Photochemistry I

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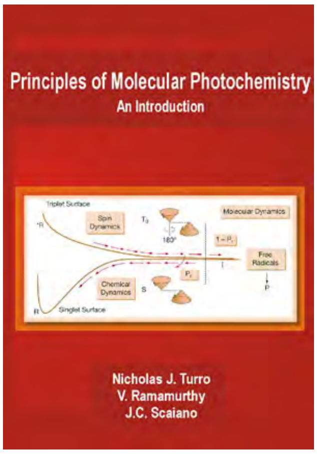
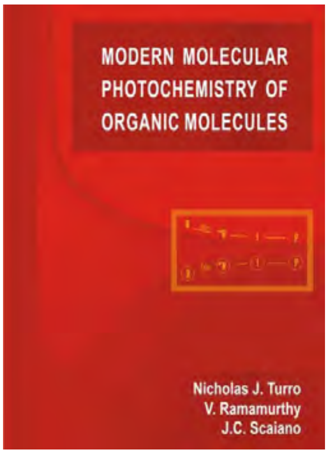
http://photochemistry.epfl.ch/PC.html

ECOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Course's website:

http://photochemistry.epfl.ch/PC.html





N. J. Turro, V. Ramamurthy & J. C. Scaiano
University Science Books
Dulles VA (USA), 2010

Content

PHOTOCHEMISTRY I

Content (contd)

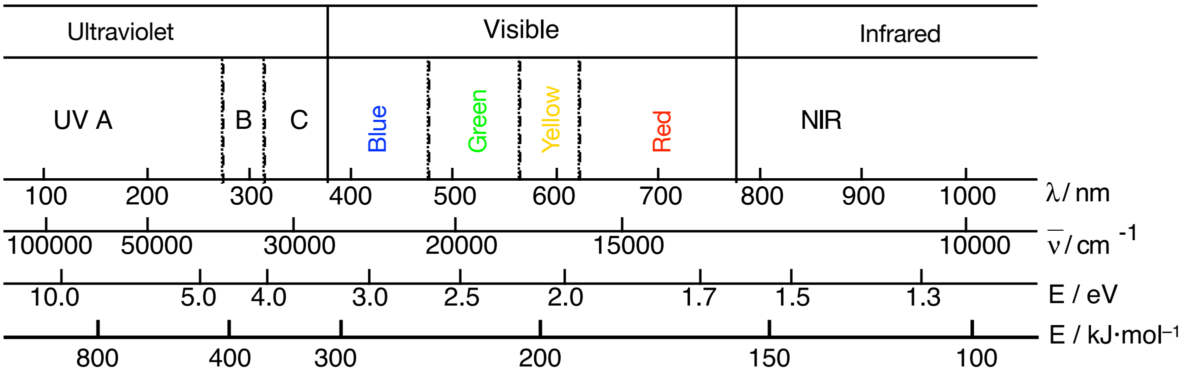
1. Basic principles

Photochemistry (light-induced chemistry)

Chemistry: forming or breaking of chemical bonds and charge transfer within or between molecules.

Photochemical reactions are processes during which the energy required for their *activation* ($\Delta U^{\ddagger}$) or their development (ΔG_r) is provided by an electromagnetic radiation.

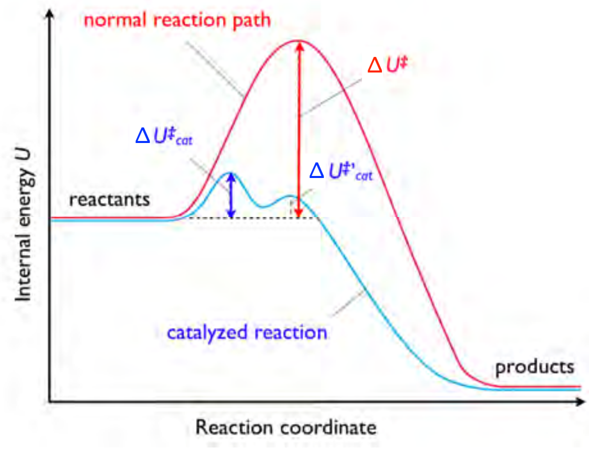
Activation energies of the order of $\Delta U^{\ddagger}$ = 100 kJ·mol^{-1} and bond energies of the order of ΔG = 200-400 kJ·mol^{-1} imply absorption of photons that should individually carry an equivalent amount of energy.



