A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest

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The Henry's law constants (air-water partition coefficients) of hydrophobic organic compounds of environmental concern are reviewed. An outline of the thermodynamic principles which govern the relationships between vapor pressure, solubility and Henry's law constant for solid and liquid compounds is presented and experimental techniques for obtaining these quantities with the required accuracy are discussed. Vapor pressure, solubility, and Henry's law constant data are tabulated and reviewed for a total of 150 compounds in 12 tables consisting of gaseous, liquid and solid alkanes, cycloalkanes, alkenes, alkynes, monoaromatics, polynuclear aromatics, halogenated alkanes, alkenes and aromatics, and selected pesticides.

Key words: Alkanes; aromatics; critical review, evaluated data; gases; halogenated hydrocarbons; Henry's law constants; liquids; pesticides, solids; solubility; vapor pressure.

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1. Introduction

1.1. Background

For elucidating the environmental dynamics of many natural and anthropogenic compounds, it is essential to have reliable data for the compounds' air-water partition coefficient or Henry's law constant. When a compound (here referred to as the solute) is introduced into the environment, it tends to diffuse from phase to phase in the direction towards establishing equilibrium between all phases. Frequently, the physical-chemical properties of the solute dictate that it will partition predominantly into a different phase from the one into which it is normally emitted. For example, benzene emitted in waste water will tend to partition or transfer from that water into the atmosphere where it becomes subject to atmospheric photolytic degradation processes. Sulfur dioxide is normally emitted into the atmosphere and undergoes the reverse process of deposition into water bodies. A knowledge of the air-water partition characteristics of a solute is thus important for elucidating where the solute will tend to accumulate and also in calculating the rates of transfer between phases. Conventionally these rates are expressed as the product of a kinetic constant such as a mass transfer coefficient (or diffusivity divided by a diffusion path length) and the degree of departure from equilibrium which exists between the two phases. Elucidating the direction and rate of transfer of such solutes thus requires accurate values for the Henry's law constant.

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The objective of this review is to provide first a detailed account of the physical chemical principles which underlie the Henry's law constant, demonstrating that it can be deduced from either appropriate (and independent) measurements of solubility and vapor pressure or by direct or indirect measurement of equilibrium concentrations.

This review clarifies the relationships between the several forms in which air-water partition data are recorded, including Henry's law constants, partition coefficients on a mass/volume basis, Bunsen coefficients, Ostwald coefficients, and even relative volatilities.

Techniques for measurement of these quantities are reviewed with particular emphasis on the error limits. An awareness of likely errors in reported data is particularly important since many compounds of environmental interest have high molecular weights, low vapor pressures, and are sparingly soluble. Accurate determination of vapor pressure and solubility are thus experimentally difficult and regrettably many reported data contain a substantial error thus leading to highly inaccurate estimates of environmental transport rates and even directions.

Finally, a compilation of critically reviewed data is presented for hydrophobic organic compounds, principally hydrocarbons and halogenated hydrocarbons. These data were obtained from a search of the literature through 1979 using Chemical Abstracts. Organic compounds with alcohol, phenol, carboxyl, carboxylic, nitrogen, phosphorus and sulfur groups and ionizing species were generally excluded, with the exception of some pesticides. Their exclusion does not imply any lack of environmental significance, rather it implies that volatilization from water is judged to be a less significant environmental process than other processes such as oxidation, hydrolysis, or biodegradation. Since the purpose of this review is to assist the elucidation of environmental processes, emphasis is on data relevant to environmental temperatures and pressures. Many data for high temperature or pressure conditions as may occur in chemical processes are thus not included.

1.2. Format

The units of aqueous concentration used are g/m^3 or mol/m^3. Although concentrations are frequently expressed in mg/liter (which is numerically equal to g/m^3) or as molarities, i.e., mol/liter or mol/dm^3, these forms have been avoided here since in environmental fate calculations or models dimensions are best expressed in meters. Pressures are expressed as Pa rather than atm or mm Hg. The gas constant R is thus 8.314 Pa m^3/mol K or the identical J/mol K. Henry's law constants, which are a ratio of pressure to concentration, may thus have units of $Pa/(mol/m^3)$ or Pa m^3/mol or the identical J/mol. This latter form, although simpler and more fundamental is conceptually less convenient since the units of pressure and concentration are not expressed directly and may not therefore be immediately clear to the user.

2. Thermodynamic Basis

2.1. Fundamental Equilibrium Expressions

If a solute is present in air and water phases at equilibrium and at constant temperature and pressure, then the solute's chemical potential or fugacity is equal in both phases. In the following analysis the fugacity approach used by Prausnitz [1][1] is used.

$$f = y\phi p_T$$

where y is the solute mole fraction in the air phase, ϕ is the fugacity coefficient and p_T is the total pressure (Pa), usually atmospheric pressure of 101.3 kPa in environmental applications. The fugacity coefficient ϕ characterizes the degree of "non-ideality" of the solute in the air phase. Normally it is close to unity in value, the exceptions being situations in which the solute associates (as occurs with carboxylic acids) or at high gas densities. An estimate of the magnitude of ϕ can be obtained from data or correlations for the second virial coefficient of the solute in air following the procedures described by Prausnitz [1] or Reid *et al.* [2]. For all the compounds considered here at environmental pressures, ϕ is negligibly different from unity and can thus be ignored. The fugacity thus becomes equal to the solute partial pressure p(Pa) which is the product of mole fraction and total pressure.

In the water phase the fugacity is given by

$$f = x\gamma f_r$$

where x is the mole fraction in the water phase, γ is the activity coefficient (which characterizes the degree of non-ideality between water and the solute) expressed on a Raoult's law convention such that by definition γ becomes unity when x is unity. This contrasts with the opposite convention in which γ is unity at infinite dilution, i.e., when x is zero. The reference fugacity f_r (Pa) is then the fugacity exerted by the solute when pure and in the liquid state at the system temperature. At environmental pressures this reference fugacity can be assumed to equal the vapor pressure of the liquid.

In two situations this reference fugacity becomes hypothetical and is thus not directly accessible experimentally. When the solute critical temperature is below the system temperature (as occurs with methane which has a critical temperature of 190.6 K [2]) no vapor pressure can be measured although a hypothetical value can be assigned. Second, when the solute's triple or melting point exceeds the system temperature only the solid vapor is accessible (as occurs with anthracene with a melting point of 489 K). Again a hypothetical sub-cooled liquid vapor pressure can be calculated and assigned from a knowledge of the compound's thermal properties. A useful approximation for estimating the ratio of solid fugacity (f_s) to liquid or reference fugacity (f_r) is given by Prausnitz [1] as

$$\ln(f_s/f_r) = -\Delta S((T_M/T) - 1)/R \qquad (1)$$

where ΔS is the entropy of fusion (J/mol K), R is the gas constant (8.31 J/mol K), T_M is the normal melting point and T is the system temperature (K). Yalkowsky has shown that many organic compounds have entropies of fusion of approximately 56 J/mol K [3] thus this relationship simplifies at a temperature T of 298 K to approximately

$$\ln(f_s/f_r) = -0.023(T_M - 298)$$

the error introduced by assuming this equation to apply is often small compared to the experimental error in measuring solubility, vapor pressure or Henry's law constant.

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[1] Figures in brackets indicate literature references at the end of this paper.

The principal determinant of the water phase fugacity (and the principal source of its error) is the activity coefficient γ. There is no reliable method of calculating γ from a knowledge of molecular structure and the only source of data is experimental measurement, usually of aqueous solubility. Activity coefficients of hydrophobic organics expressed on a Raoult's law convention can become very high, for example millions, as is illustrated later. Several attempts have been made to correlate γ with molecular structure or other physical properties. Notable among these attempts are those of Yalkowsky and Valvani [4] using total molecular surface area, Leinonen et al. [5] using molar volume, Mackay and Shiu [6], Tsonopolous and Prausnitz [7], and Kabadi and Danner [8] using carbon number. A satisfactory degree of correlation is often found between γ and such properties for a homologous series. Another approach is the "group contribution" method developed by Derr and Deal and the UNIFAC method both of which are reviewed by Reid et al. [2].

Such correlations are invaluable as a means of estimating γ for compounds for which no data exist and for checking the "reasonableness" of other data.

Values of γ are most easily obtained from solubility measurements. For a liquid solute in equilibrium with its aqueous solution, equating fugacities yields

$$x_L \gamma_L f_r = x_W \gamma_W f_r$$

where subscripts L and W refer to the liquid and the water solution phases, respectively. If the solubility of water in the liquid solute is negligible then x_L and γ_L become unity, thus x_W the mole fraction solubility is simply the reciprocal of γ_W. At high dilutions (i.e., $x_W < < 1$), γ_W can be assumed to be constant since its logarithm normally varies approximately in proportion to $(1 - x_W)^2$ which is essentially constant at low values of x_W.

For solid solutes if the water does not affect the solid phase fugacity

$$f_s = x_W \gamma_W f_r, \quad \text{thus} \quad x_W = f_s / f_r \gamma_W.$$

A knowledge of (f_s / f_r) is thus necessary to calculate γ_W from the solubility x_W. It is noteworthy that since f_s / f_r is always less than unity below the melting point, the solubility of a solid solute is invariably lower than that of a liquid solute of similar γ_W. Low solubilities thus result from high values of γ_W (i.e., high hydrophobicity) and high melting points which cause low f_s / f_r ratios.

For gaseous solutes above the critical point the conventional approaches are either to extrapolate the vapor pressure beyond the critical point to estimate f_r, or to lump f_r and γ in a single term which is a form of Henry's law constant (H_M Pa) expressed as a ratio of partial pressure p(Pa) to mole fraction, i.e.,

$$p \simeq f = x\gamma f_r = xH_M, \text{ where } H_M = \gamma f_r.$$

The various forms in which gas solubilities or Henry's law constants can be expressed can be shown to be fundamentally traceable to the quantities introduced above, especially activity coefficient (γ) and vapor pressure.

