As is often the case, the formulation of a law is more complicated than its name suggests. This is the case, for example, with Beer's law, which also is known as the Beer-Lambert law or the Beer-Lambert-Bouguer law. Pierre Bouguer, in 1729, and Johann Lambert, in 1760, noted that the transmittance of light decreases exponentially with an increase in the sample's thickness.

$$T \propto e^{-b}$$

Later, in 1852, August Beer noted that the transmittance of light decreases exponentially as the concentration of the absorbing species increases.

$$T \propto e^{-C}$$

Together, and when written in terms of absorbance instead of transmittance, these two relationships make up what we know as Beer's law.

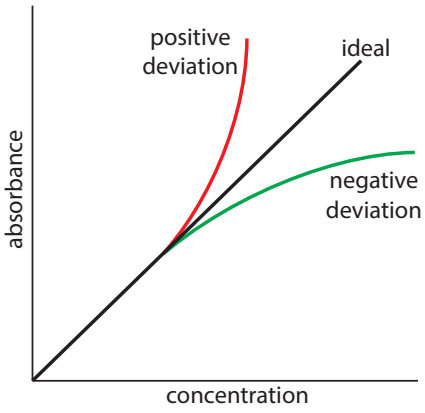

Figure 10.23 Plots of absorbance vs. concentration showing **positive** and **negative** deviations from the **ideal** Beer's law relationship, which is a straight line.

Equation 10.4 and equation 10.5, which establish the linear relationship between absorbance and concentration, are known as BEER'S LAW. Calibration curves based on Beer's law are common in quantitative analyses.

10B.4 Beer's Law and Multicomponent Samples

We can extend Beer's law to a sample that contains several absorbing components. If there are no interactions between the components, then the individual absorbances, A_i, are additive. For a two-component mixture of analyte's X and Y, the total absorbance, A_{tot}, is

$$A_{tot} = A_X + A_Y = \varepsilon_X b C_X + \varepsilon_Y b C_Y$$

Generalizing, the absorbance for a mixture of n components, A_{mix}, is

$$A_{mix} = \sum_{i=1}^{n} A_i = \sum_{i=1}^{n} \varepsilon_i b C_i \qquad 10.6$$

10B.5 Limitations to Beer's Law

Beer's law suggests that a plot of absorbance vs. concentration—we will call this a Beer's law plot—is a straight line with a y-intercept of zero and a slope of ab or εb. In some cases a Beer's law plot deviates from this ideal behavior (see Figure 10.23), and such deviations from linearity are divided into three categories: fundamental, chemical, and instrumental.

Fundamental Limitations to Beer's Law

Beer's law is a limiting law that is valid only for low concentrations of analyte. There are two contributions to this fundamental limitation to Beer's law. At higher concentrations the individual particles of analyte no longer are independent of each other. The resulting interaction between particles of analyte may change the analyte's absorptivity. A second contribution is that an analyte's absorptivity depends on the solution's refractive index. Because a solution's refractive index varies with the analyte's concentration, values of a and ε may change. For sufficiently low concentrations of analyte, the refractive index essentially is constant and a Beer's law plot is linear.

Chemical Limitations to Beer's Law

A chemical deviation from Beer's law may occur if the analyte is involved in an equilibrium reaction. Consider, for example, the weak acid, HA. To construct a Beer's law plot we prepare a series of standard solutions—each of which contains a known total concentration of HA—and then measure each solution's absorbance at the same wavelength. Because HA is a weak acid, it is in equilibrium with its conjugate weak base, A^-.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

If both HA and A^- absorb at the selected wavelength, then Beer's law is

$$A = \varepsilon_{HA} b C_{HA} + \varepsilon_{A^-} b C_{A^-} \quad 10.7$$

Because the weak acid's total concentration, C_{total}, is

$$C_{total} = C_{HA} + C_{A^-}$$

we can write the concentrations of HA and A^- as

$$C_{HA} = \alpha_{HA} C_{total} \quad 10.8$$

$$C_{A^-} = (1 - \alpha_{HA}) C_{total} \quad 10.9$$

where α_{HA} is the fraction of weak acid present as HA. Substituting equation 10.8 and equation 10.9 into equation 10.7 and rearranging, gives

$$A = (\varepsilon_{HA}\alpha_{HA} + \varepsilon_{A^-} - \varepsilon_{A^-}\alpha_{A^-}) b C_{total} \quad 10.10$$

To obtain a linear Beer's law plot, we must satisfy one of two conditions. If ε_{HA} and ε_{A^-} have the same value at the selected wavelength, then equation 10.10 simplifies to

$$A = \varepsilon_{A^-} b C_{total} = \varepsilon_{HA} b C_{total}$$

Alternatively, if α_{HA} has the same value for all standard solutions, then each term within the parentheses of equation 10.10 is constant—which we replace with k—and a linear calibration curve is obtained at any wavelength.

$$A = k b C_{total}$$

Because HA is a weak acid, the value of α_{HA} varies with pH. To hold α_{HA} constant we buffer each standard solution to the same pH. Depending on the relative values of α_{HA} and α_A, the calibration curve has a positive or a negative deviation from Beer's law if we do not buffer the standards to the same pH.

