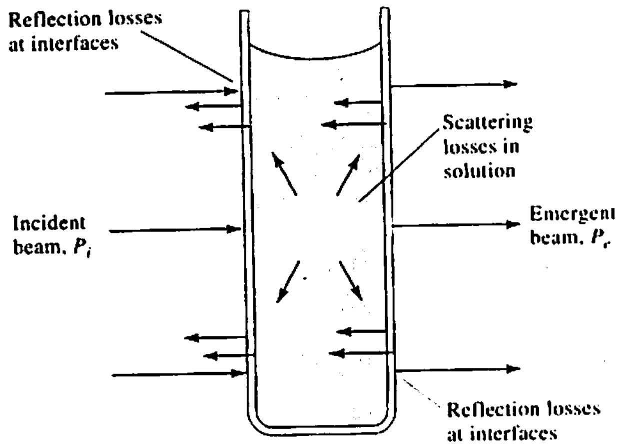

Figure 22-11
Reflection and scattering losses.

an identical cell containing only solvent. Experimental transmittances and absorbances that closely approximate the true transmittance and absorbance are then obtained with the equations

$$T = \frac{P_{solution}}{P_{solvent}} = \frac{P}{P_0} \qquad (22\text{-}10)$$

$$A = \log \frac{P_{solvent}}{P_{solution}} \approx \log \frac{P_0}{P} \qquad (22\text{-}11)$$

The terms P_0 and P, as used in the rest of this book, refer to the power of radiation after it has passed through cells containing the solvent and the analyte, respectively.

FEATURE 22-2
Derivation of Beer's Law

Beer's law can be derived as follows.[3] Consider the block of absorbing matter (solid, liquid, or gas) shown in Figure 22-12. A beam of parallel monochromatic radiation with power P_0 strikes the block perpendicular to a surface; after passing through a length b of the material, which contains n absorbing particles (atoms, ions, or molecules), its power is decreased to P as a result of absorption. Consider now a cross section of the block having an area S and an infinitesimal thickness dx. Within this section there are dn absorbing particles; associated with each particle, we can imagine a surface at which photon capture will occur. That is, if a photon reaches one of these areas by chance, absorption will follow immediately. The total projected area of these capture surfaces within the section is designated as dS; the

[3]The discussion that follows is based on a paper by F. C. Strong, *Anal. Chem.*, 1952, *24*, 338.

ratio of the capture area to the total area, then, is dS/S. On a statistical average, this ratio represents the probability for the capture of photons within the section.

The power of the beam entering the section P_x is proportional to the number of photons per square centimeter per second, and dP_x represents the quantity removed per second within the section; the fraction absorbed is then $-dP_x/P_x$, and this ratio also equals the average probability for capture. The term is given a minus sign to indicate that P undergoes a decrease. Thus,

$$-\frac{dP_x}{P_x} = \frac{dS}{S} \tag{22-12}$$

Recall, now, that dS is the sum of the capture areas for particles within the section; it must therefore be proportional to the number of particles, or

$$dS = a\,dn \tag{22-13}$$

where dn is the number of particles and a is a proportionality constant, which can be called the *capture cross section.* Combining Equations 22-12 and 22-13 and summing over the interval between 0 and n, we obtain

$$-\int_{P_0}^{P} \frac{dP_x}{P_x} = \int_0^n \frac{a\,dn}{S}$$

which, upon integration, gives

$$-\ln \frac{P}{P_0} = \frac{an}{S}$$

Upon converting to base 10 logarithms and inverting the fraction to change the sign, we obtain

$$\log \frac{P_0}{P} = \frac{an}{2.303\,S} \tag{22-14}$$

where n is the total number of particles within the block shown in Figure 22-12. The cross-sectional area S can be expressed in terms of the volume of the block V in cm^3 and its length b in cm. Thus,

$$S = \frac{V}{b}\ \text{cm}^2$$

Substitution of this quantity into Equation 22-14 yields

$$\log \frac{P_0}{P} = \frac{anb}{2.303\,V} \tag{22-15}$$

Note that n/V has the units of concentration (that is, number of particles per cubic centimeter); we can readily convert n/V to moles per liter. Thus, the number of moles is given by

$$\text{number mol} = \frac{n \text{ particles}}{6.02 \times 10^{23} \text{ particles/mol}}$$

and c in mol/L is given by

$$c = \frac{n}{6.02 \times 10^{23}} \text{ mol} \times \frac{1000 \text{ cm}^3\text{/L}}{V \text{ cm}^3}$$
$$= \frac{1000\, n}{6.02 \times 10^{23}\, V} \text{ mol/L}$$

Combining this relationship with Equation 22-15 yields

$$\log \frac{P_0}{P} = \frac{6.02 \times 10^{23}\, abc}{2.303 \times 1000}$$

Finally, the constants in this equation can be collected into a single term ε to give

$$\log \frac{P_0}{P} = \varepsilon bc = A \qquad (22\text{-}16)$$

which is a statement of Beer's law.

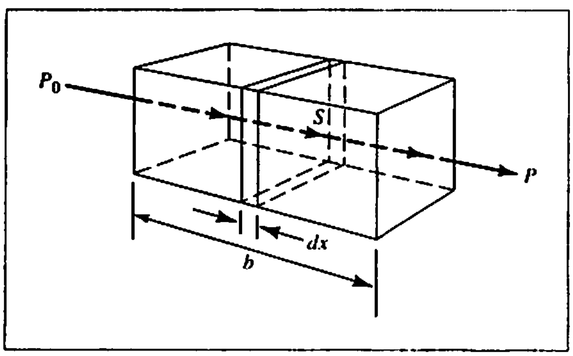

Figure 22-12 Attenuation of radiation with initial power P_0 by a solution containing c mol/L of absorbing solute and a path length of b cm ($P < P_0$).

22C-7 The Application of Beer's Law to Mixtures

Beer's law also applies to a medium containing more than one kind of absorbing substance. Provided there is no interaction among the various species, the total absorbance for a multicomponent system is given by

Absorbances are additive.