

William Henry: His Achievements and His Law

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Abstract: Henry is a well-known name to all students of physical chemistry. Despite physical handicaps resulting from a childhood accident, he went on to a brilliant career in chemistry and medicine. The extensive and careful measurements that he made of the solubility of gases have given us the law that carries his name. Not many are familiar with his work on the steam sterilization of fabrics and other materials used as a medical tool to avoid spreading disease. He also did the basic work that proved that carbon is an element and not a compound.

Introduction

Chemists and chemical engineers are familiar with William Henry (1774–1836) through the law that bears his name, a law that states that the solubility of a gas is proportional to its partial pressure, although Henry never stated his law as we know it today. He also made other contributions to science that include the analysis of gases derived from coal; the determination of the composition of gases like methane, ethylene, and ammonia; and contributions to public medicine. Here, we describe his personal life and career, his scientific achievements, and, in particular, how his empirical law (Henry's law) has been developed into the modern equations that correlate the solubility of a gas as a function of temperature and pressure.

Life and career [1, 2]

William Henry was born in Manchester, England, on December 12, 1774, the son of Thomas Henry, an apothecary that developed a process for the manufacture of magnesia for medicinal purposes and put up a very successful manufacturing plant that provided a very comfortable income for the family for many years. William Henry went to a private school and then to the Manchester Academy. At the age of ten, a falling beam hit him on his right side, resulting in serious injuries that threatened his life for sometime. This injury was so serious that it affected his physical development and prevented from him normal boyhood activities. He was also left with acute neuralgic pains, which recurred often after long periods of remission and were particularly severe some months before his death.

After leaving the Manchester Academy, he became secretary to Thomas Percival (1740–1804, the founder of the Manchester Literary and Philosophical Society) and began premedical studies. In 1795 he entered Edinburgh University but left a year later to assist in his father's practice and to manage the family manufacturing business. He was also engaged with his father in general medical practice. At Edinburgh, he attended the lectures of Joseph Black (1728–1799, rediscovered CO_2 , discovered bicarbonates and latent heat), a supporter of the caloric theory.

Henry became a member of the Manchester Literary and Philosophical Society in 1796 and began to carry out original research in chemistry. He returned to Edinburgh University in 1805 and received his M.D. in 1807, submitting a dissertation on uric acid. This was published years later in the *Memoirs of the Manchester Literary and Philosophical Society* [3]. He later specialized in urinary diseases and contributed papers to British and German medical journals on this subject. In 1808 Henry was elected a fellow of the Royal Society and awarded the Copley medal for papers communicated to the society and printed in the *Philosophical Transactions*.

Henry's textbook, *Elements of Experimental Chemistry*, based on lectures he gave at Manchester, was dedicated to John Dalton (1766–1844), with whom he had a very close friendship. This work went through eleven editions and was the most popular and successful chemistry text in England for more than thirty years. The first American edition of the book was published in Philadelphia in 1819, by Dr. Robert Hare, professor of chemistry in the Medical Department of the University of Pennsylvania.

In 1801 Henry read his first paper [4] to the Manchester Literary and Philosophical Society, rebutting Davy's argument against the materiality of heat. As Black's student he remained a lifetime adherent to the caloric theory. The solubility of gases [5], which eventually would be the basis of Henry's law, was read to the Literary and Philosophical Society in 1802.

Henry was forced to abandon experimental work because of surgical operations performed on his hands. He began to study contagious diseases, which he believed were spread by chemical substances different from gases. Henry believed that *contagion*, the disease carrier, was heat labile and could be inactivated by moderate heat. The arrival of Asian cholera in 1831 made his work relevant and he devised a cheap and simple apparatus for disinfecting clothing and other items using heat.

Henry suffered from chronic ill health besides the neuralgic pains resulting from his injury during childhood. In the last months of his life, pain become so acute as to deprive him of sleep, and this drove him to suicide on September 2, 1836.

Scientific Activities

We will now discuss some of Henry's most relevant contributions, with particular emphasis on his work on the solubility of gases.