Bond energies

Bond	ΔH [kJ mol^{-1}]	λ [nm]	Bond	ΔH [kJ mol^{-1}]	λ [nm]
H–H	436	274	N–N	160	748
C–H	413	290	N=N	631	190
N–H	393	304	N≡N	941	127
P–H	297	403	N–O	201	595
C–C	347	345	N–P	297	403
C–O	358	334	O–H	464	258
C–N	305	392	O–S	265	451
C-Cl	397	301	O–Cl	269	445
C=C	607	197	O–O	204	586
C=O	805	149	C–F	552	216
O=O	498	240	C–S	259	461

Types of photochemical reactions



a) $\underline{\Delta G_r < 0}$ *(exergonic reaction, spontaneous)*

Light enable for overcoming the activation barrier or to lower it by acting as a catalyst. Such reactions are called "*photocatalytic*"

Example: $H_2 + Cl_2 \rightarrow 2\ HCl$

b) $\underline{\Delta G_r > 0}$ *(endergonic, non spontaneous)*

Energy required by the reaction is brought by light. Light energy is (partially) converted into chemical energy.

Example:

Natural photosynthesis

$$CO_2 + H_2O \xrightarrow[chloroplastes]{h\nu} \frac{1}{6}\ C_6H_{12}O_6 + O_2 \qquad \Delta G = 496\ \text{kJ} \cdot \text{mol}^{-1}$$

Functions associated with light

$$A \xrightarrow{h\nu} B\ \ (\pm \Delta G)$$

a) Light as a reactant

- synthesis of B
- reaction inhibition (photo-stabilization of A)

b) Light as an energy vector

- endergonic formation of B
- energy storage

c) Light as information vector

- optical absorption profile (photography, information storage)
- charge density profile (xerography)
- 3D material profile (photolithography)

Fundamental laws of photochemistry

Theodor von Grotthuss
(1785-1822)

John W. Draper
(1811-1882)

Grotthuss-Draper law (1812, 1842)

Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

Stark-Einstein law (1908-1913)

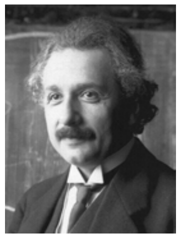
Also known as the "photo-equivalence law"

For each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

$$\Delta G_{molecule} = N_A \cdot h\nu = N_A \cdot \frac{hc}{\lambda}$$

1 Einstein = 1 mol of photons = N_A photons

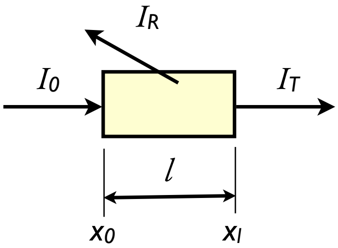
Johannes Stark
(1874-1957)



Albert Einstein
(1879-1955)

1.2 Laws of light absorption

Phenomenological (macroscopic) law of absorption



$$I_T = I_0 - I_A - I_R$$

$T = \frac{I_T}{I_0}$ transmittance $\quad \frac{I_R}{I_0}$ reflectance $\quad \frac{I_A}{I_0}$ absorptance

$A = -\log\left(\frac{I_T}{I_0}\right) = -\log T$ absorbance

Lambert's law

$$I(x) = I_0 \cdot \exp(-\alpha x)$$

$$\ln \frac{I(x)}{I_0} = -\alpha x \longrightarrow \ln \frac{I_T}{I_0} = \ln T = -\alpha l$$

α = *absorption constant* *[cm^{-1}]*

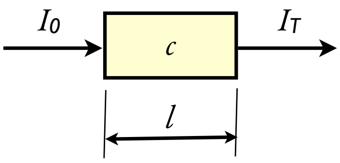
Link with the medium's complex refractive index:

$\hat{n} = n - i\kappa \quad [-]$ $\qquad \kappa$ = absorption coefficient [-] (imaginary part of the refractive index)

$$\alpha = \frac{4\pi \cdot \kappa}{\lambda_0}$$

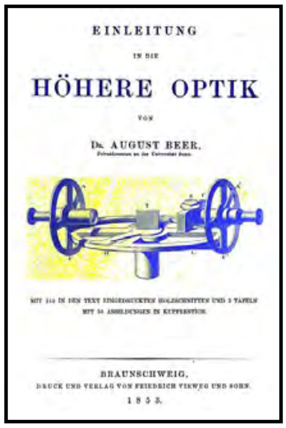
Johann H. Lambert
(1728-1777)

Beer-Lambert Law



$$A = -\log \frac{I_T}{I_0} = -\log T = \varepsilon \cdot c \cdot l \quad [-]$$

c molar concentration [mol l^{-1}]
l optical pathlength [cm]
ε molar decadic extinction coefficient



August Beer
(1825-1863)

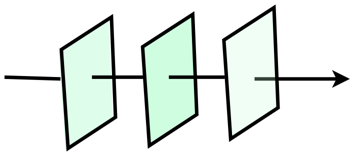
Example: $c = 10^{-3}$ M, $\varepsilon = 10^4$ mol^{-1} · l · cm^{-1}

$\Rightarrow$ $T = 0.01$, $A = 2 \Rightarrow$ 99% of the light is absorbed within the first 2 mm of the solution

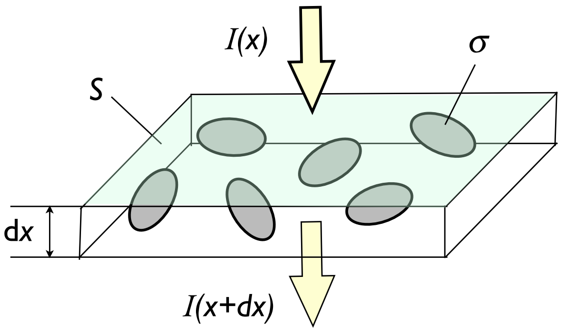
Superimposition of absorbing systems

Transmittance is multiplicative: $T_{tot} = \prod_i T_i$

Absorbance is additive: $A_{tot} = \sum_i A_i$



Justification of Beer-Lambert law



Initial assumptions

- individual molecules totally block light within a characteristic cross-section σ
- monochromatic light
- molecules do not cast any shadow on each other (only conceivable if the concentration c is very low)

Absorptance of a solution volume S·dx containing *n* molecules :

$$\frac{-dI}{I(x)} = \frac{I(x+dx) - I(x)}{I(x)} = \frac{n \cdot \sigma}{S} = \frac{c \cdot S \cdot N_A \cdot dx \cdot \sigma}{S} = c \cdot \sigma \cdot N_A \cdot dx$$

$$-\frac{1}{I(x)} dI = c \cdot \sigma \cdot N_A \cdot dx \quad \xrightarrow{\int_0^l} \quad -\ln \frac{I}{I_0} = c \cdot \sigma \cdot l \cdot N_A$$

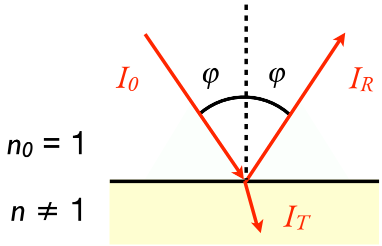
By defining : $\varepsilon = \sigma \cdot N_A \cdot \log(e) = \dfrac{\sigma \cdot N_A}{2.303} \quad \Rightarrow \quad -\log \dfrac{I}{I_0} = A = \varepsilon \cdot c \cdot l$

Absorption by non-continuous media

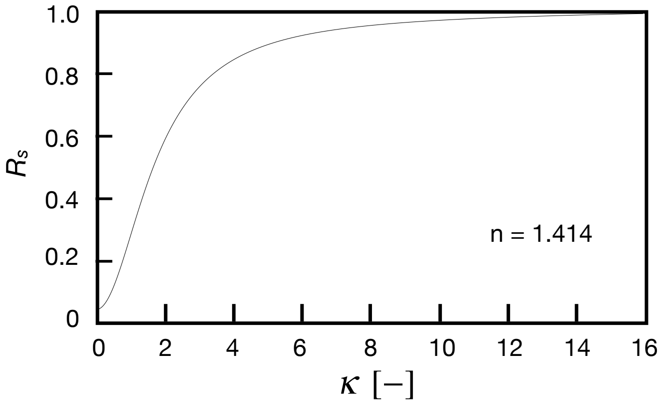
Absorption and reflexion by a specular (mirror-like) surface

