This handbook is a compilation of environmentally relevant physical-chemical data for similarly structured groups of chemical substances. These data control the fate of chemicals as they are transported and transformed in the multimedia environment of air, water, soils, sediments, and their resident biota. These fate processes determine the exposure experienced by humans and other organisms and ultimately the risk of adverse effects. The task of assessing chemical fate locally, regionally, and globally is complicated by the large (and increasing) number of chemicals of potential concern; by uncertainties in their physical-chemical properties; and by lack of knowledge of prevailing environmental conditions such as temperature, pH, and deposition rates of solid matter from the atmosphere to water, or from water to bottom sediments. Further, reported values of properties such as solubility are often in conflict. Some are measured accurately, some approximately, and some are estimated by various correlation schemes from molecular structures. In some cases, units or chemical identity are wrongly reported. The user of such data thus has the difficult task of selecting the “best” or “right” values. There is justifiable concern that the resulting deductions of environmental fate may be in substantial error. For example, the potential for evaporation may be greatly underestimated if an erroneously low vapor pressure is selected.

To assist the environmental scientist and engineer in such assessments, this handbook contains compilations of physical-chemical property data for over 1000 chemicals. It has long been recognized that within homologous series, properties vary systematically with molecular size, thus providing guidance about the properties of one substance from those of its homologs. Where practical, plots of these systematic property variations can be used to check the reported data and provide an opportunity for interpolation and even modest extrapolation to estimate unmeasured properties of other substances. Most handbooks treat chemicals only on an individual basis and do not contain this feature of chemical-to-chemical comparison, which can be valuable for identifying errors and estimating properties. This most recent edition includes about 1250 compounds and contains about 30 percent additional physical-chemical property data. There is a more complete coverage of PCBs, PCDDs, PCDFs, and other halogenated hydrocarbons, especially brominated and fluorinated substances that are of more recent environmental concern. Values of the physical-chemical properties are generally reported in the literature at a standard temperature of 20 or 25°C. However, environmental temperatures vary considerably, and thus reliable data are required on the temperature dependence of these properties for fate calculations. A valuable enhancement to this edition is the inclusion of extensive measured temperature-dependent data for the first time. The data focus on water solubility, vapor pressure, and Henry’s law constant but include octanol/water and octanol/air partition coefficients where available. They are provided in the form of data tables and correlation equations as well as graphs.

We also demonstrate in Chapter 1 how the data may be taken a stage further and used to estimate likely environmental partitioning tendencies, i.e., how the chemical is likely to become distributed between the various media that comprise our biosphere. The results are presented numerically and pictorially to provide a visual impression of likely environmental behavior. This will be of interest to those assessing environmental fate by confirming the general fate characteristics or behavior profile. It is, of course, only possible here to assess fate in a “typical” or “generic” or “evaluative” environment. No claim is made that a chemical will behave in this manner in all situations, but this assessment should reveal the broad characteristics of behavior. These evaluative fate assessments are generated using simple fugacity models that flow naturally from the compilations of data on physical-chemical properties of relevant chemicals. Illustrations of estimated environmental fate are given in Chapter 1 using Levels I, II, and III mass balance models. These and other models are available for downloading gratis from the website of the Canadian Environmental Modelling Centre at Trent University (www.trent.ca/cemc).

It is hoped that this new edition of the handbook will be of value to environmental scientists and engineers and to students and teachers of environmental science. Its aim is to contribute to better assessments of chemical fate in our multimedia environment by serving as a reference source for environmentally relevant physical-chemical property data of classes of chemicals and by illustrating the likely behavior of these chemicals as they migrate throughout our biosphere.
We would never have completed the volumes for the first and second editions of the handbook and the CD-ROMs without the enormous amount of help and support that we received from our colleagues, publishers, editors, friends, and family. We are long overdue in expressing our appreciation.

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His awards include the SETAC Founders Award, the Honda Prize for Eco-Technology, the Order of Ontario, and the Order of Canada. He has served on the editorial boards of several journals and is a member of SETAC, the American Chemical Society, and the International Association of Great Lakes Research.

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# Introduction

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1.1 THE INCENTIVE

It is believed that there are some 50,000 to 100,000 chemicals currently being produced commercially in a range of quantities with approximately 1000 being added each year. Most are organic chemicals, and many are pesticides and biocides designed to modify the biotic environment. Of these, perhaps 1000 substances are of significant environmental concern because of their presence in detectable quantities in various components of the environment, their toxicity, their tendency to bioaccumulate, their persistence and their potential to be transported long distances. Some of these chemicals, including pesticides, are of such extreme environmental concern that international actions have been taken to ensure that all production and use should cease, i.e., as a global society we should elect not to synthesize or use these chemicals. They should be “sunsetted.” PCBs, “dioxins” and DDT are examples. A second group consists of less toxic and persistent chemicals which are of concern because they are used or discharged in large quantities. They are, however, of sufficient value to society that their continued use is justified, but only under conditions in which we fully understand and control their sources, fate and the associated risk of adverse effects. This understanding is essential if society is to be assured that there is negligible risk of adverse ecological or human health effects. Other groups of more benign chemicals can presumably be treated with less rigor.

A key feature of this “cradle-to-grave” approach to chemical management is that society must improve its skills in assessing chemical fate in the environment. We must better understand where chemicals originate, how they migrate, and between, the various media of air, water, soils, sediments and their biota which comprise our biosphere. We must understand how these chemicals are transformed by chemical and biochemical processes and, thus, how long they will persist in the environment. We must seek a fuller understanding of the effects that they will have on the multitude of interacting organisms that occupy these media, including ourselves.

It is now clear that the fate of chemicals in the environment is controlled by a combination of three groups of factors. First are the prevailing environmental conditions such as temperatures, flows and accumulations of air, water and solid matter and the composition of these media. Second are the properties of the chemicals which influence partitioning and reaction tendencies, i.e., the extent to which the chemical evaporates or associates with sediments, and how fast the chemical is eventually destroyed by conversion to other chemical species. Third are the patterns of use, into which compartments the substance is introduced, whether introduction is episodic or continuous and in the case of pesticides how and with which additives the active ingredient is applied.

In recent decades there has emerged a discipline within environmental science concerned with increasing our understanding of how chemicals behave in our multimedia environment. It has been termed environmental chemistry or “chemodynamics.” Practitioners of this discipline include scientists and engineers, students and teachers who attempt to measure, assess and predict how this large number of chemicals will behave in laboratory, local, regional and global environments. These individuals need data on physical-chemical and reactivity properties, as well as information on how these properties translate into environmental fate. This handbook provides a compilation of such data and outlines how to use them to estimate the broad features of environmental fate. It does so for classes or groups of chemicals, instead of the usual approach of treating chemicals on an individual basis. This has the advantage that systematic variations in properties with molecular structure can be revealed and exploited to check reported values, interpolate and even extrapolate to other chemicals of similar structure.