The Nature of Carbon. Henry's first paper [6] was a refutation of William Austin's claim that carbon was not an element [7]. Austin arrived at this conclusion by performing a series of experiments on "heavy inflammable air" that was later proved to consist of a "solution of pure coal in light inflammable air, in the new nomenclature, carbonated hydrogen gas (resulting from the decomposition of water in the presence of carbon)." In his experiments Austin passed an electrical current through the gas, pure or enriched with oxygen, and found that different amounts of oxygen were required for complete combustion. From this result he inferred that the "light inflammable gas disengaged by the electrization, proceeded from the decomposition of some substance within the influence of the electric fluid."

Henry analyzed the experimental procedure used by Austin and found it was at fault in that not enough oxygen was present to completely burn both the carbon and the hydrogen present. He then performed a series of experiments under different conditions and concluded that the electrical spark did not result in the decomposition of carbon, because the same amount was present before and after the spark. According to Henry, hydrogen did not arise from the decomposition of coal but from decomposed water. The oxygen from the decomposition of water combined afterwards with carbon to produce CO. His conclusion was that carbon should be considered as an "elementary body."

Decomposition of Hydrogen Chloride and Ammonia. In 1800 Henry reported his experiments on the decomposition of "muriatic acid gas" (HCl) [8]. This work is of particular importance because it recalls the state of chemical science before Davy's discoveries. This period was marked by preconceived ideas concerning the interpretation of facts. Oxygen was considered to be the sole contributor to acidity, and muriatic acid was supposed to be constituted of oxygen associated with an unknown radical. In order to detach this imaginary element from oxygen, Henry exposed the gas alone and the gas with gaseous matter possessing a strong affinity for oxygen to repeated electrical discharges. When muriatic acid gas was electrified alone over mercury, hydrogen was released and a white deposit (calomel) was collected. In the absence of mercury, chlorine was evolved. Because of the prevalent chemical thought, of which Henry was in favor, he assumed that the hydrogen was coming from the minute amounts of water present in the gas (although he had dried it very thoroughly before the experiment!). In 1809 Henry used the same experiment to resolve ammonia into its constituent gases [9].

Solubility of Gases in Water: Henry's Law. In December of 1802, Henry communicated to the Royal Society a paper entitled "Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures" [5] where he reported the number of cubic inches of gas [H₂, O₂, N₂, H₂S, CO, CO₂, PH₃, and carbureted hydrogen gas (methane)] absorbed by 100 in³ of water at 60 °F and 1 atm. For some of the gases, Henry gave an indication of the effect of temperature, for example, 100 volumes of water absorbed 108 volumes of CO₂ at 55 °F and 84 at 85 °F. The effect of

pressure was more significant. A series of more than 50 experiments at 1, 2, and 3 atm, with N₂O, O₂, N₂, H₂S, and CO₂, showed that "water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, etc. the volume absorbed under the common pressure of one atmosphere. . . ., for all practical purposes, I apprehend the law has been announced with sufficient accuracy" [5].

In his paper Henry did not express the results in a mathematical form, but if we assume ideal gas behavior and that water is incompressible, then his results indicate that

$$\frac{V_1}{22,400} = n_1 = k \frac{V_2}{18} P = kn_2 P \quad (1)$$

where the subscript 1 refers to the solute gas, the subscript 2 to the solvent, and k is a constant of proportionality that includes the various unit conversion factors. If the gases are assumed to be sparingly soluble then

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad (2)$$

and $x_2 = kP_2$, which is the common form of Henry's law.

To the credit of Henry, we must recall that at his time the concepts of molecule, mole, mole fraction, and Avogadro's number, did not exist or were not established.

A reading of Henry's paper gives a clear feeling of the care with which he performed his experiments and the extreme precautions he took to assure elimination of the air dissolved in the water (by long boiling), before dissolving the gas being tested. In addition, he describes with exquisite detail the changes in the equipment for gases of very low solubility. This is substantiated even more in an appendix that Henry published shortly after the original paper. In this appendix, he reported an improvement in the experimental technique and corrected some of his previous results [10].

The reader interested in the development of Henry's law using modern thermodynamics concepts should look at Appendix I.

