] >>0 .

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + M$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{P}$$

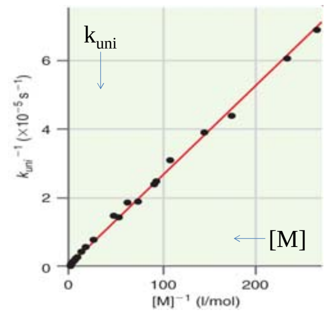
uni

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} = k_{uni}[\mathrm{A}]$$

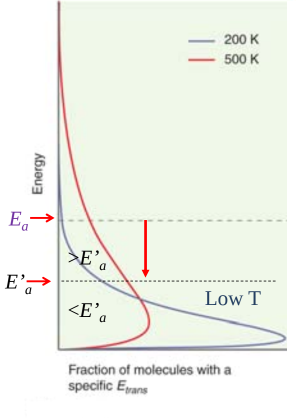
with $k_{uni} = \dfrac{k_1 k_2[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$

[M] ~ constant
$k_{app} = k_{uni}$ is not simplistic.

Upon rearrangement; $\dfrac{1}{k_{uni}} = \dfrac{k_{-1}}{k_1 k_2} + \left(\dfrac{1}{k_1}\right)\dfrac{1}{[\mathrm{M}]}$



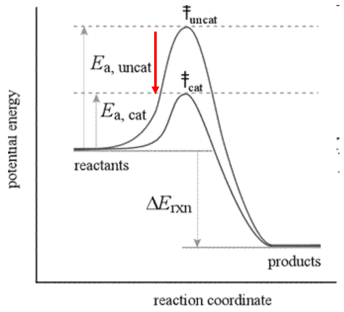
Catalysis



Increasing reaction rates amounts to increasing reaction rate constants.

$$k = Ae^{-E_a/RT}$$

One strategy would be to lower E'_a. Thereby increase the fraction of molecules with energy > E'_a.



Catalyst remain unchanged after the reaction, it changes the reaction mechanism by combining with reactant(s)/ intermediates and therefore changes the reaction coordinate.

Catalysis – a mechanism

$$\mathrm{S} + \mathrm{C} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SC}$$ ← S-C complex

Reactant = S

$$\mathrm{SC} \xrightarrow{k_2} \mathrm{P} + \mathrm{C}$$

Reaction rate; $\dfrac{d[\mathrm{P}]}{dt} = k_2[\mathrm{SC}]$

Applying SSA to SC;

$$\frac{d[\mathrm{SC}]}{dt} = k_1[\mathrm{S}][\mathrm{C}] - k_{-1}[\mathrm{SC}] - k_2[\mathrm{SC}] = 0$$

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

$$\boxed{K_m = \frac{k_{-1} + k_2}{k_1}}$$

Determining reaction parameters k_2 and K_m;
Intial rate method.

$$\because \quad \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{SC}]$$

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

Conservation of matter:
$$\begin{cases} [\mathrm{S}]_0 = [\mathrm{S}] + [\mathrm{SC}] + [\mathrm{P}] \\ [\mathrm{C}]_0 = [\mathrm{C}] + [\mathrm{SC}] \end{cases}$$

$$\begin{cases} [\mathrm{S}] = [\mathrm{S}]_0 - [\mathrm{SC}] - [\mathrm{P}] \\ [\mathrm{C}] = [\mathrm{C}]_0 - [\mathrm{SC}] \end{cases}$$

Substituting for [S] and [C] in $[\mathrm{SC}] = \frac{[\mathrm{S}][\mathrm{C}]}{K_m}$

and rearranging ;

$$K_m[\mathrm{SC}] = [\mathrm{S}][\mathrm{C}] = ([\mathrm{S}]_0 - [\mathrm{SC}] - [\mathrm{P}])\,([\mathrm{C}]_0 - [\mathrm{SC}])$$

$$0 = [[\mathrm{C}]_0([\mathrm{S}]_0 - \cancel{[\mathrm{P}]})] - [\mathrm{SC}]([\mathrm{S}]_0 + [\mathrm{C}]_0 - \cancel{[\mathrm{P}]} + K_m) + \cancel{[\mathrm{SC}]^2}$$

