

3.9 Separation of Solutions and Mixtures; Chromatography

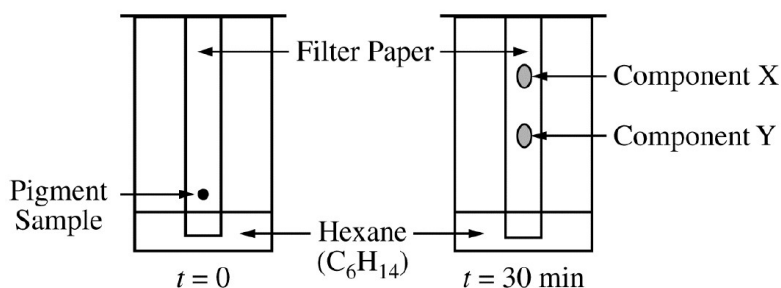
Essential knowledge statements from the AP Chemistry CED:

- The components of a liquid solution cannot be separated by filtration. They can, however, be separated using processes that take advantage of differences in the intermolecular interactions of the components.
 - Chromatography (paper, thin-layer, and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components of the solution (the mobile phase) and with the surface components of the stationary phase.
 - Distillation separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components and the effects these interactions have on the vapor pressures of the components in the mixture.

Stationary phase A solid that provides support for the chromatography experiment, but does not move. It can be a piece of paper, a piece of metal or glass coated with a porous solid, or a glass column filled with a porous solid.

Mobile phase A liquid or gas that moves, carrying the components of the mixture over or through the stationary phase.

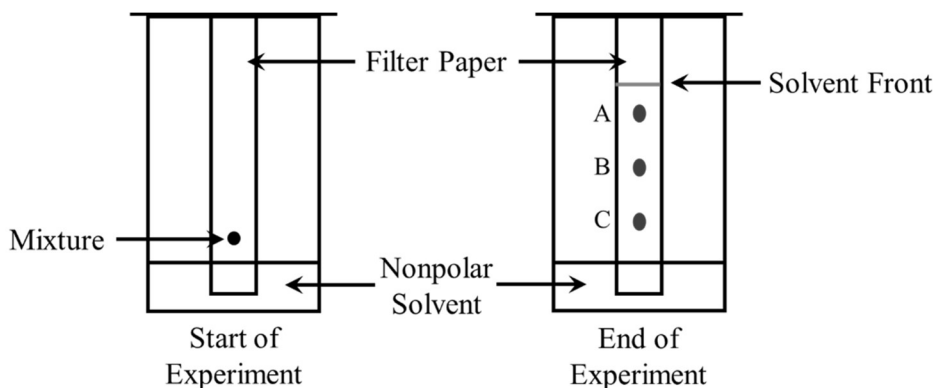
In AP Chemistry, questions related to chromatography often involve polarity. As you will see in Topic 3.10 (Solubility), substances with similar intermolecular interactions tend to be soluble in one another. *Polar solutes mix well with polar solvents; nonpolar solutes mix well with nonpolar solvents.*



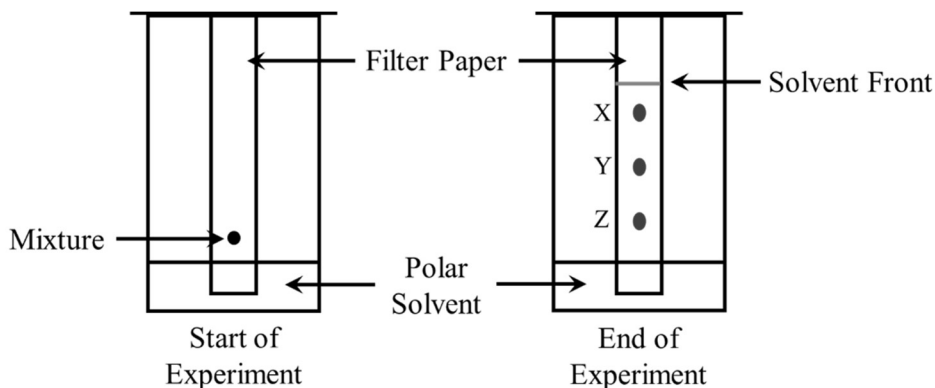
1. In the diagram above, the stationary phase is the paper, which is a moderately polar substance. The mobile phase is hexane (C_6H_{14}), which is a nonpolar solvent. A mixture of substances X and Y are separated in a chromatography experiment. Based on the results shown above, a student makes the claim that component Y is more polar than component X. Do you agree or disagree with the student's claim? Justify your answer.

The solvent is the liquid that travels up the paper in a paper chromatography experiment. The solvent is also known as the mobile phase. The **solvent front** is the mark on the paper that indicates how far the solvent has moved up the paper.

The component of the mixture that travels the farthest distance up the paper will be the one that is the most soluble in, or has the best interactions with, the solvent.



