Lecture 3: Energy of Electromagnetic Waves and Spectra, Rate of Chemical Reaction and Energy

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Week 11; 30th June: Experiment 7
Determination of concentration by absorption photometry (Lambert – Beer law)

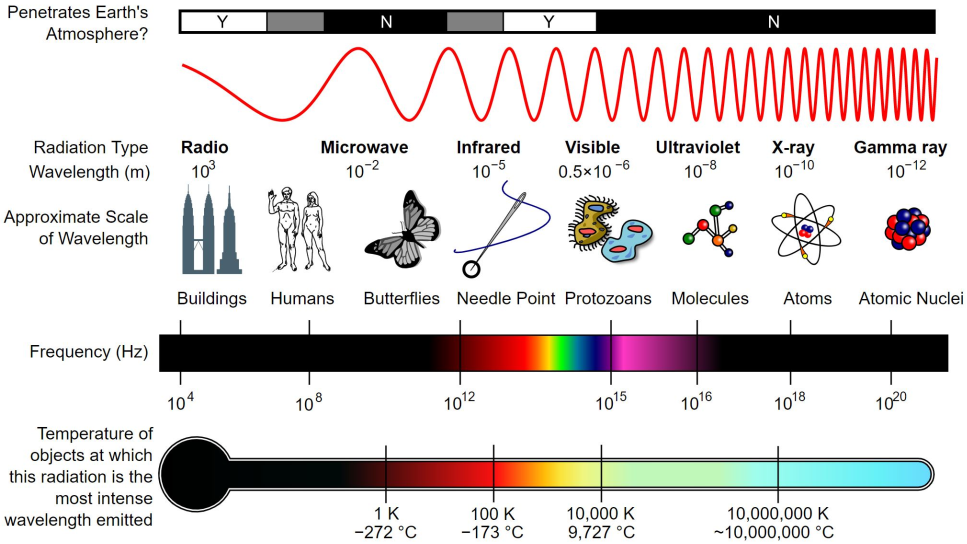
Week 12; 7th July: Experiment 8
Absorption spectra of bromothymol blue (BTB) at different pH

Week 13; 14th July: Experiment 9
Chemical oscillation reactions (online only)

Chapter 5: Energy of Electromagnetic Radiation And Spectra

Spectra of Various Light Sources (skip)

Main theme: In this experiment, you will study the relation between color, wavelength and energy of light.



https://en.wikipedia.org/wiki/Electromagnetic_spectrum

$$\text{Wavelength} \times \text{Frequency} = \text{Speed}$$

$$\lambda(\mathrm{m}) \times \nu\left(\mathrm{s}^{-1}\right) = c(\mathrm{m\,s}^{-1})$$

c: the rate of travel of all electromagnetic energy in a vacuum and is a **constant exact** value—speed of light.

c = 2.997 924 58 × 10^8 m s^{-1}, usually rounded off to 3.00 × 10^8 m s^{-1}

A beam of light behaves as if it were a stream of small particles, called photons, whose energy (E) is related to their frequency, ν (or wavelength, λ)

$$E = h\nu = \frac{hc}{\lambda}$$

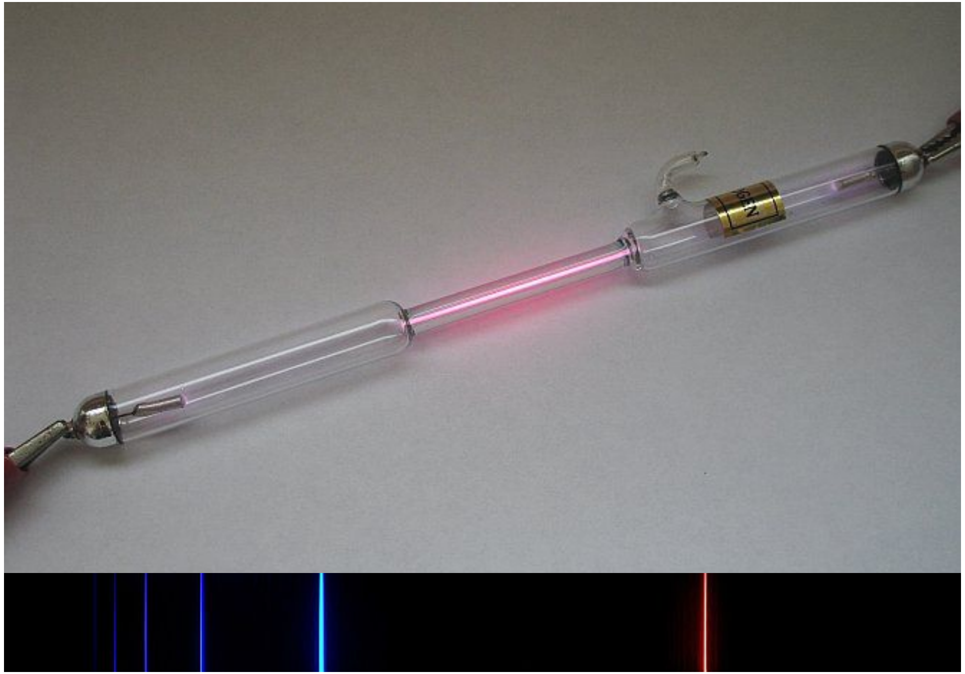
$h = 6.626 \times 10^{-34}$ J s
Planck's constant

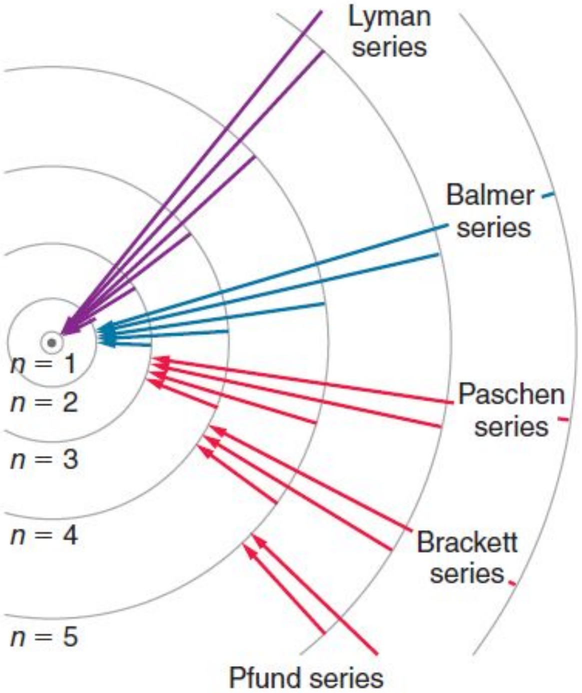
Unit:

J s × s^{-1} = J (Energy of 1 photon)

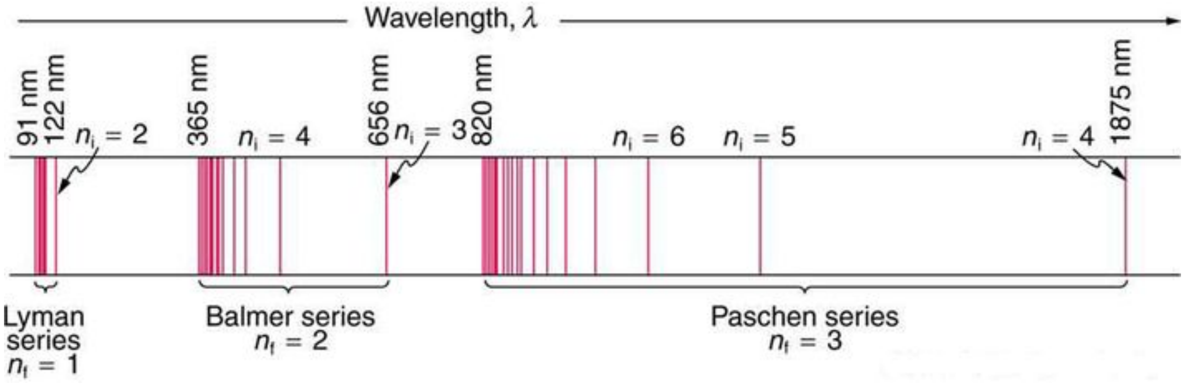
Sometimes in kJ mol^{-1} (Energy of N_A photons)

Line Spectrum: A series of discrete lines on an otherwise dark background as a result of light emitted by an excited atom





Line Spectra and the Bohr Model. (2021, November 8). https://chem.libretexts.org/@go/page/21730



The “visible” H emission spectrum lines in the Balmer series.

The Hydrogen Atomic Spectrum. (2021, October 3). https://chem.libretexts.org/@go/page/210778

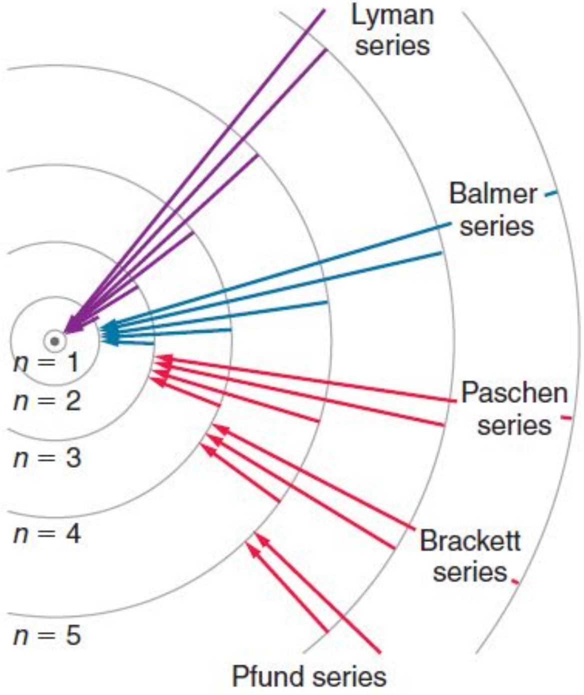
Rydberg formula (1888)

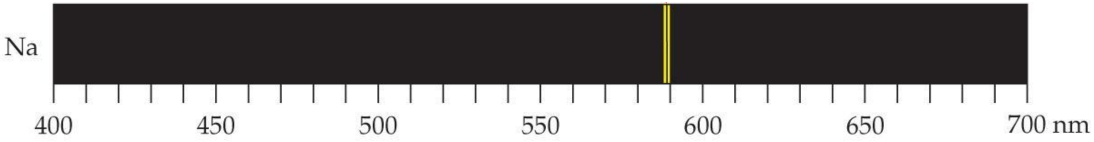
$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$n_2 > n_1$$