@ t = 0, where $R = R_0$

Simplifies to; $$[\mathrm{SC}] = \frac{[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$$

yields; $$R_0 = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$$

yields; $$R_0 = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$$

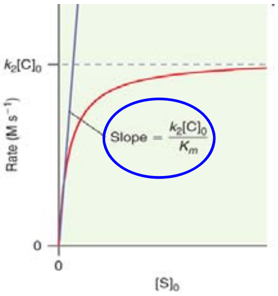
(1) For $[\mathrm{C}]_0 << [\mathrm{S}]_0$

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

(a) and also if $[\mathrm{S}]_0 < K_m$

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

$[\mathrm{R}]_0$ linear to $[\mathrm{S}]_0$.



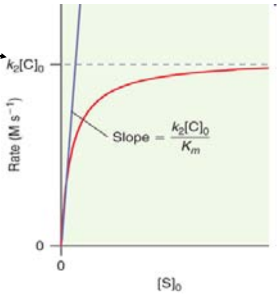
Starting with; $$R_0 = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$$

For $[\mathrm{S}]_0 >> [\mathrm{C}]_0$ experimental conditions

(b) and also if $[\mathrm{S}]_0 > K_m$

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

At large $[\mathrm{S}]_0$, $R_0 = k_2[\mathrm{C}]_0$

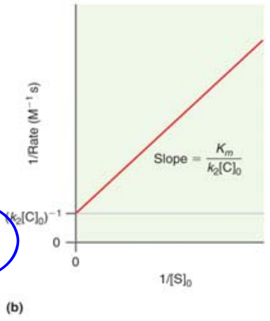


alternatively

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

invert ↓

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



Reciprocal plot

Again, $R_0 = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$

(1) For $[\mathrm{C}]_0 << [\mathrm{S}]_0$

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

(b) if $[\mathrm{S}]_0 >> \mathrm{K}_\mathrm{m}$

$$\Downarrow$$

$$R_0 = k_2[\mathrm{C}]_0 = R_{max}$$

$[\mathrm{R}]_0$ reaches a *limiting value* and zero order w.r.t. [S] .

using; $R_0 = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{S}]_0[\mathrm{C}]_0}{[\mathrm{S}]_0 + [\mathrm{C}]_0 + K_m}$

(2) For $[\mathrm{C}]_0 >> [\mathrm{S}]_0$

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

(a) if $[\mathrm{C}]_0 < \mathrm{K}_\mathrm{m}$

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

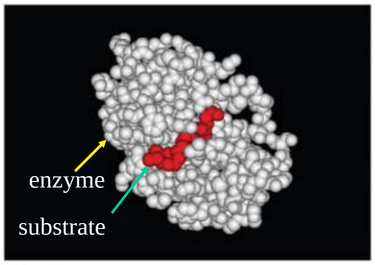
$[\mathrm{R}]_0$ linear to $[\mathrm{C}]_0$ & $[\mathrm{S}]_0$.

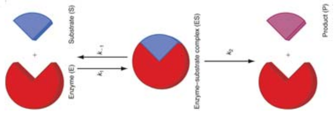
(b) if $[\mathrm{C}]_0 > \mathrm{K}_\mathrm{m}$

$$R_0 = k_2[\mathrm{S}]_0$$

$[\mathrm{R}]_0$ linear to $[\mathrm{S}]_0$.

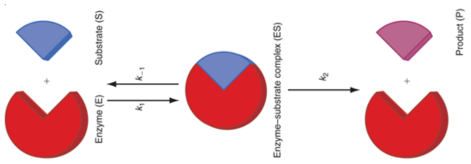
Michaelis-Menten Enzyme Kinetics





Michaelis-Menten Enzyme Kinetics

Enzymes are reaction specific catalysts.