2. Based on the results shown above, component A is the (least most) polar, and component C is the (least most) polar.



3. Based on the results shown above, component X is the (least most) polar, and component Z is the (least most) polar.

After a paper chromatography experiment has been completed, you can calculate the R_f value (which is known as the retention factor) for each component of the mixture. The R_f value is calculated as follows.

$$R_f = \frac{\text{distance traveled by one component}}{\text{distance traveled by the solvent}}$$

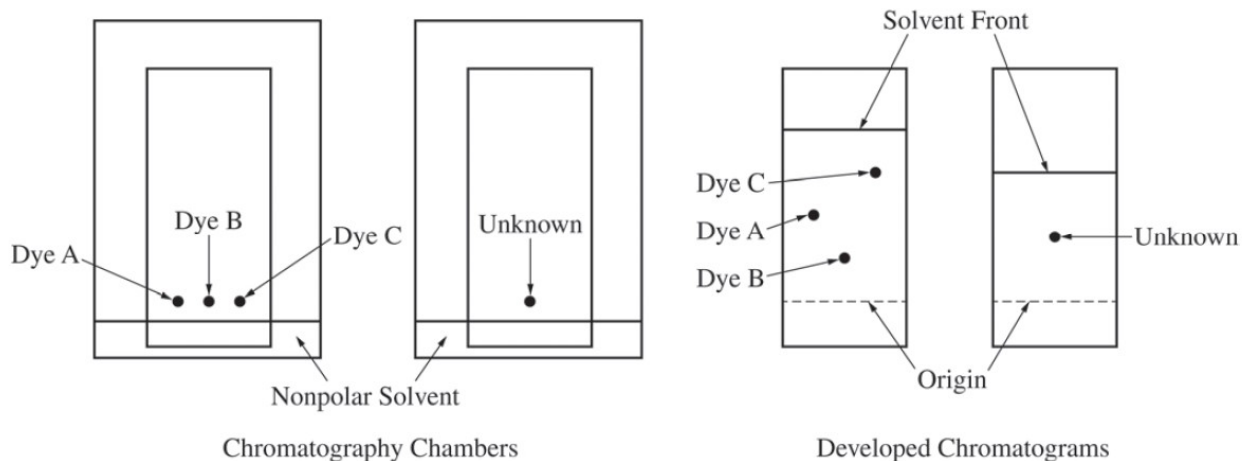
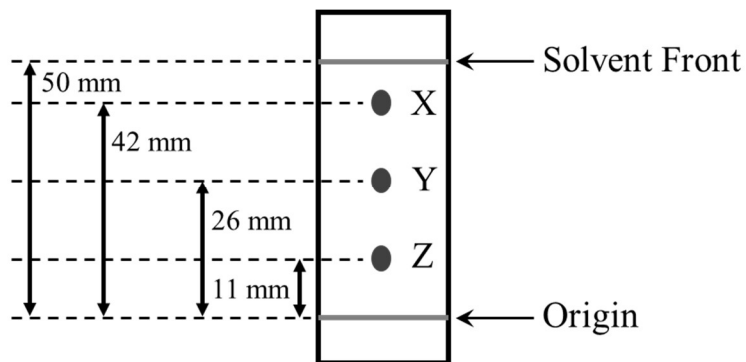
The R_f value will always be in a range of 0 to 1. The larger the R_f value is, the farther up the paper the component of the mixture has traveled relative to the solvent front.

In the example shown on the next page, the R_f values for three different components of a mixture have been calculated.