With the advent of inexpensive and rapid computation there has been a remarkable growth of interest in this general area of quantitative structure-property relationships (QSPRs). The ultimate goal is to use information about chemical structure to deduce physical-chemical properties, environmental partitioning and reaction tendencies, and even uptake and effects on biota. The goal is far from being fully realized, but considerable progress has been made. In this series of handbooks we have adopted a simple and well-tried approach of using molecular structure to deduce a molar volume, which in turn is related to physical-chemical properties. In the case of pesticides, the application of QSPR approaches is complicated by the large number of chemical classes, the frequent complexity of molecules and the lack of experimental data. Where there is a sufficient number of substances in each class or homologous series QSPRs are presented, but in some cases there is a lack of data to justify them. QSPRs based on other more complex molecular descriptors are, of course, widely available, especially in the proceedings of the biennial QSAR conferences.

Regrettably, the scientific literature contains a great deal of conflicting data, with reported values often varying over several orders of magnitude. There are some good, but more not-so-good reasons for this lack of accuracy. Many of these properties are difficult to measure because they involve analyzing very low concentrations of 1 part in 10^9 or 10^12. For many purposes an approximate value is adequate. There may be a mistaken impression that if a vapor pressure is low, as is the case with DDT, it is not important. DDT evaporates appreciably from solution in water, despite its low vapor pressure, because of its low solubility in water. In some cases the units are reported incorrectly. There may be uncertainties about temperature or pH. In other cases the chemical is wrongly identified. Errors tend to be perpetuated.
by repeated citation. The aim of this handbook is to assist the user to identify such problems, provide guidance when selecting appropriate values and where possible determine their temperature dependence.

The final aspect of chemical fate treated in this handbook is the depiction or illustration of likely chemical fate. This is done using multimedia “fugacity” models as described later in this chapter. The aim is to convey an impression of likely environmental partitioning and transformation characteristics, i.e., a “behavior profile.” A fascinating feature of chemodynamics is that chemicals differ so greatly in their behavior. Some, such as chloroform, evaporate rapidly and are dissipated in the atmosphere. Others, such as DDT, partition into the organic matter of soils and sediments and the lipids of fish, birds and mammals. Phenols and carboxylic acids tend to remain in water where they may be subject to fairly rapid transformation processes such as hydrolysis, biodegradation and photolysis. By entering the physical-chemical data into a model of chemical fate in a generic or evaluative environment, it is possible to estimate the likely general features of the chemical’s behavior and fate. The output of these calculations can be presented numerically and pictorially.

In summary, the aim of this series of handbooks is to provide a useful reference work for those concerned with the assessment of the fate of existing and new chemicals in the environment.

1.2 PHYSICAL-CHEMICAL PROPERTIES

1.2.1 THE KEY PHYSICAL-CHEMICAL PROPERTIES

In this section we describe the key physical-chemical properties and discuss how they may be used to calculate partition coefficients for inclusion in mass balance models. Situations in which data require careful evaluation and use are discussed.

The major differences between behavior profiles of organic chemicals in the environment are attributable to their physical-chemical properties. The key properties are recognized as solubility in water, vapor pressure, the three partition coefficients between air, water and octanol, dissociation constant in water (when relevant) and susceptibility to degradation or transformation reactions. Other essential molecular descriptors are molar mass and molar volume, with properties such as critical temperature and pressure and molecular area being occasionally useful for specific purposes. A useful source of information and estimation methods on these properties is the handbook by Boethling and Mackay (2000).

Chemical identity may appear to present a trivial problem, but most chemicals have several names, and subtle differences between isomers (e.g., cis and trans) may be ignored. The most commonly accepted identifiers are the IUPAC name and the Chemical Abstracts System (CAS) number. More recently, methods have been sought of expressing the structure in line notation form so that computer entry of a series of symbols can be used to define a three-dimensional structure. For environmental purposes the SMILES (Simplified Molecular Identification and Line Entry System, Anderson et al. 1987) is favored, but the Wismesser Line Notation is also quite widely used.

Molar mass or molecular weight is readily obtained from structure. Also of interest for certain purposes are molecular volume and area, which may be estimated by a variety of methods.

When selecting physical-chemical properties or reactivity classes the authors have been guided by:

1. The acknowledgment of previous supporting or conflicting values,
2. The method of determination,
3. The perception of the objectives of the authors, not necessarily as an indication of competence, but often as an indication of the need of the authors to obtain accurate values, and
4. The reported values for structurally similar, or homologous compounds.

The literature contains a considerable volume of “calculated” data as distinct from experimental data. We have generally not included such data because they may be of questionable reliability. In some cases an exception has been made when no experimental data exist and the calculation is believed to provide a useful and reliable estimate.

1.2.2 PARTITIONING PROPERTIES

Solubility in water and vapor pressure are both “saturation” properties, i.e., they are measurements of the maximum capacity that a solvent phase has for dissolved chemical. Vapor pressure \( P \) (Pa) can be viewed as a “solubility in air,” the corresponding concentration \( C \) (mol/m\(^3\)) being \( P/RT \) where \( R \) is the ideal gas constant (8.314 J/mol.K) and \( T \) is absolute temperature (K). Although most chemicals are present in the environment at concentrations well below saturation, these concentrations are useful for estimating air-water partition coefficients as ratios of saturation values. It is usually assumed...
that the same partition coefficient applies at lower sub-saturation concentrations. Vapor pressure and solubility thus provide estimates of the air-water partition coefficient \( K_{AW} \), the dimensionless ratio of concentration in air (mass/volume) to that in water. The related Henry’s law constant \( H \) (Pa·m³/mol) is the ratio of partial pressure in air (Pa) to the concentration in water (mol/m³). Both express the relative air-water partitioning tendency.

When solubility and vapor pressure are both low in magnitude and thus difficult to measure, it is preferable to measure the air-water partition coefficient or Henry’s law constant directly. It is noteworthy that atmospheric chemists frequently use \( K_{WA} \), the ratio of water-to-air concentrations. This may also be referred to as the Henry’s law constant.

The octanol-water partition coefficient \( K_{OW} \) provides a direct estimate of hydrophobicity or of partitioning tendency from water to organic media such as lipids, waxes and natural organic matter such as humin or humic acid. It is invaluable as a method of estimating \( K_{OC} \), the organic carbon-water partition coefficient, the usual correlation invoked being that of Karickhoff (1981)

\[
K_{OC} = 0.41 \ K_{OW}
\]

Seth et al. (1999) have suggested that a better correlation is

\[
K_{OC} = 0.35 \ K_{OW}
\]

and that the error limits on \( K_{OC} \) resulting from differences in the nature of organic matter are a factor of 2.5 in both directions, i.e. the coefficient 0.35 may vary from 0.14 to 0.88.

\( K_{OC} \) is an important parameter which describes the potential for movement or mobility of pesticides in soil, sediment and groundwater. Because of the structural complexity of these agrochemical molecules, the above simple relationship which considers only the chemical’s hydrophobicity may fail for polar and ionic compounds. The effects of pH, soil properties, mineral surfaces and other factors influencing sorption become important. Other quantities, \( K_{OW} \), (adsorption partition coefficient to the whole soil on a dry weight basis) and \( K_{OM} \), (organic matter-water partition coefficient) are also commonly used to describe the extent of sorption. \( K_{OM} \) is often estimated as 0.56 \( K_{OC} \), implying that organic matter is 56% carbon.