Rydberg constant for hydrogen 109677 cm^{-1}

principal quantum number

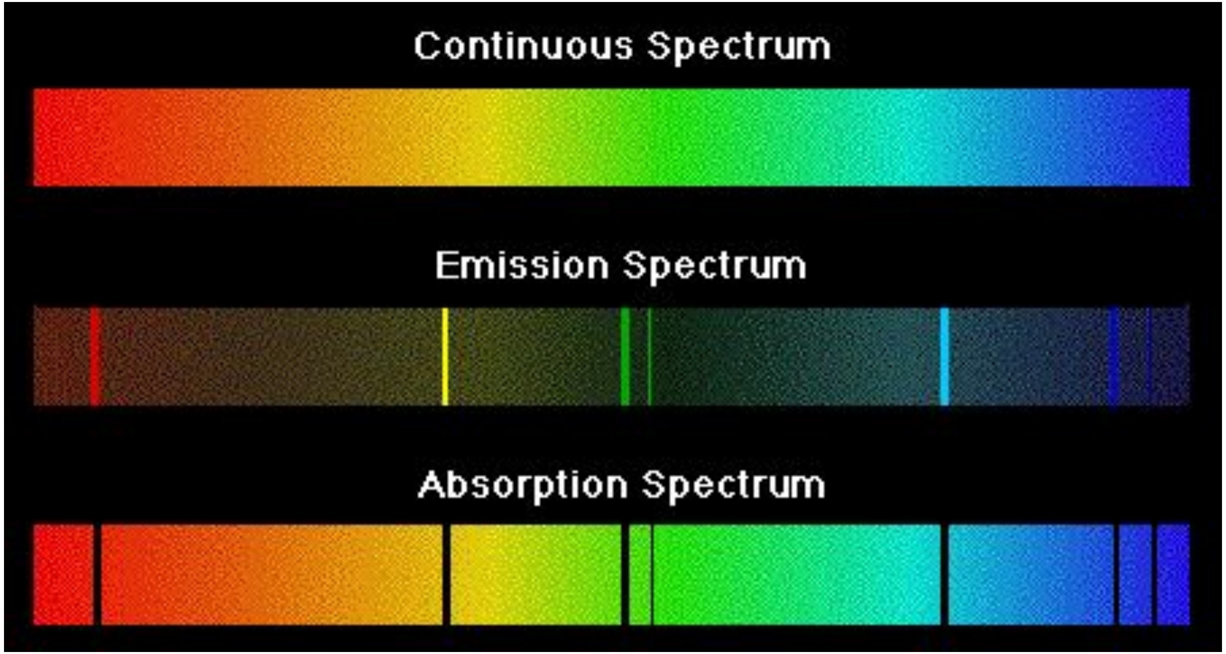




Emission spectrum of atomic sodium

each element has its own unique spectral "signature"

The Bohr Atom. (2015, September 24). https://chem.libretexts.org/@go/page/37017



Absorption vs. emission spectra

http://faculty.sdmiramar.edu/fgarces/labmatters/instruments/aa/AAS_Theory/AASTheory.htm

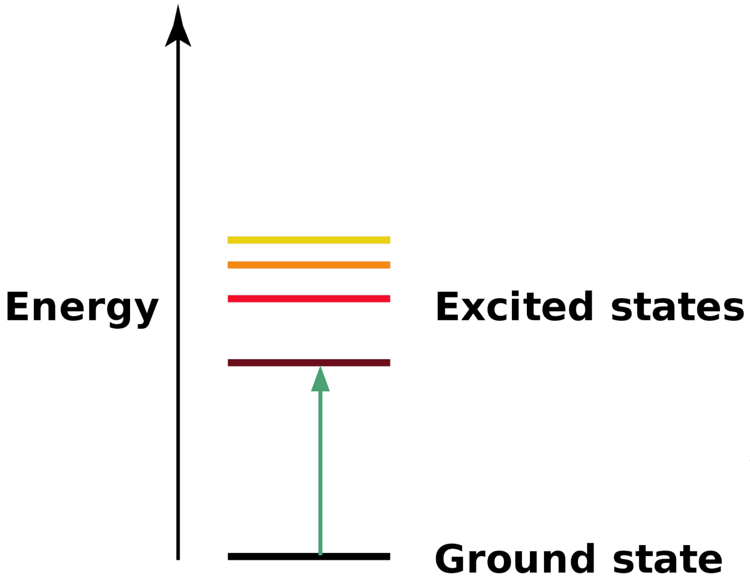
Absorption spectra and structure of molecules

Main theme: In this experiment, you will

- measure molecular absorption spectrum.
- learn how absorption spectrum relates to molecular structure.

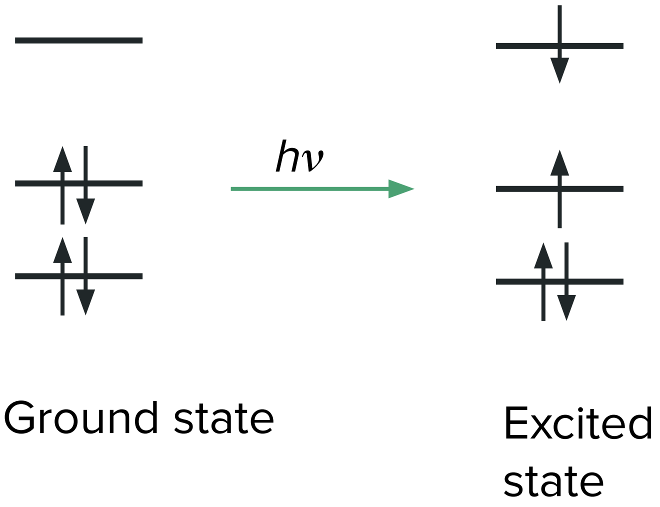
Light absorption

When a molecule interacts with light and energy is absorbed ➔ the molecule is excited.



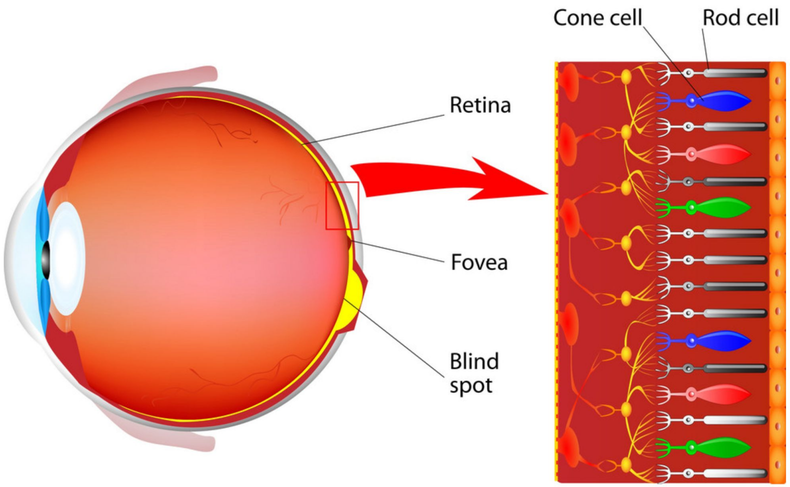
$$\Delta E = E_{\text{excited state}} - E_{\text{ground state}} = h\nu$$

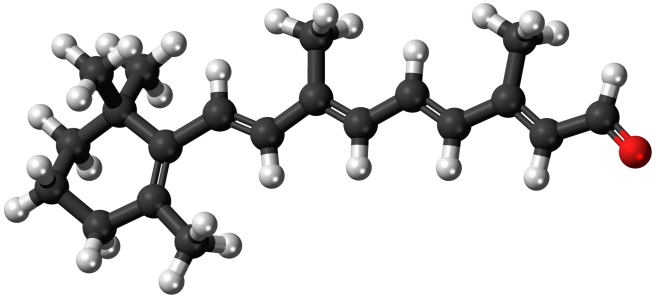
Molecular orbital (MO) picture: promotion of an electron from an occupied MO to an unoccupied MO.



Color

Our perception of color is determined by the wavelengths of radiation reaching our eyes and the sensitivity of the receptors in our eyes.

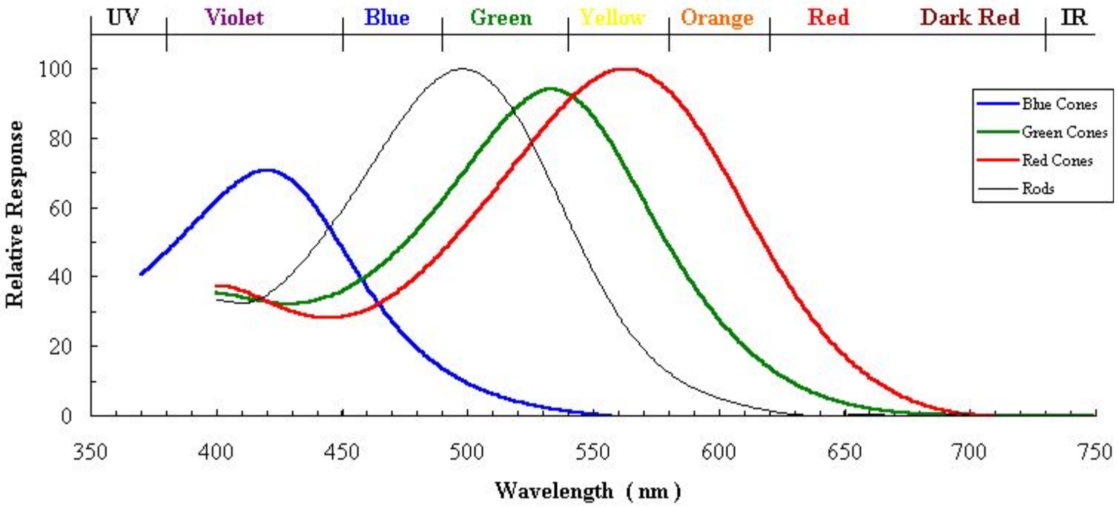


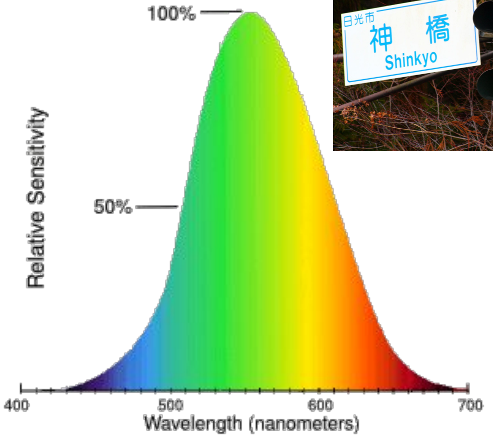


Retinal

Chromophores convert light into electrical impulse.

https://www.aao.org/eye-health/anatomy/cones





Human eye is the most sensitive to green color

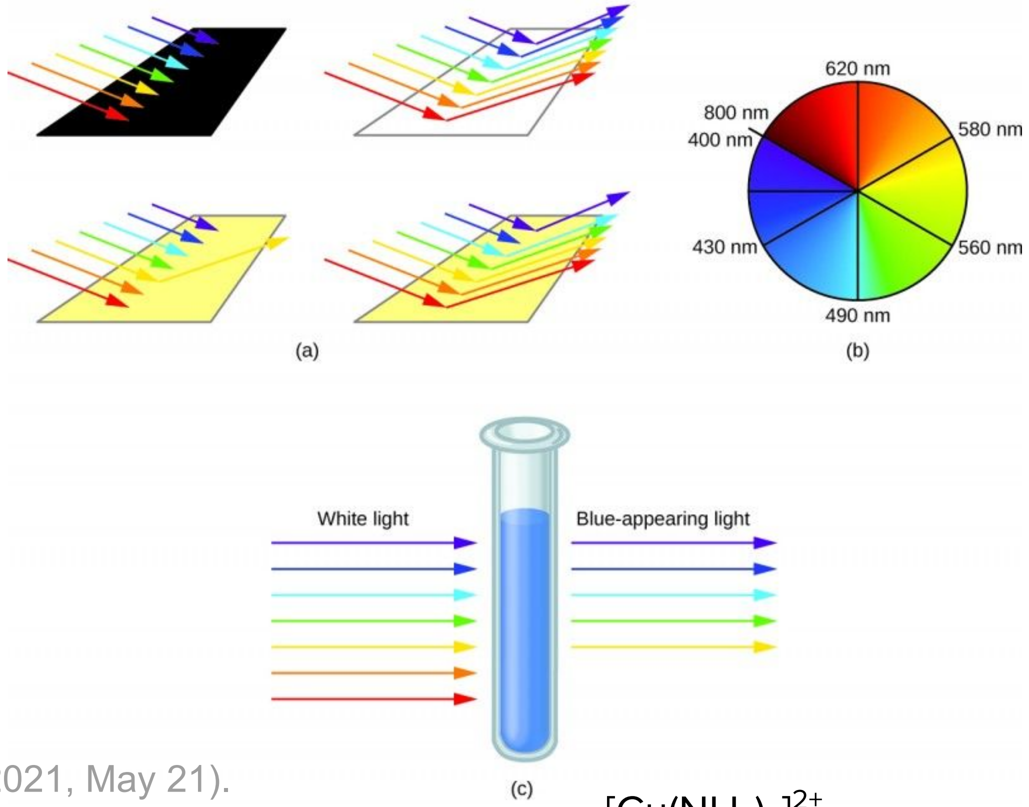
Rods work under low intensity conditions ➜ black, grey, and white.

