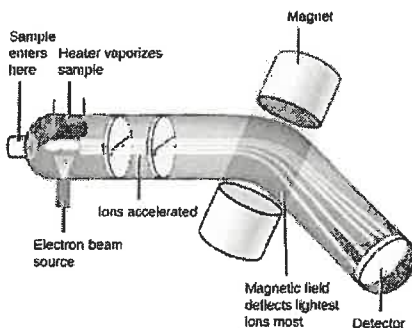


Key

## Mass Spectroscopy

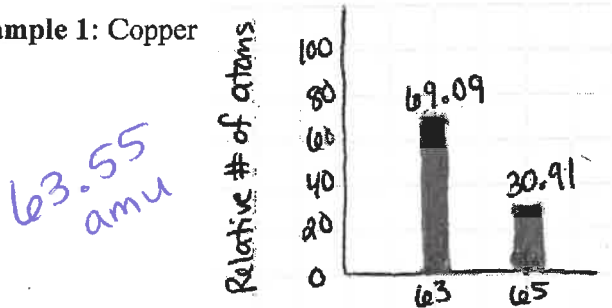
**Objectives:** Explain the quantitative relationship between the mass spectrum of an element and the masses of the element's isotopes.



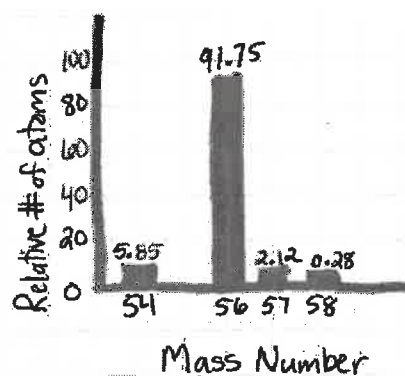
- **How a mass spectrometer works:**
  - Atoms or molecules are passed into a beam of high-speed electrons, which knock electrons off the atoms or molecules and change them into positive ions.
  - An electric field accelerates these ions into a magnetic field. Because an accelerating ion produces its own magnetic field, an interaction with the applied field occurs, which change the path of the ion.
  - The amount of path deflection for each ion depends on its mass.
  - The more massive the ion, the less it is deflected. The ions separate and a comparison of the positions where the ions hit the detector plate gives very accurate values of their relative masses.

Use the data on the following mass spectrums to estimate the average atomic mass of the element and compare it to the value given on the periodic table.

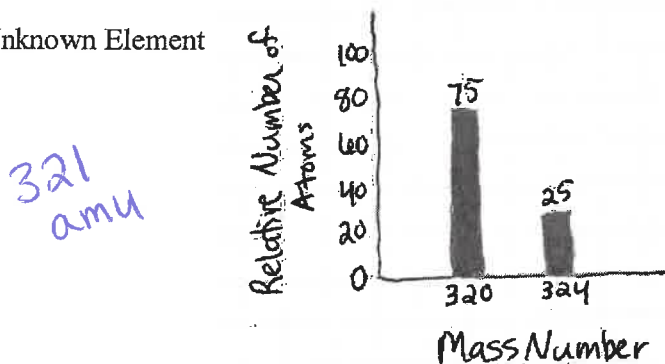
Example 1: Copper

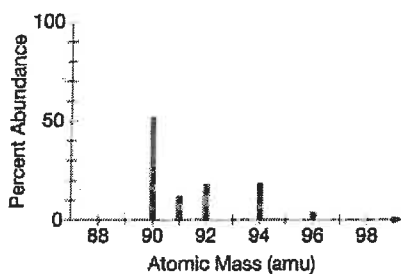


Example 2: Iron



Example 3: Unknown Element





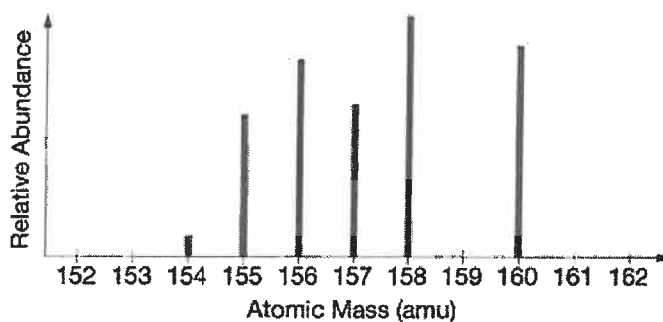
4. The mass spectrum for an unknown element is shown above. According to the information in the spectrum, the atomic mass of the unknown element is closest to