\( K_{OW} \) is also used to estimate equilibrium fish-water bioconcentration factors \( K_B \), or BCF using a correlation similar to that of Mackay (1982)

\[
K_B = 0.05 \ K_{OW}
\]

where the term 0.05 corresponds to a lipid content of the fish of 5%. The basis for this correlation is that lipids and octanol display very similar solvent properties, i.e., \( K_{LW} \) (lipid-water) and \( K_{OW} \) are equal. If the rate of metabolism is appreciable, equilibrium will not apply and the effective \( K_B \) will be lower to an extent dictated by the relative rates of uptake and loss by metabolism and other clearance processes. If uptake is primarily from food, the corresponding bioaccumulation factor also depends on the concentration of the chemical in the food.

For dissociating chemicals it is essential to quantify the extent of dissociation as a function of pH using the dissociation constant \( pK_a \). The parent and ionic forms behave and partition quite differently; thus pH and the presence of other ions may profoundly affect chemical fate. This is discussed later in more detail in Section 1.2.4.

The octanol-air partition coefficient \( K_{OA} \) was originally introduced by Paterson et al. (1991) for describing the partitioning of chemicals from the atmosphere to foliage. It has proved invaluable for this purpose and for describing partitioning to aerosol particles and to soils. It can be determined experimentally using the technique devised by Harner and Mackay (1995). Although there are fewer data for \( K_{OA} \) than for \( K_{OW} \), its use is increasing and when available, data are included in this handbook. \( K_{OA} \) has been applied to several situations involving partitioning of organic substances from the atmosphere to solid or liquid phases. Finizio et al. (1997) have shown that \( K_{OA} \) is an excellent descriptor of partitioning to aerosol particles, while McLachlan et al. (1995) and Tolls and McLachlan (1994) have used it to describe partitioning to foliage, especially grasses. Hippelein and McLachlan (1998) have used \( K_{OA} \) to describe partitioning between air and soil.

An attractive feature of \( K_{OA} \) is that it can replace the liquid or supercooled liquid vapor pressure in a correlation. \( K_{OA} \) is an experimentally measurable or accessible quantity, whereas the supercooled liquid vapor pressure must be estimated from the solid vapor pressure, the melting point and the entropy of fusion. The use of \( K_{OA} \) thus avoids the potentially erroneous estimation of the fugacity ratio, i.e., the ratio of solid and liquid vapor pressures. This is especially important for solutes with high melting points and, thus, low fugacity ratios.
The availability of data on $K_{AW}$, $K_{OW}$ and $K_{OA}$ raises the possibility of a consistency test. At first sight it appears that $K_{OA}$ should equal $K_{OW}/K_{AW}$, and indeed this is often approximately correct. The difficulty is that in the case of $K_{AW}$, the water phase is pure water, and for $K_{OA}$ the octanol phase is pure “dry” octanol. For $K_{OW}$, the water phase inevitably contains dissolved octanol, and the octanol phase contains dissolved water and is thus not “dry.” Beyer et al. (2002) and Cole and Mackay (2000) have discussed this issue.

If the partition coefficients are regarded as ratios of solubilities $S$ (mol/m$^3$)

$$K_{AW} = S_A/S_W \text{ or } \log K_{AW} = \log S_A - \log S_W$$

$$K_{OA} = S_O/S_A \text{ or } \log K_{OA} = \log S_O - \log S_A$$

$$K_{OW} = S_{OW}/S_{WO} \text{ or } \log K_{OW} = \log S_{OW} - \log S_{WO}$$

where subscript $A$ applies to the gas phase or air, $W$ to pure water, $O$ to dry octanol, $OW$ to “wet” octanol and $WO$ to water saturated with octanol. It follows that the assumption that $K_{OA}$ is $K_{OW}/K_{AW}$ is essentially that

$$(\log S_{OW} - \log S_O) - (\log S_{WO} - \log S_W) = 0$$

or $S_{OW}/(S_O \cdot S_{WO})$ is 1.0

This is obviously satisfied when $S_{OW}$ equals $S_O$ and $S_{WO}$ equals $S_W$, but this is not necessarily valid, especially when $K_{OW}$ is large.

There are apparently two sources of this effect. The molar volume of water changes relatively little as a result of the presence of a small quantity of dissolved octanol, however the quantity of dissolved water in the octanol is considerable, causing a reduction in molar volume of the octanol phase. The result is that even if activity coefficients are unaffected, $\log S_O/S_W$ will be about 0.1 units less than that of $\log K_{OW}$. Effectively, the octanol phase “swells” as a result of the presence of water, and the concentration is reduced. In addition, when $\log K_{OW}$ exceeds 4.0 there is an apparent effect on the activity coefficients which causes $\log (S_O/S_W)$ to increase. This increase can amount to about one log unit when $\log K_{OW}$ is about 8. A relatively simple correlation based on the analysis by Beyer et al. (2002) (but differing from their correlation) is that

$$\log K_{OA} = \log (K_{OW}/K_{AW}) - 0.10 + [0.30 \log K_{OW} - 1.20]$$

when $\log K_{OW}$ is 4 or less the term in square brackets is ignored

when $\log K_{OW}$ is 4 or greater that term is included

### 1.2.3 TEMPERATURE DEPENDENCE

All partitioning properties change with temperature. The partition coefficients, vapor pressure, $K_{AW}$ and $K_{OA}$, are more sensitive to temperature variation because of the large enthalpy change associated with transfer to the vapor phase. The simplest general expression theoretically based temperature dependence correlation is derived from the integrated Clausius-Clapeyron equation, or van’t Hoff form expressing the effect of temperature on an equilibrium constant $K_p$,

$$R \ln K_p = A_o - B/T$$

which can be rewritten as

$$\ln (\text{Property}) = A - \Delta H/RT$$

where $A_o$, $B$ and $A$ are constants, $\Delta H$ is the enthalpy of the phase change, i.e., evaporation from pure state for vapor pressure, dissolution from pure state into water for solubility, and for air-water transition in the case of Henry’s law constant.
The fit is improved by adding further coefficients in additional terms. The variation of these equilibrium constants with temperature can be expressed by (Clarke and Glew 1966),

\[ R \cdot \ln K_p(T) = A + B/T + C \cdot \ln T + D \cdot T + E \cdot T^2 + F \cdot T^3 + \ldots \]

where \( A, B, C, D, E, F \) are constants.

There have been numerous approaches to describing the temperature dependence of the properties. For aqueous solubility, the most common expression is the van’t Hoff equation of the form (Hildebrand et al. 1970):

\[ \frac{d}{d(1/T)} \ln x = -\frac{\Delta_{sol} H}{R} \]

where \( x \) is the mole fraction solubility, \( T \) is the temperature in K, \( R \) is the ideal gas constant, and \( \Delta_{sol} H \) is the enthalpy of solution of the solute. The enthalpy of solution can be considered as the sum of various contributions such as cavity formation and interactions between solute-solute or solute-solvent as discussed by Bohon and Claussen (1951), Arnold et al. (1958), Owen et al. (1986) and many others. Assuming the enthalpy of solution is constant over a narrow temperature range, integrating gives,

\[ \ln x = -\frac{\Delta_{sol} H}{RT} + C \]

where \( C \) is a constant.