Cones work under high intensity conditions ➜ colors.

https://www.unm.edu/~toolson/human_cone_response.htm
https://commons.wikimedia.org/wiki/File:Eyesensitivity.png
https://www.flickr.com/photos/veisto/8389740249

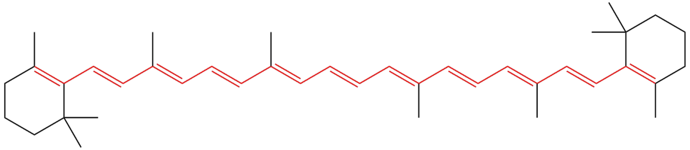
Complementary Colors

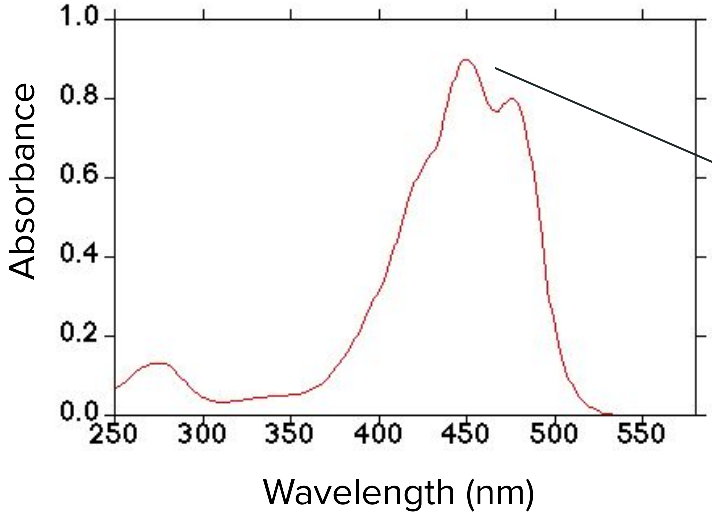
If wavelengths of light from a certain region of the spectrum are absorbed by a material, then the material will appear to be the complementary color.

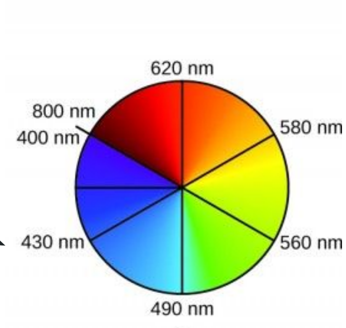


$[Cu(NH_3)_4]^{2+}$

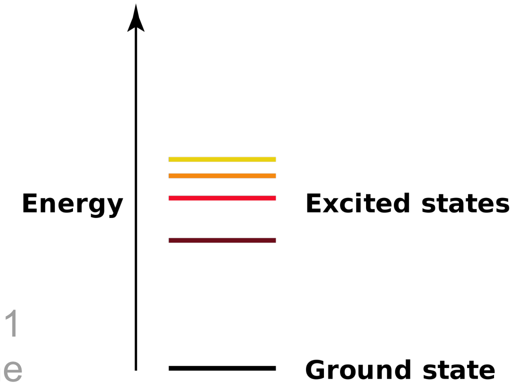
Theopold, P. F., Klaus, & Richard Langley et al. (2021, May 21). Color and the Colors of Complexes. OpenStax CNX. https://chem.libretexts.org/@go/page/24356





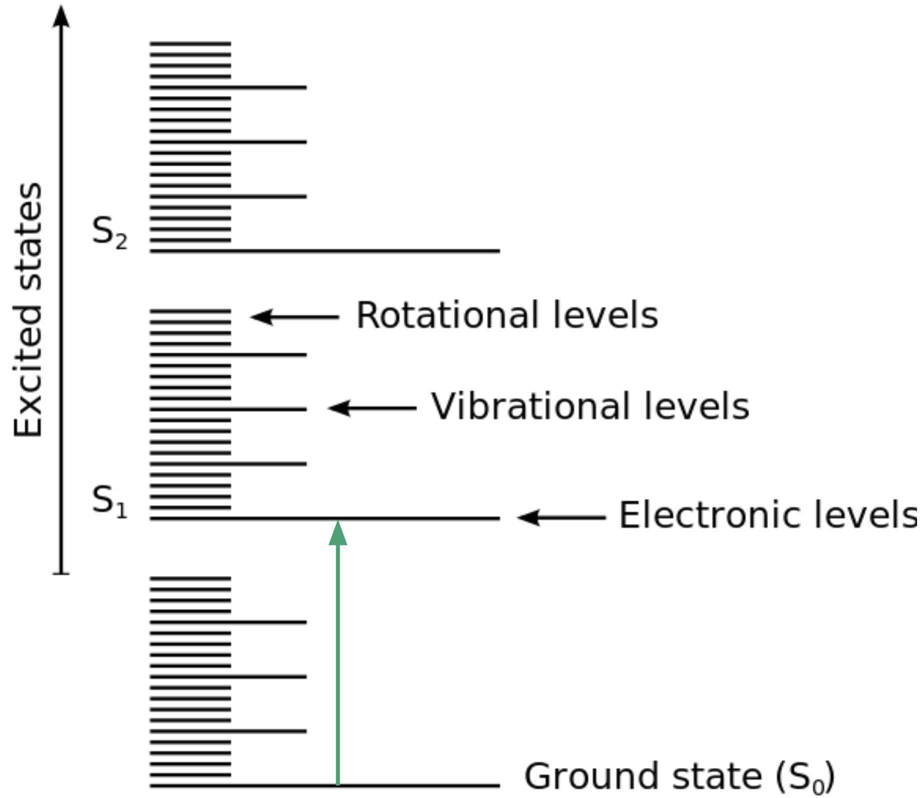


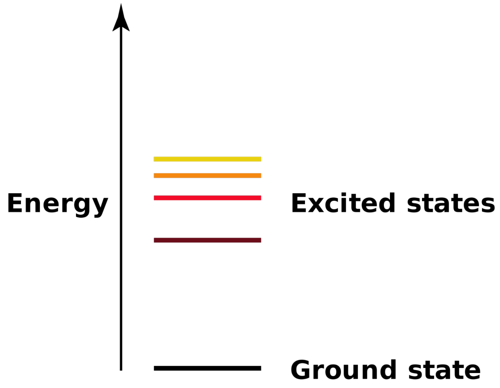
UV-Vis spectrum of
□-Carotene in methanol



Why do atoms produce line spectra, while molecules produce band spectra?

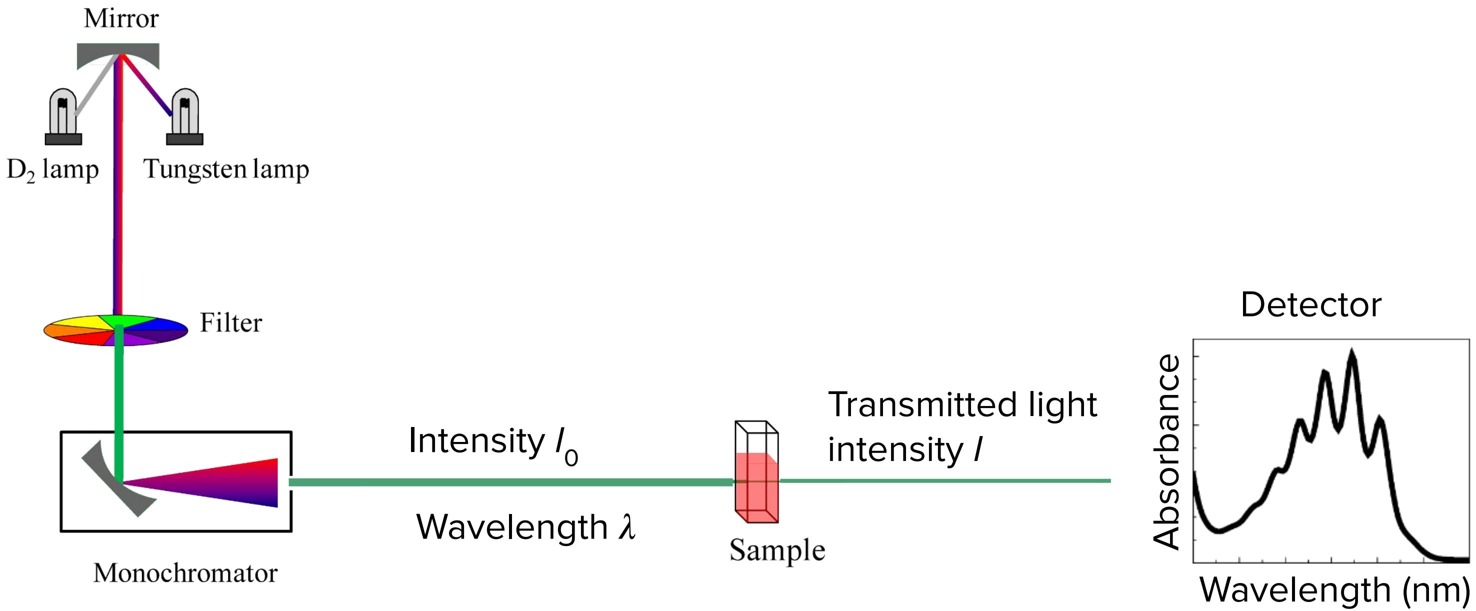
http://lipidbank.jp/cgi-bin/detail.cgi?id=VCA0001
https://en.wikipedia.org/wiki/%CE%92-Carotene





Each electronic energy level has many sublevels associated with vibration and rotation of the molecule