A. 90 amu

B. 91 amu

C. 93 amu

D. 94 amu



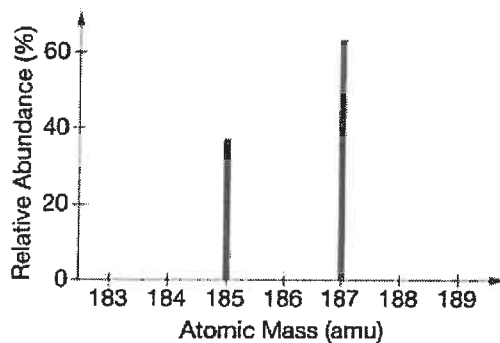
5. The mass spectrum represented above is most consistent with which of the following elements?

A. Eu

B. Gd

C. Tb

D. Dy



6. Based on the mass spectrum of a pure element represented above, the average atomic mass of the element is closest to which of the following?

A. 185.7 amu

B. 186.0 amu

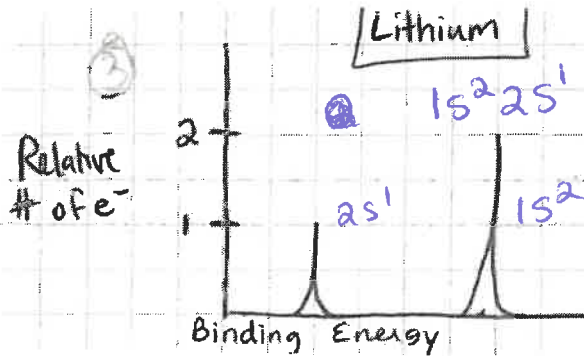
C. 186.3 amu

D. 186.9 amu

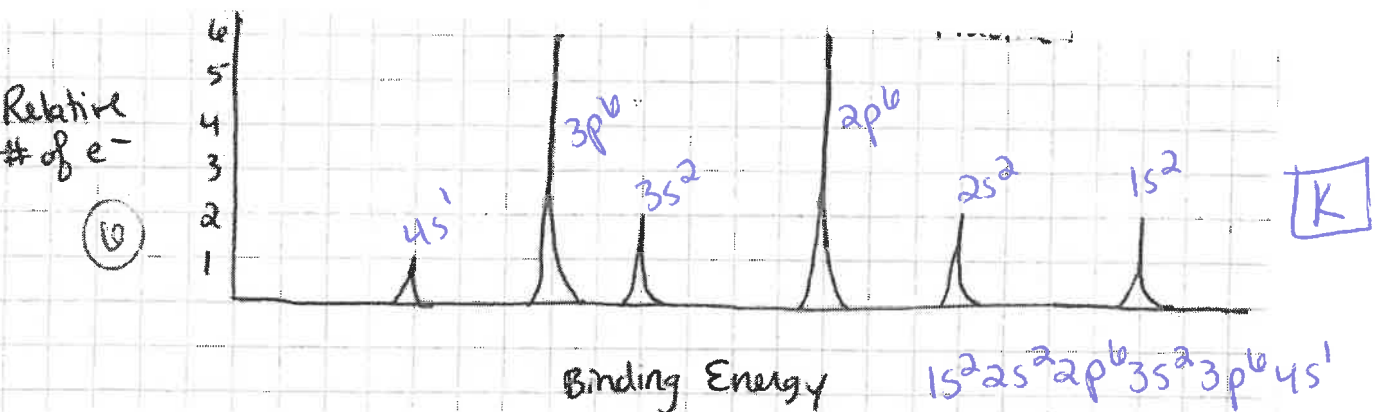
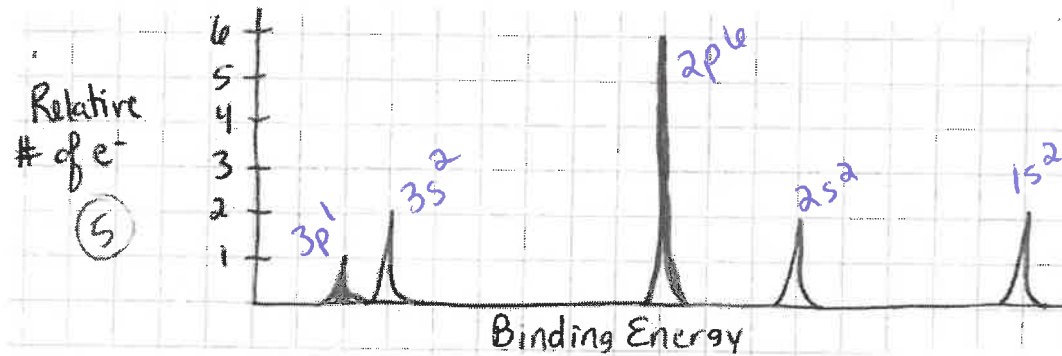
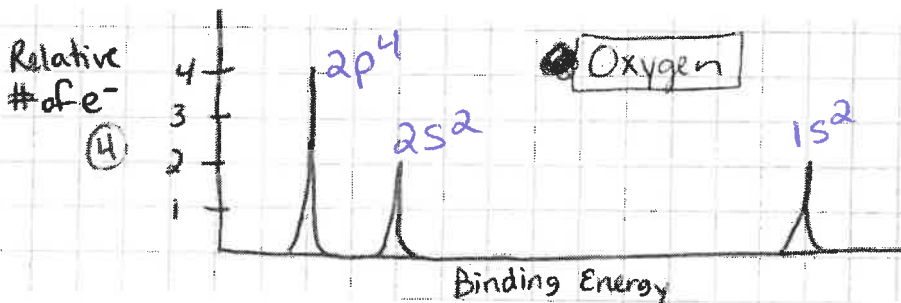
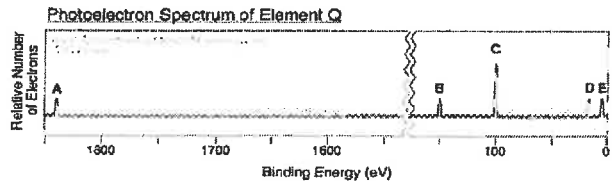
## Photoelectron Spectroscopy