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

↕

C

Michaelis-Menten rate law

For $[E]_0 << [S]_0$; **Rate =** $R_0 = \dfrac{k_2[S]_0[E]_0}{[S]_0 + K_m}$

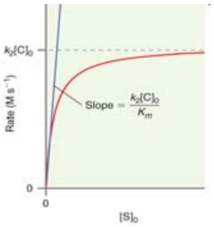
K_m= Michaelis-Menten constant

and also if $[S]_0 >> K_m$ above equation simplifies to,

$$R_0 = k_2[E]_0 = R_{max}$$

The reaction rate plateau is at $k_2[E]_0$

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



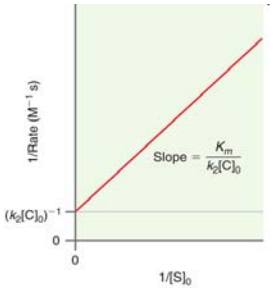
Lineweaver-Burk Equation

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

invert

K_m?

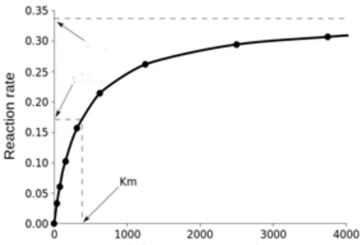
$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \frac{1}{[S]_0}$$



Determination of K_m

With R_{max} known, evaluate $R_{max}/2$ substitute in

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



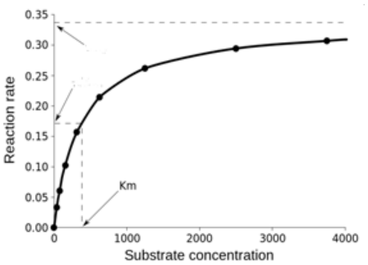
$$R_0 = \frac{k_2[S]_0[E]_0}{[S]_0 + K_m} = \frac{R_{max}[S]_0}{[S]_0 + K_m}$$

$$\frac{\cancel{R_{max}}}{2} = \frac{\cancel{R_{max}}[S]_0}{[S]_0 + K_m}$$

$$[S]_0 + K_m = 2[S]_0$$

$$K_m = [S]_0 \Leftarrow$$

Determination of K_m



With R_{max} known, evaluate $R_{max}/2$ substitute in

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

$$R_0 = \frac{\mathrm{k}_2[\mathrm{S}]_0[\mathrm{E}]_0}{[\mathrm{S}]_0 + K_m} = \frac{R_{\max}[\mathrm{S}]_0}{[\mathrm{S}]_0 + K_m}$$

$$\frac{\cancel{R_{\max}}}{2} = \frac{\cancel{R_{\max}}[\mathrm{S}]_{@\mathrm{Rmax}/2}}{[\mathrm{S}]_{@\mathrm{Rmax}/2} + K_m}$$

$$[\mathrm{S}]_{@\mathrm{Rmax}/2} + K_m = 2[\mathrm{S}]_{@\mathrm{Rmax}/2}$$

$$K_m = [\mathrm{S}]_{@\mathrm{Rmax}/2} \quad \Leftarrow$$

Photochemistry – physical processes

Photochemistry deals with the chemical and physical changes of molecules following absorption of photons in the visible/UV region.

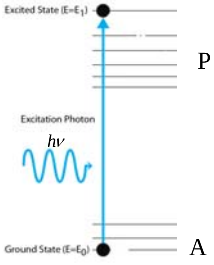
Following the absorption of photons molecules undergo electronic and vibrational and rotational (rotational in gas phase) excitation (photoexcitation).

