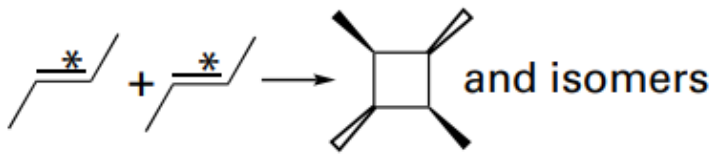
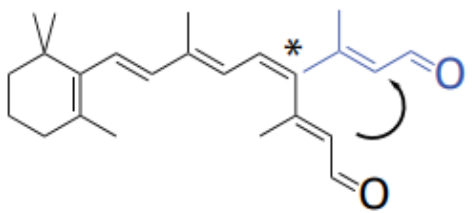
Focus 17: Chemical Kinetics

- The rates of chemical reactions
- Integrated rate laws
- Reactions approaching equilibrium
- The Arrhenius equation
- Reaction mechanisms
- Photochemistry

Photochemical processes

Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \rightarrow NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$Ru(bpy)_3^{2+*} + Fe^{3+} \rightarrow Ru(bpy)_3^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow B + C$	$O_3^* \rightarrow O_2 + O$
	$A^* + B\text{–}C \rightarrow A + B + C$	$Hg^* + CH_4 \rightarrow Hg + CH_3 + H$
Addition	$A^* + A^* \rightarrow B$	 and isomers
	$A^* + B \rightarrow AB$	$Hg^* + H_2 \rightarrow HgH + H$
Abstraction	$A^* + B\text{–}C \rightarrow A\text{–}B + C$	$Hg^* + CH_3\text{–}H \rightarrow Hg\text{–}CH_3 + H$
Isomerization or rearrangement	$A^* \rightarrow A'$	

* Excited state.

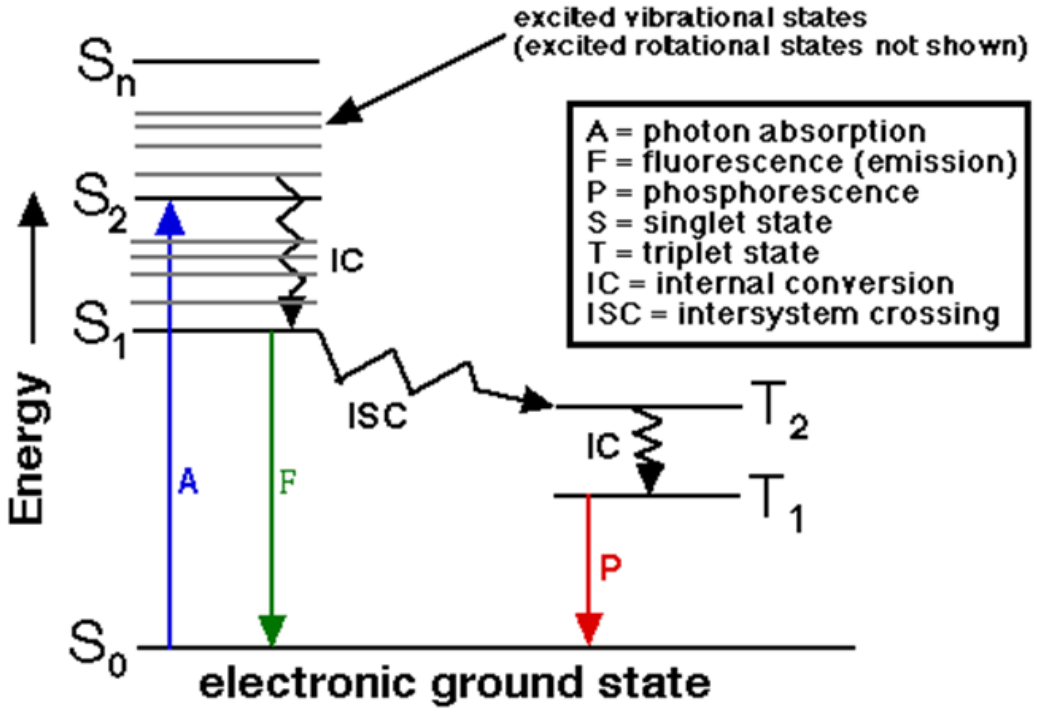
Photochemical processes

Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet–singlet	$S^* + S \rightarrow S + S^*$
Triplet–triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet–singlet	$S^* + S^* \rightarrow S^{**} + S$
Triplet–triplet	$T^* + T^* \rightarrow S^{**} + S$

Photochemical processes

Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet–singlet	$S^* + S \rightarrow S + S^*$
Triplet–triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet–singlet	$S^* + S^* \rightarrow S^{**} + S$
Triplet–triplet	$T^* + T^* \rightarrow S^{**} + S$

Jablonski diagram



Primary quantum yield

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

Primary quantum yield

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$$\phi = \frac{\text{rate of process}}{\text{rate of photon absorption}} = \frac{v}{I_{\text{abs}}}$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$N_{events} = N_{decomposed}$

$$N_{\text{decomposed}} = (3.44 \times 10^{-3}\,\text{mol}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$$E_{\text{abs}} = fPt$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$$E_{\text{abs}} = fPt$$

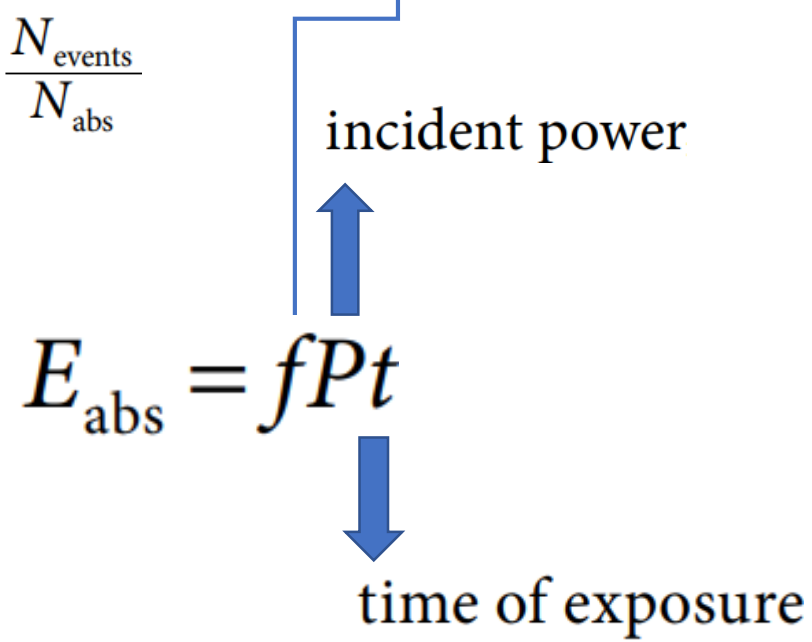
incident power

time of exposure

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$



Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

incident power

time of exposure

$$E_{\text{abs}} = fPt = N_{\text{abs}} h\nu = N_{\text{abs}} hc/\lambda$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$fPt = N_{\text{abs}}\left(\frac{hc}{\lambda}\right)$$

$$\phi = \frac{N_{\text{decomposed}}}{N_{\text{abs}}} = \frac{N_{\text{decomposed}}hc}{fPt\lambda}$$