2.2. Forms of Expressing Air-Water Partition Data

a. Henry's Law Constants

The Henry's law constant is conventionally expressed as a ratio of partial pressure in the vapor (in various units such as Pa, atm, or torr) to the concentration in the liquid (also in various units such as mole fraction and mass or mole concentration or ratio). The most commonly used measures of concentration are mole fraction (x) and amount-of-substance concentration (c, expressed in mol/m^3) which yield either

$$p = H_M x \text{ in which } H_M \text{ has units Pa}$$
$$= H_c c \text{ in which } H_c \text{ has units Pa m}^3/\text{mol}.$$

Comparison of these equations with the fugacity equations shows that H_M is equivalent to $(\gamma_W f_r)$. The mole fraction x is related to c since x is the ratio c/c_S where c_S is the total number of moles of solute and water per m^3 of solution. At low concentration of solute c_S is essentially the molar concentration of water in solution or the reciprocal of the molar volume v_W which is 18×10^{-6} m^3/mol, thus $x \simeq v_W c$. The Henry's law constant H_c or p/c is thus $(v_W \gamma_W f_r)$ or $(v_W H_M)$.

Both constants are strongly temperature dependent because of the temperature dependencies of f_r (or vapor pressure) and of solubility. H_c is also slightly dependent on the temperature dependence of water density and hence molar volume. Both constants may be concentration dependent because of variations in γ_W although the effect is believed to be negligible at low concentrations of non-associating solutes. It should be noted that these simple relationships break down at high concentrations, i.e., at mole fractions in excess of 0.01. For most environmental situations the concentrations are (fortunately) usually much lower. For thermodynamic purposes H_M is usually preferred whereas for environmental purposes H_c is more convenient.

It should be noted that the frequently quoted expression for H_c as the ratio of solute vapor pressure to solubility is valid only for solutes with a low water mixibility. When the solubility of water in the solute becomes large, i.e., greater than a few percent, the solute vapor pressure or fugacity exerted is less than that of the pure solute because of its dilution by water. To a first approximation the vapor pressure can be estimated to be $f_r(1 - w)$ where w is the mole fraction solubility of water in the liquid state. This effect may be appreciable for solutes such as alcohols.

b. Partition Coefficients or Concentration Ratios

It is often convenient to express air-water partitioning directly as a dimensionless ratio of concentrations K_{AW}, for example the ratio c_A / c_W with both quantities expressed in mol/m^3. The value of K_{AW} is independent of the units used provided that consistent mass or mole units per unit of volume are used in both phases. Invoking the ideal gas law shows that c_A is equivalent to p/RT thus K_{AW} is equivalent to H_c/RT. Since RT normally ranges in value from 2200 to 2500 Pa m^3/mol at environmental conditions, the implication is that a compound with values of H_c in this range will partition between air and water at equal concentrations.

c. Relative Volatility

In estimating whether or not a compound will increase or decrease in water concentration on exposure to the atmosphere it is convenient to examine its relatively volatility with respect to water. The relative volatility α is usually expressed as

$$\alpha = y(1-x)/x(1-y)$$

where x and y are the mole fractions in liquid and vapor phases of the more volatile component, here of the solute. When x and y are small compared to unity, i.e., the solution in water and air are dilute, α becomes y/x and thus $(\gamma f_r/p_T)$ or (H_M/p_T) or $(H_c/p_T v_W)$.

Considering first for simplicity an air-free system, the total pressure p_T is essentially the water vapor pressure p_W. The Henry's law constant H_c for water between pure water and its vapor is $p_W v_W$ since the concentration of pure water is $(1/v_W)$. It follows that α is thus simply the ratio of H_c for the solute to H_c for the water. Volatilization of solute and water simultaneously will result in a decrease in liquid concentration of the solute if α exceeds unity, i.e., H_c exceeds $p_W v_W$. Compounds which have H_c values less than $p_W v_W$ will thus tend to become more concentrated in the liquid phase due to faster volatilization of water in the environment.

The presence of dry air does not alter this deduction because air does not affect the fugacities, it merely increases p_T and correspondingly reduces the vapor mole fractions. Volatilization in the presence of humid air is more complex since the presence of water vapor reduces or prevents water evaporation but does not affect solute evaporation.

For many solutes of environmental interest, solute-water vapor liquid equilibrium data and predictive methods are available either to give α or the equivalent $(\gamma f_r/p_W)$ with f_r usually being the liquid solute vapor pressure. This form of equation is interesting because it illustrates that compounds such as DDT which have very low vapor pressures (i.e., f_r) compared to water (p_W) may still have high relative volatilities with respect to water because of the large value of γ, corresponding to the high hydrophobicity. This was first noted by Mackay and Wolkoff [9] and was previously wrongly attributed to a "codistillation" phenomenon.

d. Bunsen and Ostwald Coefficients

Gas solubilities are often expressed as the Bunsen or absorption coefficient which is the volume of gas (at 0 °C and 1 atm) in liters which is dissolved in 1 liter of water, or the Ostwald coefficient in which the volume is expressed at the system temperature and the solute partial pressure. The Ostwald coefficient can be shown to be the reciprocal of the air-water partition coefficient K_{AW} and thus RT/H_c. The Bunsen coefficient is thus $273\,R/H_c$.

e. Other Systems

Solubilities of solute gases such as ammonia or sulfur dioxide are usually expressed as mass dissolved per unit mass of water at some defined partial pressure. Freid and Adler [10] have reviewed these systems in more detail.

3. Experimental Techniques

3.1. Required Environmental Accuracy

It is first useful to examine the accuracy which is required in the Henry's law constant (referred to in this section as H) for environmental assessment purposes. Two environmental questions can be posed which require H data; (i) "in which direction is the solute diffusing?"; and (ii) "how fast is it diffusing?". Both questions require data on the ambient values of concentration in the water and the atmosphere. These concentrations tend to fluctuate in time and space as source strengths vary (diurnally, or with industrial production changes, periodic accidental releases or in the case of pesticides with periodic application). They also vary as a result of changing atmospheric and aquatic advection and degradation rates. For example, a hydrocarbon may photolyze rapidly on a hot sunny day but slowly during cold cloudy weather. Precipitation (rain, snow, or dustfall) may scavenge the solute from the atmosphere and analogous processes may occur in the water column. The net result of these processes is that only in cases such as CO_2 or CH_4 where the solute is present in consistently high and thus "buffered" concentrations as a result of very slow or non-existent degradation it is possible to establish concentrations with an accuracy (expressed as a standard deviation) of better than 5 to 10% of the prevailing average.

Accordingly, a reasonable target for H could be that its error contribute no more than an additional one tenth to the existing error, thus implying an accuracy on the order of 1%. This is certainly attainable with current techniques for all but the most sparingly soluble and involatile solutes. Clearly, in cases where there exists near-equilibrium conditions between water and atmosphere high accuracy in H is desirable. This occurs usually for natural solutes such as CO_2 or CH_4 rather than anthropogenic solutes and the most important application is to air-sea equilibria rather than aquatic (fresh water) systems which are more variable and more contaminated. The general conclusion is that for certain specific solutes, principally natural in origin, which have reached near-equilibrium conditions, the required accuracy in H is approximately 1%, and usually the critical data needed are for salt water rather than fresh water.

Most anthropogenic solutes present a different situation in that the direction of transfer is clear and the problem is to estimate the rate of the volatilization or absorption process. It is useful to examine the structure of the rate equations to elucidate the sensitivity of the rate to H.

Application of the two resistance model [11] of inter-phase transfer yields the equation for mass flux N (mol/m^2·s) in terms of the liquid and vapor phase mass transfer coefficients (k_L and k_G m/s, respectively) and the ambient concentration as,

$$N = (c - p/H)\{1/(1/k_L + RT/Hk_G)\}.$$

It is instructive to obtain the derivative of N with respect to H (i.e., dN/dH) and thus the fractional change in N arising from a fractional change in H, namely,

$$(\mathrm{d}N/N)(\mathrm{d}H/H) = (\mathrm{d}N/\mathrm{d}H)(H/N) = \frac{(c - pk_{\mathrm{G}}/RTk_{\mathrm{L}})}{(c - p/H)(1 + Hk_{\mathrm{G}}/RTk_{\mathrm{L}})}.$$

Under normal environmental conditions k_{G} has a value of approximately 0.01 m/s and k_{L} a value of 0.00005 m/s [11] thus the group $(k_{\mathrm{G}}/RTk_{\mathrm{L}})$ is typically 0.083 mol/m^{3}Pa, thus

$$(\mathrm{d}N/\mathrm{d}H)(H/N) \approx (c - 0.083p)/\{(c - p/H)(1 + 0.083H)\}.$$

When the solute is volatilizing into an atmosphere in which p is negligible this reduces to $1/(1 + 0.083H)$. When H is large, for example, greater than 100 Pa m^3/mol this quantity becomes very small implying that N is insensitive to errors in H. In the limit as H approaches infinity N becomes $k_{\mathrm{L}}c$ and is independent of H. The physical reason is that the flux becomes entirely controlled by the liquid phase diffusion rate which is unaffected by H. When H is small, for example, less than 1.0 Pa m^3/mol, N becomes almost proportionately sensitive to H, i.e., a 10% error in H causes a 10% error in N. This is the gas phase diffusion control regime in which N approaches $Hk_{\mathrm{G}}c/RT$. In the intermediate regime when H lies between 1 and 100 Pa m^3/mol the sensitivity of N to H varies between these limits and there is diffusive resistance in both phases.