$$R_f \text{ of component X} = \frac{42 \text{ mm}}{50 \text{ mm}} = 0.84$$

$$R_f \text{ of component Y} = \frac{26 \text{ mm}}{50 \text{ mm}} = 0.52$$

$$R_f \text{ of component Z} = \frac{11 \text{ mm}}{50 \text{ mm}} = 0.22$$

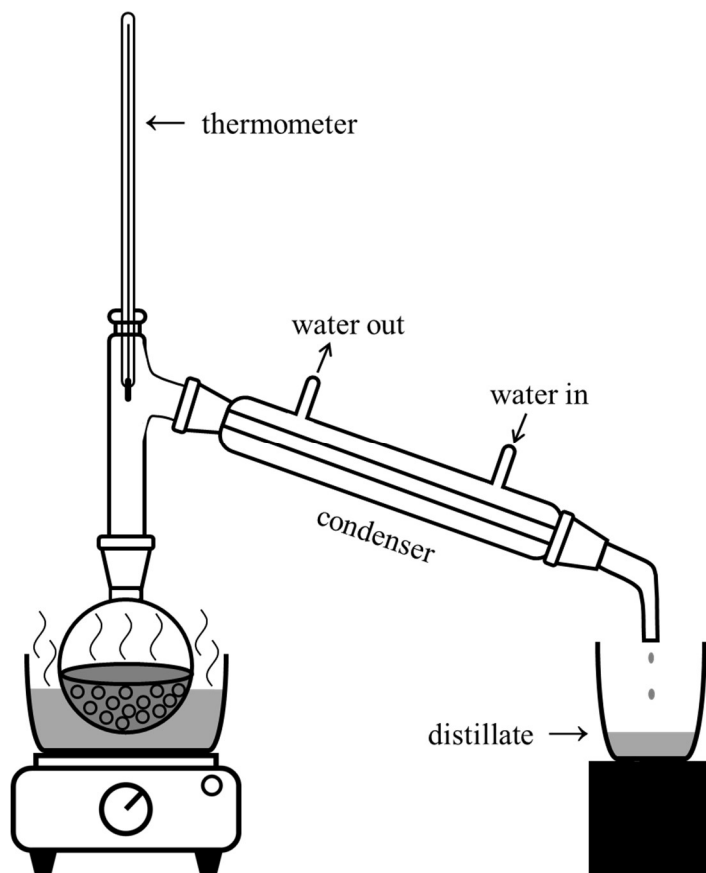


4. A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.

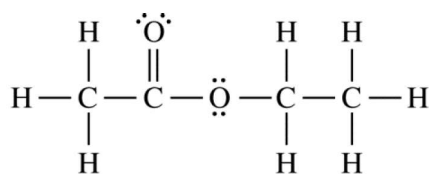
(a) Which dye (A, B, or C) is the least polar? Which dye is the most polar?

Justify your answers in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

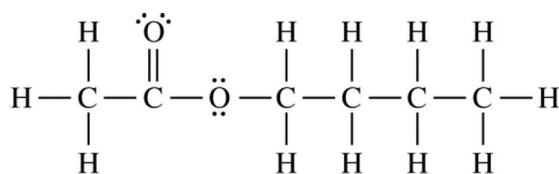
(b) Which dye is present in the unknown sample? Justify your answer.



The diagram above shows the setup for a **distillation** experiment. Distillation is used to separate the components of a mixture that have different boiling points. The mixture is heated gently until the component with the lowest boiling point begins to boil. The vapor rises up through the glassware, and reaches the **condenser**, which is the portion of the apparatus that is surrounded by cool water. The vapor condenses into a liquid and is collected in a separate container. The liquid that is produced in a distillation experiment is known as the **distillate**. The component of the mixture that appears first in the distillate is the one with the lowest boiling point.



Ethyl Acetate



Butyl Acetate

5. A mixture containing equal numbers of moles of ethyl acetate and butyl acetate was separated using distillation. Use the Lewis diagrams shown above to answer the following questions.

(a) Identify all types of intermolecular forces present in each substance.

ethyl acetate _____

butyl acetate _____

5. (continued)

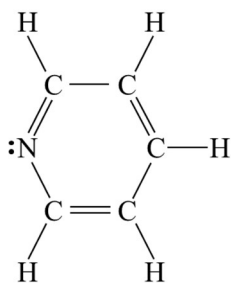
(b) Which substance, ethyl acetate or butyl acetate, should have a higher boiling point? Justify your answer in terms of the relative strength of the intermolecular forces.

(c) Which substance, ethyl acetate or butyl acetate, should be initially present in a higher concentration in the distillate? Justify your answer.

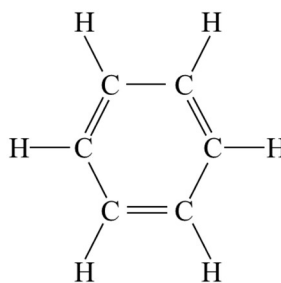
3.10 Solubility

Essential knowledge statement from the AP Chemistry CED:

- Substances with similar intermolecular interactions tend to be miscible or soluble in one another.
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Pyridine



Benzene

6. The structures of pyridine and benzene are shown above. A chemist adds a sample of each substance to a sample of water in order to compare the relative solubility in water.

(a) Classify each substance as polar or nonpolar.

water _____ pyridine _____ benzene _____

(b) Identify all types of intermolecular forces present between each solute and water.

pyridine and water _____

benzene and water _____

6. (continued)

(c) Which substance, pyridine or benzene, do you predict should be more soluble in water? Justify your choice in terms of the relative strength of the intermolecular forces between each solute and water.

7. Carbon tetrachloride, $\text{CCl}_4(l)$, is miscible with pentane, $\text{C}_5\text{H}_{12}(l)$, whereas methanol, $\text{CH}_3\text{OH}(l)$, is immiscible with pentane. Explain these two observations in terms of polarity and the relative strength of the intermolecular forces between each solute and water.

8. Will $\text{NaCl}(s)$ be more soluble in $\text{H}_2\text{O}(l)$ or in $\text{C}_6\text{H}_{14}(l)$? Justify your answer in terms of the interparticle attractions between $\text{NaCl}(s)$ and each solvent.

3.11 Spectroscopy and the Electromagnetic Spectrum

Essential knowledge statements from the AP Chemistry CED:

- Differences in absorption or emission of photons in different spectral regions are related to the different types of molecular motion or electronic transition
 - Microwave radiation is associated with transitions in molecular rotational levels.
 - Infrared radiation is associated with transitions in molecular vibrational levels.
 - Ultraviolet/visible radiation is associated with transitions in electronic energy levels.
-

Spectroscopy is the study of how electromagnetic radiation (EMR) interacts with a sample of matter. A sample of matter can absorb energy, and it can also emit energy.

