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The Beer-Lambert Law

The Laws of Lambert and Beer relate the radiant power in a beam of electromagnetic radiation, usually ordinary light, to the length of the path of the beam in an absorbing medium and to the concentration of the absorbing species, respectively. The laws are normally combined in the relation

$$A = -\log_{10} \frac{P}{P_0} = abc$$

where

  A = absorbance, formerly called the optical density,
  P = radiant power, formerly called the intensity,
  a = absorptivity, formerly called the extinction coefficient,
  b = length of the beam in the absorbing medium,
  c = concentration of the absorbing species.

In this paper we use the nomenclature recommended by a Joint Committee on Nomenclature of the Society for Applied Spectroscopy and the ASTM (1). The older terms are indicated above for reference.

These laws, so vital to colorimetric analysis and spectrophotometry in general, are very poorly treated or not treated at all in a mathematical sense in most books on physical chemistry, quantitative analysis, or instrumental analysis. The two laws are most easily and intuitively stated in the form of differential equations as is true of so many physical problems. In most cases the integrated form is merely stated, or one of the two differential equations is treated while the total solution is assumed (2–12). It is obvious that the integrated form as presented is a solution to the differential equations, but it is not obvious that it is the only possible solution. The best attempt to solve the equations is to be found in one book on analysis (13).

Also textbook authors do not usually present a precise definition of the radiant powers, P and P_0, which appear in the integrated form of the law. It is not made clear to the student what relations these quantities have to light reflections at interfaces or absorption by the solvent. Reflections from the walls in complex geometries, such as a beam across the diameter of a test tube, may greatly complicate the treatment. But for a parallel light beam traveling axially through a cylindrical cell, wall reflections should not complicate the case. This is not true, however, for reflections from windows normal to the beam, even in this idealized case.

Comments on the history of the laws have appeared elsewhere in THIS JOURNAL (14–16). It appears that Beer did not explicitly introduce the concentration variable into the law that bears his name (14) but that another author gave him this credit (14, 17).

This paper is written to present a reasonably rigorous treatment of the differential equations and to include a treatment of reflections at cell windows and solvent absorption.

The radiant power of a parallel light beam is defined as the flow of radiant energy in the beam (in ergs/sec) which crosses one square centimeter of surface in a plane normal to the beam. The power is proportional to the photocurrent produced in a high vacuum photocell (18). Thus the power is usually measured by measuring the photocurrent where relative powers are sufficient as is the case in spectrophotometry.

We consider a very general case where reflections occur at cell windows and the solvent and a single dissolved species both absorb.

Figure 1 is a schematic drawing of an absorption cell. A parallel monochromatic light beam of power P' originates at the left. At each interface a fixed fraction of the incident radiant power at that interface is reflected, dependent on the refractive indices of the two media at the interface (19). Thus the power just inside the left-hand solution-window interface is $(1-f)P'$ where f is the fraction reflected at the two left interfaces. The fraction reflected at the right interfaces is m. The distances x and b and functions of these quantities and of the concentration, c, of the dissolved species are defined by the drawing.
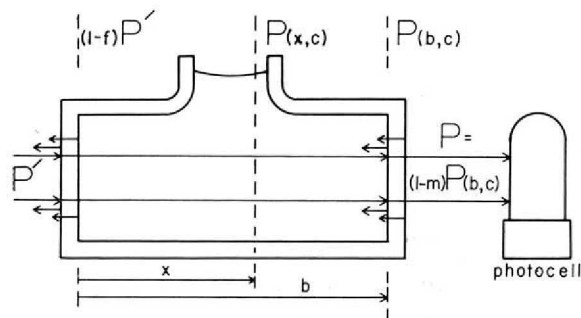

Figure 1. Absorption cell.

In general the powers and other functions of distances and concentrations in what follows are also functions of the wave length of the radiation. We shall content ourselves with leaving this functionality implicit in the functional notation. In general, then, P is a function of x and c, i.e., $P = P(x,c)$.