The conclusion is that if H exceeds 100 Pa m^3/mol there is usually no need for high accuracy (for environmental purposes) but as H falls to 1.0 Pa m^3/mol the error in H becomes directly reflected in N. In environmental calculations of flux the principal source of error (apart from c) is the mass transfer coefficients which are probably subject to an error of a factor of at least 1.5 and in many cases considerably more. There is even greater doubt about the transfer coefficients applicable to large lakes, for example it has been recently suggested that published k_{L} values based on laboratory determinations may greatly overestimate transfer rates [12]. Given this present uncertainty in k_{L} and k_{G} and speculating that these quantities will become more accurately predictable in the future, a reasonable target for the standard error in H (for environmental purposes) is 5% and certainly less than 10%. Although a higher degree of accuracy is inherently desirable it is unlikely that models of environmental transport of chemical substances will ever achieve a level of accuracy greater than 10%.

If p is not negligible the sensitivity in N becomes inversely proportional to $(c - p/H)$ implying that when near equilibrium conditions prevail and this group approaches zero, N becomes very sensitive to errors in H. Fortunately such cases occur rarely and in any event N tends to be small thus a relatively high percentage error may be tolerable.

3.2. Methods and Accuracy of Determination

There are, in principle, three methods of obtaining H data: (i) from the ratio of vapor pressure and solubility, these quantities being measured independently, (ii) by direct measurement of p and c in a system at equilibrium, and (iii) by measurement of p or c during an equilibrium air-water-exchange process.

The first method is subject to the error discussed earlier in section 2 when the solubility of the solute in water (or water in the solute) exceeds a mole fraction of a few percent but it is satisfactorily accurate for less soluble compounds. The overall variance in H is essentially the sum of the variances in the vapor pressure and solubility determinations, which are discussed later.

The second method is usually applied only to fairly high concentrations because of the difficulty of sampling and analyzing the absolute values of the low concentrations in both phases. Such concentrations rarely apply environmentally thus there is a danger that error may be introduced by the concentration dependence of H. This method tends to be used for more soluble solutes such as CO_2 or SO_2 or gases at higher pressures but not for hydrophobic organic compounds of concern here. The error in H arises from the combined errors in the absolute concentration or pressure measurements. A precise and rapid method of this type has been described by Rivas and Prausnitz [13].

The third method developed by Mackay et al. [14] requires only measurement of relative (not absolute) concentration changes in one phase thus it is inherently simpler and potentially more accurate. In principle the method involves passing a gas stream through a vessel containing the dissolved solute under conditions such that near equilibrium is reached. The falling liquid concentration is measured. The value of H is obtained from the slope of a semilogarithmic plot of concentration versus time and requires a knowledge of the gas flow rate, liquid volume, temperature, and assurance that equilibrium is reached. With care, the standard error in H is judged by the authors to be less than 5% but with very sparingly soluble compounds which tend to sorb on vessel walls 10 to 15% is more realistic. This is sufficiently accurate for environmental purposes since such compounds will also display this sorptive behavior in aquatic systems thus depressing volatilization rates. The principal merit of this approach is that it is readily applicable to compounds of very low solubility and vapor pressure thus neither of these measurements is necessary.

3.3. Aqueous Solubility

The measurement of aqueous solubility of hydrophobic compounds is very difficult and it is only in recent years that accurate values have been established. Unfortunately many inaccurate data have been reported. For example, the Handbook of Chemistry and Physics (Hodgman [15]) quotes the aqueous solubility of benzene as 800 g/m^3 whereas the accepted value is 1770 to 1780 g/m^3. The advent of gas chromatography and later liquid chromatography has permitted accurate solubilities to be determined in the part per million and part per billion range. Notable was the early work of McAuliffe [16] whose measurements of the solubilities of lower hydrocarbons down to 1 g/m^3 (ppm) have proved to be reliable. Preparation of saturated solutions below 1 g/m^3 is difficult because of sorption on glassware and inadvertant formation of colloidal solute particles during dissolution. Neither filtering or centrifuging are entirely satifactory methods of overcoming these difficulties.

It is generally accepted that the most accurate technique of solubility determination for sparingly soluble solid hydrophobic compounds is the use of generator column as first developed by May et al. [17,18].

The precision of this method is judged to be better than 3% which is entirely adequate for environmental purposes. The principle of the method is that a measured flow of water is passed through a column containing glass beads coated with the solute to achieve saturation, the dissolved solute then being extracted in a short packed column with a suitable stationary phase. After extraction of a known volume of water the solute is eluted on to a liquid chromatographic column and analyzed by *UV* spectrophotometry.

Most solubility data are reported at 25 °C and there is a lack of reliable temperature coefficient (i.e., enthalpy of solution) data. The importance of such data is illustrated by the work of Schwartz [19] who has shown that the enthalpies of solution of polycyclic aromatic hydrocarbons vary from 14 kJ/mol for 1-ethylnaphthalene to 48 kJ/mol for pyrene. A typical enthalpy of solution of 35 kJ/mol implies a doubling of solubility between 10 °C and 24 °C which is clearly a significant variation even for environmental purposes.

3.4. Vapor Pressure

A similar situation exists for vapor pressure data. Accurate measurements have been possible for many years using standard isoteniscopic techniques which are applicable down to approximately 1 mm Hg or 100 Pa. Most of these data are published in the form of correlation equations such as the Antoine equation with three constants A, B, and C,

$$\log p = A - B/(T + C),$$

or the Clapeyron equation which omits the constant C and is applicable only over narrower temperature ranges in which the enthalpy of vaporization is relatively constant. Again highly erroneous data have been reported, for example, Spencer et al. [20] quote previously reported vapor pressures for ethyl parathion varying by a factor of over eight. It is difficult to estimate the accuracy of much published data since the values reported are usually the fitted data or the regression constants. The largest single compilation of this type is the several American Petroleum Institute Research Projects hydrocarbons and related compounds, for example Zwolinski and Wilhoit [21]. The accuracy of these published values is certainly adequate for environmental purposes but other compilations may have been prepared with less rigor.

The preferred experimental technique for determination of low vapor pressures is similar in principle to that of the "generator column" solubility technique except that a gas stream is saturated with solute. Methods have been described by Spencer and Cliath [22], Sinke [23], and Macknick and Prausnitz [24] in which a standard error better than 3% is attainable which is clearly adequate for environmental purposes.

Again it is desirable to have data over a range of temperatures as may apply environmentally. The temperature coefficient (enthalpy of vaporization) is typically 45 kJ/mol thus the vapor pressure may double from 10 to 20 °C necessitating accurate environmental temperature data. Since solubility also increases with temperature (but usually more slowly) the net effect may be an approximately 10 kJ/mol enthalpy of volatilization effect on H, i.e., a doubling in H between 10 °C and 65 °C but this effect is very solute-specific and no generalization is possible.

4. Literature Data Review

4.1. Introduction

For convenience, the compounds are categorized into alkanes, cycloalkanes, aromatics, polynuclear aromatics, halogenated hydrocarbons, and pesticides. Tabulated data are presented for each category, there being a further subdivision into compounds which are gaseous, liquid, and solid at environmental temperatures. In all cases the vapor pressures and solubilities are at 25 °C unless otherwise stated. Melting points and boiling points are given for each compound, the values being taken directly from the Handbook of Chemisry and Physics (Weast, [25]). These values are presented largely to indicate the phase transition temperatures and are not critically reviewed. In most cases an accurate value is not required since these temperatures do not enter into the calculation of H. The exception occurs when a fugacity ratio is calculated to estimate liquid from solid vapor pressures as is discussed later.

For solid compounds the solubility reported is usually that of the solid whereas the vapor pressure may be that of the subcooled liquid, estimated by extrapolation below the melting point. In such cases it is essential to estimate and use the solid vapor pressure to estimate H. This estimation introduces an error of extrapolation. The approach adopted is to use vapor pressure data obtained by one of the following methods which are listed in decreasing order of preference, i.e., with decreasing perceived accuracy.

First are data obtained in the relevant temperature range and reported either as experimental values or regression coefficients.

Second are data obtained by extrapolation using the reported regression equation, there being no phase changed involved.

Third are data for solids obtained from the extrapolated liquid vapor pressure and application of the fugacity ratio $f_s/f_r = \exp(-0.023(T_M - 298))$ as described earlier where T_M is the melting point (K).

Fourth are data for solids obtained from the liquid boiling point assuming Trouton's Rule to apply, to give a constant enthalpy of vaporization and application of the fugacity ratio f_s/f_r.

In this last case the enthalpy of vaporization ΔH^v is assumed to be 88.6 T_B J/mol where T_B is the normal boiling point. Applying the Clapeyron equation between T_B at which the vapor pressure is 101 kPa and 298 K at which the vapor pressure is p kPa yields

$$\ln(p/101) = 88.6T_B(1/298 - 1/T_B)/R$$

which, since the gas constant R has a value of 8.31 J/mol K, becomes

$$\ln(p/101) = -0.036(T_B - 298)$$

The fugacity ratio expression can then be used to convert p (or f_r) to the solid vapor pressure f_s yielding in total

$$\ln(f_s/101) = -0.036(T_B - 298) - 0.023(T_M - 298).$$

It is recognized that the constants in this equation vary with molecular configuration but in the absence of more accurate data, this simple correlation is applied, unfortunately, to all compounds.

Footnotes indicating which assumption applies are included. Error limits are widened considerably when the less preferred methods are used, especially the last which must be regarded as a very approximate estimate possibly in error by a factor of 3 or more. This procedure is regrettably necessitated by the lack of experimental vapor pressure data, especially for the solid polynuclear aromatic hydrocarbons.

A reason for estimating such vapor pressures is that it appears that H tends to vary relatively little for a homologous series when compared to the variation in solubility and vapor pressure. It is thus possible to detect inconsistencies and estimate H not only from solubilities and vapor pressures but also from the H values of homologs.

The dimensionless concentration ratio of air-water partition coefficient can be obtained from the H values expressed here in kPa m^3/mol by dividing by RT which at 298 K has a value of 2.48 kPa m^3/mol.