Different forms of radiation will have different effects on a sample of matter, as shown in the table below.

Form of EMR	What effect will this form of EMR have on the molecule?	Relative Energy
microwave	It causes the molecule to rotate.	low
infrared	It causes the chemical bonds in the molecule to stretch and vibrate.	medium
visible and ultraviolet	It causes the electrons to move up to higher energy levels. It may also cause certain bonds to break.	high

You can explore the PhET simulation on molecules and light by visiting the following website.

bit.ly/PhET_light

Mnemonic Devices to help you remember how each form of EMR affects a sample

Imagine a microwave oven with a glass dish inside it, that rotates when the microwave oven is used.

Microwave radiation causes the molecule to rotate.

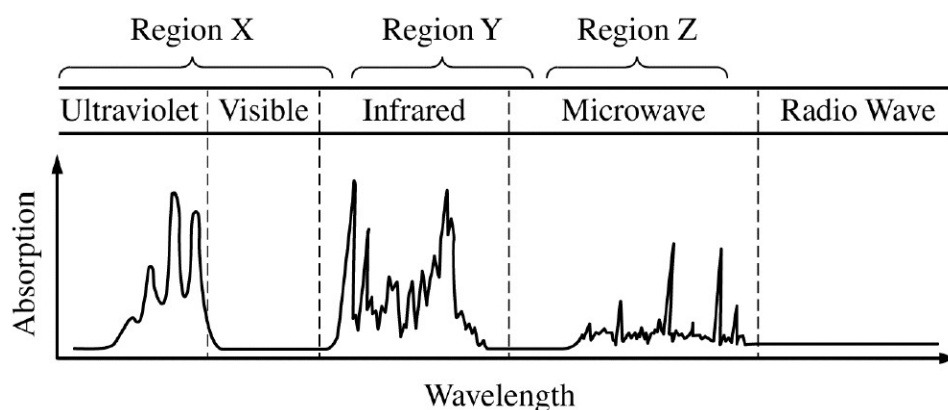
Imagine your phone is set on vibrate. Your phone buzzes, and you say, “It’s Ringing.” (I.R.)

Infrared (IR) radiation causes the bonds in the molecule to vibrate.

You think about visible light and UV radiation when you look “up” at the sun. Now think about the electrons that are jumping “up” to higher energy levels.

Visible or UV radiation causes electrons in the molecule to move up to higher energy levels.

ABSORPTION SPECTRUM



9. The diagram above represents the absorption spectrum for a pure molecular substance. Match each region in the absorption spectrum to the correct type of transition. Your choices are, in no particular order, **molecular rotation**, **molecular vibration**, and **electronic transition**.

Region X	Region Y	Region Z

3.12 Photoelectric Effect

Essential knowledge statements from the AP Chemistry CED:

- When a photon is absorbed (or emitted) by an atom or molecule, the energy of the species is increased (or decreased) by an amount equal to the energy of the photon.
- The wavelength of the electromagnetic wave is related to its frequency and the speed of light by the following equation: $c = \lambda\nu$
- The energy of a photon is related to the frequency of the electromagnetic wave through the following equation: $E = h\nu$.

In spectroscopy, a sample is exposed to a source of electromagnetic radiation. This radiation causes the sample to be affected in some way, involving both the absorption and the emission of energy. The changes in energy are processed through a detector, producing a spectrum.

The energy absorbed or emitted from a sample can be described in terms of **photons**. A photon refers to a particle of radiation that has a specific wavelength, frequency, and energy.

The units of wavelength are usually expressed in units of meters, but another common unit is nanometers. ($1 \text{ m} = 10^9 \text{ nm}$)

Frequency is usually expressed in units of Hz or s^{-1} . These units are equivalent to each other.

Energy is usually expressed in joules (J) or kilojoules (kJ).

Here is a portion of the AP Chemistry Equations and Constants Sheet that includes information about the speed of light, wavelength, frequency, energy, and Planck's constant.

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

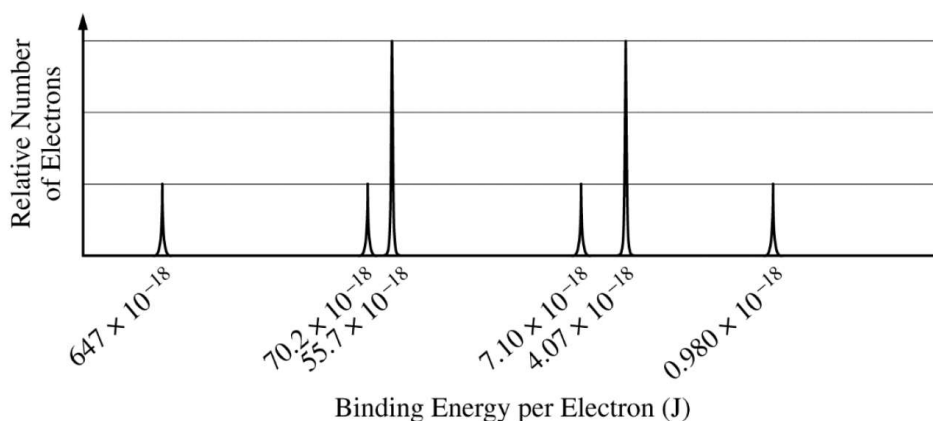
Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

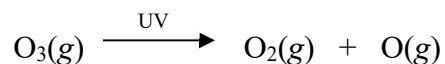
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

10. The complete photoelectron spectrum of an element in its ground state is represented below.



- (a) Write the ground state electron configuration, and elemental symbol of this element.
- (b) Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of this element.