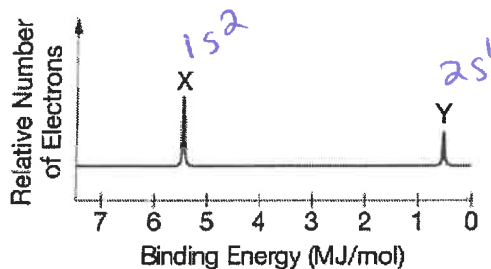
**Objectives:** Be able to explain the relationship between the PES of an atom or ion and: a) the electron configuration of the species and b) the interactions between the electrons and the nucleus.

- The energies of the electrons in a given shell can be measured experimentally with photoelectron spectroscopy (PES).
- The position of each peak in the PES spectrum is related to the energy required to remove an electron from the corresponding subshell, and the height of each peak is (ideally) proportional to the number of electrons in that subshell.



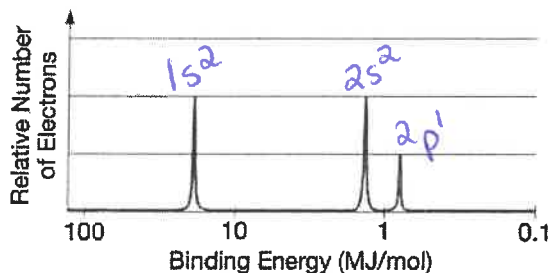
- 1) What is the electron configuration for the element whose photoelectron spectrum is shown below?
- 2) Explain why peak A corresponds to such a high "binding energy".





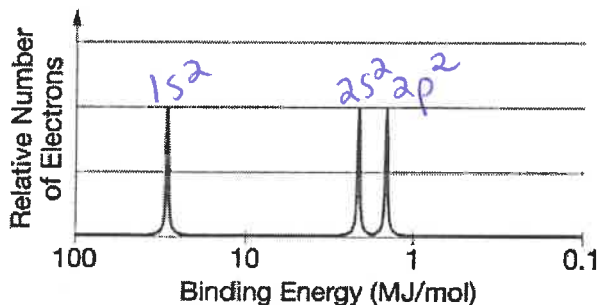
7. The complete photoelectron spectrum of an element is given above. Which labeled peak corresponds to the 1s electrons and why?