The relation between aqueous solubility and temperature is complicated because of the nature of the interactions between the solute and water structure. The enthalpy of solution can vary greatly with temperature, e.g., some liquid aromatic hydrocarbons display a minimum solubility corresponding to zero enthalpy of solution between 285 and 320 K. For instance, benzene has a minimum solubility at 291 K (Bohon and Claussen 1951, Arnold et al. 1958, Shaw 1989a) and alkylbenzenes display similar behavior (Shaw 1989a,b, Owens 1986). As is illustrated later in chapter 3, solid aromatic hydrocarbons show a slight curvature in plots of logarithm of mole fraction solubility versus reciprocal absolute temperature. For narrow ranges in environmental temperatures, the enthalpy of solution may be assumed to be constant, and the linear van’t Hoff plot of \( \ln x \) versus \( 1/T \) is often used (Dickhut et al. 1986). Other relationships such as quadratic or cubic equations have been reported (May et al. 1978), and polynomial series (Clarke and Glew 1966, May et al. 1983, Owens et al. 1986) have been used when the data justify such treatment.

Equations relating vapor pressure to temperature are usually based on the two-parameter Clausius-Clapeyron equation,

\[ \frac{d}{dT} \ln P_\infty = \frac{\Delta_{vap} H}{RT^2} \]

where \( P_\infty \) is vapor pressure, \( \Delta_{vap} H \) is the enthalpy of vaporization. Again assuming \( \Delta_{vap} H \) is constant over a narrow range of temperature, this gives,

\[ \ln P_\infty = -\frac{\Delta_{vap} H}{RT} + C \]

which can be rewritten as the Clapeyron equation

\[ \log P_\infty = A - \frac{B}{T} \]

This can be empirically modified by introducing additional parameters to give the three-parameter Antoine equation by replacing \( T \) with \( (T + C) \), where \( C \) is a constant, which is the most common vapor pressure correlation used to represent experimental data (Zwolinski and Wilhoit 1971, Boublík et al. 1984, Stephenson and Malanowski 1987, and other handbooks).

\[ \log P_\infty = A - \frac{B(t + C)}{t} \]

where \( A, B \) and \( C \) are constants and \( t \) often has units of °C.

Other forms of vapor pressure equations, such as Cox equation (Osborn and Douslin 1974, Chao et al. 1983), Chebyshev polynomial (Ambrose 1981), Wagner’s equation (Ambrose 1986), have also been widely used. Although
the enthalpy of vaporization varies with temperature, for the narrow environmental temperature range considered in environmental conditions, it is often assumed to be constant, for example, for the more volatile monoaromatic hydrocarbons and the less volatile polynuclear aromatic hydrocarbons.

The van’t Hoff equation also has been used to describe the temperature effect on Henry’s law constant over a narrow range for volatile chlorinated organic chemicals (Ashworth et al. 1988) and chlorobenzenes, polychlorinated biphenyls, and polynuclear aromatic hydrocarbons (ten Hulscher et al. 1992, Alaee et al. 1996). Henry’s law constant can be expressed as the ratio of vapor pressure to solubility, i.e., \( p/c \) or \( p/x \) for dilute solutions. Note that since \( H \) is expressed using a volumetric concentration, it is also affected by the effect of temperature on liquid density whereas \( k_H \) using mole fraction is unaffected by liquid density (Tucker and Christian 1979), thus

\[
\ln \left( \frac{k_H}{Pa} \right) = \ln \left[ \left( \frac{P}{Pa} \right) x \right];
\]

or,

\[
\ln \left( \frac{H}{Pa \cdot m^3 \cdot mol^{-1}} \right) = \ln \left[ \left( \frac{P}{Pa} \right)/(C_S^w/mol \cdot m^{-3}) \right];
\]

where \( C_S^w \) is the aqueous solubility.

By substituting equations for vapor pressure and solubility, the temperature dependence equation for Henry’s law constant can be obtained, as demonstrated by Glew and Robertson (1956), Tsonopoulos and Wilson (1983), Heiman et al. (1985), and ten Hulscher et al. (1991).

Care must be taken to ensure that the correlation equations are applied correctly, especially since the units of the property, the units of temperature and whether the logarithm is base \( e \) or base 10. The equations should not be used to extrapolate beyond the stated temperature range.

### 1.2.4 Treatment of Dissociating Compounds

In the case of dissociating or ionizing organic chemicals such as organic acids and bases, e.g., phenols, carboxylic acids and amines, it is desirable to calculate the concentrations of ionic and non-ionic species, and correct for this effect. A number of authors have discussed and reviewed the effect of pH and ionic strength on the distribution of these chemicals in the environment, including Westall et al. (1985), Schwarzenbach et al. (1988), Jafvert et al. (1990), Johnson and Westall (1990) and the text by Schwarzenbach, Gschwend and Imboden (1993).

A simple approach is suggested here for estimating the effect of pH on properties and environmental fate using the phenols as an example. A similar approach can be used for bases. The extent of dissociation is characterized by the acid dissociation constant, \( K_a \), expressed as its negative logarithm, \( pK_a \), which for most chlorophenolic compounds range between 4.75 for pentachlorophenol and 10.2 to phenol, and between 10.0 and 10.6 for the alkylphenols. The dissolved concentration in water is thus the sum of the undissociated, parent or protonated compound and the dissociated phenolate ionic form. When the \( pK_a \) exceeds \( pH \) by 2 or more units, dissociation is 1% or less and for most purposes is negligible. The ratio of ionic to non-ionic or dissociated to undissociated species concentrations is given by,

\[
\frac{\text{ionic/non-ionic}}{\text{dissociated}} = 10^{(\text{pH} - \text{pK}_a)} = I
\]

The fraction ionic \( x_i \) is \( I/(1 + I) \). The fraction non-ionic \( x_n \) is \( 1/(1 + I) \). For compounds such as pentachlorophenol in which pH generally exceeds \( pK_a \), \( I \) and \( x_i \) can be appreciable, and there is an apparently enhanced solubility (Horvath and Getzen 1985, NRCC 1982, Yoshida et al. 1987, Arcand et al. 1995, Huang et al. 2000). There are other reports of pH effects on octanol-water partition coefficient (Kaiser and Valdmanis 1982, Westall et al. 1985, Lee et al. 1990, Smejtek and Wang 1993), soil sorption behavior (Choi and Amoine 1974, Lee et al. 1990, Schellenberg et al. 1984, Yoshida et al. 1987, Lee et al. 1990), bioconcentration and uptake kinetics to goldfish (Steihly and Hayton 1990) and toxicity to algae (Smith et al. 1987, Shigeoka et al. 1988).

