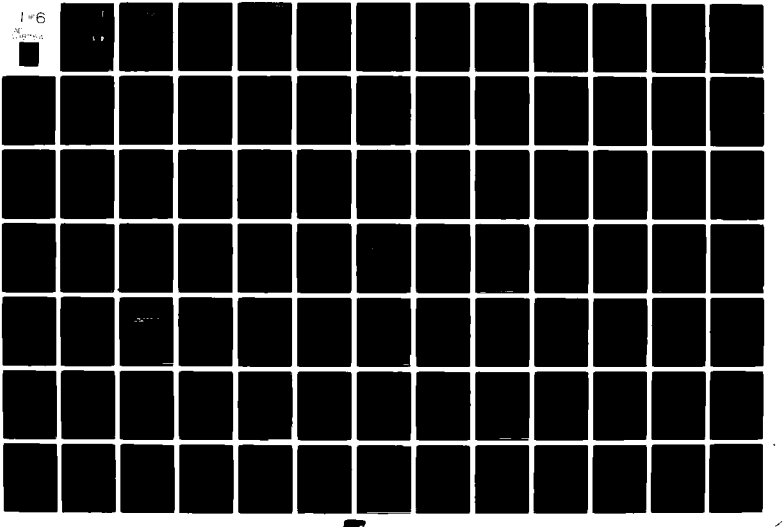
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RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEMICAL PROPERTIES OF ORGANIC COMPOUNDS OF ENVIRONMENTAL CONCERN

FINAL REPORT, PHASE II
(PART 1 OF 2 PARTS)

by

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US Army Medical Bioengineering Research and Development Laboratory

June 1981

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Cambridge, Massachusetts 02140

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This report contains selected, evaluated estimation methods for 26 environmentally important physicochemical properties of organic chemicals. The methods selected are applicable to a variety of chemical classes, are easy to use, require a minimum of input data, and are reasonably accurate. Each method has a descriptive text, step-by-step instructions, worked-out examples, and supplementary information allowing the user to estimate the likely uncertainty of an estimated value. Approximately 800 literature references cited.

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EXECUTIVE SUMMARY

This document is the final report for Phase II of a program carried out by Arthur D. Little, Inc., for the U.S. Army Medical Bioengineering Research and Development Laboratory. The report contains selected estimation methods for several environmentally important physicochemical properties of organic chemicals. The general style of the report is that of a handbook with specific instructions for the use of each estimation method.

Our goal in this program was to distill the widely scattered literature, much of recent origin, in order to select and present in an organized manner the most appropriate estimation methods for particular chemical properties. This information should be useful to environmental chemists, environmental program managers, and even some chemical process engineers, who must frequently deal with problematic chemicals for which even the most basic physicochemical properties may be unknown. The methods described here permit rapid estimation of properties and thereby facilitate studies of these problematic chemicals for such purposes as chemical fate modeling, exposure assessments, priority ranking of large lists of chemicals, and process design.

Each of the 26 chapters of this handbook covers one physicochemical property or parameter. (See list on inside cover.) With few exceptions, each chapter provides: (1) a general discussion of the property and its importance in environmental considerations, (2) an overview of available estimation methods, (3) a description plus step-by-step instructions for each selected method, (4) worked-out examples for each method, (5) a listing of sources of available data on the property, (6) a list of symbols used, and (7) the cited references. The chapters on Rate of Aqueous Photolysis (Chap. 8) and Rate of Biodegradation (Chap. 9) depart from the usual format and provide only qualitative or semiquantitative information; neither of these properties can be estimated at present.

Most chapters provide two or more estimation methods. In selecting the methods, we favored those that: (1) are applicable to a variety of chemical classes and structures, (2) are relatively simple to use with no more than a desk calculator, (3) require a minimum of input data; and (4) are reasonably accurate. Information on method errors is provided with each chapter; an appendix describes a procedure to estimate propagated and total error in situations where one or more inputs must first be estimated. None of the selected methods is intended to be applicable to organic mixtures, polymers, solutions, or inorganic compounds.

ACKNOWLEDGMENTS

The original idea for an environmentally oriented handbook of chemical property estimation methods was by our Project Officer, Dr. David H. Rosenblatt of the U.S. Army Medical Bioengineering Research and Development Laboratory (Fort Detrick, Frederick, MD). His initiative, guidance, and subsequent assistance in the preparation of the handbook — especially as an editor — were essential to the successful completion of this program.

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The authors of individual chapters are listed on the first page of each chapter. Special credit should be given to William F. Reehl, who served as both a technical and style editor for every chapter.

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INTRODUCTION

OVERVIEW

This report contains selected estimation methods for several physicochemical properties of organic chemicals. The full list of properties covered is shown in Table 1. The general style of the report is that of a handbook with specific instructions for the use of each estimation method. It is hoped that the descriptions and examples will be useful to environmental chemists and environmental program managers, who must frequently deal with problem chemicals for which even the most basic physicochemical properties may be missing from the literature or data collections. The report should also be of use to process engineers when they must estimate properties of chemicals at or near ambient temperatures and pressures.

The "properties" covered by this handbook include a variety of conventional properties of pure materials (e.g., density, boiling point, refractive index), some properties that describe how a chemical behaves or interacts with a second substance (e.g., solubility in water, diffusion coefficient in air, interfacial tension with water), and a set that describe the fate of trace concentrations of the chemical in specific environmental situations (e.g., rate of hydrolysis in water, atmospheric residence time, and volatilization from soil). The latter group — in particular, Chapters 8, 10, 15 and 16 — are related more to environmental fate than to physicochemical properties; these models require input information on the environmental compartment of concern as well as chemical-specific properties.

TABLE 1

Physicochemical Properties Covered in this Report

Chapter	Property
1	Octanol/Water Partition Coefficient
2	Solubility in Water
3	Solubility in Various Solvents
4	Adsorption Coefficient for Soils and Sediments
5	Bioconcentration Factor in Aquatic Organisms
6	Acid Dissociation Constant
7	Rate of Hydrolysis
8	Rate of Aqueous Photolysis
9	Rate of Biodegradation
10	Atmospheric Residence Time
11	Activity Coefficient
12	Boiling Point
13	Heat of Vaporization
14	Vapor Pressure
15	Volatilization from Water
16	Volatilization from Soil
17	*Diffusion Coefficients in Air and Water*
18	Flash Points of Pure Substances
19	Densities of Vapors, Liquids and Solids
20	Surface Tension
21	Interfacial Tension with Water
22	Liquid Viscosity
23	Heat Capacity
24	Thermal Conductivity
25	Dipole Moment
26	Index of Refraction

Two important properties, rate of aqueous photolysis (Ch. 8) and rate of biodegradation (Ch. 9), are included in this handbook even though the current state of the art does not permit quantitative estimation. These two chapters stress the importance of photolysis and biodegradation in environmental fate and should allow a qualitative determination of the susceptibility of an organic chemical to these forms of degradation. Additional research is required before quantitative estimation methods can be developed.

A few additional properties that are not the subject of separate chapters may be estimated from instructions given in this handbook. These properties are used as input parameters for other estimation methods and frequently must be estimated themselves. Included are:

Property	See
Critical temperature	§12-4
Critical pressure	§13-4
Henry's law constant	§15-5 (see also §11-4, Example 11-2)
Mass transfer coefficients[1]	§15-5
Molar refractivity	Ch. 26 (also §12-3)
Molar volume at the boiling point	§12-5 (or §19-5)
Parachor	§20-3 (or §12-3)

Most of the estimation methods in this handbook (excluding those dealing with environmental fate models) are based upon one of the following:

(1) Theoretical equations, usually containing parameters that are empirically derived (e.g., via fragment constants),

(2) Group or atomic fragment constants derived by regression analysis of data sets, or

(3) Correlations (usually in the form of linear regression equations) between two properties.

Types 1 and 2 are most frequently encountered for properties of the pure chemical (e.g., boiling point, heat of vaporization, density, heat capacity), while type 3 is more commonly used for certain environmental properties (e.g., aqueous solubility, soil adsorption coefficient, bioconcentration factor). Combinations of the above approaches are also possible. Because of the increasing importance of linear regression equations, a detailed discussion of this subject is provided in Appendix B. Type 2 methods (i.e., those requiring only the use of fragment constants) are favored in many circumstances where little is known about the chemical, since they require only a knowledge of the chemical's structure. In most other methods, one or more different properties of the chemical must be known (or estimated) before the desired property can be estimated.

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1. In air and water near the air/water interface.

Some aspects of the novelty and innovation associated with this work should be noted. It is, to our knowledge, the first attempt to review and evaluate available estimation methods for a group of environmentally important physicochemical properties (particularly those covered in Chapters 1—10, 15, 16 and 18). For many of the remaining properties we relied heavily on the excellent review of estimation methods by Reid *et al.*[2] Secondly, although the original objective of this report was to cover only available (i.e., previously published) estimation methods, several authors found ways to improve or expand them. This has permitted the inclusion of some new or modified methods with enhanced utility.

APPENDICES

The following four appendices to this report provide important supplemental information:

A. "Bibliography of Standard Chemical Property Data Sources" lists selected reference books and articles that contain compilations of measured physicochemical properties of organic chemicals.

B. "Simple Linear Regression" describes linear regression analysis and explains (with examples) how readers can use regression analysis to formulate new estimation equations.

C. "Evaluating Propagated and Total Error in Chemical Property Estimates" discusses propagated and total error in chemical property estimates to cover those cases when both propagated error (i.e., error associated with an estimated or otherwise uncertain input parameter) and method error (i.e., that associated with the method when all input parameters are exactly known) must be considered. Detailed instructions and examples are given.

D. "Recommendations for Future Research" suggests avenues of investigation that will either improve present methods or lead to new methods for estimating various properties — not only those covered in this handbook but also some that cannot presently be estimated.

OBJECTIVES

Over the past decade, the chemical contamination of our environment has justifiably aroused growing concern. A proper assessment of

2. Reid, R.C., J.M. Prausnitz and T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill Book Co., New York (1977).

the risk — to man and the environment — created by exposure to these chemicals generally includes attempts to measure or predict the concentrations in various environmental compartments in conjunction with toxicological data. Frequently, however, neither the concentration data nor the toxicological data are adequate for any realistic assessment. In addition, basic physical and chemical data are often unavailable, especially for new organic chemicals being considered for bulk manufacture. If, however, the most important physical and chemical properties of these chemicals could be estimated, their transport and fate in the environment could be better understood — even modeled in some cases — and the eventual environmental concentrations might be estimated.

In September 1978, with support from the U.S. Army Medical Bioengineering Research and Development Laboratory (Fort Detrick, Frederick, MD), Arthur D. Little, Inc., undertook a preliminary problem definition study to answer the following questions: (1) What are the important properties of organic chemicals with regard to their transport and fate in the environment? (2) What methods are available for the estimation of these properties? (3) What limitations and/or uncertainties are associated with these methods? and (4) Can a comprehensive user's manual incorporating the basic elements of these methods be prepared so they become not only easy to comprehend and use, but hard to misuse?

The results of this preliminary study[3] included a recommendation that a property estimation handbook be prepared covering 26 specific properties. In this study, a review of environmental fate models, hazard ranking schemes, federal regulations, and other material first led to the identification of about 50 physicochemical properties of interest. Additional literature surveys indicated that estimation methods were available for only half of the properties.

For the estimable properties, it has been our goal to select (and recommend) two or more estimation methods for each property. Our selection of methods was based upon the following considerations:

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3. Lyman, W.J., J.C. Harris, L.H. Nelken and D.H. Rosenblatt, "Research and Development of Methods for Estimating Physicochemical Properties of Organic Compounds of Environmental Concern, Final Report, Phase I," NTIS Report No. AD-A074829, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD (February 1979).

- *Range of applicability* — Methods should be adaptable to a variety of chemical classes and structures and should be applicable over the range of values of interest to environmental chemists.
- *Ease of use* — The rules and equations should be relatively simple and capable of solution without a computer. We have presumed that the user would have at least one year of college-level organic chemistry and a reasonable facility with common mathematical functions.
- *Minimum input data requirements* — Very little property data (from actual measurements) is available for some chemicals. Thus, methods requiring minimum input data are desired. In several cases, estimation methods requiring only the chemical structure are available.
- *Accuracy* — While the highest possible accuracy is desirable, it should not overshadow the first three considerations. For environmental fate models, hazard assessments, etc., precise chemical property data are not always needed.

BENEFITS OF ESTIMATION

With such estimation methods at their disposal, environmental scientists and environmental program managers should find their tasks much simplified. In particular, we expect estimated values of organic chemicals to be used in lieu of measured values (temporarily, at least) to:

(1) Obtain a sufficient understanding of a chemical's fate and transport in the environment to allow decisions and actions (for environmental protection) to proceed in a timely manner;

(2) Run a variety of environmental fate models to predict concentrations in various environmental compartments (air, water, soil);

(3) Set research priorities, especially in cases where large numbers of chemicals must be considered;

(4) Check the reliability of reported measurements; and

(5) Design laboratory and/or field experiments.

Associated with the use of estimated values of physicochemical properties will be a significant saving of both time and funds. To obtain

a measured value of many of the selected properties, several days to several weeks and hundreds to thousands of dollars (per property) are commonly required. For example, the cost of obtaining a measured value for all 26 properties of just one chemical could be in the range of $10,000 to $50,000, or perhaps higher. In some situations, estimation methods could be preferable to the usual literature search, which could cost $50-$500 for a single property of just one chemical. Estimation of a chemical property (excluding the models in Chapters 8, 10, 15 and 16) usually takes only 15 to 30 minutes if the user is reasonably familiar with the methods and there are no significant problems with input data requirements. This time will normally allow for some checking for calculational errors and for documentation of the method used.

CONTENTS OF EACH CHAPTER

A degree of uniformity of style and content has been imposed on each chapter in this handbook to facilitate its use. Each property estimation chapter (excepting Chapters 8 and 9) generally contains the following elements:

- *Introductory material* describing the property, its importance, range of values, and factors affecting the value.
- *Overview of available estimation methods,* including summary information on each recommended method (applicability, input requirements, method error) and a discussion of which methods the user should consider for a particular chemical.
- *Method description* (for each recommended method), including basis for method, necessary equations and tables, and an explicit set of instructions (labeled *Basic Steps)* for the use of the method. Additional information on method error is usually included.
- *Examples.* Two or more examples of each method are usually provided.
- *Available data.* References to major compilations of data on the property are provided. Supplemental information is given in Appendix A for the more common physicochemical properties.
- *Symbols used.* A listing, with definitions, of all symbols used.
- *References.* An alphabetical listing of the references cited in the chapter.

LIMITATIONS OF THIS HANDBOOK

As noted above, this is the first attempt to review, evaluate, and recommend estimation methods for a large group of environmentally important physicochemical properties. Several deficiencies and errors are likely to be present, which we hope to eliminate in future editions.

The basic limitation of this handbook is that only single-component (i.e., pure) organic chemicals are covered. Future editions may be able to cover organic mixtures (e.g., gasoline, fuel oil, or simple two-component mixtures) for some properties. Extensions to include polymers, salts, solutions, and inorganic chemicals are not presently contemplated.

For several estimation methods the reader will find that some chemical classes or structures cannot be handled, i.e., no estimate can be calculated. This may be due to a lack of appropriate fragment constants, to an unacceptably high method error for that class (or no information on method error at all for that class), or to the lack of an appropriate constant or equation. This is particularly true of organometallics. Improvisation is not recommended unless the reader is familiar with the method(s) and aware of the large errors that may result.

Another problem is the limited capability of many of the recommended methods to provide estimates either as a function of temperature (and pressure), or to provide estimates at temperatures (and pressures) outside of the normal range of ambient values. In addition, the value of many properties (e.g., solubility, adsorption coefficient, rate of hydrolysis) may be affected by other environmental factors in ways that are not understood.

Finally, the preparation of this handbook did not involve the compilation and evaluation of large sets of *measured* data on each property. As a result, we have not analyzed method applicability and method error for as many chemicals (and chemical classes) as would be desirable.

ERRORS ASSOCIATED WITH CHEMICAL PROPERTY ESTIMATES

Each chapter in this handbook contains some information on method error, i.e., the errors found when estimated values are compared with measured values for a set of chemicals. These method

errors (the absolute average errors for the selected test sets) vary greatly. Some are as low as 1-2% (e.g., density, vapor pressure for values >10 mm Hg, heat capacity, and index of refraction); several are in the range of 3-20% (e.g., boiling point, heat of vaporization, diffusion coefficients, surface tension); and some have errors that are nearly one order of magnitude (e.g., aqueous solubility, soil adsorption coefficient, bioconcentration factors). Uncertainties of one order of magnitude for this last group are not a serious problem, when one considers the normal use to which these estimates will be put (risk assessments, fate modeling) and the fact that their values range over six orders of magnitude.

The error associated with a particular estimate obviously cannot be predicted until a measured value is obtained. We recommend that all reported estimates be listed with their associated uncertainty, taken from the information on method error given in each chapter. If method errors are given for several chemical classes, the value for the appropriate chemical class should be selected. If the information on method error for a particular class of chemicals is insufficient, the reader may wish to evaluate the likely method error by using the method to estimate values for several chemicals (of related structure) for which measured values are available.

In many instances the user will have to estimate one or more of the input parameters for a particular method. For example, method 3 for estimating liquid viscosity (§22-6) requires a value for the boiling point as input. If no measured value of the boiling point is available, it can be estimated by the methods described in Chapter 12. The uncertainty of this estimate should be combined with the method error for the viscosity estimation when one is calculating the likely total error, as described in Appendix C.

DOCUMENTATION AND REPORTING OF ESTIMATED VALUES

It is strongly recommended that all reported chemical property estimates be clearly labeled as estimates, and that the methods used to obtain them be explained in a footnote or reference. The uncertainty in the estimate (see above) should also be reported. It will often be desirable to prepare a more formal record of the procedures used to obtain an estimate; Figure 1 is a sample of one kind of form that could be used for internal documentation.

Chemical _____ Estimate of _____

Estimated Value _____ Uncertainty _____ Temperature _____

Estimated by _____ Date _____

Method Used _____ Ref. _____

Equations Used _____ _____ Ref. _____

Values of Input Parameters:

	Parameter	Value	Comments	Ref.
1)	_____	_____	_____	_____
2)	_____	_____	_____	_____
3)	_____	_____	_____	_____
4)	_____	_____	_____	_____

List below: (1) important assumptions made, (2) values of key intermediate parameters, (3) key equations, and (4) other pertinent comments on the method used and the estimated value. (Attach details of complex calculations on separate sheet.)

Checked by _____ Date _____

References

1.
2.
3.

FIGURE 1. Sample Form for Reporting Estimated Chemical Properties

1

OCTANOL/WATER PARTITION COEFFICIENT

Warren J. Lyman

1-1 INTRODUCTION

Definition and Measurement. The octanol/water partition coefficient (K_{ow})[1] is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system.

$$K_{ow} = \frac{\text{Concentration in octanol phase}}{\text{Concentration in aqueous phase}} \qquad (1\text{-}1)$$

Values of K_{ow} are thus unitless. The parameter is measured using low solute concentrations, where K_{ow} is a very weak function of solute concentration. Values of K_{ow} are usually measured at room temperature (20 or 25°C). The effect of temperature on K_{ow} is not great — usually on the order of 0.001 to 0.01 log K_{ow} units per degree — and may be either positive or negative [28].

Measured values of K_{ow} for organic chemicals have been found as low as 10^{-3} and as high as 10^{7}, thus encompassing a range of ten orders of magnitude. In terms of log K_{ow}, this range is from −3 to 7. As noted later in this chapter, it is frequently possible to estimate log K_{ow} with an uncertainty (i.e., method error) of no more than ±0.1-0.2 log K_{ow} units.

1. The symbol P is also commonly used.

The octanol/water partition coefficient is not the same as the ratio of a chemical's solubility in octanol to its solubility in water, because the organic and aqueous phases of the binary octanol/water system are not pure octanol and pure water. At equilibrium, the organic phase contains 2.3 mol/L of water, and the aqueous phase contains 4.5×10^{-3} mol/L of octanol [27]. Moreover, K_{ow} is often found to be a function of solute concentration for concentrations $\gg$0.01 mol/L.

References 7, 20, and 28 describe various measurement techniques. The chemical in question is added to a mixture of octanol and water whose volume ratio is adjusted according to the expected value of K_{ow}. Very pure octanol and water must be used, and the concentration of the solute in the system should be less than 0.01 mol/L [7]. The system is shaken gently until equilibrium is achieved (15 min to 1 hr). Centrifugation is generally required to separate the two phases, especially if an emulsion has formed. An appropriate analytical technique is then used to determine the solute concentration in each phase.

A rapid laboratory estimate of K_{ow} may be obtained by measuring the retention time in a high-pressure liquid chromatography system; the logarithm of the retention time and the logarithm of K_{ow} have been found to be linearly related [1,7,20,30,31,43,44,45,48].

Environmental Significance. Interest in the K_{ow} parameter developed first with the study of structure-activity relationships, primarily with pharmaceuticals. Numerous studies showed that K_{ow} was useful for correlating structural changes of drug chemicals with the change observed in some biological, biochemical, or toxic effect. The observed correlations could then be used to predict the effect of new drugs for which a value of K_{ow} could be measured or estimated. References 14 and 28 contain interesting discussions of the history of this parameter.

In recent years the octanol/water partition coefficient has become a key parameter in studies of the environmental fate of organic chemicals. It has been found to be related to water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life. (Estimation of these three parameters solely on the basis of K_{ow} is described in Chapters 2, 4, and 5 respectively.) Because of its increasing use in the estimation of these other properties, K_{ow} is considered a required property in studies of new or problematic chemicals.

Values of K_{ow} can be considered to have some meaning in themselves, since they represent the tendency of the chemical to partition

itself between an organic phase (e.g., a fish, a soil) and an aqueous phase. Chemicals with low K_{ow} values (e.g., less than 10) may be considered relatively hydrophilic; they tend to have high water solubilities, small soil/sediment adsorption coefficients, and small bioconcentration factors for aquatic life. Conversely, chemicals with high K_{ow} values (e.g., greater than 10^4) are very hydrophobic.

Estimation Methods Described in this Handbook. Table 1-1 summarizes the methods for estimating K_{ow} that are discussed in this handbook. (A more detailed review of available methods, including several not covered in this handbook, is provided in §1-2 of this chapter.) This chapter presents two different methods by which K_{ow} may be estimated:

(1) *From fragment constants* (see §1-3). This method requires only a knowledge of the chemical structure; for structurally complex molecules, however, it is helpful to have a measured value of K_{ow} for a structurally similar compound. If, for example, K_{ow} is sought for a complex compound R-OH and a measured value is available for the compound R-NH_2, the fragment constants for $-NH_2$ (f_{NH_2}) and $-OH$ (f_{OH}) would be used as follows:

$$\log K_{ow} \text{ for R-OH} = \log K_{ow} \text{ for R-NH}_2 - f_{NH_2} + f_{OH} \qquad (1\text{-}2)$$

When K_{ow} must be calculated "from scratch," a variety of fragment constants and structural factors must be combined. Users require some practice in order to become proficient in this method.

(2) *From other solvent/water partition coefficients* (K_{sw}) (see §1-4). If a measured value of the chemical's partition coefficient between an organic solvent and water (K_{sw}) is available, K_{ow} can be calculated from linear regression equations that relate log K_{sw} (for a particular solvent) and log K_{ow}. The method is straightforward, and the calculations are simple.

These two methods should be given preference over the approach that uses regression equations with solubility (No. 3 in Table 1-1), which has larger method errors. However, the latter method provides a rough check on K_{ow} if the fragment-constant method is used and the user is unfamiliar with the procedure.

TABLE 1-1

Overview of Estimation Methods for K_{ow} Provided in This Handbook

No.	Location	Basis for Method	Information Required[a]	Comments
1	This chapter § 1-3	Fragment constants and structural factors	Structure (K_{ow} for structurally related compound)[b]	– Fairly accurate – Wide range of applicability – Requires some practice
2	This chapter § 1-4	Regression equations	K_{sw}	– Easy, rapid calculations – Limited applicability – Fairly accurate (less than No. 1)
3	Chapter 2	Regression equations	S	– Easy, rapid calculations – Wide range of applicability – Less accurate
The following two approaches are not recommended[c]				
4	Chapter 4	Regression equations	K_{oc}	– Relatively large method error
5	Chapter 5	Regression equations	BCF	– Relatively large method error
A method for the venturesome[d]				
6	Chapter 11 plus § 1-5 of this chapter	Uses estimated activity coefficients	Structure	– Calculations are lengthy and difficult – Limited applicability for functional groups – Fairly accurate

a. K_{ow} = octanol/water partition coefficient; K_{sw} = organic solvent/water partition coefficient; S = water solubility; K_{oc} = soil adsorption coefficient based on organic carbon; BCF = bioconcentration factors for aquatic life.

b. Helpful, but not required.

c. These methods involve relatively large method errors because values of K_{oc} and BCF are highly variable.

d. This method is only described in general terms; it has not been evaluated by this author. Detailed instructions for the calculation of activity coefficients are provided in Chapter 11.

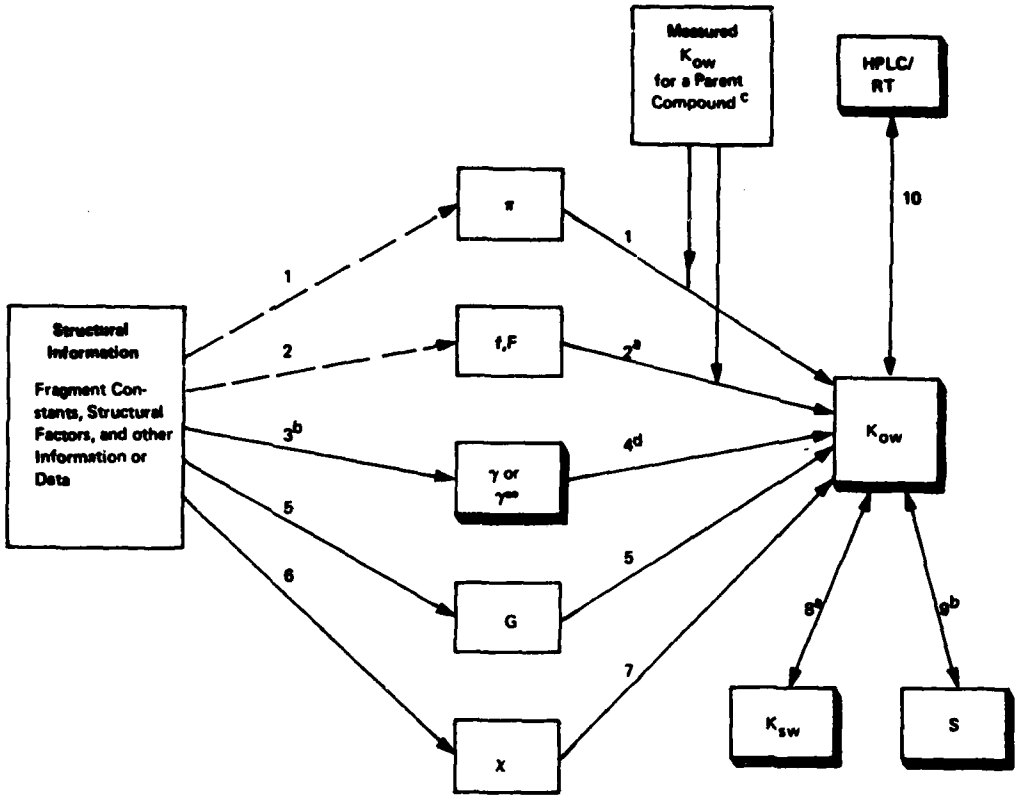
Methods using regression equations with soil adsorption coefficients or bioconcentration factors (Nos. 4 and 5 in Table 1-1) are not recommended because of the relatively large method errors that would be involved.

A sixth possible estimation method, via the use of estimated activity coefficients, is outlined in §1-5. Activity coefficients are estimated via the methods described in Chapter 11. The calculations involved are relatively difficult, but the method promises to be fairly accurate.

1-2 OVERVIEW OF AVAILABLE ESTIMATION METHODS

Several pathways are available for the estimation of octanol/water partition coefficients (K_{ow}) for organic chemicals. These pathways are shown schematically in Figure 1-1 and described briefly in Table 1-2. (Each of the pathways in Figure 1-1 is numbered, and this number is used as the index for Table 1-2.) Some comments about these pathways are given below.

- Two pathways involve the use of substituent constants (#1) or fragment constants (#2) that, when summed for the molecule, yield values of K_{ow} directly. (Structural factors must also be considered for both #1 and #2.) The methods are closely related, but each has particular advantages in practical application. Method 1 requires a measured value of K_{ow} for a structurally related or base compound; this method is primarily of interest for aromatic compounds. A measured value for a structurally related compound is desirable for method 2 -- especially if the compound in question has a complex structure — but is not required. When, as is often the case, no K_{ow} is available for a parent compound, one must start "from scratch" using the fragment-constant pathway (#2). Values of π and f are available for a large number of functional groups; in addition, measured values of K_{ow} for thousands of chemicals have been compiled [14,28]. Thus, these two pathways allow the (direct) estimation of K_{ow} for a broad range of chemicals.
- Two different sets of fragment constants, f, for pathway #2 have been reported, one by Hansch and Leo [14] (Leo's method) and one by Nys and Rekker [33,34,39]. A detailed analysis and comparison of the two methods have not been made, but the method of Hansch and Leo [14] appears to be



π = "pi" (substituent) constants

f,F = fragment constants and structural factors

γ = activity coefficient (in water and octanol)

γ^{∞} = infinite dilution activity coefficient (water and octanol)

G = free energy of solution

HPLC/RT = high-pressure liquid chromatography/ retention time

K_{sw} = solvent/water partition coefficient

K_{ow} = octanol/water partition coefficient

S = solubility in water

χ = molecular connectivity

Pathway (unidirectional) leading to K_{ow}

Bidirectional pathways

Pathway leading to tabulated constants

1,2(etc.) Pathway number (see Table 1-1)

a. Pathways covered by this chapter

b. Pathways covered in other chapters (see Table 1-1)

c. Required for pathway # 1.
Desirable for pathway # 2, especially for structurally-complex molecules.

d. Outline of method given in §1-5.
Details not provided

Properties that may directly or indirectly be measured in the laboratory

FIGURE 1-1 Pathways for the Estimation of Octanol/Water Partition Coefficients

TABLE 1-2

Pathways Leading to the Estimation of Octanol/Water Partition Coefficients

Pathway	References	Approach[a]	Chemical Classes Covered	Comments
1	[4, 11, 14, 15, 28, 39]	G	Best for aromatic compounds, but works for aliphatic as well. π values for most functional groups are available. Few restrictions.	Need measured value of K_{ow} for structurally related compound.
2	[14, 27, 33, 34, 39]	G	Few restrictions. f values for most functional groups are available. Calculations may be difficult for complex structures.	Two different sets of f values are available, one in [14] and the other in [33,34,39].
3	[8, 9, 10, 29, 35, 36, 42]	G,R	Most of the more common classes/functional groups are covered. Structure must not be too complex.	Estimation methods are described in Chapter 11.
4	–	I	No restrictions beyond those for pathway 3.	Basic equations and approach are outlined in §1-5.
5	[19, 37]	I	Most chemical classes can apparently be handled. Fewer problems with complex structures.	Computer required for calculations.
6	[13, 23]	I	Organics with one or more of the following functional groups: $-NH_2$, $>NH$, $>N-$, $=N-$ (pyridine), $C\equiv N$, $-OH$, $-O-$, $=O$, $-Cl$, $-Br$, $-I$, $-F$, nitro N, furan O, and a few other special cases. Structure must not be too complex.	Computer program is available for the calculation of X values [12].
7	[23, 32]	R	Hydrocarbons, carboxylic acids, esters, ethers, alcohols, ketones, amines, mixed classes with functional groups.	Regression equations primarily for mono-functional chemical classes.

(continued)

TABLE 1-2 (Continued)

Pathway	References	Approach[a]	Chemical Classes Covered	Comments
8	[18, 27, 28, 39, 41]	R	Organic acids, alcohols, phenols, ketones, esters, ethers, amides, imines, imides, nitriles, aromatic amines, sulfonamides, barbiturates, aromatic hydrocarbons, other miscellaneous groups.	Regression equations for calculation of K_{ow} from K_{av} in any of 20 different solvent/water systems are given. Equations primarily for monofunctional chemical classes.
9	[2, 5, 16, 22, 40, 46, 47]	R	Most of the common chemical classes are covered. A few equations cover mixed chemical classes.	Estimation methods are described in Chapter 2.
10	[1, 30, 31, 43, 44, 45, 48]	R	Many studies have used mixed chemical classes.	Requires a measured value of retention time (RT) on a calibrated HPLC system.

a. G = group, fragment, and/or structure-related constants; R = regression equation; I = other types of instructions or equations.

better suited for inclusion in this handbook, since more fragment constants are available and the rules for considering structural factors are better explained. In addition, the Leo method is more amenable to computerization; two computer programs using this method have been reported [3,6]. For these reasons, the method of Nys and Rekker is not included here.

- The pathway via intermediate values of activity coefficients (#3-4) has not, to our knowledge, been described in the open literature. One industry group that has used this approach has reported fairly accurate estimates (errors typically <10%). The method requires the estimation of the of the activity coefficient for the chemical in both octanol and water; for compounds that are hydrophobic, it may suffice to estimate these values in pure water and octanol, but for hydrophilic compounds it may be necessary to estimate the values in octanol-saturated water and water-saturated octanol.
- The more complex parts of pathways #3, 5 and 6 have been computerized, but only pathway #5 actually requires a computer because of the difficult and lengthy calculations.
- Pathway #5 calculates the free energy of solvation (G) of the solute in both octanol (G_o) and water (G_w). This is done via a solvent-dependent conformational analysis procedure (SCAP) which allows G to be calculated as a function of molecular conformation; preferred minimum-energy conformations are then selected for subsequent use. In the computer program now being used, only the structure of the molecule (via a special numerical code) and output format instructions are necessary for a complete conformational analysis. The free-energy values (G_o and G_w) are then used to calculate activities which are, in turn, used to calculate K_{ow}. In one test of 20 compounds, SCAP was able to estimate log K_{ow} values with an average absolute error of 9% [19]. (Log K_{ow} values with an absolute average error of 5% were obtained for the same 20 compounds using the π-constant approach, pathway #1 [19].
- Pathway #6 requires the calculation of an intermediate, χ (the molecular connectivity index), which is a topological index. The regression equations that link χ to K_{ow} (pathway #7) cover only a relatively small number of monofunctional-group chemical classes.

- Pathways #8, 9 and 10 all involve two-parameter, linear regression equations using the log of each parameter. The utility of pathway #9 is enhanced by an available compilation of various solvent/water partition coefficients (K_{sw}) for thousands of chemicals [28]. The utility of pathway #9 is fairly well recognized; the regression equations are included in Chapter 2, which covers estimation methods for solubility (S). Pathway #10 is more of a laboratory estimation method than a computational method; it derives its main benefit from the fact that the measurement of retention time takes only about 25 minutes [44]. In a test of 18 compounds, the HPLC/RT method estimated values of log K_{ow} with average absolute error of ~23% [44].
- Only pathway #3 is intrinsically capable of estimating K_{ow} at any (reasonable) temperature. Essentially all of the other approaches use, or are derived from, data or fragment constants that come from measurements at room temperature. Quite frequently, data covering a range of temperatures (e.g., 15-30°C) have been used in the derivation of these approaches. Data from a number of solvent systems indicate that the effect of temperature on K_{ow} (actually, log K_{ow}) is on the order of 0.001 to 0.01 log units/deg and may be either positive or negative [28].

1-3 LEO'S FRAGMENT CONSTANT METHOD

Principles of Use. Leo's approach (Hansch and Leo [14]) to the estimation of octanol/water partition coefficients uses empirically derived atomic or group fragment constants (f) and structural factors (F). All calculations are carried out in terms of log K_{ow}:

$$\log K_{ow} = \text{sum of fragments (f)} + \text{factors (F)} \qquad (1\text{-}3)$$

The only input information required for this method is the structure of the chemical, since the fragment values and factors are known.

Fragment values (f) are provided in this chapter for over 100 atoms or atom groups. A fragment has different f values, depending on the type of structure (e.g., aliphatic or aromatic) it is bonded to. Thus, in total, about 200 f values are available. Fourteen different factors must be considered; these take into account molecular flexibility (e.g., possible rotation around bonds), unsaturation, multiple halogenation, branching, and interactions with H-polar fragments.

Because of the large number of f and F values available, this method is a fairly powerful one, and there are relatively few man-made chemicals for which a value of log K_{ow} cannot be calculated. One study [3], using a computerized version of this method, looked at several large data sets for organic compounds and found that, on average, log K_{ow} could be estimated for 84.5% of the compounds. Details are provided in Table 1-3.

TABLE 1-3

Percentage of Compounds for Which log K_{ow} Could Be Calculated

No. of Compounds	Class	Percentage Calculated
209	Heterogeneous set of mutagens and carcinogens	80.4
200	Polycyclic aromatic hydrocarbons	97.5
155	N-Nitroso compounds	75.5
90	Random selection from the 3052 compounds in Ref. 28	84.4
	Average	84.4

Source: Chou and Jurs [3]

For complex molecules it is very desirable to have a measured value of log K_{ow} for a structurally similar compound.[2] This measured value can then be modified by adding or subtracting, as required, the appropriate f or F values:

$$\log K_{ow} \text{ (new chemical)} = \log K_{ow} \text{ (similar chemical)} \pm \text{fragments (f)} \pm \text{factors (F)} \quad (1\text{-}4)$$

If, for example, an estimate of log K_{ow} is desired for the compound R-Br (R = any organic base structure) and a measured value is available for R-Cl, then

$$\log K_{ow} \text{ (R-Br)} = \log K_{ow} \text{ (R-Cl)} - f_{Cl} + f_{Br} \quad (1\text{-}5)$$

2. References 14 and 28 contain measured values of K_{ow} for thousands of chemicals.

This approach is recommended whenever a reliable measured value of K_{ow} is available for a base compound that differs from the compound of interest by the substitution of only one or just a few fragments. However, if different factors (F values) are involved in the two structures, the application of Eq. 1-4 can be rather difficult.

Because of the numerous f values and sometimes confusing F values involved in the use of this method, *the user is urged to study the procedure and the examples carefully and practice with a few compounds before tackling the first real estimate.* For complex structures it may be desirable to number each fragment and bond so that their f and F values can be considered in a systematic way. Use of an alternative method is advised if the user is unsure of the correct procedure here.

Method Error. This method assumes that log K_{ow} depends upon the structure of the solute in an additive-constitutive fashion, and that the more important structural effects are adequately described by the available factors (F values). Test calculations have shown that these assumptions are justified for most chemicals, but the user should keep in mind that some chemicals deviate seriously from the norm.

The results of one set of test calculations are shown in Table 1-4. For each chemical a value of log K_{ow} was calculated by a computer program from the fragment and factor values of Hansch and Leo [14]. The average absolute error for the 76 compounds was 0.14 log K_{ow} unit. Fifty chemicals (66%) had errors of less than 0.1 log K_{ow} unit, and 63 chemicals (83%) had errors of less than 0.2 log K_{ow} unit.[3] An average absolute error of 0.09 log K_{ow} unit is obtained from a comparison of the estimated and measured values for the chemicals used in Examples 1-1 to 1-37 (given later in this section). Three chemicals had no measured value, so the test set (chosen to exemplify the rules for the method) contined 34 chemicals. In this set, absolute errors were $\leq$0.1 log K_{ow} unit for 23 chemicals (68%) and $\leq$0.2 log K_{ow} unit for 31 chemicals (91%). The maximum error was +0.30 log K_{ow} unit.