Example

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to light of wavelength 490 nm from a 1.00 W laser source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 3.44 mmol of the absorbing substance decomposed. What is the primary quantum yield?

$$fPt = N_{abs}\left(\frac{hc}{\lambda}\right)$$

$$\phi = \frac{N_{decomposed}}{N_{abs}} = \frac{N_{decomposed}hc}{fPt\lambda}$$

$$N_{decomposed} = (3.44 \times 10^{-3}\,mol) \times (6.022 \times 10^{23}\,mol^{-1})$$

$$\phi = \frac{(2.07\ldots\times10^{21})\times(6.626\times10^{-34}\,Js)\times(2.998\times10^{8}\,ms^{-1})}{0.60\times(1.00\,Js^{-1})\times(2700\,s)\times(4.90\times10^{-7}\,m)}$$

$$= 0.52$$

Primary quantum yield

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$$\phi = \frac{\text{rate of process}}{\text{rate of photon absorption}} = \frac{v}{I_{\text{abs}}}$$

Primary quantum yield

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{N_{\text{events}}}{N_{\text{abs}}}$$

$$\phi = \frac{\text{rate of process}}{\text{rate of photon absorption}} = \frac{v}{I_{\text{abs}}}$$

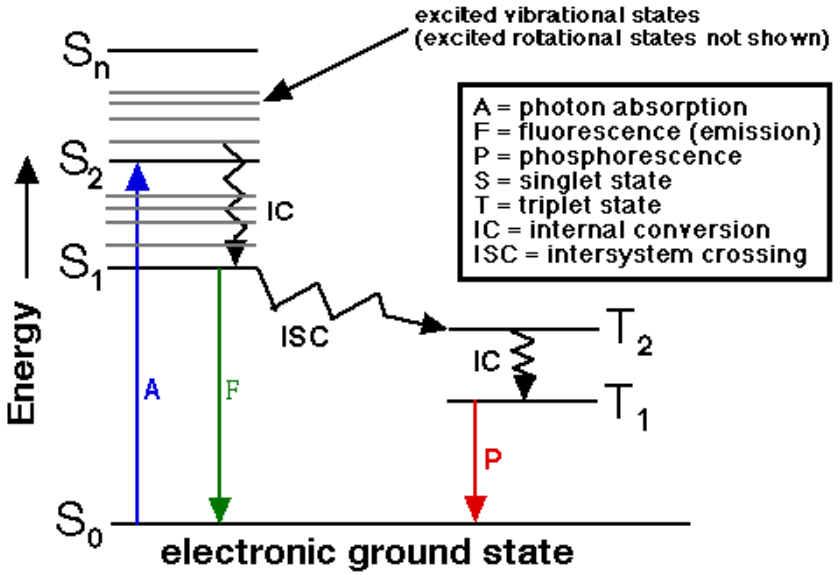
$$\sum_i \phi_i = \sum_i \frac{v_i}{I_{\text{abs}}} = \frac{1}{I_{\text{abs}}} \sum_i v_i = 1$$

The sum of all primary quantum yields for all events must be equal to 1

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

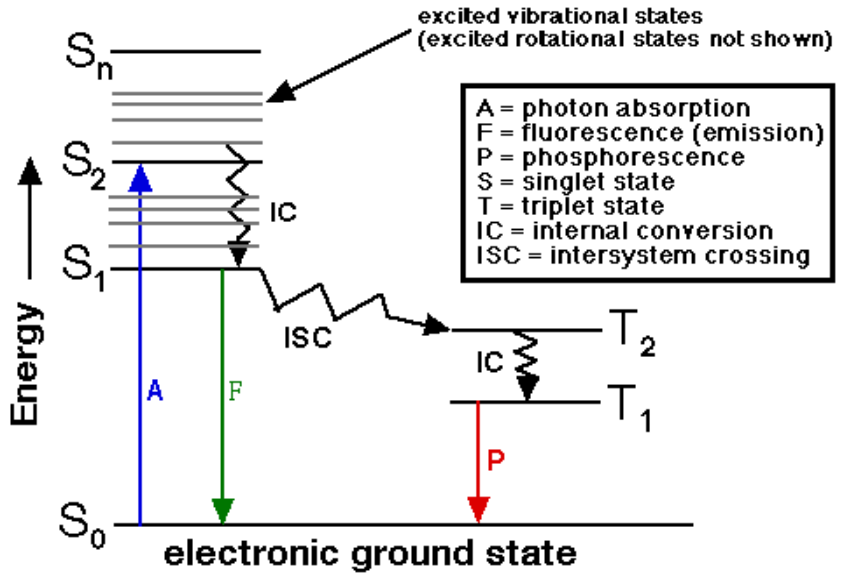
Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$

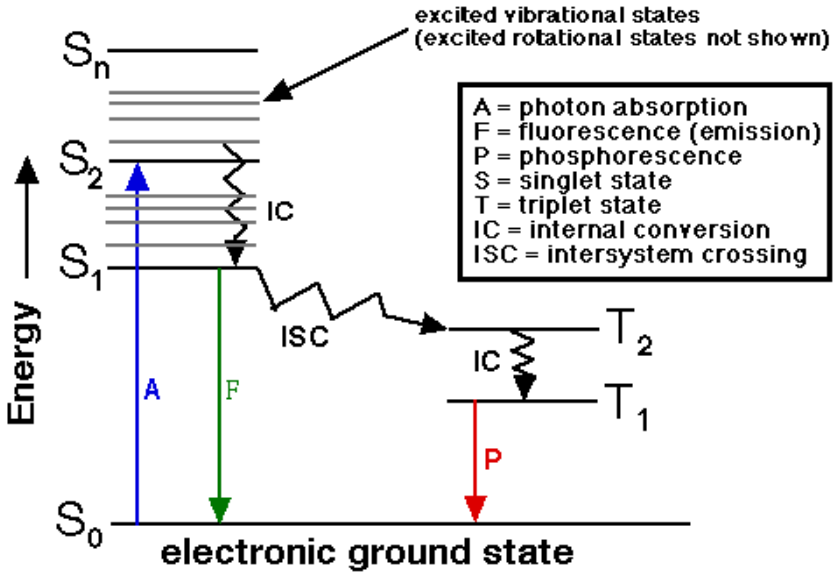


Rate of formation of $S^* = I_{abs}$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