Analysis of Gases. During Henry's time experiments on the use of coal gas for lighting purposes began; this encouraged Henry to start a very long research program on the properties of mixtures of flammable gases to determine their relative power of illumination and to explain any differences in terms of their composition. Eventually, Henry's results helped confirm Dalton's conclusions on the composition of methane and ethylene and also that carbon and hydrogen and combined only in definite proportions to form a limited number of compounds. In a paper published in 1824 [11], Henry discussed previous findings on the action of spongy platinum on combustible gases below their combustion temperature. Mixtures of hydrogen and oxygen ignited immediately, sometimes silently, sometimes with explosion, but mixtures of oxygen with gases like ethylene, methane, or NO did not react at all. Henry thought that this fact could be used as a tool for gas analysis and to separate the gases one from another. To test his idea he prepared synthetic mixtures of the combustible gases with oxygen and hydrogen in different compositions, and he subjected them to the action of spongy platinum at room and higher temperatures. The results at room temperature

confirmed his expectations, the gases reacted in a different form: CO was the most prone to react with oxygen, followed by ethylene and methane. By changing the proportion of hydrogen in the mixture, it was possible to convert CO completely to CO₂ without burning the ethylene or methane present. With mixtures of methane and CO it was possible to oxidize the latter completely without changing the amount of methane present. The effect of temperature was studied by immersing the glass retort, containing the gas mixture, in a bath of mercury that could be heated to the desired temperature. The results indicated, again, that each gas reacted at a different temperature. CO reacted between 300 and 310 °F, ethylene at 480 °F, NO did not burn at all, HCl at 250 °F, NH₃ at 380 °F, and so on. By combining all the experimental results, Henry was able to develop a quantitative method to analyze the mixtures of methane, ethylene, and CO obtained from coal distillation and used as illuminating gases.

An interesting corollary to this investigation was Henry's observation that certain gases (like CO and CO₂) have the property of "retarding the action of the platina sponge when added to an explosive mixture of hydrogen and oxygen." Today we know that CO and CO₂ adsorb preferentially on the platinum catalyst, thus poisoning it.

Studies on Disinfection. At a late stage in his career, Henry was approached by William Garnett, a leading importer of Egyptian cotton, to see if it was possible to develop a procedure to avoid the introduction of plagues by means of this material without incurring the cost attached to the quarantine laws related to cotton import into England. Chlorine had been once considered for this purpose and discarded because of its chemical activity on the fiber and the need for subsequent washing and drying of the cotton. Analysis of the various possibilities led Henry to suggest the use of heat, which should destroy any contagious virus and not injure the cotton [12]. He based his arguments on the fact that if the plague was present in the state of *fomites* (infectious matter existing in absorbent matter), it would be rendered innocuous by a temperature below that of boiling water, because it was known that plagues ceased as soon as the weather became hot. According to Henry, the *contagion* (the disease carrier) was different from any of the known gases, which were not affected by temperatures below 212 °F. They were probably of a complex nature and "owed their existence to affinities that are nicely balanced and easily disturbed."

Henry conducted a series of experiments in which cotton was exposed in a closed vessel (today, autoclave) to steam heat for two to three hours. The first results were very discouraging; the cotton suffered serious loss of its mechanical properties and was unfit for spinning. Surprisingly, if the treated cotton was left at room temperature for three days it recovered its original properties completely. Henry explained this result by the cotton recovering its equilibrium humidity, lost during the heat treatment. Additional experiments with delicate textures, fugitive colors, furs, and feathers yielded the same results. In order to test his hypothesis of the effect of heat on contagion by infectious diseases, he obtained from Dr. Robertson, a surgeon at Manchester's Hospital, vaccine lymph taken from pustules. The vaccine (treated and untreated) was injected into the arms of a group of healthy children (the Helsinki Protocols were yet to be approved!!) with very encouraging results, only the nonheated vaccine was efficient.

Henry ended this paper with a suggestion on how to build the closed vessel required for sterilization. Inspection of his design shows no difference with a modern sterilizing autoclave!

The arrival of Asian cholera at Sunderland in 1831 made his work topical and he reinstated his research in the subject of disinfection. In two following publications [13, 14], Henry extended his experiments using clothes taken from people affected with typhus and measles, found again that these could be disinfected without difficulty, and gave improved designs for a cheap autoclave. He reported that an equipment-manufacturing factory had quoted a price of 52 shilling (!) for a turnkey installation, which included the autoclave and the boiler for generating the steam.