Three Henry's law constants may be presented. First are values calculated from reported vapor pressures and solubilities. In such cases, the value presented is the ratio in units of kPa m^3/mol. Second are values which has been measured experimentally and are reported as experimental Henry's law constants. Third are recommended values reflecting the author's judgement as to the most accurate determinations. Error limits are given which are estimated from the stated or judged accuracy of the source data and comparison of data from various sources. In most cases the solubility is less accurate than the vapor pressure, especially for volatile hydrocarbons for which accurate Antoine equation constants are available. The sources of the vapor pressure, solubility, and Henry's law constant data are given in the tables with each entry.

When the substance is a gas at 25 °C the vapor pressure reported is that obtained from the Antoine equation, possibly involving extrapolation, even beyond the critical point. The solubility data refer however to atmospheric pressure thus in calculating H, a pressure of 101 kPa has been used instead of the actual vapor pressure. The tabulated vapor pressure is thus not used directly to calculate H. A footnote to this effect is included where appropriate.

4.2. Tabulated Data

Table 1 gives data for gaseous alkanes all of which boil below 25 °C. The solubilities refer to atmospheric pressure vapor and the H values are calculated on the basis of atmospheric pressure. These compounds partition predominantly into the atmosphere, i.e., the air concentrations exceeds that in the water by a factor of 28 to 155.

Table 2 gives data for liquid alkanes. The variation in reported solubilities is apparent, and is reflected in the wide error limits. The values of H are high, corresponding to a factor of 50 to 400 ratio in air to water concentration. There is a trend for H to increase with increasing molecular weight, the solubility falling more than the vapor pressure. The data for the long chain alkanes $> C_{10}$ are regarded as suspect principally because of uncertainties about the solubilities which are in the range of 50 parts per billion or lower and were not determined using the preferred "generator column" method [17,18]. Accordingly no recommended values are given for tetradecane and hexadecane. Examination of the trend with increasing carbon number suggests that H for these compounds may be in the range of 500 to 1000 kPa m^3/mol. This represents a concentration ratio of 200 to 400 in favor of the air.

Table 3 gives data for solid alkanes in which H is calculated from extrapolated liquid vapor pressures using an appropriate fugacity ratio. No recommended values are given since the solubility data are regarded as suspect. The reported solubility data suggest that despite the increase in molecular weight there is no substantial decrease in solubility below 0.005 g/m^3. This seems unlikely and is attributed to erroneous data caused by inclusion of colloidal hydrocarbon in the solution. In the absence of accurate solubility data the best approach may be to adopt a value in the range, 500 to 1500 kPa m^3/mol for these compounds on the basis of extrapolation from lower molecular weight compounds. The implication is that if octadecane has an H value of (say) 1000 kPa m^3/mol and a vapor pressure of 2×10^{-5} kPa its solubility will be 2×10^{-8} mol/m^3 or 5×10^{-6} g/m^3, a factor of 400 less than the reported value. Between heptane and decane there is an approximately 4 fold decrease in solubility per carbon added. Use of this rule suggests a dodecane solubility of approximately 2400×10^{-6} g/m^3 (in fair agreement with reported values) a tetradecane solubility of 150×10^{-6} (which is a factor of 15 to 46 lower than the reported values), a hexadecane solubility of 10×10^{-6} and an octadecane solubility of the order of 0.5×10^{-7} a factor of 4000 smaller than the measured values. It is thus concluded that for carbon numbers above C_{12} the solubility is not known with sufficient accuracy to permit H to be estimated within a factor of ten. No values are therefore recommended.

Table 4 gives data for cycloalkanes. These compounds, having a smaller molar volume than the corresponding alkanes, are more soluble and thus have lower H values, but again partitioning is dominantly into the air phase.

Table 5 gives data for gaseous alkenes and as in table 1 the vapor pressure used to calculate H is atmospheric pressure. These values are a factor of approximately three lower than the alkanes reflecting the increased solubility.

Table 6 gives data for liquid alkenes which lie in the range 22 to 96 kPa m^3/mol; again lower than the alkanes. Such componds still partition preferentially into the air phase by a concentration factor of 10 to 40.

Table 7 gives data for dienes which have still lower H values than the alkenes because of the higher solubilities.

Table 8 gives data for alkynes which have high solubilities resulting in H values of 1.1 to 2.5 kPa m^3/mol corresponding to almost equal partitioning between air and water.

The single ring aromatics in table 9 have very high solubilities and correspondingly low H values generally in the range 0.3 to 0.7 kPa m^3/mol giving preferential partitioning into the water phase by a factor of 3 to 8. Increased substitution reduces solubility and vapor pressure about equally, thus there is no distinct trend in H. The highly alkylated benzenes tend to have higher H values presumably because of their low solubilities caused by the large molecular size. This class of compounds is of considerable environmental interest because of their greater toxicity than the alkanes and their greater tendency to be retained in aquatic systems.

The polynuclear (or polycyclic) aromatics in table 10 are also of considerable environmental interest because of their direct toxicity and in some cases suspected carcinogenicity. As with the benzene derivatives in table 9, there is no distinct trend in H, the values generally lying in the range of 0.02 to 0.06 kPa m^3/mol, i.e., a concentration ratio of 40 to 120 in favor of the water phase. This class of compounds thus lies in the region in which the volatilization process in influenced by both the water and air phase resistances, whereas for those discussed earlier the water phase resistance dominates.

Only for napthalene are solid vapor pressure data available. For the others, most of which are solids, the vapor pressures are obtained from higher temperature liquid state data. As the number of rings increases the vapor pressure becomes very small and less accurately known, thus *H* values have wide error limits.

There are considerable discrepancies in the vapor pressures, solubilities and experimental *H* values for the higher polynuclear aromatics and no recommended values are given. The lower polynuclear aromatics including the substituted naphthalenes show better agreement. It is clear that the preferred method of obtaining reliable data for this class of compounds is to measure solubility, vapor pressure, and *H* and check the internal consistency of the values.

Table 11 gives data for halogenated alkanes and alkenes. The lower molecular weight saturated compounds have values generally in the range 0.1 to 3.0, i.e., in the same range as the mono-aromatics with similar concentrations in air and water phases. In many cases, the data are at 20 °C. For certain compounds no value is recommended in view of the discrepancies in solubility data.

The effect of substituting the larger halogen atom is to reduce both the vapor pressure and solubility thus there is no distinct trend in *H*. The brominated alkanes have very low vapor pressures and thus correspondingly low values of *H*.

The halogenated mono-aromatics in table 12 generally have *H* values in the range 0.1 to 0.4 kPa m^3/mol which are smaller by a factor of approximately 3 than the corresponding non-halogenated aromatics. It is interesting that substitution by halogens in aromatics has this relatively small effect on *H* whereas it reduces *H* of alkanes by two orders of magnitude.

The selected pesticides in table 13 are almost all solids of very low vapor pressure, typically 10^{-6} kPa, with variable solubilities. Most *H* values are in the range 10^{-4} to 10^{-3} kPa m^3/mol thus partitioning is predominantly into the water phase. The very low solubility of DDT results in higher value of *H*, greater partitioning into the atmosphere, an effect which has had implications regarding global distribution of this compound by atmospheric transport.

An interesting class of environmentally important compounds which are not reviewed here because of lack of reliable data is the chlorinated and brominated biphenyls. Accurate solubility, vapor pressure, and *H* data for these compounds are clearly very desirable as part of any assessment of their environmental behavior. Mackay et al. [106] have recently reviewed solubility data for these compounds and have suggested that some experimental solubility data are in error by two orders of magnitude. No reliable vapor pressure data are available thus it was judged to be unwise to estimate *H* values at this time.

Table 1. Data at 25°C for gaseous alkanes

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom	Reference p	S	H_{ex}
Methane	16.04	-182.5	-164	27260	24.1	67.4		67.4± 2.0	21	16	
Ethane	30.7	-183.3	-88.6	3990	60.4	50.6		50.6± 1.1	21	16	
Propane	44.11	-189.7	-42.1	941	62.4	71.6		71.6± 2.4	21	16	
n-Butane	58.13	-138.4	- 0.5	243	61.4	95.9		95.9± 4.1	21	16	
Isobutane	58.13	-159.6	-11.7	357	48.9	120		120± 5.2	21	16	
2,2-Dimethyl-propane	72.15	- 16.6	9.5	172	33.2	373		373± 11.2	21	16	

[a] Calculated using atmospheric pressure (see text).

Table 2. Data at 25°C for liquid alkanes

Compound	MW	mp,°C	bp,°C	Vapor pressure, p kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
n-Pentane	72.15	-129.7	36.1	68.4	38.5	128		125±10	21	16	
					39.5	125				26	
					40.0	123				27	
					40.4	122.2				28	
					47.6	103.7				29	
Isopentane	72.15	-159.9	27.9	92.6	47.8	140		138±5	21	16	
					48.0	139				26	
					49.6	134.7				29	
n-Hexane	86.17	- 95	68.95	20.2	9.5	190		170±25	21	16	
					9.47	191				26	
					9.52	190				27	
					12.3	147				30	
					12.4	144				29	
					16.2	110				31	
					18.3	98.9				28	
2-Methyl-pentane	86.17	-153.7	60.3	28.2	13.8	175		170±15	21	16	
					13.0	186				26	
					15.7	154				29	
3-Methyl-pentane	86.17		63.3	25.3	12.8	172		172±8	21	16	
					13.1	171				26	
2,2-Dimethyl-butane	86.17	- 99.9	49.7	42.6	18.4	199		173±16	21	16	
					21.2	173				26	
					23.8	154				29	
2,3-Dimethyl-butane	86.17	-128.5	58.0	31.3	19.1	141		130±10	21	26	
					22.5	120				29	
n-Heptane	100.21	- 90.6	98.4	6.11	2.93	209		230±50	21	16	
					2.24	273				26	
					2.66	230				20	
					2.19	280				27	
					3.37	182				29	
2-Methyl-hexane	100.21	-118.3	90.0	8.78	2.54	346		346±21	21	26	
3-Methyl-hexane	100.21	-119	92	8.21	2.64	312		240±75	21	26	
					4.95	166				29	
2,2-Dimethyl-pentane	100.21	-123.8	79.2	14	4.40	318		318±8	21	26	
2,3-Dimethyl-pentane	100.21		89.8	9.18	5.25	175		175±7	21	26	
2,4-Dimethyl-pentane	100.21	-119.2	80.5	13.1	4.06	323		300±25	21	16	
					4.41	298				26	
					5.50	239				29	
3,3-Dimethyl-pentane	100.21	-134.5	86.06	11.0	5.94	186		186±10	21	26	
n-Octane	114.23	-56.23	125.7	1.88	0.66	325		300±50	21	16	
					0.431	499				26	
					0.493	438				27	
					0.85	253				29	
					0.88	244				28	
3-Methyl-heptane	114.23	-120.5	115	2.6	0.792	376		376±15	21	26	
2,2,4-Tri-methyl-pentane	114.23	-107.4	99.2	6.56	2.44	308		330±30	21	16	
					2.05	365				29	

