

ランベルト・ベールの法則、質量作用の法則、およびヘンリーの法則に 原子分子論を適用する方法 高見知秀^{*1}

Application of Atomic Molecular Theory to Beer–Lambert Law, Law of Mass Action, and Henry’s Law Tomohide TAKAMI^{*1}

Abstract

本論文は化学を学ぶ初学者を教える先生方のために書かれたものであり、量子化学のような専門的な知識を必要としません。化学で使用されるいくつかの法則は、原子分子の概念が科学的に受け入れられる前に確立されており、それらは原子分子論、すなわちすべての物質は元素からなる、ということに基づいて再考される必要があります。本論文では、ランベルト・ベールの法則、質量作用の法則、およびヘンリーの法則に原子分子論を適用する方法について述べます。また、グーグル翻訳がある時代に日本語で書く意味はないため、本論文は英語で記述しました。

This paper is written for those who teach beginners learning chemistry in university and does not require the subject of study such as quantum chemistry. Some laws used in chemistry were established before the concepts of atom and molecule had been scientifically accepted, and they need to be reconsidered based on atomic molecular theory; all materials are made from elements. Here, the author describes a way to develop the Beer–Lambert law, the law of mass action, and Henry’s law from the perspective of atomic molecular theory. It is also noted that this paper is written in English, not Japanese, because there is no point in writing in Japanese when there is a Google translation.

Keywords: Beer–Lambert law, the law of mass action, Henry’s law

1. Introduction

When a bongo player, Richard Feynman, was asked to think of a sentence that would impart the most important scientific knowledge, he answered that matter was made of atoms.¹ Einstein demonstrated theoretically the existence of molecules with his explanation of Brownian motion.² Perrin performed the precise experiments to prove the existence of molecules.³ Since the proofs of the existence of atoms and molecules, many improvements and discoveries have occurred.

Whereas, some important laws and theories, including thermodynamics, were established before the general acceptance of the existence of

molecules. Thus, thermodynamics has been re-derived from the point of view of molecular theory evolving into statistical thermodynamics. However, some laws in analytical and basic chemistry still exist without reference to the molecular theory.

Here, the author demonstrates how the Beer–Lambert law, the law of mass action, and Henry’s law can be based on molecular theory.

2. Beer–Lambert Law

It should be noted that this section was inspired by the homepage⁴ and textbook⁵ written by Koichi Ohno, Professor Emeritus of Tohoku University indicated last century. It is also noted that Akul Mehta mentioned the similar approach on line in 2012.⁶

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The Beer-Lambert law was typically taught by starting with a differential equation based on the hypothesis that the logarithm of the transmittance through a substance is proportional to its concentration and the optical path length. However, textbooks do not, in general, show how that hypothesis is derived. Here, the Beer-Lambert law is derived from molecular theory.

Figure 1 displays a schematic illustration of the deduction of the Beer-Lambert law. First, we consider a single molecule ($n = 1$) with cross section a in a cell with volume $V = SL$ (S : cross section of the cell, L : optical path length in the cell), as shown on the left of Fig. 1. The transmission probability T_1 is

$$T_1 = \frac{I_1}{I_0} = 1 - \frac{a}{S} \quad (1.1).$$

Next, we consider number N of molecules in the same cell, as shown on the right of Fig. 1. The event shown in the left of Fig. 1 occurs N -times when the molecules are small enough to neglect the correlation between the molecules. Thus, the transmission probability T is the N -times multiplication of the individual probabilities;

$$T = \frac{I}{I_0} = \left(1 - \frac{a}{S}\right)^N \quad (1.2).$$

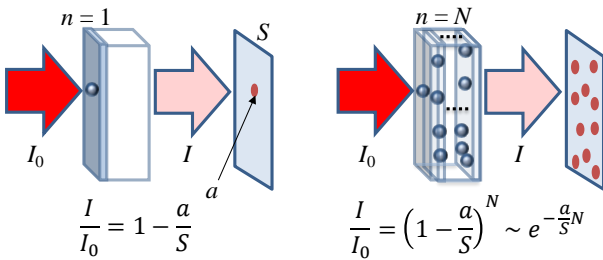


Figure 1. Illustration of the Beer-Lambert law using molecular theory. Left: Single-molecule scattering where the molecule is in a thin slab ($n = 1$). Right: Multiple-molecule scattering where the molecules are in the pile of the slabs ($n = N$).