UV-Vis spectrophotometer



$$A = \log \frac{I_0}{I}$$

https://en.wikibooks.org/wiki/Methods_and_Concepts_in_the_Life_Sciences/Spectroscopy

Lambert-Beer law

Absorbance

$$A = \log \frac{I_0}{I} = \varepsilon[J]L$$

sample length
cm

molar absorption (extinction)
coefficient
$dm^3\ mol^{-1}\ cm^{-1}$

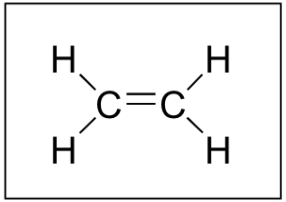
molar concentration
$mol\ dm^{-3}$

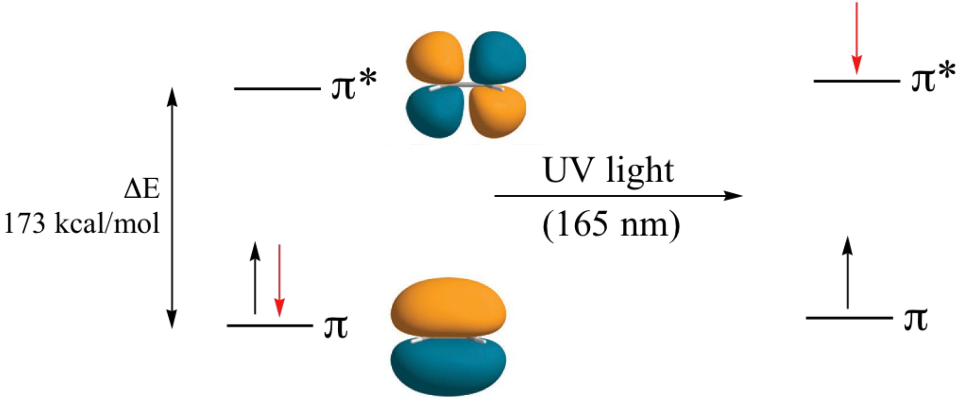
Transmittance

$$T = \frac{I}{I_0}$$

ε depends on wavelength of the light λ, solvent, and temperature
ε can be evaluated by plotting A with $[J]$ (linear)

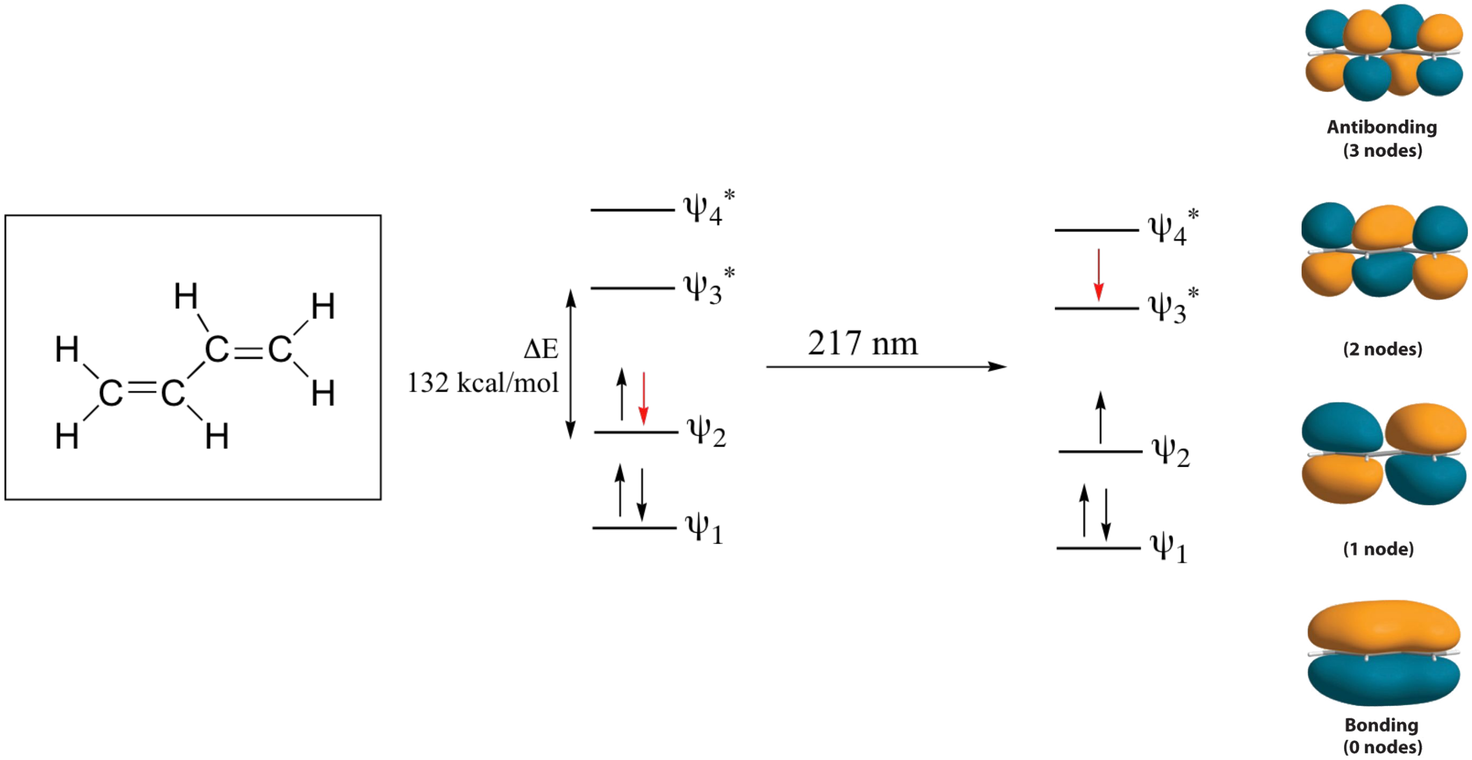
Absorption spectra of conjugated systems

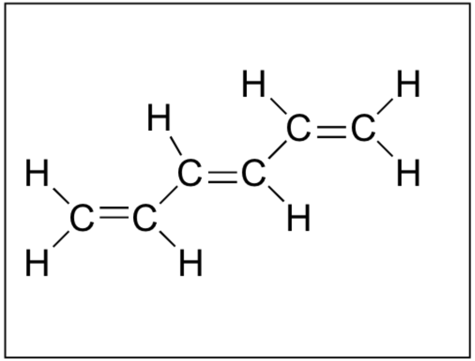


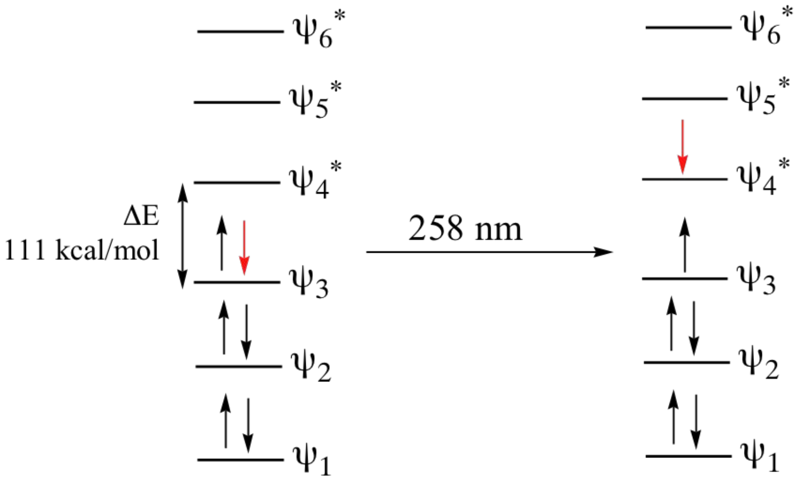


1 kcal/mol =
4.184 kJ/mol

π-π^*
transition

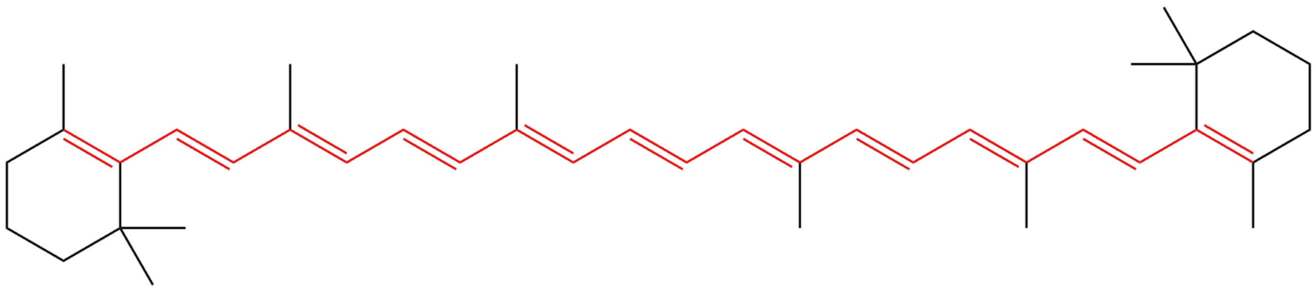

H
H
H
H
H
H
C=C
C=C
ΔE
132 kcal/mol
ψ4*
ψ3*
ψ2
ψ1
217 nm
ψ4*
ψ3*
ψ2
ψ1
Antibonding
(3 nodes)
(2 nodes)
(1 node)
Bonding
(0 nodes)

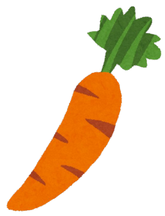




The longer the conjugated system, the smaller the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

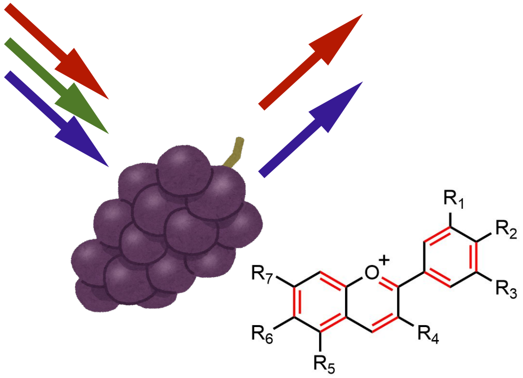
Short conjugated systems exhibit absorption in UV.