Table 2. Data at 25 C for liquid alkanes - continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
2,3,4-Trimethylpentane	114.23	-109.2	113.5	3.60	1.36	302		190±15	21	26	
					2.30	179				29	
2,2,5-Trimethylhexane	128.26	-105.8	124.1	2.21	1.15	219		350±120	21	16	
					0.54	467				29	
n-Nonane	128.26	- 51	150.8	0.571	0.122	601		500±200	21	26	
					0.098	748				27	
					0.22	333				32	
4-Methyloctane	128.26	-113.2	142.4	0.903	0.115	1010		1000±100	21	26	
n-Decane	148.28	- 29.7	174.1	0.175	0.052	500		700±300	21	32	
					0.024	1080				33	
Undecane	156.32	- 25.59	195.9	0.0522	0.044	185		1855±760	21	32	
Dodecane	170.33	- 9.6	216.3	0.0157	0.0034	723		750±250	21	32	
					0.0037	786				34	
					0.00844	317				33	
				0.0154					35		
Tetradecane	190.38	5.86	253.7	0.00127	0.00696	34.7			21	33	
					0.0022	110				34	
				0.00124					35		
Hexadecane	226.44	18.17	287	0.0000898	0.00628	3.24			21	33	
					0.0009	22.6				34	
				0.000917					35		

Table 3. Data at 25°C for solid alkanes

Compound	MW	mp, C	bp, C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Octadecane	254.4	28.18	316.1	7.44×10^{-6a}	0.0021	0.84			21	34	
				1.30×10^{-5a}		1.463			35		
				2.59×10^{-5a}		2.92			24		
				6.92×10^{-6b}							
					0.00608					27	
Eicosane	282.6	36.8	343	2.18×10^{-7a}	0.0019	0.025			21	34	
				2.67×10^{-6a}		0.288			24		
				1.58×10^{-7b}							
Hexacosane	366.7	56.4	412.2	7.32×10^{-12a}	0.0017	7.7×10^{-7}			21	34	
				3.55×10^{-12b}							

[a] Extrapolated value from liquid state.

[b] Calculated from the extrapolated vapour pressure with a fugacity ratio correction.

Table 4. Data at 25°C for cycloalkanes.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S g/m³	Henry's law constant kPa m³/mol calc	exptl	recom	Reference p	S	H_{ex}
Cyclopentane	70.14	-93.88	49.26	42.4	156 160	19.1 18.6		18.5±1.1	21	16 26	
Cyclohexane	84.16	6.55	80.7	12.7	55 57.5 66.5	19.4 18.6 16.1		18.0±2.0	21	16 31 26	
Methyl-cyclopentane	84.16	-142.14	71.8	18.3	42 41.8	36.7 36.8		36.7±1.4	21	16 26	
Methyl-cyclohexane	98.19	-126.6	100.9	6.18	14 16	42.8 38.0		40±3.0	21	16 26	
1-cis-2-Dimethylcyclohexane	112.2	- 50.1	129.7	1.93	6.0	36.1		36±5.0	21	16	
1,4,-trans-Dimethyl-cyclohexane	112.2	- 37	119.4	3.02	3.84	88.2		88.2±4.0	21	26	
1,1,3-Trimethylcyclopentane	112.2	- 14.2	104.9	5.3	3.73	159		159±8	21	26	
Propylcyclopentane	112.2	-117.3	103.0	1.64	2.04	90.2		90.2±4.4	21	26	
Pentylcyclopentane	140.26	- 83		0.152	0.115	185		185±18	21	26	

Table 5. Data at 25°C for gaseous alkenes.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S g/m³	Henry's law constant kPa m³/mol[a] calc.	exptl	recom	Reference p	S	H_{ex}
Ethene	28.5	-169.2	-103.7	6070	131	21.7		21.7±2.0	21	16	
Propene	42.08	-185.3	- 47.4	1140	200	21.3		21.3±3.0	21	16	
1-Butene	56.12	-185.4	- 6.3	297	222	75		75±4.0	21	16	
2-Methyl-propene	56.12	-140.4	- 6.9	304	263	64.8		64.8±6	21	16	
3-Methyl-1-butene	70.14	-168.5	20.0	120	130	54.7		54.7±6	21	16	

[a] Calculated using atmospheric pressure.

Table 6. Data at 25°C for liquid alkenes.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p, kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
1-Pentene	70.14	-138	30.0	85	148	40.3		40.3±2.0	21	16	
2-Pentene (cis)	70.14	-151.4	36.9	66	203	22.8		22.8±1.0	21	16	
1-Hexene	84.16	-139.8	63.4	24.8	50	41.8		41.8±1.0	21	16	
2-Methyl-1-pentene	84.16	-135.7	60.7	26.0	78	28.1		28.1±1.2	21	16	
4-Methyl-1-pentene	84.16	-153.6	53.9	36.1	48	63.2		63.2±3.5	21	16	
2-Heptene (trans)	98.19	-136.6	95.7	6.45	15	42.3		42.3±4.0	21	16	
1-Octene	112.2	-101.7	121.3	2.32	2.7	96.4		96.4±7.1	21	16	

Table 7. Data at 25°C for dienes.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p, kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Butadiene	54.09	-108.9	- 4.4	281	735	7.46[a]		7.46±0.2	21	16	
2-Methyl-1, 3-butadiene	68.13	-146	34	73.3	642	7.78		7.78±0.12	21	16	
1,4-Pentadiene	68.13	-148.3	26	98	558	12.0		12±0.6	21	16	

[a] Calculated using atmospheric pressure.

Table 8. Data at 25°C for alkynes.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p, kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Propyne	40	-101	-23.2	558	3640	1.11[a]		1.11±.04	21	16	
1-Butyne	50.09	-125.7	8.1	188	2870	1.91[a]		1.91±0.07	21	16	
1-Pentyne	68.13	- 90	40.18	57.6	1570	2.5		2.5±.05	21	16	

[a] Calculated using atmospheric pressure.

Table 9. Data at 25°C for monoaromatics.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S g/m³	Henry's law constant kPa m³/mol			Reference		
						calc	exptl	recom	p	S	H_{ex}
Benzene	78.11	5.53	80.1	12.7	1780	0.557	0.562	0.550±.025	21	16	14
					1755	0.565				36	
					1769	0.561				30	
					1790	0.554				37	
					1779.5	0.557				38	
					1740	0.570				26	
					1869	0.533				39	
					1770	0.560					
Toluene	92.13	-95	110.6	3.80	515	0.68	0.673	0.670±.035	21	16	14
					517	0.677				31	
					544	0.632				26	
					534.3	0.655				40	
					500	0.70				39	
					519.5	0.674				38	
					627	0.558				37	
Ethylbenzene	106.2	-95	136.2	1.27	152	0.887	0.854	0.80±.07	21	16	14
					177	0.762				29	
					131	1.03				26	
					208	0.648				37	
					161	0.837				41	
					175	0.771				39	
p-Xylene	106.2	13.2	138	1.17	185	0.671		0.710±.08	21	29	
					198	0.628				37	
					157	0.791				26	
					156	0.797				41	
					200	0.621				42	
m-Xylene	106.2	-47.9	139	1.10	162	0.721		0.700±0.10	21	29	
					196	0.596				37	
					173	0.675				42	
					146	0.80				41	
					134	0.872				26	
o-Xylene	106.2	-25.2	144.4	0.882	175	0.535		0.50±0.06	21	16	
					170.5	0.549				41	
					167	0.561				26	
					204	0.459				41	
					213	0.440				29	
1,2,3-Trimethylbenzene	120.2	-25.4	176.1	0.202	75.2	0.323		0.323±0.02	21	41	
1,2,4-Trimethylbenzene	120.2	-43.8	169.4	0.271	57	0.571		0.590±.04	21	16	
					51.9	0.627				26	
					59	0.552				41	
1,3,5-Trimethylbenzene	120.2	-44.7	164.7	0.328	97.0	0.407		0.60±.20	21	43	
					48.2	0.818				41	
Propylbenzene	120.2	-101.6	159.2	0.449	55	0.981		0.700±.30	21	43	
					120	0.450				44	
Isopropylbenzene	120.2	-96.6	154.2	0.611	50	0.147		0.130±.025	21	16	
					48.3	0.152				26	
					65.3	0.112				41	
1-Ethyl-2-methylbenzene	120.2	-80.8	165.2	0.330	93.05	0.427		0.427±.025	21	44	
1-Ethyl-4-methylbenzene	120.2	-62.4	162	0.393	94.85	0.498		0.498±.03	21	44	