Conclusion

Henry's life and scientific contributions is another example of overcoming physical handicaps and turning life into an enriching experience. Henry's contributions are numerous, but he is mostly remembered by the law carrying his name, which describes the solubility of gases. Although this law has been superseded by more exact relations, it is still a scientific landmark and an example of fine experimental work.

Appendix I

Henry's Law Using Modern Thermodynamic Concepts

Today, Henry's law can be derived without recourse to experiments and using only thermodynamic concepts. To do so, consider the Gibbs–Duhem equation for a binary system,

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0 \quad (3)$$

where \bar{M}_i is the partial property of the extensive property M . Let us consider that property M is the excess of the Gibbs energy, G^E , defined as

$$G^E \equiv G - G^{\text{id}}$$

where G and G^{id} are the actual and ideal values of G . Then

$$x_1 \frac{d\bar{G}_1^E}{dx_1} + x_2 \frac{d\bar{G}_2^E}{dx_1} = 0 \quad (4)$$

At infinite dilution of the solvent, $x_1 \rightarrow 0$ and $x_2 \rightarrow 1$, we have

$$\left(\frac{d\bar{G}_2^E}{dx_1} \right)_{x_1=0} = 0 \quad (5)$$

and at infinite solution of the solute ($x_1 \rightarrow 1$, $x_2 \rightarrow 0$)

$$\left(\frac{d\bar{G}_1^E}{dx_1} \right)_{x_2=0} = 0 \quad (6)$$

What is the meaning of these results? If we plot the functions $\bar{G}_1^E(x)$ and $\bar{G}_2^E(x)$, then each curve must converge to the value zero with slope zero as the concentration of the component approaches the unit value. Since $\bar{G}_i^E = RT \ln \gamma_i$ [15], where γ_i is the activity coefficient, we conclude that the activity coefficients must decrease (or increase) steadily to the value of 1 as the concentration of the particular component increases from infinite dilution to pure component. Now, if we remember that an ideal solution is defined by $\gamma_i = 1$ (Lewis–Randall law, [15]), then the results imply that as the solution becomes more and more concentrated in one component, it behaves more and more ideal with respect to it.

We now ask the question: if the solution tends to ideal behavior regarding the concentrated component, how does it behave regarding the diluted one? To answer this question we look at the Gibbs–Duhem equation again, this time written in terms of the activity coefficient

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (7)$$

Imposing the condition that $x_1 \rightarrow 1$, then

$$x_2 \frac{d \ln \gamma_2}{dx_1} \rightarrow 0 \quad (8)$$

or

$$x_2 \frac{d \ln \gamma_2}{dx_2} \rightarrow 0 \quad (9)$$

From the definition of the activity coefficient, γ_2 , we have

$$\gamma_2 = \frac{\hat{f}_2}{x_2 f_2^0} \quad (10)$$

where \hat{f}_2 is the fugacity of the component in the solution and f_2^0 is the reference state for the calculation of the fugacity. Taking the logarithm of eq 10 and differentiating with respect to x_2 we get

$$\begin{aligned} \frac{d \ln \gamma_2}{dx_2} &= \frac{d \ln \hat{f}_2}{dx_2} - \frac{1}{x_2} \\ x_2 \frac{d \ln \gamma_2}{dx_2} &= x_2 \frac{d \ln \hat{f}_2}{dx_2} - 1 \end{aligned} \quad (11)$$

For increasing dilution, $x_1 \rightarrow 1$ or $x_2 \rightarrow 0$ and

$$\begin{aligned} \lim [x_2 \frac{d \ln \hat{f}_2}{dx_2} - 1] &= 0 \\ (x_2 \rightarrow 0) \end{aligned} \quad (12)$$

$$\frac{d \ln \hat{f}_2}{d \ln x_2} = 1 \quad (13)$$

Integration of eq 13 yields

$$\hat{f}_2 = H_{2,1} x_2 \quad (14)$$

$$(x_2 \rightarrow 0)$$

Equation 14 is also known as Henry's law, and it indicates that at infinite dilution the fugacity of the solute (gas) is proportional to its concentration. The proportionality constant, $H_{2,1}$, is called Henry's constant, and its value will depend on the particular solute–solvent pair, the temperature, and the pressure. For the case of an ideal system, we would say that the solubility of a gas in a liquid is proportional to its partial pressure in the gas phase.