Both of the test sets mentioned above contained relatively simple chemicals, and for these a method error $\pm$0.12 log K_{ow} unit appears valid. However, errors for more complex chemicals (including many pesticides and drugs) would probably be substantially larger. In addition, estimates

3. Not all of the fragment constants and factors of the Leo method were incorporated in this program. Their inclusion would have reduced the error for a few compounds and thus slightly lowered the average method error.

TABLE 1-4

Comparison of Observed Values of log K_{ow} with Those Calculated from Fragment Constants[a]

Compound	Observed log K_{ow}	Δ log K_{ow} (Calculated –Observed)
Methylacetylene	0.94	–0.04
Fluoroform	0.64	0.00
Isobutylene	2.34	–0.16
Ethanol	–0.31	0.10
Dimethyl ether	0.10	0.02
Cyclohexane	3.44	0.07
Propane	2.36	–0.04
2-Propanol	0.05	0.06
tert-Butylamine	0.40	0.13
2-Phenylethylamine	1.41	0.03
N-Phenylacetamide	1.16	0.01
Halothane	2.30	0.16
Benzimidazole	1.34	0.17
p-Nitrophenol	1.91	0.06
Cyclohexene	2.86	0.10
1,2-Dichlorotetrafluoroethane	2.82	0.04
Hexachlorophene	3.93	–0.04
1,2-Methylenedioxybenzene	2.08	0.02
2-Phenyl-1,3-indandione	2.90	–0.08
Carbon tetrachloride	2.83	0.13
Dioxane	–0.42	0.43
2-Bromoacetic acid	0.41	0.07
2-Chloroethanol	0.03	0.00
Indene	2.92	0.07
Fluorene	4.12	–0.09
Anthracene	4.45	0.00
Pyrene	4.88	0.02
Quinoxaline	1.08	0.05
Carbozole	3.51	0.01
Menadione	2.20	–0.45
Chloramphenicol	1.14	–0.58
2-Hydroxy-1,4-naphthoquinone	1.46	–0.94
2-Methyl-3-hydroxyl-1,4-naphthoquinone	1.20	–0.02
2-Methoxy-1,4-naphthoquinone	1.35	–0.09
Benzothiazole	2.01	0.00
o-Phenanthroline	1.83	0.10
Thiazole	0.44	–0.02

(continued)

TABLE 1-4 (Continued)

Compound	Observed log K_{ow}	Δ log K_{ow} (Calculated –Observed)
Piperazine	–1.17	–0.08
Morpholine	–1.08	0.09
Salicylic acid	2.24	–0.27
Imidazole	–0.08	0.00
Cyclohexanol	1.23	0.19
o-Phenyleneurea	1.12	0.27
Tripropylamine	2.79	0.06
Di-*n*-propylamine	1.62	0.05
Coumarin	1.39	0.05
Trifluoromethylbenzene	2.90	–0.70
Trifluoromethylsulfonanilide	3.05	0.01
1,3-Indandione	0.61	0.66
9-Fluorenone	3.58	–0.71
Phenazine	2.84	–0.12
Morphine	0.83	0.35
2,2,2-Trifluoroethanol	0.41	0.00
2,2,2-Trifluoroacetamide	0.12	0.00
2,2,2-Trichloroethanol	1.35	0.04
2,2,2-Trichloroacetamide	1.04	0.00
Pyrimidine	–0.40	–0.06
Glucose	–3.24	–0.15
Cyclohexylamine	1.49	0.03
Neopentane	3.11	0.03
2-Methylpropane	2.76	–0.03
Crotonic acid	0.72	0.13
Cinnamonitrile	1.96	–0.04
Cinnamic acid	2.13	0.05
Cinnamamide	1.41	–0.41
Methyl cinnamate	2.62	–0.15
Phenyl vinyl ketone	1.88	–0.30
Styrene	2.95	–0.03
1-Phenyl-3-hydroxypropane	1.95	–0.48
Methyl styryl ketone	2.07	–0.09
1,1,2-Trichloroethylene	2.29	–0.01
2-Methoxyanisole	2.08	–0.08
Ethyl vinyl ether	1.04	–0.06
Pyrazole	0.13	0.11
1,1-Difluoroethylene	1.24	–0.12
1,2,3,4-Tetrahydroquinoline	2.29	0.19
Average absolute Δ		0.14
Maximum Δ		–0.94

a. See note 3 on page 1-12.

Source: Chou and Jurs [3].

of log K_{ow} >6 are likely to be overestimates of the measured log K_{ow}, perhaps by one or more log units.[4]

It is recommended that the user consider the method error to be in log K_{ow} units (e.g., the average uncertainty of ±0.12 log K_{ow} unit from the two test sets described) and apply this to any log K_{ow} value calculated from scratch. For example, if an estimate of 2.86 is obtained for log K_{ow} (for a structurally simple compound), report the estimate as log K_{ow} = 2.86 ± 0.12. In terms of K_{ow}, this would be written as $K_{ow} = 720^{-170}_{+220}$.

If an estimated value of log K_{ow} is derived by modification of a reliable measured value for a structurally related compound (as in Eq.1-4), the method error is likely to be less than if log K_{ow} were calculated "from scratch." To a large extent, the method error will reflect the uncertainty in the specific fragment constants (f values) and factors (F values) that are employed. Data provided in Refs. 11, 28, and 34 indicate that fragment constants (f or π values) and factors for the more common group interactions generally have uncertainties in the range of 0.02 to 0.05 log K_{ow} unit. More complex fragments or factors may have larger uncertainties. For example, an uncertainty of ±0.08 log K_{ow} unit was assigned to the f-value for the fragment NH_2COO- on the basis of log K_{ow} values for twelve pairs of chemicals (H-R vs NH_2COOR in each pair) [3].

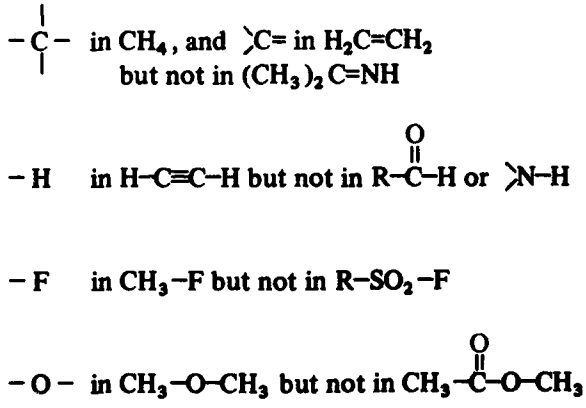
Hansch and Leo [14] do not give the uncertainties for each of their f and F values, but a typical value of 0.03 log K_{ow} unit can be assumed for common fragments and factors and 0.05 for less common ones. The total uncertainty in any estimate derived via the method outlined in Eq. 1-4 can then be calculated by the method outlined in Appendix C of this handbook. Since simple addition and subtraction of terms is involved here, the total method error is the square root of the sum of the squares of the individual uncertainties. Using the example given previously in Eq. 1-5, and assuming that the uncertainties for f_{Cl} and f_{Br} are both 0.03 log K_{ow} unit (Cl and Br are common fragments), the total uncertainty is $(0.03^2 + 0.03^2)^{1/2}$ = 0.04 log K_{ow} unit. Note that this does not consider any uncertainty in the measured value of log K_{ow} for the base chemical. Accordingly, method errors of 0.04 to 0.1 log K_{ow} unit should be expected when this method is used.

4. Personal communication from C. Hansch and A. Leo, Pomona College, Claremont, CA, 1980.

Fragments and Factors[5]. The basic fragment constants (f values) and factors (F values) for this method are given in Tables 1-5 and -6, respectively. Table 1-7 provides the F values for one special factor which considers the interaction between halogens and certain polar groups. This chapter does not contain the fragment constants and factors that Hansch and Leo [14] derived for calculating log K_{ow} of ions; the reader is referred to their work for this information. The following paragraphs explain the terms used and refer to specific examples that show how each rule is applied.

- *Fragments.* A fragment is an atom, or string of atoms, whose exterior bonds are to isolating carbon atoms. (An isolating carbon is one that either has four single bonds, at least two of which are to non-hetero atoms, or is multiply bonded to other carbon atoms.) The fragments for which f values are available are listed in the left-hand column of Table 1-5. Superscripts on f denote the type of attachment; superscript symbols are defined on p. 1-24.

A **single-atom fragment** can only be (1) an isolating carbon atom, or (2) a hydrogen or hetero atom, all of whose bonds are isolating carbons. For example:



[See Examples 1-1 and -2]

A **multiple-atom fundamental fragment** can be formed by any combination of (a) a non-isolating carbon, (b) hydrogen, and/or (c) hetero atoms. A fundamental fragment is complete when all its

(continued on p. 1-21)

5. The information provided here is a condensation of a much more detailed text by Hansch and Leo [14].

TABLE 1-5

Fragment Constants[a]

Fragment[b]	f	f^{ϕ}	$f^{\phi\phi}$	Special Types
Without C or H				
–F	–0.38	0.37		$f^{\phi/2}$ = .00
–Cl	0.06	0.94		$f^{\phi/2}$ = 0.50
–Br	0.20	1.09		f^{1R} = 0.48, $f^{\phi/2}$ = 0.64
–I	0.59	1.35		$f^{\phi/2}$ = 0.97
–N<	–2.18	–0.93	–0.50[c]	f^{1R} = –1.76
–O–	–1.82[d]	–0.61	0.53	f^{X1} = –0.22, f^{X2} = +0.17, $f^{\phi/2}$ = –1.21
–S–	–0.79	–0.03	0.77	
–NO		0.11		
$-NO_2$	–1.16	–0.03		f^{X2} = 0.09
$-ONO_2$	–0.36			
$-IO_2$		–3.23		
$-OP(O)O_2<$	–2.29	–1.71		f^{X1} = –1.50
–P(O)<				Triple aromatic = –2.45
$-P(O)O_2<$		–2.33		
$-OP(S)O_2<$		–0.30[c]		
$>NP(S)(N<)_2$	–3.37			
$-SP(S)O_2<$	–2.89			
$-SO_2F$		0.30		
$-SO_2N<$		–2.09		
–S(O)–	–3.01	–2.12	–1.62	
$-SO_2-$	–2.67	–2.17	–1.28	
$-SO_2O-$	–2.11	–2.06	–0.62	$f^{1/\phi}$ = –1.42
$-SF_5$		1.45		
$-SO_2O^{-e}$	–5.87	–4.53		
$-OSO_3^{-e}$	–5.23			
–N=N–			0.14	
–NNN–		0.69		
–N=NN<		–0.85		f^{X1} = –0.67
>NNO	–2.40	–0.84		
$-O^{-e}$		–3.64		
–Si<	–0.09[c]	0.65[c]		f^{1R} = –0.38[c]

(continued)

TABLE 1-5 (Continued)

Fragment[b]	f	f^{ϕ}	$f^{\phi\phi}$	Special Types
Without C, with H				
–H	0.23	0.23		
–NH–	–2.15	–1.03	–0.09	$f^{X1} = -0.37$
$–NH_2$	–1.54	–1.00		$f^{X1} = -0.23$, $f^{1R} = -1.35$
–OH	–1.64	–0.44		$f^{X1} = 0.32$, $f^{1R} = -1.34$
–SH	–0.23	0.62		
$–SO_2NH–$		–1.75[c]	–1.10	$f^{1/\phi} = -1.72$
$–SO_2(NH_2)$		–1.59		$f^{X1} = -1.04$
$–SO_2NH(NH_2)$	–2.04			
$–NHSO_2(NH_2)$		–1.50		
–NH(OH)		–1.11		
–NHNH–			–0.74	$f^{1R} = -2.84$
$–NH(NH_2)$		–0.65		
$–SP(O)(O–)NH–$	–2.18[c]			
$–SP(O)(NH_2)O–$	–2.50			
$–As(OH)_2O–$		–1.84		
$–As(O)(OH)_2$		–1.90		
$–B(OH)_2$		–0.32		
With C, without H				
	0.20	0.20		
$–CF_3$		1.11		
–CN	–1.27	–0.34		$f^{1R} = -0.88$
–C(O)N<	–3.04	–2.80	–1.93	$f^{1/\phi} = -2.20$
–SCN	–0.48	0.64		$f^{1R} = -0.45$
–C(O)–	–1.90	–1.09	–0.50	$f^{X1} = -0.83$, $f^{1R} = -1.77$
–C(O)O–	–1.49	–0.56	–0.09	$f^{X1} = -0.36$, $f^{1R} = -1.38$, $f^{1/\phi} = -1.18$
$–C(O)O^{-\ominus}$	–5.19	–4.13		
$–N=CCl_2$		0.64		
–OC(O)N<	–2.54?	–1.84		
–C(O)N–N=N–				$f^{1/\phi} = -0.87$
–C(=S)O–	–1.11			

(continued)

TABLE 1-5 (Continued)

Fragment[b]	f	f^{ϕ}	$f^{\phi\phi}$	Special Types
With C and H				
$-CH_3$	0.89	0.89		
$-C_6H_5$ (benzene)	1.90			
–C(O)H	-1.10	–0.42		
–C(O)OH	–1.11	–0.03		$f^{1R} = -1.03$
–C(O)NH–	–2.71	–1.81	–1.06	$f^{1/\phi} = -1.51$
$-C(O)NH_2$	–2.18	–1.26		$f^{X1} = -0.82$, $f^{1R} = -1.99$
–OC(O)NH–	–1.79	–1.46		$f^{1/\phi} = -0.91$
$-OC(O)NH_2$	–1.58	–0.82		$f^{1R} = -1.24$
–CH=N–		–1.03	+0.08[c]	
–CH=NOH	–1.02	–0.15		
–CH=NNH–	–2.75			
–NHC(O)NH–	–2.18	–1.57	–0.82	
$-NHC(O)NH_2$	–2.18	–1.07		
$>NC(O)NH_2$		–2.25	–2.15	
>C=NH			–1.29	
>NC(O)H	–2.67	–1.59		
–OC(O)NH–	–1.79	–1.45		$f^{1/\phi} = -0.91$
–C(=S)NH–	–2.00			$f^{1/\phi} = -0.96$
–NHCN		–0.03		
–CH=NN<		–1.71		
–NHC(O)N<		–2.29		$f^{1/\phi} = -2.42$
–NNO(C(O)NH–)	–1.50			$f^{1/\phi} = -0.76$
–OC(O)H	–1.14	–0.64		
–NHC(O)H		–0.64		
–C=NOH(OH)		–1.64		
$-C(=S)NH_2$		–0.41		
$-N(C(O)NH_2)-$		–2.25	–2.07	
$-SO_2NHN=CH-$				$f^{1/\phi} = -1.47$
–NHC(=S)NH–		–1.79		
$-NNO(C(O)NH_2)$	–0.95			
$-C(O)NHNH_2$		–1.69		
$-NHC(=S)NH_2$	–1.29	–1.17		
$-CNH_2(=NH\cdot HCl)$		–3.49		
$-NHC=NH(NH_2)$	–5.65			
–C(O)C(O)–	–3.00		–0.30	

(continued)

TABLE 1-5 (Continued)

Fragment[b]	f	f^{ϕ}	$f^{\phi\phi}$	Special Types
–C(O)NHC(O)–	–3.31		–3.00[c]	
–C(O)NHC(O)H	–2.84			
–C(O)NHN=CH–			–1.12	
$–C(O)NHC(O)NH_2$	–1.91			$f^{1R} = –1.57$
$–CH(NH_2)C(O)OH$	–3.97			
$–CH=NNHC(O)NH_2$	–0.63	–0.66		
$–CH=NNHC(=S)NH_2$		–0.05		
$–CH=NNHC(O)NHNH_2$		–1.09		
–C(O)NHC(O)NHC(O)–	–2.38			

Fused in Aromatic Ring[f]

Fragments[b] Without C	f^{ϕ}	Fragments[b] With C	f^{ϕ}
–N=	–1.12	C	0.13
–N<	–1.10[c]	Ċ (ring fusion carbon)	0.22_5
$–N<^{\phi}$	–0.56	Ċ* (ring fusion hetero)[g]	0.44
–N=N–	–2.14	CH	0.35_5
$–N=^{O}$	–3.46	–C(O)–	–0.59
–O–	–0.08	–OC(O)–	–1.40
–S–	0.36	–CH=NNH–	–0.47
$–S<^{O}$	–2.08	–N=CHNH–	–0.79
–Se–	0.45	–NHC(O)–	–2.00
–NH–	–0.65	–N=CH–O–	–0.71
–NHN=N–	–0.86	–N=CH–S–	–0.29
		–CH=N–O–	–0.63
		–N=CHN=	–1.46
		–NHC(O)NH–	–1.18
		–C(O)NHC(O)–	–1.08[c]
		–C(O)NHC(O)NH–	–1.78
		–C(O)NHC(O)NHN=	–1.36

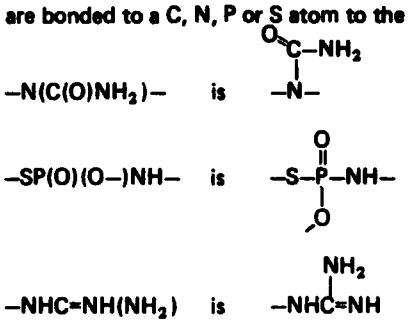
a. The superscript symbols used with f are defined on p. 1-24.

b. The fragment notation is simplified and does not show all bonds. Intrafragment single bonds are not shown. A carbonyl oxygen is always shown in parentheses – e.g., $–OC(O)NH_2$ is $–O–\overset{O}{\overset{\|}{C}}–NH_2$. A $–\overset{S}{\overset{\|}{C}}–$ group is represented by –C(=S)–. Portions of a fragment shown in

(continued)

TABLE 1-5 (Continued)

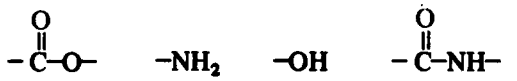
parentheses are bonded to a C, N, P or S atom to the left of the parentheses. For example:



c. Hansch, C., Pomona College, Claremont, CA, personal communication, October 16, 1980.
d. For methyl ethers and ethylene oxide, use −1.54.
e. These fragments are negatively charged ions.
f. A ring system is considered aromatic unless interrupted by a saturated carbon.
g. This factor is also used for fusion to a non-isolating carbon.

Source: Hansch and Leo [14], except as noted in note c.

remaining bonds are to isolating carbons. Some common multiple-atom fundamental fragments are:



[See Examples 1-3 and -4]

Multiple-atom derived fragments can be any combination of single-atom or multiple-atom fundamental fragments that is common or convenient to use. For example, one can *derive* the fragment value for $-CH_3$ (a common fragment): 3(0.23) + 0.20 = 0.89. Similarly, for the fragment C_6H_5 the derived fragment value is 5(CH) + C = 5(0.355) + 0.13 = 1.91. A slightly better value of 1.90 is derived by subtracting 0.23 (for one H) from the measured value of 2.13 for benzene.

[See Examples 1-5 and -6]

An H-polar fragment is one that can be expected to participate in hydrogen bonding, either as a donor or an acceptor, such as $-NH_2$, $-OH$, $-O-$, and $-CO_2H$. For such fragments a factor may have to be added that takes into account hydrogen bonding or interactions with nearby halogens.

[See Examples 1-32, -33 and -34]

TABLE 1-6

Summary of Rules for Calculating Factors

• Involving BONDS

Unsaturation

Double	Triple
Normal: $F_{(=)} = -0.55$	$F_{(\equiv)} = -1.42$
Conjugate to ϕ: $F^{\phi}_{(=)} = -0.42$	$F^{\phi\phi}_{(\equiv)} = 0.00$
Conjugate to 2ϕ: $F^{\phi\phi}_{(=)} = -0.00$	
Conjugate to second = in chain: $F_{(=)} = -0.38$	

Geometric

Proportional to length: $x(n-1)$		Branching in short chains: one-time	
Chain:	$F_b = -0.12$	Alkane chain:	$F_{cBr} = -0.13$
Ring:[a]	$F_b = -0.09$	H-polar fragment:	$F_{gBr} = -0.22$
Branching:	$F_{bYN} = -0.20$ (-amine)	Ring cluster:	$F_{rCl} = -0.45$
	$F_{bYP} = -0.31$ (phosphorus esters)		

• Involving MULTIPLE HALOGENATION

On same carbon (geminal) F_{mhGn}: $\begin{cases} (n=2) = 0.30^b \\ (n=3) = 0.53^b \\ (n=4) = 0.72^b \end{cases}$

On adjacent carbon (vicinal) $F_{mhVn} = 0.28\,(n-1)$

• Involving H-POLAR PROXIMITY

Chain: $F_{P1} = -0.42\,(f_1 + f_2)$

$F_{P2} = -0.26\,(f_1 + f_2)$

$F_{P3} = -0.10\,(f_1 + f_2)$

Aromatic ring: $F^{\phi}_{P1} = -0.16\,(f_1 + f_2)$

$F^{\phi}_{P2} = -0.08\,(f_1 + f_2)$

Aliphatic ring: $F_{P1} = -0.32\,(f_1 + f_2)$

$F_{P2}{}^c = -0.20\,(f_1 + f_2)$

• Involving INTRAMOLECULAR H-BOND

$F_{HBN} = 0.60$ for nitrogen

$F_{HBO} = 1.0$ for oxygen

a. Aromatic rings excluded.
b. Values per halogen atom, if α or β to H-polar fragment, additional factor required: see Table 1-7.
c. For morpholine and piperazine derivatives, use coef. = −0.10

Source: Hansch and Leo [14].

TABLE 1-7

Aliphatic H/S-Polar Interactions: α-Halogen Factors ($F_{H/SP}$)

Fragment[a]	No. α-F Atoms[b]			No. α-Cl Atoms[b]			No. α-Br Atoms[b]		
	1	2	3	1	2	3	1	2	3
$-SO_2NH-AR$	1.13	1.86	2.70						
$-SO_2-AR$			2.78						
$-\overset{O}{\overset{\parallel}{C}}-NH_2$	0.97	*1.49*	2.01	1.05	*1.33*	1.61	0.92		
$-\overset{O}{\overset{\parallel}{C}}-NH-Alk$	0.91	1.31	1.70	0.91	1.15	1.28	0.91	1.09	1.06
$-\overset{O}{\overset{\parallel}{C}}-NH-AR$			1.65	0.76					
$-O-AR$			1.71						
$-S-AR$			1.47			(0.36)			
$-CH_2OH$[c]	(0.02)		1.22	0.53	0.56	0.88	0.59		
$-CH_2CO_2H$[c]				*0.68*					
$-\overset{O}{\overset{\parallel}{C}}-AR$			1.17				*0.86*		
$-\overset{O}{\overset{\parallel}{C}}-Alk$				*0.87*					
$-\overset{O}{\overset{\parallel}{C}}-O-Alk$			1.07				*0.85*		
$-CO_2H$	*0.89*			*0.90*	*0.98*	*1.20*	*0.85*		

a. Fragment attached to α carbon. AR = aromatic group; Alk = alkane.
b. Italicized values are less reliable; parenthetical values are doubtful.
c. Note β attachment to fragment.

Source: Hansch and Leo [14]

A S-polar (or σ-polar) fragment is one with strong electron-withdrawing power but little or no tendency to hydrogen bond — i.e., any of the halogens. For such fragments a factor may have to be added that takes into account interactions with nearby H-polar fragments.

[See Examples 1-32 and -33]

Underlining any symbol associated with a fragment constant means the fragment is present in a ring. [See Examples 1-31, -35, -36 and -37.] Factor symbols may also be underlined to show association with a ring, as in $\underline{F_b} = -0.09$. A ring system is considered aromatic unless interrupted by a saturated carbon.

- *Superscripts Denoting Attachment.* The type of isolating carbon atom to which a fragment is attached affects the f value. Superscripts on f (and sometimes F) denote the type of attachment associated with each f value as follows:

Superscript	Attachment	See Examples
None	Aliphatic structural attachment	1-1 to -5
ϕ	Attached to aromatic ring; if bivalent (e.g., $-CO_2-$, $-SO_2N\langle$, $-CH=N-$) the attachment is from the left as written ($Ar-CO_2-$, $Ar-SO_2N\langle$, $Ar-CH=N-$).	1-6 to -8
$1/\phi$	Attached to aromatic ring from right (as written) for bivalent fragments (e.g., $-CO_2-Ar$, $-SO_2N\langle_{Ar}$, $-CH=N-Ar$)	1-9
$\phi\phi$	Bivalent fragment with two aromatic attachments (e.g., $Ar-NH-Ar$)	1-10
X	Aromatic attachment; value enhanced by second, electron-withdrawing substituent ($\sigma_I > +0.50$).[6] f^{X1} used when σ_I for second substituent is between 0.50 and 0.75 (e.g., F, NO_3, CN, SCN, NH_3^+, $OCCl_3$). f^{X2} is used when σ_I for second substituent is > 0.75 (e.g., NO_2, OCN). The other halogens (Cl, Br, I) all have $\sigma_I < 0.5$; the f^{X1} factor may be used if two of these are present to enhance the f value of a third substituent (e.g., use $f^{X1}_{NH_2}$ for 3,4-dichloroaniline).	1-11

6. σ_I is a measure of the static inductive effect of a substituent on an aromatic ring. Values are tabulated in Appendix I of Ref. 14.

Superscript	Attachment	See Examples
1R	Benzyl attachment (i.e., attachment to $C_6H_5CH_2-$)	1-12, -13
$\phi/2$	Attachment to vinyl carbon (i.e., to $>C=C<$). Values of $f^{\phi/2}$ are halfway between f and f^{ϕ}.	

• *Factors.* Many molecular structures require the consideration of *factors* in addition to the fragment values:

F_b	=	bond factor (special cases: F_{bYN}, F_{bYP})
F_{cBr}	=	chain branch factor
F_{gBr}	=	group branch factor
F_{rCl}	=	ring cluster branch factor
$F_{=}$	=	double bond factor
$F_{\equiv}$	=	triple bond factor
F_{mhG}	=	multiple halogenation, geminal
F_{mhV}	=	multiple halogenation, vicinal
F_P	=	proximity factor for two H-polar fragments; f_{P1}, one-carbon separation; F_{P2}, two-carbon separation; F_{P3}, three-carbon separation
$F_{H/SP}$	=	proximity factor for H-polar fragment and S-polar (halogen) fragment. (Values are listed in Table 1-7.)
F_{BHN},F_{BHO}	=	intramolecular H-bond factors

Each of these factors is briefly explained below with reference to specific examples where these factors are required. The rules for each factor are summarized in Table 1-6.

F_b [See especially Examples 1-1 through -4 and 1-14 through -20.] A bond factor of −0.12 for chains and −0.09 for non-aromatic rings is taken (n−1) times, where n is the number of bonds in the molecule, with the following provisions:

- Do not count bonds between hydrogen and any other atom.
- Do not count any bonds *within* any multi-atom fundamental fragment. [Examples 1-3 and -4]
- Double and triple bonds are considered equivalent to single bonds (only for the calculation of F_b). [Examples 1-14, -15, -17 and -25]
- In ring-chain combinations, consider that the ring stops the count; e.g., in CH_3-CH_2- Ar−$CONH_2$, n=2 on the left side

of the aromatic ring (Ar) and n=1 on the right side. Thus, $F_b = 1\ (-0.12) + 0(-0.12)$. [See also Example 1-18.]

- There are special bond factors (Table 1-6) for amines (F_{bYN}) and phosphorus esters (F_{bYP}). These are used for all "counted" bonds in the molecule if the radiating chains are purely hydrophobic (i.e., contain C and H atoms only). [Examples 1-5 and -19] However, if one (and only one) chain contains an H-polar group, use the F_{bY} factor for all bonds up to the one that connects the H-polar fragment; use F_b for any beyond it. [Example 1-20] If two chains contain H-polar fragments, then all bonds are treated as F_b.

No bond factor applies to the bonds in an aromatic ring.

F_{cBr}, F_{gBr} and F_{rCl} "One-time" chain branching factors are applied whenever there is branching on the molecule. The rules are:

- The length of each branch must be just one or two carbon atoms; or, two or more of the branches must contain hydrophilic groups.
- The factor is required for each branch in the molecule.
- No branching factor is used if either F_{mhG} or F_{mhV} factor is required at that site.
- If the branching is an alkane chain or single S-polar fragment, use $F_{cBr} = -0.13$. [Examples 1-21 and -29] Note that $CH_3CH_2C(CH_3)_3$ has two branches and would require the factor $2F_{cBr}$.
- If the branching is an H-polar fragment, use $F_{gBr} = -0.22$. [Examples 1-22 and -29]
- If the branching is on a ring cluster (peri-fused rings), use $F_{rCl} = -0.45$. This factor is used only once per ring cluster. [Example 1-23]
- If the branching is more than two carbons long, use the factor F_{bYN} (even if the compound is not an amine), which is taken $(n-1)$ times as described above for F_b factors.

$F_=$ For every double bond, *excluding* those contained within fundamental fragments (e.g., $>C=O$, $-C(=O)NH_2$), add the $F_=$ factor according to the following rules:

- Do not count any double bonds in aromatic rings if you are using the fragment constants (f values) for fragments fused in an aromatic ring.
- When a double bond is present, the site of unsaturation should be considered *saturated* for the purposes of fragment constants (i.e., assume >C=C< is >CH-CH<) and bond factors (i.e., F_b).
- For normal (isolated) double bonds, use $F_{=} = -0.55$. [Examples 1-14, -15 and -17]
- For double bonds conjugate to an aromatic ring, use $F_{=}^{\phi} = -0.42$. [Example 1-24]
- For all double bonds conjugate to another double bond in a chain (e.g., in 1,3-butadiene), use $F_{=} = -0.38$.
- For double bonds conjugate to two aromatic rings, use $F_{=}^{\phi\phi} = 0.00$.

$\boxed{F_{\equiv}}$ For every triple bond, *excluding* those contained within fundamental fragments (e.g., $-C\equiv N$), add the $F_{\equiv}$ factor according to the following rules:

- When a triple bond is present, the site of unsaturation should be considered *saturated* for the purposes of fragment constants (i.e., assume $-C\equiv C$ is $-CH_2CH_2-$) and bond factors (F_b).
- For normal (isolated) triple bonds, use $F_{\equiv} = -1.42$. [Example 1-25]
- For triple bonds conjugate to two aromatic rings, use $F_{\equiv}^{\phi\phi} = 0.00$.

$\boxed{F_{mhG}}$ When two or more halogens (−F, −Cl, −Br, −I) are *bonded to the same carbon atom,* the F_{mhG} factor is applied as follows [Examples 1-14, -15, -26 and -27]:

- Two halogens: $F_{mhG} = 0.30$ per halogen atom.
- Three halogens: $F_{mhG} = 0.53$ per halogen atom.
- Four halogens: $F_{mhG} = 0.72$ per halogen atom.
- No branching factor (F_{cBr} or F_{gBr}) is needed for the carbon-halogen groups requiring the F_{mhG} factor.

$\boxed{F_{mhV}}$ When two or more halogens are *bonded to adjacent carbon atoms,* the F_{mhV} factor (0.28) is taken n−1 times, where n is the number

of halogens involved. [Examples 1-18 and -27] The following are qualifications:

- This factor applies only when the two carbon atoms are separated by *single* bonds.
- No branching factor (F_{cBr} or F_{gBr}) is needed for carbon-halogen groups requiring the F_{mhv} factor.

F_{P1}, F_{P2}, F_{P3} When two H-polar fragments (e.g., $-NH_2$, $-OH$, $-O-$, $-CO_2H$) in the molecule are separated by one, two, or three carbon atoms, a correction factor for their interaction is calculated from the sum of the individual H-polar fragment constants ($f_1 + f_2$) as follows:

- If the H-polar fragments are on (or in) a *chain:*

Separation	Factor	
1 carbon	$F_{P1} = -0.42\,(f_1 + f_2)$	[Example 1-28]
2 carbons	$F_{P2} = -0.26\,(f_1 + f_2)$	[Example 1-29]
3 carbons	$F_{P3} = -0.10\,(f_1 + f_2)$	

- If the H-polar fragments are in an *aliphatic ring:*

Separation	Factor	
1 carbon	$\underline{F_{P1}} = -0.32\,(f_1 + f_2)$	[Example 1-29]
2 carbons	$\underline{F_{P2}} = -0.20\,(f_1 + f_2)$	[Example 1-29]
	[For morpholine, dioxane, and piperazine derivatives use $\underline{F_{P2}} = -0.10\,(f_1 + f_2)$.]	

- If the H-polar fragments are on (or in) an *aromatic ring:*

Separation	Factor	
1 carbon	$F^{\phi}_{P1} = -0.16\,(f_1 + f_2)$	
2 carbons	$F^{\phi}_{P2} = -0.08\,(f_1 + f_2)$	[Example 1-31]

Important points for all F_P factors:

- The factor must be applied to each hydrophobic chain connecting two H-polar fragments. [Examples 1-30 and -31]

- The factor must be applied to every pair of H-polar fragments as long as at least one of the hydrocarbon links between them is not otherwise involved. [Example 1-29]
- Fragments on an aliphatic ring are considered to be on a chain. [Example 1-29]
- Where the placement of the two fragments would imply two different coefficients, an average may be used. If, for example, one fragment is on a chain and the other in an aliphatic ring, use $F_{P1} = (-0.42 - 0.32)/2 = -0.37$ and $F_{P2} = (-0.26 - 0.20)/2 = -0.23$. [Example 1-29]

$F_{H/SP}$ If a halogen (S-polar fragment) is located on the same *aliphatic carbon (i.e., an* α-halogen) as an H-polar fragment, add the appropriate factors from the listing provided in Table 1-7. [Examples 1-32 and -33] The $F_{H/SP}$ values in this table also allow a factor to be added for β-halogens (1 carbon separation) for the $-OH$ and $-CO_2H$ fragments.

F_{HBN}, F_{HBO} If intramolecular hydrogen bonding is possible with a nitrogen atom, add the factor $F_{HBN} = 0.60$; if the bonding is with an oxygen atom, add the factor $F_{HBO} = 1.0$. Both factors are per H-bond. [Example 1-34].

Basic Steps

Note: For those unfamiliar with this method, all of the information provided above (i.e., starting at the beginning of §1-3) should be considered prerequisite reading.

(1) Draw the structure of the chemical.

(2) Two estimation pathways are possible:

- Check to see if a measured value of K_{ow} is available for one or more structurally similar compounds.[7] If so, proceed to Step 3. (This approach is preferred for structurally complex chemicals, as it generally provides a more accurate estimate.)
- If no measured value of K_{ow} is available for a structurally similar compound, or if the approach of Step 3 is unworkable or otherwise undesirable, proceed to Step 4.

7. Refs. 14 and 28 provide compilations of measured values for thousands of chemicals.

(3) Select the structurally similar compound(s) closest in structure to the problem chemical; if possible, select only those that differ in the number or type of functional groups (fragments) attached to a base molecule. Then, for each structurally similar compound of interest:

- Identify the fragments (f) and factors (F) that have to be added or subtracted to change the similar chemical to the problem chemical. Fragments are listed in Table 1-5 and factors in Tables 1-6 and 1-7 and the text of §1-3.
- Calculate the log K_{ow} value for the new chemical as follows:

$$\log K_{OW} \text{ (new chemical)} = \log K_{OW} \text{ (similar chemical)} \pm \text{fragments (f)} \pm \text{factors (F)} \quad (1\text{-}4)$$

A general example of the method is given in Eq. 1-5. Specific examples are provided in the following subsection; see Examples 1-38 to -43.

(4) Identify the fragments (f) and Factors (F) associated with the molecule, considering the rules described previously. Fragments are listed in Table 1-5, and factors are summarized in Tables 1-6 and -7 and the text of §1-3. Obtain log K_{ow} for the chemical by summing the fragment and factor values. Examples 1-1 to -37 illustrate the use of this method.

Several of the examples that follow are taken from Hansch and Leo [14], which is also the source of the observed ("obsd.") values cited. References 14 and 26 contain additional examples that readers may wish to examine.

Example 1-1 $CH_3CH_2-O-CH_2CH_3$

$4f_C$	= 4(0.20)	= 0.80
$+10f_H$	= 10(0.23)	= 2.3
$+f_{-O-}$	=	= −1.82
$+(4-1)F_b$	= 3(−0.12)	= −0.36
	log K_{ow}	= 0.92

(Obsd. = 0.77, 0.83, 0.89)

Example 1-2 $ClCH_2CH_2CH_2Cl$

$3f_C$	= 3(0.20)	= 0.60
$+6f_H$	= 6(0.23)	= 1.38
$+2f_{Cl}$	= 2(0.06)	= 0.12
$+(4-1)F_b$	= 3(−0.12)	= −0.36
	log K_{ow}	= 1.74

(Obsd. = 2.00)

Example 1-3 $CH_3\overset{O}{\overset{\|}{C}}-O-CH_3$

$2f_C$	= 2(0.20) =	0.40
$+6f_H$	= 6(0.23) =	1.38
$+f_{CO_2}$	=	−1.49
$+(2-1)F_b$	=	−0.12
	$\log K_{ow}$ =	0.17

(Obsd. = 0.18)

Example 1-4 $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}NH_2$

$3f_C$	= 3(0.20) =	0.60
$+7f_H$	= 7(0.23) =	1.61
$+f_{CONH_2}$	=	−2.18
$+(3-1)F_b$	= 2(−0.12) =	−0.24
	$\log K_{ow}$ =	−0.21

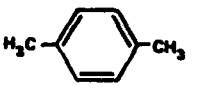
(Obsd. = −0.21)

Example 1-5 $(CH_3)_3N$

$3f_{CH_3}$	= 3(0.89) =	2.67
$+f_{-N<}$	=	−2.18
$+(3-1)F_{bYN}$	= 2(−0.20) =	−0.40
	$\log K_{ow}$ =	0.09

(Obsd. = 0.16, 0.27)

Example 1-6

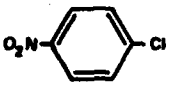


(Note: $f^{\phi}_{CH_3} = f_{CH_3}$)

$f_{C_6H_5}$	=	1.90
$-f^{\phi}_{H}$	=	−0.23
$+2f^{\phi}_{CH_3}$	= 2(0.89) =	1.78
	$\log K_{ow}$ =	3.45

(Obsd. = 3.15)

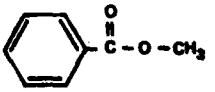
Example 1-7



$f_{C_6H_5}$	=	1.90
$-f^{\phi}_{H}$	=	−0.23
$+f^{\phi}_{NO_2}$	=	−0.03
$+f^{\phi}_{Cl}$	=	0.94
$\log K_{ow}$	=	2.58

(Obsd. = 2.39)

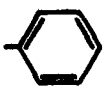
Example 1-8



$f_{C_6H_5}$	=	1.90
$+f^{\phi}_{CO_2}$	=	−0.56
$+f_{CH_3}$	=	0.89
$+(2-1)F_b$	=	−0.12
$\log K_{ow}$	=	2.11

(Obsd. = 2.12, 2.23)

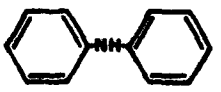
Example 1-9



$f_{C_6H_5}$	=	1.90
$+f^{1/\phi}_{CO_2}$	=	−1.18
$+f_{CH_3}$	=	0.89
$+(2-1)F_b$	=	−0.12
$\log K_{ow}$	=	1.49

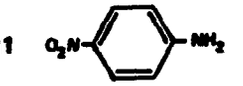
(Obsd. = 1.49)

Example 1-10



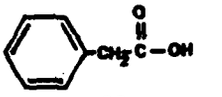
$2f_{C_6H_5}$	= 2(1.90) =	3.80
$+f^{\phi\phi}_{NH}$	=	−0.09
$+(2-1)F_{bYN}$	=	−0.20
	$\log K_{ow}$ =	3.51

(Obsd. = 3.22, 3.34, 3.50, 3.72)

Example 1-11 

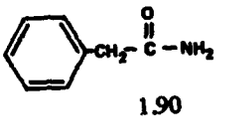
$f_{C_6H_5}$ =	1.90
$-f^{\phi}_{H}$ =	−0.23
$+f^{XI}_{NH_2}$ =	−0.23
$+f^{\phi}_{NO_2}$ =	−0.03
log K_{ow} =	1.41

(Obsd. = 1.39)

Example 1-12 

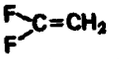
$f_{C_6H_5}$ =	1.90
$+f^{\phi}_{C}$ =	0.20
$+2f_{H}$ = 2(0.23) =	0.46
$+f^{1R}_{CO_2H}$ =	−1.03
$+(2\text{-}1)F_b$ =	−0.12
log K_{ow} =	1.41

(Obsd. = 1.41, 1.51)

Example 1-13 

$f_{C_6H_5}$ =	1.90
$+f^{\phi}_{C}$ =	0.20
$+2f_{H}$ = 2(0.23) =	0.46
$+f^{1R}_{CONH_2}$ =	−1.99
$+(2\text{-}1)F_b$ =	−0.12
log K_{ow} =	0.45

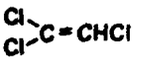
(Obsd. = 0.45)

Example 1-14 

(Note the second rule given for the $F_=$ factor)

$2f_{C}$ = 2(0.20) =	0.40
$+4f_{H}$ = 4(0.23) =	0.92
$+2f^{\phi/2}_{F}$ = 2(0.00) =	0
$+F_=$ =	−0.55
$+(3\text{-}1)F_b$ = 2(−0.12) =	−0.24
$+2F_{mhG_2}$ = 2(0.30) =	0.60
log K_{ow} =	1.13

(Obsd. = 1.24)

Example 1-15 

$2f_{C}$ = 2(0.20) =	0.40
$+3f_{H}$ = 3(0.23) =	0.69
$+3f^{\phi/2}_{Cl}$ = 3(0.50) =	1.50
$+F_=$ =	−0.55
$+(4\text{-}1)F_b$ = 3(−0.12) =	−0.36
$+2F_{mhG_2}$ = 2(0.30) =	0.60
log K_{ow} =	2.28

(Obsd. = 2.29)

Example 1-16 

$5f_{C}$ = 5(0.20) =	1.00
$+10f_{H}$ = 10(0.23) =	2.30
$+(5\text{-}1)F_b$ = 4(−0.09) =	−0.36
log K_{ow} =	2.94

(Obsd. = 3.00)

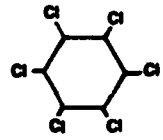
Example 1-17



$6f_C$	= 6(0.20)	=	1.20
$+12f_H$	= 12(0.23)	=	2.76
$+(6-1)F_b$	= 5(−0.09)	=	−0.45
$+F_=$	=		−0.55
	$\log K_{ow}$	=	2.96

(Obsd. = 2.86)

Example 1-18



$6f_C$	= 6(0.20)	=	1.20
$+6f_H$	= 6(0.23)	=	1.38
$+6f_{Cl}$	= 6(0.06)	=	0.36
$+(6-1)F_b$	= 5(−0.09)	=	−0.45
$+(6-1)F_{mhV}$	= 5(0.28)	=	1.40
	$\log K_{ow}$	=	3.89

(Obsd. = 3.61, 3.72, 3.80 for α isomer
= 3.78 for β isomer
= 4.14 for δ isomer
= 3.72 for γ isomer)

Example 1-19 $(CH_3CH_2CH_2)_3N$

$9f_C$	= 9(0.20)	=	1.80
$+21f_H$	= 21(0.23)	=	4.83
$+f_{-N<}$	=		−2.18
$+(9-1)F_{bYN}$	= 8(−0.20)	=	−1.60
	$\log K_{ow}$	=	2.85

(Obsd. = 2.79)

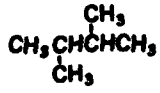
Example 1-20

$(CH_3CH_2)_2NCH_2CH_2-O-CH_2CH_3$
(Note the final rule given for the F_b' factor).