- A. Peak X, because 1s electrons are the easiest to remove from the atom.  
 B. Peak X, because 1s electrons have the strongest attractions to the nucleus.  
 C. Peak Y, because electrons in the 1s sublevel are the farthest from the nucleus.  
 D. Peak Y, because there are fewer electrons in an s sublevel than in a p sublevel.



8. The photoelectron spectrum for the element boron is represented above. Which of the following best explains how the spectrum is consistent with the electron shell model of the atom?

- A. The spectrum shows an odd number electrons.  
 B. The spectrum shows a single electron in the 2p subshell.  
 C. The spectrum shows equal numbers of electrons in the first and second electron shells.  
 D. The spectrum shows three electrons with the same binding energy in the second electron shell.



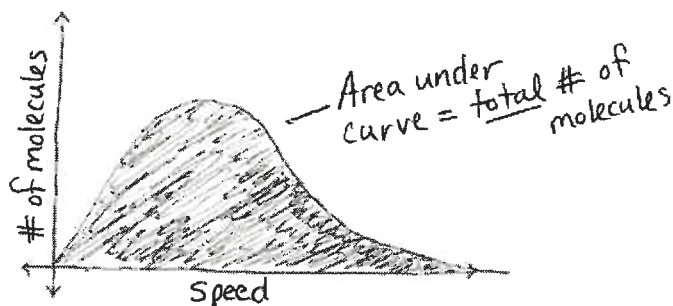
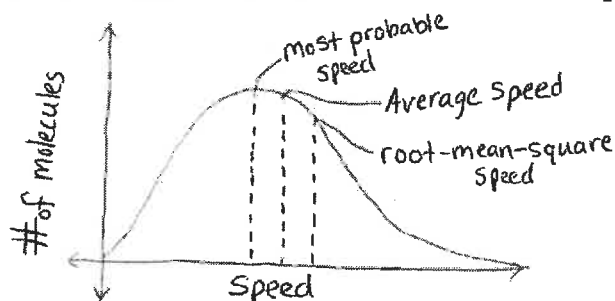
9. The complete photoelectron spectrum of the element carbon is represented above. Which of the following best explains how the spectrum is consistent with the electron shell model of the atom?

- A. The spectrum shows four electrons in the inner electron shell.  
 B. The spectrum shows equal numbers of electrons in the three occupied electron subshells.  
 C. The spectrum shows that all the electrons in the valence shell have the same binding energy.  
 D. The spectrum shows more electrons in the inner electron shell than in the outer electron shell.

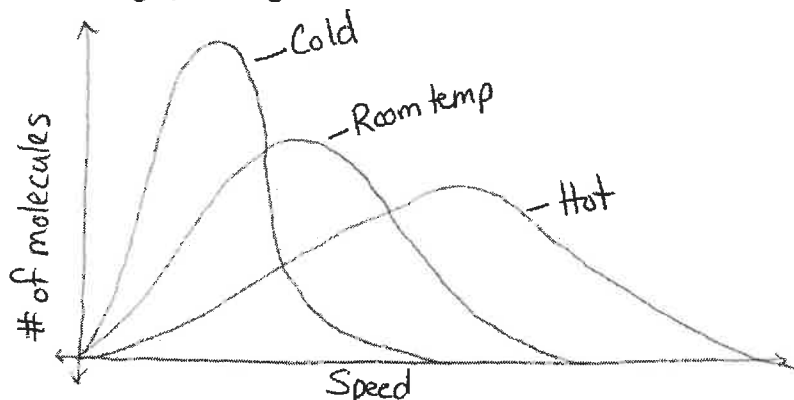
## Maxwell-Boltzmann distribution

**Explanation:** Not all gas particles move at the same speed. So instead of focusing on one gas molecule, we look at the distribution of speeds in a gas at a certain temperature.

