Is Henry's Law Constant?
A Review of Its Description in Environmental Engineering Texts

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Abstract

A survey of how Henry's Law is cited in a wide range of texts suggests that there is significant variation in the presentation of the definition, breadth of theory, applications and limitations of this relationship in technical resources used by students. This is of importance because students and practitioners must be able to evaluate and apply the theory of engineering principles in order to effectively design and model environmental systems. Critical design errors may result from incomplete or inaccurate explanations of a principle in a technical resource. Most topic-specific texts provided detailed descriptions of Henry's Law. The presentation of Henry's Law in more general environmental engineering texts and other technical resources provided less detailed descriptions. In many cases the theory and application of Henry's Law appear to have been oversimplified. This paper reviews the descriptions of Henry's Law in texts and other resources to demonstrate potential effects on student learning and professional practice that may result from oversimplifications of this engineering principle.

Introduction

One of the critical skills of an engineer is the ability to approximate how a system will perform in the absence of system-specific data. Handbooks of thermodynamic data, texts, papers and other technical publications serve as resources to formulate such approximations. Engineers learn early in their academic and practicing careers that assumptions about an environmental system such as equilibrium, steady state and ideal solutions help in making approximations and estimations about a system. Engineers also know that theory guides and experiment decides and environmental systems don't generally behave as ideal, well-defined systems. Limitations of the approximation methods need to be understood. Henry's Law is one of the most fundamental principles of environmental engineering and use of it in characterizing a gas/liquid system demands an understanding of its limitations.

Credit for first characterizing concentration equilibria in gas/liquid systems has been given to William Henry. Henry was an early nineteenth century English physician turned chemist who focussed his energies on chemical manufacturing when poor health prohibited him from practicing medicine (Partington, 1960). His postulate that the weight of a gas dissolved in dilute solution by a liquid is proportional to the pressure of the gas upon the liquid was formulated in 1803. Although engineers and scientists identify Henry with this well known principle, perhaps Henry's most important contribution to chemistry was the influence of his experiments on his friend John Dalton's formulation of fundamental principles of modern atomic theory (Greenaway, 1966).

Environmental engineering practitioners use Henry's Law to investigate the measurement and transport of volatile organic compounds in and across air, soil and groundwater interfaces. "Henry's Law" is not a law but, rather, an empirical principle that applies for dilute solutions in ideal liquids when the gas phase behaves as an ideal gas. The following definition is a synthesis of definitions reviewed while researching this paper:

At a constant temperature the mass of substance dissolved in a fixed amount of a liquid at a stable dynamic equilibrium maintained by two-way diffusion across a planar interface is proportional to the partial pressure of the substance. The proportionality constant that holds for the substance in the gas/liquid system is called the Henry's Law Constant. This relationship holds only for dilute solutions that do not react, ionize or dissociate with the solvent liquid.

This relationship is used to predict equilibrium concentrations of a contaminant in a gas/liquid system. In environmental engineering, it is often used to describe the extent of transport across air/water systems such as:

- the solubility of oxygen in natural waters, wastewater and drinking water supplies;
- the indirect measurement of contaminants in groundwater when soil gas concentrations are known;
- the design and performance of air stripping and other air-water mass transfer-based treatment/ remediation systems; and
- the mobility potential of volatile organic compounds through soil gas, soil, groundwater and indoor air systems.

Although its derivation has been explained using conventional thermodynamic theory, a Henry's Law Constant is based on empirical observations of a well-defined system. In practice, gas/liquid systems may not be well defined and may not resemble the system upon which a published Henry's Law Constant is based. It is incorrect to assume Henry's Law Constants are thermodynamic equilibrium constants. Nonetheless, engineers routinely use a tabulated Henry's Law Constant to approximate transport phenomena for an environmental system or unit operation. In order to understand the applications of Henry's Law, an engineer must possess the ability to evaluate and synthesize its supporting theory.