In other words, the thin slabs with the scattering molecules pile up N -times. For small number a/S , the following approximation can be applied,

$$\left(1 - \frac{a}{S}\right)^N \sim e^{-\frac{a}{S}N} \quad (1.3),$$

and the approximation is explained later.

Then, the following expression can be obtained,

$$\ln \frac{I}{I_0} = \ln \left(1 - \frac{a}{S}\right)^N \sim -\frac{a}{S}N \quad (1.4).$$

The concentration, c , of the sample liquid in the cell in our model for the deviation of the Beer-Lambert law is

$$c = \frac{N/N_A}{V} = \frac{N}{SLN_A} \quad (1.5),$$

where N_A is Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

We define the molar attenuation coefficient ε as

$$\varepsilon \equiv \log_{10} e \times aN_A = 2.303aN_A \quad (1.6);$$

then, the logarithm of the transmittance is

$$\begin{aligned} \log \frac{I_0}{I} &= -\log_{10} e \ln \left(\frac{I}{I_0}\right) = \log_{10} e \times \frac{a}{S}N \\ &= \frac{\varepsilon}{N_A} \frac{N}{S} = \varepsilon cL \end{aligned} \quad (1.7).$$

Thus, we have derived the reason why the logarithm of the transmittance is proportional to the concentration c and the optical path length L .

Now, how the approximation of the equation 1.3 can be obtained is shown. From a Maclaurin-series expansion, we can obtain the following approximation:

$$\ln \frac{I}{I_0} = \ln \left(1 - \frac{a}{S}\right)^N = N \ln \left(1 - \frac{a}{S}\right) \sim N \left(-\frac{a}{S}\right) \quad (1.9),$$

so that we can obtain the approximated equations 1.3 and 1.4.

The physical meaning of the logarithmic dependence in the Beer - Lambert equation is described. Note that $a/S = acLN_A/N$ (from equation 1.5) $= b/N$ ($b \equiv acLN_A$) and N is a very large number. Then, the following equation related to Napier's constant e could be obtained,

$$\lim_{N \rightarrow \infty} \left(1 - \frac{b}{N}\right)^N = (1/e)b \quad (1.10).$$

Figure 2 illustrates the physical meaning of Napier's constant e . A sheet of paper with area S is cut into a number N of tiny pieces of paper, and the

tiny pieces of paper are randomly deposited on a different sheet of paper with the same area S as the original sheet. Then, the probability to cover the deposited area with a piece of the paper is $(S-S/N)/S = 1-1/N$. The behavior of each piece should be considered an independent event, so that the ratio of the area that is not covered with the pieces of the paper is the N -th power of the probability, *i.e.*, $(1-1/N)^N$. Therefore, the ratio of the deposited domain to the exposed domain is approximately $1-e^{-1} : e^{-1} = e-1 : 1$ when the number N is large enough because

$$\lim_{N \rightarrow \infty} \left(1 - \frac{1}{N}\right)^N = 1/e \quad (1.11).$$

This is the meaning of Napier's constant according to the stochastic interpretation.

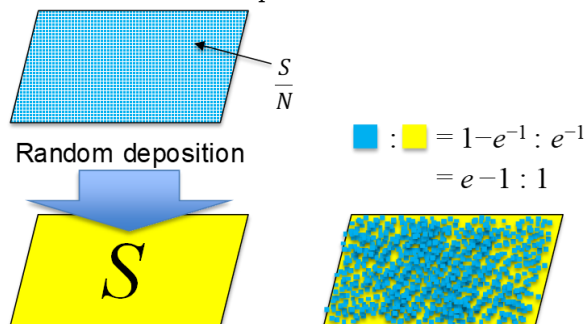


Figure 2. Explanation of Napier's constant e . The ratio of the deposited area (blue) to the exposed area (yellow) is $e-1 : 1$, which is the physical meaning of Napier's constant.