We can summarize our results as follows: In a concentrated solution the solution behaves like the Lewis–Randall law (ideal) for the concentrated component and like Henry's law for the diluted one.

Experience indicates that Henry's law is satisfied, in general, at very low concentrations ($x < 0.01$); at higher concentrations, the linear relationship given by eq 14 fails. Nevertheless, we can take care of this “nonideality” by introducing an activity coefficient (γ_2^*) that will correct the concentration to the required value

$$\hat{f}_2 = H_{2,1} \gamma_2^* x_2 \quad (15)$$

We should realize that this new activity coefficient is different from the usual one, defined by eq 10. This can be seen immediately if we consider that Henry's law is a special case of eq 15; the equation must be valid at infinite dilution of component 2, that is, γ_2^* must satisfy the condition $\gamma_2^* \rightarrow 1$ as $x_2 \rightarrow 0$ (whereas the usual activity coefficient, γ_2 , tends to unity as $x_2 \rightarrow 1$).

The relation between the two activity coefficients is easily found from the definition of γ_2 , eq 10. For physical equilibrium, it is advantageous to use as standard state of the pure component at the same pressure and temperature as that of the system; that is, $f_2^0 = f_2$, so that $\gamma_2 = \hat{f}_2 / x_2 f_2$. For infinite dilution we have

$$\lim \left(\frac{\hat{f}_2}{x_2} \right) = \lim (y_2 f_2) = \gamma_2^\infty f_2; \quad x_2 \rightarrow 0 \quad (16)$$

where γ_2^∞ is the activity coefficient of the solute at infinite dilution, based on the Lewis–Randall rule. But, from Henry's law

$$\lim \left(\frac{\hat{f}_2}{x_2} \right) = H_{2,1}; \quad x_2 \rightarrow 0 \quad (17)$$

so that

$$H_{2,1} = \gamma_2^\infty f_2 \quad (18)$$

and

$$\hat{f}_2 = \gamma_2 x_2 f_2 = H_{2,1} \gamma_2^* x_2 = \gamma_2^* x_2 \gamma_2^\infty f_2 \quad (19)$$

and finally

$$\gamma_2^* = \frac{\gamma_2}{\gamma_2^\infty} \quad (20)$$

As has been mentioned previously, the usual definition of Henry's law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas, but, even at obviously low partial pressures, some systems deviate significantly from this definition. Using classical thermodynamics, the strict Henry's law can be modified to account for the difference between the simple prediction and the experimental observations. As the pressure increases, nonidealities in the vapor must be accounted for by including fugacity coefficients. As the concentration of the solute increases, activity coefficients must be included to account for the nonidealities in the liquid. In addition, as the pressure increases, the Poynting term must be included to account for the effect of pressure on the liquid-phase reference fugacity. Additional complications may arise if the solvent contains other solutes such as gases, electrolytes, or nonelectrolytes.

Let us consider only the effect of pressure and temperature and see how it is possible to considerably extend the original Henry's law to higher-pressure ranges.

Effect of Pressure on Gas Solubility. The constant of proportionality, $H_{2,1}^{P_0}$, is not a function of composition, but depends on the temperature and, to a lesser degree, pressure. The pressure dependence can be neglected as long as the pressure is not high. At high pressures, however, the effect is not negligible; therefore, it is necessary to consider how $H_{2,1}$ depends on pressure. This dependence is easily obtained by using the exact equation [15]

$$\left(\frac{\partial \ln \hat{f}_2^L}{\partial P} \right)_T = \frac{\bar{v}_2^L}{RT} \quad (21)$$

where \bar{v}_2^L is the partial volume of component i in the liquid phase. Substitution of eq 14 into eq 21 gives

$$\left(\frac{\partial \ln H_{2,1}}{\partial P} \right)_T = \frac{\bar{v}_2^{L,\infty}}{RT}; \quad x_2 \rightarrow 0 \quad (22)$$