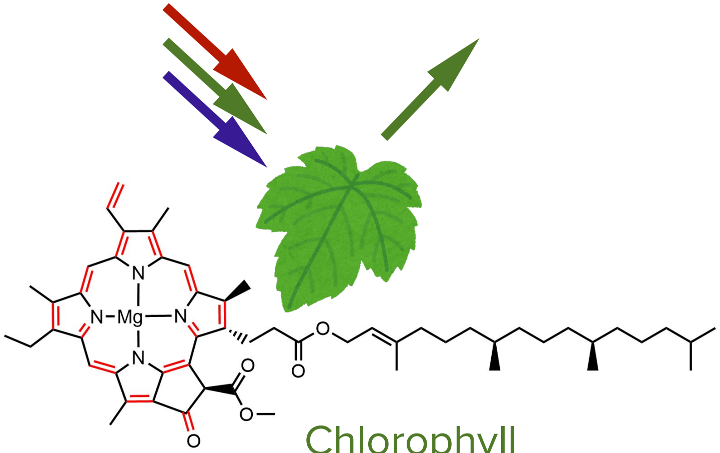


beta carotene

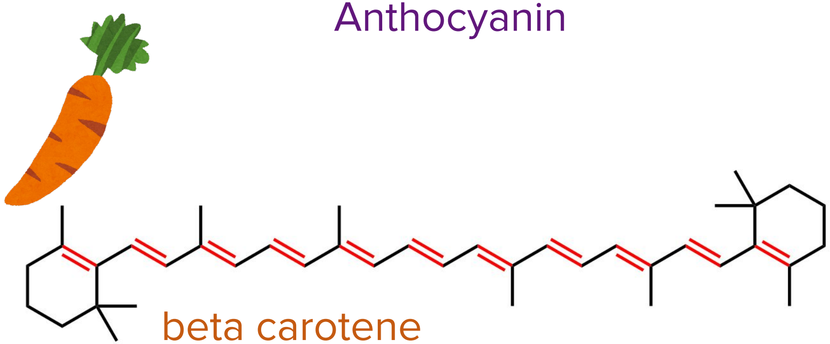
In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum.



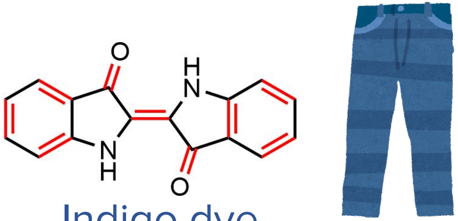
Anthocyanin



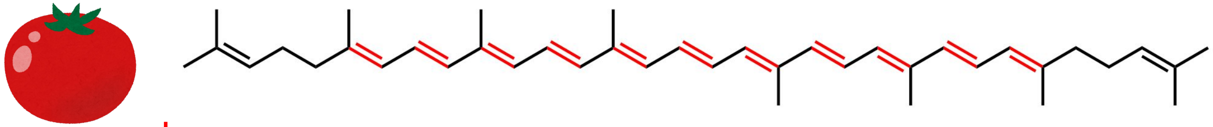
Chlorophyll



beta carotene

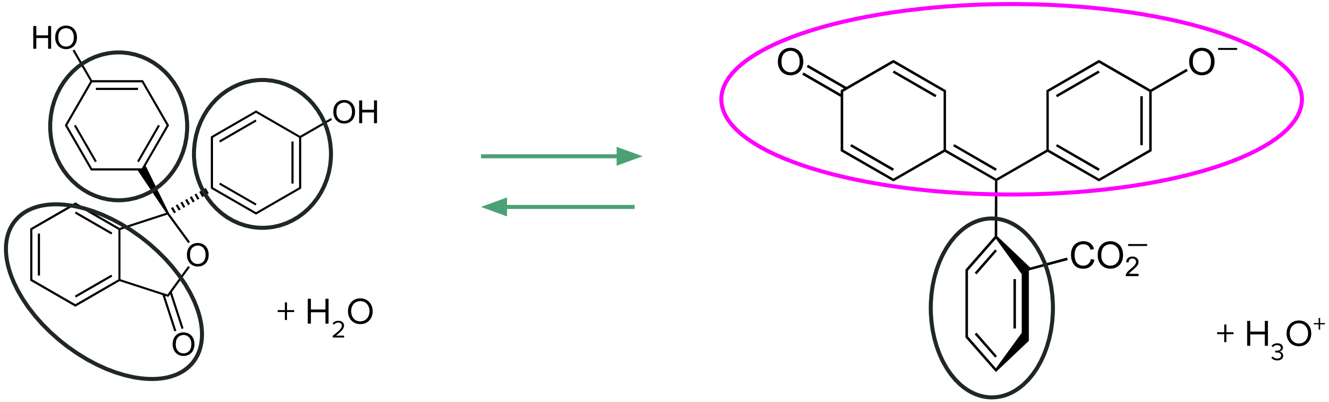


Indigo dye



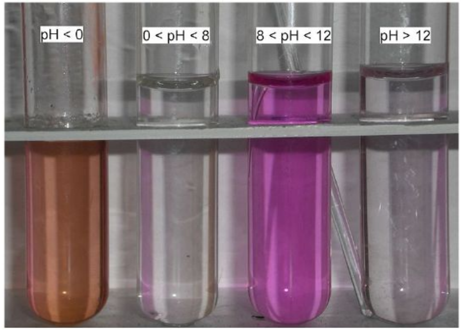
Lycopene

Experiment 0: UV-Vis spectrum of Phenolphthalein (skip)



Colorless
pH = 0–8.3

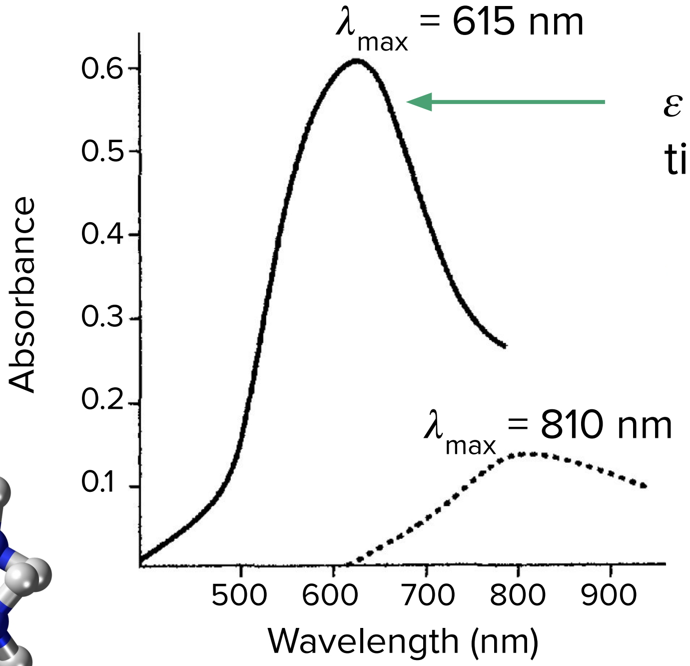
Pink
pH = 8.3–10.0



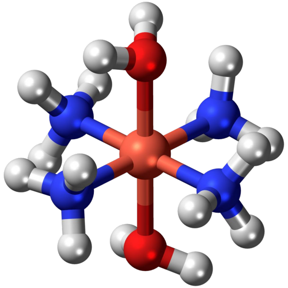
Can you see the difference in the length of the conjugated pi-electron system?
Where are the two form absorption peaks located in the electromagnetic spectrum?

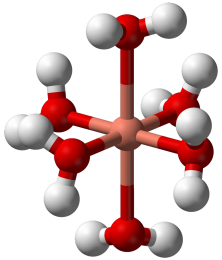
Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, E. V., John W., & Hahn, A. (2020, November 6). Indicators. Chemical Education Digital Library (ChemEd DL). https://chem.libretexts.org/@go/page/49692

Experiment 1: UV-Vis spectra of Cu^{2+} and $[Cu(NH_3)_4]^{2+}$



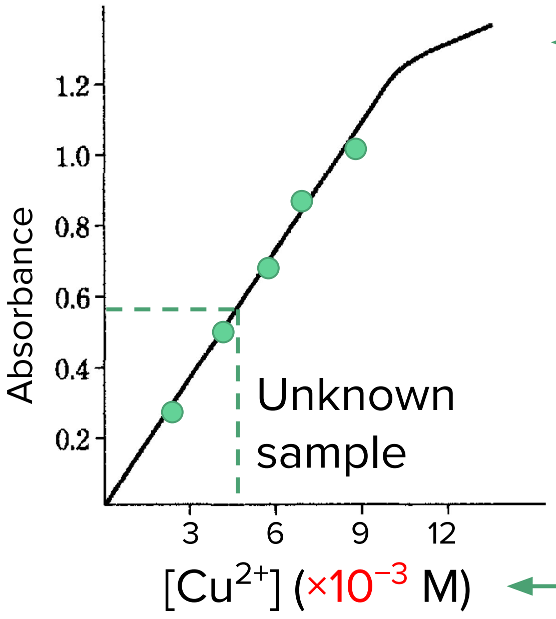
ε of $[Cu(NH_3)_4]^{2+}$ is several times higher





Experiment 1: Determine the concentration of Cu^{2+}

$$A = \varepsilon[J]L$$



High concentrations, stronger intermolecular interaction

Calibration curve for Cu^{2+}

$A = k[Cu^{2+}] + b$

High sensitivity (can be up to 10^{-6} M)

Technical Details

Results are sensitive with respect to impurities:

- Highly purified solvents and chemicals are necessary.
- Clean glassware.

  - ➢ Avoid contact with clear sides of cuvettes with any hard surface.
  - ➢ Avoid spillage of the solution on the outer side of the cuvettes.
  - ➢ Hold the cuvettes such that transparent sides are not being touched.
  - ➢ Ensure that transparent sides of the cuvettes are in the optical path.

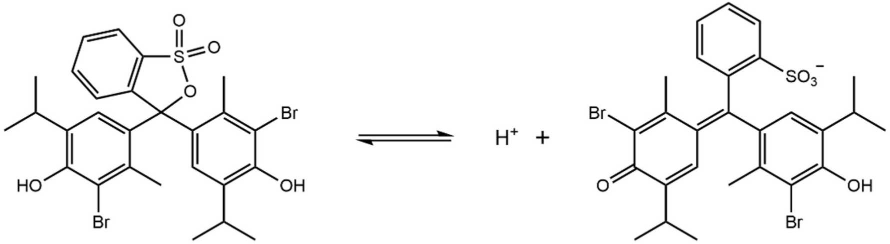
Technical Details

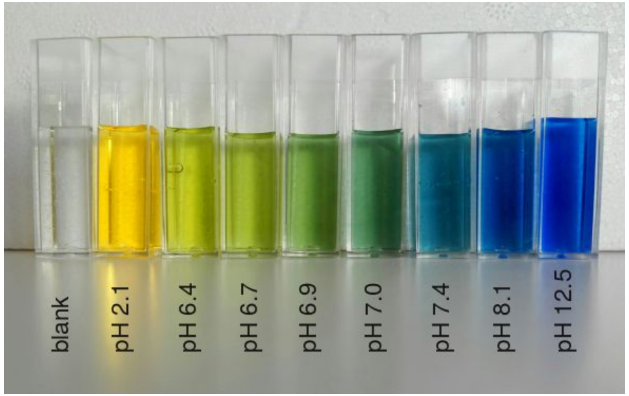
The absorption of solvent must be taken into account by measuring the absorption spectrum of a reference solution (containing the same volume of solvent—2.4 M aqueous NH_3).