**Maxwell-Boltzmann distribution:** shows how the speeds of molecules are distributed for an ideal gas.

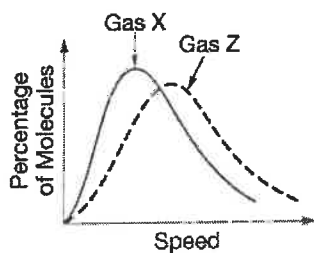


- The y-axis is the number of molecules per unit speed. So if the graph is higher in a region, it means there are more gas molecules moving with those speeds.
- The graph is not symmetrical. There is a longer "tail" on the high speed right end of the graph. It continues to the right longer because molecules can move at very high speeds (although it's short so few molecules are doing that).
- The left end of the graph must end at zero because that is the slowest a molecule can move.
- **Most probable speed** – is located at the highest peak (that is the speed that the most molecules have).
- **Average speed** – is located slightly to the right of the peak. That is due to the fact that the graph is not symmetrical and there is a longer "tail" on the right side. It shifts the average.
- **Root-mean-square speed** – The square root of the mean of the squares of the velocities.
- **The area under the graph = the total number of molecules.**
- **If heated**, the peak will shift to the right (because the average speed of the molecules will increase). As it shifts to the right, the height has to decrease in order to maintain the same total area under the curve.



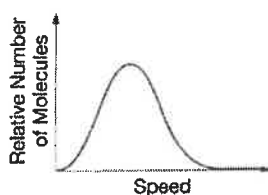
**Practice:** What happens to the following quantities as the gas cools? (Select 2 correct statements.)

- The peak height of the graph of number of molecules vs. speed gets shorter.
- The average molecular speed of the gas decreases.
- The graph of number of molecules vs. speed becomes more narrow.
- The root-mean-square molecular speed of the gas increases.

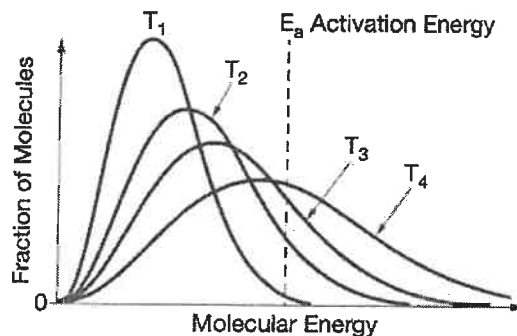
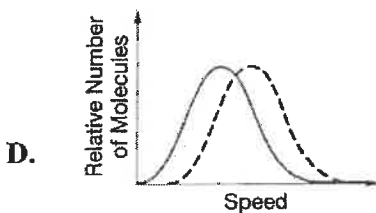
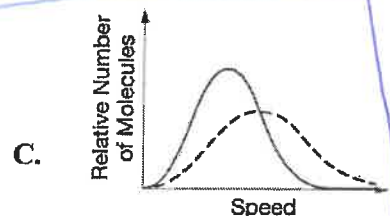
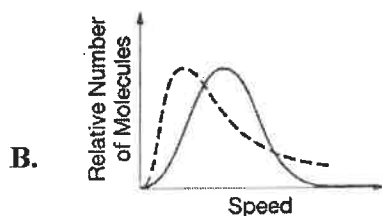
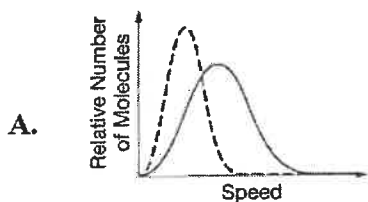


1. The two gas samples represented in the graph above are at the same temperature. Which of the following statements about the gases is correct?

- a. The molecules of gas Z have a higher average kinetic energy than the molecules of gas X.
- b. There are fewer molecules in the sample of gas Z than in the sample of gas X.
- c. Gas Z has a smaller molar mass than gas X.
- d. Gas Z has a greater molar mass than gas X.



2. The diagram above shows the distribution of speeds for a sample of  $O_2(g)$ . Which of the following graphs shows the distribution of speeds for the same sample at a higher temperature (dashed line)?



3. The diagram above shows the distribution of molecular energies for equimolar samples of a reactant at different temperatures. Based on the diagram, at which temperature will the reactant be consumed at the fastest rate, and why?

- a. At  $T_1$ , because a larger fraction of the molecules have about the same energy.
- b. At  $T_1$ , because at this temperature most of the molecules undergo collisions frequently.
- c. At  $T_1$ , because at this temperature the rate of consumption for about half of the molecules is determined by their orientation.
- d. At  $T_4$ , because a larger fraction of the molecules have an energy that is equal to or greater than the activation energy.

## Beer's Law

Watch Bozeman's video on light and matter, from 5:30 – 7 minute mark.

Also – experiment with the PHET simulation about Beer's law.