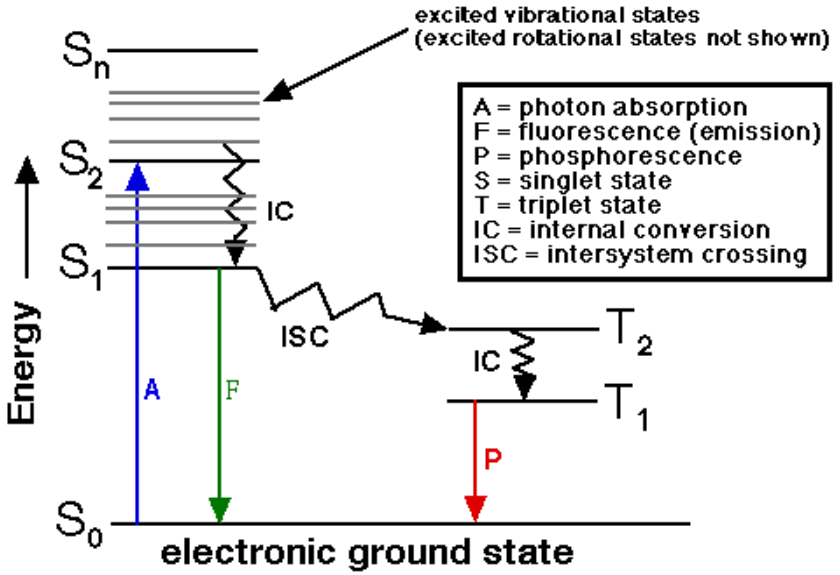
$$\text{Rate of formation of } S^* = I_{abs}$$

$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



$$\text{Rate of formation of } S^* = I_{abs}$$

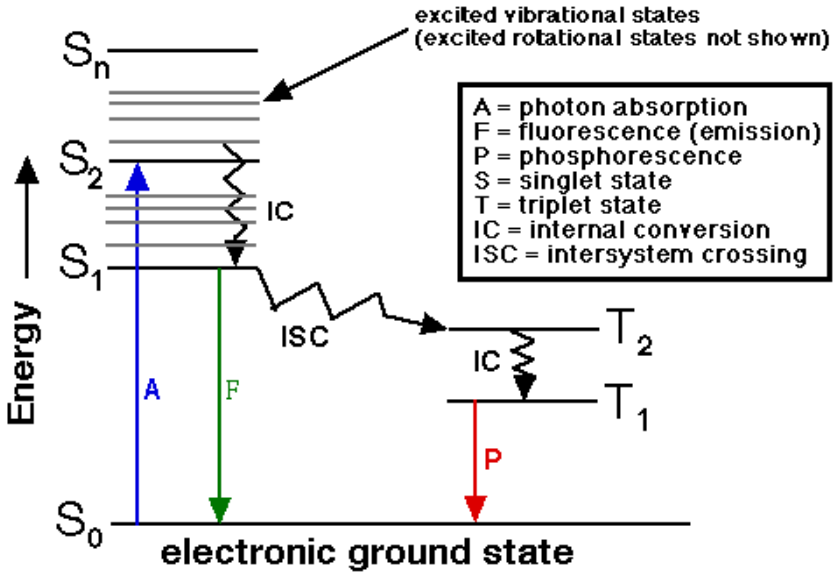
$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$

$$= (k_F + k_{ISC} + k_{IC})[S^*]$$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



$$\text{Rate of formation of } S^* = I_{abs}$$

$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$

$$= (k_F + k_{ISC} + k_{IC})[S^*]$$

The excited state decays by a first-order process!

Lifetime of an excited state

If you excite a big group of molecules at time zero, the lifetime τ is how long, on average, a molecule stays excited before relaxing (by fluorescence, internal conversion, ISC, etc.).

Lifetime of an excited state

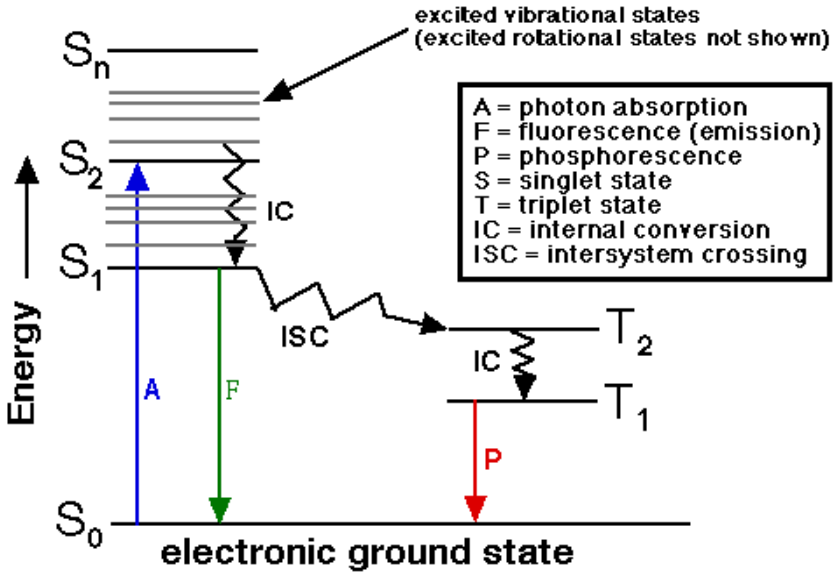
If you excite a big group of molecules at time zero, the lifetime τ is how long, on average, a molecule stays excited before relaxing (by fluorescence, internal conversion, ISC, etc.).

	Lifetime τ
First-order	Average survival time of molecules ($\tau = 1/k$)
Zero-order	τ linked to half-depletion ($[A]_0/2k$)
Second-order	Lifetime depends on $[A]_0$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



$$\text{Rate of formation of } S^* = I_{abs}$$

$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$

$$= (k_F + k_{ISC} + k_{IC})[S^*]$$

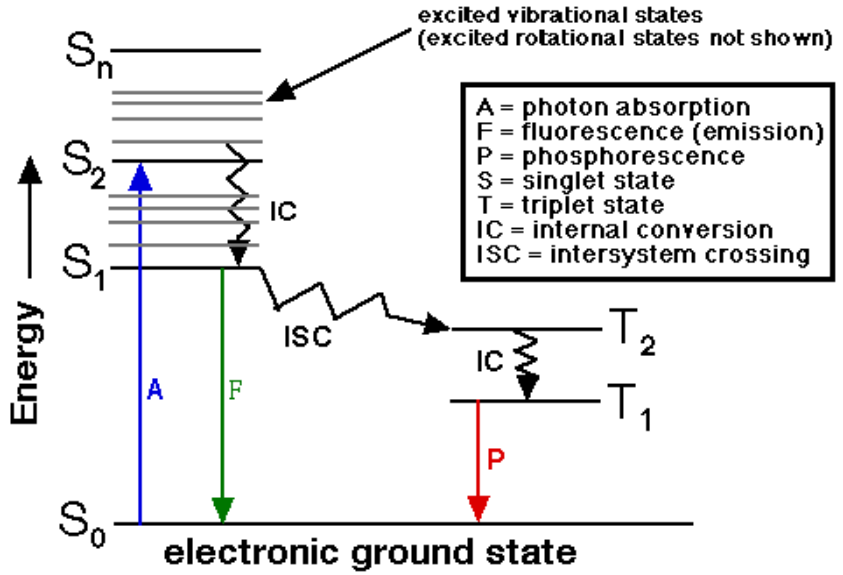
The excited state decays by a first-order process!