Absorbance of the reference solution is set to 0

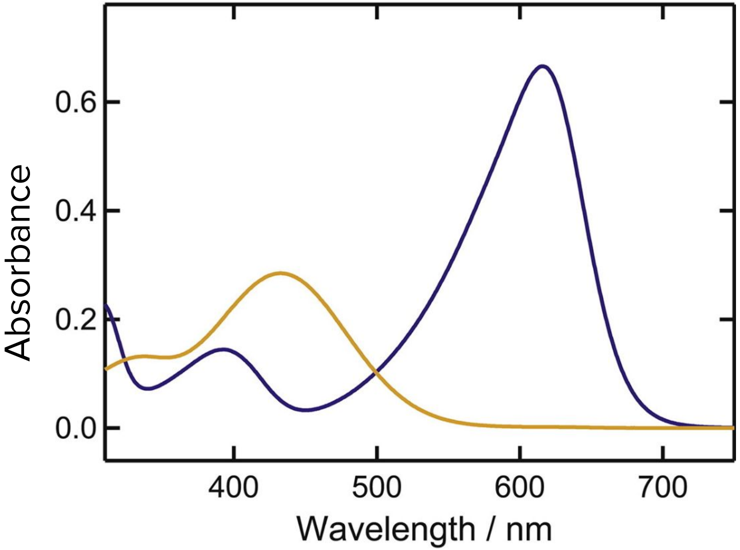
Absorbance of the sample solution is 0.3–0.6 (optimal range)

Experiment 2: Absorption spectrum of bromothymol blue (BTB) at different pH





https://en.wikipedia.org/wiki/Bromothymol_blue



Can you see the difference in the length of the conjugated pi-electron system?

Shimada, T., Hasegawa, T. (2017). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *185*, 104-110.

$$K_a = \frac{[\mathrm{H^+}][\mathrm{L^-}]}{[\mathrm{HL}]}$$

$$\frac{[\mathrm{L^-}]}{[\mathrm{HL}]} = 10^{(\mathrm{pH} - \mathrm{p}K_a)}$$

Total concentration of BTB (HL and L⁻)

$$A = \varepsilon_{\mathrm{HL}}[\mathrm{HL}] + \varepsilon_{\mathrm{L}}[\mathrm{L^-}]$$

(Ignore sample length)

Acidic solution:

$$A = \varepsilon_{\mathrm{HL}} C = A_1$$

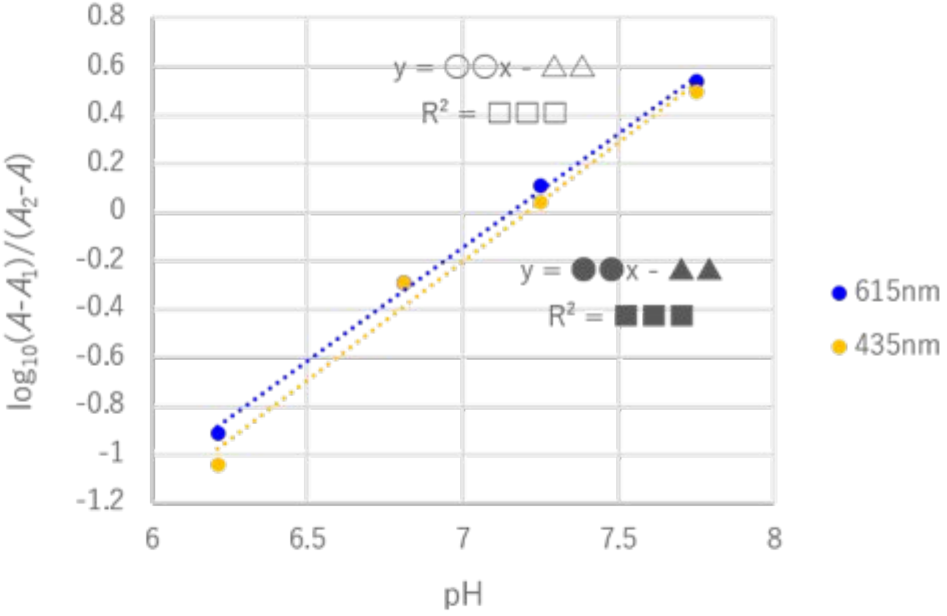
Basic solution:

$$A = \varepsilon_{\mathrm{L}} C = A_2$$

$$\log_{10} \frac{A - A_1}{A_2 - A} = \mathrm{pH} - \mathrm{p}K_a$$

$$\log_{10} \frac{A - A_1}{A_2 - A} = \mathrm{pH} - \mathrm{p}K\mathrm{a}$$

Intercept



Chapter 6: Rate of Chemical Reactions and Energy

Main theme: In this experiment, you will learn

The Arrhenius equation (the relationship between temperature and the reaction rate) and the Belousov-Zhabotinsky reaction (chemical oscillation reactions).

Rate of reaction

The rate of a chemical reaction or **reaction rate**

- speed at which a chemical reaction takes place
- how quickly amounts (moles) of reactants are converted into amounts (moles) of products

Rusting - slow

$$4Fe + 3O_2 + 2xH_2O \longrightarrow 2Fe_2O_3 \cdot xH_2O$$

https://en.wikipedia.org/wiki/Iron_oxide

Sodium in water - fast

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2(g)$$

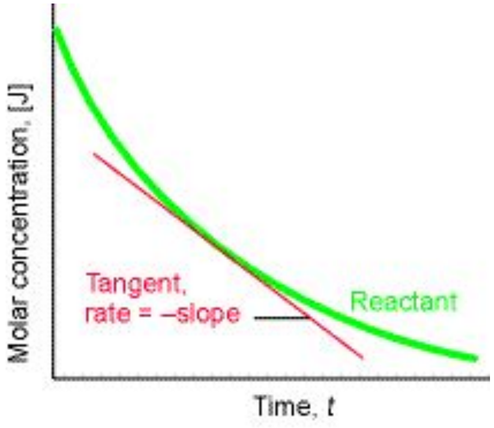
https://www.youtube.com/watch?v=dmcfsEEogxs

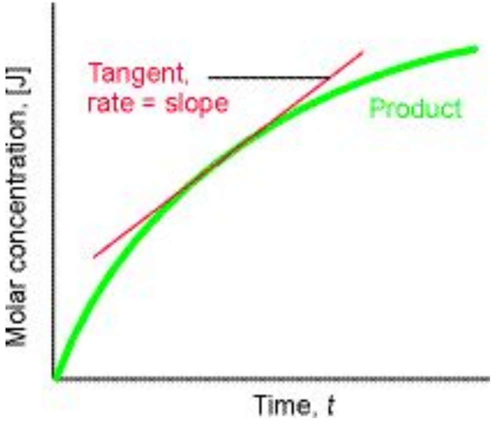
A + 2B → 3C + D

$$-\frac{d[A]}{dt} \quad -\frac{d[B]}{dt} \qquad \frac{d[C]}{dt} \quad \frac{d[D]}{dt}$$

Rate of consumption of reactants

Rate of formation of products





$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = v$$

Rate of the reaction

http://staff.um.edu.mt/jgri1/teaching/che2372/notes/06/01/intro_kinetics.html

$aA + bB \longrightarrow cC + dD$

$$\text{rate} = v = -\frac{1}{a}\cdot\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{b}\cdot\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \frac{1}{c}\cdot\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \frac{1}{d}\cdot\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}$$

Unit: mol dm^{-3} s^{-1} (liquid reactions)
molecule cm^{-3} s^{-1} (gas phase reaction)

Rate law

$aA + bB + ... \rightarrow$ product

$$v = k_r [A]^m [B]^n \cdots$$

order of the reaction with respect to A

order of the reaction with respect to B

Rate constant

Generally, there is **no** connection between the order of the reaction and the stoichiometry coefficients!

The overall order = $m + n + ...$

Order	Unit of k_r
0	$mol \cdot L^{-1} \cdot s^{-1}$
1	s^{-1}
2	$L \cdot mol^{-1} \cdot s^{-1}$
3	$L^2 \cdot mol^{-2} \cdot s^{-1}$

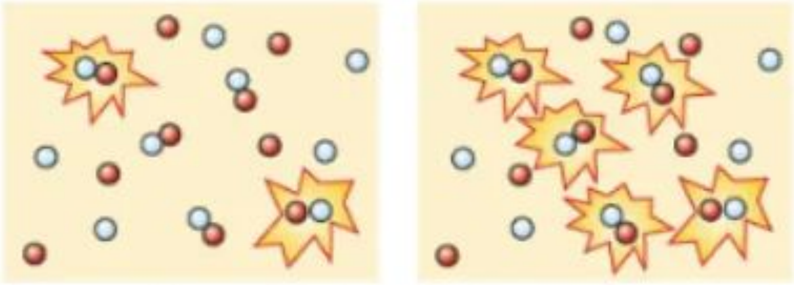
Arrhenius Equation

Most reaction rates increase with T: in solution, by about a factor of 2 to 4 with an increase of 10 °C.

Milk turns sour much more rapidly if stored at room temperature.

https://en.wikipedia.org/wiki/Soured_milk

Low T High T



Less collisions More collisions

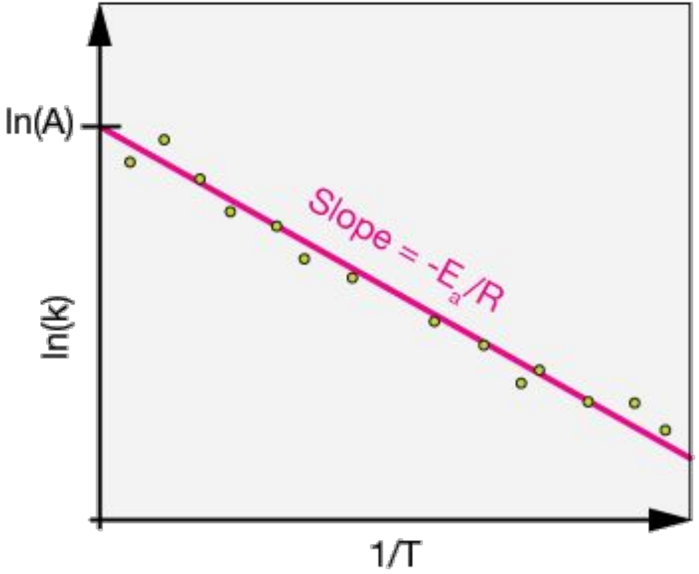
https://igcseandialchemistry.com/factors-affecting-the-rate-of-reaction/

$$k_\mathrm{r} = A \cdot e^{-E_\mathrm{a}/RT}$$

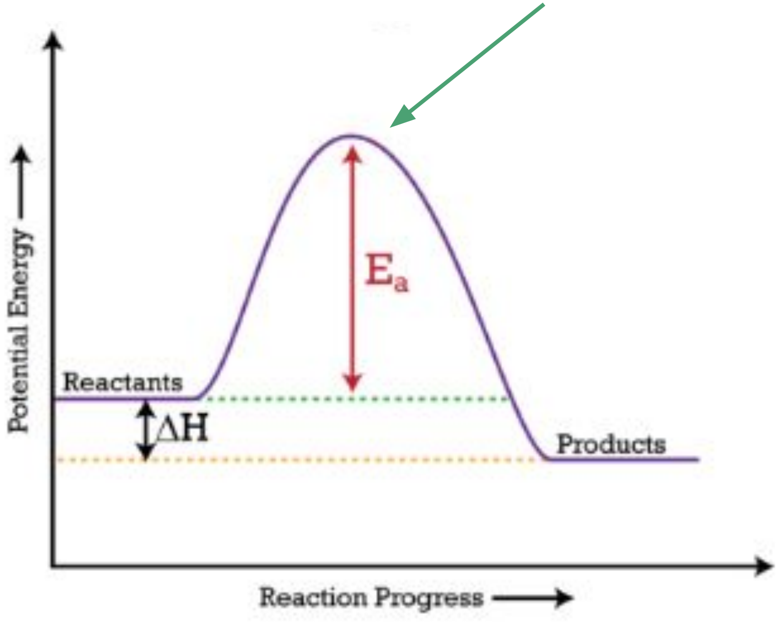
Activation energy
Unit: kJ mol^{-1}

frequency factor or the pre-exponential factor
Unit: same of k_r
$A > 0$

$$\underbrace{\ln k_\mathrm{r}}_{y} = \underbrace{\ln A}_{\text{intercept}} + \underbrace{\left(-\frac{E_\mathrm{a}}{R}\right)}_{\text{slope}} \underbrace{\frac{1}{T}}_{x}$$