$8f_C$	= 8(0.20)	=	1.60
$+19f_H$	= 19(0.23)	=	4.37
$+f_{-N<}$	=		−2.18
$+f_{-O-}$	=		−1.82
$+(7-1)F_{bYN}$	= 6(−0.20)	=	−1.20
$+(2-1)F_b$	=		−0.12
	$\log K_{ow}$	=	0.65

(No obsd. value)

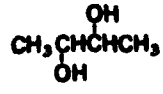
Example 1-21



$6f_C$	= 6(0.20)	=	1.20
$+14f_H$	= 14(0.23)	=	3.22
$+(5-1)F_b$	= 4(−0.12)	=	−0.48
$+2F_{cBr}$	= 2(−0.13)	=	−0.26
	$\log K_{ow}$	=	3.68

(Obsd. = 3.85)

Example 1-22



$4f_C$	= 4(0.20)	=	0.80
$+8f_H$	= 8(0.23)	=	1.84
$+2f_{OH}$	= 2(−1.64)	=	−3.28
$+(5-1)F_b$	= 4(−0.12)	=	−0.48
$+2F_{gBr}$	= 2(−0.22)	=	−0.44
$+F_{P2}$	= (−0.26)(2)(−1.64)	=	0.85
		$\log K_{ow}$ =	−0.71

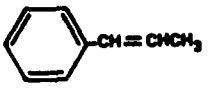
(Obsd. = −0.92)

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Example 1-23 

$10f_C$	= 10(0.20)	= 2.00
$+16f_H$	= 16(0.23)	= 3.68
$+(12-1)F_b$	= 11(−0.09)	= −0.99
$+F_{rCl}$		= −0.45
	$\log K_{ow}$	= 4.24

(No Obsd. value)

Example 1-24 

$f_{C_6H_5}$	=	1.90
$3f_C$	= 3(0.20)	= 0.60
$+7f_H$	= 7(0.23)	= 1.61
$+(3-1)F_b$	= 2(−0.12)	= −0.24
$+F^{\phi}_{=}$	=	−0.42
	$\log K_{ow}$	= 3.45

(Obsd. = 3.35)

Example 1-25 $CH_3C{\equiv}CCH_3$

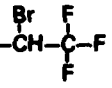
$4f_C$	= 4(0.20)	= 0.80
$+10f_H$	= 10(0.23)	= 2.30
$+(3-1)F_b$	= 2(−0.12)	= −0.24
$+F_{\equiv}$	=	−1.42
	$\log K_{ow}$	= 1.44

(Obsd. = 1.46)

Example 1-26 

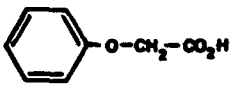
f_C	=	0.20
$+f_H$	=	0.23
$+f_F$	=	−0.38
$+2f_{Cl}$	= 2(0.06)	= 0.12
$+(3-1)F_b$	= 2(−0.12)	= −0.24
$+3F_{mhG_3}$	= 3(0.53)	= 1.59
	$\log K_{ow}$	= 1.52

(Obsd. = 1.55)

Example 1-27 

$2f_C$	= 2(0.20)	= 0.40
$+f_H$	=	0.23
$+f_{Cl}$	=	0.06
$+f_{Br}$	=	0.20
$+3f_F$	= 3(−0.38)	= −1.14
$+(6-1)F_b$	= 5(−0.12)	= −0.60
$+2F_{mhG_2}$	= 2(0.30)	= 0.60
$+3F_{mhG_3}$	= 3(0.53)	= 1.59
$+(5-1)F_{mhV^F_S}$	4(0.28)	= 1.12
	$\log K_{ow}$	= 2.46

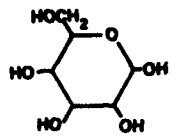
(Obsd. = 2.30)

Example 1-28 

$f_{C_6H_5}$	=	1.90
$+f^{\phi}_{-O-}$	=	−0.61
$+f_C$	=	0.20
$+2f_H$	= 2(0.23)	= 0.46
$+f_{CO_2H}$	=	−1.11
$+(3-1)F_b$	= 2(−0.12)	= −0.24
$+F_{P1}$	= −0.42(−0.61 −1.11)	= 0.72
	$\log K_{ow}$	= 1.32

(Obsd. = 1.26)

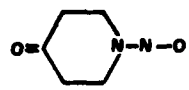
Example 1-29



$6f_C$	= 6(0.20)	= 1.20
$+7f_H$	= 7(0.23)	= 1.61
$+f_{-O-}$	=	−1.82
$+5f_{OH}$	= 5(−1.64)	= −8.20
$+(6\text{-}1)F_b$	= 5(−0.09)	= −0.45
$+F_b$	=	−0.12
$+F_{cBr}$	=	−0.13
$+4F_{gBr}$	= 4(−0.22)	= −0.88
$+F_{P1}$	= −0.37(−1.82 −1.64)	= 1.28
$+2F_{P2}$	= 2(−0.23)(−1.82 −1.64)	= 1.59
$+3F_{P2}$	= 3(−0.26)(−1.64 −1.64)	= 2.56
	$\log K_{ow}$	= −3.36

(Obsd. = −3.24)

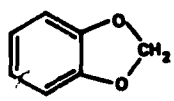
Example 1-30



$4f_C$	= 4(0.20)	= 0.80
$+8f_H$	= 8(0.23)	= 1.84
$+f_{NNO}$	=	= −2.40
$+f_{CO}$	=	= −1.90
$+(6\text{-}1)F_b$	= 5(−0.09)	= −0.45
$+2F_{P2}$	= 2(−0.20)(−2.40 −1.90)	= 1.72
	$\log K_{ow}$	= −0.39

(Obsd. = −0.47)

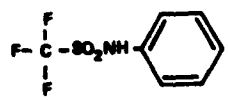
Example 1-31



$4f_{CH}$	= 4(0.355)	= 1.42
$+2f^{\phi}_{C}$	= 2(0.44)	= 0.88
$+2f_H$	= 2(0.23)	= 0.46
$+2f^{\phi}_{-O-}$	= 2(−0.61)	= −1.22
$+f_C$	=	0.20
$+(4\text{-}1)F_b$	= 3(−0.09)	= −0.27
$+F_{P1}$	= (−0.32)(2) (−0.61)	= 0.39
$+F^{\phi}_{P2}$	= (−0.08)(2) (−0.61)	= 0.10
	$\log K_{ow}$	= 1.96

(Obsd. = 2.08)

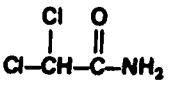
Example 1-32



$3f_F$	= 3(−0.38)	= −1.14
$+f_C$	=	0.20
$+f^{1/\phi}_{SO_2NH}$	=	−1.72
$+f_{C_6H_5}$	=	1.90
$+(5\text{-}1)F_b$	= 4(−0.12)	= −0.48
$+3F_{mhG_3}$	= 3(0.53)	= 1.59
$+F_{H/SP_3}$	=	2.70
	$\log K_{ow}$	= 3.05

(Obsd. = 3.05)

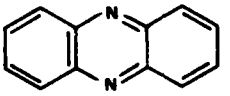
Example 1-33



$2f_{Cl}$	= 2(0.06) =	0.12
$+f_C$	=	0.20
$+f_H$	=	0.23
$+f_{CONH_2}$	=	–2.18
$+(3-1)F_b$	= 2(–0.12) =	–0.24
$+2F_{mhG_2}$	= 2(0.30) =	0.60
$+F_{H/SP_2}$	=	1.33
	log K_{ow} =	0.06

(No obsd. value)

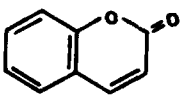
Example 1-35



$8f^{\phi}_{\underline{CH}}$	= 8(0.355) =	2.84
$+4f^{\phi}_{\underline{\underline{C}}}$	= 4(0.44) =	1.76
$+2f^{\phi}_{\underline{N}}$	= 2(–1.12) =	–2.24
$+2F^{\phi}_{P2}$	= 2(–0.08)(–1.12–1.12) =	0.36
	log K_{ow} =	2.72

(Obsd. = 2.84)

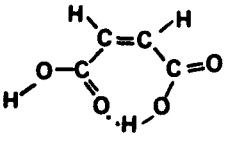
Example 1-36



$6f^{\phi}_{\underline{CH}}$	= 6(0.355) =	2.13
$+f^{\phi}_{\underline{\underline{C}}}$	=	0.225
$+f^{\phi}_{\underline{\underline{C}}}$	=	0.44
$+f^{\phi}_{\underline{OCO}}$	=	–1.40
	log K_{ow}	1.40

(Obsd. = 1.39)

Example 1-34 **Maleic Acid**

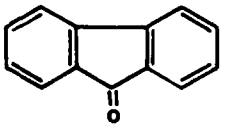


(Dotted line indicates hydrogen bond)

$2f_C$	= 2(0.20) =	0.40
$+4f_H$	= 4(0.23) =	0.92
$+2f^{\phi/2}_{C(O)OH}$	= 2(–0.57) =	–1.14
$+F_=$	=	= –0.55
$+(3-1)F_b$	=	= –0.24
$+F_{HBO}$	=	= 1.00
	log K_{ow} =	0.39

A similar calculation of log K_{ow} for the trans isomer of this compound (fumaric acid) yields an estimate of –0.61 since the F_{HBO} factor is not used. No observed values of log K_{ow} are available for these compounds, but estimates of 0.26 (fumaric) and –0.55 (maleic) may be obtained by the methods in §1-4 using the diethyl ether/water partition coefficients reported in Ref. 14.

Example 1-37

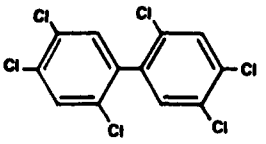


$8f^{\phi}_{\underline{CH}}$	= 8(0.355) =	2.84
$+2f^{\phi}_{\underline{\underline{C}}}$	= 2(0.225) =	0.45
$+2f^{\phi}_{\underline{\underline{C}}}$	= 2(0.44) =	0.88
$+f^{\phi\phi}_{\underline{CO}}$	=	= –0.50
	log K_{ow} =	3.67

(Obsd. = 3.58)

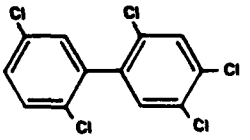
Note that the carbonyl carbon is considered to be in an aromatic ring according to footnote f of Table 1-5.

Example 1-38



2,4,5,2',4',5'-PCB

I. $\log K_{ow} = ?$



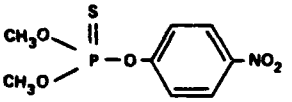
2,4,5,2',5'-PCB

II. $\log K_{ow} = 6.11$ [2]

$$\log K_{ow}(II) = 6.11$$
$$-f_H^{\phi} = -0.23$$
$$+f_{Cl}^{\phi} = 0.94$$
$$\log K_{ow}(I) = 6.82$$

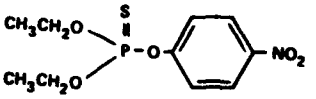
(Obsd. = 6.72 [2])

Example 1-39



Methyl Parathion

I. $\log K_{ow} = ?$



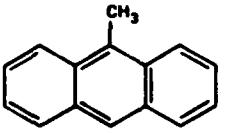
Parathion

II. $\log K_{ow} = 3.81$ [2].

$$\log K_{ow}(II) = 3.81$$
$$-2f_C = -2(0.20) = -0.40$$
$$-4f_H = -4(0.23) = -0.92$$
$$-2F_{bYP} = -2(-0.31) = 0.62$$
$$\log K_{ow}(I) = 3.11$$

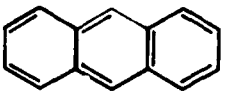
(Obsd. values are 2.04 [14], 2.99 [14], 1.91 [22] and 3.22 [38].
The estimate of 3.11 casts suspicion on the two lowest measured values.)

Example 1-40



9-Methyl anthracene

I. $\log K_{ow} = ?$



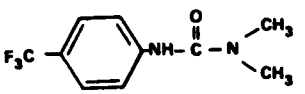
Anthracene

II. $\log K_{ow} = 4.54$ [21]

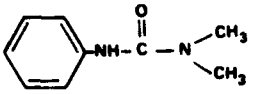
$$\log K_{ow}(II) = 4.54$$
$$-f_H^{\phi} = -0.23$$
$$+f_{CH_3}^{\phi} = 0.89$$
$$\log K_{ow}(I) = 5.20$$

(Obsd. = 5.07 [21])

Example 1-41



Fluometuron



Fenuron

I. $\log K_{ow}$ = ?

II. $\log K_{ow}$ = 1.00 [22]

$\log K_{ow}$(II) = 1.00

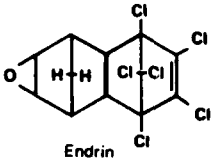
$-f^{\phi}_{H}$ = –0.23

$+f^{\phi}_{CF_3}$ = 1.11

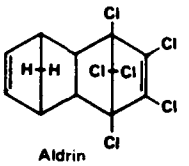
$\log K_{ow}$(I) = 1.88

(Obsd. = 1.34 [22])

Example 1-42



Endrin



Aldrin

I. $\log K_{ow}$ = ?

II. $\log K_{ow}$ = 3.01 [14]

$\log K_{ow}$(II) = 3.01

$-F_{=}$ = 0.55

$+f_{-O-}$ = –1.54

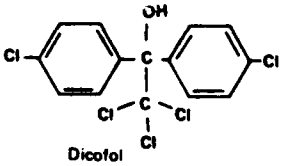
$+2F_{b}$ = –0.18

$\log K_{ow}$(I) = 1.84

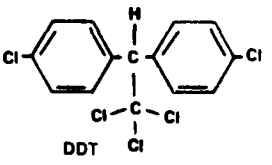
(Obsd. = 3.21 [38], 5.34 [22])

Note: Estimates of 4.96 and 3.91 for $\log K_{ow}$ (II) may be obtained by the methods of §1-3 and §1-4, respectively. These would yield estimates of 3.79 and 2.74 for $\log K_{ow}$ (I), in closer agreement with the reported values. The reported value of 3.01 for $\log K_{ow}$ (II) is thus questionable.

Example 1-43



Dicofol



DDT

I. $\log K_{ow}$ = ?

II. $\log K_{ow}$ = 5.98 [22]

$\log K_{ow}$(II) = 5.98

$-f_{H}$ = –0.23

$+f_{OH}$ = –1.64

$+F_{gBr}$ = –0.22

$+F_{b}$ = –0.12

$+F_{H/SP_3}$ = 0.88

$\log K_{ow}$(I) = 4.65

(No. obsd. value)

1-4 ESTIMATION WITH SOLVENT REGRESSION EQUATIONS

Principles of Use. Solvent/water partition coefficients (K_{sw}) have been measured for numerous solutes in a large variety of solvent systems. These K_{sw} values, like K_{ow}, have found wide use in structure-activity correlations, especially for pharmaceuticals. Some of the more frequently used organic solvents are ethyl ether, n-butanol, chloroform, cyclohexane, benzene, and vegetable oils. In analogy with Eq. 1-1, K_{sw} is defined as the ratio of the solute's concentration in the organic phase to that in the aqueous phase of the two-phase system at equilibrium. Low solute concentrations are employed in the measurement.

The most comprehensive set of solvent regression equations is that given by Leo and Hansch [27] and repeated in the subsequent publication by Leo, Hansch, and Elkins [28]. Their original equations were written with log K_{sw} as the dependent variable but are restated here in the following form:

$$\log K_{ow} = a \log K_{sw} + b \qquad (1\text{-}6)$$

Thirty-one such equations are provided, allowing K_{ow} to be calculated if a value of K_{sw} for the solute is available with one or more of approximately twenty different solvents. A modified solvent regression equation, developed by Seiler [41], is provided if the K_{sw} value is for the cyclohexane/water system. Several solvent regression equations are also given by Rekker [39], but most of them involve the use of special fragment constants or correction factors and are thus slightly more difficult to use. Rekker's equations are not included in this chapter.

Solvent Regression Equations. The selection of the appropriate solvent regression equation sometimes depends upon the nature of the solute. Table 1-8 lists a number of solute classes in two basic groups: A (hydrogen donors) and B (hydrogen acceptors). Table 1-9 provides values of a and b for the basic set of solvent regression equations (Eq. 1-7 to -37), all of which are of the form shown in Eq. 1-6. If the solute (the chemical for which K_{ow} is to be calculated) is listed under Group A or B in Table 1-8 *and* if the solvent (associated with the available K_{sw} value) is one of those listed in the first two sections of Table 1-9, then a choice between two equations must be made. For example, if a value of K_{sw} is available from the xylene/water system, one must choose between Eqs. 1-10 and 1-21. The choice depends on where the solute is listed in Table 1-8 — e.g., Eq. 1-10 would be used if the solute were an alcohol, and Eq. 1-21 would be used if it were an ether.

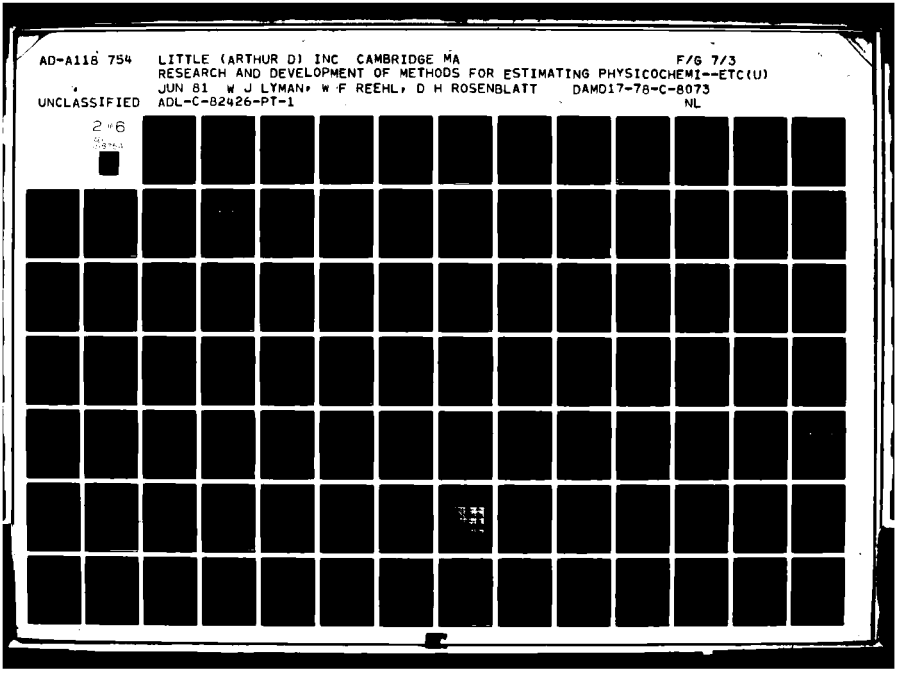

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RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEMI--ETC(U)
JUN 81 W J LYMAN, W F REEHL, D H ROSENBLATT DAMD17-78-C-8073
UNCLASSIFIED ADL-C-82426-PT-1 NL
2 #6

TABLE 1-8

General Solute Classes

Group A – H donors		1. Acids
		2. Phenols
	a	3. Barbiturates
		4. Alcohols
		5. Amides (negatively substituted, but not di-N-substituted)
		6. Sulfonamides
		7. Nitriles
		8. Imides
		9. Amides[b]
Group B – H acceptors		10. Aromatic amines[b] (not di-N-substituted)
		11. Miscellaneous acceptors
		12. Aliphatic[c] and aromatic hydrocarbons
		13. Intramolecular H bonds[d]
		14. Ethers
		15. Esters
		16. Ketones
		17. Aliphatic amines and imines
		18. Tertiary amines (including ring N compounds)

a. "Neutral" in chloroform and carbon tetrachloride; use "N" equations (Eq. 1-36, -37) for these two solvents.

b. Classes 9 and 10 must be reversed when considering the ether and oils solvent systems.

c. Classification assigned by the author of this chapter.

d. E.g., *o*-nitrophenol.

Source: Leo, Hansch and Elkins [28]

TABLE 1-9

Solvent Regression Equations[a]
($\log K_{ow} = a \log K_{sw} + b$)

Eq.	Solvent	a	b	No.	r
	Equations for Group A Solutes				
1-7	Cyclohexane	1.481	2.729	26	0.761
1-8	Heptane	0.947	2.700	10	0.764
1-9	Carbon tetrachloride	0.856	1.852	24	0.974
1-10	Xylene	1.062	1.798	19	0.963
1-11	Toluene	0.881	1.566	22	0.980
1-12	Benzene	0.985	1.381	33	0.962
1-13	Chloroform	0.888	1.193	28	0.967
1-14	Oils[b]	0.910	1.192	65	0.981
1-15	Nitrobenzene	0.850	0.912	9	0.977
1-16	Isopentyl acetate	0.974	−0.070	22	0.986
1-17	Ethyl ether	0.885	0.150	71	0.988
	Equations for Group B Solutes				
1-18	Cyclohexane	0.941	0.690	30	0.957
1-19	Heptane	0.541	1.203	11	0.954
1-20	Carbon tetrachloride	0.829	0.181	11	0.959
1-21	Xylene	0.974	0.579	21	0.986
1-22	Toluene	0.715	0.660	14	0.971
1-23	Benzene	0.818	0.469	19	0.958
1-24	Chloroform	0.784	0.134	21	0.976
1-25	Oils[b]	0.894	0.290	14	0.988
1-26	Ethyl ether	0.876	0.937	32	0.957
	Equation Set C				
1-27	Oleyl alcohol	1.001	0.576	37	0.985
1-28	Methyl isobutyl ketone	0.914	−0.046	17	0.993
1-29	Ethyl acetate	1.073	−0.056	9	0.969
1-30	Cyclohexanone	0.966	−0.866	10	0.972
1-31	Primary pentanols	1.238	−0.335	19	0.987
1-32	sec- and tert-Pentanols	1.121	−0.323	11	0.996
1-33	2-Butanone	2.028	−0.639	9	0.987
1-34	Cyclohexanol	1.342	−1.162	12	0.985
1-35	Primary butanols	1.435	−0.547	57	0.993
	Equations for Group N Solutes				
1-36	Carbon tetrachloride	1.160	0.726	6	0.809
1-37	Chloroform	0.909	0.561	32	0.974

a. The values of a and b are the slope and intercept, respectively, for the solvent regression equation; No. = number of chemicals in data set; r = correlation coefficient for equation as originally written by Leo *et al.* [28]. Their equations were in the form $\log K_{sw} = a' \log K_{ow} + b'$.

b. Most liquid glyceryl triesters fit these equations; olive, cottonseed, and peanut oils were the most frequently used.

Source: Adapted from Leo, Hansch and Elkins [28], Table VIII.

If the solvent is one of those listed in the third section (set "C") of Table 1-9, the appropriate equation (from Eqs. 1-27 to -35) is selected irrespective of the solute class. Three equations are available for the instances when K_{sw} is from the carbon tetrachloride/water or chloroform/water systems: 1-9, -20, and -36 for the former and 1-13, -24, and -37 for the latter. Footnote "a" of Table 1-8 explains how the correct equation is selected based upon considerations of solute class.

It has been noted in several places [18,27,28,41] that solvent regression equations linking K_{ow} with K_{sw} for such solvents as cyclohexane and heptane have a poorer quality of fit (lower *r* values — see Table 1-9). This is attributed to the effects of hydrogen bonding (solute-solute interactions). Cyclohexane and heptane dissolve very small amounts of water ($\sim 3 \times 10^{-3}$ mol/L); other organic solvents dissolve greater amounts, which tends to inhibit solute-solute hydrogen bonding effects when K_{sw} is measured.

Seiler [41] has proposed a modified solvent regression equation to cover the cyclohexane/water → octanol/water calculation:

$$\log K_{ow} = \log K_{cw} + \Sigma I_H + 0.16 \qquad (1\text{-}38)$$

$$\text{No.} = 195, \; r = 0.967$$

In this equation K_{cw} is the cyclohexane/water partition coefficient and I_H values are hydrogen bonding corrections for specific functional groups in the solute. The I_H values are given in Table 1-10. Note that the correlation coefficient (r) for Eq. 1-38 (0.967) is significantly better than for Eq. 1-7 (0.761) for H donors but is about the same as for Eq. 1-18 (0.957) for H acceptors.

Method Errors. Table 1-11 compares observed and estimated values of K_{ow} for 39 examples, excluding those where K_{sw} was from the cyclohexane/water or heptane/water systems. For the examples listed, the average absolute error is 0.38 log K_{ow} unit and the maximum error is 1.4 log K_{ow} units. The method error for Eq. 1-38 is assumed to be of similar magnitude.

Basic Steps

(1) Obtain a measured value of K_{sw} for any of the solvent systems listed in Table 1-9. (Measured values of K_{sw} for numerous chemicals are tabulated in Refs. 14 and 28. Reference 17 gives some values for the cyclohexane/water system.)

TABLE 1-10

Hydrogen Bonding Corrections, I_H, for Eq. 1-38

Molecular Segment[a]	I_H	No.[b]
–N=N–NH– (triazolo)	4.24	2
$NH_2OC...CONH_2$ (in malonamides)	3.41	4
–Ç·CO·NH·CO·NH·ÇO	3.06	2
–COOH, aliphatic	2.88	1
–COOH, aromatic	2.87	4
–OH, aromatic	2.60	33
–CONH–	2.56	7
$–SO_2NH–$	1.93	3
–OH, aliphatic	1.82	11
$–NH_2$, aliphatic	1.33	2
$–NH_2$, aromatic	1.18	21
=N–	1.01	9
$–P(OR)_2=O$, R≠H	0.84	2
–NHR, R≠H	0.61	9
$–CO–CH_2–CO–$	0.59	26
$–NR_1R_2$, R≠H	0.55	10
$–NO_2$	0.45	31
>C=O	0.31	26
–CN	0.23	13
–O–	0.11	34
Ortho substitution to –OH, –COOH, $–NR_1R_2$	–0.62	16
Per ΔpK unit (phenols)[c]	0.30	33
Per ΔpK unit (anilines)[c]	0.16	21

a. Inclusion of the following molecular segments as additional independent variables in the least-squares analysis did not improve the correlation significantly: chlorine (No.=40); bromine (No.=4); iodine (No.=2); fluorine (No.=12); –COOR, R≠H (No.=55); $–SO_2–$ (No.=1); number of carbon atoms in each molecule; and ΔpK value for benzoic acids (No.=4).

b. Total number of each of the molecular segments used in the least-squares calculation.

c. $\Delta pK = pK_a (R=H) - pK_a (R\neq H)$.

Source: Seiler [41].

TABLE 1-11

Comparison of Observed log K_{ow} with Values Estimated from Solvent/Water Partition Coefficients

Chemical[a]	Solvent	log K_{sw}[b]	Eq. Type	log K_{ow} Observed	log K_{ow} Calculated[b]	Error (log K_{ow} units)
Chloroform	Oils	1.86	B	1.97	1.98	0.01
Thiourea	Diethyl ether	−2.15(3)	A	−1.14	−1.48(3)	−0.34
	Chloroform	−3.10	N		−2.38	−1.24
	Oils	−2.92	A		−1.43	−0.29
Chloroacetamide	Diethyl ether	−1.02(2)	A	−0.53	−0.78	−0.25
	Chloroform	−0.96	N		−0.29	0.24
Acetic acid, methyl ester	Diethyl ether	0.43	A	0.18	0.49	0.31
	Oils	−0.37	B		0.20	0.02
	Benzene	0.47	B		0.87	0.69
	Carbon tetrachloride	0.41	B		0.32	0.14
α-Bromobutyric acid	Chloroform	0.08	A	1.42	1.29	−0.13
	Oils	0.14	A		1.12	−0.30
	Benzene	−0.08	A		1.33	−0.09
	Isobutanol	1.46	C		1.55	0.13
	Toluene	−0.27	A		1.32	−0.10
β,β,β-Trichloro-*t*-butanol	Oils	1.36	A	2.03	2.44	0.41
Piperazine	Diethyl ether	−3.28	B	−1.17	−2.03	−0.86
Diethanolamine	Diethyl ether	−3.27	B	−1.43	−2.02	−0.59
	Isobutanol	−0.70	C		−1.49	−0.06
Pentanol	Oils	0.36	A	1.40	1.52	0.12
	Benzene	0.19	A		1.56	0.16

(continued)

TABLE 1-11 (Continued)

Chemical[a]	Solvent	log K_{sw}[b]	Eq. Type	log K_{ow} Observed	log K_{ow} Calculated[b]	Error (log K_{ow} units)
2,4,6-Trinitrophenol	Chloroform	1.20	A	2.03	2.31	0.28
	Benzene	1.69	A		3.02	0.99
	n-Butanol	0.96	C		0.82	−1.21
	Toluene	1.30(2)	A		2.72(2)	0.69
	Primary pentanols	1.85	C		2.01	−0.02
	sec-Pentanols	0.82	C		0.63	−1.40
m-Bromophenol	Oleyl alcohol	2.02	C	2.63	2.57	−0.06
p-Bromobenzene-sulfonamide	Chloroform	0.39	N	1.36	0.92	−0.44
o-Dihydroxybenzene	Diethyl ether	0.93(3)	A	0.94(2)	0.93(3)	−0.01
	Benzene	−1.19	A		0.21	−0.73
Triethylamine	Benzene	1.13	B	1.44	1.30	−0.14
	Isobutanol	1.32	C		1.47	0.03
	Xylene	1.11	B		1.77	0.33
	Toluene	0.89(3)	B		1.30(3)	−0.14
	Primary pentanols	1.42	C		1.42	−0.02
Phenylthiourea	Diethyl ether	0.23	A	0.73	0.32	−0.41
	Chloroform	0.54	N		0.54	−0.19
2-Naphthol	Diethyl ether	1.77	A	2.84	1.67	−1.17
					Average absolute error =	0.38[c]
					Maximum error =	1.4

a. Entries were selected from a much larger listing in Table XVII of Ref. 28.

b. Where more than one value of log K_{sw} or log K_{ow} was given, an average was taken for use in this table. *The number in parentheses indicates the number of data points in the original source.*

c. Higher errors are likely to be associated with K_{ow} values derived from K_{sw} values from the cyclohexane or heptane systems.

Source: Leo, Hansch and Elkins [28].

(2) If the solvent is one of those in "Set C" in Table 1-9, select the appropriate solvent regression equation from this group. Substitute the given values of a and b, along with log K_{sw}, in the generalized equation shown at the head of Table 1-9 (also shown as Eq. 1-6) and solve for log K_{ow}.

(3) If the solvent is listed in the first two sections of Table 1-9, see Table 1-8 to determine whether the solute is in Group A or B and select the regression equation accordingly. (See Step 4 for an alternate method if the solvent is cyclohexane.) Substitute the selected values of a, b and log K_{sw} into the generalized equation shown at the head of Table 1-9 (also shown as Eq. 1-6) and solve for log K_{ow}.

(4) If K_{sw} is from the cyclohexane/water system *and* the chemical is a H-donor, the preferred equation is Eq. 1-38 (given in the text). Values of I_H needed for this equation are obtained from Table 1-10. This method may also be used if the chemical is a H-acceptor.

(5) If K_{sw} values are available for two or more solvents, it is suggested that a value of log K_{ow} be estimated from each K_{sw} value and averaged.

Example 1-44 Estimate K_{ow} for *m*-bromoaniline, given log K_{sw} (benzene) = 2.20 [28].

(1) There are two benzene equations (Eqs. 1-12 and -23) in Table 1-9. Table 1-8 indicates that the equation in group "B" (Eq. 1-23) should be used for an aromatic amine.

(2) From Eq. 1-23,

$$\log K_{ow} = 0.818\,(2.20) + 0.469$$

$$= 2.27 \quad (\therefore K_{ow} = 186)$$

The reported value of log K_{ow} is 2.10 [28]; thus, the error is +0.17 log unit.

Example 1-45 Estimate K_{ow} for *t*-butanol, given log K_{sw} (chloroform) = −0.04 [28].

(1) There are three chloroform equations in Table 1-9. Table 1-8 indicates that the "N" equation (Eq. 1-37) should be used for alcohols.

(2) From Eq. 1-37,

$$\log K_{ow} = 0.909\,(-0.04) + 0.561$$

$$= 0.52 \quad (\therefore K_{ow} = 3.3)$$

The reported value of $\log K_{cw}$ is 0.37 [28]; thus, the error is +0.15 log unit.

Example 1-46 Estimate K_{ow} for *m*-bromophenol, given $\log K_{sw}$ (cyclohexane) = −0.52 and $\log K_{sw}$ (oleyl alcohol) = 2.02 [28].

(1) For the cyclohexane number, Step 4 (of Basic Steps) states that Eq. 1-38 is preferred. The −OH substituent requires a hydrogen bonding correction (I_H) of 2.60, as indicated in Table 1-10. Substituting in Eq. 1-38:

$$\log K_{ow} = -0.52 + 2.60 + 0.16$$

$$= 2.24 \quad (\therefore K_{ow} = 174)$$

(2) For the oleyl alcohol number, only one equation (Eq. 1-27) is available in Table 1-9; there is no choice to be made based on solute class. Substituting in Eq. 1-27:

$$\log K_{ow} = 1.001\,(2.02) + 0.576$$

$$= 2.60 \quad (\therefore K_{ow} = 397)$$

The measured value of $\log K_{ow}$ is 2.63 [28]; thus, the errors involved in the two estimates are −0.39 and −0.03 log units, respectively.

1-5 ESTIMATION FROM (ESTIMATED) ACTIVITY COEFFICIENTS

Introduction. This section briefly outlines how K_{ow} values can be estimated with activity coefficients that have been estimated via the methods described in Chapter 11. It is not considered a recommended method, since the calculations (primarily those associated with estimating the activity coefficient) are too complex for those without access to a programmable calculator or small computer. Accordingly, not all details of the procedure are given, there are no step-by-step instructions or examples, and the method error is not stated.

Relating K_{ow} to γ. The activity of a chemical that has been allowed to equilibrate between the phases of the octanol/water system must be the same in each phase. It follows that

$$x_c^o \gamma_c^o = x_c^w \gamma_c^w \qquad (1\text{-}39)$$

where

x_c^o = mole fraction of chemical (c) in octanol (o) phase

x_c^w = mole fraction of chemical (c) in water (w) phase

γ_c^o = activity coefficient of chemical in octanol phase

γ_c^w = activity coefficient of chemical in water phase

Thus

$$x_c^o / x_c^w = \gamma_c^w / \gamma_c^o \tag{1-40}$$

From the definition of mole fraction, it follows that

$$x_c^w = \frac{n_c^w}{n_w^w + n_c^w + n_o^w} = \frac{C_c^w}{C_w^w + C_c^w + C_o^w} \tag{1-41}$$

where n = number of moles

superscript w = water phase

subscripts w, c, o = water, chemical, and octanol, respectively

C = concentration (mol/L)

In the measurement of K_{OW}, C_c^w is typically $\lesssim 0.01$. C_o^w is the solubility of octanol in water (4.5×10^{-3} M) and C_w^w is 55.5 M. Thus, Eq. 1-41 may be reduced to:

$$C_c^w = 55.5\ x_c^w \text{ (mol/L)} \tag{1-42}$$

Similarly,

$$x_c^o = \frac{n_c^o}{n_o^o + n_c^o + n_w^o} = \frac{C_c^o}{C_o^o + C_c^o + C_w^o} \tag{1-43}$$

where the symbols have the same meaning as described above. Again, C_c^o is typically small ($\lesssim 0.01$ M) and may be neglected. C_w^o is the solubility of water in octanol (2.30 M). C_o^o is then found to be 6.07 M, using a density of 0.825 g/mL for octanol and assuming no volume change upon mixing of the octanol in water. Equation 1-43 may now be reduced to:

$$C_c^o = 8.37\ x_c^o \text{ (mol/L)} \tag{1-44}$$

Now K_{ow}, by definition (cf. Eq. 1-1), is

$$K_{ow} = C_c^o / C_c^w \tag{1-45}$$

Substituting Eqs. 1-42 and -44 into 1-45 we obtain

$$K_{ow} = 0.151\ x_c^o/x_c^w \tag{1-46}$$

Finally, substituting Eq. 1-40 in the above:

$$K_{ow} = 0.151\ \gamma_c^w/\gamma_c^o \tag{1-47}$$

Estimating γ^w and γ^o. Chapter 11 provides detailed instructions for calculating activity coefficients in binary systems. These instructions are adequate for estimating γ_c^w for most chemicals, since the presence of 4.5 $\times$ 10^{-3}M octanol may be ignored.[8] In addition, since $C_c^w < 0.01$M, one can assume that $\gamma_c^w = (\gamma_c^w)^\infty$, where $(\gamma_c^w)^\infty$ is the activity coefficient at infinite dilution. This assumption simplifies the calculations.