The following treatment has been suggested by Shiu et al. (1994) and is reproduced briefly below. The simplest, “first-order” approach is to take into account the effect of dissociation by deducing the ratio of ionic to non-ionic species \( I \), the fraction ionic \( x_i \) and the fraction non-ionic \( x_n \) for the chemical at both the pH and temperature of experimental data determination \((I_D, x_{ID}, x_{ND})\) and at the pH and temperature of the desired environmental simulation \((I_E, x_{IE}, x_{NE})\). It is assumed that dissociation takes place only in aqueous solution, not in air, organic carbon, octanol or lipid phases. Some ions and ion pairs are known to exist in the latter two phases, but there are insufficient data to justify a general procedure for estimating the quantities. No correction is made for the effect of cations other than \( H^+ \). This approach must be regarded as merely a first correction for the dissociation effect. An accurate evaluation should preferably be based on experimental...
Most hydrophobic substances have low solubilities in water, and in the case of liquids, water is also sparingly soluble in pressure and a solubility as described earlier. From a known apply existing models to hydrophilic chemicals if this pseudo-solubility is calculated from the activity coefficient or temperature. Above this temperature, no mutual solubilities exist. A simple plot of solubility versus temperature thus ends temperature increases, these mutual solubilities increase until a point of total miscibility is reached at a critical solution point. At low temperatures near freezing, the phase diagram also become complex. Example of such systems is to input the "pseudo-solubilities" that have been derived from QSPR correlations with molecular descriptors for alcohols, aldehydes and amines (by Leahy 1986; Kamlet et al. 1987, 1988 and Nirmalakhandan and Speece 1988a, b). The obvious option "pseudo-solubilities" that have been derived from QSPR correlations with molecular descriptors for alcohols, aldehydes and amines (by Leahy 1986; Kamlet et al. 1987, 1988 and Nirmalakhandan and Speece 1988a, b). The obvious option is to input the $H$ or $K_{AW}$ directly. If the chemical’s activity coefficient $\gamma$ in water is known, then $H$ can be estimated as $v_wP_S/C$, where $v_w$ is the molar volume of water and $P_S$ is the liquid vapor pressure. Since $H$ can be regarded as $P_S/C$, where $C$ is the solubility, it is apparent that $(1/\gamma)\gamma$ is a "pseudo-solubility." Correlations and measurements of $\gamma$ are available in the physical-chemical literature. For example, if $\gamma$ is 5.0, the pseudo-solubility is 11100 mol/m$^3$ since the molar volume of water $v_w$ is $18 \times 10^{-6}$ m$^3$/mol or 18 cm$^3$/mol. Chemicals with $\gamma$ less than about 20 are usually miscible in water. If the liquid vapor pressure in this case is 1000 Pa, $H$ will be 1000/11100 or 0.090 Pa·m$^3$/mol and $K_{AW}$ will be $H/RT$ or $3.6 \times 10^{-5}$ at 25°C. Alternatively, if $H$ or $K_{AW}$ is known, $C_L$ can be calculated. It is possible to apply existing models to hydrophilic chemicals if this pseudo-solubility is calculated from the activity coefficient or from a known $H$ (i.e., $C_L^{sec}P_S^L/H$ or $P_S$ or $K_{AW}-RT$). This approach is used here. In the fugacity model illustrations all pseudo-solubilities are so designated and should not be regarded as real, experimentally accessible quantities.

1.2.5 Treatment of Water-Miscible Compounds

In the multimedia models used in this series of volumes, an air-water partition coefficient $K_{AW}$ or Henry’s law constant ($H$) is required and is calculated from the ratio of the pure substance vapor pressure and aqueous solubility. This method is widely used for hydrophobic chemicals but is inappropriate for water-miscible chemicals for which no solubility can be measured. Examples are the lower alcohols, acids, amines and ketones. There are reported “calculated” or “pseudo-solubilities” that have been derived from QSPR correlations with molecular descriptors for alcohols, aldehydes and amines (by Leahy 1986; Kamlet et al. 1987, 1988 and Nirmalakhandan and Speece 1988a, b). The obvious option is to input the $H$ or $K_{AW}$ directly. If the chemical’s activity coefficient $\gamma$ in water is known, then $H$ can be estimated as $v_wP_S/C$, where $v_w$ is the molar volume of water and $P_S$ is the liquid vapor pressure. Since $H$ can be regarded as $P_S/C$, where $C$ is the solubility, it is apparent that $(1/\gamma)\gamma$ is a "pseudo-solubility." Correlations and measurements of $\gamma$ are available in the physical-chemical literature. For example, if $\gamma$ is 5.0, the pseudo-solubility is 11100 mol/m$^3$ since the molar volume of water $v_w$ is $18 \times 10^{-6}$ m$^3$/mol or 18 cm$^3$/mol. Chemicals with $\gamma$ less than about 20 are usually miscible in water. If the liquid vapor pressure in this case is 1000 Pa, $H$ will be 1000/11100 or 0.090 Pa·m$^3$/mol and $K_{AW}$ will be $H/RT$ or $3.6 \times 10^{-5}$ at 25°C. Alternatively, if $H$ or $K_{AW}$ is known, $C_L$ can be calculated. It is possible to apply existing models to hydrophilic chemicals if this pseudo-solubility is calculated from the activity coefficient or from a known $H$ (i.e., $C_L^{sec}P_S^L/H$ or $P_S$ or $K_{AW}-RT$). This approach is used here. In the fugacity model illustrations all pseudo-solubilities are so designated and should not be regarded as real, experimentally accessible quantities.

1.2.6 Treatment of Partially Miscible Substances

Most hydrophobic substances have low solubilities in water, and in the case of liquids, water is also sparingly soluble in the pure substance. Some substances such as butanols and chlorophenols display relatively high mutual solubilities. As temperature increases, these mutual solubilities increase until a point of total miscibility is reached at a critical solution temperature. Above this temperature, no mutual solubilities exist. A simple plot of solubility versus temperature thus ends at this critical point. At low temperatures near freezing, the phase diagram also become complex. Example of such systems have been reported for sec-butyl alcohol (2-butanol) by Ochi et al. (1996) and for chlorophenols by Jaoui et al. (1999).

1.2.7 Treatment of Gases and Vapors

A volatile substance may exist in one of three broad classes that can be loosely termed gases, vapors and liquids. A gaseous substance such as oxygen at normal environmental conditions exists at a temperature exceeding its critical temperature of 155 K. No vapor pressure can be defined or measured under this super-critical condition, thus no Henry’s law constant can be calculated. Empirical data are required.

A substance such as propane with a critical temperature of 370 K has a measurable vapor pressure of 998000 Pa, or approximately 10 atm at 27°C, which exceeds atmospheric pressure of 101325 Pa, the boiling point being –42°C or 231 K. It is thus a vapor at normal temperatures and pressures. A Henry’s law constant can be calculated from this vapor pressure and a solubility as described earlier.
Most substances treated in this handbook are liquids or solids at environmental conditions; thus their boiling points exceed 25°C. Benzene, for example, has a critical temperature of 562 K, a boiling point of 80°C and a vapor pressure of 12700 Pa at 25°C.