11. In the upper atmosphere, ozone (O_3) molecules decompose as they absorb ultraviolet (UV) radiation, as shown by the equation below. Ozone serves to block harmful ultraviolet radiation that comes from the Sun.



A molecule of $\text{O}_3(\text{g})$ absorbs a photon with a frequency of $1.00 \times 10^{15} \text{ s}^{-1}$.

- (a) How much energy, in joules, does the $\text{O}_3(\text{g})$ molecule absorb per photon?

- (b) The minimum energy needed to break an oxygen-oxygen bond in ozone is 387 kJ mol^{-1} . Does a photon with a frequency of $1.00 \times 10^{15} \text{ s}^{-1}$ have enough energy to break this bond? Support your answer with a calculation.

12. The Cl–Cl bond has a bond energy of 242 kJ mol^{-1} .

- (a) Calculate the amount of energy, in joules, needed to break a single Cl–Cl bond.

- (b) Calculate the longest wavelength of light, in meters, that can supply the energy per photon necessary to break the Cl–Cl bond.

3.13 Beer–Lambert Law

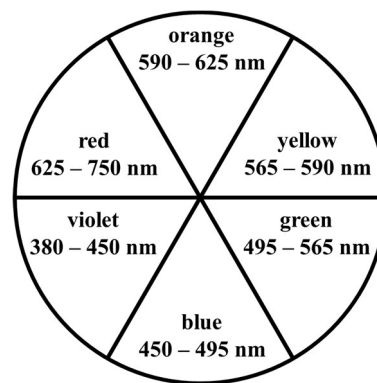
Essential knowledge statements from the AP Chemistry CED:

- The Beer–Lambert law relates the absorption of light by a solution to three variables according to the following equation: $A = \epsilon bc$
- The molar absorptivity ϵ describes how intensely a sample of molecules or ions absorbs light of a specific wavelength. The path length b and concentration c are proportional to the number of absorbing species.
- In most experiments the path length and wavelength of light are held constant. In such cases, the absorbance is proportional only to the concentration of absorbing molecules or ions.

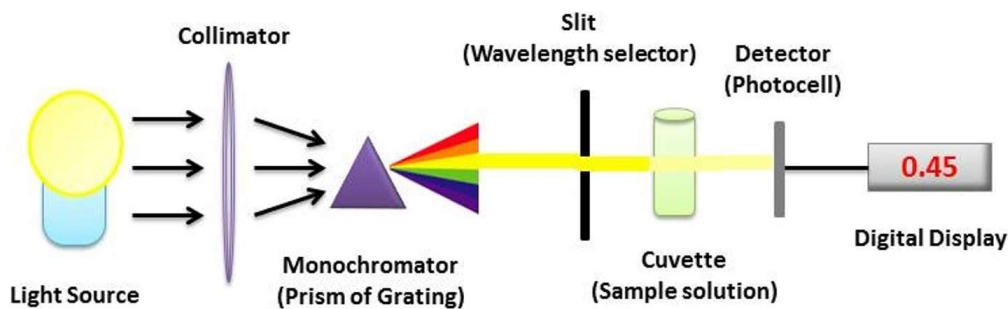
Instruments such as **spectrophotometers** or **colorimeters** are designed to measure the **absorbance** of a particular sample. When a substance absorbs light, electrons in the ground state become excited and move up to higher energy levels. For many transition metal ions, electrons absorb photons of light in the visible portion of the electromagnetic spectrum. That is why many transition metal ions appear colored. The table below lists a few examples of transition metal cations and the colors associated with them in aqueous solution.

Co^{2+}	Cr^{3+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	MnO_4^-
red	orange	yellow	green	blue	pink-purple

The color wheel shown at right illustrates that the perceived color has a complementary relationship with the color of visible light that is absorbed. For example, $\text{Cu}^{2+}(aq)$ ions appear blue to our eyes because the solution has a strong absorbance in the orange portion of the visible spectrum (around 600 nm).



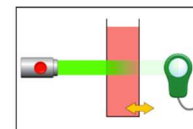
A spectrophotometer or colorimeter is an instrument that consists of a light source and a diffraction grating that separates the light into different wavelengths. The light passes through a **cuvette**, which is a small test tube or a square container used to hold the sample that is being analyzed. After the light passes through the sample, a detector measures how much light passes through the sample. Most spectrophotometers are designed to measure absorbance in the visible or the ultraviolet region of the electromagnetic spectrum.



Basic Instrumentation of a Spectrophotometer

You can explore the PhET simulation on the Beer-Lambert Law, also known as Beer's Law, by visiting the following website.