**Explanation:** Beer's Law states that the absorbance of light at a certain wavelength is directly proportional to the concentration of a solution. The more concentrated a solution is, the more the molecules will absorb the light and the less light will be transmitted through the substance. The concentration can be found by using this formula:  $A = \epsilon bc$

A is absorbance (no units).

$\epsilon$  is molar absorptivity ( $L \text{ mol}^{-1} \text{ cm}^{-1}$ ).

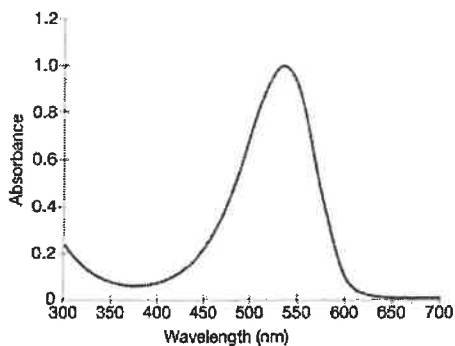
b is the path length of the sample.

c is the concentration of the solution (mol/L)

**Example 1:** A solution with a concentration of 0.14 M is measured to have an absorbance of 0.43. Another solution of the same chemical is measured under the same conditions and has an absorbance of 0.37. What is the concentration of the second solution? (Answer 0.12 M)

$$\frac{0.14 \text{ M}}{0.43} = \frac{x}{0.37}$$

$$x = 0.12 \text{ M}$$



**Example 2:** The absorption spectrum of a certain red dye is shown above. If a student analyzing the same concentration of this dye neglected to wipe fingerprints off the cuvette before placing it in the spectrophotometer, how would the absorption curve be affected?

A

- The peak of the curve would be higher because more light would be absorbed.
- The peak of curve would be lower because less light would be absorbed.
- The peak of the curve would be shifted to the left because less light would be absorbed.
- The peak of the curve would be shifted to the right because more light would be absorbed.

**Example 3:** A student measures the absorbance of a solution containing  $\text{FeSCN}^{2+}$  ion using a spectrophotometer. The cuvette used by the student has two frosted walls and two transparent walls. The student properly orients the cuvette so that the path of the light goes through the transparent sides of the cuvette when calibrating the spectrophotometer. How will the measured absorbance of the  $\text{FeSCN}^{2+}$  be affected if the student incorrectly orients the cuvette so that the path of the light is through the frosted sides of the cuvette?

- B
- a. The measured absorbance of the  $\text{FeSCN}^{2+}$  solution will not be affected.
  - b. The measured absorbance of the  $\text{FeSCN}^{2+}$  solution will be higher than the actual absorbance.
  - c. The measured absorbance of the  $\text{FeSCN}^{2+}$  solution will be lower than the actual absorbance.
  - d. The effect on the measured absorbance of the  $\text{FeSCN}^{2+}$  solution depends on the concentration of the  $\text{FeSCN}^{2+}$  solution.

**Example 4:** A student uses a spectrophotometer to analyze a solution of blue food 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, how would the measured absorbance be affected?

- A
- a. The measured absorbance would be too low, because the distilled water left in the cuvette would slightly dilute the solution.
  - b. The measured absorbance would be too low, because the distilled water would change the optimum wavelength of absorbance.
  - c. The measured absorbance would be too high, because the 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.

- More water means less concentrated.

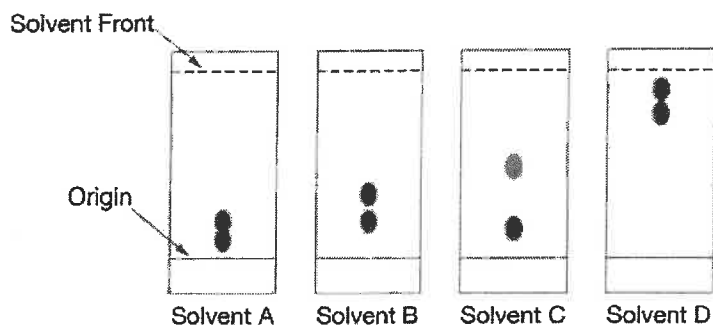
$$A = \epsilon bc$$

A and c are directly related. So  $\downarrow$  conc. means  $\downarrow$  absorbance.