the activated complex
or the transition state

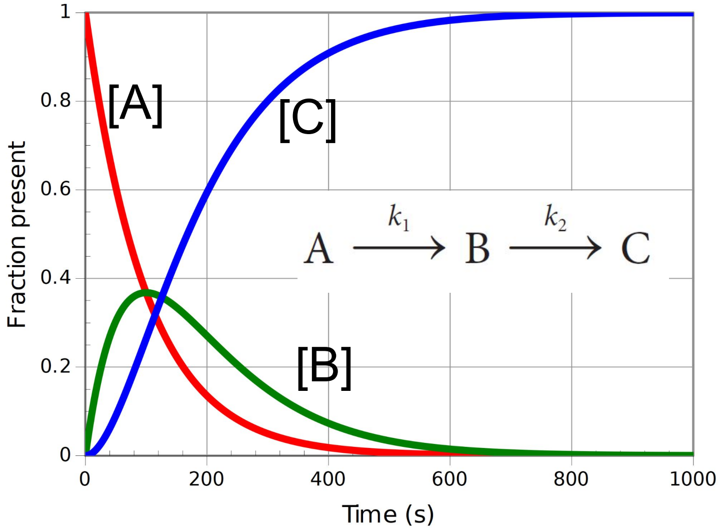


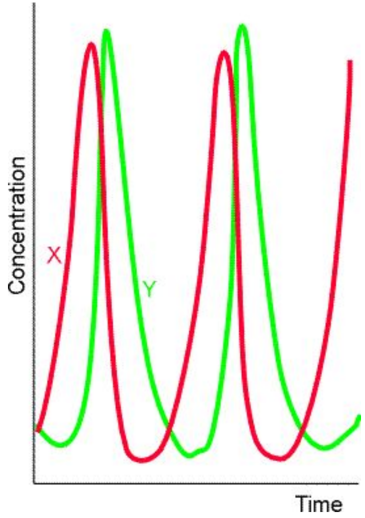
The activation energy is the **minimum** energy reactants must have in order to form products.

Potential Energy Diagrams. (2021, July 10).
https://chem.libretexts.org/@go/page/53890

Oscillating reactions

http://staff.um.edu.mt/jgri1/teaching/che2372/notes/09/04/catalysis.html





Normal reactions:
the concentration of species displays a single maximum during the course of the reaction.

Oscillating reactions:
the concentration of species oscillates with time.
Is it possible?

Lotka-Volterra Model

step 1: $A + X \rightarrow 2X$

step 2: $X + Y \rightarrow 2Y$

step 3: $Y \rightarrow B$

$$A \rightarrow B$$

autocatalytic reaction
[X] and [Y] accelerates its own production

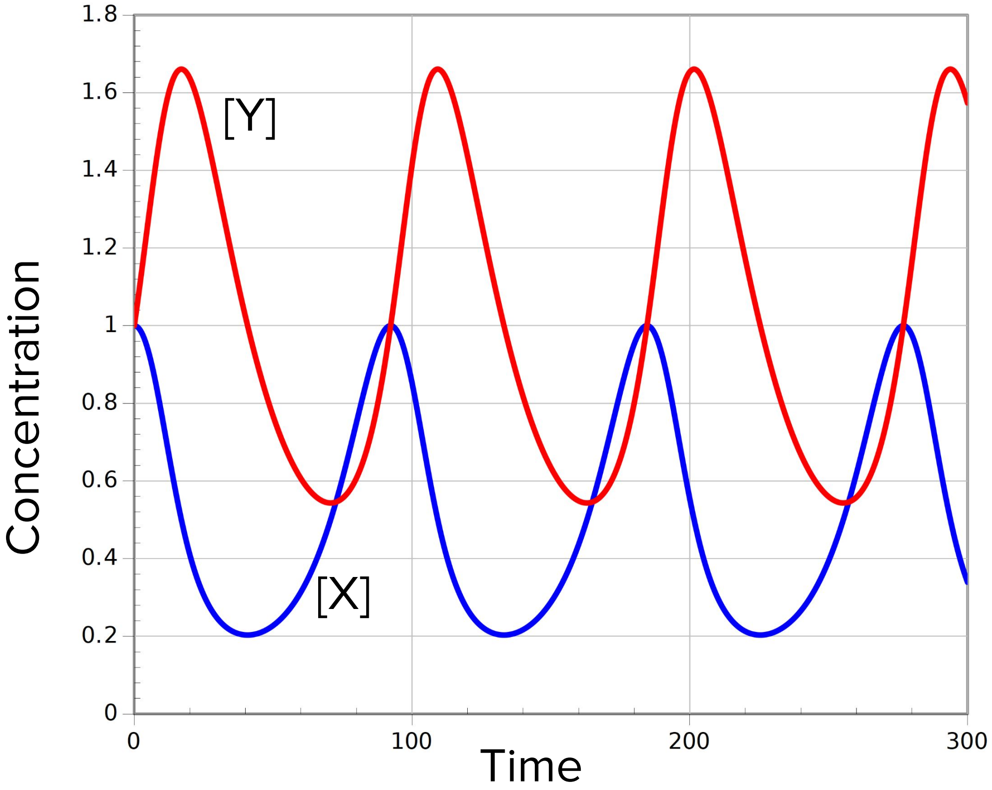
Assumption:

[A] = constant, A is continuously replaced from an external source as it is consumed in the reaction

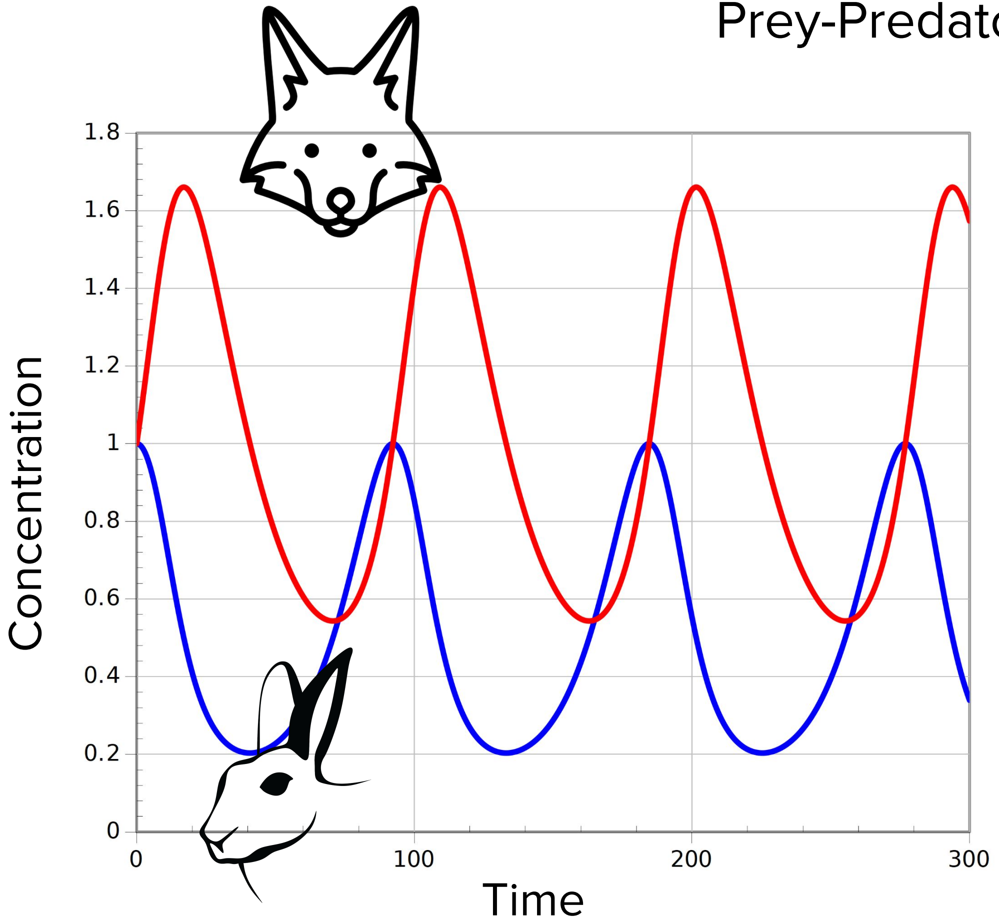
B plays no part in the reaction

X: activation species

Y: inhibitor species


1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Concentration
[Y]
[X]
0
100
200
300
Time

Prey-Predator Model

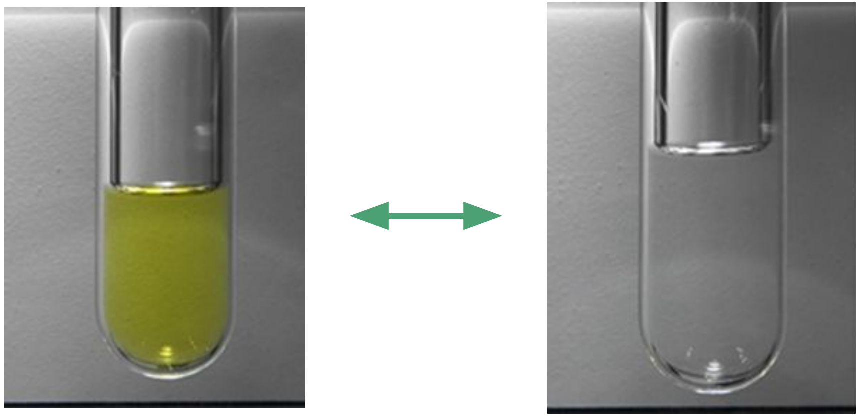


Experiment 3: Belousov-Zhabotinsky (BZ) reaction (online)

Oxidation of malonic acid ($CH_2(COOH)_2$) with bromate ion (BrO_3^-) in an acidic solution with the presence of cerium ions (catalyst)

$$3\ BrO_3^- + 5\ CH_2(COOH)_2 + 3\ H^+ \rightarrow 3\ BrCH(COOH)_2 + 2\ HCOOH + 4\ CO_2 + 5\ H_2O$$