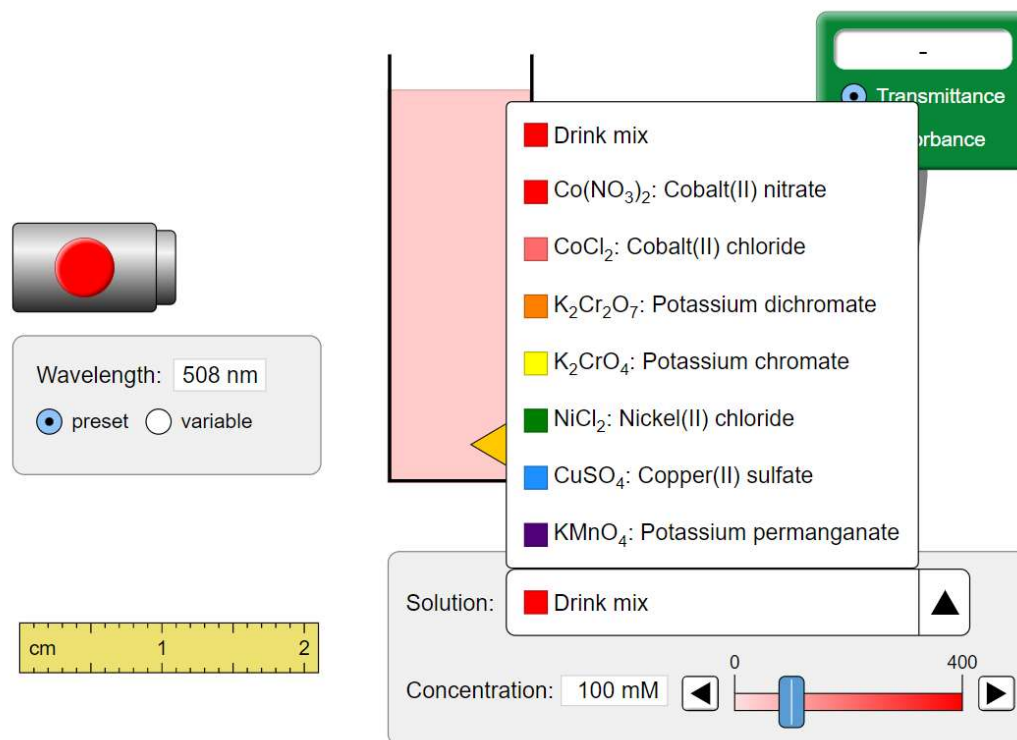
bit.ly/PhET_BeersLaw



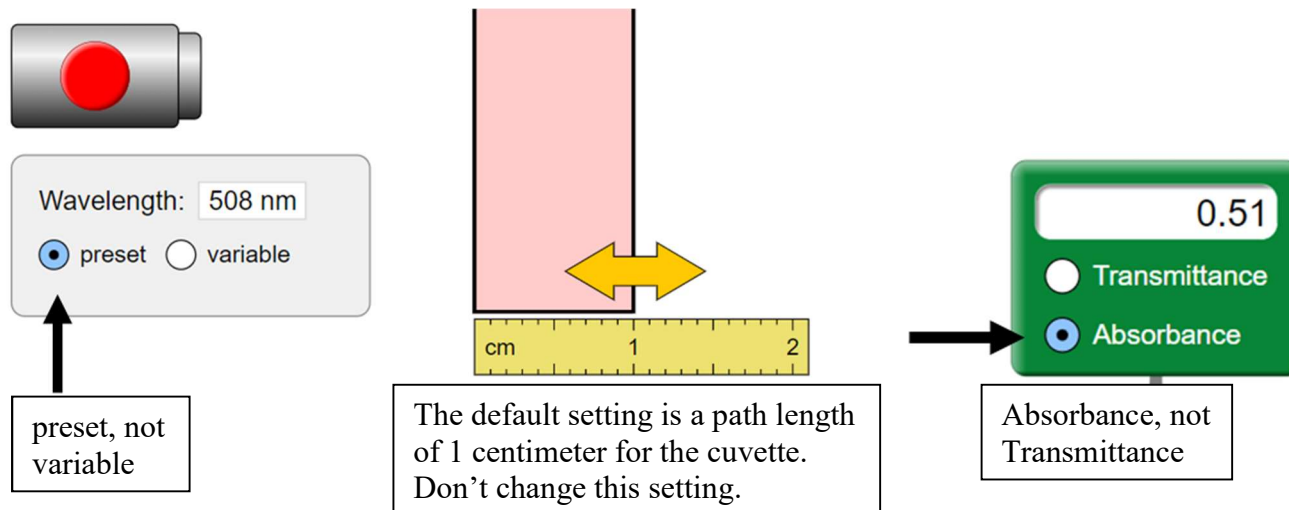
Beer's Law

Once the website loads, select the "Beer's Law" icon on the right side of the screen.

Use the menu to select one of eight different solutions to be analyzed.



Make sure that the following settings are selected.