where $\bar{v}_2^{L,\infty}$ is the partial volume of solute i in the liquid phase at infinite dilution. Equation 22 can be integrated if we assume that the fugacity of the solute at constant pressure and temperature is proportional to the concentration, x_2

$$\ln \frac{\hat{f}_2}{x_2} = H_{2,1}^{P_0} + \frac{\int_{P_0}^P \bar{v}_2^{L,\infty} dP}{RT} \quad (23)$$

where $H_{2,1}^{P_0}$ is Henry's constant evaluated at some reference pressure, P_0 . The second term on the right hand side is known as Poynting's correction. As the solution becomes more and more diluted ($x_2 \rightarrow 0$), the total pressure approaches the vapor pressure of the solvent P_1^0 , and, thus, it is often convenient to use this value as P_0 .

If the temperature is well below the critical temperature of the solvent, it is reasonable to assume that $\bar{v}_2^{L,\infty}$ is independent of the pressure and eq 23 becomes

$$\ln \frac{\hat{f}_2}{x_2} = H_{2,1}^{P_0} + \frac{\bar{v}_2^{L,\infty} (P - P_1^0)}{RT} \quad (24)$$

Equation 24 is known as the Krichevsky–Kasarnovsky equation [16], and it is very useful for representing the solubility of sparingly soluble gases ($x < 0.01$) to very high pressures. The structure of the equation indicates that in the range of existence it will plot as a straight line in a semilog plot of \hat{f}_2/x_2 against the pressure, with a slope of $\bar{v}_2^{L,\infty}$ and an intercept of $H_{2,1}^{P_0}$.

The Krichevsky–Kasarnovsky equation can be used to demonstrate the experimental fact that the solubility of a gas may go through a maximum as the pressure is increased. To illustrate this phenomenon, let us consider the particular case of a slightly soluble gas in a solvent with negligible vapor pressure. Differentiating eq 24 with respect to the pressure at constant temperature we have

$$\left(\frac{\partial \ln \hat{f}_2}{\partial P} - \frac{\partial \ln x_2}{\partial P} \right)_T = \frac{\bar{v}_2^{L,\infty}}{RT} \quad (25)$$

if we assume the liquid to be incompressible, then, for the situation in question, we can make the approximations $\hat{f}_2 \approx f_2$ and

$$\left(\frac{\partial \ln \hat{f}_2}{\partial P} \right)_P \approx \left(\frac{\partial \ln f_2}{\partial P} \right)_P = \frac{v^L}{RT} \quad (26)$$

so that the solubility will achieve a maximum value when

$$v^L = \bar{v}_2^L \quad (27)$$

Effect of Temperature on Gas Solubility. The question of how temperature affects the solubility of a gas has yet to be answered in a quantitative form. The experimental evidence indicates that an increase in temperature may result in larger or smaller solubility, depending on the pressure and the nature of the solute–solvent pair. For example, at atmospheric pressure the solubility of hydrogen sulfide in water passes through a

minimum at about 450 K [17]. Since Henry's first observations, many have tried to tackle the problem with only partial success. For example, Robert Bunsen (1811–1899) in his paper "The Law of Absorption of Gases" [18] stated clearly that "gases are absorbed in liquids on which they exert no chemical reaction, in quantities that depend upon the nature of the gas and the liquid, the temperature, and the pressure." He defined the absorption coefficient, α , as the volume of gas at STP that is absorbed by the unit of volume of the liquid. The parameter α is known today as the Bunsen absorption coefficient. Later, Körösy [19] pointed out that it was commonly supposed that all gases show a decrease in solubility with rise in temperature, but that the experimental data that appear in the Landolt–Börstein tables show that this is not so. Körösy claimed that the temperature coefficient of solubility was a function of the cohesive forces (expressed as the critical temperature), and that all gases with low critical temperatures and small solubilities have a positive temperature coefficient. In addition, Körösy affirmed that gases having a critical temperature above 180 K have a negative coefficient. The only exception he found to his rules was water as a solvent, in which all gases, even helium, show a negative coefficient.