Ce^{4+}



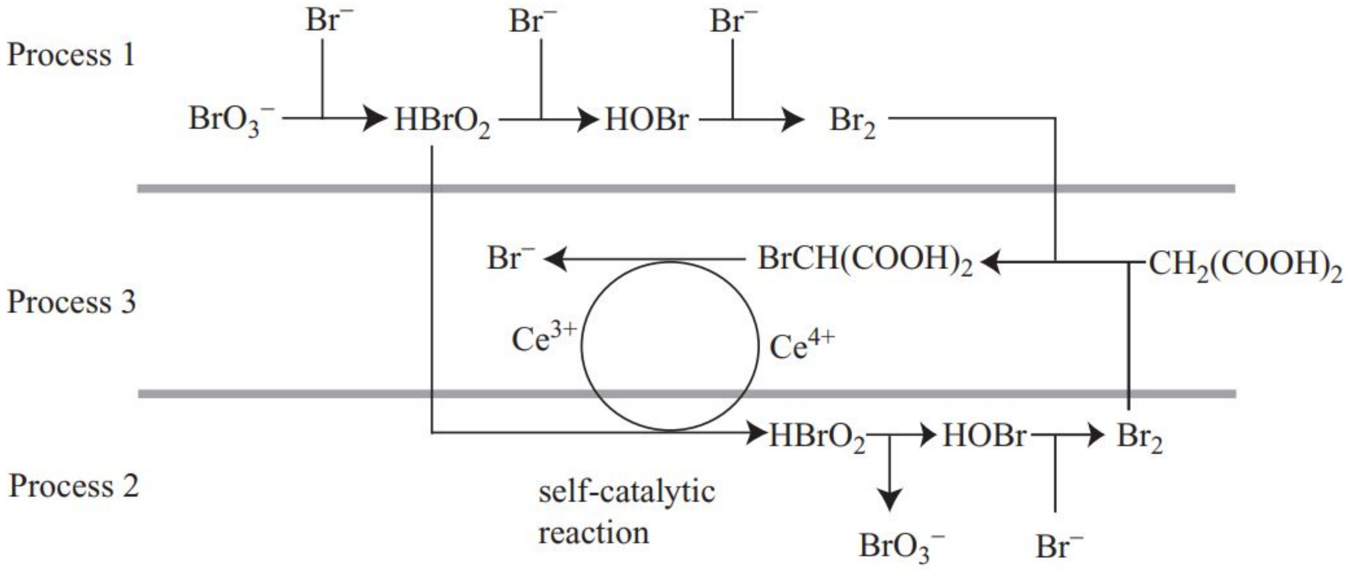
https://en.wikipedia.org/wiki/Ammonium_cerium(IV)_sulfate

FNK (Field, Körös and Noyes) mechanism

(R1) $Br^- + BrO_3^- + 2H^+ \leftrightarrow HOBr + HBrO_2$
(R2) $Br^- + HBrO_2 + H^+ \leftrightarrow 2HOBr$
(R3) $Br^- + HOBr + H^+ \leftrightarrow Br_2 + H_2O$
(R4) $2HBrO_2 \leftrightarrow HOBr + BrO_3^- + H^+$
(R5) $HBrO_2 + BrO_3^- + H^+ \leftrightarrow 2 \cdot BrO_2 + H_2O$
(R6) $\cdot BrO_2 + Ce^{3+} + H^+ \leftrightarrow HBrO_2 + Ce^{4+}$
(R7) $\cdot BrO_2 + Ce^{4+} + H_2O \leftrightarrow BrO_3^- + Ce^{3+} + 2H^+$
(R8) $Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+$
(R9) $6Ce^{4+} + CH_2(COOH)_2 + 2H_2O \rightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+$
(R10) $4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \rightarrow 4Ce^{3+} + HCOOH + Br^- + 2CO_2 + 5H^+$

Miyazaki, J. (2013). Belousov–Zhabotinsky Reaction. In *Pattern Formations and Oscillatory Phenomena* (pp. 61-83). Elsevier.

Process 1: dominant at high [Br⁻]

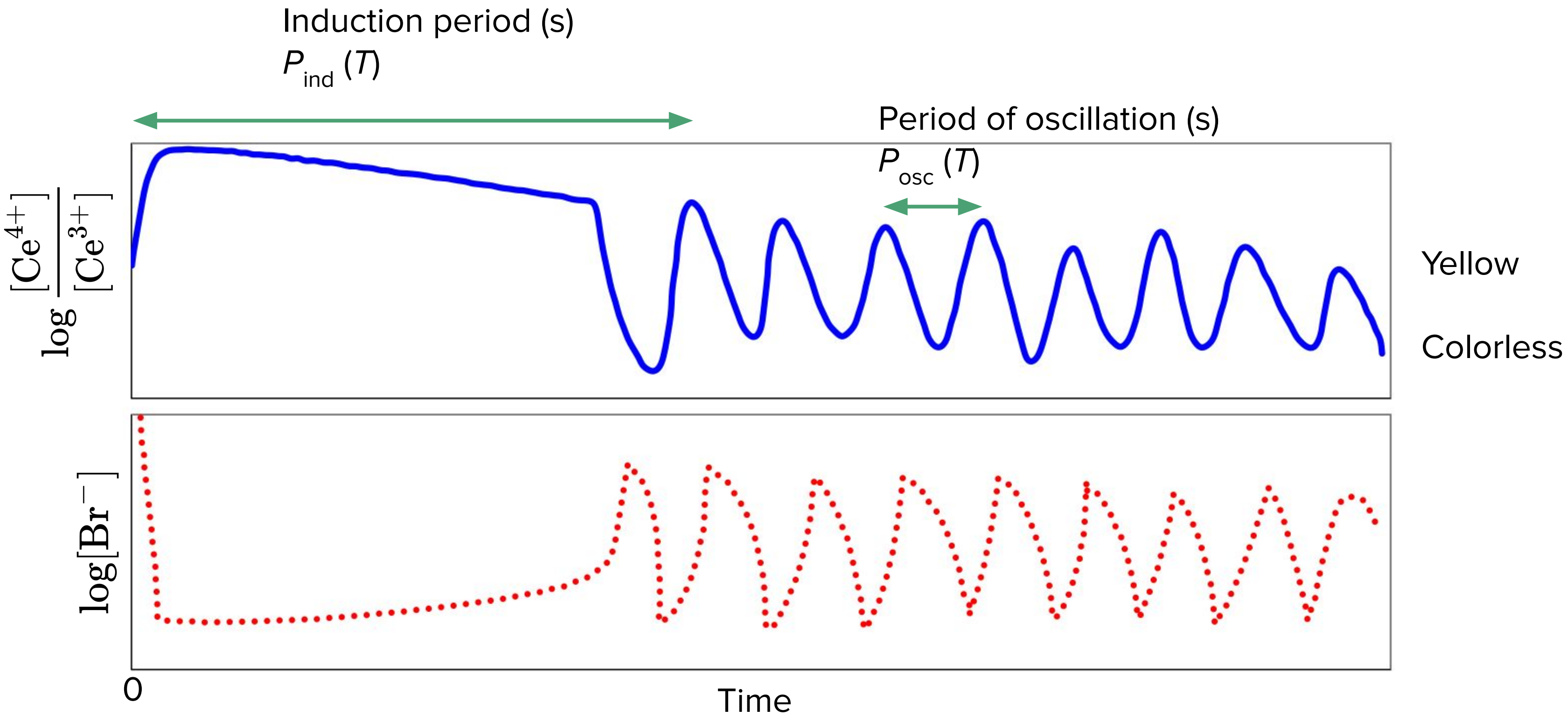


Process 2: dominant at low [Br⁻]

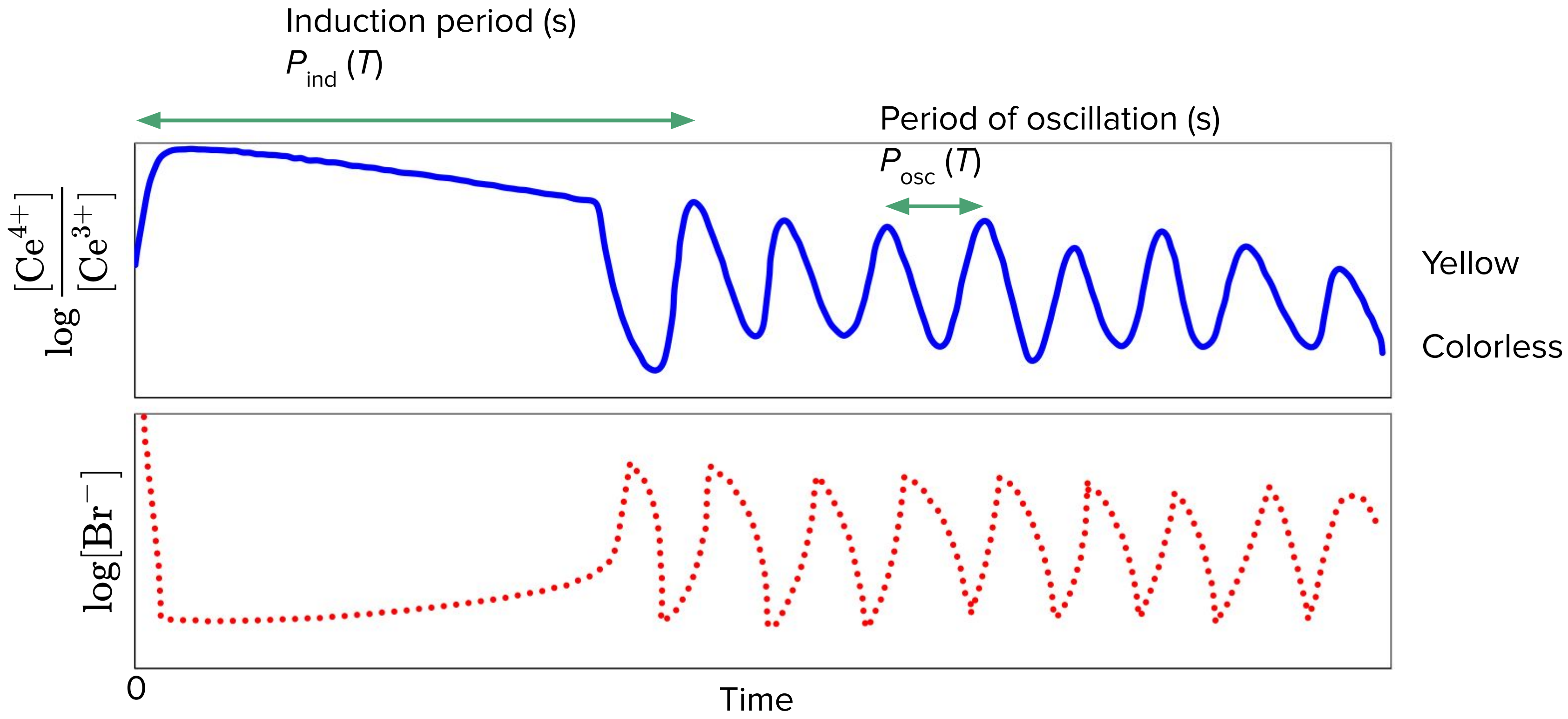
$$\boxed{HBrO_2} + BrO_3^- + 3H^+ + 2Ce^{3+} \rightarrow \boxed{2HBrO_2} + H_2O + 2Ce^{4+}$$

Bromous acid

Br^- is not presented at the beginning of the reaction ➔ induction period



Task: measure P_{osc} and P_{ind} at different temperatures ➔ Activation energy



https://www.youtube.com/watch?v=LL3kVtc-4vY