When a solubility in water is measured and reported for gases and vapors an ambiguity is possible. For gases the solubility and the corresponding partial or total pressure in the gas phase must be reported since the solubility is dependent on this pressure as dictated by Henry’s Law. For liquids and solids the solubility is presumably measured under conditions when the partial pressure equals the vapor pressure. For vapors such as propane the solubility can be measured either at a specified pressure (usually 1 atmosphere) or under high-pressure conditions (e.g., 10 atm) when the substance is a liquid. When calculating \( H \) or \( K_{AW} \) it is essential to use the correct pressure corresponding to the solubility measurement. Care must be exercised when treating substances with boiling points at or below environmental temperatures to ensure that the solubility is interpreted and used correctly.

### 1.2.8 Solids, Liquids and the Fugacity Ratio

Saturation properties such as solubility in water and vapor pressure can be measured directly for solids and liquids. For certain purposes it is useful to estimate the solubility that a solid substance would have if it were liquid at a temperature below the melting point. For example, naphthalene melts at 80°C and at 25°C the solid has a solubility in water of 33 g/m³ and a vapor pressure of 10.9 Pa. If naphthalene was a liquid at 25°C it is estimated that its solubility would be 115 g/m³ and its vapor pressure 38.1 Pa, both a factor of 3.5 greater. This ratio of solid to liquid solubilities or vapor pressures is referred to as the fugacity ratio. It is 1.0 at the melting point and falls, in this case at lower temperatures to 0.286 at 25°C.

Solubilities and vapor pressures of a solid substance in the liquid state are often reported for the following four reasons.

- Measurements of gas chromatographic retention time are often used as a fast and easy method of estimating vapor pressure. These estimated pressures are related to the gas/substrate partition coefficient, which can be regarded as a ratio of solubility of the substance in the gas to that in the substrate, both solubilities being of the substance in the liquid state. As a result the estimated vapor pressures are of the liquid state. To obtain the solid vapor pressure requires multiplication by the fugacity ratio. It is important to establish if the estimated and reported property is of the vapor or liquid.

- QSRRs in which solubilities and vapor pressures are correlated against molecular structure are done exclusively using the liquid state property. This avoids the complication introduced by the effect of fugacity ratio or melting point on the solid state property.

- When a solid is in liquid solution it behaves according to its liquid state properties because it is in a liquid mixture. When applying Raoult’s Law or similar expressions, the pure substance property is that of the liquid. Liquids such as crude oils and PCB mixtures consist largely of solid substances, but they are in the liquid state and generally unable to precipitate as solid crystals because of their low individual concentrations.

- When estimating air-aerosol partitioning of gas phase substances such as PAHs, most of which are solids, it is usual to use the liquid state vapor pressure as the correlating parameter. This is because the PAH is effectively in a liquid-like state on or in the aerosol particle. It does not exist in crystalline form.

When calculating partition coefficients such as \( K_{AW} \), \( K_{OW} \) or \( K_{OA} \) from solubilities it is immaterial if the values used are of solids or liquids, but it is erroneous to mix the two states, e.g., a solid solubility and a liquid vapor pressure.

The fugacity ratio \( F \) can be estimated at temperature \( T \) (K) from the expression

\[
\ln F = -\Delta S (T_M - T)/RT
\]

where \( \Delta S \) is the entropy of fusion, \( T_M \) is the melting point, and R is the gas constant. \( \Delta S \) is related to the measurable enthalpy of fusion \( \Delta H \) at the melting point as \( \Delta H/T_M \). The reader should use experimental data for \( \Delta H \), \( \Delta S \) and melting point whenever possible. The most reliable method is to measure \( \Delta H \) calorimetrically, calculate \( \Delta S \) and use this value to estimate \( F \). Only in the absence of \( \Delta H \) data should a QSRR be used or Walden’s Rule applied that \( \Delta S \) is approximately 56.5 J/mol K. This assumption leads to the equations

\[
F = \exp(-6.79(T_M/T - 1))
\]

\[
\log F = -0.01(T_M - 298)
\]
F is thus 1.0 at the melting point, with lower values at lower temperatures. It is not applied at temperatures exceeding $T_M$.

This issue is discussed by Mackay (2001), Tesconi and Yalkowsky (2000), Yalkowsky and Banerjee (1992) and Chickos et al. (1999).

### 1.2.9 Chemical Reactivity and Half-Lives

Characterization of chemical reactivity presents a challenging problem in environmental science in general and especially in handbooks. Whereas radioisotopes have fixed half-lives, the half-life of a chemical in the environment depends not only on the intrinsic properties of the chemical, but also on the nature of the environmental compartments. Factors such as sunlight intensity, hydroxyl radical concentration and the nature of the microbial community, as well as temperature, affect the chemical’s half-life so it is impossible (and misleading) to document a single reliable half-life. We suggest that the best approach is to suggest a semi-quantitative classification of half-lives into groups or ranges, assuming average environmental conditions to apply. Obviously, a different class will generally apply between compartments such as in air and bottom sediment. In this compilation we use the following class ranges for chemical reactivity in a single medium such as water.

These times are divided logarithmically with a factor of approximately 3 between adjacent classes. With the present state of knowledge it is probably misleading to divide the classes into finer groupings; indeed, a single chemical is likely to experience half-lives ranging over three classes, depending on season. These half-lives apply to the reaction of the parent substance. Often a degradation product or metabolite is formed that is of environmental concern. Since it has different properties it requires separate assessment. The ultimate degradation to inorganic species may require a much longer time than is indicated by the initial half-life.

<table>
<thead>
<tr>
<th>class</th>
<th>mean half-life (hours)</th>
<th>range (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 &lt; 10</td>
<td>10–30</td>
</tr>
<tr>
<td>2</td>
<td>17 (~ 1 day)</td>
<td>30–100</td>
</tr>
<tr>
<td>3</td>
<td>55 (~ 2 days)</td>
<td>100–300</td>
</tr>
<tr>
<td>4</td>
<td>170 (~ 1 week)</td>
<td>300–1,000</td>
</tr>
<tr>
<td>5</td>
<td>550 (~ 3 weeks)</td>
<td>1,000–3,000</td>
</tr>
<tr>
<td>6</td>
<td>1700 (~ 2 months)</td>
<td>3,000–10,000</td>
</tr>
<tr>
<td>7</td>
<td>5500 (~ 8 months)</td>
<td>10,000–30,000</td>
</tr>
<tr>
<td>8</td>
<td>17000 (~ 2 years)</td>
<td>30,000–100,000</td>
</tr>
<tr>
<td>9</td>
<td>55000 (~ 6 years)</td>
<td>&gt; 100,000</td>
</tr>
<tr>
<td>10</td>
<td>&gt; 11 years</td>
<td></td>
</tr>
</tbody>
</table>

When compiling the suggested reactivity classes, the authors have examined the available information on reaction rates of the chemical in each medium by all relevant processes. These were expressed as an overall half-life for transformation. The product of the half-life and the corresponding rate constant is ln2 or 0.693. For example, a chemical may be subject to biodegradation with a half-life of 20 days or 480 hours (rate constant 0.0014 h$^{-1}$) and simultaneous photolysis with a rate constant of 0.0011 h$^{-1}$ (half-life 630 hours). The overall rate constant is thus 0.0025 h$^{-1}$ and the half-life is 277 hours or 12 days. Data for homologous chemicals have also been compiled, and insights into the reactivity of various functional groups considered. In most cases a single reaction class is assigned to the series; in the above case, class 4 with a mean half-life of 170 hours would be chosen. These half-lives must be used with caution, and it is wise to test the implications of selecting longer and shorter half-lives.