The assumption of a binary system cannot, however, be used for the calculation of γ_c^o. The octanol phase is a ternary one, with 0.725 mole fraction octanol, 0.275 mole fraction water, and $\sim 10^{-4}$ mole fraction of the test chemical. Thus, for the calculation of γ_c^o, the instructions of Chapter 11 must be slightly modified (see references cited in Chapter 11) to extend the method to ternary systems.[9] It can again be assumed that $\gamma_c^o = (\gamma_c^o)^\infty$

1-6 AVAILABLE DATA

A large collection of measured K_{ow} and K_{sw} values (nearly 15,000 data points) is given by Hansch and Leo [14]. This supersedes the list (nearly 6,000 data points) published earlier by Leo, Hansch and Elkins [28]. More up-to-date lists — the result of a continuing project by these researchers — may be purchased from the Pomona College Medicinal Chemistry Project, Pomona College, Claremont, CA 91711. All of these lists are indexed by molecular formula.

Other publications that list substantial amounts of data include the following:

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8. This was demonstrated by Dec *et al.* [5], who measured the solubility of three chemicals (1,3,5-triaza-1,3,5-trinitrocyclohexane, 1,2,3,5-tetrachlorobenzene, and o-dichlorobenzene) in both pure water and octanol-saturated water and found no significant difference in the results.

9. The general method described in Chapter 11 *is* applicable to ternary systems, and other investigators have carried out numerous calculations to demonstrate this. See Ref. 9 or § 3-4 of Chapter 3 for additional information.

Rekker [39] — Numerous K_{ow} and K_{ew} values

Nys and Rekker [33] — K_{ow} values

Kenaga and Goring [22] — K_{ow} for many pesticides

Rao and Davidson [38] — K_{ow} for many pesticides

Karickhoff, Brown and Scott [21] — K_{ow} for several polynuclear aromatics

Holmes [17] — Some emphasis on K_{ew} for the cyclohexane/water system

Holmes and Lough [18] — K_{ow} for substituted phenols with intramolecular hydrogen bonding.

Additional sources include the references cited in Table 1-2 of this chapter. Appropriate references in Chapters 2, 4, and 5 may also be helpful; these chapters describe regression equations between K_{ow} and (1) solubility, (2) soil adsorption coefficients, and (3) bioconcentration factors.

1-7 SYMBOLS USED

a = parameter in solvent regression equation (Eq. 1-6)

b = parameter in solvent regression equation (Eq. 1-6)

BCF = bioconcentration factor for aquatic life

C = concentration, mol/L (superscripts o, w, and c for octanol, water, and chemical)

f = fragment constant (See §1-3 for meaning of superscripts. Subscripts are molecular fragments as identified in Table 1-5. Underline indicates fragment is present in a ring.)

F = structural factor (See §1-3 for meaning of subscripts and superscripts.)

G = free energy of solution (subscripts o and w for octanol and water)

HPLC/RT = high-pressure liquid chromatography/retention time

I_H = correction factor for hydrogen bonding in Eq. 1-38

K_{cw} = cyclohexane/water partition coefficient in Eq. 1-38

K_{oc} = soil or sediment adsorption coefficient based on organic carbon

K_{ow} = octanol/water partition coefficient

K_{sw} = solvent/water partition coefficient

n = number of bonds when used with F_b or number of halogens when used with F_{mhG} or F_{mhV} (See Table 1-6)

$n^{\{\}}$ = number of moles in Eqs. 1-41 and -43. (Superscripts o and w for octanol and water phases. Subscripts o, w and c for octanol, water and chemical.)

pK_a = negative log of acid dissociation constant for acid (Table 1-10)

pK_o = negative log of acid dissociation constant for a chemical having a hydrogen atom substituted for the acid function (Table 1-10)

ΔpK = pK_o—pK_a (Table 1-10)

r = correlation coefficient for regression equation

S = solubility in water

X = concentration, mole fraction (Superscripts o and w for octanol and water phases. Subscripts o, w and c for chemical.)

Greek

γ = activity coefficient (Superscripts o and w for octanol and water. Subscript c for chemical.)

γ^{∞} = activity coefficient at infinite dilution

π = "pi" substituent constant

σ_I = static (or sigma) inductive effect parameter

χ = molecular connectivity parameter

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2

SOLUBILITY IN WATER

Warren J. Lyman

2-1 INTRODUCTION

Of the various parameters that affect the fate and transport of organic chemicals in the environment, water solubility is one of the most important. Highly soluble chemicals are easily and quickly distributed by the hydrologic cycle. These chemicals tend to have relatively low adsorption coefficients for soils and sediments and relatively low bioconcentration factors in aquatic life; they also tend to be more readily biodegradable by microorganisms in soil, surface water, and sewage treatment plants. Other degradation pathways (e.g., photolysis, hydrolysis, and oxidation) and specialized transport pathways (e.g., volatilization from solution and washout from the atmosphere by rain) are also affected by the extent of water solubility.

Water solubility, as an environmental parameter, is much less important for gases than it is for liquids or solids. The solubility of gases is usually measured when the partial pressure of the gas above the solution is one atmosphere, an unlikely situation under most environmental conditions. A more important parameter for gases is Henry's law constant, which describes the ratio of atmospheric to solution concentrations at low partial pressures. (This constant is discussed in Chapters 3, 11, and 15.)

Definition. The solubility of a chemical in water may be defined as the maximum amount of the chemical that will dissolve in pure water at

a specified temperature. Above this concentration, two phases will exist if the organic chemical is a solid or a liquid at the system temperature: a saturated aqueous solution and a solid or liquid organic phase.

Units and Range of Values. Aqueous concentrations are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, μg/L, moles/L, etc.). Less common units are mole fraction and molal concentration (moles per kg of solvent). At low concentrations all units are proportional to one another. At high concentrations this is not the case, and it becomes important to distinguish if the solubility is per volume of pure water or per volume of solution.

No organic chemical is completely insoluble in water; all are soluble to some extent. At the low end, solubilities below 1 ppb have been measured (e.g., 0.26 ppb for benzo[g,h,i]perylene). The solubilities of most common organic chemicals are in the range of 1 to 100,000 ppm at ambient temperatures, but several are higher, and some compounds (e.g., ethyl alcohol) are infinitely soluble — i.e., miscible with water in all proportions. An overall range covering at least nine orders of magnitude is thus involved.

As will be noted later, the available estimation methods usually yield values that are, on average, uncertain by less than one order of magnitude, but errors of over two orders of magnitude occur in about 10% of the cases with some equations.

Estimation Methods Provided. Five basically different approaches to the estimation of water solubility (S) are given in this handbook (see Table 2-1), but only two are described in this chapter. A more detailed review of available estimation methods, including several not included in this handbook, is presented in §2-2.

It is difficult to recommend any one method as the "best." The method(s) of choice may be determined by, for example, the information available on the chemical, the desired accuracy, and the time available for the calculations. The following are some of the considerations involved:

- Methods 1, 2, 4, and 5 give an estimate of S only for ~25°C. Only method 3 allows the calculation of S at any temperature.
- Method 1 is probably the most generally applicable (i.e., to various chemical classes and structures) and should provide

TABLE 2-1

Overview of Solubility Estimation Methods Provided in this Handbook

Method No.	Where Described	Basis for Method	Information Required[a]	Comments
1	§ 2-4	Regression equations (several available)	K_{ow}, T_m[b]	K_{ow} easy to estimate from structure (see Chapter 1)
				Simple calculations
2	§ 2-5	Addition of atomic fragments (only for hydrocarbons and halocarbons)	Structure, T_m[b]	Limited applicability (chemicals with C, H, Cℓ, Br, I, F only)
3	Chapters 3 and 11	Theoretical equations using estimated activity coefficients	Structure, ΔH_f, T_m[b]	Allows calculation of S at any temperature
				Calculations may be difficult
				Somewhat limited applicability
				May be more accurate
4	Chapter 4	Regression equations	K_{oc}	Simple calculations
				Somewhat less accurate
5.	Chapter 5	Regression equations	BCF	Simple calculations
				Less accurate

a. K_{ow} = octanol/water partition coefficient; T_m = melting point; ΔH_f = heat of fusion; K_{oc} = soil or sediment adsorption coefficient based on organic carbon; BCF = bioconcentration factors for aquatic life.

b. T_m is required only if the chemical is a solid at the system temperature. It is not required at all for some of the regression equations in the first method listed, but some of the equations are applicable to liquids only. Thus, it is only necessary to know if the substance is a liquid or a solid.

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a reasonably accurate estimate of S if a value of K_{ow} (measured or estimated) is available.

- Even if measured values of K_{oc} and BCF are available (and no measured value of K_{ow} is available), methods 4 and 5 should not necessarily be considered better than method 1. Measured values of K_{oc} and BCF can have large uncertainties, while K_{ow} values can usually be estimated fairly accurately.
- Method 3, which proceeds via the calculation of activity coefficients, can be tedious. The general method is applicable to solubility in organic solvents as well as in water. Besides allowing the calculation of S at any temperature, it may, in some cases, provide a more accurate estimate.
- Only methods 2 and 3 make a clear distinction between liquids and solids and provide modified procedures for solids to account for their generally lower solubility. Some of the regression equations in method 1 cover both liquids and solids, while others are either limited to liquids or include a correction factor for solids.

If it is important to obtain the most accurate estimate of S, all applicable methods should be investigated in detail. S should be estimated by each method, and one value (or a range of values) should then be reported.

2-2 OVERVIEW OF AVAILABLE ESTIMATION METHODS

The aqueous solubility of organic chemicals can be estimated via numerous pathways. These are shown schematically in Figure 2-1 and described briefly in Table 2-2. To our knowledge, the relative merits, applicability, and accuracy of these pathways have not been reviewed elsewhere. Furthermore, many of the reported correlations and equations have been used primarily to test some theory or to show that two or more parameters were correlated in a certain way; few have actually been presented (and tested) as predictive tools.

The following characteristics of these pathways should be noted:

(1) Most of the pathways can start with only structural information for the chemical, but few can handle complex structures or uncommon functional groups.

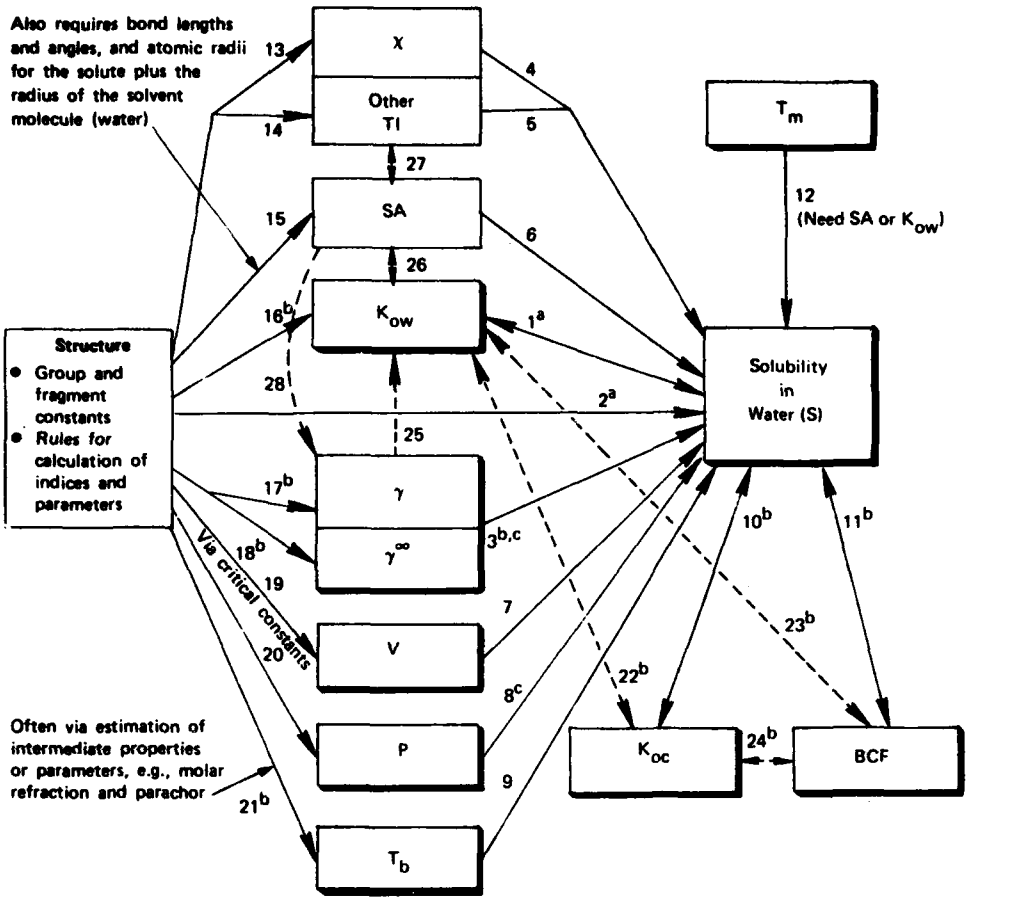


FIGURE 2–1 Pathways for Estimating the Aqueous Solubility of Organic Chemicals

TABLE 2-2

Pathways Leading to the Estimation of Aqueous Solubility for Organic Chemicals

Pathway	Reference	Gives[a]	t(°C)[b]	Chemical Classes Covered[c]	Comments
1	[7b,14]	R	25	Mixed	Liquids and solids
	[30]	R	V	Mixed	
	[13]	R	V	Mixed	
	[24]	R	V	(1) Alcohols, (2) ketones, (3) esters, (4) ethers, (5) alkyl halides, (6) alkynes, (7) alkenes, (8) aromatics, (9) alkanes, (10) all exc. alkanes, (11) all	Liquids only
	[58]	R	V	Alkyl and aryl phosphate esters	
	[71]	R	25	Rigid aromatic hydrocarbons	T_m also required
	[70]	R	25	Halobenzenes	T_m also required
2	[27]	G	25	Aliphatic (saturated and unsaturated) and aromatic hydrocarbons plus halogenated hydrocarbons	
	[35]	R	25	n-Alcohols	Correlation with N[d]
	[45]	P	25	n-Alkanes	Plot vs N
3	—	I	Any T	(Few restrictions)	Methods described in Chapter 3
4	[22,32]	R	V	(1) Alkanes, (2) alkyl substituted benzenes, (3) alcohols, (4) ethers, (5) esters, (6) combined classes	
5	[4]	R	V	(1) Acyclic saturated hydrocarbons, (2) acyclic and cyclic saturated hydrocarbons	Equations given for three topological indices
				(1) Hydrocarbons, (2) alcohols, (3) ethers, (4) ketones and aldehydes, (5) esters, (6) acids, (7) olefins. (All acyclic monofunctional compounds.)	Uses various "branching indices"
6	[6]	R	V	(1) Aliphatic alcohols, (2) aliphatic alcohols and hydrocarbons	
	[4]	R	V	(1) Hydrocarbons, (2) alcohols, (3) ethers, (4) ketones and aldehydes, (5) esters, (6) acids, (7) olefins	Functional group index also required
	[5]	R	V	Same classes as item above. Two or more equations given for each class using different SA parameters	Functional group index also required

(continued)

TABLE 2-2 (Continued)

Pathway	Reference	Gives[a]	t(°C)[b]	Chemical Classes Covered[c]	Comments
6 (cont.)	[26]	P	25	Hydrocarbons (acyclic, cyclic, aromatic)	
	[71]	R	25	Rigid aromatic hydrocarbons	T_m also required
	[70]	R	25	Halobenzenes	T_m also reouired
7	[46]	P	25	(1) Alkanes, (2) olefin hydrocarbons, (3) diolefin hydrocarbons, (4) acetylenes, (5) cycloparaffins, (6) aromatic hydrocarbons	
	[36]	R+I	25	C_4 to C_{10} hydrocarbons (all types)	Structure-related factors also used in equation
8	[47]	R	V	(1) Hydrocarbons and halogenated hydrocarbons, (2) alcohols, esters, ethers, ketones, phenols, (3) solids	ΔH_f and T_m also required for (3)
9	[1]	R	25	Aromatic hydrocarbons (including arenes, PAH, and some halogenated benzenes)	
10	[30]	R	V	Mixed classes	Equations given in Chapter 4 for estimation of K_{oc}
	[29]	R		Aromatics, mostly PAHs; two chlorinated	
11	[30]	R	V	Mixed classes	Equations given in Chapter 5 for estimation of BCF; other equations may also be listed there
	[13]	R	V	Mixed classes	
	[40]	R	27	Benzene derivatives	
	[49]	R	27	Organochlorine pesticides	
12	[70]	R	25	Halobenzenes	K_{ow} or SA also required
13	[21,32-34]	I	—	Organics which may have one or more of the following functional groups: $-NH_2$, $-NH-$, $-N<$, $=N-$ (pyridine), $C\equiv N$, $-OH$, $-O-$, $=O$, $-Cl$, $-Br$, $-I$, $-F$, pyridine N, furan O, nitro N, + few other special cases	

(continued)

TABLE 2-2 (Continued)

Pathway	Reference	Gives[a]	t(°C)[b]	Chemical Classes Covered[c]	Comments
14	—	I	—	Hydrocarbons	See Ref. 4 for overview of various methods
15	[4-6,26,70,71]	I	—	Hydrocarbons, alcohols, ethers, ketones, aldehydes, esters, acids, olefins, and few others	
16	[23,37,55]	G	—	Organics (very few restrictions)	Methods covered in Chapter 1
17	[17-19,50]	G+I	Any T	Organics with common functional groups (~25 possibilities); structure must not be too complex	Methods covered in Chapter 11
18	[17-19,50]	G+I	Any T	Same as for pathway 17	
	[52]	R	25, 60, or 100	(1) n-Acids, (2) n-primary alcohols, (3) n-sec-alcohols, (4) n-tert-alcohols, (5) alcohols, general, (6) n-allyl alcohols, (7) n-aldehydes, (8) n-alkene aldehydes, (9) n-ketones, (10) n-acetals, (11) n-ethers, (12) n-nitriles, (13) n-alkene nitriles, (14) n-esters, (15) n-formates, (16 n-monoalkylchlorides, (17) n-paraffins, (18) n-alkylbenzenes	Uses N. Methods covered in Chapter 11
	[62]	R	25	(1) Arenes with straight-chain aliphatic part, (2) polymethylbenzenes, (3) branched arenes, (4) polycyclic aromatic hydrocarbons (PAH). Side chains in (1) and (3) may contain C=C or C≡C bonds. Chemicals in (4) may contain F, Cl, Br, I, OH, COOH, NH_2 or NO_2	Methods covered in Chapter 11; uses N
	[42]	R	25	Polynuclear aromatic hydrocarbons (PAH)	In Chapter 2
19	—	G	—	Organics with fairly common functional groups	See Ref. 54. Estimate via critical constants

(continued)

TABLE 2-2 (Continued)

Pathway	Reference	Gives[a]	t(°C)[b]	Chemical Classes Covered[c]	Comments
20	[53]	G	—	Organics with fairly common functional groups	
21	—	—		—	Methods covered in Chapter 12
22	—	R	V	—	Methods to estimate K_{oc} covered in Chapter 4
23	—	R	V	—	Methods to estimate BCF covered in Chapter 5
24	—	R	V	—	
25	—	I	Any T	Same as for pathway 17	Basis for methods given in Refs. 7a, 17, 18, 19
26	[71]	R	25	Rigid aromatic hydrocarbons	
27	[4]	—	V	Acyclic and cyclic saturated hydrocarbons	Correlations between SA and certain topological indices suggested
28	[69]	I	25	n-Alkyl-p-aminobenzoates	Interfacial tension also required

a. R = regression equation(s); P = plot; G = group, fragment and/or structure-related constants; I = other types of instructions or equations.
b. Temperature at which solubility data in data set were measured. V = various temperatures, usually between 15°C and 30°C.
c. Where more than one *numbered* class is given, a separate regression equation is given for each numbered group.
d. N = number of carbon atoms in molecule.

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(2) Only one pathway (#2) allows S to be estimated *directly* from structural information; all others go through some intermediate property or parameter. Within pathway #2 only one method [27] has a degree of general applicability.

(3) Most of the pathways that proceed through an intermediate parameter do so with a parameter that is measurable, either directly or indirectly. This is considered to be an advantage, since a measured value of this intermediate property will simplify the estimation of S and usually improve its accuracy.

(4) Most of the pathways leading from structural information to the intermediate parameters do so via the use of group and fragment constants; the remainder (principally 13, 14 and 15) use rules for the calculation of topological indices (TI) and/or surface area (SA).

(5) Most of the pathways leading from some other parameter to S do so via a regression equation which describes the correlation between the two properties.

(6) Also, most of the pathways leading to S, whether through some intermediate parameter or not, either are limited to liquids explicitly or make no distinction between liquids and solids. Other factors (e.g., main structural characteristics) being equal, solids tend to have lower solubilities than do liquids; between solids with similar chemical formulas and melting points, the one with the larger heat of fusion has the lower solubility. Only pathways 3 and 8 (and some of the regression equations) allow the solubility of solids in water to be explicitly considered; both of these pathways require ΔH_f and T_m.

(7) Almost all of the fragment-constant pathways and all of the regression equations (except those in Ref. 52) apply to only one temperature. In some cases the data sets from which the constants or equations were derived were obtained at a single temperature (e.g., 25°C); others used data from several sources and thus represent a mix of temperatures (indicated by V in the table). Since S is a function of temperature, the latter approach reduces the accuracy of the method. Only one general pathway (#17 followed by #3) allows S to be estimated at essentially any temperature.

(8) Some of the pathways are bidirectional; i.e., they are simple regression equations relating two properties or pa-

rameters. In cases where the second parameter cannot be measured as accurately as S or is not commonly available (e.g., pathways 10 and 11), the regression equations are generally better suited for estimating the second parameter from S.

(9) Most of the regression equations between an intermediate property and S are for specific, simple chemical classes (alcohols, esters, alkanes, etc.). Only for pathway #1 are equations given for "mixed chemical classes," where the mix is sufficiently broad to cover almost any chemical. Such equations, understandably, involve larger method errors than those for specific chemical classes.

(10) Of all the pathways leading to an intermediate property, only #16 has been developed sufficiently to be applicable to almost any new chemical. A particular strength of this pathway is that the group/fragment constants can be applied to a measured value of K_{ow} for a structurally related compound,[1] thus significantly reducing the effort involved (and improving the accuracy) in obtaining an estimate of K_{ow} for the new chemical.

2-3 FACTORS INFLUENCING SOLUBILITY

Method of Measurement. Several methods are available for measuring the solubility of organic chemicals, but no single method is usable over the entire range of solubilities in water [16]. Because of special problems encountered in measuring S for very hydrophobic (i.e., low solubility) compounds [28], various methods may yield different values. In general, an excess of the chemical is added to *very pure* water and allowed to equilibrate at constant temperature. Equilibration may take several days for very hydrophobic compounds. The solution is then filtered and/or centrifuged to remove undissolved material before the solution concentration is measured.

Temperature. Solubility in water is a function of temperature, but the strength and direction (i.e., sign) of this function varies. Many, if not most, organic compounds become more soluble as the temperature increases, but some behave in the opposite way. The solubility of benzene, for example, increases with increasing temperature (at temperatures near ambient) [44], but the solubility of p-dichlorobenzene decreases [65]. For

1. Compilations of measured values [23,37] contain data for thousands of chemicals.

some chemicals S may either increase or decrease at higher temperatures, depending on the nature of the chemical and the temperature range involved (see Figure 3-1c in Chapter 3); an example is 2-butanone, whose solubility increases with increasing temperature above ~80°C but decreases with increasing temperature between ~ − 6°C and 80°C [59]. If it is necessary to estimate a solubility at some temperature other than ~25°C and the literature does not report the effect of temperature on structurally similar compounds, the combined methods of Chapters 3 and 11 must be used.

Salinity. The presence of dissolved salts or minerals in water leads to moderate decreases in S. For example, the solubilities of several polynuclear aromatics (e.g., naphthalene, biphenyl, anthracene, fluorene) in sea water, which contains about 35 g/L NaCl, are from 30% to 60% below their fresh water solubilities [10]. The general relationship between salinity and solubility can be expressed in the following form [15]:

$$\log (S^\circ/S') = K_s C_s \qquad (2\text{-}1)$$

where

S° = molar solubility in pure water

S' = molar solubility in salt solution

K_s = empirical salting parameter

C_s = molar salt concentration

Values of K_s for polynuclear aromatics range from ~ 0.04 to 0.4.

Dissolved Organic Matter. A number of studies have shown that the presence of dissolved organic material, such as the naturally occurring humic and fulvic acids in rivers and other surface waters, leads to an increase in the solubility of many organic chemicals. For example, in one study using the waters of Narragansett Bay and the Providence River, removal of the dissolved organic matter resulted in a 50-99% decrease in the amounts of n-alkanes and isoprenoid hydrocarbons that could be solubilized; the decrease was directly related to the amount of dissolved organic matter removed. The solubilities of aromatic hydrocarbons, however, were unaffected by the process [9]. Another study showed that 500 mg/L of humic material (extracted from soil) increased the solubility of DDT 20 to 40 times [67]. Other studies have shown increases in solubility for 2,2',5,5'-tetrachlorobiphenyl and cholesterol [25], and phthalate esters [43]. Surfactants can also increase the apparent solubility by forming micelles into which the solute partitions.

pH. Hydrogen ion concentration also affects the solubility of organic compounds. Organic acids may be expected to increase in solubility with increasing pH, while organic bases may act in the opposite way. Even the solubility of "neutral" organic chemicals (e.g., alkanes and chlorinated hydrocarbons) may be affected by pH. Significant increases in solubility above pH 8 have been reported for some chemicals [9,48].

2-4 ESTIMATION OF S FROM K_{ow}

Equations Available. Eighteen different regression equations were found that correlate water solubility (S) with the octanol/water partition coefficient (K_{ow}) for different groups of chemicals. Table 2-3 lists these equations (and Eq. 2-20) along with such information as the kind and number of chemicals represented in each data set and the quality of fit (r^2). Table 2-4 gives additional data for each equation, including the range of S and K_{ow} values involved and the temperatures at which the solubility data were obtained. Table 2-4 also refers to subsequent tables (Tables 2-5 to 2-13) which list the actual chemicals used to obtain each regression equation.

One of the listed equations (2-20), which is used for polynuclear aromatic hydrocarbons, does not require a value of K_{ow}; one need only know the number of carbon atoms (N) in the molecule and the melting point (t_m). In its original form [42], this equation was an expression for the infinite dilution activity coefficient (γ^∞), but since S is directly proportional to $1/\gamma^\infty$ at low solubilities (see Chapter 3), the equation has been rewritten here in terms of S in units of mole fraction.[2]

All of these equations provide an estimate of S at ~25°C. Some of the correlations are based on solubility data from a range of temperatures (e.g., 15-30°C) while others use only data measured at 25°C. Clearly, the latter would be expected to provide more accurate estimates.

Note also that Eqs. 2-5 to 2-15 were obtained from data on liquid organics only. Use of these equations for solid solutes will (on average) result in overestimation of the solubility.[3] Most of the other equations include data for both liquid and solid solutes. Equations 2-17, -18 and -20 use a correction factor for solids that requires a knowledge of the melting point; the other equations do not attempt to include any correction factor and may be used for either liquid or solid solutes.

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2. Mole fraction = number of moles of solute divided by total number of moles (solute plus solvent) present.

3. Correction factors for solids, which require a knowledge of the melting point, are given later in this chapter for use with Eqs. 2-14 and 2-15.

TABLE 2-3

Regression Equations for the Estimation of S

Eq. No.	Equation[a]	Units of S	No.[b]	r^2 [c]	Chemical Classes Represented	Ref.
2-2[i]	$\log S = -1.37 \log K_{ow} + 7.26$	μ mol/L	41	0.903	Mixed classes; aromatics and chlorinated hydrocarbons well represented	[14]
2-3	$\log S = -0.922 \log K_{ow} + 4.184$	mg/L	90	0.740	Mixed classes; pesticides well represented	[30]
2-4	$\log S = -1.49 \log K_{ow} + 7.46$	μ mol/L	34	0.970	Mixed classes; several pesticides	[13]
2-5	$\log 1/S = 1.113 \log K_{ow} - 0.926$	mol/L[d]	41	0.935	Alcohols[e]	[24]
2-6	$\log 1/S = 1.229 \log K_{ow} - 0.720$	mol/L[d]	13	0.960	Ketones[e]	[24]
2-7	$\log 1/S = 1.013 \log K_{ow} - 0.520$	mol/L[d]	18	0.980	Esters[e]	[24]
2-8	$\log 1/S = 1.182 \log K_{ow} - 0.935$	mol/L[d]	12	0.880	Ethers[e]	[24]
2-9	$\log 1/S = 1.221 \log K_{ow} - 0.832$	mol/L[d]	20	0.861	Alkyl halides[e]	[24]
2-10	$\log 1/S = 1.294 \log K_{ow} - 1.043$	mol/L[d]	7	0.908	Alkynes[e]	[24]
2-11	$\log 1/S = 1.294 \log K_{ow} - 0.248$	mol/L[d]	12	0.970	Alkenes[e]	[24]
2-12	$\log 1/S = 0.996 \log K_{ow} - 0.339$	mol/L[d]	16	0.951	Aromatics[e] (benzene and benzene derivatives)	[24]
2-13	$\log 1/S = 1.237 \log K_{ow} + 0.248$	mol/L[d]	16	0.908	Alkanes[e]	[24]
2-14	$\log 1/S = 1.214 \log K_{ow} - 0.850$	mol/L[d]	140	0.912	All chemicals represented by Eqs. 2-5 to -12 plus propionitrile[e]	[24]

(continued)

TABLE 2-3 (Continued)

Eq. No.	Equation[a]	Units of S	No.[b]	r^2[c]	Chemical Classes Represented	Ref.
2-15	$\log 1/S = 1.339 \log K_{ow} - 0.978$	mol/L[d]	156	0.874	All chemicals represented by Eqs. 2-5 to -13 plus propionitrile[e]	[24]
2-16	$\log S = -2.38 \log K_{ow} + 12.90$	μ mol/L	11	0.656	Phosphate esters	[56]
2-17[f]	$\log S = -0.9874 \log K_{ow} - 0.0095\ t_m + 0.7178$	mol/L	35	0.990	Halobenzenes	[70]
2-18[f]	$\log S = -0.88 \log K_{ow} - 0.01\ t_m - 0.012$	mol/L	32	0.979	Rigid aromatic hydrocarbons (polynuclear aromatics)	[71]
2-19	$\log S = -0.962 \log K_{ow} + 6.50$	μ mol/L	9	0.878	Halogenated 1- and 2-carbon hydrocarbons (8 with Cl, 1 with Br)	[12]
2-20[g]	$\log S = -0.00987\ (t_m - 25) - 3.5055 - 0.3417\ (N-6) + 0.002640\ (N-6)^2$	mole fraction	21	[h]	Polynuclear aromatic hydrocarbons (See note g for alkyl-substituted naphthalenes and anthracenes.)	[42]

a. S = aqueous solubility; K_{ow} = octanol/water partition coefficient; t_m = melting point (°C), $t_m \geq 25$°C; N = number of carbon atoms in molecule.

b. No. = number of compounds in data set used to obtain equation.

c. r^2 = square of correlation coefficient.

d. Actually, moles/1000 g of water (i.e., molar solubility). For most chemicals this is very close to the molar solubility (moles/liter of solution), and no correction need be applied.

e. All chemicals used were liquids. Values of K_{ow} for many of these chemicals were estimated.

f. If t_m is less than 25°C, a value of 25°C should be used for t_m in Eqs. 2-17 and 2-18.

g. If t_m is less than 25°C, the first term on the right side of Eq. 2-20 should be set equal to zero. For alkyl-substituted naphthalenes and anthracenes, multiply the last three terms on the right side of Eq. 2-20 by a factor of 2 before solving for S. This equation is a combination of three equations given in Ref. 42.

h. Not available.

i. [Note added in final proof.] The published version of this equation [7b] differs from the version given here, which was taken from the draft [14]. The revised equation, based on a 27-compound subset of the 41 compounds used for Eq. 2-2, is [7b]: $\log S = -1.12 \log K_{ow} + 7.30 - 0.015\ t_m$. For this equation $r^2 = 0.922$; the melting point of the compound, t_m (°C), is set equal to 25°C if the compound is a liquid at 25°C.

TABLE 2-4

Additional Information on Equations for Estimating S

Eq. No.	Range of S Values[a]	Range of K_{ow} Values	t(°C)[b]	Chemicals Used for Regression Listed in Table
2-2	$5 \times 10^{-2} - 2 \times 10^{6}$	$8 - 2 \times 10^{6}$	25	2-5
2-3	$5 \times 10^{-4} - 2 \times 10^{6}$	$1 \times 10^{-3} - 4 \times 10^{6}$	Var.	2-6
2-4	$1 \times 10^{-3} - 1.7 \times 10^{4}$	$19 - 5 \times 10^{6}$	Var.	2-7
2-5	$5 \times 10^{-3} - 1$	$4 - 7 \times 10^{2}$	Var.	2-8
2-6	$3 \times 10^{-3} - 5$	$2 - 6 \times 10^{2}$	Var.	2-8
2-7	$8 \times 10^{-5} - 1$	$2 - 5 \times 10^{4}$	Var.	2-8
2-8	$5 \times 10^{-2} - 1$	$7 - 1 \times 10^{2}$	Var.	2-8
2-9	$1 \times 10^{-3} - 0.1$	$25 - 1 \times 10^{3}$	Var.	2-8
2-10	$6 \times 10^{-5} - 3 \times 10^{-2}$	$1 \times 10^{2} - 1 \times 10^{4}$	Var.	2-8
2-11	$2 \times 10^{-5} - 1 \times 10^{-2}$	$56 - 5 \times 10^{3}$	Var.	2-8
2-12	$4 \times 10^{-4} - 0.4$	$8 - 5 \times 10^{3}$	Var.	2-8
2-13	$6 \times 10^{-6} - 7 \times 10^{-4}$	$1 \times 10^{2} - 1 \times 10^{4}$	Var.	2-8
2-14	$2 \times 10^{-5} - 5$	$2 - 5 \times 10^{4}$	Var.	2-8
2-15	$6 \times 10^{-6} - 5$	$2 - 5 \times 10^{4}$	Var.	2-8
2-16	$(0.36 - 1 \times 10^{3})$[c]	$1 \times 10^{4} - 5 \times 10^{5}$	d	2-9
2-17	$2 \times 10^{-8} - 2 \times 10^{-2}$	$1 \times 10^{2} - 3 \times 10^{6}$	25	2-10
2-18	$9 \times 10^{-10} - 9 \times 10^{-4}$	$2 \times 10^{3} - 1.3 \times 10^{7}$	25	2-11
2-19	$1 \times 10^{3} - 1 \times 10^{5}$	25 – 2400	20	2-12
2-20	$9 \times 10^{-12} - 1.7 \times 10^{-5}$	(Not pertinent)	25	2-13

a. Units of S are as shown in Table 2-3, except for Eq. 2-16.

b. Temperature at which solubility of chemicals in data set was measured. "Var." indicates that various temperatures are represented by the solubility data, usually in the 15-30°C range.

c. Units are mg/L.

d. Exact value not specified, but is presumably ~ 20°C.