first-order exponential decay has a direct relationship between the decay rate and the lifetime $\tau_0 = \frac{1}{k_{total}}$ or $k_{total} = \frac{1}{\tau_0}$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



$$\text{Rate of formation of } S^* = I_{abs}$$

$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$
$$= (k_F + k_{ISC} + k_{IC})[S^*]$$

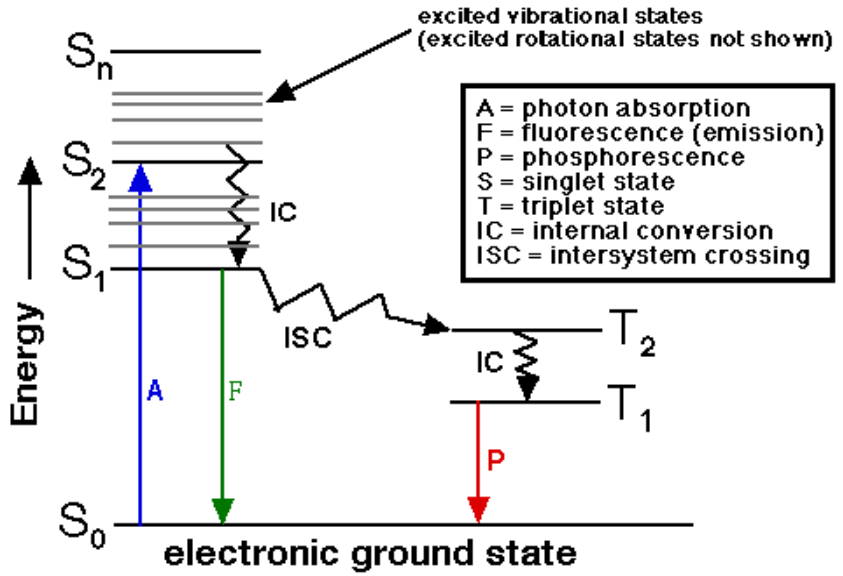
Decay–When the light is turned off,

$$[S^*](t) = [S^*]_0 e^{-t/\tau_0}$$

Mechanism of decay of excited singlet states

In the absence of a chemical reaction:

Absorption:	$S + h\nu_i \rightarrow S^*$	$\upsilon_{abs} = I_{abs}$
Fluorescence:	$S^* \rightarrow S + h\nu_f$	$\upsilon_F = k_F[S^*]$
Internal conversion:	$S^* \rightarrow S$	$\upsilon_{IC} = k_{IC}[S^*]$
Intersystem crossing:	$S^* \rightarrow T^*$	$\upsilon_{ISC} = k_{ISC}[S^*]$



$$\text{Rate of formation of } S^* = I_{abs}$$

$$\text{Rate of disappearance of } S^* = k_F[S^*] + k_{ISC}[S^*] + k_{IC}[S^*]$$
$$= (k_F + k_{ISC} + k_{IC})[S^*]$$

Decay–When the light is turned off,

$$[S^*](t) = [S^*]_0 e^{-t/\tau_0}$$

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}} = \frac{1}{k_{total}}$$

Observed lifetime of the excited singlet state

Quantum yield of fluorescence

$$\phi_{F,0} = k_F \tau_0$$

Quantum yield of fluorescence

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}}$$

$$\phi_{F,0} = \frac{k_F}{k_F + k_{ISC} + k_{IC}}$$

Quantum yield of fluorescence

Rate x time

$$\phi_{F,0} = k_F \tau_0$$

Quantum yield of fluorescence

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}}$$

$$\phi_{F,0} = \frac{k_F}{k_F + k_{ISC} + k_{IC}}$$

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

$$\phi_{F,0} = \frac{k_F}{k_F + k_{ISC} + k_{IC}}$$

Without Q

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

$$\phi_{F,0} = \frac{k_F}{k_F + k_{ISC} + k_{IC}}$$

Without Q

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{without\ Q}{with\ Q}$$

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

$$\phi_{F,0} = \frac{k_F}{k_F + k_{ISC} + k_{IC}}$$

Without Q

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \times \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F}$$

With and without a Q

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \times \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F}$$

$$= \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F + k_{ISC} + k_{IC}}$$

With and without a Q

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \times \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F}$$

$$= \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F + k_{ISC} + k_{IC}}$$

$$= 1 + \frac{k_Q}{k_F + k_{ISC} + k_{IC}}[Q]$$

With and without a Q

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}}$$

Observed lifetime of the excited singlet state

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \times \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F}$$

$$= \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F + k_{ISC} + k_{IC}}$$

$$= 1 + \frac{k_Q}{k_F + k_{ISC} + k_{IC}}[Q]$$

Quenching

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

Quenching: $S^* + Q \rightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$

$$\frac{d[S^*]}{dt} = I_{abs} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] \approx 0$$

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}}$$

Observed lifetime of the excited singlet state

The ratio of the quantum yields

$$\frac{\phi_{F,0}}{\phi_F} = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \times \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F}$$

$$= \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F + k_{ISC} + k_{IC}}$$