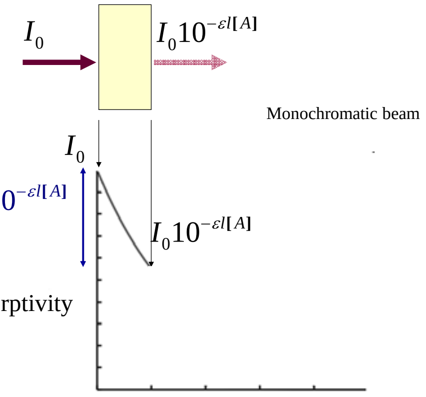
$$A \xrightarrow{h\nu} A^* \rightarrow \left\{\begin{array}{l} \left.\begin{array}{l} A(radiatively) \\ A(non-radiatively) \end{array}\right\} \text{physical processes} \\ \text{Photoproducts} \end{array}\right.$$

A^* =excited molecule

Photo-excitation; $\mathrm{A} \xrightarrow{h\nu} \mathrm{P}$

Rate of A undergoing photo excitation; $\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$





$$I_{abs} = I_0 - I_0 10^{-\varepsilon l[A]}$$

ε = molar absorptivity

$$10^{-\varepsilon l[\mathrm{A}]} = 1 - 2.303\varepsilon l[\mathrm{A}] + \cancel{\frac{(2.303\varepsilon l[\mathrm{A}])^2}{2!}} - \cdots$$

Setting [A] low, $10^{-\varepsilon l[\mathrm{A}]} = 1 - 2.303\varepsilon l[\mathrm{A}]$

$$\because I_{abs} = I_0(1-10^{-\varepsilon l[A]})$$

$$I_{abs} = I_0(2.303)\varepsilon l[\mathrm{A}]$$

$$\frac{d[\mathrm{A}]}{dt} = -I_{abs}$$

Keeping I_0 a constant and $l = 1$, substitute for I_{abs};

$$\frac{d[\mathrm{A}]}{dt} = -I_0(2.303)\varepsilon[A]$$ First order loss

$$\Downarrow$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-I_0(2303)\varepsilon t} = [\mathrm{A}]_0 e^{-kt}$$

$$\frac{d[\mathrm{A}]}{dt} = -I_0(2.303)\varepsilon[A]$$

In terms of number of molecules; A = # molecules of A,

$$-\frac{d\mathrm{A}}{dt} = I_0 \frac{2303\varepsilon}{N_A}\mathrm{A}$$

$$\Downarrow$$

$$\mathrm{A} = \mathrm{A}_0 e^{-I_0(2303\varepsilon/N_A)t} = \mathrm{A}_0 e^{-\overbrace{I_0\sigma_A}^{k_a} t}$$

σ_A = absorption cross section.

Jablonski Diagram

(paths)

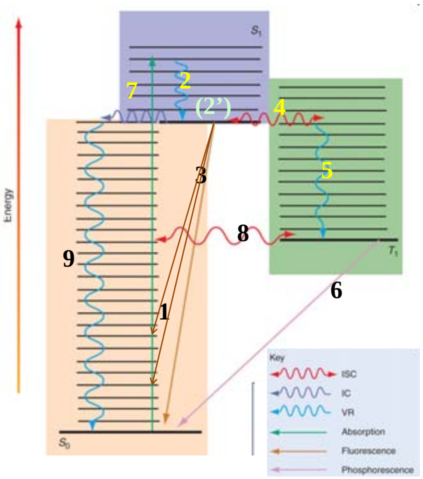
1→2’ →(2’) →3 F

1→2→4→5→6 P

4, 8 ISC T ↔ S

7 IC $S_1 \leftrightarrow S_0$

2, 5, 9 VR



Jablonski Diagram shows the electronic states of a molecule and the photo-physical transformations between them in an energy diagram.

The energy states are grouped horizontally by their spin multiplicity.

Non-radiative transitions are shown by wavy arrows and radiative transitions by straight arrows.

The vibrational ground state of each electronic state is indicated by heavy lines.