TABLE 2-5

Compounds Used for Regression Equation 2-2

Acenaphthene	*n*-Decane	Nitrobenzene
Acrolein	Dibenzofuran	N-Nitroso-diphenylamine
Acrylonitrile	*o*-Dichlorobenzene	Pentachlorobenzene
Benzene	*m*-Dichlorobenzene	Pentachloroethane
Biphenyl	*p*-Dichlorobenzene	α-Pinene
Butylbenzylphthalate	3,3'-Dichlorobenzidine	Styrene
n-Butylether	1,2-Dichloroethane	1,2,3,5-Tetrachlorobenzene
Camphene	Diethylphthalate	1,1,2,2-Tetrachloroethane
Carbon tetrachloride	2,4-Dimethylphenol	Tetrachloroethylene
Chloroethane	Dimethylphthalate	Toluene
2-Chloroethylether	Diphenylether	1,1,1-Trichloroethane
Chloroform	Docosane	Trichloroethylene
o-Chlorophenol	Hexachloroethane	Vinylidene chloride
p-Cymene	Isophorone	

Source: Dec *et al.* [14]

TABLE 2-6

Compounds Used for Regression Equation 2-3

Halogenated Hydrocarbon Insecticides

DDD
DDE
DDT
Endrin
Methoxychlor

Substituted Benzenes and Halobenzenes

Bromobenzene
Chlorobenzene
p-Dichlorobenzene
Hexachlorobenzene
Pentachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,4-Trichlorobenzene
Aniline
Diethylaniline
Nitrobenzene
Phthalic anhydride
Captan

Halogenated Biphenyls and Diphenyl Oxides

4-Chlorobiphenyl
4,4'-Dichlorobiphenyl
2,4,4'- and 2,2',5-Trichlorobiphenyl
2,2',4,4'- and 2,2',5,5'-Tetrachlorobiphenyl
2,2',4,5,5'-Pentachlorobiphenyl
2,2',4,4',5,5'-Hexachlorobiphenyl
Diphenyloxide
4-Chlorodiphenyloxide
x-sec-Butyl-4-chlorodiphenyloxide
x-hexyl-x'-Chlorodiphenyloxide
x-dodeca-x'-Chlorodiphenyloxide

Aromatic Hydrocarbons

Anthracene
Benzene
Biphenyl
9-Methylanthracene
2-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene
Tetracene

Fumigants

Carbon tetrachloride
Tetrachloroethylene

Phosphorus-containing Insecticides

Malathion
Trichlorfon
Dimethoate
Dichlorvos
Crufomate
Chlorpyrifos
Chlorpyrifos-methyl
Leptophos
Methyl parathion
Parathion
Ronnel
Fenitrothion
Phosmet
Phosalone
Dichlofenthion
Dialifor

Carbamates, Thiocarbamates and Carbamoyl Oximes

Carbaryl
Carbofuran
Propoxur
Mexacarbate
Methomyl

Carboxylic Acids and Esters

6-Chloropicolinic acid
2,4-D acid
Dalapon
Picloram
2,4,5-T
Triclopyr (triethylamine salt)
Triclopyr (butoxyethyl ester)
Trichlopyr
Di-2-ethylhexylphthalate

(continued)

TABLE 2-6 (Continued)

Dinitroanilines	Ipazine
Trifluralin	Propazine
Ureas and Uracils	Simazine
Diuron	Trietazine
Fenuron	**Miscellaneous Nitrogen Heterocyclics**
Fluometuron	2-Methoxy-3,5,6-trichloropyridine
Linuron	Nitrapyrin
Monolinuron	3,5,6-Trichloro-2-pyridinol
Monuron	**Miscellaneous**
Urea	Dinoseb
Symmetrical Triazines	Alachlor
Atrazine	Propachlor
Cyanazine	Bentazon

Source: Kenaga and Goring [30]

TABLE 2-7

Compounds Used for Regression Equation 2-4

Benzene	*p,p'*-DDT	Phosmet
Toluene	*p,p'*-DDE	Malathion
Fluorobenzene	Benzoic acid	Fenitrothion
Chlorobenzene	Salicylic acid	Dicapthon
Bromobenzene	Phenylacetic acid	Parathion
Iodobenzene	Phenoxyacetic acid	Phosalone
p-Dichlorobenzene	2,4-D	Methyl chlorpyrifos
Naphthalene	2,4,5,2',5'-PCB	Dialifor
Diphenylether	2,4,5,2',4',5'-PCB	Ronnel
Tetrachloroethylene	4,4'-PCB	Chlorpyrifos
Chloroform		Dichlofenthion
Carbon tetrachloride		Leptophos

Source: Chiou *et al.* [13]

TABLE 2-8

Compounds Used for Regression Equations 2-5 to 2-15[a]

Alcohols (Eq. 2-5)

Butanol
2-Methyl-1-propanol
2-Butanol
Pentanol
3-Methyl-1-butanol
Methylbutanol
2-Pentanol
3-Pentanol
3-Methyl-2-butanol
2-Methyl-2-butanol
2,2-Dimethylpropanol
Hexanol
2-Hexanol
3-Hexanol
3-Methyl-3-pentanol
2-Methyl-2-pentanol
2-Methyl-3-pentanol
3-Methyl-2-pentanol
4-Methyl-2-pentanol
2,3-Dimethyl-2-butanol
3,3-Dimethyl-1-butanol
3,3-Dimethyl-2-butanol
Heptanol
2-Methyl-2-hexanol
3-Methyl-3-hexanol
3-Ethyl-3-pentanol
2,3-Dimethyl-2-pentanol
2,3-Dimethyl-3-pentanol
2,4-Dimethyl-2-pentanol
2,4-Dimethyl-3-pentanol
2,2-Dimethyl-3-pentanol
Octanol
2,2,3-Trimethyl-3-pentanol
Cyclohexanol
4-Penten-1-ol
3-Penten-2-ol
1-Penten-3-ol
1-Hexen-3-ol
2-Hexen-4-ol
2-Methyl-4-penten-3-ol
Benzyl alcohol

Ketones (Eq. 2-6)

2-Butanone
2-Pentanone
3-Pentanone
3-Methyl-2-butanone
2-Hexanone
3-Hexanone
3-Methyl-2-pentanone
4-Methyl-2-pentanone
4-Methyl-3-pentanone
2-Heptanone
4-Heptanone
2,4-Dimethyl-3-pentanone
5-Nonanone

Esters (Eq. 2-7)

Ethyl formate
Propyl formate
Methyl acetate
Ethyl acetate
Propyl acetate
Isopropyl acetate
Butyl acetate
Isobutyl acetate
Methyl propionate
Methyl butyrate
Ethyl butyrate
Propyl butyrate
Ethyl valerate
Ethyl hexanoate
Ethyl heptanoate
Ethyl octanoate
Ethyl nonanoate
Ethyl decanoate

Ethers (Eq. 2-8)

Diethyl ether
Methyl butyl ether
Methyl isobutyl ether
Methyl sec-butyl ether
Methyl t-butyl ether
Ethyl propyl ether
Ethyl isopropyl ether
Dipropyl ether
Propyl isopropyl ether
Methyl propyl ether
Methyl isopropyl ether
Cyclopropyl ethyl ether

Alkyl Halides (Eq. 2-9)

Chloroethane
Chloropropane
2-Chloropropane
Chlorobutane
Isobutyl chloride
1,3-Dichloropropane
Chloroform
Bromoethane
Bromopropane
2-Bromopropane
Bromobutane
Isobutyl bromide
Isoamyl bromide
1,3-Dibromopropane
Iodomethane
Iodoethane
Iodopropane
Iodobutane
Diiodomethane
$(ClCH_2CH_2)_2S$

Alkynes (Eq. 2-10)

1-Pentyne
1-Hexyne
1-Heptyne
1-Octyne
1-Nonyne
1,8-Nonadiyne
1,6-Heptadiyne

Alkenes (Eq. 2-11)

1-Pentene
2-Pentene
1-Hexene
2-Heptene
1-Octene
4-Methyl-1-pentene
1,6-Heptadiene
1,5-Hexadiene
1,4-Pentadiene
Cyclopentene
Cyclohexene
Cycloheptene

(continued)

TABLE 2-8 (Continued)

Aromatics (Eq. 2-12)		
Benzene	*m*-Nitrotoluene	Hexane
Toluene	*o*-Dichlorobenzene	Heptane
Ethylbenzene	*m*-Dichlorobenzene	2,4-Dimethylpentane
Propylbenzene	Ethyl benzoate	2,2-Dimethylpentane
Fluorobenzene	Aniline	Octane
Chlorobenzene		Cyclopentane
Bromobenzene	**Alkanes (Eq. 2-13)**	Cyclohexane
Nitrobenzene	Pentane	Methylcyclopentane
1,2,4-Trimethylbenzene	Isopentane	Cycloheptane
o-Xylene	2-Methylpentane	Methylcyclohexane
Isopropylbenzene	3-Methylpentane	Cyclooctane
		1,2-Dimethylcyclohexane

a. Data set for Eq. 2-15 includes all compounds listed plus propionitrile. Data set for Eq. 2-14 does not include alkane group but is otherwise the same.

Source: Hansch *et al.* [24]

TABLE 2-9

Compounds Used for Regression Equation 2-16

tert-Butylphenyl diphenyl phosphate
Cresyl diphenyl phosphate
Dibutyl phenyl phosphate
2-Ethylhexyl diphenyl phosphate
Isodecyl diphenyl phosphate
Isopropylphenyl diphenyl phosphate
Tributyl phosphate
Tricresyl phosphate
Triphenyl phosphate
Tris(2-ethylhexyl) phosphate
Trixylenyl phosphate

Source: Saeger *et al.* [56]

TABLE 2-10

Compounds Used for Regression Equation 2-17

Hexachlorobenzene	1,2-Difluorobenzene
Pentachlorobenzene	1,3-Difluorobenzene
1,2,3,4-Tetrachlorobenzene	1,4-Difluorobenzene
1,2,3,5-Tetrachlorobenzene	1,2-Diiodobenzene
1,2,4,5-Tetrachlorobenzene	1,3-Diiodobenzene
1,2,4,5-Tetrabromobenzene	1,4-Diiodobenzene
1,2,4-Tribromobenzene	Bromobenzene
1,3,5-Tribromobenzene	Chlorobenzene
1,2,3-Trichlorobenzene	Fluorobenzene
1,2,4-Trichlorobenzene	Iodobenzene
1,3,5-Trichlorobenzene	Benzene
1,2-Dibromobenzene	2-Bromochlorobenzene
1,3-Dibromobenzene	3-Bromochlorobenzene
1,4-Dibromobenzene	4-Bromochlorobenzene
1,2-Dichlorobenzene	4-Bromoiodobenzene
1,3-Dichlorobenzene	2-Chloroiodobenzene
1,4-Dichlorobenzene	3-Chloroiodobenzene
	4-Chloroiodobenzene

Source: Yalkowsky *et al.* [70]

TABLE 2-11

Compounds Used for Regression Equation 2-18

Indan	2-Methylanthracene
Naphthalene	9-Methylanthracene
1-Methylnaphthalene	9,10-Dimethylanthracene
2-Methylnaphthalene	Pyrene
1,3-Dimethylnaphthalene	Fluoranthene
1,4-Dimethylnaphthalene	1,2-Benzofluorene
1,5-Dimethylnaphthalene	2,3-Benzofluorene
2,3-Dimethylnaphthalene	Chrysene
2,6-Dimethylnaphthalene	Triphenylene
1-Ethylnaphthalene	Naphthacene
1,4,5-Trimethylnaphthalene	1,2-Benzanthracene
Biphenyl	7,12-Dimethyl-1,2-benzanthracene
Acenaphthene	Perylene
Fluorene	3,4-Benzopyrene
Phenanthrene	3-Methylcholanthrene
Anthracene	Benzo [g,h,i] perylene

Source: Yalkowsky and Valvani [71]

TABLE 2-12

Compounds Used for Regression Equation 2-19

1,2-Dibromoethane	Trichloroethylene
1,2-Dichloroethane	1,1,1-Trichloroethane
1,2-Dichloropropane	Chloroform
Tetrachloroethylene	Carbon tetrachloride
1,1,2,2-Tetrachloroethane	

Source: Chiou and Freed [12]

TABLE 2-13

Compounds Used for Regression Equation 2-20

Indan	Chrysene
Naphthalene	Triphenylene
Biphenyl	Naphthacene
Acenaphthene	1,2-Benzanthracene
Fluorene	7,12-Dimethyl-1,2-benzanthracene
Phenanthrene	Perylene
Anthracene	3,4-Benzopyrene
Pyrene	3-Methylcholanthrene
Fluoranthene	Benzo[g,h,i] perylene
1,2-Benzofluorene	Coronene
2,3-Benzofluorene	

Source: Mackay and Shiu [42]

The principal input information required for these equations is K_{ow}, the octanol/water partition coefficient, measured at or near room temperature. Compilations of measured (and some estimated) values of K_{ow} are available for thousands of chemicals [23,37]. If the K_{ow} for a particular compound cannot be found, however, it can usually be estimated fairly accurately by the methods described in Chapter 1.

General instructions for selecting the most appropriate equation(s) and for calculating S are given below after an explanation of the basis for the method and a discussion of method errors.

Basis for Estimation Method. The basis for the correlation between S and K_{ow} has been briefly discussed by Mackay [41] and Chiou and Freed [11]. The correlation between log K_{ow} and log S for hydrophobic pollutants is shown actually to be a correlation between

$$(\log \gamma_{w/oct} - \log \gamma_{oct/w} - 0.94) \qquad \text{[log K term]}$$

and

$$(-\log \gamma_w + \log (f_S/f_R) + 7.74) \qquad \text{[log S term]}$$

where

γ_w = activity coefficient of solute in pure water

$\gamma_{w/oct}$ = activity coefficient of solute in octanol-saturated aqueous phase

$\gamma_{oct/w}$ = activity coefficient of solute in water-saturated octanol phase

f_S/f_R = ratio of solid fugacity to reference fugacity (ratio = 1 for liquids)

If one assumes that $\gamma_{w/oct} \approx \gamma_w$ and that γ_w dominates the two terms, then the correlation between log K and log S is a correlation of one quantity (log γ_w) against its reciprocal (−log γ_w). With these assumptions, a slope of −1 is predicted for the regression equations of the form log S = a log K_{ow}+b. (The predicted slope is +1 for equations of the form log(1/S) = a log K_{ow}+b.) Note that except for Eq. 2-16, most of the equations in Table 2-3 do have slopes (i.e., coefficients of log K_{ow}) close to the predicted value. Chiou and Freed [11] suggest that a slope close to 1 is more likely for a highly soluble liquid solute, since it is expected that $\gamma_{w/oct}/\gamma_w \approx 1$, log $\gamma_{oct/w} \approx$ constant, and $f_S/f_R = 1$.

Dec *et al.* [14] have also pointed out that a plot of log S vs. log K_{ow} will have a slope of −1 only if log (K_{ow}S) is a constant. Using the data set from which Eq. 2-2 was obtained, they divided it into five subgroups having similar values of log (K_{ow}S). While the equation for the complete data set had a slope of −1.37, the slopes of the equations for the five subgroups were −0.96, −1.02, −1.02, −0.90, and −1.05. The chemicals in these subgroups were frequently structurally dissimilar from one another.

The basis for the correction term for solids (the term involving t_m) in some equations has been explained by Irmann [27] and Yalkowsky and Valvani [71].[4] To account for crystal lattice interactions in solids, the term $-\Delta H_f(T_m - T)/2.30\ RT_mT$ may be added to the right-hand side of equations for log S. (ΔH_f is the heat of fusion, T_m the melting point in K, T the system temperature (K), and R the gas constant.) Since $\Delta H_f = T_m\Delta S_f$ at the melting point (ΔS_f being the entropy change associated with fusion), the previous term becomes $-\Delta S_f\ (T_m - T)/2.30RT$. At room temperature (25°C), this becomes $-\Delta S_f\ (t_m - 25)/1360$, where t_m is the melting point in °C and ΔS_f is in cal/mol-°C. If an average value of 13 cal/mol-°C is assumed ΔS_f, the correction factor is $-0.0095\ (t_m - 25)$.

Method Errors. The true method error for a linear correlation between log S and log K_{ow} is difficult to determine, since most of the data sets that have been used to date incorporate some erroneous values of S and K_{ow}, and many are also based on values of S measured over a range of temperatures. Estimated values of K_{ow} have been used, in part, in some

4. See also §3-5 of Chapter 3 and the references cited therein for additional discussion.

of the data sets. Even under such conditions, values of r^2 (square of the correlation coefficient) are usually above 0.9; one data set covering mixed classes of chemicals (Eq. 2-4) reaches 0.97. On the other hand, a relatively low value of 0.656 for r^2 has been reported for one data set (Eq. 2-16) that is limited to a single class of chemicals (phosphate esters) whose solubilities were all measured at the same temperature. The values of r^2 associated with the equations of Hansch *et al.* [24] (Eqs. 2-5 to -15) also indicate that one should not necessarily expect lower method errors with regression equations derived for a single class of chemicals.

The likely method errors can be visualized from Figure 2-2, which is a plot of the data set and regression equation given by Dec *et al.* [14]. Most data points are well represented by the equation. The data for two chemicals, 1,3,5-triazo-1,3,5-trinitrocyclohexane (RDX) and hexachloro-1,3-butadiene, were not included in the regression analysis; if the K_{ow} values for these chemicals were used to estimate their solubility, the results would be about three orders of magnitude too high. The authors concluded, "While the correlation obviously applies to the majority of the compounds studied, it is *not* universal, and caution is required for the interpretation of results obtained from it." This statement should also be considered applicable to other equations of this kind.

A more quantitative analysis of method errors is provided by Tables 2-14 and -15. The former compares measured values of S for 78 chemicals with estimated values obtained from five selected regression equations. The method errors are summarized by chemical class for each of the five equations in Table 2-15. All of the selected equations were derived from data on mixed chemical classes. The equations were used to estimate a value of S for every chemical, even if it would not appear appropriate to do so normally; for example, some were used outside the range of K_{ow} and S values in their original data sets, and Eqs. 2-14 and 2-15 were used for solids even though the original data sets were limited to liquids. In addition, several of the K_{ow} values used were estimates, although this was limited primarily to simple, monosubstituted compounds for which fairly accurate K_{ow} estimates could be obtained. Although the indicated errors therefore include propagated error in some cases, method errors are presumed to predominate. Note that an estimate is within a factor of 10 of the measured value if the error is between −90% and + 900%.

The following general conclusions may be drawn from Tables 2-14 and -15:

- Most equations estimated two thirds of the chemicals within a factor of 10. Equation 2-3 was less accurate.

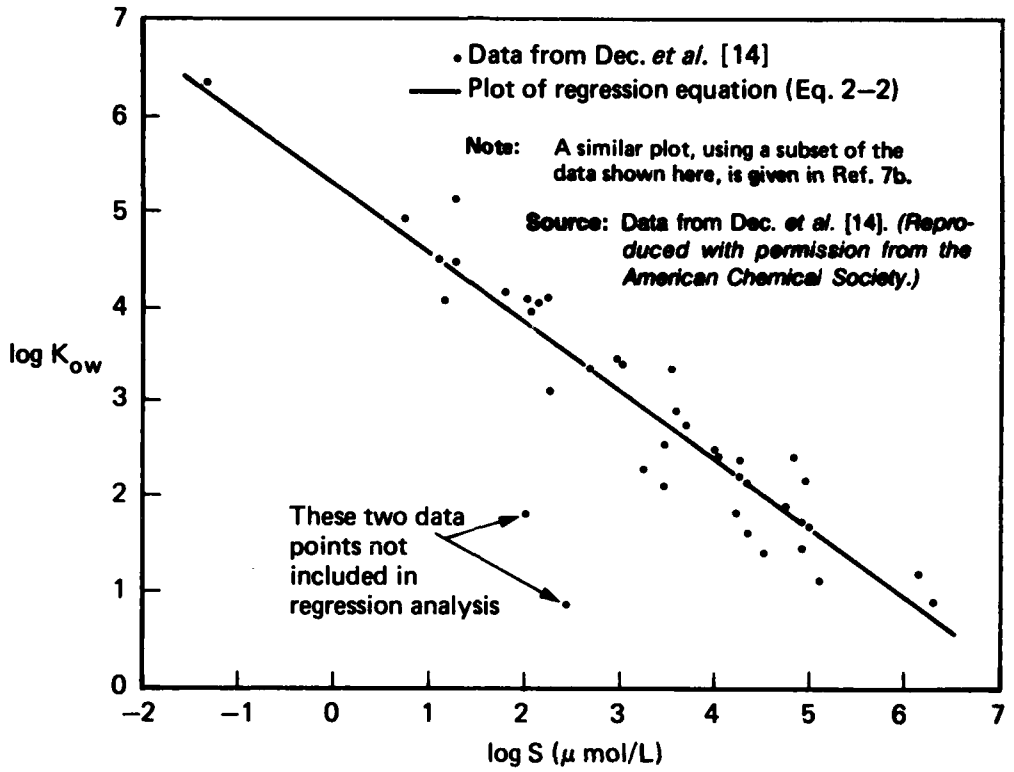


FIGURE 2–2 CORRELATION BETWEEN SOLUBILITY AND OCTANOL/WATER PARTITION COEFFICIENT

- Between 5% and 14% of the estimates were in error by more than a factor of 100. Equation 2-3 was better in this regard. Many of these large errors occurred with the nitrogen-containing compounds, and almost all were overestimates.
- Equations 2-14 and -15 were relatively quite accurate when limited to liquids; approximately 77% of the estimates were within a factor of 10 and 93% within a factor of 100.
- All of the equations showed a significant bias (i.e., tendency to continually overestimate or underestimate S) for selected classes of chemicals. For example, four of the five equations showed strong positive bias in their estimates for nitrogen-containing compounds. The same equations had smaller positive bias when estimating S for miscellaneous pesticides and aliphatic hydrocarbons. Equation 2-3 showed a significant negative bias for halogenated hydrocarbons, oxygen-containing hydrocarbons, and phosphate esters.

TABLE 2-14

Comparison of Measured and Estimated Values of S for Selected Chemicals

Chemical	t_m (°C)[a]	log K_{ow}[b]	Measured S (mg/L)[c]	Percentage Error in Estimated S Using: Eq. 2-2	Eq. 2-3	Eq. 2-4	Eq. 2-14	Eq. 2-15
Aliphatic Hydrocarbons								
2-Butene	—	1.85	78.5	−96	+280	+3500	+2800	+2200
1-Pentene	—	2.20	202	+510	−29	+450	+430	+270
1-Heptene	—	3.20	560	−87	−97	−91	−84	−91
Neopentane	—	3.11	53.5	+35	−60	−10	+60	−12
Cyclohexane	—	2.46	55.6	+1100	+48	+370	+1000	+630
2,2,4-Trimethylpentane	—	5.02	8.46	−97	−96	−98	−92	−98
n-Octane	—	4.00	0.657	+950	+380	+450	+1600	+630
Cyclooctane	—	3.28	7.94	+720	+82	−96	+940	+440
Methyl cyclopentane	—	2.35	42.7	+2100	+140	+1700	+1900	+1300
Isopentane	—	2.30	47.7	+1800	+140	+1500	+1600	+1100
Aromatic Hydrocarbons								
1,2,4-Trimethylbenzene	—	3.65	57.6	−62	−89	−78	−45	−74
Isopropylbenzene	—	3.43	50.1	−13	−79	−46	+16	−42
Indan	—	3.57	109	−75	−93	−85	−64	−83
1-Ethylnaphthalene	—	4.39	10.7	−74	−87	−88	−52	−82
Fluorene	115.8	4.47	1.98	+15	−42	−47	+120	−17
2,3-Benzofluorene	208.8	5.75	0.0020	+2500	+3700	+740	+7800	+1900
3,4-Benzopyrene	175	6.50	0.0038	+50	+310	−60	+500	+25
Benzo[g,h,i] perylene	276.8	7.10	0.00026	+260	+1600	−19	+1700	+210
Halogenated Hydrocarbons								
Vinylidene chloride	—	2.12	273	+700	−38	+610	+570	+390
Trichloroethylene	—	2.42	1,470	−21	−94	−36	−27	−51
Hexachloroethane	—	3.93	27.2	−35	−87	−65	+4	−55
1,3-Dibromopropane	—	2.70	1,680	−56	−97	−67	−55	−72

(continued)

TABLE 2-14 (Continued)

Chemical	t_m (°C)[a]	log K_{ow}[b]	Measured S (mg/L)[c]	Percentage Error in Estimated S Using: Eq. 2-2	Eq. 2-3	Eq. 2-4	Eq. 2-14	Eq. 2-15
Halogenated Hydrocarbons (cont.)								
Diiodomethane	—	2.50	1,220	+50	−94	+19	+43	−7
Fluorobenzene	—	2.27	1,540	−12	−92	−25	−22	−46
1,4-Diiodobenzene	129.4	4.64	1.85	+42	−56	−37	+190	+4
3-Chloroiodobenzene	—	4.12	67.2	−85	−96	−93	−75	−89
1,2,4-Tribromobenzene	44	4.98	9.95	−91	−96	−97	−80	−94
Pentachlorobenzene	86	5.79	0.561	−90	−88	−97	−70	−92
4,4'-Dichlorobiphenyl	148	5.58	0.062	+48	+76	−50	+330	+15
Oxygen-containing Hydrocarbons								
2-Methyl-1-propanol	—	0.61	75,800	+160	−94	+250	+26	+42
3-Hexanol	—	1.61	16,400	−29	−97	−28	−51	−58
2,4-Dimethyl-3-pentanol	< 70	1.71	7,050	+36	−94	+35	−2	−20
4-Nonanol	—	3.57	317	−89	−98	−94	−85	−93
2-Ethyl-1-hexanol	—	3.03	880	−81	−97	−87	−78	−88
3-Pentanone	—	0.79	50,500	+160	−94	+230	+33	+42
3-Methyl-2-pentanone	—	1.09	21,300	+170	−93	+220	+58	+55
Cyclopropylethyl ether	—	1.24	20,000	+58	−94	+78	−4	−10
Propylisopropyl ether	—	1.83	4,720	+23	−93	+17	−8	−27
n-Butyl ether	—	2.27	219	+740	−44	+610	+640	+420
Diphenyl ether	28	4.08	18.0	−56	−85	−77	−26	−69
Ethyl formate	—	0.23	88,200	+640	−89	+100	+210	+640
Butyl acetate	—	1.73	23,600	−62	−98	−62	−72	−77
Benzoic acid	122	1.87	2,700	+130	−89	+110	+72	+35
Phenylacetic acid	76.7	1.41	16,600	+75	−95	+87	+13	+1
Diethyl phthalate	—	1.40	7,040	+590	−89	+650	+350	+300
Butylbenzyl phthalate	(?)	4.05	42.2	−62	−93	−80	−36	−73

(continued)

TABLE 2-14 (Continued)

Chemical	t_m (°C)[a]	log K_{ow}[b]	Measured S (mg/L)[c]	Percentage Error in Estimated S Using: Eq. 2-2	Eq. 2-3	Eq. 2-4	Eq. 2-14	Eq. 2-15
Phosphate Esters								
Tributyl phosphate	—	4.00	280	−94	−99	−97	−91	−96
Cresyl diphenyl phosphate	(?)	4.51	2.6	+58	−59	−28	+210	+14
Trixylenyl phosphate	(?)	5.63	0.89	−84	−89	−95	−52	−87
Tricresyl phosphate	77	5.11	0.36	+86	−18	−28	+350	+40
Nitrogen-containing Compounds								
Acrylonitrile	—	−0.92	80,000	$+2.2 \times 10^4$	+35	$+4.5 \times 10^4$	+6000	$+1.1 \times 10^4$
Nitromethane	—	−0.33	95	$+3.3 \times 10^6$	$+3.2 \times 10^4$	$+5.7 \times 10^6$	$+1.1 \times 10^6$	$+1.7 \times 10^6$
1-Nitrobutane	—	1.47	5	$+3.6 \times 10^5$	−43	$+3.8 \times 10^5$	$+2.4 \times 10^5$	$+2.1 \times 10^5$
m-Nitrotoluene	—	2.42	498	+140	−82	+97	+125	+51
m-Nitroaniline	111.8	1.37	890	+3600	−6	+4000	+2300	+2100
Nitrobenzene	—	1.79	1,780	+340	−81	+330	+230	+160
Aniline	—	0.84	36,600	+230	−93	+311	+72	+81
Diethylaniline	—	0.95	670	$+2.0 \times 10^4$	+200	$+2.5 \times 10^4$	$+1.1 \times 10^4$	$+1.1 \times 10^4$
Diphenylamine	53	3.39	36	+94	−68	+20	+150	+29
Triethylamine	—	1.35	15,000	+74	−94	+90	+10	0
Diethanolamine	28	−1.43	954,000	$+1.8 \times 10^4$	−67	$+4.3 \times 10^4$	+4200	+8500
dl-Alanine	295	−2.83	166,000	$+7.4 \times 10^6$	+3600	$+2.6 \times 10^7$	$+1.0 \times 10^6$	$+3.1 \times 10^6$
N-Acetylglycine	206	−1.56	21,700	$+1.3 \times 10^6$	+1800	$+3.3 \times 10^6$	$+3.0 \times 10^5$	$+6.3 \times 10^5$
Acrylamide	84	−1.76	2,050,000	$+1.6 \times 10^4$	−69	$+4.2 \times 10^4$	+3300	+7400
Sulfur-containing Compounds								
Ethyl mercaptan	—	1.20	15,000	+71	−92	+23	+3	−2
Diethyl sulfide	—	1.95	3,130	+12	−62	+3	−12	−33
Thiourea	182	−1.06	91,800 (13°C)	$+4.2 \times 10^4$	+58	$+9.0 \times 10^4$	$+1.1 \times 10^4$	$+2.1 \times 10^5$

(continued)

TABLE 2-14 (Continued)

Chemical	t_m (°C)[a]	log K_{ow}[b]	Measured S (mg/L)[c]	Percentage Error in Estimated S Using: Eq. 2-2	Eq. 2-3	Eq. 2-4	Eq. 2-14	Eq. 2-15
Miscellaneous Pesticides (classification)								
Malathion (organophosphate)	—	2.89	145	+360	−77	+220	+400	+190
Dichlorvos (organophosphate)	—	1.40	10,000	+380	−92	+420	+210	+180
Parathion (organophosphate)	—	3.81	24	+33	−80	−26	+100	−9
Dichlofenthion (organophosphate)	—	5.14	0.245	+110	+14	−19	+420	+60
Carbaryl (carbamate)	142	2.36	40	+5200	+150	+4300	+4800	+3200
Carbofuran (carbamate)	151	1.60	415	+6100	+23	+6200	+4200	+3500
Dalapon (chlorinated carboxylic acid)	—	0.78	502,000	−56	−99	−43	−77	−76
Fluometuron (substituted urea)	164	1.34	90	$+6.8 \times 10^4$	+890	$+7.5 \times 10^4$	$+4.3 \times 10^4$	$+3.9 \times 10^4$
Atrazine (triazine)	174	2.68	33	+2400	+56	+1800	+2500	+1500
Methoxychlor (organochlorine)	89	4.68	0.003	$+8.1 \times 10^4$	$+2.4 \times 10^4$	$+3.5 \times 10^4$	$+1.7 \times 10^5$	$+5.9 \times 10^4$
DDT (organochlorine)	108	5.98	0.0017	+2300	$+2.7 \times 10^4$	+640	+8000	+1800

a. Melting point of compound if greater than 25°C. A dash (—) indicates the melting point is below 25°C.
b. Many of these values were calculated (i.e., estimated) by the methods described in Chapter 1.
c. From Refs. 5, 6, 13, 14, 24, 30, 42, 56, 64, 69, 70 and 71. All values are for a temperature at or near 25°C.

TABLE 2-15

Analysis of Errors Associated with Methods Using Correlations with K_{ow}

Chemical Class	No.[a]	No. of Calculated Values within a Factor of 10 (< x 10)[b] and Bias in Calculated Values[c]									
		Eq. 2-2		Eq. 2-3		Eq. 2-4		Eq. 2-14[f]		Eq. 2-15[f]	
		< x 10	Bias[c]	< x 10	Bias	< x 10	Bias	< x 10	Bias	< x 10	Bias
Aliphatic hydrocarbons	10 (10)	4	7/3	8	6/4	4	6/4	3	8/2	5	7/3
Aromatic hydrocarbons	8 (4)	7	4/4	5	3/5	8	1/7	6 (4)	5/3 (1/3)	7 (4)	3/5 (0/4)
Halogenated hydrocarbons	11 (7)	10	4/7	5	1/10	8	2/9	11 (7)	5/6 (3/4)	9 (7)	3/8 (1/6)
Oxygen-containing hydrocarbons	17 (12)	17	11/6	4	0/17	16	11/6	17 (12)	8/9 (6/6)	16 (11)	8/9 (6/6)
Phosphate esters	4 (1)	3	2/2	3	0/4	2	0/4	3 (0)	2/2 (0/1)	3 (0)	2/2 (0/1)
Nitrogen-containing compounds[d]	15 (8)	5	15/0	10	6/9	5	15/0	5 (4)	15/0 (8/0)	5 (4)	14/0 (7/0)
Sulfur-containing compounds[e]	2 (2)	2	2/0	1	0/2	2	2/0	2	1/1	2	0/2
Miscellaneous pesticides	11 (5)	5	10/1	7	7/4	6	8/3	5 (5)	10/1 (4/1)	5 (5)	9/2 (3/2)
Total	78 (49)	53	55/23	43	23/55	51	45/33	52 (37)	54/24 (31/18)	52 (38)	46/31 (24/24)
% of total no. of chemicals estimated within a factor of 10		68		55		65		67 (76)		67 (78)	
% of total no. of chemicals estimated within a factor of 100		86		95		86		90 (92)		90 (94)	

a. Number of chemicals in chemical class for which calculations were performed. Number in parentheses is number of chemicals which are known to be liquids at 25°C. (See t_m values in Table 2-14.)

b. A calculated value is within a factor of ten of the measured value if the error is between −90% and +900%.

c. Bias is the tendency of the equation to over- or underestimate the solubility. The number of chemicals with positive and negative errors is given as no. +/no. −. (See Table 2-14 for magnitude of bias.)

d. Includes thioures.

e. Excludes thioures.

f. Numbers in parentheses consider the results only with liquid solutes.

A separate analysis of the applicability of Eq. 2-14 to solids was made with $+0.0095(t_m-25)$ as a correction factor on the right side of the equation. The corrected equation was used to estimate the solubilities of the 25 solids in Table 2-14 for which melting points (t_m) were available. The results were as follows:

	Corrected Eq. 2-14	Uncorrected Eq. 2-14
No. overestimated/No. underestimated	+ 14/−11	+ 22/−3
Average bias	+ 2,300%	+ 63,000%
No. (%) within a factor of ± 10	17 (68%)	11 (44%)
No. (%) within a factor of ± 100	24 (96%)	20 (80%)

Similar results could be expected for Eq. 2-15 and for the revised form of Eq. 2-2 given in footnote i of Table 2-3. When the results above are combined with those for the 49 liquids in Table 2-14, the corrected Eq. 2-14 yields estimates within a factor of 10 for 73% of the chemicals.

Selection of Appropriate Equation(s). One or more equations should be selected on the basis of the following considerations:

(1) *Chemical class represented.* If the chemical belongs to a chemical class that is well represented in (or, better, is the sole data base for) a particular data set, select the appropriate equation. Table 2-3 lists the types of chemicals or chemical classes represented in each regression equation. Tables 2-5 to -13 list the specific chemicals in each set. For example:

(a) For benznaphthene, use Eq. 2-18 or 2-20.

(b) For *p*-bromoiodobenzene, use Eq. 2-17.

(c) For isoamyl alcohol, use Eq. 2-5.

Check also items 3 to 5 below.

(2) *Chemical class not well represented.* If the chemical is in a class that is not strongly represented in any of the data sets, use one or more of the equations based on mixed chemical classes (Eqs. 2-2, -3, -4, -14, or -15). Select the equation(s) on the basis of the remaining considerations below.

(3) *Range of values.* Exclude any equation that is incompatible with the input value of K_{ow} or the estimated value of S. (The ranges of K_{ow} and S associated with each data set are given

in Table 2-4.) A small amount of extrapolation may be acceptable, but considerable extrapolation outside the original range can lead to significantly larger errors. For example:

(a) If K_{ow} = 0.1 and a mixed-class equation is acceptable, only Eq. 2-3 is appropriate.

(b) If K_{ow} = $1x10^4$ and the chemical is an alkene, Eq. 2-11 should probably not be used.

(4) *Method errors and bias.* Give appropriate consideration to the quality of fit of the regression equation (r^2 values in Table 2-3) and the likely method error and bias (discussed in the previous subsection). If Tables 2-14 and -15 do not provide sufficient information, errors may be calculated for chemicals of similar structure that have known K_{ow} and S values.

Specifically, if the chemical is a liquid, use any of the equations given by Hansch *et al.* [24], Eqs. 2-5 to -15, other considerations permitting. Conversely, these equations should not be used for solids (t_m > 25°C), since much larger errors are involved. For example:

(a) Tripropylamine (liquid): Although Table 2-15 indicates that Eq. 2-3 is best for nitrogen-containing compounds, inspection of Table 2-14 indicates that Eq. 2-15 is probably better for amines, especially those of the form R_3N, and for liquids in general.

(b) 1,3-Dichloro-2-propanol (liquid): According to Table 2-15, Eq. 2-14 estimates S for halogenated and oxygen-containing hydrocarbons slightly better than do the other equations. In addition, Eq. 2-14 is generally better for liquids.

(5) *Solids.* If the chemical is a solid at 25°C and one of the five mixed-class equations must be chosen, first consideration should be given to a corrected version of Eq. 2-14 or -15:

$$\log(1/S) = 1.214 \log K_{ow} - 0.85 + 0.0095 (t_m - 25) \quad \text{(2-14 corr.)}$$

$$\log(1/S) = 1.339 \log K_{ow} - 0.978 + 0.0095 (t_m - 25) \quad \text{(2-15 corr.)}$$

where t_m is the melting point in °C and S is in moles/L. The revised version of Eq. 2-2 (footnote i, Table 2-3) may also be used. Other factors being equal, these equations should

provide, on average, more accurate estimates than Eqs. 2-2, -3, or -4. However, the applicability of the latter three equations should be assessed before they are rejected, since all of them included solids in their data sets. If no value of t_m is available, Eqs. 2-2, -3, and -4 are the only mixed-class equations that can be used. For example:

Baygon® (t_m = 91°C) is a carbamate. Table 2-14 indicates that Eq. 2-3 is best, with errors of +150% and +23% for the two carbamates listed. Application of the corrected versions of Eqs. 2-14 and -15 show errors of +270% and +170% (Eq. 2-14) and +160% and +130% (Eq. 2-15) for the two carbamates. Thus, Eq. 2-3 still appears to be best, although all three might be used and the results averaged.

Basic Steps

(1) Obtain the octanol/water partition coefficient, K_{ow}, for the chemical. Large compilations of measured (and some estimated) values are available in Refs. 23 and 37. If no measured value is available, the methods given in Chapter 1 may be used to obtain a reasonable estimate for most chemicals. No value of K_{ow} is required for Eq. 2-20, but this equation is only for polynuclear aromatic hydrocarbons.

(2) Determine if the chemical is a liquid or a solid at 25°C. If it is a solid, it is desirable (but not absolutely necessary) to obtain the melting point, t_m(°C).

(3) Select the most appropriate regression equation(s) on the basis of the considerations discussed in the previous subsection.

(4) Use the value of K_{ow} (and t_m, if required) to calculate a value of the solubility, S, at approximately 25°C. The units of S associated with each equation are given in Table 2-3. Only two significant figures should be reported.

(5) If two or more regression equations were used, and each equation can be presumed to be equally valid (i.e., the likely error in log S is about the same), then it is probably better to calculate a geometric mean than a simple average of the individual answers. To obtain the geometric mean, take the log of each individual estimate (after they have all been converted to the same units), average the logs, and then find the antilog.

Example 2-1 Estimate S for 2-isopropoxyphenyl-N-methylcarbamate (also called Baygon® and Propoxur). It is a solid with t_m = 91°C. Measured values of 1.52 and 1.58 have been reported for log K_{ow} [23]. The molecular weight is 209.2 g/mole.

(1) As there is no separate regression equation for carbamates, one of the mixed-class equations must be used. Table 2-14 indicates that, of the three equations that cover both liquids and solids (Eqs. 2-2, -3 and -4), Eq. 2-3 is probably the best with errors of +150% and +23% for the two carbamates listed. However, application of the corrected versions of Eqs. 2-14 and 2-15 to the two carbamates in Table 2-14 shows errors of +270% and +170% (for Eq. 2-14 corr.) and +160% and +130% (for Eq. 2-15 corr.). The differences in these three sets of error values are not significant; thus, it appears appropriate to use all three equations and average the results.

(2a) Using an average value of 1.55 for log K_{ow} in Eq. 2-3,

$$\log S = -0.922\,(1.55) + 4.184 = 2.755$$

$$S = 570 \text{ mg/L}$$

(2b) Similarly, with Eq. 2-14 (corr.),

$$\log (1/S) = 1.214\,(1.55) - 0.850 + 0.0095\,(91\text{-}25) = 1.659$$

$$S = 0.022 \text{ mol/L} = 4600 \text{ mg/L}$$

(2c) And with Eq. 2-15 (corr.),

$$\log (1/S) = 1.339\,(1.55) - 0.978 + 0.0095\,(91\text{-}25) = 1.724$$

$$S = 0.019 \text{ mol/L} = 3900 \text{ mg/L}$$

(3) The measured value of S is 2,000 mg/L [30]; the errors associated with each estimate and the geometric mean are:

Eq.	S (mg/L)	% Error
2-3	570	−72%
2-14 (corr.)	4,600	+130%
2-15 (corr.)	3,900	+95%
Geometric Mean	2,200	+10%

Example 2-2 Estimate S for 2-chloroethylether, a liquid. The molecular weight is 108.6 g/mole. The measured value of log K_{ow} is 1.12 [14].

(1) As there is no separate regression equation for chloroethers, it appears that one of the mixed-class equations must be used. Table 2-15 indicates that Eqs. 2-2, -4, -14 and -15 all do well for oxygen- and chlorine-containing compounds. Of these, Eqs. 2-14 and -15 are favored, since they are for

liquids only. However, Table 2-3 shows that the slopes and intercepts of Eqs. 2-8 (for ethers) and -9 (for alkyl halides) are fairly similar to each other; thus, an average of the results from these two equations should also provide a reasonable estimate.

(2a) With log K_{ow} = 1.12 in Eq. 2-14,

$$\log (1/S) = 1.214\,(1.12) - 0.850 = 0.510$$

$$S = 0.309 \text{ mol/L}$$

(2b) Similarly with Eq. 2-15,

$$\log (1/S) = 1.339\,(1.12) - 0.978 = 0.522$$

$$S = 0.301 \text{ mol/L}$$

(2c) With Eq. 2-8,

$$\log (1/S) = 1.182\,(1.12) - 0.935 = 0.389$$

$$S = 0.408 \text{ mol/L}$$

(2d) With Eq. 2-9,

$$\log (1/S) = 1.221\,(1.12) - 0.832 = 0.536$$

$$S = 0.291 \text{ mol/L}$$

(3) The measured value of S is 0.120 mol/L [14]; the errors associated with each estimate and the average are:

Eq.	S (mol/L)	% Error
2-14	0.309	+160%
2-15	0.301	+150%
2-8	0.408	+240%
2-9	0.291	+140%
Geometric Mean	0.32	+170%

Example 2-3 Estimate S for 2- chloroiodobenzene, a liquid. An estimated value for log K_{ow} is 4.12 [70].

(1) Equation 2-17 should be the most appropriate, since it was derived for halobenzenes. Note (Table 2-14) that Eq. 2-2 also did fairly well for halobenzenes. Both equations will be used and the results compared.