## Chromatography

**Chromatography** – the general name for a series of methods for separating mixtures by using a system with a mobile phase and a stationary phase. The stationary phase is a solid and the mobile phase is either a liquid or a gas. The separation process occurs because components of the mixture have different affinities for the two phases and thus move through the system at different rates. A component with a high affinity for the mobile phase moves more slowly.

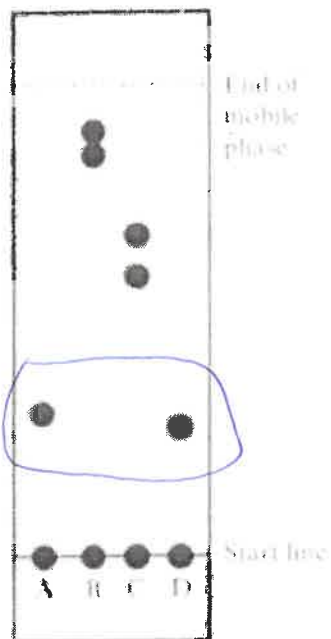


1. The diagram above shows thin-layer chromatograms of the same mixture of two compounds. Based on the chromatograms, which solvent would be most effective at separating the two compounds if the same stationary phase is used for column chromatography?
- a. Solvent A      b. Solvent B      **c. Solvent C**      d. Solvent D

Four different kinds of inks are placed on chromatography paper, and a solvent is introduced and allowed to move up the paper.

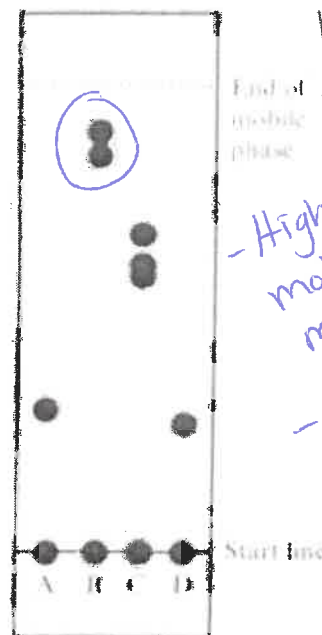
2. From the diagram below, which two inks are likely to contain molecules that have the most similar molecular structures?

- a. A and D**  
 b. B and D  
 c. B and C  
 d. A and C



3. From the diagram below, which ink contains a component likely to have a molecular structure most similar to that of the solvent?

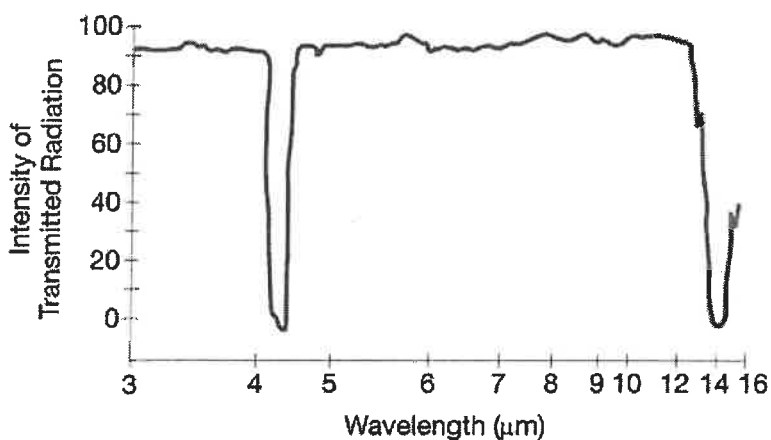
- a. A  
**b. B**  
 c. C  
 d. D



*- High affinity for mobile phase (solvent) moves quickly.  
 - High affinity for solid phase moves slowly.*

## Infrared Spectroscopy

**Infrared spectroscopy (IR spectroscopy)** - is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.



1. The infrared spectrum above represents the absorption of certain wavelengths of radiation by molecules of CO<sub>2</sub>. Which of the following best explains what occurs at the molecular level as the CO<sub>2</sub> molecules absorb photons of the infrared radiation?

- i. The atoms in the CO<sub>2</sub> molecules increase their vibration as the bonds between the atoms bend and stretch.
- ii. The molecules of CO<sub>2</sub> increase the energy of their rotational motions.
- iii. The electrons in the valence shells of the atoms in the CO<sub>2</sub> molecules are promoted to higher electronic energy levels.
- iv. The bonds between the atoms in the CO<sub>2</sub> molecules are continuously broken and then reform.