The most reliable kinetic data are for atmospheric oxidation by hydroxyl radicals. These data are usually reported as second-order rate constants applied to the concentration of the chemical and the concentration of hydroxyl radicals (usually of the order of $10^6$ radicals per cm$^3$). The product of the assumed hydroxyl radical concentration and the second-order rate constant is a first-order rate constant from which a half-life can be deduced.

Extensive research has been conducted into the atmospheric chemistry of organic chemicals because of air quality concerns. Recently, Atkinson and coworkers (1984, 1985, 1987, 1988, 1989, 1990, 1991), Altshuller (1980, 1991) and Sabljic and Güsten (1990) have reviewed the photochemistry of many organic chemicals of environmental interest for their gas phase reactions with hydroxyl radicals (OH), ozone ($O_3$) and nitrate radicals ($NO_3$) and have provided detailed information on reaction rate constants and experimental conditions, which allowed the estimation of atmospheric lifetimes. Klöpffer (1991) has estimated the atmospheric lifetimes for the reaction with OH radicals to range from 1 hour to 130 years, based on these reaction rate constants and an assumed constant concentration of OH...
radicals in air. As Atkinson (1985) has pointed out, the gas phase reactions with OH radicals are the major tropospheric loss process for the alkanes, haloalkanes, the lower alkenes, the aromatic hydrocarbons, and a majority of the oxygen-containing organics. In addition, photooxidation reactions with O₃ and NOₓ radicals can result in transformation of these compounds. The night-time reaction with NOₓ radicals may also be important (Atkinson and Carter 1984, Sabljic and Güsten 1990).

There are fewer studies on direct or indirect photochemical degradation in the water phase; however, Klöpffer (1991) had pointed out that the rate constant or lifetimes derived from these studies “is valid only for the top layer or surface waters.” Mill (1982, 1989, 1993) and Mill and Mabey (1985) have estimated half-lives of various chemicals in aqueous solutions from their reaction rate constants with singlet oxygen, as well as photooxidation with hydroxyl and peroxo radicals. Buxton et al. (1988) gave a critical review of rate constants for reactions with hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions. Mabey and Mill (1978) also reviewed the hydrolysis of organic chemicals in water under environmental conditions. Recently, Ellington and coworkers (1987a,b, 1988, 1989) also reported the hydrolysis rate constants in aqueous solutions for a variety of organic chemicals.

In most cases, a review of the literature suggested that reaction rates in water by chemical processes are 1 to 2 orders of magnitude slower than in air, but with biodegradation often being significant, especially for hydrocarbons and oxygen-containing chemicals. Generally, the water half-life class is three more than that in air, i.e., a factor of about 30 slower. Chemicals in soils tend to be shielded from photolytic processes, and they are less bioavailable, thus the authors have frequently assigned a reactivity class to soil of one more than that for water. Bottom sediments are assigned an additional class to that of soils largely on the basis that there is little or no photolysis, there may be lack of oxygen, and the intimate sorption to sediments renders the chemicals less bioavailable.

Because of the requirements of regulations for certain chemicals such as pesticides, extensive data usually exist on partitioning properties and reactivity or half-lives of active ingredients. In some cases these data have been peer-reviewed and published in the scientific literature, but often they are not generally available. A reader with interest in a specific pesticide can often obtain additional data from manufacturers or from registration literature, including accounts of chemical fate under field application conditions. Frequently these data are used as input to pesticide fate models, and the results of these modeling exercises may be available or published in the scientific literature.

The chemical reactivity of these substances is a topic which continues to be the subject of extensive research; thus there is often detailed, more recent information about the fate of chemical species which are of particular relevance to air or water quality. The reader is thus urged to consult the original and recent references because when considering the entire multimedia picture, it is impossible in a volume such as this to treat this subject in the detail it deserves.

1.3 EXPERIMENTAL METHODS

1.3.1 SOLUBILITY IN WATER AND pKₐ

Most conventional organic contaminants are fairly hydrophobic and thus exhibit a low but measurable solubility in water. Solubility is often used to estimate the air-water partition coefficient or Henry’s law constant, but this is not possible for miscible chemicals; indeed the method is suspect for chemicals of appreciable solubility in water, i.e., exceeding 1 g/100 g. Direct measurement of the Henry’s law constant is thus required.

The conventional method of preparing saturated solutions for the determination of solubility is batch equilibration. An excess amount of solute chemical is added to water and equilibrium is achieved by shaking gently (generally referred to as the “shake flask method”) or slow stirring with a magnetic stirrer. The aim is to prevent formation of emulsions or suspensions and thus avoid extra experimental procedures such as filtration or centrifuging which may be required to ensure that a true solution is obtained. Experimental difficulties can still occur with sparingly soluble chemicals such as longer chain alkanes and polycyclic aromatic hydrocarbons (PAHs) because of the formation of emulsion or microcrystal suspensions. An alternative approach is to coat a thin layer of the chemical on the surface of the equilibration flask before water is added. An accurate “generator column” method is also used (Weil et al. 1974, May et al. 1978a,b) in which a column is packed with an inert solid support, such as glass beads and then coated with the solute chemical. Water is pumped through the column at a controlled, known flow rate to achieve saturation.

The method of concentration measurement of the saturated solution depends on the solute solubility and its chemical properties. Some common methods used for solubility measurement are listed below.

1. Gravimetric or volumetric methods (Booth and Everson 1948)

An excess amount of solid compound is added to a flask containing water to achieve saturation solution by shaking, stirring, centrifuging until the water is saturated with solute and undissolved solid or liquid
residue appears, often as a cloudy phase. For liquids, successive known amounts of solute may be added to water and allowed to reach equilibrium, and the volume of excess undissolved solute is measured.

2. Instrumental methods
   a. UV spectrometry (Andrews and Keefer 1950, Bohon and Claussen 1951, Yalkowsky and Valvani 1976);
   b. Gas chromatographic analysis with FID, ECD or other detectors (McAuliffe 1966, Mackay et al. 1975, Chiu et al. 1982, Bowman and Sans 1983);
   c. Fluorescence spectrophotometry (Mackay and Shiu 1977);
   d. Interferometry (Gross and Saylor 1931);
   e. High-pressure liquid chromatography (HPLC) with I.R., UV or fluorescence detection (May et al. 1978a,b, Wasik et al. 1983, Shiu et al. 1988, Doucette and Andren 1988a);
   f. Liquid phase elution chromatography (Schwarz 1980, Schwarz and Miller 1980);
   g. Nephelometric methods (Davis and Parke 1942, Davis et al. 1942, Hollifield 1979);
   h. Radiotracer or liquid scintillation counting (LSC) method (Banerjee et al. 1980, Lo et al. 1986).