When pure solvent fills the cell, Lambert's law only applies. This law states, as seems reasonable intuitively, that the fraction of radiant power absorbed when it passes through an infinitesimal thickness of the absorbing medium is proportional to the infinitesimal thickness, i.e.,

$$-\frac{dP(x, 0)}{P(x, 0)} = a'dx \tag{1}$$

where a' is a proportionality constant called the absorptivity for the pure medium (at wavelength λ). The solution to equation(1) is direct and simple.

$$-\ln P(x,0) = a'x + q$$

or

$$P(x,0) = e^{-q}e^{-a'x} = Qe^{-a'x}$$

At $x = 0$,

$$P(0,0) = (1 - f)P'$$

or

$$(1 - f)P' = Q$$

and

$$P(x,0) = (1 - f)P'e^{-a'x} \qquad (2)$$

Now if an absorbing solute is added at concentration c moles/liter, where $c << 1$ as is usually the case, absorption by the solvent is independent of c.

For this case then Lambert's law becomes

$$-\frac{\partial P(x,c)}{P(x,c)} = a'\partial x + g(c)\partial x \qquad (3)$$

Here the proportionality "constant," $g(c)$, will in general be a function of the concentration, a function to be found.

Beer's law also applies. It states that the fractional loss of power due to absorption when an infinitesimal increase is made in the concentration is proportional to that infinitesimal increase. In general this proportionality "constant" is a function of the length of the light path in the solution, thus

$$-\frac{\partial P(x,c)}{P(x,c)} = k(x)\partial c \qquad (4)$$

The problem is to find the solution to equations (3) and (4), consistent with the boundary conditions of the problem. Partial integration of these equations holding c constant in (3) and x constant in (4), yields

$$-\ln P(x,c) = a'x + g(c)x + h(c)$$

$$-\ln P(x,c) = k(x)c + j(x)$$

where the "constants" of integration in each case are functions of the opposite variable. Written in exponential form, these become

$$P(x,c) = H(c)e^{-a'x}e^{-g(c)x} \qquad (5)$$

$$P(x,c) = J(x)e^{-k(x)c} \qquad (6)$$

where

$$H(c) = e^{-h(c)}$$

and

$$J(x) = e^{-j(x)}$$

Applying boundary conditions, we have at $x = 0$,

$$P(0,c) = (1 - f)P' = H(c) \qquad (7)$$

and at $c = 0$, from equations (2) and (6):

$$P(x,0) = (1 - f)P'e^{-a'x} = J(x) \qquad (8)$$

To obtain forms for $g(c)$ and $k(x)$ we proceed as follows. Putting (7) into (5) and differentiating with respect to c we have

$$-\frac{\partial P(x,c)}{\partial c} = (1 - f)P'e^{-a'x} x \frac{dg(c)}{dc}e^{-g(c)x}$$

and compare this with equation (4), eliminating $P(x,c)$ with (5) and (7)

$$-\frac{\partial P(x,c)}{\partial c} = k(x)(1 - f)P'e^{-a'x}e^{-g(c)x}$$

This yields

$$\frac{dg(c)}{dc} = \frac{k(x)}{x} \qquad (9)$$

The left side is a function of c only and the right side of x only. This equation must hold for *all values* of x and c. Thus each side must be equal to a constant separately, say a'', so

$$g(c) = a''c + r \qquad (10)$$

$$k(x) = a''x \qquad (11)$$

Similar treatment of equations (6) and (8), differentiation with respect to x, and comparison with equation (3), yields

$$\frac{dk(x)}{dx} = \frac{g(c)}{c} \qquad (12)$$

Each side of this equation must also be a constant, say a'''. Then

$$k(x) = a'''x + s \qquad (13)$$

$$g(c) = a'''c \qquad (14)$$

Comparison of (13) and (14) with (10) and (11) requires that $a'' = a'''$ and $r = s = 0$.