$$= 1 + \frac{k_Q}{k_F + k_{ISC} + k_{IC}}[Q]$$

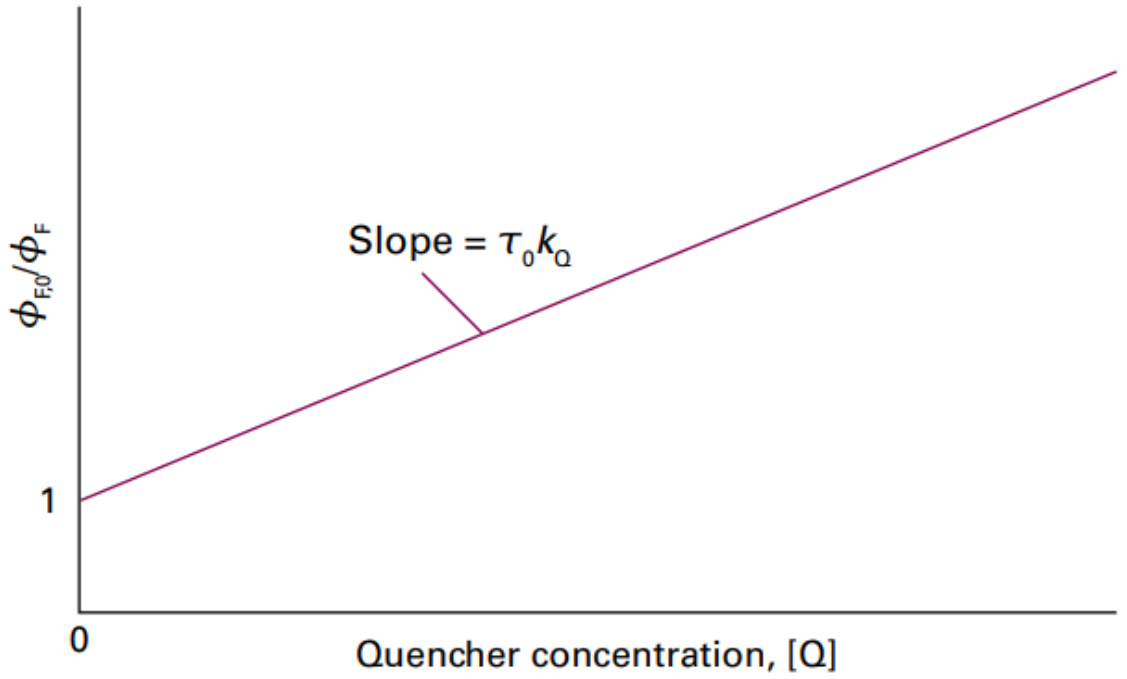
$$\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q[Q]$$

Stern–Volmer equation

relates fluorescence quenching to the concentration of quencher

Stern-Volmer plot

$$\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q [Q]$$



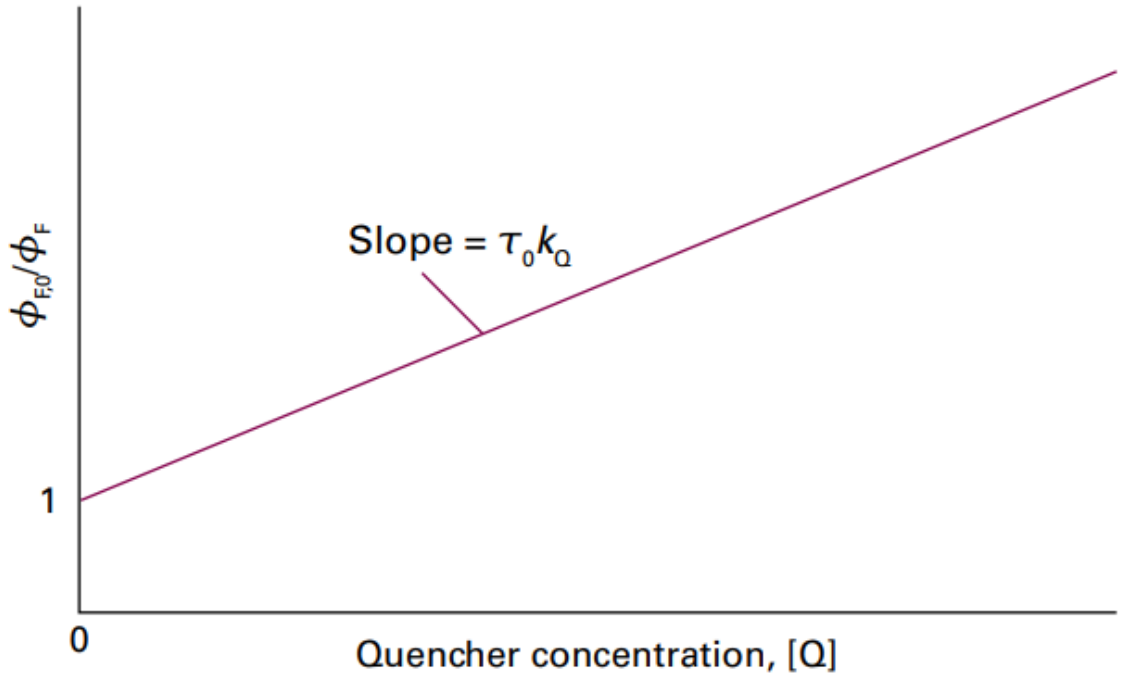
A Stern-Volmer plot is a useful tool for studying fluorescence quenching and provides valuable information about the interaction between a fluorophore and a quencher molecule.

Stern-Volmer plot

$$\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q [Q]$$

$$K_{SV} = \tau_0 k_Q$$

Stern–Volmer constant



A Stern-Volmer plot is a useful tool for studying fluorescence quenching and provides valuable information about the interaction between a fluorophore and a quencher molecule.

Quenching

Three common mechanisms for bimolecular quenching of an excited singlet (or triplet) state are:

Collisional deactivation: $S^* + Q \rightarrow S + Q$

Resonance energy transfer: $S^* + Q \rightarrow S + Q^*$

Electron transfer: $S^* + Q \rightarrow S^{+/-} + Q^{-/+}$

resonance energy transfer is efficient when the donor and acceptor are separated by a short distance (of the order of nanometres).

Focus 18: Reaction Dynamics

Collision theory

Diffusion-controlled reactions

Transition-state theory

The dynamics of molecular collisions

Electron transfer in homogeneous systems

Reactive encounters

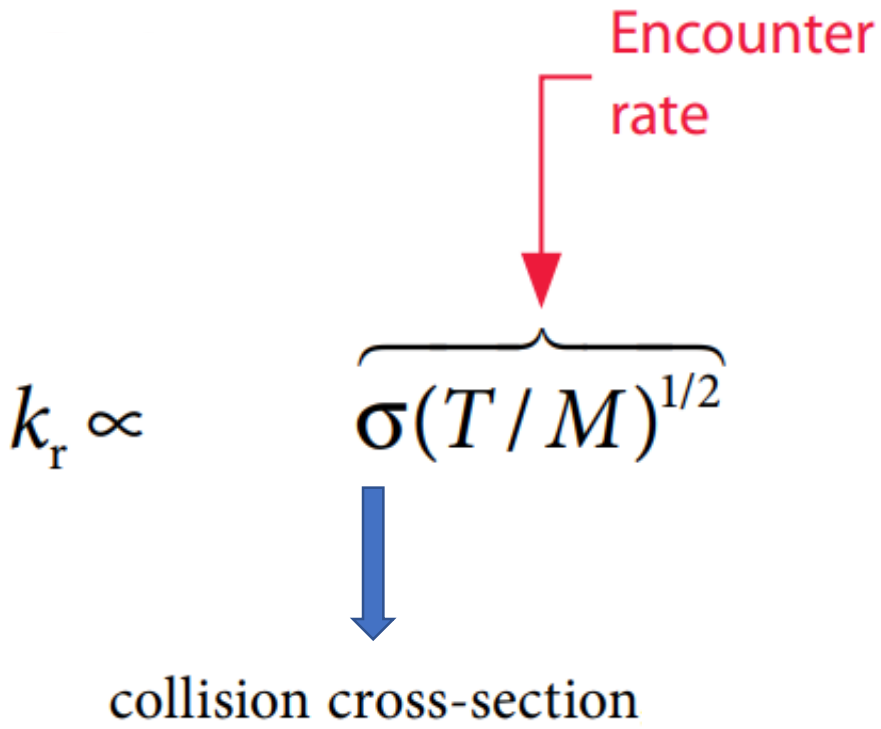
$$A + B \rightarrow P \qquad v = k_r[A][B]$$