Theory

Dilute Solutions

While a review of the relevant theory is provided here, the reader may refer to thermodynamic texts for a more in-depth explanation of dilute solutions. The phenomena of dilute species in gas/liquid systems can be described by applying some standard thermodynamic principles. Henry's Law can be explained with the use of the fugacity function. Fugacity can be thought of as a convenient means to measure system deviations from ideal gas behavior. In terms of the Gibbs free energy, the fugacity of a pure substance, f_i, is defined by the following equations (Perry's Chemical Engineers Handbook, 1997):

$$dG_i = RT \, d \ln f_i$$

$$\lim_{P \to 0} \frac{f_i}{P} = 1$$

where,
R = ideal gas constant
T = temperature
G_i = Gibbs free energy of substance i

The ratio of the fugacity of a material to its pressure is called the fugacity coefficient, ϕ_i:

$$\phi_i = f_i / P$$

The fugacity of substance i that has a mole fraction of x_i in a solution, (f^*_i), is expressed as:

$$\lim_{P \to 0} \frac{f^*_i}{x_i P} = 1$$

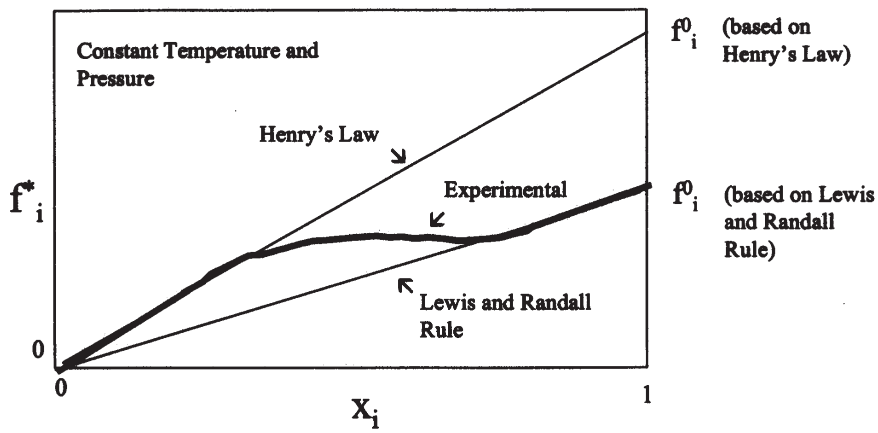
where,
P = vapor pressure of pure i.

These relationships apply at constant temperature. Also, as pressure of substance i approaches zero, ideal gas behavior is a reasonable expectation and the fugacity of i, in effect, equals its pressure. As x_i of a solution approaches 1, f^*_i would equal f_i if the gas phase behaves as an ideal gas. However, for real solutions, this rule (known as the Lewis and Randall rule) does not apply. The deviation from ideality is shown in Figure 1.

For real solutions the relationship between f^*_i and x_i is not a straight line over the entire range of x_i and must be determined experimentally. For dilute solutions, Henry's Law suggests that there is a linear relationship between f^*_i and x_i. The slope of f^*_i vs x_i is known as the Henry's Law Constant. As shown in Figure 1, the Henry's Law Constant applies at dilute solutions (i.e., low values of x_i) and is dependent on the temperature and pressure of the system. The Henry's Law Constant does not apply for concentrated solutions, since the standard state (f^0_i) for the Henry's Law line in Figure 1 is hypothetical and does not exist. To summarize, any given Henry's Law Constant:

- is empirically derived by gas/liquid systems at equilibrium.
- applies for a substance i that exists in a gas/liquid system at equilibrium.
- is unique to a substance i in a given gas/liquid system at equilibrium.
- is both temperature and pressure dependent.

Also, it is important to note that changes to either media, (for example changing the ionic strength of the liquid phase; or changes that may affect the ideal gas behavior of the gas phase) may substantially affect the value of a Henry's Law Constant for a given substance.



Fugacity-composition relationships, showing standard-state fugacities based on Henry's Law and the Lewis-Randall Rule(Perry, 1997).

Figure 1.