Table 9. Data at 25°C for monoaromatics – continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
n-Butylbenzene	134.2	-88	183	0.137	12.6	1.46		1.30±.25	21	43	
					11.8	1.56				41	
					15.4	1.04				45	
					17.7	1.04				46	
					50.0	0.368				39	
Isobutylbenzene	134.2	-51.4	172.8	0.248	10.1	3.30		3.30±.13	21	26	
s-Butylbenzene	134.2	-75.5	173	0.241	17.6	1.84		1.40±.40	21	41	
					30.9	1.05				43	
t-Butylbenzene	134.2	-57.8	169	0.286	34.0	1.13		1.20±0.10	21	43	
					29.5	1.30				41	
1,2,4,5-Tetramethylbenzene	134.2	-79.2	196.8	0.0659	3.48	2.54		2.54±0.20	21	26	
1-iso-Propyl-4-methylbenzene	134.2	-67.9	177.1	0.204	34.15	0.80		0.80±.10	21	47	
n-Pentylbenzene	148.25	-75.0	205.4	0.0437	10.5	0.62		0.60±.06	21	43	

Table 10. Data for polynuclear aromatics at 25°C.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Naphthalene	128.19	80.2	218	1.09×10^{-2}	34.4	0.0407	0.0489	0.0430±.004	23	37	14
					31.2	0.0448				48	44
					31.7	0.0441				6	
					33.5	0.0417				49	
					31.3	0.0446				50	
					30.8	0.0454				19	
					31.69	0.0441				18	
					30.0	0.0466				40	
					22.0	0.0635				51	
				1.04×10^{-2}					24		
				1.16×10^{-2}					25		
				3.11×10^{-2}[a]					21		
				1.08×10^{-2}[a]					52		
1-Methylnaphthalene	142.2	-22	244.6	8.84×10^{-3}	28.5	0.0441	0.0263	0.0450±.004	24	6	44
					30.0	0.0419				19	
					25.8	0.0487				50	
					29.9	0.0420				40	
				7.90×10^{-3}[a]					21		
				7.17×10^{-3}[a]					35		
2-Methylnaphthalene	142.2	34.6	241.1	9.03×10^{-3}[a]	25.4	0.0405			21	6	
				7.24×10^{-3}[b]	24.6	0.0419				50	
				9.07×10^{-3}[a]					24		
1-Ethylnaphthalene	156.2	-13.8	258.7	2.51×10^{-3}[a]	10.7				21	6	
					10.0					19	
2-Ethylnaphthalene	156.2	liquid		4.21×10^{-3}	8.0	0.0822			24	50	
				3.24×10^{-3}[a]					21		

Table 10. Data for polynuclear aromatics at 25°C - continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Biphenyl	154.21	71	255.9	1.30x10^{-3}	7.48	0.0268	0.0413	0.028±.002	52	37	14
					7.0	0.0286	0.0304			6	44
					7.45	0.0269				50	
					7.50	0.0267				54	
					7.08	0.0283				48	
					5.94	0.0337				42	
					3.87	0.0518				55	
				5.80x10^{-4}					53		
				3.92x10^{-3}[a]					35		
				7.55x10^{-3}[a]					25		
Acenaphthene	154.21	96.2	277.5	3.07x10^{-3}[a]	3.88	0.0237	0.0148	0.024±.002	35	48	14
				5.96x10^{-4}[b]	3.93	0.0234	0.0157			6	44
					3.47	0.0265				50	
				4.02x10^{-3}[a]					25		
Fluorene	166.2	116	295	8.86x10^{-5}[c]	1.90	0.00775	0.0101	0.0085±.002	52	48	44
					1.98	0.00744				6	
				1.13x10^{-3}[a]					35		
				1.66x10^{-3}[a]					25		
Phenanthrene	178.23	101	339	2.67x10^{-5}[c]	1.18	0.00403	0.00398	0.0040±.0008	24	48	14
					1.07	0.00445	0.00365			50	44
					1.29	0.00367				6	
					1.60	0.00297				39	
					1.15	0.00414				19	
					1.002	0.00475				18	
				2.27x10^{-5}[c]					52		
				1.59x10^{-4}[a]					35		
				4.64x10^{-4}[a]					25		
Anthracene	178.23	216.2	340	1.44x10^{-6}[c]	0.075	0.0034	0.073	0.0060±.003	24	48	44
					0.073	0.0034	0.676			6	57
					0.041	0.0063				19	
					0.046	0.0056				18	
					0.030	0.0085				51	
				8.32x10^{-7}[c]					52		
				3.17x10^{-5}[a]					25		
				1.44x10^{-4}[a]					35		
Pyrene	202.3	156	360	8.86x10^{-7}[c]	0.148	0.00121	0.0011	0.0012±.002	52	48	44
					0.135	0.00133				6	
					0.132	0.00136				18	
					0.175	0.00102				39	
					0.171	0.00105				51	
Fluorathene	202.3	111	375	1.79x10^{-3}[a]	0.260	0.198		0.22±.03	35	6	
				2.54x10^{-4}[b]	0.265	0.194				39	
					0.206	0.249				18	
					0.236	0.218				51	
1,2-Benzanthracene	228.3	160		6.67x10^{-13}	0.014				58	6	
				(20°)	0.01					56	
3,4-Benzopyrene	252.3	175		6.67x10^{-13}	0.0012	1.4x10^{-7}			59	59	
					0.0038	4.43x10^{-8}				6	
					0.0040	4.21x10^{-8}				56	

[a] Extrapolated values from liquid state.

[b] Calculated from the extrapolated vapor pressure with a fugacity ratio correction..

[c] Extrapolated from solid vapor pressure.

Table 11. Data for halogenated alkanes and alkenes at 25°C unless otherwise stated.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p kPa	Solubility S, g/m³	Henry's law constant kPa m³/mol			Reference		
						calc	exptl	recom	p	S	H_{ex}
Chloromethane	50.5	-97.7	-24.2	570	5350	0.951^a		0.95±.05	35	61	62
				480(20°)	7400(20°)	0.691^a (20°)	0.731 (20°)		60	60	
					6270(20°)	0.817^a (20°)				62	
				499(20°)	7250(20°)	0.706^a (20°)			67	67	
Dichloromethane	84.9	-95.1	39.7	58.40	19400	0.256	0.272	0.26±.02	62	62	62
					13200					63	
				46.53 (20°)	13200(20°)	0.299 (20°)	0.301		60	60	63
				48.31 (20°)					63		
				21.08 (1.5°)	22700(1.5°)	0.079 (1.5°)			64	64	
Trichloromethane	119.4	-63.5	61.7	25.60	7900	0.387	0.322	0.38±.03	62	65	62
					7950	0.383				66	
				32.80 (20°)	8000(20°)	0.496 (20°)			60	60	
				20.06 (20°)	8200(20°)	0.292 (20°)	0.283 (20°)		63	63	63
				8.8 (1.5°)	10300(1.5°)	0.102 (1.5°)			64	64	
Carbon tetrachloride	153.8	-22.9	76.5	15.06	1160	1.586	2.16	2.0±0.4	62	54	62
					800	2.895				65	
				12.13 (20°)	800(20°)	2.331 (20°)		2.30±.2 (20°)	60	60	
				12.0 (20°)	785(20°)	2.351 (20°)	2.21 (20°)		63	63	63
Chloroethane	64.9	-136.4	12.27	100.7 (20°)	5710(20°)	1.145 (20°)		(.20±.20 (20°))	60	60	
					4700(20°)	1.391 (20°)				66	
1,1-Dichloroethane	98.97	-96.98	57.5	30.10	5100	0.585		0.58±.02	60	60	
				24.42 (20°)	5500(20°)	0.439 (20°)			62	62	
1,2-Dichloroethane	98.97	-35.36	83.47	10.93	8700	0.124	0.099	0.11±.01	62	62	62
				8.52	8800	0.096			63	63	
				8.40	8000	0.104			67	67	
				8.93	8000(20°)	0.111 (20°)			60	60	
1,1,1-Trichloroethane	133.4	-30.4	74.1	16.53	720	3.06		2.8±.04	62	62	
				13.20 (20°)	730(20°)	2.41 (20°)	3.47 (20°)		62	62	62
				13.33 (20°)	950(37°)				60	60	
				12.80 (20°)	480(20°)	3.56 (20°)			63	63	
				5.33 (1.5°)	880(1.5°)	0.808 (1.5°)			62	62	
1,1,2-Trichloroethane	133.4	-36.5	113.8	4.04	4420	0.122		0.12±.02	62	62	
				3.30 (20°)	4500(20°)	0.8978 (20°)			62	62	
1,1,1,2-Tetrachloroethane	167.85	-70.2	130.5	1.853	1100	0.283		0.28±.02	62	62	

Table 11. Data for halogenated alkanes and alkenes at 25°C unless otherwise stated -continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S, g/m³	Henry's law constant kPa m³/mol calc	exptl	recom	Reference p	S	H_{ex}
1,1,2,2-Tetrachloroethane	167.85	-36	146.2	0.867	3000	0.0485		0.048±.04	62	62	
					3200	0.0455				60	
				0.647(20°)					60		
1,1,2,2,2-Pentachloroethane	202.3	-29	162	0.60	480	0.253		0.22 ±.04	62	62	
				0.444(20°)	500 (20°)	0.180(20°)			60	60	
Hexachloroethane	236.7	-	186	0.044	8	1.302			62	62	
				0.028(20°)	50 (22°)				60	60	
Vinylchloride	62.5	-153.8	-13.4		2700	2.35[d]				68	
				344(20°)	90 (20°)	70.4(20°)[d]			60	60	
				308(20°)					67		
					60 (10°)	105.6(10°)[d]	117.6 (10°)			62	62
1,1-Dichloroethene	96.94	-122.1	37	79.73	400	13.32			62	62	
				66.0(20°)	400 (20°)	16.06 (20°)	15.61 (20°)		67	67	67
				66.0(20°)	5500 (20°)	1.16 (20°)			60	60	
1,2-Dichloroethene (cis)	96.94	-80.5	60.3	27.46	3500	0.761			62	62	
1,2-Dichloroethene (trans)	96.94	50	47.5	43.47	6300	0.669			64	65	
				34.65(20°)	300 (10°)				60	60	
1,1,2-Trichloroethene	131.4	-73	87	9.87	1100	1.179			62	62	
					1000	1.30				60	
				7.86(20°)	1100 (20°)	0.939 (20°)	0.904 (20°)		62	62	62
				8.0(20°)					60		
				3.27 (1.5°)	1000 (1.5°)	0.430 (1.5°)			62	62	
Tetrachloroethene	165.83	-19	121	2.48	140	2.94	1.239	2.3±.4	62	62	62
					400	1.03				60	
				1.90(20°)	120 (20°)	2.62 (20°)	2.03 (20°)		62	62	67
				1.80(20°)	150 (20°)	1.99 (20°)			67	67	
				0.64(1.5°)	130 (1.5°)				62	62	
Trichloropropane	147.5	-14.7	156.9	0.413	1900 (20°)				67	62	
3-Chloropropane	76.53	-134.5	45	48.13	3370	1.09		1.10±0.1	62	62	
					3000	1.228				60	
1-Chloro-2-methyl-propane	92.57	-131	68	12.06	9164	0.122		0.12±.01	54	54	
2,3-Dichloropropane	110.97		94	7.06	2150	0.365		0.36±.04	62	62	
1,3-Dichloropropane (cis)	110.97		104.3	5.735	2700	0.236		0.24±.03	62	62	
1,3-Dichloropropane	110.97		112	4.53(20°)	2800 (20°)	0.18 (20°)		0.18±.02 (20°)	62	62	