For most organic chemicals the solubility is reported at a defined temperature in distilled water. For substances which dissociate (e.g., phenols, carboxylic acids and amines) it is essential to report the pH of the determination because the extent of dissociation affects the solubility. It is common to maintain the desired pH by buffering with an appropriate electrolyte mixture. This raises the complication that the presence of electrolytes modifies the water structure and changes the solubility. The effect is usually “salting-out.” For example, many hydrocarbons have solubilities in seawater about 75% of their solubilities in distilled water. Care must thus be taken to interpret and use reported data properly when electrolytes are present.

The dissociation constant $K_a$ or its commonly reported negative logarithmic form $pK_a$ is determined in principle by simultaneous measurement or deduction of the ionic and non-ionic concentrations and the pH of the solution.

The most common problem encountered with reported data is inaccuracy associated with very low solubilities, i.e., those less than 1.0 mg/L. Such solutions are difficult to prepare, handle and analyze, and reported data often contain appreciable errors.

As was discussed earlier, care must be taken when interpreting solubility data for gases, i.e., substances for which the temperature exceeds the boiling point. Solubility then depends on the pressure which may be atmospheric or the higher vapor pressure.

1.3.2 Vapor Pressure

In principle, the determination of vapor pressure involves the measurement of the saturation concentration or pressure of the solute in a gas phase. The most reliable methods involve direct determination of these concentrations, but convenient indirect methods are also available based on evaporation rate measurements or chromatographic retention times. Some methods and approaches are listed below.

   a. Static method, the equilibrium pressure in a thermostatic vessel is directly measured by use of pressure gauges: diaphragm gauge (Ambrose et al. 1975), Rodebush gauge (Sears and Hopke 1947), inclined-piston gauge (Osborn and Douslin 1975);
   b. Dynamic method (or boiling point) for measuring relatively high vapor pressure, e.g., comparative ebulliometry (Ambrose 1981);
   c. Effusion methods, torsion and weight-loss (Balson 1947, Bradley and Cleasby 1953, Hamaker and Kerlinger 1969, De Kruijff 1980);
   e. Dynamic coupled-column liquid chromatographic method- a gas saturation method (Sonnefeld et al. 1983);
   f. Calculation from evaporation rates and vapor pressures of a reference compound (Gückel et al. 1974, 1982, Dobbs and Grant 1980, Dobbs and Cull 1982);

The greatest difficulty and uncertainty arises when determining the vapor pressure of chemicals of low volatility, i.e., those with vapor pressures below 1.0 Pa. Vapor pressures are strongly dependent on temperature, thus accurate temperature control is essential. Data are often regressed against temperature and reported as Antoine or Clapeyron constants. Care
must be taken if the Antoine or other equations are used to extrapolate data beyond the temperature range specified. It must be clear if the data apply to the solid or liquid phase of the chemical.

1.3.3 Octanol-Water Partition Coefficient $K_{OW}$

The experimental approaches are similar to those for solubility, i.e., employing shake flask or generator-column techniques. Concentrations in both the water and octanol phases may be determined after equilibration. Both phases can then be analyzed by the instrumental methods discussed above and the partition coefficient is calculated from the concentration ratio $C_O/C_W$. This is actually the ratio of solute concentration in octanol saturated with water to that in water saturated with octanol.

As with solubility, $K_{OW}$ is a function of the presence of electrolytes and for dissociating chemicals it is a function of pH. Accurate values can generally be measured up to about $10^7$, but accurate measurement beyond this requires meticulous technique. A common problem is the presence of small quantities of emulsified octanol in the water phase. The high concentration of chemical in that emulsion causes an erroneously high apparent water phase concentration.

Considerable success has been achieved by calculating $K_{OW}$ from molecular structure; thus, there has been a tendency to calculate $K_{OW}$ rather than measure it, especially for “difficult” hydrophobic chemicals. These calculations are, in some cases, extrapolations and can be in serious error. Any calculated log $K_{OW}$ value above 7 should be regarded as suspect, and any experimental or calculated value above 8 should be treated with extreme caution.

For many hydrophilic compounds such as the alcohols, $K_{OW}$ is low and can be less than 1.0, resulting in negative values of log $K_{OW}$. In such cases, care should be taken when using correlations developed for more hydrophobic chemicals since partitioning into biota or organic carbon phases may be primarily into aqueous rather than organic media.

Details of experimental methods are described by Fujita et al. (1964), Leo et al. (1971), Hansch and Leo (1979), Rekker (1977), Chiou et al. (1977), Miller et al. (1984, 1985), Bowman and Sans (1983), Woodburn et al. (1984), Doucette and Andre (1987), and De Bruijn et al. (1989).

1.3.4 Henry’s Law Constant

The Henry’s law constant is essentially an air-water partition coefficient which can be determined by measurement of solute concentrations in both phases. This raises the difficulty of accurate analytical determination in two very different media which usually requires different techniques. Accordingly, effort has been devoted to devising techniques in which concentrations are measured in only one phase and the other concentration is deduced from a mass balance. These methods are generally more accurate. The principal difficulty arises with hydrophobic, low-volatility chemicals which can establish only very small concentrations in both phases.

Henry’s law constant can be regarded as a ratio of vapor pressure to solubility, thus it is subject to the same effects that electrolytes have on solubility. Temperature affects both properties. Some methods are as follows:

a. Volatility measurement of dilute aqueous solutions (Butler et al. 1935, Burnett 1963, Buttery et al. 1969);
b. Multiple equilibration method (McAuliffe 1971, Munz and Roberts 1987);
c. Equilibrium batch stripping (Mackay et al. 1979, Dunnivant et al. 1988, Betterton and Hoffmann 1988, Zhou and Mopper 1990);
d. GC-determined distribution coefficients (Leighton and Calo 1981);
e. GC analysis of both air/water phases (Vejrostova et al. 1982, Jonsson et al. 1982);
f. EPICS (Equilibrium Partitioning In Closed Systems) method (Lincoff and Gossett 1984, Gossett 1987, Ashworth et al. 1988);
g. Wetted-wall column (Fendinger and Glotfelty 1988, 1989, 1990);
h. Headspace analyses (Hussam and Carr 1985);
i. Calculation from vapor pressure and solubility (Mackay and Shiu 1981);
j. GC retention volume/time determined activity coefficient at infinite dilution $\gamma^*$ (Karger et al. 1971a,b, Sugiyama et al. 1975, Tse et al. 1992).

When using vapor pressure and solubility data, it is essential to ensure that both properties apply to the same chemical phase, i.e., both are of the liquid, or of the solid. Occasionally, a solubility is of a solid while a vapor pressure is extrapolated from higher temperature liquid phase data.

As was discussed earlier under solubility, for miscible chemicals it is necessary to determine the Henry’s law constant directly, since solubilities are not measurable.