Thus

$$k(x) = a''x$$

and

$$g(c) = a''c$$

and equations (5) and (6) become

$$P(x,c) = (1 - f)P'e^{-a'x}e^{-a''cx} \qquad (15)$$

The radiant power striking the photocell is P. So

$$P = (1 - m)P(b,c)$$
$$= (1 - m)(1 - f)P'e^{-a'b}e^{-a''bc} \qquad (16)$$

When $c = 0$, the radiant power *striking the photocell* is, by convention, P_0. Then

$$P_0 = (1 - m)(1 - f)P'e^{-a'b} \qquad (17)$$

Some authors' drawings (4) indicate that $P_0 = P'$ but clearly this is not so. Even if the solvent does not absorb, i.e., if $a' = 0$,

$$P_0 = (1 - m)(1 - f)P'$$

In any case then

$$P = P_0e^{-a''bc}$$

or if

$$a'' = (2.303)a$$

$$P = P_010^{-abc}$$

or

$$A = -\log_{10}\frac{P}{P_0} = abc$$

If c is in moles per liter and b in centimeters, a is called the "molar absorptivity." This is the usual form of the law as stated in texts. It is hoped that this treatment will clarify the formal combination of the two laws and will clearly show the relation of the conventional radiant powers *as measured* to other physical factors encountered in absorption measurements.

From this discussion it should also be clear why it is important in accurate measurements that P_0 (or what corresponds to it, 100% transmittance) be measured with the same cell and *same surface conditions* as is used in the measurements of absorbance.

As a concluding comment, we note that most authors discuss "failures" of the Beer-Lambert Law. While these discussions are not incorrect in principle, it seems to the author that the very term "failure" is misleading to say the least. It can safely be said that the Beer-Lambert Law *never* fails (1) if monochromatic light is used and (2) if the concentration factor in the law is

actually the concentration of the absorbing species. Manifestly the law will not hold in general if the concentration of some other species is introduced as *c*, even if the absorbing species is in equilibrium with the other species.

Literature Cited

(1) HUGHES, H. K., ET AL., *Anal. Chem.*, **24,** 1349 (1952).
(2) BARROW, G. M., "Physical Chemistry," McGraw-Hill Book Co., Inc., New York, **1961,** p. 375.
(3) DANIELS, F., ALBERTY, R. A., "Physical Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, **1961,** p. 521.
(4) DIEHL, H., AND SMITH, G. F., "Quantitative Analysis," John Wiley and Sons, Inc., New York, **1952,** p. 347.
(5) KOLTHOFF, I. M., AND SANDELL, E. B., "Textbook of Quantitative Analysis," 3rd ed., The Macmillan Company, New York, **1952,** p. 614.
(6) MOORE, W. J., "Physical Chemistry," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., **1955,** p. 596.
(7) PIERCE, W. C., HAENISCH, E. L., AND SAWYER, D. T., "Quantitative Analysis," 4th ed., John Wiley and Sons, Inc., New York, **1958,** p. 400.
(8) SANDELL, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, **1944,** p. 33.
(9) SHEEHAN, W. F., "Physical Chemistry," Allyn and Bacon, Inc., Boston, **1961,** p. 575.
(10) STROBEL, H. A., "Chemical Instrumentation," Addison-Wesley Publishing Company, Inc., Reading, Mass., **1960,** p. 150.
(11) WILLARD, H. H., FURMAN, N. H., AND BRICKER, C. E., "Elements of Quantitative Analysis," 4th ed., D. Van Nostrand Co., Inc., New York, **1956,** p. 485.
(12) WILLARD, H. H., MERRITT, L. L., JR., AND DEAN, J. A., "Instrumental Methods of Analysis," 3rd ed., D. Van Nostrand Co., Inc., New York, **1958,** p. 5.
(13) WILLARD, H. H., AND DIEHL, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., Inc., New York, **1943,** p. 112.
(14) PFEIFFER, H. G., AND LIEBHAFSKY, H. A., J. CHEM. EDUC., **28,** 123 (1951).
(15) LIEBHAFSKY, H. A., AND PFEIFFER, H. G., J. CHEM. EDUC., **30,** 450 (1953).
(16) MALININ, D. R., AND YOE, J. H., J. CHEM. EDUC., **38,** 129 (1961).
(17) WALTER, B., *Ann. Physik.*, **36,** 502 (1889).
(18) RICHTMYER, F. K., AND KENNARD, E. H., "Introduction to Modern Physics," 4th ed., McGraw-Hill Book Co., Inc., New York, **1947,** p. 87.
(19) SLATER, J. C., AND FRANK, N. H., "Electromagnetism," McGraw-Hill Book Co., Inc., **1947,** p. 120.