Lykos demonstrated a similar route to the Beer-Lambert law following the process of deriving the Napier's constant $e = 2.71828...$ and the natural logarithm;⁷ however, a thin "slab" was only used in the model of the explanation. Using molecular theory might allow students to understand the Beer-Lambert law more easily, based on the adsorption of a single molecule.

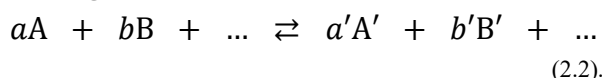
3. Law of Mass Action

Guldberg and Waage proposed the law of mass action in 1864.^{8,9} According to the original paper, the word "mass" in the law of mass action means

"active mass",¹⁰ "chemical force",¹¹ or concentration, because the concept of the amount of a substance did not exist when the law of mass action was proposed. For the student learning the law of mass action, however, there can be some confusion over fact that no mass variable, m , appears in the law of mass action,

$$K = \frac{[A']^{a'}[B']^{b'} \dots}{[A]^a[B]^b \dots} \quad (2.1),$$

for the general reaction



Therefore, when evaluating this expression for a particular reaction, students are liable to make the error of using the mass percentage (%) in place of the concentration $[A]$, which should be a molar percentage (*e.g.*, in units of mol L^{-1} for each of the components of a solution-phase reaction).

Although the historical discovery of the law of mass action should be respected, the words of the law of "mass" action should be reconsidered, *e.g.*, "the law of chemical equilibrium".¹² could be used as an alternative.

4. Henry's Law

Henry's law was proposed in 1802, and William Henry published an article on the solubility of gases in water in 1803.¹³ Naturally, this law pre-dates the general acceptance of the concept of molecules. The most commonly used definition of Henry's law is that the solubility of a gas is proportional to the partial pressure of the corresponding gas.^{14,15}

However, some teachers and textbooks present the law by stating that the dissolved volume of a gas is constant with increasing pressure in the case of an ideal gas.¹⁶ This expression can generate confusion for students.

Henry's law can be expressed by the following equation:

$$S_g = n/V_s = k_p P \quad (3.1),$$

where S_g is the solubility of the dissolved gas per the volume of the solvent, n is the amount of substance of the dissolved gas, V_s is the volume of the solvent, k_p is the Henry's constant, and P is the pressure applied to the gas. The volume of dissolved

gas V_g in the case of an ideal gas follows the equation

$$PV_g = nRT \quad (3.2),$$

where R is the gas constant and T is the temperature. This leads to the expression

$$V_g/V_s = k_p RT \quad (3.3),$$

and hence, when the temperature T is constant, the dissolved volume of the gas per the volume of the solvent V_g/V_s is constant. Though the amount substance n dissolved in the solvent increase with the applied pressure P , according to the equation 3.1, the volume of the dissolved gas V_g is constant because the Boyle's law says that V_g is inverse proportional to the applied pressure P . A textbook described that the volume of the dissolved gases in the solvents were often converted to the same condition, *e.g.*, standard state in case of the comparison of the solubility using the volumes, and that the volume of the dissolved gas was proportional to the pressure when the gas was dissolved at the constant pressure (as translated by the author),¹⁵ which makes more confusion to the students.

Considering from the concept of the amount of substance n , this approach does not cause any confusion. Therefore, considering molecular theory, Henry's law has been defined as in most of the modern university textbooks¹⁷ that "*the mole fraction of the dissolved gas*" is proportional to its pressure.

5. Conclusion

A number of chemical laws were discovered or proposed before the concepts of the atom, the amount of substance, and molecular theory had been established, and some of these laws should be re-expressed for the benefit of students learning chemistry. The Beer-Lambert law equation can be derived from molecular theory and the hypothesis that the logarithm of the transmittance is proportional to the concentration and optical path length can be explained via this approach. The name of the law of mass action should be reconsidered based on the concept of the molar amount of substance. Henry's law, also, should be

reconsidered based on the concept of the amount of substance per amount of solvent; "the mole fraction of the dissolved gas is proportional to the partial pressure of the gas" as in most of the modern university textbooks.