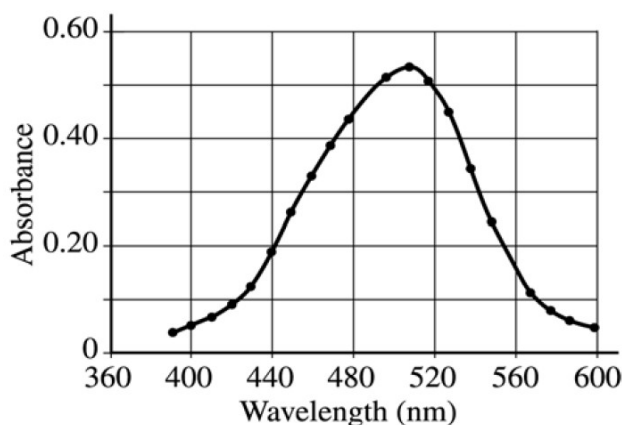
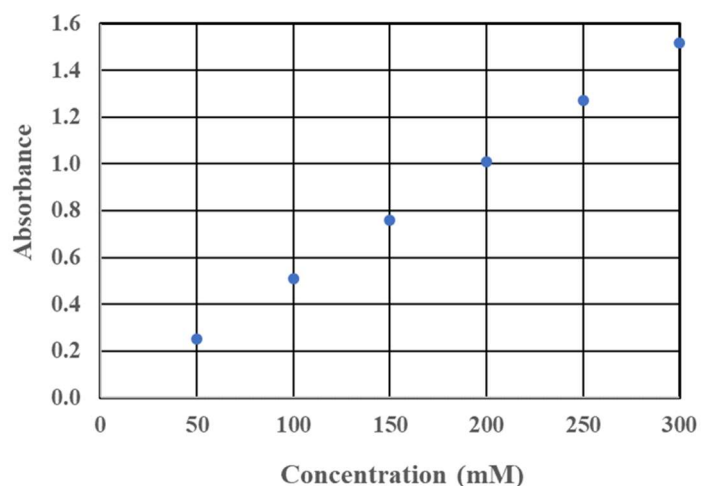


Once you have chosen one of the eight solutions to analyze, click the circle on the left side of the screen on the light source to turn on the beam of light. With the “preset” option, the wavelength of the light source has already been chosen. This should be the wavelength that will give the best results for that particular solution.

You can observe both the concentration of the solution at the bottom of the screen and the absorbance of the solution at the top right. You can use the slider at the bottom of the screen to adjust the concentration of the solution. As the concentration of the solution increases, the absorbance increases. The appearance of the solution in the cuvette should get darker as the concentration increases.

Data for concentration and absorbance for the “Drink mix” solution is shown below.

Concentration (mM)	Absorbance
50	0.25
100	0.51
150	0.76
200	1.01
250	1.27
300	1.52



A spectrophotometer can be used to scan the sample over a wide range of wavelength values. The instrument produces an **absorption spectrum** for that particular sample. In the spectrum shown above, the maximum value for absorbance is at a wavelength of approximately 500 nm.

When using a spectrophotometer to analyze a sample, it is important to set the instrument to a particular wavelength in which there is a relatively high absorbance value. Based on the absorbance spectrum shown above, any wavelength that is between 480 nm and 520 nm would be an appropriate setting for the instrument. On the other hand, it would not be appropriate to set the instrument at a wavelength of 400 nm or 600 nm, because the absorbance of that particular sample would be too low.

Before inserting a sample into the spectrophotometer, a blank sample is inserted to calibrate the instrument. If the sample to be analyzed is present in an aqueous solution, the blank sample usually consists of distilled water. The absorbance value for the blank sample is set to zero. When the samples are analyzed in the instrument, the absorbance values are compared to that of the blank sample. The cuvette should be filled with enough solution so that the beam of light passes entirely through the solution and not through empty air space.

A standard cuvette normally has a diameter (path length) of 1.0 cm. If it is a square container, it normally has two opaque or frosted sides and two transparent sides. The light passes through the transparent sides of the cuvette. Cuvettes are normally wiped with a lint-free tissue to remove any moisture or fingerprints before they are placed in the instrument. Cuvettes are handled with care in order to avoid getting scratches on them. If you are not wearing gloves, you normally hold a cuvette with your fingers touching the opaque sides only.

Any smudges, dirt, or fingerprints on the transparent sides of the cuvette will scatter or block the light, preventing it from reaching the detector. This will result in measured value for absorbance that will be too high.