$I_0 = I_R + I_A + I_T$

$R_s = I_R / I_0$ specular reflectance

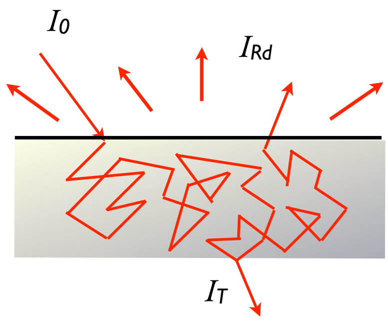


Fresnel law
$$R_s = \frac{I_R}{I_0} = \frac{(n-1)^2 + n^2 \cdot \kappa^2}{(n+1)^2 + n^2 \cdot \kappa^2} \quad \text{at} \quad \varphi = 0$$



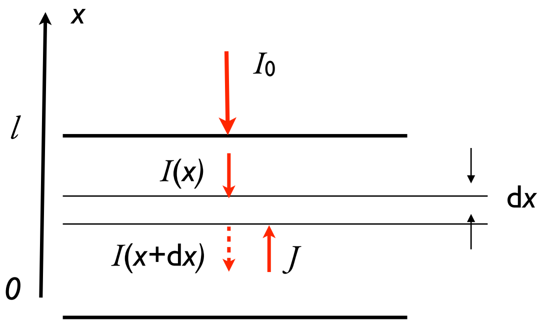
Augustin Fresnel
(1788-1827)

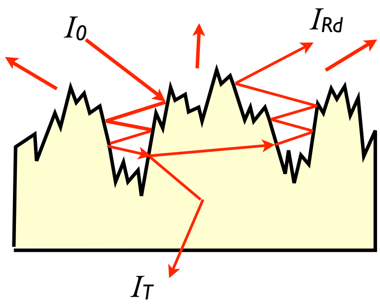
Absorption by a scattering medium



Diffuse reflectance $I_0 = I_{Rd} + I_A + I_T$

Schuster-Kubelka-Munk theory





Phenomenological extinction constants:

$k\ [cm^{-1}]$ absorption $\quad k_{s \to 0} = -\frac{1}{dx} \cdot \ln \frac{dI}{I_0}$

$s\ [cm^{-1}]$ scattering $\quad s_{k \to 0} = -\frac{1}{dx} \cdot \ln \frac{dI}{I_0}$

$$\begin{cases} -dI = -kI \cdot 2dx - sI \cdot 2dx + sJ \cdot 2dx \\ dJ = -kJ \cdot 2dx - sJ \cdot 2dx + sI \cdot 2dx \end{cases}$$

Kubelka and Kubelka-Munk equations

Kubelka's hyperbolic solutions

$$R = \frac{1 - R_g (a - b \cdot \coth (b \cdot 2s \cdot l))}{a + b \cdot \coth (b \cdot 2s \cdot l) - R_g}$$

$$T = \frac{b}{a \cdot \sinh (b \cdot 2s \cdot l) + b \cdot \cosh (b \cdot 2s \cdot l)}$$

with: $R_g = \text{background reflectance}$

$$a = 1 + \frac{k}{s} \qquad b = \sqrt{a^2 - 1}$$

Kubelka-Munk simplified solution

$$l \to \infty \quad \Rightarrow \quad F(R_\infty) = \frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty}$$

Absorber homogeneously dispersed in a scattering medium (powder)

$$k\ [\text{cm}^{-1}] = \ln(10) \cdot \varepsilon\ [\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}] \cdot c\ [\text{mol} \cdot \text{l}^{-1}]$$

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \varepsilon \cdot c \cdot \frac{\ln(10)}{s}$$