Three aspects of a successful collision:

Reactive encounters

$$A + B \rightarrow P \qquad v = k_r[A][B]$$

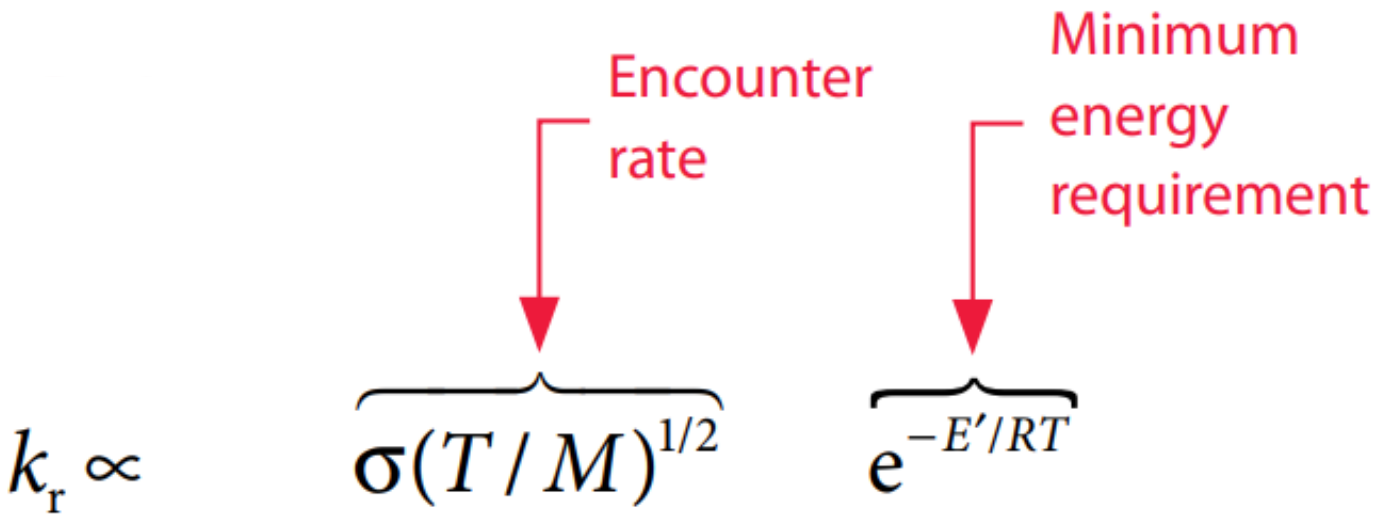
Three aspects of a successful collision:



Reactive encounters

$$A + B \rightarrow P \qquad v = k_r[A][B]$$

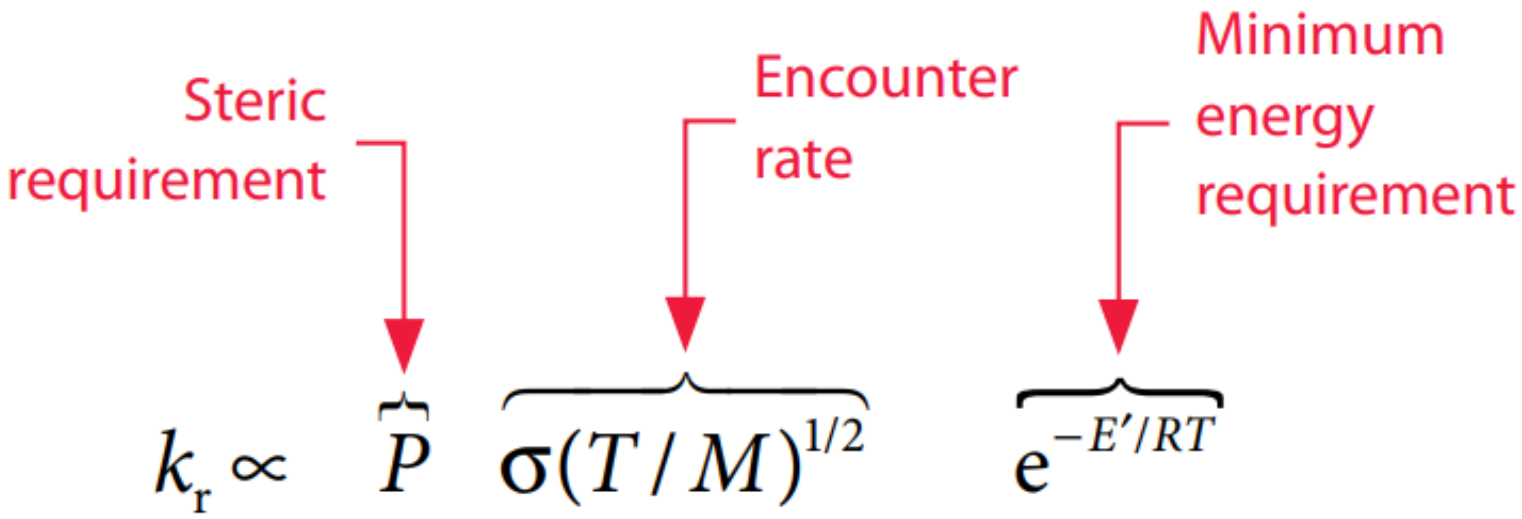
Three aspects of a successful collision:



Reactive encounters

$$A + B \rightarrow P \qquad v = k_r[A][B]$$

Three aspects of a successful collision:



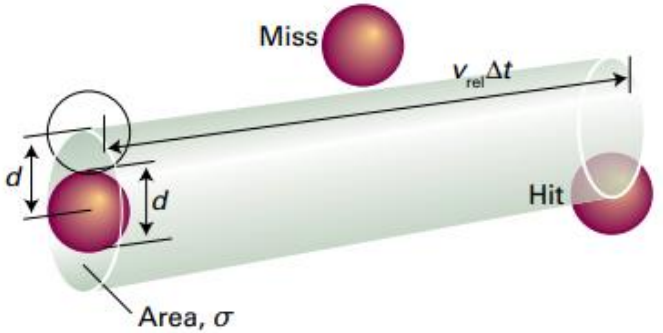
Collision density in gases

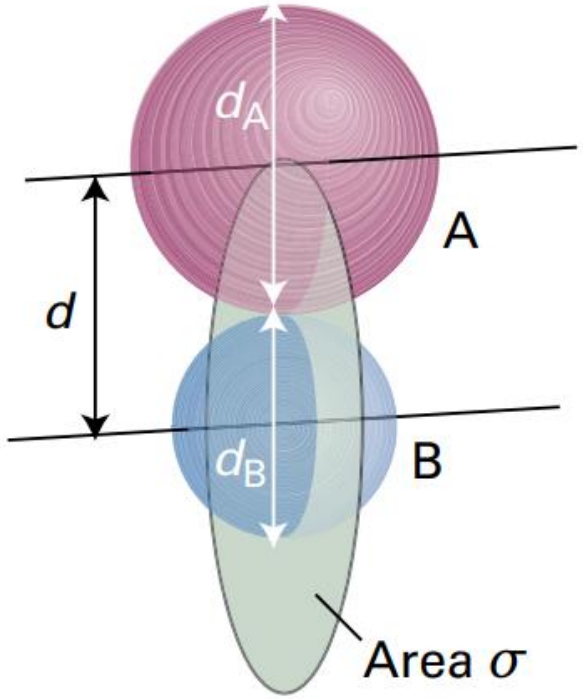
Z_{AB} is the collision frequency per unit volume

$$Z_{AB} = \sigma \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B]$$

Collision density in gases

Z_{AB} is the collision frequency per unit volume



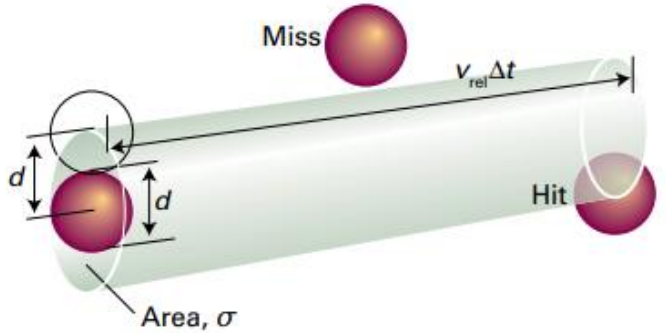


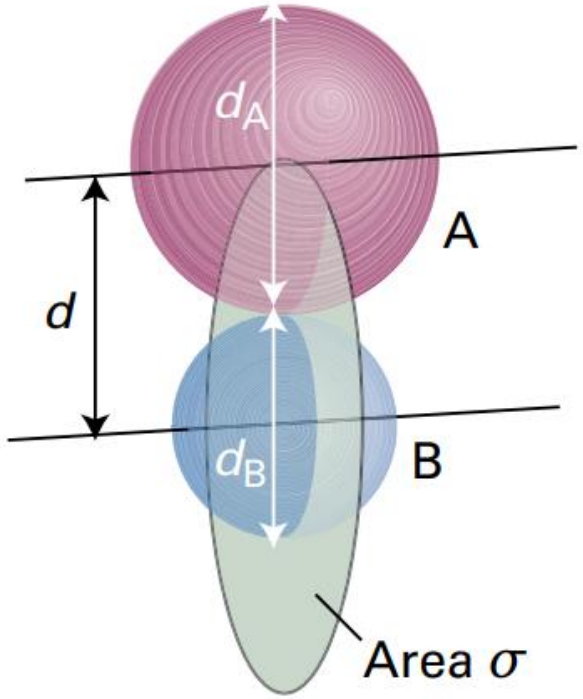
$$\sigma = \pi d^2, \text{ with } d = \tfrac{1}{2}(d_A + d_B),$$

$$Z_{AB} = \sigma \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B]$$

Collision density in gases

Z_{AB} is the collision frequency per unit volume





$$\sigma = \pi d^2, \text{ with } d = \tfrac{1}{2}(d_A + d_B),$$

$$Z_{AB} = \sigma \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B]$$

$$\mu = m_A m_B / (m_A + m_B)$$

Collision rate in gases

For A-A collision

$$Z_{AA} = \tfrac{1}{2}\sigma\left(\frac{16kT}{\pi m_A}\right)^{1/2} N_A^2[A]^2$$

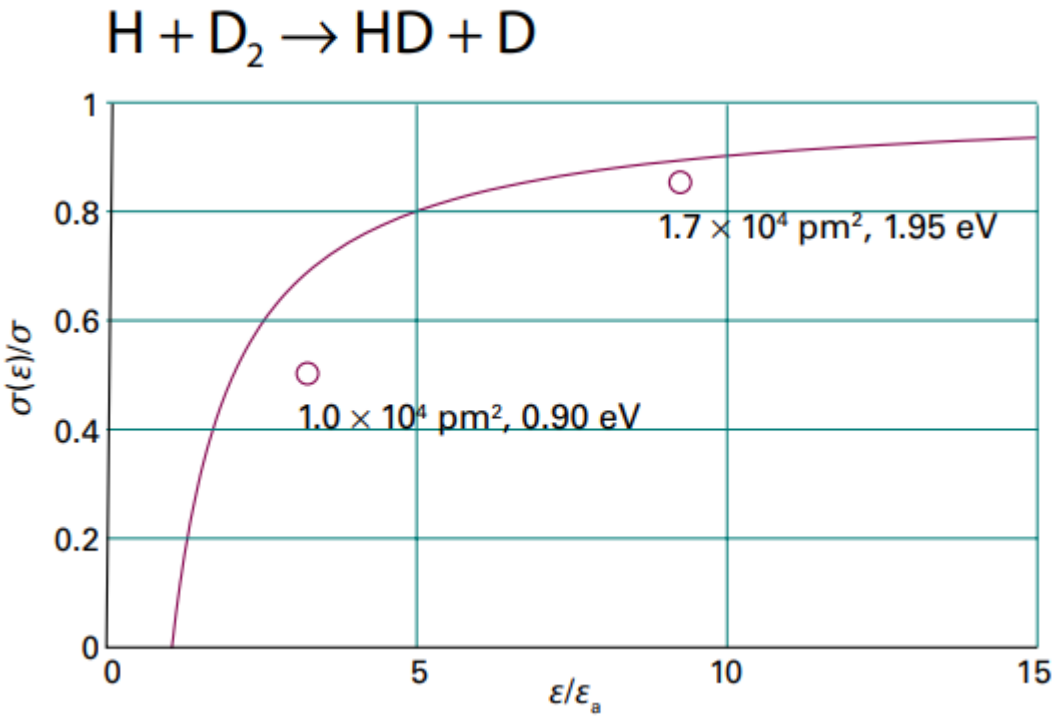
$$= \sigma\left(\frac{4kT}{\pi m_A}\right)^{1/2} N_A^2[A]^2$$

Collision density [identical molecules]