(2a) With log K_{ow} = 4.12 and t_m = 25° (Table 2-3, note f), Eq. 2-17 is:

$$\log S = -0.9874\,(4.12) - 0.0095\,(25) + 0.7178 = -3.588$$

$$S = 2.58 \times 10^{-4} \text{ mol/L}$$

(2b) With Eq. 2-2,

$$\log S = -1.37\,(4.12) + 7.26 = 1.616$$

$$S = 41.3\ \mu \text{ mol/L} = 4.13 \times 10^{-5} \text{ mol/L}$$

(3) The measured value of S is 2.88×10^{-4} mol/L [70]. Thus, the errors associated with the use of Eqs. 2-17 and 2-2 are −10% and −86%, respectively.

Example 2-4 Estimate S for naphthacene ($C_{18}H_{12}$), given log K_{ow} = 5.91 and t_m = 357°C [71].

(1) Table 2-3 indicates two equations, 2-18 and -20, that are specifically for polynuclear aromatic hydrocarbons. Each will be used and the errors compared.

(2a) With Eq. 2-18,

$$\log S = -0.88\,(5.91) - 0.01\,(357) - 0.012 = -8.783$$

$$S = 1.65 \times 10^{-9} \text{ mol/L}$$

(2b) With Eq. 2-20,

$$\log S = -0.00987\,(357-25) - 3.5055 - 0.3417\,(18-6) + 0.002640\,(18-6)^2 = -10.50$$

$$S = 3.14 \times 10^{-11} \text{ mole fraction, which is equivalent}^5 \text{ to } 1.75 \times 10^{-9} \text{ moles/L.}$$

(3) The measured value of S is 2.05×10^{-9} mol/L [42]. Thus, the errors associated with the use of Eqs. 2-18 and -20 are −20% and −15%, respectively.

---

5. Mole fraction is the ratio of the moles of solute to the total moles present (solute plus water). At very low concentrations, this can be simplified to moles of solute per mole of water. One liter of water is equivalent to 55.49 moles. Thus,

$$\text{Mole fraction} = \frac{\text{solute (moles)}}{\text{water (moles)}} = \frac{\text{solute (moles/L)}}{\text{water (moles/L)}} = \frac{\text{solute (moles/L)}}{55.49}$$

and solute (moles/L) = 55.49 × mole fraction.

2-5 ESTIMATION OF S FROM STRUCTURE (METHOD OF IRMANN)

Irmann [27] developed a means for estimating the aqueous solubilities of hydrocarbons and halo hydrocarbons from structural information alone. The method is intended primarily for organic liquids at 25°C. For solids, the melting point is required.

The basic method involves the substitution of atomic and structural constants, derived from the measured solubilities of nearly 200 compounds, into the following equation:

$$-\log S = x + \Sigma y_i n_i + \Sigma z_j n_j \qquad (2\text{-}21)$$

The negative logarithm of the solubility, S (g/gH_2O), is calculated from (1) a basic value, x, which is dependent on the compound type, (2) contributions, y_i, of the various atom types multiplied by their frequency, n_i, in the molecule, and (3) the contributions, z_j, of various structural elements that are present with frequencies, n_j, in the molecule. The x,y, and z values are given in Table 2-16.

For a material that is gaseous under normal pressure (1 atm), the correlation gives the solubility of the liquefied gas at the vapor pressure of both coexisting phases. This can be converted to the approximate value of S at 1 atm by dividing it by the vapor pressure (in atm) of the pure compound.

For a material that is solid at 25°C, Eq. 2-21 gives the solubility of the supercooled liquid. The true solubility of the solid (S_{sol}) can be obtained by the following approximation suggested by Irmann:

$$-\log S_{sol} = -\log S + 0.0095\,(t_m - 25) \qquad (2\text{-}22)$$

In this equation, $-\log S$ is the value from the right side of Eq. 2-21 and t_m is the melting point of the solid in °C. The 0.0095 factor is based on an assumed melting entropy of 13 cal/mol-°C.

Method Errors. Table 2-17 summarizes the errors involved in the use of Irmann's method for the data set from which the atomic and structural constants were obtained. Over 60% of the estimates were within 25% of the measured values. The solubilities of only three compounds could not be estimated within a factor of 10; all were high-molecular-weight hydrocarbons (octadecane, picene, dibenzanthracene).

TABLE 2-16

Parameters for the Calculation of Water Solubility

a. Values of x

	Type of Compound	No.[a]	x[b]
C_6H_6	Aromatic compound	53	0.50
X,H,=C	Halogen[c] derivative, unsaturated aliphatic, with halogen on the unsaturated C, as well as with H in the molecule (no F).	6	
F,H,(Cl),–C	Halogen derivative, saturated aliphatic, containing H besides F	8	
X,H,–C	Halogen derivative, saturated aliphatic (without F)	47	0.90
X,–C or F,(X),–C	Perhalogenated derivative (also with F), saturated aliphatic (without H in molecule)	12	1.25
X,=C	Perhalogenated derivative (no F), unsaturated aliphatic	—	0.90[d]
H,C	Hydrocarbon, aliphatic	21	1.50
—	Cycloaliphatic	—	-0.35[d]

b. Values of y

Atom	Location	No.[a]	y
C			0.25
H			0.12_5
F	On aromatic C	1	0.19
	On saturated C	19	0.28
Cl	On aromatic and unsaturated C	22	0.67_5
	On saturated C	41	0.37_5
Br	On aromatic and unsaturated C	31	0.79_5
	On saturated C		0.49_5
I	On aromatic and unsaturated C	13	1.12_5
	On saturated C		0.82_5

(continued)

TABLE 2-16 (Continued)

c. Values of z

Structural Element		No.[a]	z
–C=C–	Double bond (not conjugated) in pure aliphatic compound	16	–0.35
–C=C–C=C–	Two conjugated double bonds in aliphatic compound	—	–0.55[d]
–C≡C–	Triple bond (individual) in pure aliphatic compound	9	–1.05
>CH, –CH$_2$ (X substituents)	Group with H besides halogen(s) (also F) on the same saturated C	54	–0.30
–CHX–	Group occurring repeatedly non-terminal	—	–0.10[d]
–C–C, –C–R (C substituents)	Aliphatic chain branching or non-terminal monosubstitution	17	–0.10

a. Number of compounds available for the determination of the parameter.
b. If more than one compound type is represented in the molecule, use the smallest x value.
c. Unless otherwise specified, X indicates any halogen (Cl,Br,F,I).
d. Approximate value, considered "provisional" by author.

Source: Irmann [27]

A number of the measured solubilities in the data set used by Irmann had uncertainties greater than 20%. A better evaluation of method errors is given in Table 2-18, which lists deviations of calculated solubilities for only those chemicals whose measured solubility was known within 10 — 20%. These data show that the estimates for nearly 90% of the compounds were within ± 15% of the measured values; none deviated by a factor greater than 1.6.

Basic Steps

(1) Draw the molecular structure.

(2) Using Table 2-16, determine the compound type and the appropriate x value.

TABLE 2-17

Deviations Between Measured and Calculated Solubilities Using Irmann's Method

	Deviation in:		No. of Chemicals	Percentage of Total
	log S	S		
Up to:	± 0.05	± 10%	75	45
	± 0.1	± 25%	103	61
	± 0.2	Factor of 1.6	144	86
	± 0.5	Factor of 3	162	96
	± 1.0	Factor of 10	165	98
Greater than:	± 1.0	Factor of 10	3	2

Source: Irmann [27]

TABLE 2-18

Deviations Between Measured and Calculated Solubilities for Compounds with More Accurately Measured Solubilities

	Deviation in:		No. of Chemicals	Percentage of Total
	log S	S		
Up to:	± 0.02	± 5%	24	68
	± 0.06	±15%	31	89
	± 0.2	Factor of 1.6	35[a]	100

a. Included 10 aromatic hydrocarbons, 9 halogenated aromatics, and 15 chlorinated aliphatics. Measured solubilities of all were known within 10-20%.

Source: Irmann [27]

(3) Using Table 2-16 (and, if necessary, the text following Eq. 2-21) find the appropriate values of y and z and total them in proportion to their frequency (n_i and n_j, respectively) in the molecule.

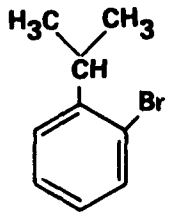
(4) Substitute the values from steps 2 and 3 in Eq. 2-21 to find S in g/gH_2O at 25°C.

(5) If the compound is a solid at 25°C, use Eq. 2-22 to find the corrected solubility, S_{sol}.

(6) If the compound is a gas at 25°C, note that the solubility obtained from Eq. 2-21 is that of the liquefied gas at the vapor pressure of the two coexisting phases. (See text.)

Example 2-5 Estimate S for o-bromoisopropylbenzene, $C_9H_{11}Br$.

(1) The structure is



(2) The basic compound type is aromatic; thus, from Table 2-16, x = 0.50

(3) The atomic and structural contributions from Table 2-16 are:

9C	= 9 (0.25)	= 2.25
11H	= 11 (0.125)	= 1.375
Aromatic Br		= 0.795
	$\Sigma y_i n_i$	= 4.42
Aliphatic chain branching		= − 0.10 = $\Sigma z_j n_j$

(4) Substituting in Eq. 2-21,

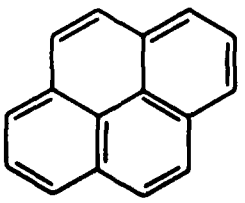
$$-\log S = 0.50 + 4.42 + (-0.10) = 4.82$$

$$S = 1.51 \times 10^{-5} \text{ g/g} = 15.1 \text{ mg/L}$$

The measured value of S = 13 mg/L [27], indicating a deviation of + 16%.

Example 2-6 Estimate S for pyrene, $C_{16}H_{10}$ (t_m = 150°C).

(1) The structure is



(2) The basic compound type is aromatic; thus, from Table 2-16, x = 0.50.

(3) The atomic and structural contributions from Table 2-16 are:

$$16C = 16\,(0.25) = 4.00$$

$$10H = 10\,(0.125) = 1.25$$

$$\Sigma y_i n_i = 5.25$$

As there are no special structural elements, $\Sigma z_j n_j = 0$.

(4) Substituting in Eq. 2-21,

$$-\log S = 0.50 + 5.25 + 0 = 5.75$$

(5) Since the compound is a solid at 25°C, we use Eq. 2-22 to find the corrected solid solubility:

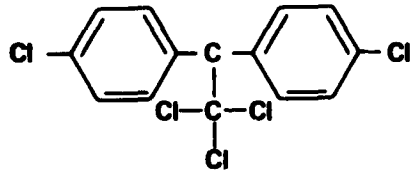
$$-\log S_{sol} = 5.75 + 0.0095\,(150-25) = 6.94$$

$$S_{sol} = 1.15 \times 10^{-7}\ g/g = 0.115\ mg/L$$

The measured value of S_{sol} = 0.160 mg/L [27] or 0.135 [42], indicating deviations of −28% and −15%, respectively.

Example 2-7 Estimate S for DDT, $CCl_3CH(C_6H_4Cl)_2$ (t_m = 110°C).

(1) The structure is



(2) The basic compound type is aromatic; thus, from Table 2-16, x = 0.50.

(3) The atomic and structural contributions from Table 2-16 are:

14C	= 14 (0.25)	= 3.50
9H	= 9 (0.125)	= 1.125
3Cl on saturated C	= 3 (0.375)	= 1.125
2 aromatic Cl	= 2 (0.675)	= 1.35
	$\Sigma y_i n_i$	= 7.10

As there are no special structural elements, $\Sigma z_j n_j = 0$.

(4) Substituting in Eq. 2-21,

$$-\log S = 0.50 + 7.10 + 0 = 7.60$$

(5) Since the compound is a solid at 25 °C, we use Eq. 2-22 to find the corrected solubility:

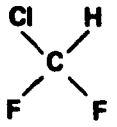
$$-\log S_{sol} = 7.60 + 0.0095\,(110-25) = 8.41$$

$$S_{sol} = 3.89 \times 10^{-9}\ g/g = 3.89\ \mu g/L$$

The measured value of S_{sol} = 1.2 μg/L [27] or 1.7 μg/L [30], indicating deviations of +220% and +130%, respectively.

Example 2-8 Estimate S for chlorodifluoromethane, $CHClF_2$ (boiling point = −40.8°C, vapor pressure = 10.4 atm at 25°C).

(1) The structure is



(2) The basic compound type is "halogen derivative, saturated aliphatic, containing H besides F"; thus, from Table 2-16, x = 0.50.

(3) The atomic and structural contributions from Table 2-16 are:

1C		= 0.25
1H		= 0.125
1Cl on saturated C		= 0.375
2F on saturated C	= 2 (0.28)	= 0.56
		$\Sigma y_i n_i$ = 1.31

Group with H and halogen on same saturated C = −0.30 = $\Sigma z_j n_j$

(4) Substituting in Eq. 2-21,

$$-\log S = 0.50 + 1.31 + (-0.30) = 1.51$$

$$S = 0.031\ g/g$$

The measured value of S is 0.028 g/g [27], indicating a deviation of +11%.

2-6 AVAILABLE DATA

A number of sources of aqueous solubility data are listed below.

Weast and Astle (1979) [66], *Handbook of Chemistry and Physics*

Perry and Chilton (1973) [51], *Chemical Engineers' Handbook*

Verschueren (1977) [64], *Handbook of Environmental Data on Organic Chemicals*

U.S. Coast Guard (1974) [63], *CHRIS Hazardous Chemical Data*

Wilhelm, *et al.* (1977) [68] — for gases in water

Battino and Clever (1966) [8] — for gases in liquids

American Petroleum Institute (1976) [2] — primarily hydrocarbons

American Petroleum Institute (1969) [3] — focus on hydrocarbons

Freed (1976) [20] — data on pesticides

Linke (1958) [38] and (1965) [39] — inorganic and metal-organic compounds

Seidell (1941) [57] — organic compounds

Seidell and Linke (1952) [58] — organic and inorganic compounds

Stephen and Stephen (1963) [61] — organic and inorganic compounds

A few publications are expected in the near future; these include a new edition (Vol. 3) for inorganic and organic compounds by Stephen [60] and a new *Solubility Data Series* to be published by Pergamon [31].

In addition to the above, the references cited in Tables 2-2 and 2-3 will frequently be helpful, e.g., the work of Kenaga and Goring [30] for pesticides.

2-7 SYMBOLS USED

a = parameter in Eq. 2-21

b = parameter in Eq. 2-21

BCF = bioconcentration factor for aquatic life

c = parameter in Eq. 2-21

C_s = molar salt concentration in Eq. 2-1

f_s/f_R = ratio of solid fugacity to reference fugacity

ΔH_f = heat of fusion (cal/mol)

K_{oc} = soil adsorption coefficient based on organic carbon

K_{ow} = octanol/water partition coefficient

K_s = empirical salting parameter in Eq. 2-1

n_i = frequency parameter in Eq. 2-21

n_j = frequency parameter in Eq. 2-21

N = number of carbon atoms in molecule, Eq. 2-20

P = parachor

r = correlation coefficient for regression equation

R = gas constant (1.987 cal/mol-deg)

S = solubility in water

S° = molar solubility in pure water, Eq. 2-1

S' = molar solubility in salt solution, Eq. 2-1

S_{sol} = solubility of a solid, Eq. 2-22

ΔS_f = entropy of fusion, cal/mol-deg

SA = molecular surface area

t = system temperature, °C

T = system temperature (K)

T_b = boiling point (K)

t_m = melting point (°C)

T_m = melting point (K)

TI = topological index

V = molar volume (cm^3/mol)

x,y,z = parameters in Eq. 2-21

Greek

γ = activity coefficient

γ^∞ = infinite dilution activity coefficient

γ_w = activity coefficient of solute in water

γ_{oct} = activity coefficient of solute in octanol

$\gamma_w oct$ = activity coefficient of solute in octanol-saturated water

$\gamma_{oct/w}$ = activity coefficient in water-saturated octanol

χ = connectivity parameter

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3

SOLUBILITY IN VARIOUS SOLVENTS

Warren J. Lyman

3-1 INTRODUCTION

This chapter provides methods for estimating the solubility limits in liquid-liquid and solid (solute)-liquid binary (i.e., two-chemical) systems. Methods for estimating the solubility of gases in liquids are not provided. All of the methods require knowledge of the activity coefficient for the solute and/or solvent at one or more points on the composition diagram. Measured activity coefficients are available for a relatively small number of chemical systems, but a fairly generalized process for estimating these coefficients from structural information alone is given in Chapter 11. The most powerful estimation method described in Chapter 11 (UNIFAC) relies on the availability of group volume and surface area parameters plus group interaction parameters; these are available for only a limited number of functional groups and can be applied only to molecules with relatively simple structures. The reader should verify that an activity coefficient can be estimated from Chapter 11 before attempting to use the methods described below.

Liquid-Liquid Systems. The methods outlined in § 3-4 allow the estimation of the solubility of one liquid in another at any temperature. One of the liquids may be water. One method is presented for estimating solubility from activity coefficients alone; this is subdivided into three modifications of increasing accuracy but also of increasing calculational difficulty. The methods involving the simpler calculations are limited to

chemicals with a low solubility in the solvent. While similar approaches are available for calculating the phase diagram of a system of three liquids, estimation methods are not provided here. The approach provided for the estimation of solubilities may be easily extended to the calculation of vapor-liquid equilibria for binary systems and partition coefficients (at infinite dilution) for ternary systems.

Solid-Liquid Systems. The method recommended in § 3-5 allows estimation of the solubility of a solid solute in a liquid solvent at any temperature. The liquid may be water. The activity coefficient, heat of fusion, and melting point of the solute must be known. As with the liquid-liquid systems, three versions of the basic method are provided that offer increasing accuracy with increasing calculational difficulty. The methods involving the simpler calculations are limited to chemicals with a low solubility in the solvent.

Gas-Liquid Systems. The estimation of the solubility of gases in liquids using (estimated) activity coefficients has not been sufficiently investigated for a method to be included here. References 12 and 25 provide some guidance on this subject.

3-2 BASIC APPROACH

All of the methods described in this chapter require the use of measured or estimated values of the activity coefficient of the solute and, in some cases, of the solvent as well. The activity coefficient, γ, is a measure of the nonideal behavior of a chemical in solution. If measured values of the activity coefficient are not available, they may be estimated by the methods described in Chapter 11. In some cases of limited solubility, only the activity coefficient at infinite dilution, γ^{∞}, is required; this parameter can be obtained from relatively simple regression equations for a very few pairs of solvents and solute chemical classes [24, 26, 34].

The estimation of solubilities from estimated activity coefficients is a fairly recent development. (Solubility data are more frequently used to obtain activity coefficients.) The approach, based upon theoretical considerations, has been made possible by recent advances in the estimation of activity coefficients from structural information alone. Because these methods are still being developed, and the use of activity coefficients to estimate solubility has been little studied, the range of applicability and accuracy of the overall method have not been established. Future investigations of this approach will probably show that it

can be used for a wide range of chemicals or chemical classes over the full range of possible solubility values and that its accuracy is more than adequate for questions relating to environmental concerns.

The theoretical basis for the approaches described derives from a consideration of the free energy of mixing (ΔG^M) in binary systems. This subject is well treated in Refs. 12, 13, 25, 26, and 30.

In keeping with most of the publications cited in this chapter, the concentration of one chemical in another is represented by the symbol x in units of mole fraction. The solute is represented by subscript 1 (x_1) and the solvent by subscript 2 (x_2). The mole fraction ranges from 0 to 1. In a binary system, $x_1 + x_2 = 1$.

3-3 OTHER ESTIMATION METHODS CONSIDERED

Three other approaches to the estimation of solubility have been suggested:

(1) Correlations with solvent/water partition coefficients, and the use of this coefficient plus the solubility in water;

(2) Various formulas based upon the use of solubility parameters; and

(3) Method of Cysewski and Prausnitz for gases in liquids.

The first approach has never been demonstrated and would require a significant amount of work to develop. The second approach, while well developed, is (in theory) limited to nonpolar systems and is often limited in other respects as well. The third approach, while valid for polar and non-polar systems, applies only to gas-liquid systems, and has other severe limitations. Each of these three approaches is further discussed below.

Use of Solvent/Water Partition Coefficients. The partition coefficient for an organic solute between some solvent(s) and water(w), K_{sw}, is frequently measured for studies of the relation between structure and activity. In such cases, K_{sw} is measured at very low solute concentrations; thus, one would expect that this parameter would not be equal to the ratio of the solute's solubility in the two phases, i.e.,

$$K_{sw} \neq \frac{x_s}{x_w} \qquad (3\text{-}1)$$

unless x_s and x_w are very small. If both x_s and x_w are believed to be small, Eq. 3-1 could provide a reasonable estimate of x_s given known or estimated values of x_w and K_{sw}.

It has been shown, however, that the solubility in water, x_w, is inversely proportional to the octanol-water partition coefficient, K_{ow}:

$$\log x_w = -a \log K_{ow} + b \tag{3-2}$$

As numerous equations of this form have been reported, one might expect a similar relationship between x_s (the solubility in solvents) and K_{sw}:

$$\log x_s = c \log K_{sw} + d \tag{3-3}$$

It is known [17, 18] that values of K_{ow} and K_{sw} can be related for a number of solvent systems by equations of the form:

$$\log K_{ow} = e \log K_{sw} + f \tag{3-4}$$

Subtracting Eq. 3-2 from Eq. 3-3 and then substituting Eq. 3-4 in the resulting equality yields

$$\log(x_s/x_w) = (c + ae)\log K_{sw} + (d + af - b) \tag{3-5}$$

or

$$x_s/x_w = k(K_{sw})^{k'} \tag{3-6}$$

where k = antilog (d+af-b) and k' = c+ae. Thus, if adequate data were available to obtain (via regression equations) values of k and k' for each solvent of interest, x_s could be estimated. This would be an extremely simple estimation method. Even better would be regression equations giving the constants c and d in Eq. 3-3 for a variety of solvents.

As previously mentioned, the author is not aware that any expressions similar to Eqs. 3-3, 3-5, and 3-6 have been published. Attempts have been made to test the validity of such equations by the use of solubility data for solutes in ether along with the ether-water partition coefficient, but the attempts were unsuccessful because of the limited quality and quantity of the data.

This approach would clearly not be applicable for solvents (e.g., ethyl alcohol) that are miscible with water. In addition, a different set of constants would have to be provided for each temperature of interest.

Use of Solubility Parameters. The use of solubility parameters (represented by the symbol δ) in estimating solubility has been treated in several publications [12, 13, 25, 30]. Equations are typically of the form shown below for the solubility of gases in liquids (subscript 1 refers to the solute, 2 to the solvent):

$$-\ln x_1 = \ln(f_1^L / f_1^V) + \frac{V_1 \phi_2^2 (\delta_1 - \delta_2)^2}{RT} \qquad (3\text{-}7)$$

where
- x_1 = mole fraction of solute
- f_1^L = fugacity of pure solute as a liquid (may be estimated from critical temperature and pressure)
- f_1^V = fugacity of solute in vapor phase
- V_1 = solute molar volume
- ϕ_2 = volume fraction of solvent = $x_2V_2/(x_1V_1 + x_2V_2)$ (≈ 1 if solubility is very low)
- δ_1 = solubility parameter for solute
- δ_2 = solubility parameter for solvent
- R = gas constant
- T = temperature

The second term on the right-hand side of Eq. 3-7 appears in similar equations for liquid-liquid and solid-liquid systems.

Data for such parameters as f_1^L, V_1, and δ_1 normally come from solubility data in some solute-solvent system and are available for a relatively small number of chemicals. Most of these parameters can be estimated if necessary, but the use of estimated values for all three (as would frequently be necessary) could lead to significant errors. Estimation methods for δ are given in Refs. 5, 12 and 30. Values of δ_2 have been compiled for numerous solvents [5].

In addition to the significant data requirements of this method (e.g., f_1^L, f_1^V, V_1, and δ_1 for the solute, and V_2 and δ_2 for the solvent), another drawback is its limitation to nonpolar systems, which derives from the theoretical basis for the equations. Various attempts have been made to add correction factors for polar systems, but this has necessarily resulted in more complex equations.

Gas Solubilities in Polar and Non-Polar Solvents. Cysewski and Prausnitz [7] have derived a semiempirical correlation which may be useful for estimating gas solubilities in limited cases. The accuracy of the

method is not high, but prediction is usually within a factor of 2. The equation allows one to calculate Henry's Law constant (the reciprocal of the solubility when the partial pressure of the solute is 1 atm) of a solute in a solvent provided one knows the molar volume of the solvent and two characteristic, temperature-independent parameters T_{12}^* and v_{12}^*. The latter two parameters must be determined empirically. For v_{12}^*, correlations are given to allow this parameter to be estimated if the critical volumes of the solvent and (for a relatively small, second-order term) the solute are known or can be estimated. Estimation of T_{12}^* is much more difficult and, at present, is possible for only a very few solutes. The derived equation also involves some lengthy calculations. Because of these limitations, the method is not included in this handbook.

3-4 LIQUID-LIQUID BINARY SOLUTIONS

Basis for Estimation Method. The solubility of one liquid in another is a function of temperature. Most binary solutions have a phase-temperature diagram like that of Figure 3-1a, but some are characterized by the curves in Figures 3-1b and -1c. For binaries of the first kind, there is a temperature (called the upper consolute temperature) above which only one phase can exist. Below this temperature two phases can exist; in this region, component 1 has a limited solubility in component 2 and vice versa.

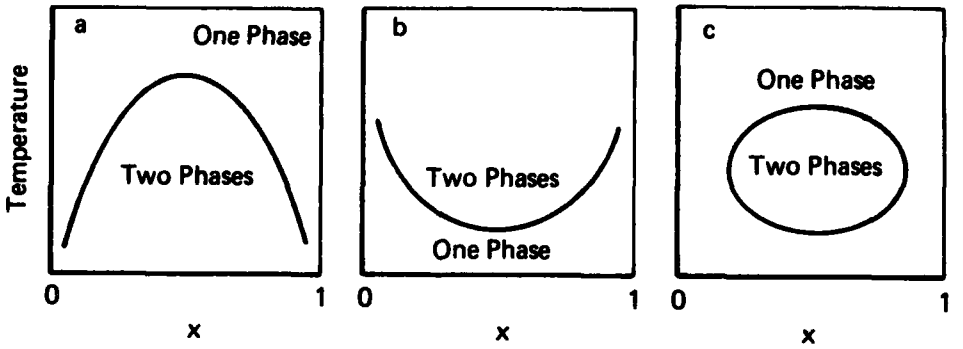


FIGURE 3–1 Phase Stability as a Function of Temperature in Three Binary Liquid Mixtures

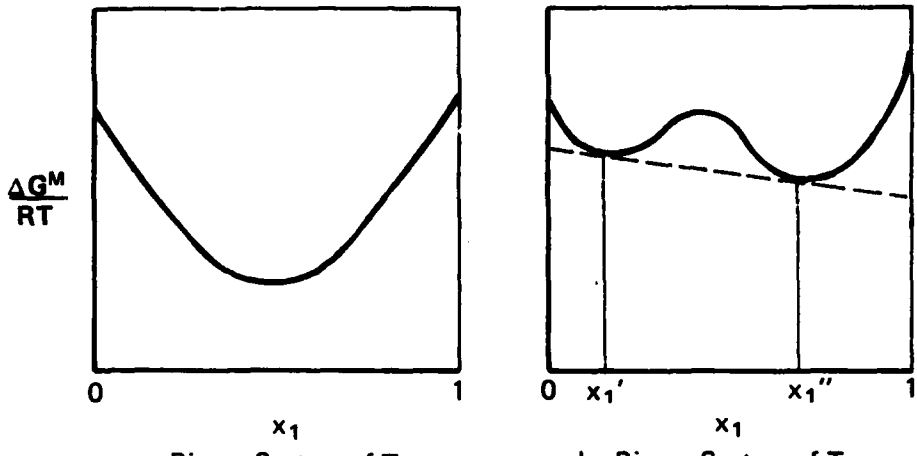
One measure of phase stability in solutions is ΔG^M, the Gibbs free energy of mixing. This parameter may be expressed as a function of the mole fraction (x) and activity (a) of each component. For a binary solution of liquids

$$\Delta G^M = RT\,(x_1 \ln a_1 + x_2 \ln a_2) \qquad (3\text{-}8)$$

where R is the gas constant and T the temperature in K. Since the activity is related to the activity coefficient, γ, by $a = x\gamma$, Eq. 3-8 may be written as

$$\Delta G^M/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_1 \ln x_1 + x_2 \ln x_2 \qquad (3\text{-}9)$$

The plot of Eq. 3-9 as a function of x has a single minimum (Fig. 3-2a) if only one phase is present at the temperature in question.



a. Binary System of Two Miscible Liquids

b. Binary System of Two Partially Soluble Liquids

FIGURE 3–2 Free Energy of Mixing Curves for Binary Solutions

If two phases are present, the curve has two minima (Fig. 3-2b), and it is possible to draw a straight line (dashed line in Fig. 3-2b) that is simultaneously tangent to the curve at two points. The values of x_1 at these two points of tangency, x_1' and x_1'', are the limits of phase stability; i.e., between these two values of x_1 two phases are present, x_1' and x_1'' being the concentrations of component 1 in the two phases. (Note that the points of tangency do not exactly coincide with the points of minima in the $\Delta G^M/RT$ curve unless the two minima are at the same value of $\Delta G^M/RT$.) Following the first minimum, the curve reverses curvature and becomes concave downward — i.e., the second derivative of the equation is negative in this region. Accordingly, if $(\partial^2 \Delta G^M/\partial x^2)_{T,P} < 0$ for any portion of the $\Delta G^M/RT$ curve, some region of phase instability will exist; this region is between x_1' and x_1''. The two minima occur when $(\partial \Delta G^M/\partial x)_{T,P} = 0$ and $(\partial^2 \Delta G^M/\partial x^2)_{T,P} > 0$. If we use the two-suffix Margules equation[1] as the

1. The two-suffix Margules equation is $RT \ln\gamma_1 = Ax_2^2$ (or $RT \ln\gamma_2 = Ax_1^2$ where A is an empirically derived constant. Evaluating this equation at x_1 (or x_2) = 0, one obtains $A = RT \ln\gamma_1^\infty$ (or $A = RT \ln\gamma_2^\infty$). See Ref. 25 or 26, or §11-2 of Chapter 11, for additional information on this equation and its limitations. It is reasonably valid for simple liquid mixtures, i.e., where the molecules are of similar size, shape, and chemical nature.

expression for the excess Gibbs energy of the binary solution, we can predict phase instability from a knowledge of the infinite dilution activity coefficient, γ^{∞}. In particular, two phases are likely to be present (at the appropriate mole fractions) at the temperature in question if

$$\ln \gamma^{\infty} > 2 \qquad (\text{or } \gamma^{\infty} > 7.4) \tag{3-10}$$

If γ^{∞} for either component in the binary is greater than 7.4, phase instability is likely at some point; as the value of γ^{∞} increases, instability will exist over a wider range of x_1 (or x_2).

If γ^{∞} is very large (>1000) for either binary component, and if the chemical does not dissociate (or associate with itself) to any significant extent in very dilute solutions, a reasonable estimate of the solubility limits may be obtained from

$$x_1 = 1/\gamma_1^{\infty} \qquad (\text{for } \gamma_1^{\infty} > 1000) \tag{3-11}$$

and

$$x_2 = 1/\gamma_2^{\infty} \qquad (\text{for } \gamma_2^{\infty} > 1000) \tag{3-12}$$

These two equations may be derived from Eqs. 3-14 and -15 (given below) by assuming that $x \ll 1$.

For values of γ^{∞} between about 50 and 1000 an acceptable estimate of x_1' may be obtained from the equation derived by taking the partial derivative of Eq. 3-9 with respect to x and setting the result equal to 0. The result is:

$$(1-4x_1 + 3x_1^2)\ \ln\gamma_1^{\infty} + (2x_1 - 3x_1^2)\ \ln\gamma_2^{\infty} + \ln x_1 - \ln(1-x_1) = 0 \tag{3-13}$$

This equation has three solutions, two of which (the ones with the lowest and highest values of x_1) correspond to the two minima in the $\Delta G^M/RT$ diagram (Fig. 3-2b). If it is not possible to obtain γ^{∞} for both components *and* it is likely that $\gamma_1^{\infty} \approx \gamma_2^{\infty}$, then Eq. 3-13 may be reduced to two simpler equations for the calculation of one solubility limit or the other. If only γ_1^{∞} is known, the expression for x_1' is:

$$(1-2x_1)\ \ln\gamma_1^{\infty} + \ln x_1 - \ln(1-x_1) = 0 \tag{3-14}$$

Similarly, if only γ_2^{∞} is known, the expression for x_1'' is:

$$(1-2x_1)\ \ln\gamma_2^{\infty} + \ln x_1 - \ln(1-x_1) = 0 \tag{3-15}$$

Equation 3-13 was derived using the three-suffix Margules equation which is described in § 11-2 of Chapter 11; Eqs. 3-14 and -15 may be

derived using the two-suffix Margules equation. These three equations allow the solubility limits to be estimated from only two input parameters, the infinite dilution activity coefficients for the two components in the binary. Whenever possible, it is clearly better to use the general equation (Eq. 3-13) than Eqs. 3-14 and -15, which require simplifying assumptions. Given a value of γ_1^∞ and/or γ_2^∞, these equations may be solved by trial and error using $1/\gamma^\infty$ as the first trial point. If Eq. 3-14 or 3-15 is used, an approximate solution may be obtained from the plot of γ^∞ vs x_1 given in Figure 3-3. The figure also shows, for comparison, a plot of $1/\gamma^\infty$ versus x_1.

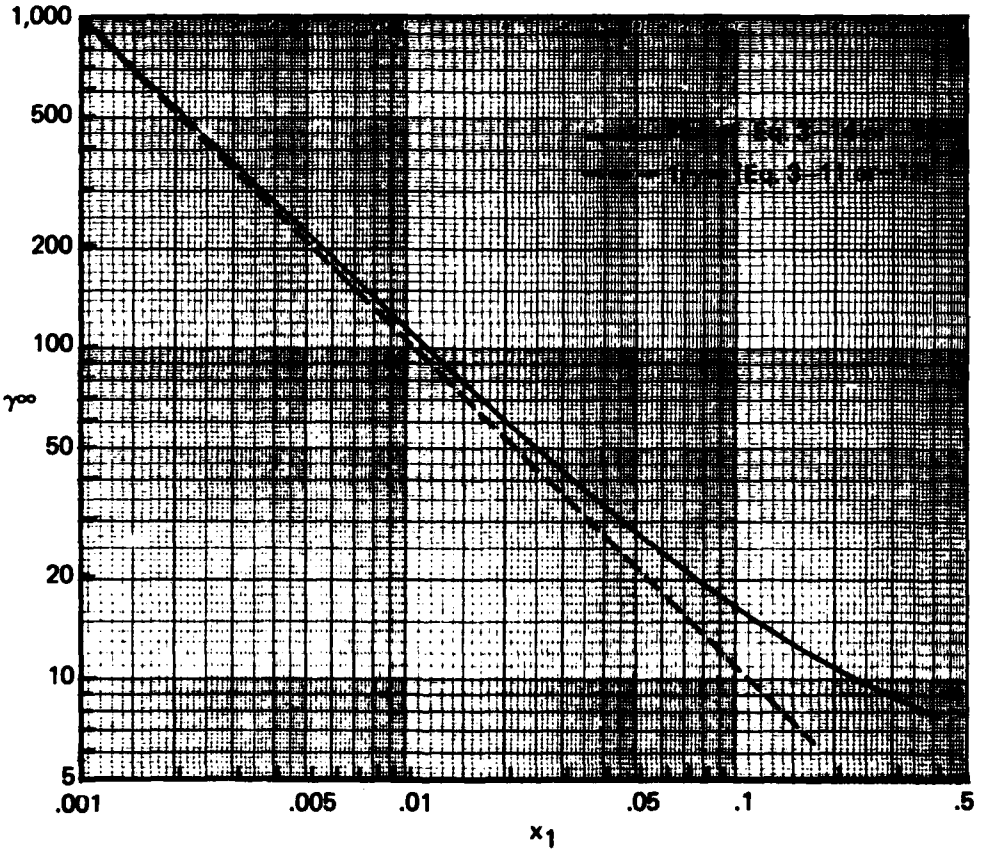


FIGURE 3–3 Plot of x_1 vs γ^∞ from Equations 3–14 and 3–15

When using the trial-and-error method, check that the left-hand side of Eqs. 3-13, -14 and -15 goes from negative to positive as x increases and passes through the value where the equality holds; if the sign changes in the opposite direction, it indicates the point at the maximum of the hump in Fig. 3-2b. Note that Eqs. 3-14 and -15 cannot predict values of x_1' above 0.5 (or x_1'' below 0.5).

For decreasing values of γ^∞ below about 50, the use of Eqs. 3-13 to -15 is likely to give increasingly erroneous results. If the activity coefficients of both components are available (e.g., estimated by the methods in Chapter 11) over the whole range of x, they may be used directly in Eq. 3-9 to plot $\Delta G^M/RT$ versus x. If two phases are present, a curve like that shown in Figure 3-2b will result, and the values of x_1' and x_1'' may be obtained from the two points tangent to the dashed straight line. This approach will always be the most accurate one, irrespective of the value of γ^∞, but the significant increase in the calculational effort is probably justified only when the values of γ^∞ are below 50.

The general method outlined above may be extended to ternary and higher systems. Examples of such calculations are given in Refs. 3 and 9.

Calculation of Vapor-Liquid Equilibria. If activity coefficients are available over the whole range of x (as required above for plotting $\Delta G^M/RT$ versus x), the composition of the vapor phase above any binary liquid solution may also be estimated if the vapor pressures of the two pure components, P_{vp_1} and P_{vp_2} are known. At any (total) system pressure, P, up to a few atmospheres [9]:

$$y_1 P = \gamma_1 x_1 P_{vp_1} \tag{3-16}$$

and

$$y_2 P = \gamma_2 x_2 P_{vp_2} \tag{3-17}$$

where y_1 and y_2 are the vapor-phase mole fractions of components 1 and 2, respectively. Note that the total system pressure (P) is a function of composition. Then, since $y_1 + y_2 = 1$ and $x_1 + x_2 = 1$, for any value of x_1 Eqs. 13-16 and -17 are a set of simultaneous equations with two unknowns and may be easily solved. Some examples of calculated vapor-liquid equilibria using estimated activity coefficients are given in Refs. 1, 2, 8, 9, 10, 23, and 31. The method is quite accurate.

Method Errors. Table 3-1 compares some observed infinite-dilution activity coefficients (γ^∞) and solubilities with the estimated values. Wherever possible, the estimated values of γ^∞ were used to estimate the solubility so that the combined error of the method could be examined. Because of the lack of data for organic-organic systems, several binaries including water are listed. Solubilities estimated from plots of $\Delta G^M/RT$ versus x are not included because of the laborious calculation required.

While most of the tabulated estimates of γ^∞ are within about 10% of the observed values, some errors are as large as 100%. Other comparisons of estimated and observed values of γ^∞ show average errors of about 10-20% [8, 9, 10, 36].