Henry's Law Constants

For systems where Henry's Law applies, the Henry's Law Constant is the ratio of the gas phase concentration and the liquid phase concentration of a substance. Numerous tabulations of the Henry's Law Constant for gases are found in standard references, texts and journal publications (such as Perry's Chemical Engineers Handbook, 1997, CRC Handbook of Chemistry and Physics, 1999, Lyman, et al., 1990, and MacKay and Shiu, 1981). Additional sources of Henry's Law Constants are listed in the References Addendum to this paper. Most often, the Henry's Law Constant is taken as the gas phase concentration divided by the liquid phase concentration of the substance. Units assigned to tabulated values usually indicate whether the Constant represents a gas/liquid or liquid/gas ratio. Sometimes, "dimensionless" values are given, i.e., when constants are given in units of mass of substance/volume in one phase divided by mass of substance/volume of the other phase. A Henry's Law Constant (H) can be converted to a dimensionless form by use of the ideal gas law as shown in the following equation:

$$H\,[\text{dimensionless}] = H\,[\text{atm} * \text{L/mol}] * 1/(R*T)$$

where,
R = ideal gas constant [atm L/mol °K]
T = temperature [°K]

Depending on the source, tabulated values may be empirically derived or predicted. Experimentally derived constants are difficult and time consuming to produce. These constants apply only to the well-defined gas/liquid systems studied and may not apply to gas/liquid systems of environmental interest. Tabulated

Henry's Law Constants are often created by using predictive methods. In general, these methods are based on either solubility and vapor pressure properties or structural properties between different substances. A simple Henry's Law Constant estimation method for air/water systems is to take the ratio of the vapor pressure of a substance to the water solubility of that substance at its vapor pressure (Thibodeaux, 1979). Excellent descriptions of these methods are provided in two chemical properties estimation texts by Lyman et al., 1990 and Baum, 1999.

Texts Survey

A review of how Henry's Law is described in current texts in use in environmental engineering curricula was performed. The review looked at how Henry's Law was described in a representative, but not exhaustive, number of texts and references. Texts were obtained using reference material found in engineering libraries and with desk copies of popular texts currently in use in undergraduate environmental engineering curricula. The texts reviewed were also considered to be resources available to and used by both the graduate student and the practitioner of environmental engineering. Resources reviewed included standard reference texts, general environmental engineering texts and topic-specific texts. The forty-four resources reviewed are listed References Addendum to this paper. For multiple edition texts, attempts were made to review the latest possible edition available.

A summary of the review and its outcomes is given in Tables 1 and 2. The Tables summarize how the Henry's Law definition and Henry's Law Constants are presented in texts. Explanations for inconsistencies between texts are offered based on these results.

Comparison of the Definition

The context in which Henry's Law is presented varies, as do the specific subject matter of each text reviewed. Nonetheless a comparison between definitions was made relative to the aforementioned definition given in **Background.** Almost half of the forty-four texts reviewed (twenty out of forty-four) provided incomplete definitions, i.e., definitions that did not identify the uses and restrictions on the applicability of the law and/or did not refer the reader to a more descriptive and complete reference. Of these texts eight out of the twenty were chemical dictionaries. Over half of all chemical dictionaries reviewed (i.e., eight out of fourteen) provided incomplete definitions. The non-"chemical dictionary" books that presented incomplete definitions tended to be general books of environmental engineering and were not topic-specific by nature. It is interesting to note that numerous general texts with "environmental engineering" in their title did not describe Henry's Law. These texts were not included in the review.

Potential Effects

Applying an incomplete definition may lead to serious errors in predicting equilibrium concentrations across gas/liquid media.

Examples:

- A common example of an incomplete definition was to state that ***"the Henry's Law Constant is equal to the ratio of the gas phase concentration to liquid phase concentration of a substance",*** without pointing out that the concentration ratio may be considered a constant only at dilute solutions. In their text, Heinsohn and Kabel, 1989, demonstrate that the misuse of a Henry's Law Constant for a substance with a significant solubility in the order of percentage mass fraction in a liquid phase may lead to an orders-of-magnitude error in predicting the equilibrium gas phase concentration of the substance.
- Another example of an incomplete definition is failure to point out that the published Henry's Law Constants apply to **a** gas/liquid system that may not resemble the environmental gas/liquid system of interest. Use of a published air/water Henry's Law Constant for oxygen in deionized water would lead to a percentage-order error in predicting the oxygen solubility in seawater.

