A. The Absorption of Light

When a substance absorbs light, an electron undergoes a transition from the lowest energy level to a higher energy level. The energy gap between these levels is given by Einstein's equation $E = h\nu$. Consequently, only one frequency ν causes this transition. More often than not, a chemist refers to the wavelength of light (λ) rather than to its frequency. Einstein's equation then becomes $E = hc/\lambda$, where c is the velocity of light.

Transmittance and absorbance

When light of the correct wavelength shines through a solution of a substance that absorbs light, the intensity of the light diminishes as it passes through the solution because absorption occurs. If the intensities of the light that enter and emerge from the solution are represented by I_o and I, respectively, *transmittance* (T) is defined as the ratio

$$T = I/I_o$$

A related quantity called the *absorbance* (A) is defined as the negative logarithm of the transmittance.

$$A = -\log_{10} T = -\log_{10}(I/I_o)$$

Spectrophotometers

Absorbance is measured with an instrument called a spectrophotometer. This instrument separates light into its component wavelengths and selectively measures the intensity of the light of a given wavelength after it passes through a solution. All spectrophotometers, regardless of the manufacturer, have certain common fundamental parts. These parts include a source of radiant energy, a prism or grating to isolate the light of a particular wavelength, a device for holding the sample, and a photoelectric cell for measuring the intensity of the light. Your laboratory instructor will explain the operation of the spectrophotometers in your laboratory.

If your spectrophotometer is a Spectronic 20 with a meter, a commonly used instrument in general chemistry laboratories, a word of advice is offered here. The meter on this spectrophotometer is calibrated linearly in percent transmittance (100 T) and logarithmically in absorbance. You will always want to obtain three significant figures in your measurements of absorbance. However, if the absorbance is relatively large, doing so will be difficult on this meter because of the logarithmic scale. Percent transmittance can always be read with high precision, however, if it is above 10%. If you cannot measure an absorbance with three significant figures, measure the percent transmittance with this precision, convert to transmittance by dividing by 100, and calculate the absorbance by taking the negative logarithm of the transmittance.

Beer's law

Beer's law states that the absorbance is directly related to the concentration (c) of the substance that absorbs light, or

$$A = kc$$

where k is a constant. Because A is a dimensionless number $[A = -\log_{10}(I/I_o)]$ and the unit of measurement for c is mol/L (M), it follows that the unit of measurement for k is L/mol (M^{-1}). This constant is a constant for a given substance at a particular wavelength. Its value may be zero if no light is absorbed at a particular wavelength, or it may be as high as $10^4\ M^{-1}$.

An absorption spectrum

Suppose the absorbance of a colored substance in a colorless liquid is measured at each of a series of wavelengths. Some typical results are given in Table A.1, where the absorbance was measured at intervals of 25 nm between 300 nm and 575 nm. These absorbances are plotted against the wavelengths in Figure A.1. After the data are plotted, the points are connected by a *smooth* curve. This curve, which represents the best estimate of the absorbance anywhere between 300 nm and 575 nm, is called an *absorption spectrum*.

Table A.1 Absorbances Obtained at Various Wavelengths for a Solution of a Hypothetical Substance (c = 0.0120 M)

λ (nm)	A	λ (nm)	A
300	0.002	450	0.558
325	0.016	475	0.281
350	0.144	500	0.092
375	0.341	525	0.031
400	0.578	550	0.004
425	0.681	575	0.001

Because the concentration of the substance is fixed in this experiment, the change in the absorbance that is shown in Figure A.1 indicates the manner in which k from Beer's law is dependent on the wavelength. The value of the constant reaches a maximum at 425 nm, where the absorption spectrum for this substance reaches a maximum.

The determination of k

The equation for Beer's law, $A = kc$, has the same form as the equation for a straight line, $y = mx + b$. A comparison of these equations indicates that

$$y = A$$

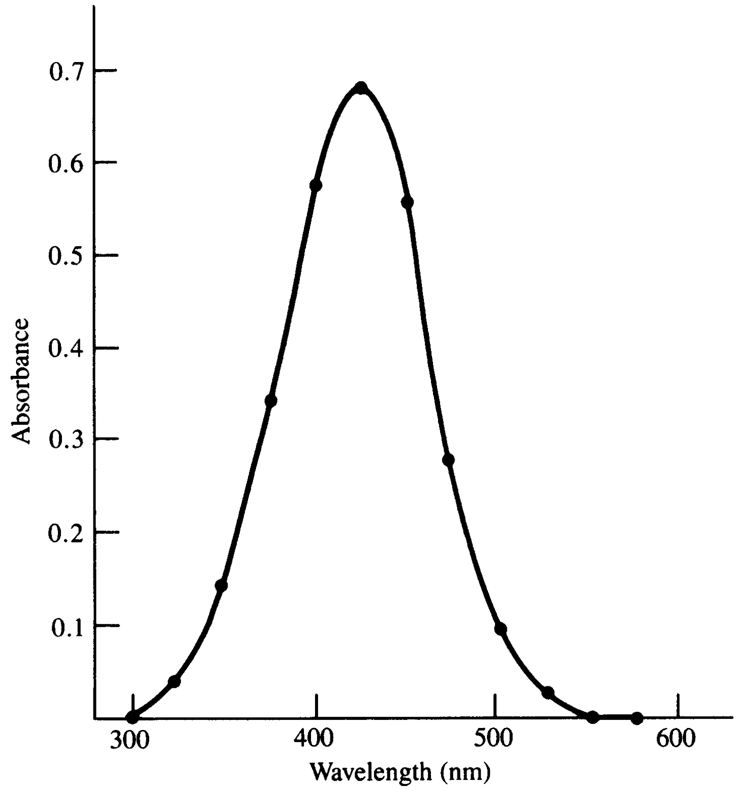
$$x = c$$

$$m = \text{slope} = k$$

$$b = \text{intercept on } y \text{ axis} = 0$$

Consequently, you should obtain a straight line when you plot the absorbances obtained at various concentrations against those concentrations. Moreover, the slope of that line will be given by k, and the line must pass through the origin ($A = 0$, $c = 0$), because the intercept is zero.