Table 11. Data for halogenated alkane and alkenes at 25°C unless otherwise stated - continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
1,2-Dibromo-methane	187.9	-34.2	167.3	0.271	1696	0.0322		0.032±.003	54	54	
Bromoform	252.75	-8.3	149.5	0.747	3033	0.0623		0.062±.006	54	54	
				0.719					69		
					3190 (30°)					54	
Fluorotri-cloromethane	137.37		23.8	88.5(20°)	1100 (20°)	11.05 (20°)	81.20 (20°)		67	67	67
Difluorodi-chloromethane	120.91	-158	-29.8	573(20°)	280	43.75 [d]	40.60		67	67	67
Bromomethane	94.94	-93.6	3.56	183.9	18040 (20°)	0.533(20°) [d]			25	61	
Fluoromethane	34.03	-141.8	-78.4	3536	1770 (30°)	1.95(30°) [d]			25	61	

[a] Extrapolated values from liquid state

[b] Calculated from the extrapolated vapor pressure with a fugacity ratio correction.

[c] Extrapolated from solid vapor pressure.

[d] Calculated using atmospheric pressure.

Table 12. Data for halogenated aromatics at 25°.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p kPa	Solubility S g/m^3	Henry's law constant kPa m^3/mol			Reference		
						calc	exptl	°recom	p	S	H_{ex}
Chlorobenzene	112.56	-45.6	132	1.581	471.7	0.377	0.382	0.35±.05	25	14	14
					500	0.356	0.314			70	44
					490	0.363				72	
					503	0.354				74	
				1.590					35		
					448(30°)					71	
					488(30°)					75	
o-Dichlorobenzene	147.01	-17.0	180.5	0.196	145.2	0.198	0.193	0.19±.01	25	73	44
					145	0.198				52	
					152	0.190					
					92.7					74	
				0.20					52		
m-Dichlorobenzene	147.01	-24.7	173	0.307	123.2	0.366		0.36±.02	25	73	
					123	0.366				52	
					120	0.367				71	
p-Dichlorobenzene	147.01	53.1	174	0.0902^c	83.1	0.160	0.240	0.16±.02	25	44	44
					87.2	0.152				48	
					79	0.168				75	
					76	0.174				70	
					90.6	0.146				74	
1,2,3-Trichlorobenzene	181.45	53	218	0.0530^a	16.6	0.306	0.127		25	44	44
					31.5	0.161				74	
				0.0280^b							
1,2,4-Trichlorobenzene	181.45	16.95	213.5	0.0606	25.03	0.439			25	7	
					34.57	0.318				74	
1,3,5-Trichlorobenzene	181.45	63	208	0.077^a	25.03	0.233			25	7	
					6.59	0.0884				74	
1,2,3,4-Tetrachlorobenzene	215.9	47.5	254	0.00876^a	4.31	0.261			25	74	
				0.00521^b							
1,2,3,5-Tetrachlorobenzene	215.9	54.5	246	0.0186^a	3.50	0.593	0.159		25	74	44
				0.0098^b							
1,2,4,5-Tetrachlorobenzene	215.9	140	243	0.0101^a	0.595	0.261			25	74	
				0.00072^b							
Pentachlorobenzene	250.3	86	277	$8.89\mathrm{x}10^{-3a}$	0.560	0.977			25	74	
				$2.19 \mathrm{x} 10^{-3b}$							
Hexachlorobenzene	284.8	230	322	$3.44\mathrm{x}10^{-4a}$	0.0050				25	74	
				$1.45\mathrm{x}10^{-6}$ (20°)		0.0050 (20°)			76		
α-Chlorotoluene	126.6	-39	179.3	0.173					25		
				0.236(30°)	466 (30°)	0.0641 (30°)			25	76	
Fluorobenzene	96.11	-41.2	85.1	10.20	1553	0.631		0.63±.06	35	39	
					1540 (30°)					78	
α,α,α-Trifluorotoluene	146.11	-29.11	102.06	4.98	450.7	1.61			25	79	
Bromobenzene	157.02	-30.82	156	0.552	410	0.211	0.247	0.21±.04	35	70	44
					360	0.241				74	
				0.570					25		
					500 (20°)					52	

Table 12. Data for halogenated aromatics at 25°C - continued.

Compound	MW	mp, °C	bp, °C	Vapor pressure, p kPa	Solubility S g/m³	Henry's law constant kPa m³/mol calc	exptl	recom	Reference p	S	H_{ex}
Bromobenzene					446 (30°)					52	
				0.997(35°)	458 (35°)	0.342 (35°)			80	80	
m-Dibromobenzene	235.92	-7	218	0.057(35°)	67.47 (35°)	0.199 (35°)			80	80	
p-Dibromobenzene	235.92	87.33	219	0.0215	20.0	0.254			25	70	
				0.018(35°)	26.42 (35°)	0.161 (35°)			80	80	
2-Bromoethylbenzene	185.07	-67.5	218	0.0326[a]	39.05				25	81	
Iodobenzene	204.01	-31.21	188.3	0.132	180	0.150		0.13±.02	35	70	
					229	0.118				74	
					340 (30°)					75	
p-Diiodobenzene	329.91	131	285		1.4					70	
					1.86					74	
1,4-Bromochlorobenzene	191.46	68	196	0.0344	44.88	0.147			25	74	
1-Chloronaphthalene	162.62	-2.3	258.8		22.4		0.355			44	44
2-Chloronaphthalene	162.62	61	256		11.7		0.0319			44	44

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[a] Extrapolated from liquid state.

[b] Calculated from the extrapolated vapor pressure with a fugacity ratio correction.

[c] Extrapolated from solid vapor pressure.

Table 13. Data for pesticides.

Compound	MW	mp, °C (Ref)	bp, °C (Ref)	Vapor pressure, p, kPa	Solubility, S g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Lindane	290.83	112.9		8.39×10^{-6}	7.3	3.34×10^{-4}		$(3.2\pm.2)\times10^{-4}$	82	83	
					7.80	3.13×10^{-4}				84	
				4.35×10^{-6} (20°)					82		
				4.13×10^{-6} (20°)					85		
				2.80×10^{-6} (20°)					86		
				1.25×10^{-6} (20°)					87		
				4.0×10^{-3} (20°)					88		
Aldrin	357.9	59.60		7.99×10^{-7}	0.2	1.43×10^{-3}		$(2.8\pm1.4)\times10^{-3}$	89	83	
					0.017	4.09×10^{-3}				84	
Dieldrin	373.9	175		6.59×10^{-7}	0.25	9.86×10^{-4}		$(1.1\pm.2)\times10^{-3}$	89	83	
					0.20	1.23×10^{-3}				84	
				3.47×10^{-7} (20°)					89		
				3.87×10^{-7} (20°)					85		
				2.53×10^{-7} (20°)					86		
				1.04×10^{-7} (20°)					90		
				2.67×10^{-8} (20°)					91		
				2.37×10^{-8} (20°)					84		
DDT	354.5	109	185	1.34×10^{-8}	1.2×10^{-3} (20°)	3.9×10^{-3} (20°)		$(5.3\pm3.8)\times10^{-3}$	89	83	89
					5.5×10^{-3} (20°)	8.64×10^{-3} (20°)				84	
					3.1×10^{-3} (20°)	1.53×10^{-3} (20°)				93, 92	
				2.53×10^{-8} (20°)	1.0×10^{-3}	8.97×10^{-3}			76	76	
Parathion	297.27	6.1 (76)	113/ .0067 (76)		24					76	
				5.04×10^{-6} (20°)	11.9(20°)	1.23×10^{-4}			94	95	
					11.0(40°)					96	
				2.61×10^{-6} (20°)					97		
				5.85×10^{-7} (20°)					98		
				7.6×10^{-7} (20°)					98		
Methyl-parathion	263.18	35-36 (76)	109/ .0067 (76)	3.94×10^{-5} (20°)	25(20°)	4.51×10^{-5}		$(2.0\pm1.0)\times10^{-5}$	20	96	
					77(40°)					96	
				1.29×10^{-6} (20°)					76, 100		
Malathion	330.36	2.85 (99)	120/ .027 (76)	1.67×10^{-5} (20°)	145(20°)	3.80×10^{-5}			76	76	
				7.33×10^{-7} (30°)					99		
Chlorpyrifos	350.58	41.5-43 (76,102, 103,104)		2.49×10^{-6}	0.4(23°)				103	101	
				2.53×10^{-6}					76		

Table 13. Data for pesticides - continued.