Burrows and Pierce [20] believed that it is difficult to draw any general conclusion about the solubility of gases, and they refer, especially, to the difficulty concerning the negative and positive temperature coefficient of solubility. They postulated a similarity between the evolution of a gas from a liquid and the evaporation of vapor from a pure liquid. According to Burrows and Pierce, the solution process can be regarded as consisting of the main stages: (a) formation of a cavity in the liquid to accommodate the gas molecule, which requires an amount of energy, ΔE_C , and (b) the interaction energy change between the gas and the solvent, which has an energy of ΔE_A , denoting the energy liberated by putting the gas into the cavity, that is, the interaction energy. Now, if $-\Delta E_A > \Delta E_C$, the temperature coefficient tends to be negative, and if $\Delta E_C > -\Delta E_A$, it may be positive. Their calculations also indicated that the values of $-\Delta E_A$ depend mainly on the kind of gas molecule and less on variations in the liquid. For the liquids they compared, $-\Delta E_A$ at room temperature varied from 2.15 to 1.62 kcal for nitrogen and from 1.65 to 1.40 kcal for oxygen.

Jolley and Hildebrand [21] concluded that the temperature dependence of the solubility depended on the sign of the entropy of solution, and they claimed that the entropy of solution is positive for any gas for which $x_2 < 10^{-3}$, and vice versa. A positive entropy of solution means that the solubility increases with temperature.

The effect of temperature on the solubility of gases has been recently analyzed in depth by Wisniak et al. [22] using the displacement theory of Malesinski [23]. We will repeat here only the basic ideas.

Starting from the condition for phase equilibrium,

$$\mu_i^V(P, T, y_2) = \mu_i^L(P, T, x_2) \quad (28)$$

and the Maxwell relations, it is possible to derive the following exact equation that describes the variation of the liquid concentration with temperature at constant pressure

$$\left(\frac{\partial x_2}{\partial T}\right)_P = -\frac{y_1 \Delta \bar{H}_1 + y_2 \Delta \bar{H}_2}{T(y_2 - x_2)} + \left(\frac{\partial^2 g^L}{\partial x_2^2}\right)_{P,T} \quad (29)$$

Let us now apply this equation to the case of a supercritical gas dissolved in a nonvolatile solvent assuming that the gas is sparingly soluble in the liquid. For this situation we have $y_2 = 1$ and $x_2 = 0$, and eq 29 becomes, approximately

$$\left(\frac{\partial x_2}{\partial T}\right)_P \approx -\frac{\Delta \bar{H}_2}{T} + \left(\frac{\partial^2 g^L}{\partial x_2^2}\right)_{P,T} \quad (30)$$

The second derivative, $(\partial^2 g^L / \partial x_2^2)_{P,T}$, is always positive because it represents the condition for phase stability; hence, the sign of the left-hand side of eq 30 will depend on the sign of the partial heat of vaporization, $\Delta \bar{H}_2$. Now, for all fluids below their critical temperature, $\Delta \bar{H}_2$ is positive, heat must be absorbed in going from the liquid to the vapor phase. What happens when the temperature is larger than the critical temperature? The experimental evidence indicates that $\Delta \bar{H}_2$ is positive near the critical temperature as long as the pressure is less than the critical pressure. Eventually, at high enough temperatures, $\Delta \bar{H}_2$ become negative. We can summarize all these facts by saying that the solubility of a gas will increase with temperature when it is well above its critical temperature, and for all other cases the solubility will decrease.

Effect of Nonideality of the Solution. To the first approximation, we can assume that the liquid phase behaves like a regular solution where [15]

$$\ln \gamma_2^* = \frac{A}{RT} (x_1^2 - 1) \quad (31)$$

The fugacity of the solute at the vapor pressure of the solvent, P_1^0 , is given by eq 25 so that eq 32 becomes

$$\ln \frac{\hat{f}_2}{x_2} = \ln H_{2,1}^{P_1^0} + \frac{A}{RT} (x_1^2 - 1) + \frac{\bar{v}_2^\infty (P - P_1^0)}{RT} \quad (32)$$

if again we assume that \bar{v}_2^∞ is independent of the pressure and composition.

Equation 32 is known as the Krichevsky–Il'inskaya equation [24] and has a wider application than eq 23 ($x < 0.1$), particularly for solutions of light gases, like hydrogen and helium in liquid solvents, where the solubility is appreciable.

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