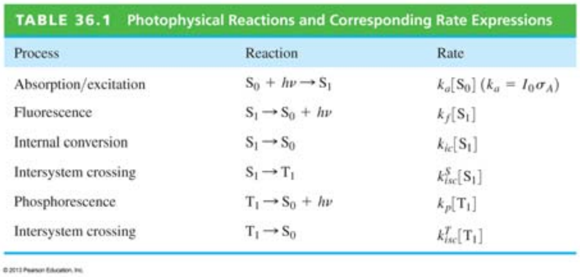
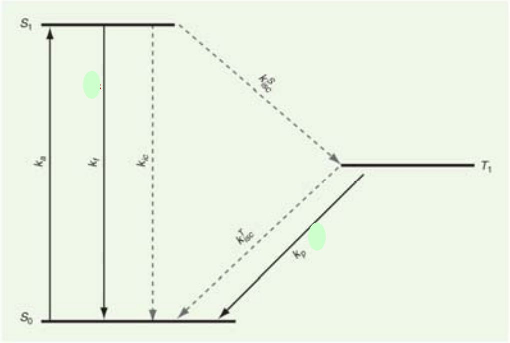


TABLE 36.1 Photophysical Reactions and Corresponding Rate Expressions

Process	Reaction	Rate
Absorption/excitation	$S_0 + h\nu \rightarrow S_1$	$k_a[S_0]$ ($k_a = I_0\sigma_A$)
Fluorescence	$S_1 \rightarrow S_0 + h\nu$	$k_f[S_1]$
Internal conversion	$S_1 \rightarrow S_0$	$k_{ic}[S_1]$
Intersystem crossing	$S_1 \rightarrow T_1$	$k_{isc}^{S}[S_1]$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu$	$k_p[T_1]$
Intersystem crossing	$T_1 \rightarrow S_0$	$k_{isc}^{T}[T_1]$



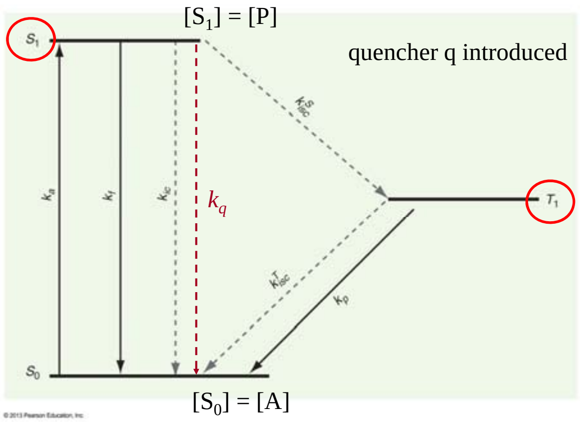
Kasha’s rule: Photon emission (fluorescence or phosphorescence) occurs *only* from the lowest-energy excited electronic state of a molecule.

Kinetics of photo-physical processes

Quenching: Excited molecules can lose its energy by way of collisions with other molecules (quenchers) and thereby relax non-radiatively. This must be considered another kinetic process.

$$S_1 + Q \xrightarrow{k_q} S_0 + Q$$

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



Applying SSA to S_1.

$$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - k_f[S_1] - k_{ic}[S_1] - k_{isc}^S[S_1] - k_q[S_1][Q]$$

$$\frac{d[S_1]}{dt} = k_a[S_0] - (k_f + k_{ic} + k_{isc}^S + k_q[Q])[S_1]$$

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

SSA $$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - \frac{[S_1]}{\tau_f}$$