For a monoprotic weak acid, the equation for α_{HA} is

$$\alpha_{HA} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

Problem 10.6 in the end of chapter problems asks you to explore this chemical limitation to Beer's law.

Instrumental Limitations to Beer's Law

There are two principal instrumental limitations to Beer's law. The first limitation is that Beer's law assumes that radiation reaching the sample is of a single wavelength—that is, it assumes a purely monochromatic source of radiation. As shown in Figure 10.10, even the best wavelength selector passes radiation with a small, but finite effective bandwidth. Polychromatic radiation always gives a negative deviation from Beer's law, but the effect is smaller if the value of ε essentially is constant over the wavelength range passed by the wavelength selector. For this reason, as shown in Figure 10.24, it is better to make absorbance measurements at the top of a broad absorption peak. In addition, the deviation from Beer's law is less serious if the source's effective bandwidth is less than one-tenth of the absorbing species' natural bandwidth.[5] When measurements must be made on a slope, linearity is improved by using a narrower effective bandwidth.

Problem 10.7 in the end of chapter problems ask you to explore the effect of polychromatic radiation on the linearity of Beer's law.

5 (a) Strong, F. C., III *Anal. Chem.* **1984**, *56*, 16A–34A; Gilbert, D. D. *J. Chem. Educ.* **1991**, *68*, A278–A281.

Another reason for measuring absorbance at the top of an absorbance peak is that it provides for a more sensitive analysis. Note that the **green** Beer's law plot in Figure 10.24 has a steeper slope—and, therefore, a greater sensitivity—than the **red** Beer's law plot. A Beer's law plot, of course, is equivalent to a calibration curve.

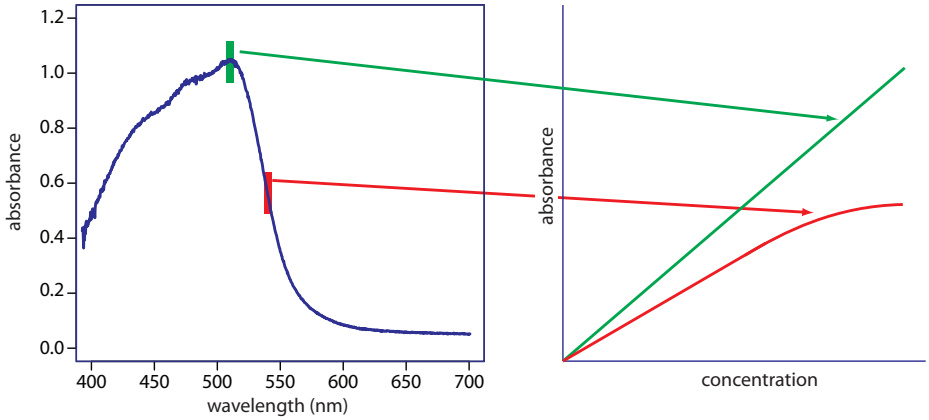

Figure 10.24 Effect of wavelength selection on the linearity of a Beer's law plot.

STRAY RADIATION is the second contribution to instrumental deviations from Beer's law. Stray radiation arises from imperfections in the wavelength selector that allow light to enter the instrument and to reach the detector without passing through the sample. Stray radiation adds an additional contribution, P_{stray}, to the radiant power that reaches the detector; thus

$$A = -\log \frac{P_T + P_{stray}}{P_0 + P_{stray}}$$

Problem 10.8 in the end of chapter problems ask you to explore the effect of stray radiation on the linearity of Beer's law.

For a small concentration of analyte, P_{stray} is significantly smaller than P_0 and P_T, and the absorbance is unaffected by the stray radiation. For higher concentrations of analyte, less light passes through the sample and P_T and P_{stray} become similar in magnitude. This results is an absorbance that is smaller than expected, and a negative deviation from Beer's law.

10C UV/Vis and IR Spectroscopy

In Figure 10.9 we examined Nessler's original method for matching the color of a sample to the color of a standard. Matching colors is a labor intensive process for the analyst and, not surprisingly, spectroscopic methods of analysis were slow to find favor. The 1930s and 1940s saw the introduction of photoelectric transducers for ultraviolet and visible radiation, and thermocouples for infrared radiation. As a result, modern instrumentation for absorption spectroscopy routinely became available in the 1940s—further progress has been rapid ever since.

10C.1 Instrumentation

Frequently an analyst must select from among several instruments of different design, the one instrument best suited for a particular analysis. In this section we examine several different instruments for molecular absorption spectroscopy, with an emphasis on their advantages and limitations. Methods of sample introduction also are covered in this section.

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