TABLE 3-1

Comparison of Observed and Estimated Activity Coefficients and Solubilities for Liquid-Liquid Binaries

Solute (1)	Solvent (2)	Activity Coefficient, γ_1^∞ T(°C)	Calc.[a]	Obs.	Ref.	Observed Solubility[b] T(°C)	x_1	Ref.	Estimated Solubility, x_1[b,c] $1/\gamma_1^\infty$	Eq. 3-14,-15	Eq. 3-13
Heptane	Acetonitrile	20	41.0	~46	[9]	20	~.04[f]	[9]	.024	.030	.030
Acetonitrile	Heptane	20	31.4	~30	[9]	20	~.05[f]	[9]	.032	.040	.039
Water	Butanol	NS[d]	4.61	~3.7	[9]	NS	~.63[f]	[9]	.22	>.50	.15
						20	.51	[33]			
Butanol	Water	NS	80.6	~70	[9]	NS	~.02[f]	[9]	.012	.015	.016
						NS	.019	[14]			
						20	.020	[33]			
2-Butanone	Water	NS	69.4	NA[g]	[9]	NS	~.03[f]	[9]	.014	.016	.018
						25	.068	[33]			
Water	Butanone	NS	9.58	NA	[9]	NS	~.35[f]	[9]	.10	.22	.11
						25	.30	[33]			
Water	Hexadiene	20	105	226	[10]		NA[g]		.0095	.010	.0093
Hexadiene	Water	25	30,600	26,900	[10]	15	.000088	[4]	.000033	.000033	.000033
n-Pentane	Acetonitrile	25	18	20	[10]		NA		.056	.082	—
		50	13.8	NA	[36]		NA		.072	.12	.11
Acetonitrile	n-Pentane	50	17	NA	[36]		NA		.059	.089	.094
Aniline	Water	100	115	80	[10]	90	.012	[14]	.0087	.0094	—
Benzene	Water	25	455	458	[10]	25	.00042	[4]	.0022	.0023	.0023
						25	.00042	[33]			
Water	Benzene	25	359	430	[10]	25	.00016	[33]	.0028	.0029	.0029
Nonane	Methylamine	0	13.2	10.7	[10]		NA		.076[h]	.13	.22
		20	7.97	7.90	[8]				.13[h]	.34	—
Methylamine	Nonane	0	5.5	4.8	[10]		NA		.18[h]	>.5	.34
		20	3.72	3.55	[8]				.27[h]	>.5	—
n-Hexane	Methylamine	0	8.6	8.3	[10]		NA		.12	.28	—
n-Propanol	1,2-Dichloroethane	84	14	23	[10]		NA		.071	.12	.22
1,2-Dichloroethane	n-Propanol	97	6.7	12.9	[10]		NA		.15	>.5	.21
n-Heptane	Ethyl alcohol	45	~ 9.1[f]		[36]	NS	.15	[14]	.11	.24	.12
		30		14.1[f]	[36]						

(Continued)

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TABLE 3-1 (Continued)

Solute (1)	Solvent (2)	Activity Coefficient, γ_1^∞ T(°C)	Calc.[a]	Obs.	Ref.	Observed Solubility[b] T(°C)	x_1	Ref.	Estimated Solubility, x_1[b,c] $1/\gamma_1^\infty$	Eq. 3-14,-15	Eq. 3-13
Ethyl alcohol	n-Heptane	45	~50.1[f]		[36]		NA		.020	.023	.026
		30		~42.7[f]	[36]						
1-Ethylnaphthalene	Water	25	NA	806,000	[22]	NS	1.16×10^{-6}	[22]	1.24×10^{-6}	1.24×10^{-6}	—
n-Heptane	N-Methylpyrrolidone	25	NA	16.2	[19]	25	.145	[19]	.062	.095	—
n-Hexane	Aniline	25	NA	26.6	[19]	25	.089	[16]	.038	.049	—

a. Calculated using the UNIFAC method, which requires only a knowledge of the structures of the solute and solvent.
b. Units are in mole fraction.
c. Estimated solubilities are based upon the calculated value of γ_1^∞ whenever possible. All estimated values of x_1 are at the temperature given for the value of γ_1^∞.
d. NS = Not specified.
e. At 350 mm Hg.
f. Observed values taken from data points in published graphs; uncertainty in cited values is due to difficulty in reading the plots accurately.
g. NA = Not available.
h. Two phases are likely at 0°C, since γ_1^∞ for nonane is significantly above 7.4. However, at 20°C the value is only slightly above 7.4 and only a single phase may exist.

Errors in the estimated values of γ^∞ will add to the method error if they are used in the calculation of x_1' or x_1''. A comparison of observed and estimated solubilities in Table 3-1 shows a wide range of errors, but they should be tolerable for environmental considerations; since only a semiquantitative evaluation of a chemical's solubility in various solvents may be needed for such purposes, the method presented in this chapter is probably more than adequate. In one study of 50 ternary liquid-liquid equilibria where two liquid phases were known to be present in some regions, the use of estimated activity coefficients[2] was shown to give reasonable predictions of phase splitting (i.e., values of mutual solubilities) for most systems [9]. The quality of the predictions was described as follows:

Rank	No. of Systems	Quality of Predictions
0	3	No phase splitting could be predicted.
1	11	Agreement between predicted values and liquid-liquid solubility curves was poor.
2	28	Predictions agreed qualitatively with experimental values.
3	8	Predictions agreed quantitively with experimental values.

Basic Steps

(1) Check that both the solute (component 1) and solvent (component 2) are liquids at the temperature of interest.

(2) Obtain the infinite dilution activity coefficient[3] for the solute (γ_1^∞) and the solvent (γ_2^∞) and proceed as follows:

- If $\gamma_1^\infty > 1000$, go to Step (3);
- If γ_1^∞ is between about 50 and 1000, go to Step (4);
- If γ_1^∞ is between about 7.4 and 50, go to Step (5);
- If both γ_1^∞ and γ_2^∞ are less than 7.4, the two liquids can be assumed to be miscible in all proportions at the temperature considered.

2. Values of γ (as a function of x). As explained earlier, this is more accurate than the shorthand method using only γ^∞.

3. Methods for estimating activity coefficients are given in Chapter 11. These coefficients are a function of temperature, and the methods described allow a calculation at any temperature.

(3) Calculate x_1 (the solubility of 1 in 2, in units of mole fraction) from Eq. 3-11. Similarly, if the solubility of 2 in 1 is desired (x_2), and $\gamma_2^\infty > 1000$, use Eq. 3-12.

(4) Calculate x_1 (the solubility of 1 in 2, in units of mole fraction) from Eq. 3-13; the equation may be solved by trial and error using $1/\gamma^\infty$ as the first approximation for x_1.

Note: Of the three solutions to this equation, the solubility of 1 in 2 is given by the lowest value of x_1 that satisfies the equality. If the left-hand side of the equation goes from negative to positive as x increases through the value where the equality holds, a minimum in the Gibbs free energy curve has been found. (See Figure 3-2b and related text for additional discussion.)

Similarly, x_2, the solubility of 2 in 1, may be calculated from Eq. 3-13; this time the solution with the *highest* value of x_1 is found and subtracted from 1 to obtain x_2.

If only γ_1^∞ is known, and if it can be assumed that $\gamma_1^\infty \approx \gamma_2^\infty$,[4] the solubility of 1 in 2 may be obtained from Eq. 3-14. Similarly, if only γ_2^∞ is known, Eq. 3-15 may be used to calculate the solubility of 2 in 1; i.e., solve for x_1 and then obtain x_2 from $x_2 = 1 - x_1$. Both equations may be solved by trial and error, using $1/\gamma^\infty$ as the first approximation or with the plot of these equations given in Figure 3-3. The note above is equally applicable to these two equations.

(5) Calculate x_1 (the solubility of 1 in 2, in units of mole fraction) by using Eq. 3-9 to plot $\Delta G^M/RT$ as a function of x_1. (This requires the calculation of activity coefficients at a number of points over the range of x_1, as described in Chapter 11.) If two phases are predicted, a curve with two minima, such as that shown in Figure 3-2b, will result; if only a single minimum is obtained, the two liquids may be assumed to be miscible in all proportions. Draw a straight line (e.g., the dashed line in Figure 3-2b) that is simultaneously tangent to the curve at the two points. The points of tangency corresponds to the solubility limits for 1 in 2 and 2 in 1 (x_1' and $1-x_1''$, respectively).

Example 3-1 Estimate the solubility of 1-ethylnaphthalene(1) in water(2) at 25°C, given $\gamma_1^\infty = 806{,}000$ [22].

4. This is seldom a good assumption unless the solute and solvent are chemically similar. However, the assumption should not lead to excessive errors unless the values are orders of magnitude apart.

(1) 1-Ethylnaphthalene melts below −14°C and decomposes at 258°C. Therefore, it is liquid at the temperature in question.

(2) Since γ_1^∞ is greater than 1000, we may use Eq. 3-11:

$$x_1 = 1/\gamma_1^\infty = 1.24 \times 10^{-6} \text{ mole fraction}$$

This is equivalent to 10.7 mg/L, which compares well with a literature value of 10.0 mg/L [22].

Example 3-2 Estimate the solubility of 2-butanone(1) in water(2) at ~25°C and 350 mm Hg, given $\gamma_1^\infty = 69.4$ and $\gamma_2^\infty = 9.58$ [9].

(1) Both the solute and the solvent are liquids at this temperature.

(2) Since γ_1^∞ is between 50 and 1000, and γ_2^∞ is less than 50, it is probably best to use Eq. 3-13:

$$(1-4x_1+3x_1^2)\ln(69.4) + (2x_1-3x_1^2)\ln(9.58) + \ln x_1 - \ln(1-x_1) = 0.$$

(3) Solve the above equation by trial and error, using $1/\gamma_1^\infty$ (=0.014) or the value from Figure 3-3 (=0.016) as the first approximation. The solution is found at $x_1 = 0.018$ mole fraction. The data given in Ref. 9 indicate an observed value of roughly 0.03 mole fraction for these conditions.

Example 3-3 Estimate the mutual solubilities for the heptane(1)-acetonitrile(2) system at 20°C, given activity coefficients (estimated) as a function of composition, and $\gamma_1^\infty = 41.0$ and $\gamma_2^\infty = 31.4$ [9].

(1) Since both γ_1^∞ and γ_2^∞ are below 50, it would seem preferable to plot $\Delta G^M/RT$ vs x, as described in Step 5 of the "Basic Steps." However, in this case the values are not much below 50 and, in addition, are approximately equal. Thus, one can probably use Eqs. 3-14 and 3-15:

$$(1-2x_1)\ln(41.0) + \ln x_1 - \ln(1-x_1) = 0$$

$$(1-2x_1)\ln(31.4) + \ln x_1 - \ln(1-x_1) = 0$$

(2) As a first approximation in solving the first equation, use $1/\gamma_1^\infty = 0.024$ or Figure 3-3 (0.030). For the second equation, use $1/\gamma_2^\infty = 0.032$ or 0.040 from Figure 3-3. Obtain x_2 from $x_2 = 1 - x_1$.

(3) Alternatively, Eq. 3-13 can be used:

$$(1-4x_1+3x_1^2)\ln(41.0) + (2x_1-3x_1^2)\ln(31.4) + \ln x_1 - \ln(1-x_1) = 0$$

To solve this equation, use $1/\gamma_1^\infty = 0.024$ or Figure 3-3 (0.030) as a first approximation for x_1' and use $1-(1/\gamma_2^\infty) = 0.968$ or $1-x_1$ (from Figure 3-3) = 0.96 as a first approximation for x_1''.

(4) Obtain x_2 from $x_2 = 1-x_1''$.

Trial-and-error solutions give a value for the solubility of heptane in acetonitrile (x_1) as 0.030 mole fraction from both Eqs. 3-14 and 3-13. The solubility of acetonitrile in heptane (x_2) is found to be 0.040 mole fraction from Eq. 3-15 and 0.039 mole fraction from Eq. 3-13. The observed values for x_1 and x_2 are about 0.04 and 0.05 mole fraction, respectively [9].

A plot of $\Delta G^M/RT$ vs x would probably look like the curve in Figure 3-4.[5] Note that the minima occur at the points predicted by Eq. 3-13.

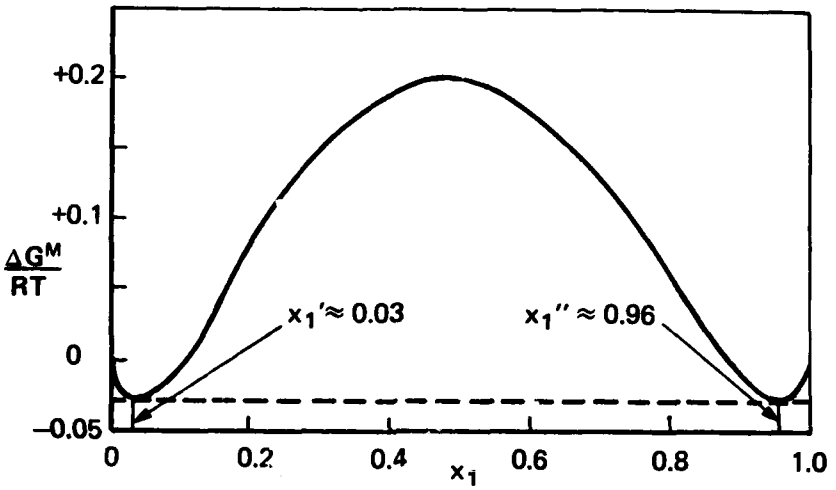


FIGURE 3–4 Sample Plot for Heptane (1) – Acetonitrile (2) System (See Example 3-3)

Example 3-4 Estimate the mutual solubilities for the water(1) butanol(2) system at ~20°C, given activity coefficients (estimated) as a function of composition and $\gamma_1^\infty = 4.61$ and $\gamma_2^\infty = 80.6$ [9].

(1) In this case, one value of γ^∞ (4.61) would imply a very high solubility or a completely miscible system, but the other value is high enough to indicate that some region of phase instability is likely. Because γ_1^∞ is so low, only Eq. 3-9 (involving a plot of $\Delta G^M/RT$ vs x_1) can be recommended for the calculation of x_1. The relatively high value of γ_2^∞ implies that Eq. 3-13, or even Eq. 3-15, might be appropriate for the calculation of x_2; however, since a plot is necessary for x_1, x_2 will be obtained from the same plot as a matter of convenience.

(2) Following Step 5 (in "Basic Steps"), a curve like the one shown in Figure 3-5 would be obtained.[5]

---

5. Activity coefficient values were not estimated directly for each value of x_1 to obtain the curves in Figures 3-4 and 3-5. It was assumed that $\ln\gamma_1 = Ax_2^2/RT$ and $\ln\gamma_2 = A'x_1^2/RT$, where $A = RT\ln\gamma_1^\infty$ and $A' = RT\ln\gamma_2^\infty$. Substituting these equations into Eq. 3-9 gives an expression for $\Delta G^M/RT$ (as a function of x_1) with only γ_2^∞ as the input parameter. The curves shown are a plot of this resulting equation.

(3) Draw a straight line (shown dashed) tangent to the curve at two points. The values of x_1' and x_1'', the points of tangency, are read as 0.185 and 0.98 mole fraction, respectively. Since $x_2 = 1-x_1''$, we predict $x_2 = 0.02$. The observed values listed in Table 3-1 for x_1 and x_2 are ~0.6 and 0.02, respectively. Note in Figure 3-5 that the point of tangency from which x_1' is found (~0.185) is not the same as the minimum in the $\Delta G^M/RT$ curve (~0.15); the latter value is the one predicted by Eq. 3-13.

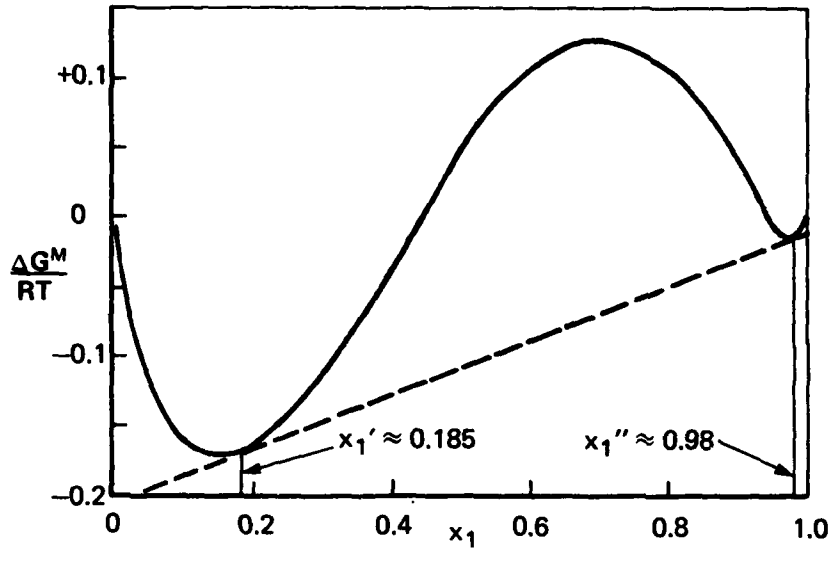


FIGURE 3–5 Sample Plot for Water (1) – Butanol (2) System (See Example 3-4)

3-5 SOLID-LIQUID BINARY SOLUTIONS

Basis for Estimation Method. The solubility of a solid in a liquid solvent is, as in liquid-liquid systems, a function of temperature. In addition, however, the heat of fusion of the solid solute must be considered, since energy is required to overcome the intermolecular forces of the molecules in the solid while it is dissolving. Accordingly, for two chemicals of similar structure (more specifically, with similar melting points), the chemical with the higher heat of fusion will have the lower solubility in any specified solvent.

The nature of the effect of temperature on solubility is shown by the two schematic phase diagrams in Figure 3-6. The point of minimum temperature is called the eutectic point; below this temperature it is not possible to have a single-phase system.

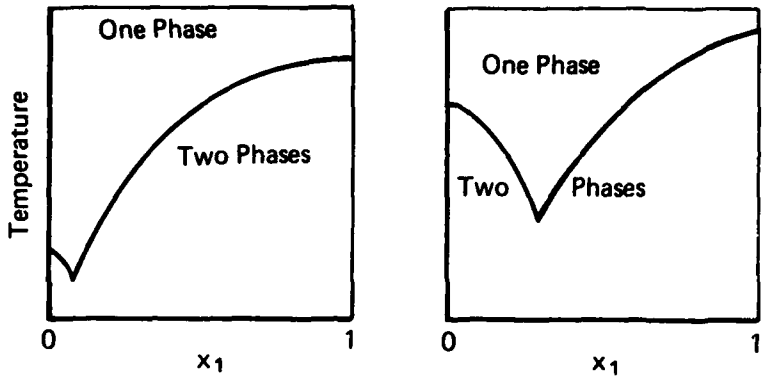


FIGURE 3–6 Phase Stability as a Function of Temperature in Two Binary Solid (1) – Solvent (2) Systems

The estimation method recommended here was proposed and evaluated by Gmehling *et al.* [11]. If the heat of fusion, ΔH_f, the melting point, T_m(K), and the activity coefficient (as a function of composition), γ_1, are known or can be estimated, then the solubility of the solid solute, x_1, (in mole fraction) may be obtained from

$$\ln \gamma_1 x_1 = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1 \right) \tag{3-18}$$

where T is the system temperature (K) and R is the gas constant. If ΔH_f is in units of calories/mole, R = 1.987 calories/mole·degree. This equation is based upon theoretical considerations which are discussed in Refs. 12, 25, 26, and 34. It neglects certain correction terms proportional to Δc_p (specific heat difference between liquid and solid), because the required c_p data are unlikely to be available; however, the uncertainties associated with neglecting the Δc_p term are expected to be small in comparison with the uncertainties in the estimated activity coefficients which will be required for Eq. 3-18.

The use of Eq. 3-18 requires three input parameters, ΔH_f, T_m and γ_1 (as a function of x_1), in order for x_1 to be calculated at a given temperature (T). Note that γ_1 is also a function of temperature. Estimation methods for activity coefficients (as a function of temperature) are provided in Chapter 11; since measured values of γ_1 are unlikely to be available, it is assumed throughout this section that estimated values are used. Thus, measured values of only ΔH_f and T_m are required. Neither of these two properties can be accurately estimated by methods that have some general applicability. Estimation methods for ΔH_f have been given by Yalkowsky [37] for organic molecules of intermediate size. If ΔH_f is not available for a compound of interest, the term $6.54 (T-T_m)/T$ may be

used as a rough approximation of the term $\Delta H_f/RT \cdot (T/T_m - 1)$ in Eq. 3-18 (and also in Eqs. 3-19 and -20 below). The basis for this approximation is explained in §2-4 (see Basis for Estimation Method) of Chapter 2; an average value of 13 cal/mole°C for ΔS_f is assumed for all organic compounds, and $\Delta H_f = T_m \Delta S_f$.

The solution of Eq. 3-18 for x_1 must be by trial and error, since γ_1 is a function of x_1 and, if the UNIFAC method of Chapter 11 is used, this function cannot be expressed in a simple, closed form. The estimation procedure thus involves three steps:

(1) Estimating γ_1 at various values of x_1 (according to the instructions in Chapter 11) so that a plot of γ_1 vs x_1 may be obtained;

(2) Calculating the value of the right-hand side of Eq. 3-18; and

(3) Using calculated and interpolated values of γ_1 (from step 1) to find the value of $\ln \gamma_1 x_1$ that matches the value from step 2. If no value of $\ln \gamma_1 x_1$ matches the value of the right side of the equation, then the two chemicals are completely miscible at the temperature in question. A first estimate of x_1 may be obtained by setting $\gamma_1 = 1$; the value of x_1 obtained with this assumption is called the "ideal solubility." The actual value of x_1 may be above or below this value.

Equation 3-18 may be simplified if one assumes that the change in γ_1 with x_1 may be described by the two-suffix Margules equation. (See footnote 1 for qualifications.) The modified form of Eq. 3-18 is:

$$\ln x_1 + (1-x_1)^2 \ln \gamma_1^\infty = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1 \right) \qquad (3\text{-}19)$$

where, as before, γ_1^∞ is the infinite dilution activity coefficient for the solute. The use of Eq. 3-19 requires only that the activity coefficient of the solute be obtained (estimated) at one point — infinite dilution — which significantly reduces the calculational effort over that associated with Eq. 3-18. The loss of accuracy in using Eq. 3-19 rather than 3-18 should not be significant if x_1 is less than 0.1, although this assumption has not been tested.

The estimation procedure may be even further simplified if x_1 is less than 0.01: the factor $(1-x_1)^2$ in Eq. 3-19 then approaches 1, and we may write

$$\ln x_1 = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1 \right) - \ln \gamma_1^\infty \qquad (3\text{-}20)$$

This equation may be solved directly for x_1 (once the input parameters on the right side are obtained) rather than by trial and error as required for Eqs. 3-18 and 3-19.

Although the methods described in this section are limited to binary systems, the basic method may be relatively easily expanded to the prediction of (solid) solute solubilities in solvent mixtures [11]. In all cases, single or mixed solvents, it is necessary to assume that the solvents are insoluble in the solid phase of the solute.

Method Errors. Although the author has not independently tested the procedure for establishing method errors using estimated activity coefficients, several calculations reported by Gmehling *et al.* [11] indicate that estimated and observed solubilities are generally in close agreement. Some of their results using Eq. 3-18 are shown in Tables 3-2 to 3-5. The first three of these tables show average errors (calculated on x_1) in the range of 10-50%, the larger errors being associated with small values of x_1. To predict the eutectic point, one must estimate the mutual solubilities of the two chemicals at several temperatures and plot a curve like those in Figure 3-6; the minimum in the curve corresponds to the eutectic point. As shown in Table 3-5, the results agree reasonably well with the observed values, reflecting the general accuracy of the estimation method.

Table 3-6 compares observed and estimated aqueous solubilities for a number of compounds using the simplified estimation method involving the use of Eq. 3-20. The errors shown, which average 36% based on mole fraction, are not directly comparable with those in the previous tables, since observed rather than estimated values of γ_1^∞ were used. As pointed out in §3-4, however, average errors in estimated values of γ^∞ are typically only 10-20%. Thus, the use of Eq. 3-20 with estimated values of γ^∞ should not involve errors much greater than those shown in Table 3-6.

It is interesting to compare the results given for naphthalene in Table 3-2 with other solubility predictions for naphthalene using the Scatchard-Hildebrand approach, which involves the use of what are now called solubility parameters (see §3-3). Scatchard [27] was able to predict the solubility of naphthalene in five nonpolar or only slightly polar solvents[6] (at 20°C) with an average error of about 7% based on mole

6. Benzene, toluene, chlorobenzene, carbon tetrachloride, and hexane.

TABLE 3-2

Observed and Estimated Solubility of Naphthalene in Various Solvents at 40°C

(T_m = 353.4K, ΔH_f = 4494 cal/mol)

	x_1 (mole fraction)		
Solvent	Observed	Estimated[a]	Error (%)
Methanol	.044	.048	+9.1
Ethanol	.073	.054	-26.
1-Propanol	.094	.093	-1.1
2-Propanol	.076	.093	+22.
1-Butanol	.116	.111	-4.3
n-Hexane	.222	.259	+17.
Cyclohexanol	.225	.205	-8.9
Acetic acid	.117	.125	+6.8
Acetone	.378	.358	-5.3
Chloroform	.473	.470	-0.6
		Average error =	10.1%

a. Eq. 3-18 used.

Source: Gmehling *et al.* [11]

fraction. However, for six polar solvents,[7] the average error in the predicted solubilities was 96%; this relatively high error is not unexpected, since, as mentioned in §3-3, the basic theory is derived from a consideration of nonpolar molecules.

Basic Steps

(1) Check that the solute is a solid at the temperature in question.

(2) Obtain the heat of fusion, ΔH_f (cal/mole), melting point, T_m(°K) and — from Chapter 11 — the infinite dilution activity coefficient, γ_1^∞, for the solute. Express the system temperature, T, in K. Use 1.987 cal/mol·deg for R. If no value of ΔH_f is available, substitute 6.54 $(T-T_m)/T$ for the term $\Delta H_f/RT \cdot (T/T_m - 1)$ in the equation selected in step 3 below.

7. Aniline, nitrobenzene, acetone, n-butyl alcohol, methanol, and acetic acid.

TABLE 3-3

Observed and Estimated Solubility of Anthracene in Various Solvents at 20°C

(T_m = 489.7K, ΔH_f = 6898 cal/mol)

Solvent	x_1 (mole fraction) Observed	Estimated[a]	Error (%)
Acetone	.0031	.0025	-19.
Diethyl ether	.0029	.0045	+55.
Chloroform	.0094	.0182	+94.
Ethanol	.0005	.0004	-20.
Carbon tetrachloride	.0041	.0053	+29.
Phenol[b]	.0099	.0113	+14.
Cyclohexane	.0012	.0031	+160.
Methanol	.0002	.0003	+50.
1-Propanol	.0006	.0006	0
2-Propanol	.0004	.0006	+50.
Aniline	.0035	.0027	-23.
n-Hexane[c]	.0018	.0024	+33.
		Average error =	46%

a. Eq. 3-18 used.
b. Solubility at 60°C.
c. Solubility at 25°C.

Source: Gmehling *et al.* [11]

(3) Use $1/\gamma_1^\infty$ as a first approximation for x_1 and proceed as follows:

- If x_1 is less than 0.01, go to Step (4).
- If x_1 is between 0.01 and 0.1, go to Step (5).
- If x_1 is greater than 0.1, go to Step (6).

(4) Calculate x_1 (the solubility of 1 in 2, in units of mole fraction) from Eq. 3-20.

(5) Calculate x_1 (the solubility of 1 in 2, in units of mole fraction) from Eq. 3-19. Trial and error must be used to find a value of x_1 that satisfies this equation.

TABLE 3-4

Observed and Estimated Solubility of Phenanthrene in Various Solvents at 20°C

(T_m = 369.5K, ΔH_f = 4456 cal/mol)

Solvent	x_1 (mole fraction) Observed	Estimated[a]	Error (%)
Diethyl ether	.133	.138	+3.8
n-Hexane[b]	.048	.070	+46.
Acetone	.145	.097	−33.
Chloroform	.238	.264	+11.
Ethanol	.0123	.0102	−17.
Carbon tetrachloride	.145	.158	+9.0
Acetic acid	.0192	.0255	+33.
Methanol	.0064	.0091	+42.
Carbon disulfide	.235	.185	−21.
		Average error =	24%

a. Eq. 3-18 used.
b. Solubility at 25°C.

Source: Gmehling *et al.* [11]

(6) Obtain (from Chapter 11) values of γ_1 at several values of x_1 over the range of 0 to 1 and plot γ_1 vs x_1 so that interpolation between calculated values is possible. Then, using the information from step (2), obtain a value for the right side of Eq. 3-18. Next, with the calculated values and plot of γ_1 vs x_1, use trial and error to find the value of ln $\gamma_1 x_1$ that satisfies the equality of Eq. 3-18. (If no value of ln $\gamma_1 x_1$ satisfies the equality, then the solute and solvent are miscible in all proportions at the system temperature.) The value of x_1, in units of mole fraction, is obtained directly from this procedure.

Example 3-5 Estimate the solubility of naphthalene in 1-butanol at 40°C, given T_m = 353.4K (80.2°C), ΔH_f = 4494 cal/mol [11], and values of γ_1 vs x_1 (estimated from Chapter 11[8]). The value of x_1 is presumed to be greater than 0.1, thus requiring the use of Eq. 3-18.

8. These values were assumed to be available for this example; they were not actually calculated.

TABLE 3-5

Observed and Calculated Eutectics in Binary Mixtures

Solute (1)	Solvent(2)	x_1 at Eutectic (mole fraction)			Temp. at Eutectic (°C)		
		Observed	Calculated	% Error	Observed	Calculated	ΔT(°C)
Acetone	Diethyl ether	.240	.320	+33	−126	−123	+3
Acetone	Ethanol	.210	.244	+16	−119	−124	−5
Benzene	1,2-Dichloroethane	.320	.316	−1.3	−55	−55	0
Benzene	Phenol	.625	.654	+4.6	−6	−7	−1
Benzene	Ethanol	.013	.009	−31	−115	−114	+1
Benzene	Chloroform	.260	.268	+3.1	−77	−82	−5
Benzene	1,4-Dioxane	.565	.569	+0.7	−26	−26	0
Benzene	Acetonitrile	.050	.126	+152.	−51	−49	+2
Benzene	Cyclohexane	.265	.266	+0.4	−44	−48	−4
Benzene	Nitrobenzene	.500	.517	+3.4	−26	−27	−1
Phenol	p-Xylene	.425	.409	−3.8	4	0	−4
Phenol	Naphthalene	.838	.837	−0.1	29	30	+1
Ethanol	Ethyl acetate	.850	.897	+5.5	−118	−118	0
Acetic acid	p-Xylene	.616	.595	−3.4	1	5	+4
Acetic acid	Benzene	.409	.453	+10.	−8	−8	0
Acetic acid	Cyclohexane	.074	.074	0	−1	−6	−5
Nitrobenzene	Carbon tetrachloride	.186	.126	−32.	−35	−37	−2
				Avg. Error = 18%			Avg. ΔT = 2.2°C

Source: Gmehling *et al.* [11]

TABLE 3-6

Observed and Estimated Aqueous Solubilities for Solid-Liquid Binaries

Solute[b]	x_1 (mole fraction)[a] Observed[c]	Estimated[d]	Error (%)
2,4,6-Trinitrotoluene	1.19×10^{-5}	1.14×10^{-5}	-4.2
1,4-Dichlorobenzene	1.02×10^{-5}	8.64×10^{-6}	-16.
1,4-Dibromobenzene	1.53×10^{-6}	1.41×10^{-6}	-7.8
1,4-Diiodobenzene	1.01×10^{-7}	5.82×10^{-8}	-43.
Naphthalene	4.38×10^{-6}	1.48×10^{-6}	-66.
Acenaphthene	4.53×10^{-7}	4.69×10^{-7}	+3.5
Biphenyl	8.27×10^{-7}	7.51×10^{-7}	-9.2
Fluorene	2.06×10^{-7}	2.26×10^{-7}	+9.7
Phenanthrene	1.19×10^{-7}	1.25×10^{-7}	+5.0
Anthracene	7.58×10^{-9}	5.56×10^{-9}	-27.
Pyrene	1.29×10^{-8}	3.87×10^{-8}	+200.
		Average error =	36%

a. At 25°C.
b. Solvent is water in all cases.
c. From Refs. 33, 35, and 38.
d. Eq. 3-20 used. All input data, including values for γ_1^∞, are measured values. Data for γ_1^∞ from Refs. 22 and 34, ΔH_f from Refs. 14 and 35, T_m from Ref. 14.

(1) The right side of Eq. 3-18 is:

$$\frac{4494}{(1.987)(313.2)}\left(\frac{313.2}{353.4}-1\right) = -0.8214 \text{ (no units)}$$

(2) From the data set (and plot) of paired γ_1 and x_1 values, it is found that the value of x_1 that satisfies the equation $\ln \gamma_1 x_1 = -0.8214$ is 0.111 mole fraction. (At this point $\gamma_1 \approx 3.85$.)

Example 3-6 Estimate the solubility of 1,4-diiodobenzene in water at 25°C, given $T_m = 402.6$K [14], $\Delta H_f = 5340$ cal/mol [14], and $\gamma_1^\infty = 1{,}660{,}000$ [34].

(1) A first approximation of x_1 is $\sim 6 \times 10^{-7}$ $(1/\gamma_1^\infty)$; since this is much less than 0.01, we may use Eq. 3-20.

(2) $$\ln x_1 = \frac{5340}{(1.987)(298.2)}\left(\frac{298.2}{402.6}-1\right) - \ln(1{,}660{,}000)$$

$= -2.337 - 14.322 = -16.659$

$\therefore x_1 = 5.8 \times 10^{-8}$ mole fraction

The reported value for x_1 at this temperature is 1.01×10^{-7} mole fraction [38].

Example 3-7 Estimate the solubility of 4-chloro-1,3-dinitrobenzene in water at 50°C, given $T_m \simeq 328K$ [14] and $\gamma_1^\infty = 27{,}500$ [34]. Assume that no value for ΔH_f is available.

(1) A first approximation of x_1 is 3.6×10^{-5} $(1/\gamma_1^\infty)$; since this is much less than 0.01, we may use Eq. 3-20 after substituting 6.54 $(T-T_m)$ T for the term containing ΔH_f.

(2) $\ln x_1 = 6.54\ (323-328)/323 - \ln (27{,}500)$

$= -0.101 - 10.222 = -10.323$

$\therefore x_1 = 3.3 \times 10^{-5}$ mole fraction.

3-6 AVAILABLE DATA

There are, unfortunately, no comprehensive, up-to-date compilations of the solubilities of organic compounds in organic solvents.[9] A few compilations that may be useful are listed below.

Seidell (1941) [28] — organic compounds.

Seidell and Linke (1952) [29] — organic and inorganic compounds.

Stephen and Stephen (1963) [33] — inorganic and organic compounds.

Linke (1958 [20] and 1965 [21]) — inorganic and metal-organic compounds.

Battino and Clever (1966) [6] — gases in liquids.

A few new publications are expected in the near future; these include a new edition (Vol. 3) for inorganic and organic compounds by Stephen [32] and a new *Solubility Data Series* to be published by Pergamon [15].

Sources of data for melting points (T_m) and heats of fusion (ΔH_f) are listed in Appendix A.

9. More recent compilations of solubilities in water are listed in Chapter 2.

3-7 SYMBOLS USED

a,b,c,d,e,g = parameters in Eqs. 3-1 to -4

a = activity in Eq. 3-8 (unitless)

A = empirical constant in two-suffix Margules Eq. (Footnotes 1 and 5)

f^L = fugacity of a liquid solute in Eq. 3-7

f^V = fugacity of a solute in the vapor phase in Eq. 3-7

ΔG^M = Gibbs free energy of mixing in Eqs. 3-8, -9,

ΔH_f = heat of fusion in Eq. 3-18, -19, -20 (cal/mol)

k,k' = parameters in Eq. 3-6

K_{ow} = octanol-water partition coefficient in Eqs. 3-3, -4,

K_{sw} = partition coefficient for substance between some solvent(s) and water(w); see §3-1

P = total pressure on system in Eqs. 3-16, -17 (e.g., atm or mm Hg)

P_{vp} = vapor pressure of pure substance in Eqs. 3-16, -17 (e.g., atm or mm Hg)

R = gas constant (1.987 cal/mol·deg)

T = temperature (K)

T_m = melting point in Eqs. 3-18, -19, -20 (K)

T_{12}^* = parameter in estimation method for gas solubilities; see §3-1

v_{12}^* = parameter in estimation method for gas solubilities; see §3-1

V = molar volume in Eq. 3-7

x = solubility (mole fraction); also used more generally to specify composition in a binary solution. Equal to ratio of moles of solute to total number of moles of solute and solvent

x_1',x_1'' = limiting solubility points in two-phase, liquid-liquid system; see Figure 3-2b

y = mole fraction of component in vapor phase over binary solution in Eqs. 3-16, -17

Greek

δ = solubility parameter in Eq. 3-7

γ = activity coefficient (mole fraction^{-1})

γ^∞ = infinite dilution activity coefficient (mole fraction^{-1})

ϕ = volume fraction of a component in a binary mixture in Eq. 3-7

Subscripts

1 = solute
2 = solvent
s = solvent
w = water

3-8 REFERENCES

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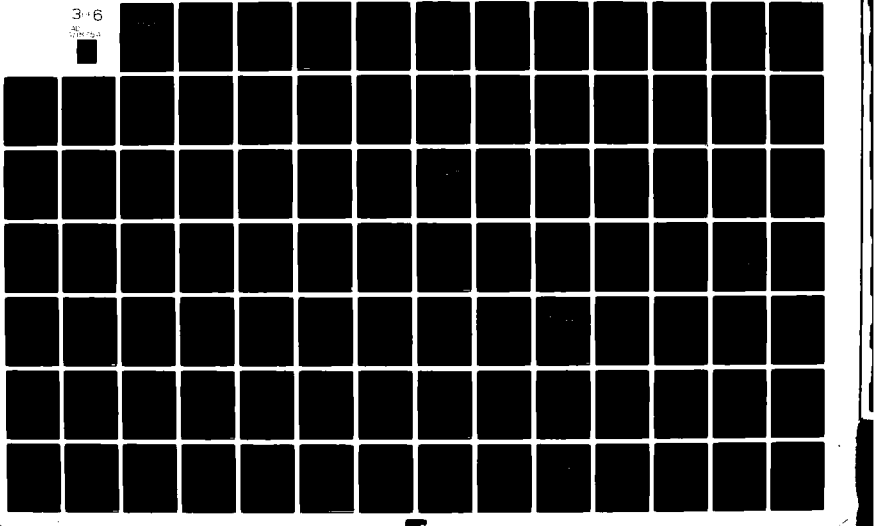
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4

ADSORPTION COEFFICIENT FOR SOILS AND SEDIMENTS

Warren J. Lyman

4-1 INTRODUCTION

The Adsorption Coefficient, K_{oc}. The extent to which an organic chemical partitions itself between the solid and solution phases of a water-saturated or unsaturated soil, or runoff water and sediment, is determined by several physical and chemical properties of both the chemical and the soil (or sediment). In most cases, however, it is possible to express the tendency of a chemical to be adsorbed in terms of a parameter, K_{oc}, which is largely independent of the properties of the soil or sediment. K_{oc} may be thought of as the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium:

$$K_{oc} = \frac{\mu g \text{ adsorbed/g organic carbon}}{\mu g/mL \text{ solution}} \qquad (4\text{-}1)$$

Values of K_{oc} (in the above units) may range from 1 to 10,000,000.[1]

The existence of this chemical-specific adsorption parameter has an important bearing on assessments of the fate and transport of chemicals in soils and sediments. K_{oc} is commonly used in river models, runoff models, and soil/groundwater models where the transport of a specific chemical is being investigated. The degree of adsorption may not only

1. See Table 4-9 for K_{oc} values for selected chemicals.

affect a chemical's mobility but may also be an important parameter in fate processes such as volatilization, photolysis, hydrolysis, and biodegradation. A value of K_{oc} for use in such assessments or models may be easily estimated by the methods described in this chapter.