Compound	MW	mp,°C	bp,°C	Vapor pressure, p, kPa	Solubility S, g/m^3	Henry's law constant kPa m^3/mol calc	exptl	recom	Reference p	S	H_{ex}
Methyl-chlor-pyrifos	322.55	44.5-45.5 (99)		4.96x10^{-6} (20°)	4.76(20°)	3.04x10^{-4}			99	99	
Fenitrothion	277.24			8.0x10^{-7} (20°)	30.0(20°)	7.39x10^{-6}			94	94	
				7.2x10^{-6} (20°)		6.65x10^{-5}			105		
Dicapthon	297.61	52-53 (76)		4.79x10^{-7} (20°)	6.25(20°)	2.28x10^{-5}			99	99	
Ronnel	321.53	41 (94)	97/.0013 (94)	7.0x10^{-6} (20°)	1.08(20°)	2.11x10^{-3} (20°)		(2.1±.5)x10^{-3} (20°)	99	99	
Phosmet	329.33	72 (94)		6.03x10^{-8} (20°)	25				99	94	
Dialifor	393.84	67-69 (94)		8.27x10^{-9} (30°)	0.18				99	99	
Leptophos	412.07	70.2-70.6 71.5-72.0 (99)		3.07x10^{-9} (20°)	0.0047(20°)	2.69x10^{-4} (20°)		(2.7±.5)x10^{-4} (20°)	99	99	
					0.03				99		

Figure 1 gives a graphical illustration of the reviewed data in the form of a wide-range logarithmic plot of vapor pressure (kPa) versus solubility (mol/m^3), most of the data being at 25 °C. Since H is the ratio of vapor pressure to solubility, a series of compounds of constant H will lie on a 45° diagonal, as shown. Each compound corresponds to a point on this plot at a given temperature and homologous series tend to form clusters. Compounds such as alkanes falling to the upper left have high H values and tend to partition into the air, whereas those falling to the lower right, such as polynuclear aromatics, tend to partition into water. A striking feature of this diagram is that the effect of increased carbon number for a series of compounds is to reduce both vapor pressure and solubility approximately equally thus the value of H tends to be relatively constant. Substitution of chlorine in aromatics also has this property. If this observation can be generalized it can permit estimates to be made of H which are possibly sufficiently accurate for environmental assessment purposes. For example it would be interesting to examine the trend in H for polychlorinated biphenyls.

Finally, it is clear from this review that considerable discrepancies exist in the literature, even for fairly common compounds. It is believed that bringing together vapor pressure, solubility, and H data for homologous series will promote the establishment of more accurate values for all three properties.

Specimen Calculation

The Henry's law constant H is expressed as

$$H = p/c = pMW/S$$

where p is vapor pressure (kPa), MW is molecular weight (g/mol) and c and S are solubility (mol/m^3) and (g/m^3), respectively.

For gaseous solutes the pressure used is atmospheric (101.3 kPa) and the solubility is that measured at a total solute partial pressure of 1 atmosphere. For example, methane (table 1)

$$H = 101.3 \times 16.04/24.1 = 67.4 \text{ kPa m}^3/\text{mol}.$$

For liquid solutes the listed vapor pressure is used. For example, n-pentane in table 2

$$H = 68.4 \times 72.15/38.5 = 128.2 \text{ kPa m}^3/\text{mol}.$$

For solid hydrocarbons the preferred approach is to calculate H from the solid vapor pressure and the solid solubility. For example, naphthalene in table 10

$$H = 1.09 \times 10^{-2} \times 128.19/34.4 = 0.0407 \text{ kPa m}^3/\text{mol}.$$

In cases such as fluorene in table 10 the vapor pressure used is that of the solid but is extrapolated from other solid data at higher pressure.

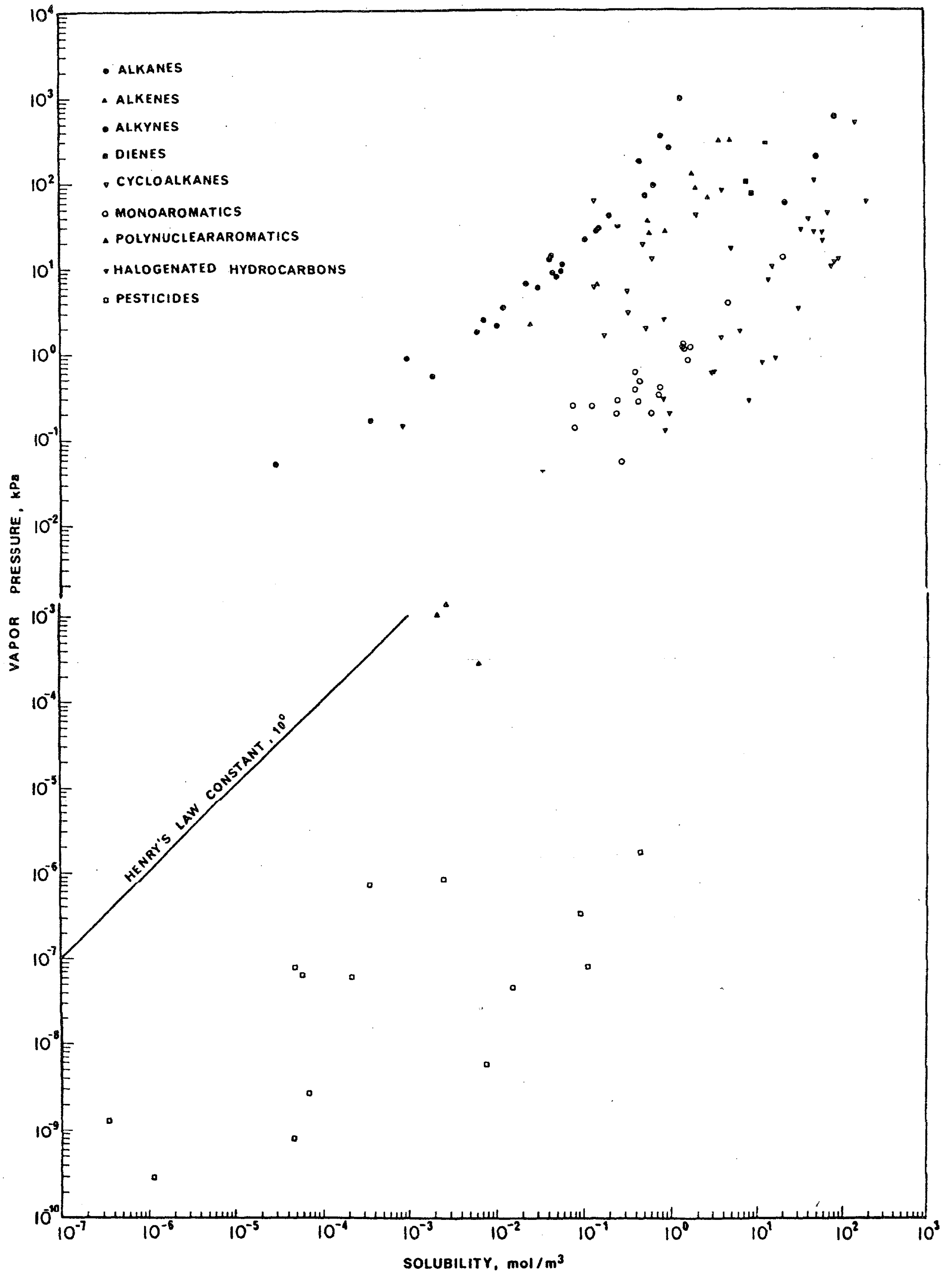

FIGURE 1. Plot of log solubility vs log vapor pressure illustrating the tendency for compounds in a homologous series to lie on a 45° diagonal of constant Henry's law constant.

When the solute is solid at 25 °C but the only vapor pressure data are for the liquid at higher temperature, the solid vapor pressure is calculated from the extrapolated liquid vapor pressure and a fugacity ratio correction is applied. For example, 2 methyl naphthalene in table 10

Extrapolated liquid vapor pressure is 9.03×10^{-3} Pa.

Fugacity ratio for melting point of 307.6 K is $\exp(-0.023(307.6-298.1))=0.805$.

Estimated solid vapor pressure is thus 7.26×10^{-3} Pa.

$$H=7.24\times10^{-3}\times142.2/25.4=0.0405 \text{ kPa m}^3/\text{mol}.$$

Although several vapor pressures and solubilities are given in the tables, only one pair of values was selected for calculating H, this selection being on the basis of judged accuracy of the data.

The references to H are in all cases to the experimental values.

List of Symbols

A, B, C	constants in Antoine equation
c	concentration, mol/m^3
c_A	concentration in air, mol/m^3
c_W	concentration in water, mol/m^3
f	fugacity, Pa or kPa
f_s	solid fugacity, Pa or kPa
f_r	reference fugacity, Pa or kPa
H	Henry's law constant, kPa m^3/mol
H_c	Henry's law constant, expressed as ratio of pressure to mole fraction, kPa
H_M	Henry's law constant, expressed as ratio of pressure to molar concentration, kPa m^3/mol
H_{ex}	experimentally determined Henry's law constant, kPa m^3/mol
ΔH^v	enthalpy of vaporization, J/mol
K_{AW}	partition coefficient of solute between air and water phases (dimensionless)
k_L	liquid phase mass transfer coefficient, m/s
k_G	vapor phase mass transfer coefficient, m/s
N	mass flux, mol/m^{2}s
p	pressure, Pa or kPa
p_T	total pressure, Pa or kPa
p_W	water vapor pressure, Pa or kPa
R	gas constant, 8.314 Pa m^3/mol K
ΔS	entropy of fusion J/mol K
T	system temperature, K
T_B	normal boiling point, K
T_M	normal melting point, K
v_W	molar volume of water, m^3/mol
w	mole fraction solubility of water in the liquid phase
x	solute mole fraction in aqueous phase
x_L	solute mole fraction in liquid phase
x_W	solute mole fraction in water phase
y	solute mole fraction in vapor phase
α	relative volatility
γ	activity coefficient
γ_L	activity coefficient of the pure liquid solute
γ_W	activity coefficient of the solute in water
ϕ	fugacity coefficient

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