The equation known as Beer's Law is written as follows: $A = \epsilon bc$

A = absorbance, which has no units

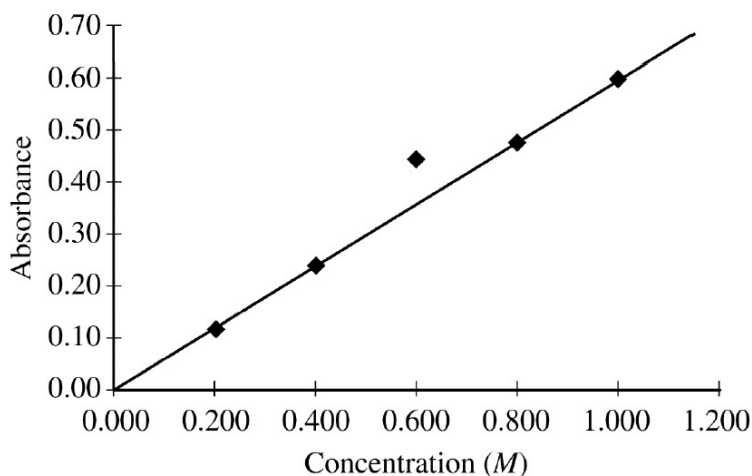
ϵ = molar absorptivity constant, which describes how intensely a sample absorbs light of a specific wavelength. This constant has units of $M^{-1} \text{ cm}^{-1}$

b = path length, which has units of cm. The standard path length is 1.00 cm.

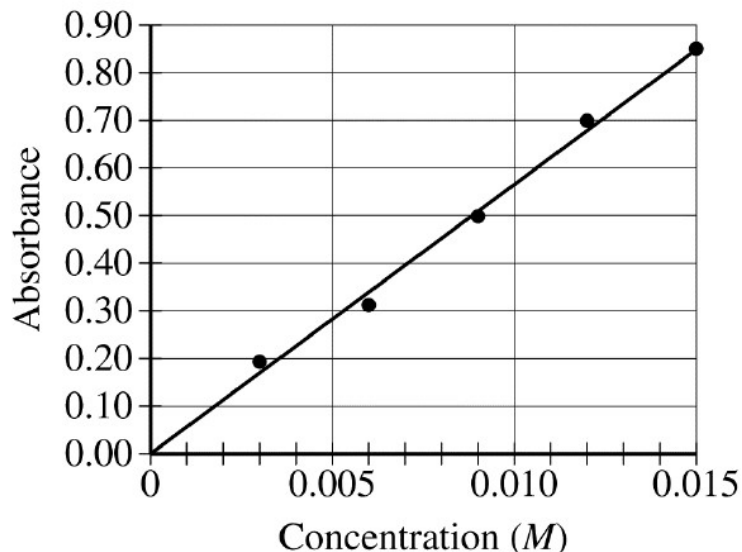
c = concentration, which has units of M (mol/L)

There is a direct relationship between absorbance and concentration. The greater the concentration of the solute being analyzed, the greater the absorbance of that substance.

13. A student uses a spectrophotometer to analyze a solution of blue dye. The student first rinses a cuvette with distilled water. Then the student adds the blue dye solution to the cuvette, forgetting to rinse the cuvette with the blue dye solution first. The student places the cuvette in the spectrophotometer and measures the absorbance of the solution. Assuming that some distilled water droplets were still in the cuvette when the blue dye solution was added to it, how would the measured absorbance be affected?
- (A) The measured absorbance would be too low, because the distilled water left in the cuvette would dilute the solution slightly.
 - (B) The measured absorbance would be too low, because distilled water would change the optimum wavelength of absorbance.
 - (C) The measured absorbance would be too high, because the distilled water would allow more light to pass through the cuvette.
 - (D) The measured absorbance would be too high, because the distilled water would also absorb some light.



14. A student prepared five solutions of CuSO_4 with different concentrations, and then filled five cuvettes, each containing one of the solutions. The cuvettes were placed in a spectrophotometer set to the appropriate wavelength for maximum absorbance. The absorbance of each solution was measured and recorded. The student plotted absorbance versus concentration, as shown in the figure above. Which of the following is the most likely explanation for the variance of the data point for the 0.600 M CuSO_4 solution?
- (A) The cuvette into which the 0.600 M solution was placed had some water droplets inside.
 - (B) The cuvette into which the 0.600 M solution was placed was filled slightly more than the other cuvettes.
 - (C) The wavelength setting was accidentally moved away from that of maximum absorbance.
 - (D) The cuvette used for the 0.600 M solution had not been wiped clean before being put in the spectrophotometer.



15. An ore containing cobalt (Co) and some inert materials is analyzed in a laboratory. A spectrophotometer is used to determine the mass percent of cobalt present in the ore sample. Solutions of known concentration of $\text{Co}^{2+}(aq)$ are prepared, and the absorbance of each solution is measured at the wavelength of optimum absorbance. The data are used to create a calibration plot, which is shown above.

A sample of the ore with a mass of 0.630 g is completely dissolved in concentrated $\text{HNO}_3(aq)$. The mixture is diluted with water to a final volume of 50.00 mL. Assume that all of the $\text{Co}(s)$ present in the ore sample is converted into $\text{Co}^{2+}(aq)$ ions. The absorbance of a sample of this solution is measured as 0.74.

- (a) Use the graph to estimate the concentration of $\text{Co}^{2+}(aq)$ in this solution.
- (b) Based on your answer to part (a), calculate the number of moles of $\text{Co}^{2+}(aq)$ in the 50.00 mL sample of solution.
- (c) Calculate the mass percent of Co in the 0.630 g sample of the ore.