Factor of 1/2 has been introduced to avoid double counting of collisions

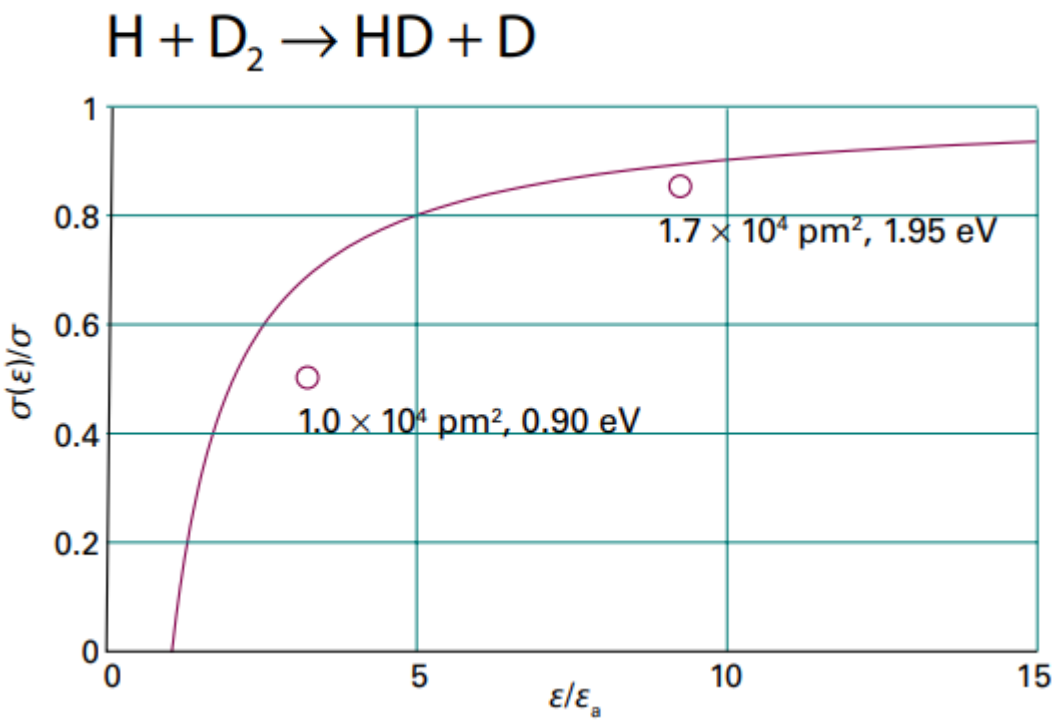
$$\mu = m_A m_B / (m_A + m_B) \quad \Longrightarrow \quad \mu = \tfrac{1}{2} m_A$$

The energy requirement



The variation of the reactive cross-section with energy

The energy requirement



The variation of the reactive cross-section with energy

energy-dependent collision cross-section

$$\sigma(\varepsilon) = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right)\sigma$$

threshold value

The minimum kinetic energy for a reaction to occur = activation energy

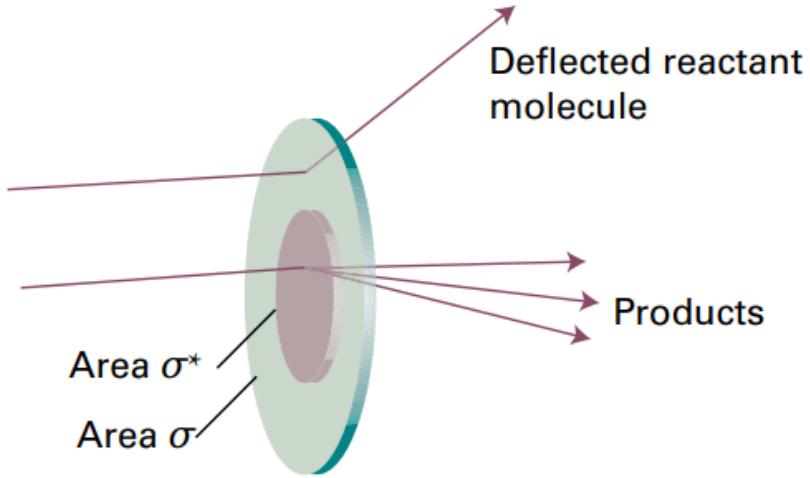
kinetic energy of two colliding species

$\sigma = \pi d^2$, with $d = \frac{1}{2}(d_A + d_B)$,

Simple collisional cross-section

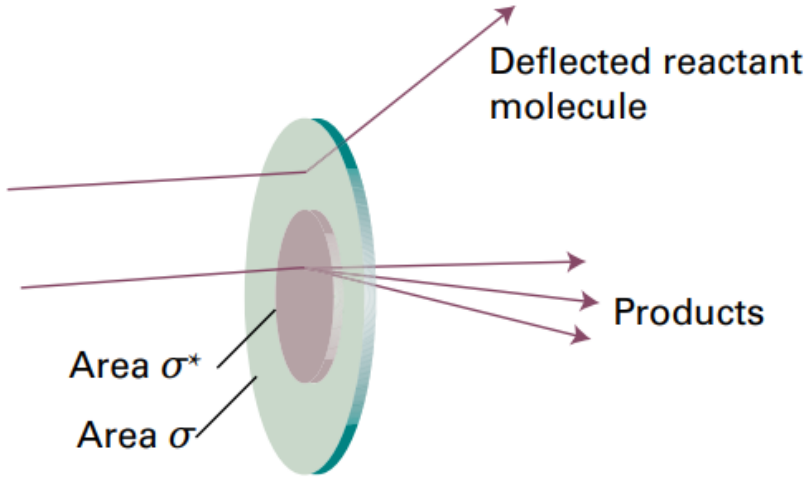
Steric requirement

The steric factor is an adjustment that takes into account the orientational requirements for a successful collision



Steric requirement

The steric factor is an adjustment that takes into account the orientational requirements for a successful collision



	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$		$E_a/(\mathrm{kJ\,mol^{-1}})$	P
	Experiment	Theory		
$2\,NOCl \rightarrow 2\,NO + 2\,Cl$	9.4×10^9	5.9×10^{10}	102	0.16
$2\,ClO \rightarrow Cl_2 + O_2$	6.3×10^7	2.5×10^{10}	0	2.5×10^{-3}
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	0	4.8

Steric requirement

The steric factor is an adjustment that takes into account the orientational requirements for a successful collision

	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$		$E_a/(\mathrm{kJ\,mol^{-1}})$	P
	Experiment	Theory		
$2\,NOCl \rightarrow 2\,NO + 2\,Cl$	9.4×10^9	5.9×10^{10}	102	0.16
$2\,ClO \rightarrow Cl_2 + O_2$	6.3×10^7	2.5×10^{10}	0	2.5×10^{-3}
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	0	4.8

Reasonably good alignment; moderate steric demand

Very poor alignment needed; hard collision geometry

Extremely specific orbital orientation needed for new bond formation.

Very large P (>1) because of long-range ionic attraction helping collisions