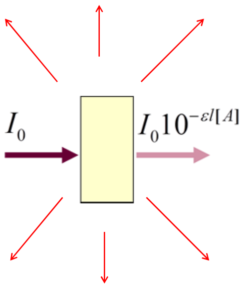
$$\Rightarrow \quad [S_1] = k_a[S_0]\tau_f$$

$$\Downarrow$$

$$I_f = k_f[S_1]$$

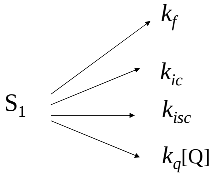
$$\Downarrow$$

$$I_f = k_a[S_0]k_f\tau_f$$



Florescence

<u>Fluorescence yield: Φ_f</u>



Parallel reactions (elementary)

$$\frac{k_f}{k_f + k_{ic} + k_{isc}^S + k_q[Q]} = \Phi_f$$

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

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

Fluorescence yield: Φ_f

$$\Phi = \frac{\text{\# photons emitted as fluorescence}}{\text{\# photons absorbed}}$$

$$I_f = k_a[\mathrm{S}_0]k_f\tau_f$$

1. invert

2. substitute $\frac{1}{\tau_f} = k_f + k_{ic} + k_{isc}^S + k_q[\mathrm{Q}]$

$$\frac{1}{I_f} = \frac{1}{k_a[\mathrm{S}]_0}\frac{1}{k_f\tau_f} = \frac{1}{k_a[\mathrm{S}]_0}\frac{k_f + k_{ic} + k_{isc} + k_q[\mathrm{Q}]}{k_f}$$

$$\frac{1}{I_f} = \frac{1}{k_a[\mathrm{S}_0]}\left(1 + \frac{k_{ic} + k_{isc}^S}{k_f}\right) + \frac{k_q[\mathrm{Q}]}{k_a[\mathrm{S}_0]k_f}$$

$$\frac{1}{I_f} = \frac{1}{k_a[\mathrm{S}_0]}\left(1 + \cancel{\frac{k_{ic} + k_{isc}^S}{k_f}}\right) + \cancel{\frac{k_q[\mathrm{Q}]}{k_a[\mathrm{S}_0]k_f}}$$

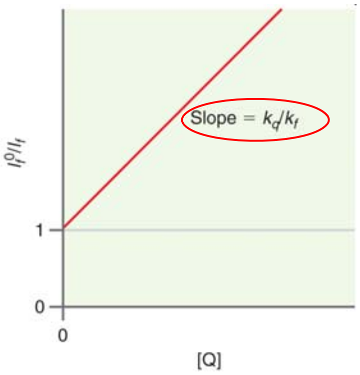
If $k_f >> k_{ic} and\ k_{isc}$

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f}[Q]$$

:Q present and k_f dominating

Stern-Volmer Plot

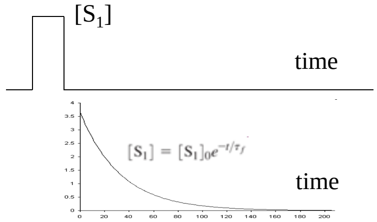
$$slope = \frac{k_q}{k_f}$$



Measurement of τ_f

Excite molecules with a short pulse of photons, monitor decay afterwards.

Creates S_1 species, with excitation turned off monitor the fluorescence decay of S_1.



For S_1;

$$\frac{d[S_1]}{dt} = -k_f[S_1] - k_{ic}[S_1] - k_{isc}^S[S_1] - k_q[Q][S_1]$$

$$\frac{d[S_1]}{dt} = -\frac{[S_1]}{\tau_f} \qquad \Rightarrow \quad [S_1] = [S_1]_0 e^{-t/\tau_f}$$

$$\ln[S_1] = \ln[S_1]_0 - \frac{1}{\tau_f}t \Rightarrow \ln[I_f] = \ln[I_f]_0 - \frac{1}{\tau_f}t$$

If conditions are such that $k_f >> k_{ic} and\ k_{isc}$

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

$$\lim_{k_f \gg k_{ic}, k^S{}_{isc}} \tau_f = \frac{1}{k_f + k_q[Q]}$$

$$\frac{1}{\tau_f} = k_f + k_q[Q]$$

Plot $\frac{1}{\tau_f} = k_f + k_q[Q]$

$slope = k_q$

$intercept = k_f$

$SVE \Rightarrow slope = \frac{k_q}{k_f}$