FIGURE A.1
A typical absorption spectrum. The experimental data plotted here are given in Table A.1.



Let's use the data in Table A.2 as an example. You may assume that the hypothetical substance whose absorption spectrum is shown in Figure A.1 was used again to obtain these data. Figure A.2 shows a graph in which the absorbances in Table A.2 are plotted against the concentrations. A straight line passing through the origin was drawn in an attempt to provide the best fit for all the data. Experimental error is the reason why some of the points deviate from that line.

Table A.2 Absorbances Obtained at Various Concentrations at 425 nm

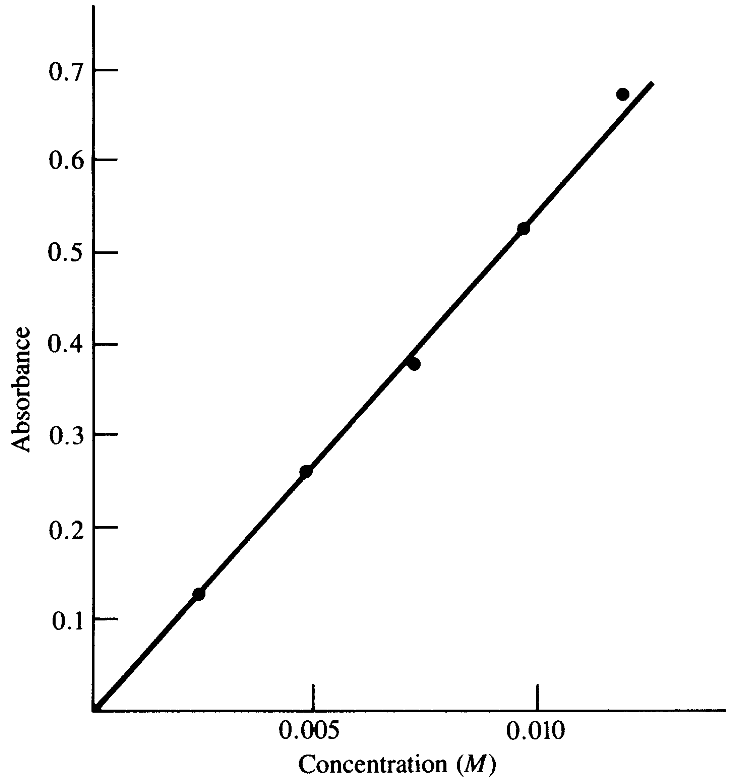
c **(*M*)**	***A***
0.0120	0.681
0.00960	0.540
0.00720	0.389
0.00480	0.270
0.00240	0.133

Any arbitrary point on the line will provide enough information for us to calculate the slope k. For example, we will choose a point with $c = 0.0100\ M$ and $A = 0.557$. The slope is given by

$$k = \frac{A}{c} = \frac{0.557}{0.0100\ M} = 55.7\ M^{-1}$$

FIGURE A.2

An example of Beer's law, $A = kc$. The slope of the straight line is given by k. The data were taken from Table A.2.



Linear regression—A better way

How do we know whether Figure A.2 shows the best straight line? If five different people used their eyes to draw what they considered to be the best straight line, five slightly different straight lines with five slightly different slopes would undoubtedly result. Clearly, visual fitting of data to a straight line is not entirely satisfactory.

Fortunately, linear regression analysis (also called *the method of least squares*) provides the means to find an entirely reproducible straight line. If five people treat the data in Table A.2 by this method, the result will be the same straight line.

To begin, we know that the best straight line must pass through the origin. Although this constraint is not necessary, it simplifies the arithmetic and lessens the tedium of the calculations. The equation for this line will be $y = mx$, and the slope m will be given by

$$m = \frac{\Sigma\, xy}{\Sigma\, x^2}$$

The quantity Σxy in the numerator is the sum of the products of each x and y, and Σx^2 in the denominator is the sum of the squares of each x. In terms of the equation for Beer's law, k becomes

$$k = \frac{\Sigma\, cA}{\Sigma\, c^2}$$

The data in Table A.2 are subjected to linear regression analysis in Table A.3. Note that k obtained in this manner differs slightly from the one derived from a visually fitted straight line. As a result, the best procedure is to use linear regression to calculate the slope and then to draw a straight line with that slope.

Table A.3 An Analysis by Linear Regression

c (M)	A	cA (M)	c^2 (M^2)
0.0120	0.681	0.0081720	0.0001440
0.00960	0.540	0.0051840	0.0000922
0.00720	0.389	0.0028008	0.0000518
0.00480	0.270	0.0012960	0.0000230
0.00240	0.133	0.0003192	0.0000058
		Sum = 0.0177720	Sum = 0.0003168

$$k = \frac{\Sigma\, cA}{\Sigma\, c^2} = \frac{0.0177720\ M}{0.0003168\ M^2} = 56.1\ M^{-1}$$

You can obtain an identical result using a computer and the Internet. The Internet site is at

http://www.hmco.com/college