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Figure Captions

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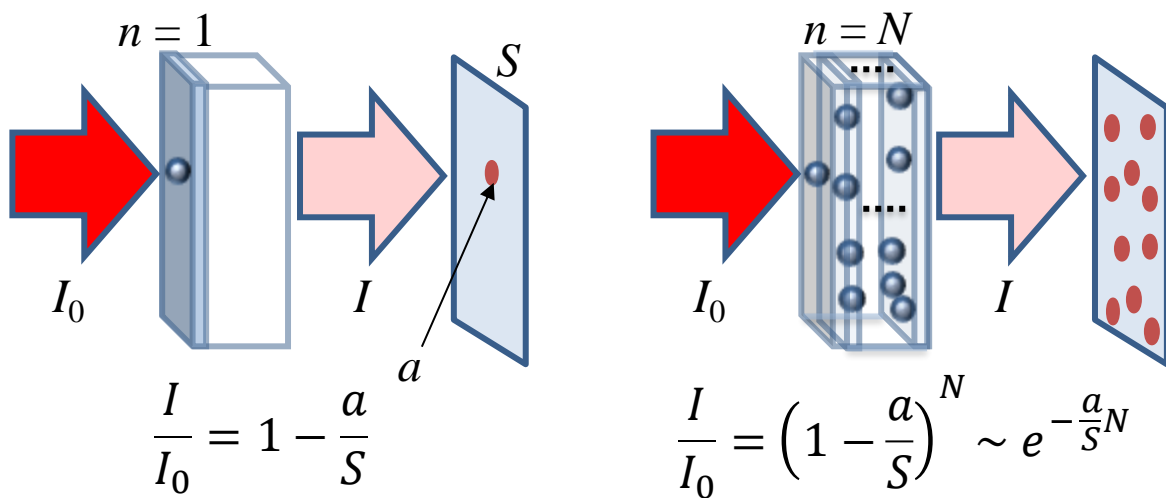


Fig.1. (Color Online)

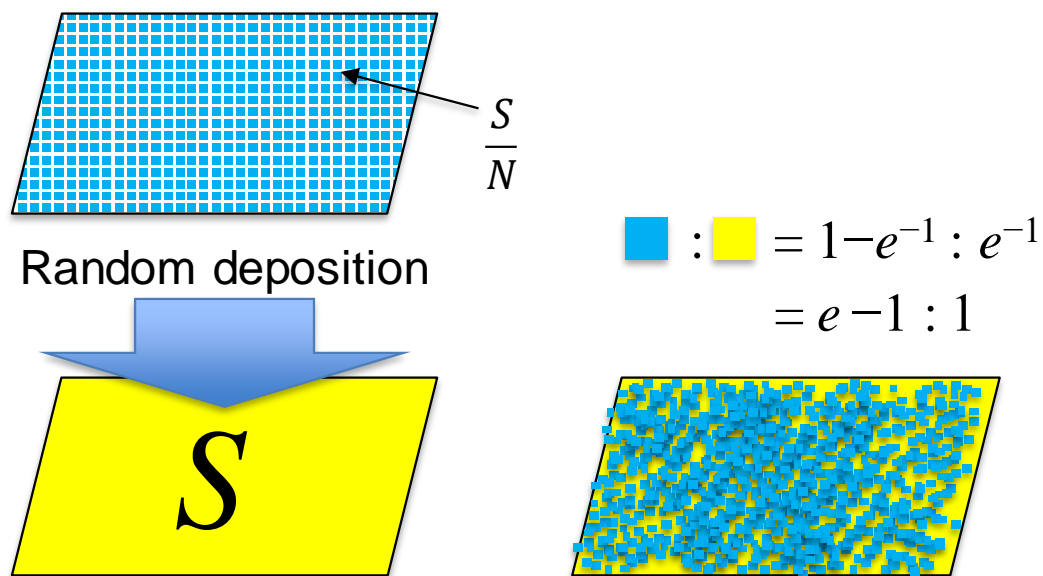


Fig. 2. (Color Online)