There are several reasons why a text might provide an incomplete definition.

Comparison of Definitions

Resource Text Type	Total Number Reviewed	Number with an Adequate Definition	Number with an Incomplete and/or Inaccurate Definition
Reference, Environmental Engineering and Topic-Specific	44	24	20
Chemical Dictionary	14	6	8

Table 1.

Comparison of Henry's Law Constant

Total Number of Resource Texts Reviewed	Texts describing H as (gas pressure/water solubility)	Texts describing H as (water solubility/gas pressure)	Texts not specifying a ratio convention for H
44	21	9	14

Table 2.

In some cases it may be presumed that the reader has already developed a good understanding of the principles of Henry's Law. However, most of the texts that might be considered appropriate for upper-level courses did provide adequate definitions. It is possible that incomplete definitions were presented as a result of space limitations. Chemical dictionaries must compromise detail for space and this survey found that the completeness of the definition suffered in many instances. Also, the few general texts of environmental engineering with incomplete definitions of Henry's Law may have done so out of an attempt to include too many concepts of engineering that is "environmental", with too little details.

Comparison of the Constant

Significant variation was noted in the definition of the Henry's Law Constant in the texts reviewed. While approximately one-third (fourteen out of forty-four) of the text definitions did not specify whether the Henry's Law Constant was a ratio of gas pressure over liquid solubility or liquid solubility over gas pressure, roughly 20% (nine out of forty-four) defined the Henry's Law Constant as the ratio of water solubility over gas pressure and almost half (twenty one out of forty-four) defined Henry's Constant as the ratio of gas pressure over water solubility. Though either form of the ratio may be used, it is interesting to note that there is not consistency with the ratio within the environmental engineering discipline. It should be also noted that the convention of the ratio didn't seem to depend on whether the text focussed on a specific sub-discipline of environmental engineering. For example, air pollution texts did not present the ratio as exclusively gas/water and water pollution texts did not present the ratio as only water/gas. The difference in form points out the caution that should be exercised in the use of published Henry's Law Constants when these constants are presented in dimensionless form. Without careful attention to the units of a published Henry's Law Constant, an orders-of-magnitude error may be made. Results underscore the point that, for dimensionless Constants, the user must know the convention of the ratio.

Conclusions

- A review of commonly used environmental engineering texts indicates that there is variation in the level of detail in the description of Henry's Law. Although most topic-specific texts provided good descriptions, many non-topic-specific texts provided incomplete descriptions. Over-reliance on an abbreviated description of Henry's Law by a student may lead to design errors in the classroom and, ultimately, in practice.
- Inconsistencies in the description of Henry's Law, such as the gas/liquid versus liquid/gas conventions for the Henry's Law Constant exist between commonly used texts. It is reasonable to assume that the different ratio conventions for the Henry's Law Constant persist with professional practitioners as well. Based on the review, it is evident that students must be made aware that both conventions exist and they must recognize the need to critically evaluate the convention used to generate published Henry's Law Constants.
- Results underscore the need for careful text selection for a topic-specific course. While general texts of environmental engineering provide broad reviews of an ever-expanding number of environmental topic areas, abbreviated descriptions of a given concept may result in unintended outcomes in student learning. Though covering a smaller range of environmental concepts, the results of this review suggest that topic-specific texts appear to be more likely to provide appropriate levels of detail. Ultimately, Instructors assume the responsibility of complementing and/or clarifying descriptions in a course's text for their students. Also, the results of this review indicate it is worthwhile for engineering program coordinators to perform program-wide reviews of texts used in an engineering curriculum to assess consistency in the presentation of critical principles to students.
- A review of Henry's Law in environmental engineering texts revealed information of adequacy and accuracy that is not unique to Henry's Law, environmental engineering or any other discipline. Similar results might be expected for the description of a fundamental concept in a science, mathematics, engineering, technology or art history discipline. Program-wide text reviews should be considered as a means to gauge how fundamental concepts are presented in texts and, ultimately, how these concepts are likely to be processed by students.

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* **Resources used for survey**

Resources provided selected Henry's Law Constants

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