Since the known methods for estimation are approximate at best, measured values should be used if they are available. The preferred method for measuring adsorption coefficients is to determine an adsorption isotherm with at least one soil or one sediment [12]. Specific soil:solution ratios of the soil and sediment are prepared using six different initial concentrations of the chemical being studied. After the solutions are shaken for about 48 hours to achieve equilibrium, the concentrations in both the solution and solid phases are measured. The amount adsorbed, x/m (μg adsorbed/g of soil or sediment), and the solution concentration, C (μg/mL of solution) are fitted to the Freundlich equation (Eq. 4-2) to determine the adsorption coefficient, K, and the parameter n.[2]

$$x/m = KC^{1/n} \tag{4-2}$$

Values of 1/n in this equation are generally found to range from 0.7 to 1.1 although values as low as 0.3 and as high as 1.7 have been reported [16]. Rao and Davidson [36] compiled measured values for 26 chemicals (mostly pesticides) and found the mean value of 1/n to be 0.87 with a coefficient of variation of ± 15%. No methods are available for estimating n; if a measured value is not available, it is frequently assumed, for convenience, to be equal to 1.

Once a value of K has been determined for a particular soil or sediment, a value of K_{oc} is calculated as follows:

$$K_{oc} = \frac{K}{\%\ oc} \cdot 100 \tag{4-3}$$

where % oc is the percentage of organic carbon contained in the soil or sediment. Numerous studies have shown that values of K_{oc} obtained in this manner (for a specific chemical) are relatively constant and reasonably independent of the soil or sediment used [16,26,36]. The spread of values obtained from a number of different soils and sediments generally results in an uncertainty (coefficient of variation) of 10% to 140%.[3]

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2. The Freundlich equation is frequently written as $x/m = KC^n$. Thus, care should be taken to determine the form of the equation used before any value of n obtained from the literature is used. Note also that K is not the same adsorption coefficient as K_{oc}.
3. See Table 4-9 for examples of uncertainty values.

Some care must be taken with the definitions of K_{oc} implied by Eqs. 4-1 and 4-3. If the adsorption isotherm is nonlinear, the K_{oc} value obtained from Eq. 4-3 would not be the same as the one obtained from a single data point and Eq. 4-1. Both values would differ from the one obtained from an isotherm (several data points) where adsorption was measured in units of $\mu g/g$ of organic carbon.

Some earlier investigations of soil adsorption coefficients reported the results on a soil-organic matter basis (K_{om}) rather than on a soil-organic carbon basis (K_{oc}). Since the organic carbon content of a soil or sediment can be measured more directly, reporting values as K_{oc} is preferred. The ratio of organic matter to organic carbon varies somewhat from soil to soil, but a value of 1.724 is often assumed when conversion is necessary; i.e., $K_{oc} \simeq 1.724\ K_{om}$.

Overview of Estimation Methods. All of the available methods for estimating K_{oc} involve empirical relationships with some other property of the chemical — water solubility (S), octanol-water partition coefficient (K_{ow}), bioconcentration factor for aquatic life (BCF), or parachor (P). The relationships are regression equations obtained from various data sets and are usually expressed in log-log form:

$$\log K_{oc} = a \log (S, K_{ow}, \text{or BCF}) + b \qquad (4\text{-}4)$$

where a and b are constants. Parachor (P) is regressed directly with log K_{oc}.

Although K_{ow} has been used most frequently, about a dozen equations of the above form have been reported. Each was derived from a different data set representing different chemicals (sometimes just one or two chemical classes) and ranges of the parameters involved. Many of the chemicals are insecticides, herbicides, fungicides, or compounds of related structure. Aromatic and polynuclear aromatic hydrocarbons are also well represented.

Many of the available K_{oc} values appear to have been used in one or more of the reported regression equations; thus, there is no independent data set (covering a range of chemical classes and K_{oc} values) with which to test the reported equations for accuracy or general applicability and to determine which are the best. Some guidance can be given, however, on the basis of (1) the chemicals or chemical classes used in the regression equation, (2) the range of K_{oc} values covered by the equation, and (3) the quality of fit (represented by the coefficient, r^2, reported for the equation).

The uncertainty associated with any value of K_{oc} estimated by one of these equations is generally less than one order of magnitude (i.e., less than ± a factor of 10). This assumes that the estimated K_{oc} is to be used for an environmental system that does not differ significantly from one implied by the normal conditions of test (temperature, soil pH, chemical concentration, salinity, etc.).[4] Attempts to extrapolate much beyond these conditions will invite additional errors. Potential errors in estimated values of K_{oc} are discussed in greater detail in §4-2.

Not all procedures for estimating K_{oc} were considered appropriate for inclusion in this handbook. One general method correlates K_{oc} with R_f values obtained from soil thin-layer chromatography tests.[5] Various authors [5,15,17,29] have shown a reasonably good correlation between these properties, but three of them gave no regression equations and the fourth [15] required an additional parameter (the pore fraction of the soil). Furthermore, only a few chemical classes were represented in these studies.

A correlation between K_{oc} and linear free-energy parameters such as Hammet and Taft constants might be expected. Briggs [4] described such a correlation for a series of substituted phenylureas, but his study is the only one reported in the literature, and it gave no regression equations. Therefore, this general approach must be excluded for the present.

Other, more theoretical approaches to the estimation of K_{oc} have been proposed (see, for example, Ref. 32), but none offers any practical solution with readily available data.

Factors Influencing the Values of K and K_{oc}. Numerous publications provide reviews and informative discussions of the various factors influencing the values of K and K_{oc} for organic chemicals.[6] The information given below provides an overview.

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4. The EPA's test recommendations [12] include the following: use of soils with pH between 4 and 8, organic matter content between 1% and 8%, cation exchange capacity greater than 7 MEQ/100g, and a sand composition less than 70%; use of distilled-deionized water adjusted to pH 7; soil:solution ratio of 1:5; initial chemical concentrations from 0.05 to about 30 μg/mL; temperature at 20°C; equilibrium conditions (48 hours). Most of the reported data derived from the shake-slurry method have used conditions roughly similar to the above.
5. The EPA's proposed protocol for this test is described in Ref. 12.
6. In particular, Refs. 1, 2, 3, 6, 10, 14, 16, 23, 25, 26, 29, 33, 36, and 42.

By basing the adsorption coefficients on soil (or sediment) organic carbon (K_{oc}) rather than on total mass (K), one can eliminate much, but not all, of the variation in sorption coefficients between different soils, sediments, etc. The remaining variation may be due to other characteristics of soils (clay content and surface area, cation exchange capacity, pH, etc.), the nature of the organic matter present, and/or variations in the test methods. Numerous studies of the correlation of K with all of these variables have found that the organic carbon content usually gives the most significant correlation. Furthermore, this correlation often extends over a wide range of organic carbon content — from ~ 0.1% to nearly 20% of the soil in some cases [42].

The emphasis in this chapter on the K_{oc} parameter should not be taken to imply that organic chemicals will not adsorb on minerals free of organic matter. Some adsorption will always take place, and it may be significant under certain conditions such as (1) in clays with very high surface area, (2) where cation exchange (e.g., for dissociated organic bases) occurs, (3) where clay-colloid-induced polymerization occurs, and/or (4) where chemisorption is a factor. Thus, the use of K_{oc} values (measured or estimated) may be completely inappropriate in soils or sediments that are essentially free of organic matter. Methods for estimating adsorption coefficients under these conditions are not currently available.

Other factors that affect the measured value of K_{oc} or are operative under actual environmental conditions are listed below and then discussed individually. Differences in laboratory procedures can also have a significant effect.

Temperature

pH of soil and water

Particle size distribution and surface area of solids

Salinity of water

Concentration of dissolved organic matter in water

Suspended particulate matter in surface water

Non-equilibrium adsorption mechanisms or failure to reach equilibrium conditions

Solids to solution ratio

Loss of chemical (in test) due to volatilization, chemical or biological degradation, adsorption on flask walls, etc.

Nonlinear isotherm

- *Temperature.* As adsorption is an exothermic process, values of K (or K_{oc}) usually decrease with increasing temperature. Heats of adsorption associated with physical adsorption are typically a few hundred calories per degree per mole [16]. With a heat of adsorption of −500 cal/degree · mole), one would expect about a 10% decrease in K (or K_{oc}) with a temperature rise from 20°C to 30°C; an 18% increase would be expected for a temperature drop from 20°C to 5°C. Care should be taken in predicting such changes; with some chemicals, temperature has no effect, or even the opposite effect, on adsorption [3].

- *pH.* Only chemicals that tend to ionize are much affected by pH; neutral chemicals are little influenced [2,16,33]. Weak acids and weak bases show the greatest sensitivity to pH changes in the range normally encountered in soils and surface waters (pH 5-9). The general rule is that the neutral species of an acid adsorbs much more strongly than the anion. For organic acids, adsorption begins to be appreciable when the pH of the bulk solution is approximately 1.0 to 1.5 units above the pK_a value of the acid [33]. The cations resulting from the dissociation of an organic base may be strongly sorbed on soils carrying net negative charges.

- *Particle size distribution and surface area.* The fine silt and clay fractions of soils and sediments have the greatest tendency to adsorb chemicals. Variation in adsorption between different size fractions is mostly a reflection of their organic carbon content, but surface area and other factors may also be involved [24,25,36,41].

- *Salinity.* An increase in salinity can significantly lower the adsorption coefficient of basic materials that are in the cation form. This may result from a displacement of the cations from the soil matrix (cation exchange) or some other action related to the lower activity of the chemical as the ionic strength of the solution increases [16]. The adsorption of some acid herbicides increases with greater salinity at pH values above the pK_a of the acid [33]. Clearly, pH significantly influences the direction and magnitude of salinity effects for organic acids and bases. Neutral molecules are generally less affected by salinity but may show increased adsorption with increasing salt concentration. For example, the adsorption of pyrene on a silt fraction of a stream sediment was found to increase 15% over the no-salt solution when 20 mg/mL of NaCl was added [25]. This salt concentration is close to that of seawater.

- *Dissolved organic matter.* The presence of dissolved organic matter commonly reduces the adsorption of a chemical. This may be due to the increased solubility of the chemical in such a solution or to competitive adsorption [19,34,44].

- *Suspended particulate matter.* In surface waters, suspended particles adsorb organic chemicals from the surrounding solution. This can increase the apparent "solution concentration," depending on the degree of filtration used to define the solution phase. In fast-flowing streams and rivers, the suspended particulate matter may not differ much in composition or nature from the bottom sediments, so K_{oc} values from soil or sediment measurements may be used to estimate the amount of chemical adsorbed on this matter. In ponds, lakes, and oceans, however, a large fraction of the suspended particulate matter may be made up of microorganisms with significantly different adsorption characteristics from those of soils and sediments. Some information on the subject of adsorption of organic chemicals on microorganisms in natural waters is given in Refs. 21, 22, and 31. Swisher [43] has compiled numerous coefficients for the adsorption of surfactants onto the solids in sewage sludge, which contains a high fraction of microorganisms.

- *Non-equilibrium adsorption.* Non-equilibrium adsorption commonly occurs when a chemical moves through an environmental compartment so rapidly that equilibrium cannot be achieved. Less commonly, it can be the result of hysteresis, which causes the adsorption and desorption processes for a chemical to follow different isotherms.[7] This usually indicates some degree of irreversible adsorption. Studies reported in the literature are sometimes conflicting; Rao and Davidson [36] have critically reviewed the available information and concluded that, while hysteresis in adsorption isotherms is often an artifact of the laboratory test methods used, it can be real and significant for some compounds.

- *Solids to solution ratio.* Changes in the water content of a soil or sediment will change the fraction of a chemical that is adsorbed: as the water content is lowered, the fraction adsorbed will increase, as does that in solution. Whether or not a change in K (or K_{oc}) is also to be expected with a change in water content is not clear, as conflicting results have been reported [16].

7. Values of K and K_{oc} are almost always measured after an adsorption process (i.e., starting with an adsorbent free of the chemical) rather than a desorption process (i.e., starting with excess chemical on the adsorbent).

- *Loss of chemical during test.* Measurements of adsorption coefficient can obviously be distorted by losses of a chemical due to volatilization, chemical or biological degradation, adsorption on walls, etc. Some chemicals may undergo clay-colloid-induced hydrolysis and polymerization. Since similar processes may alter the amount of adsorption measured in the environment, this possibility should be considered when laboratory test data are reviewed and when such data (measured or estimated) are used in environmental assessments.

- *Nonlinear isotherm.* If the adsorption isotherm is nonlinear, the reported value of K_{oc} will depend on the range of chemical concentrations used in the tests.

4-2 AVAILABLE ESTIMATION METHODS

Regression Equations. All available methods for estimating K_{oc} involve correlations with one other property of the chemical: water solubility (S), octanol-water partition coefficient (K_{ow}), bioconcentration factors for aquatic life (BCF), or parachor (P). Twelve regression equations (4-5 through 4-16) are given in Table 4-1 along with some basic information on the data set used to derive each equation. Table 4-2 provides more detailed information on the ranges of the two parameters associated with each data set and indicates the subsequent table or figure in which the chemicals and data are shown.

(Continued on p. 4-19)

TABLE 4-1

Regression Equations for the Estimation of K_{oc}

Eq. No.	Equation[a]	No.[b]	r^2[c]	Chemical Classes Represented	Ref.
4-5	$\log K_{oc} = -0.55 \log S + 3.64$ (*S in mg/L*)	106	0.71	Wide variety, mostly pesticides	[26]
4-6	$\log K_{oc} = -0.54 \log S + 0.44$ (S in mole fraction)	10	0.94	Mostly aromatic or polynuclear aromatics; two chlorinated	[25]
4-7[d]	$\log K_{oc} = -0.557 \log S + 4.277$ (S in μ moles/L)	15	0.99	Chlorinated hydrocarbons	[11]
4-8	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45	0.74	Wide variety, mostly pesticides	[26]
4-9	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	19	0.95	Aromatics, polynuclear aromatics, triazines and dinitroaniline herbicides	[9]
4-10	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10	1.00	Mostly aromatic or polynuclear aromatics; two chlorinated	[25]
4-11	$\log K_{oc} = 0.94 \log K_{ow} + 0.02$	9	e	s-Triazines and dinitroaniline herbicides	[7]
4-12	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	13	0.91	Variety of insecticides, herbicides and fungicides	[36]
4-13[d]	$\log K_{oc} = 0.524 \log K_{ow} + 0.855$	30	0.84	Substituted phenylureas and alkyl-N-phenylcarbamates	[5]
4-14[d,f]	$\log K_{oc} = 0.0067 (P - 45N) + 0.237$	29	0.69	Aromatic compounds: ureas, 1,3,5-triazines, carbamates, and uracils	[18]
4-15	$\log K_{oc} = 0.681 \log BCF(f) + 1.963$	13	0.76	Wide variety, mostly pesticides	[26]
4-16	$\log K_{oc} = 0.681 \log BCF(t) + 1.886$	22	0.83	Wide variety, mostly pesticides	[26]

a. K_{oc} = soil (or sediment) adsorption coefficient; S = water solubility; K_{ow} = octanol-water partition coefficient; BCF(f) = bioconcentration factor from flowing-water tests; BCF(t) = bioconcentration factor from model ecosystems; P = parachor; N = number of sites in molecule which can participate in the formation of a hydrogen bond.

b. No. = number of chemicals used to obtain regression equation.

c. r^2 = correlation coefficient for regression equation.

d. Equation originally given in terms of K_{om}. The relationship $K_{om} = K_{oc}/1.724$ was used to rewrite the equation in terms of K_{oc}.

e. Not available.

f. Specific chemicals used to obtain regression equation not specified.

TABLE 4-2

Information on Equations Given for Estimation of K_{oc}

Eq. No.	Parameter Required[a]	Range of Parameter[b]	Range of K_{oc} Values[b]	Chemicals Used for Regression Listed in Table	Data and/or Regression Eq. Plotted in Figure
4-5	S (mg/L)	0.0005 – 1,000,000	1 – 1,000,000	4-3	4-1
4-6	S (mole fraction)	(0.03 – 410,000) x 10^{-9}	80 – 1,000,000	4-4	4-1
4-7	S (μ moles/L)	0.002 – 100,000	30 – 380,000	4-5	4-1
4-8	K_{ow}	0.001 – 4,000,000	10 – 1,000,000	4-3	4-2
4-9	K_{ow}	100 – 4,000,000	100 – 1,000,000	4-4, 4-6	4-2
4-10	K_{ow}	100 – 4,000,000	100 – 1,000,000	4-4	4-2[e]
4-11	K_{ow}	150 – 200,000	180 – 31,000	4-6	4-2[f]
4-12	K_{ow}	0.3 – 400,000	2 – 250,000	4-7	4-2
4-13	K_{ow}[c]	3 – 2,200	10 – 400	4-8	4-2 (eq. only)
4-14	P[c,d]	g	g	g	g
4-15	BCF(f)	1 – 100,000	30 – 1,000,000	4-3	4-3
4-16	BCF(t)	0.02 – 100,000	10 – 250,000	4-3	4-3

a. S = water solubility; K_{ow} = octanol-water partition coefficient; P = parachor; BCF(f) = bioconcentration factor from flowing-water tests; BCF(t) = bioconcentration factor from model ecosystems.

b. Approximate range of data used for regression equation.

c. Equation was originally given in terms of K_{om} and rewritten in terms of K_{oc} using the relationship $K_{om} = K_{oc}/1.724$.

d. One additional parameter, obtained by visual inspection of chemical's structural formula, is required: N = number of sites in the molecule which can participate in the formation of hydrogen bonds.

e. Data included in the set used for Eq. 4-9 and are generally those with the higher K_{oc} and K_{ow} values. Regression equation not shown.

f. Data included in the set used for Eq. 4-9 and are generally those with the lower K_{oc} and K_{ow} values. Regression equation not shown.

g. The specific chemicals and data used to obtain the regression equation were not given.

TABLE 4-3

Compounds Used by Kenaga and Goring [26] for Regression Equations[a]

Compound	Used in Correlation With:[b] S	K_{ow}	BCF(f)	BCF(t)
Halogenated Hydrocarbon Insecticides				
Aldrin	X			X
DDT	X	X	X	X
Lindane	X		X	X
Methoxychlor	X	X	X	X
Substituted Benzenes and Halobenzenes				
Hexachlorobenzene	X	X	X	X
Chloroneb	X			
Chlorthiamid	X			
Dichlobenil	X			X
Methazole	X			
Norfluorazon	X			
Oxadiazon	X			
Halogenated Biphenyls and Diphenyl Oxides				
2,2',4,5,5'-Pentachlorobiphenyl (Aroclor 1254)	X	X	X	X
2,2',4,4',5,5'-Hexachlorobiphenyl	X	X	X	
Aromatic Hydrocarbons				
Anthracene	X	X		
Benzene	X	X		
9-Methylanthracene	X	X		
2-Methylnaphthalene	X	X		
Naphthalene	X	X		
Phenanthrene	X	X		
Pyrene	X	X		
Tetracene	X	X		
Fumigants				
cis-1,3-Dichloropropene	X			
trans-1,3-Dichloropropene	X			
Dibromochloropropane	X			
Ethylene dibromide	X			
Methyl isothiocyanate	X			
Phosphorus-Containing Insecticides				
Crotoxyphos	X			
Disulfoton	X			
Phorate	X			
Diamidaphos	X		X	
Carbophenothion	X			
Chlorpyrifos	X	X	X	X
Chlorpyrifos-methyl	X	X		X
Ethion	X			
Leptophos	X	X	X	X
Methyl parathion	X	X		X
Parathion	X	X		X

a. Eqs. 4-5, -8, -15, -16.

b. For symbols, see footnote a of Table 4-2.

(continued)

TABLE 4-3 (Continued)

Compound	Used in Correlation With: S	K_{ow}	BCF(f)	BCF(t)
Carbamates, Thiocarbamates, and Carbamoyl Oximes				
Carbaryl	X	X		
Chlorpropham	X			
Propham	X			
Cycloate	X			
Diallate	X			
EPTC	X			
Pebulate	X			
Triallate	X			
Methomyl	X	X		
Carboxylic Acids and Esters				
Chloramben	X			
Chloramben, methyl ester	X			
6-Chloropicolinic acid	X	X		X
2,4-D acid	X	X		
Dicamba	X			
3,6-Dichloropicolinic acid	X			
Picloram	X	X		X
Silvex	X			
2,4,5-T	X	X		X
Triclopyr	X	X		X
Dinitroanilines				
Benefin	X			
Butralin	X			
Dinitramine	X			
Fluchloralin	X			
Isopropalin	X			
Nitralin	X			
Profluralin	X			
Trifluralin	X	X	X	X
Ureas and Uracils				
Chlorbromuron	X			
Chloroxuron	X			
Diflubenzuron	X			
Diuron	X	X		
Fenuron	X	X		
Fluometuron	X	X		
Linuron	X	X		
Metobromuron	X			
Monolinuron	X	X		
Monuron	X	X		
Neburon	X			
Tebuthiuron	X			
Urea	X	X		
Bromacil	X			
Isocil	X			
Terbacil	X			

(continued)

TABLE 4-3 (Continued)

Compound	Used in Correlation With: S	K_{ow}	BCF(f)	BCF(t)
Symmetrical Triazines				
Ametryn	X			
Atrazine	X	X		X
Cyanazine	X	X		
Dipropetryn	X			
sec-Bumeton	X			
Ipazine	X	X		
Prometon	X			
Prometryn	X			
Propazine	X	X		
Simazine	X	X	X	
Terbutryn	X			
Trietazine	X	X		
Miscellaneous Nitrogen Heterocyclics				
2-Methoxy-3,5,6-trichloropyridine	X	X		
Nitrapyrin	X	X		
Pyroxychlor	X			X
3,5,6-Trichloro-2-pyridinol	X	X	X	X
Metribuzin	X			
Pyrazon	X			
Thiabendazole	X			
Miscellaneous				
Dinoseb	X	X		
Pentachlorophenol	X		X	X
Phenol	X			
Aroclor	X	X		
Napropamide	X			
Pronamide	X			
Propachlor	X	X		X
Asulam	X			

TABLE 4-4

Compounds Used by Karickhoff *et al.* [25] for Regression Equations[a]

Compounds	
Anthracene	2-Methylnaphthalene
Benzene	Naphthalene
Hexachlorobiphenyl	Phenanthrene
Methoxychlor	Pyrene
9-Methylanthracene	Tetracene

a. Eqs. 4-6, 4-10, and (in part) 4-9.

TABLE 4-5

Compounds Used by Chiou *et al.* [11] for Regression Equation[a]

Compounds	
β-BHC	Parathion
1,2-Bromo-3-chloropropane	2,4'-PCB
DDT	2,5,2',5'-PCB
1,2-Dibromomethane	2,4,5,2',4',5'-PCB
1,2-Dichlorobenzene	1,1,2,2-Tetrachloroethane
1,2-Dichloroethane	Tetrachloroethene
1,2-Dichloropropane	1,1,1-Trichloroethane
Lindane	

a. Eq. 4-7.

TABLE 4-6

Compounds Used by Brown *et al.* [7,9] for Regression Equations[a]

Compounds		
Atrazine	Propazine	Trifluralin
Cyanazine	Simazine	Two photodegradation products of trifluralin
Ipazine	Trietazine	

a. Eqs. 4-9 (in part) and 4-11.

TABLE 4-7

Compounds Used by Rao and Davidson [36] for Regression Equation[a]

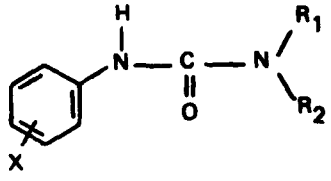
Compounds		
Atrazine	Dicamba	Malathion
Bromacil	Dichlobenil	Methylparathion
Carbofuran	Diuron	Simazine
2,4-D	Lindane	Terbacil
DDT		

a. Eq. 4-12.

TABLE 4-8

Compounds Used by Briggs [5] for Regression Equation[a,b]

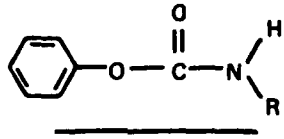
Substituted Phenylureas



X	R_1	R_2
4-Cl	CH_3	CH_3
3,4-Cl	CH_3	CH_3
3-CF_3	CH_3	CH_3
3-Cl, 4-OCH_3	CH_3	CH_3
4-Cl	CH_3	OCH_3
3,4-Cl	CH_3	OCH_3
4-Br	CH_3	OCH_3
3-Cl, 4-Br	CH_3	OCH_3
3-Cl	CH_3	H
3,4-Cl	CH_3	H
3-Cl, 4-OCH_3	CH_3	H

X	R_1	R_2
3-Cl	H	H
3,4-Cl	H	H
3-Cl, 4-OCH_3	H	H
3-F	H	H
4-F	H	H
3-CF_3	H	H
3-Br	H	H
4-Br	H	H
3-OH	H	H
4-SO_3^-	H	H
H	H	H

Alkyl-N-Phenylcarbamates



R
CH_3
CH_2CH_3
$CH_2CH_2CH_3$
$CH(CH_3)_2$
$CH_2CH_2CH_2CH_3$

a. Eq. 4-13.

b. Although Briggs [5] states that 30 compounds were used to derive the regression equation, only 28 were listed in the reference cited [4] for the original data.

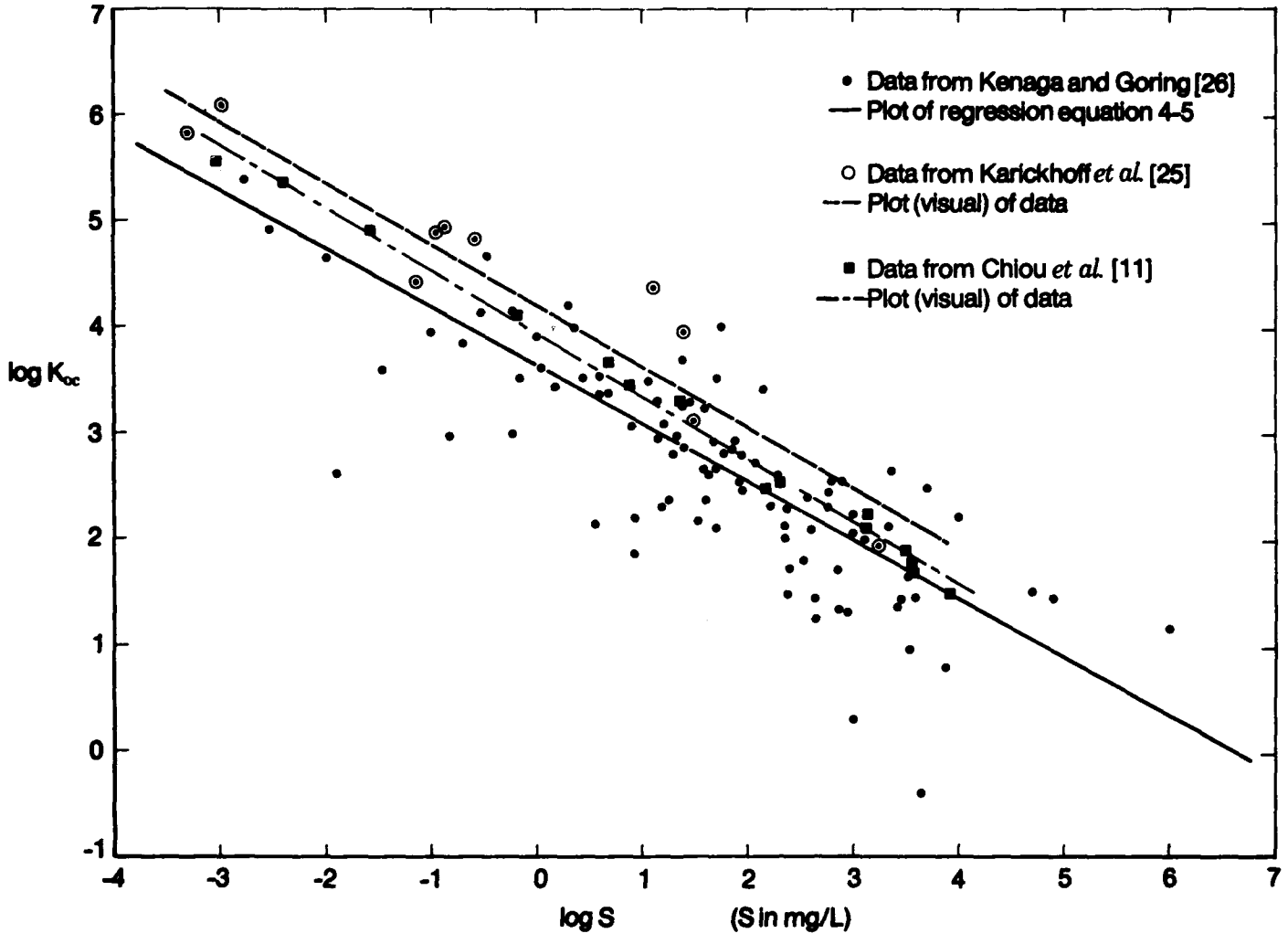


FIGURE 4-1 Correlation Between Adsorption Coefficient and Water Solubility

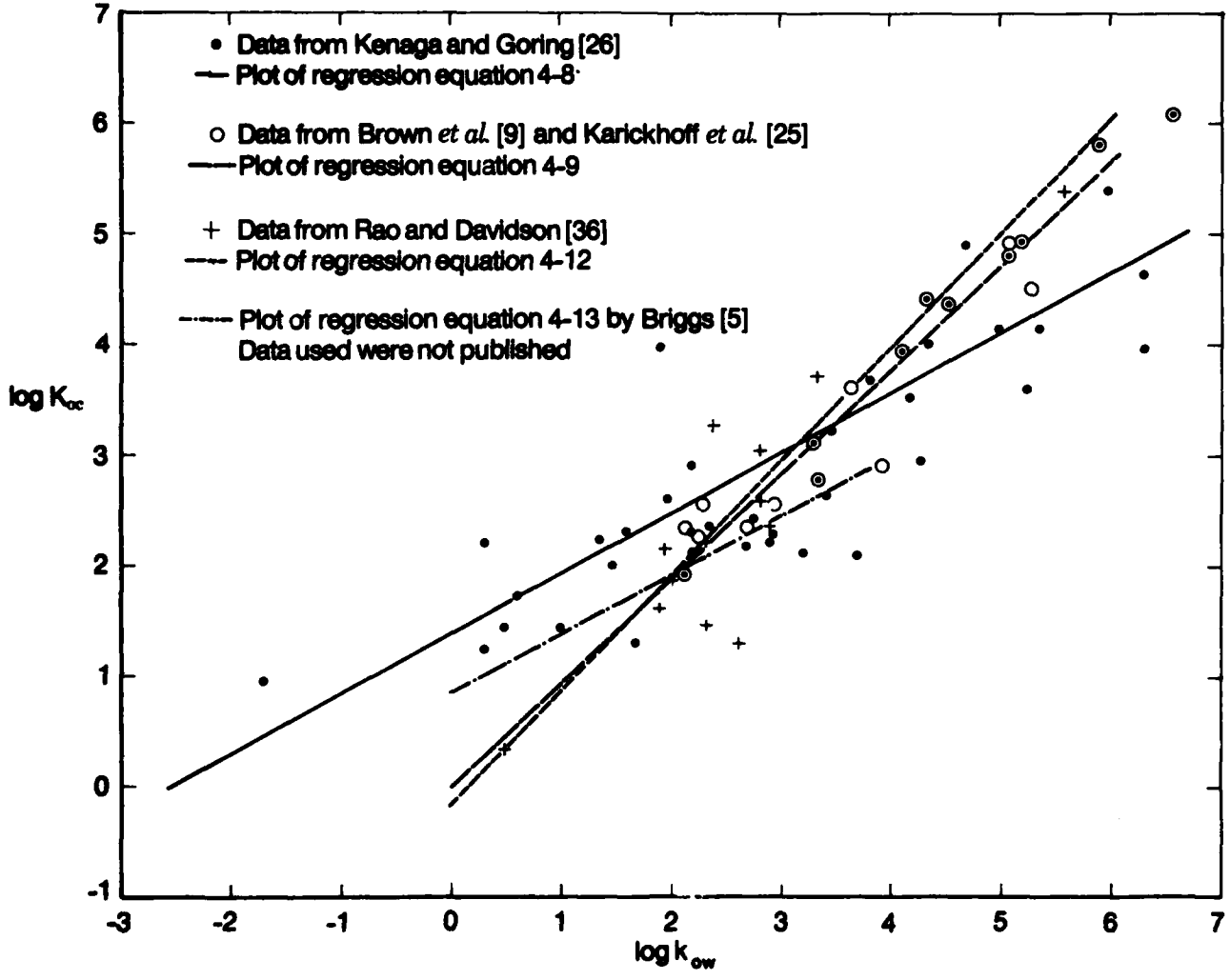


FIGURE 4-2 Correlation Between Adsorption Coefficient and Octanol-Water Partition Coefficient

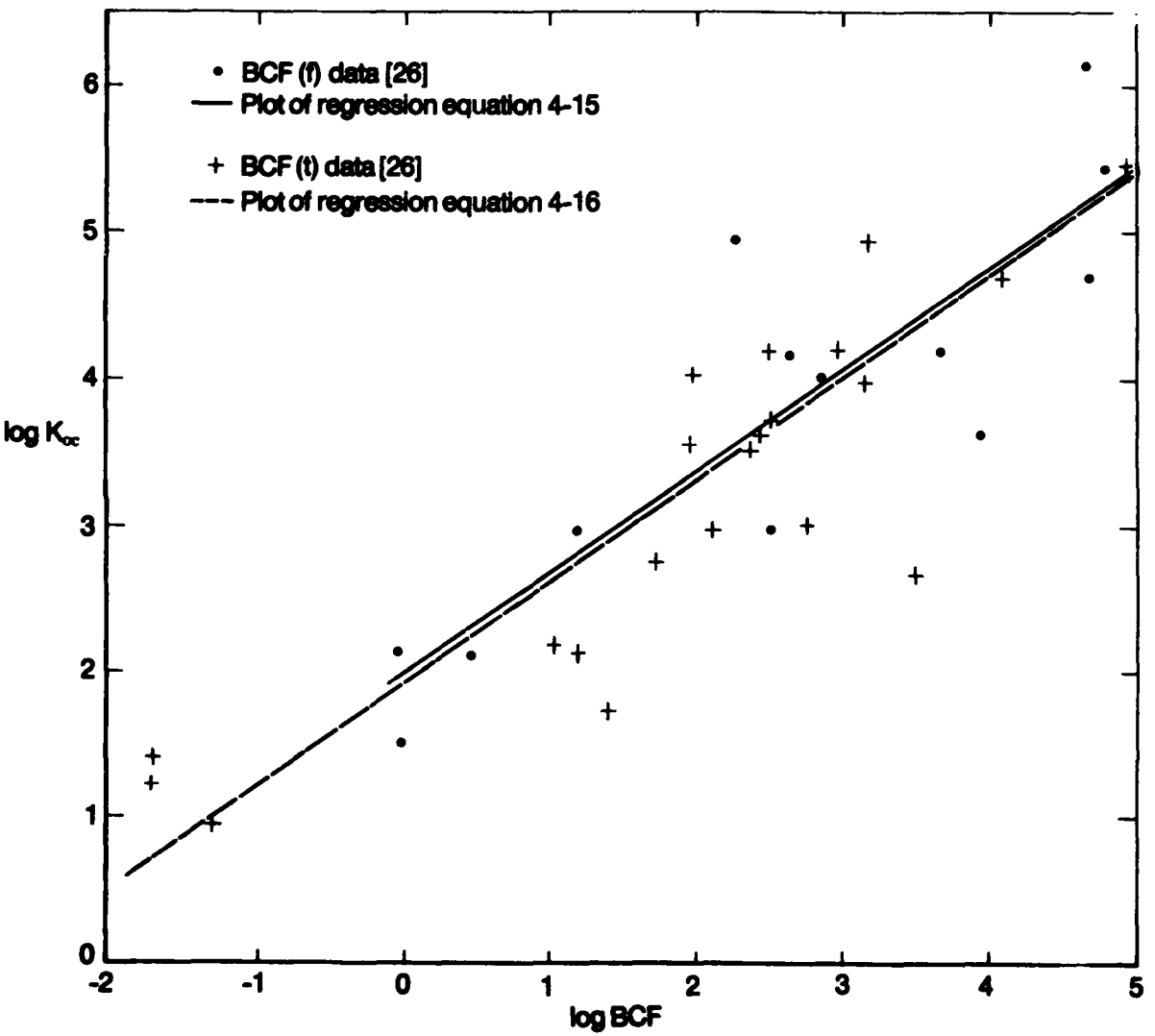


FIGURE 4-3 Correlation Between Adsorption Coefficient and Bioconcentration Factors

Except for parachor, all of the input parameters for these equations are commonly encountered with organic chemicals of environmental concern. Parachor is a constitutive and additive function of molecular structure and, for liquids, is defined as

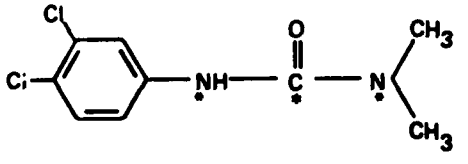
$$P = \frac{M\sigma^{1/4}}{\rho - \rho^{\circ}} \tag{4-17}$$

where M is the molecular weight, σ the surface tension, ρ the liquid density and ρ° the vapor density [28]. Since ρ° is much smaller than ρ, Eq. 4-17 may be rewritten as

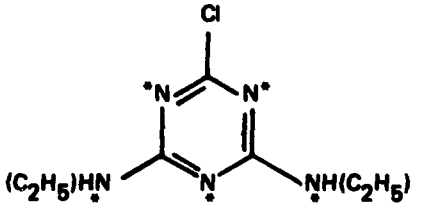
$$P = \frac{M\sigma^{1/4}}{\rho} \quad \text{or} \quad P = V\sigma^{1/4} \tag{4-18}$$

where V is the molar volume. Values of P may be obtained: (1) from Eq. 4-18 (if data are available),[8] (2) from tables of measured values in the literature (such as Ref. 35), or (3) estimated via the addition of fragment constants[8] [35,38]. Parachor values, in units of $g^{1/4} \cdot cm^3/(sec^{1/2} \cdot mol)$, are generally in the range of 100-600.

The parachor regression equation (4-14 in Table 4-1) given by Hance [18] is an extension of the work of Lambert [28], who also found a correlation between the adsorption coefficient and P for two chemical classes. The extension involved reducing the parachor value by 45N, where N is the number of proton- or electron-donating sites on the molecule that could conceivably participate in hydrogen bond formation. For the classes of compounds studied by Hance, such sites were taken to include the following groups: primary, secondary, and tertiary amines (RNH_2, R_2NH, R_3N), carbonyl ($R_2C{=}O$), heterocyclic nitrogen (nitrogen in a ring), and ether oxygen (R-O-R'). Two examples of the determination of N are shown below. The sites counted are marked with an asterisk.



Diuron (N = 3)



Simazine (N = 5)

8. Methods for estimating liquid density and surface tension are given in Chapters 19 and 20, respectively. Tables 12-3, 12-4 and 20-2 contain fragment constants for P.

Other structural groups (not in the chemicals studied by Hance) that should probably be counted in N are: hydroxyl (ROH), acid (RCOOH), ester (RCOOR), peroxide (R-O-O-R), and any other group to which hydrogen might bond.

Selection of the Most Appropriate Equation(s). One or more equations should be selected on the basis of (1) the data available on the chemical, (2) the chemical classes covered by each regression equation, and (3) the range of K_{oc} (and input parameter) values covered by each regression equation.

- *Available data.* (See Table 4-2 for input data requirements.) Highest priority should be given to the most accurate data from actual measurements. If, for example, only the solubility is known, then either Eq. 4-5, 4-6 or 4-7 must be chosen. If data are available for all input parameters, and if the other two criteria are not decisive, the following priorities can be applied: $K_{ow} \gtrsim S > P > BCF(t) \gtrsim BCF(f)$. If no measured data are available, estimated values may be used with the following suggested priority: $K_{ow} > S > P$.[9]

- *Chemical classes.* If the chemical for which K_{oc} is to be estimated is in a class covered by one or more of the regression equations (see Tables 4-1 and 4-2), these equations should be given priority. If there is no clear match of chemical classes, it is suggested that Eq. 4-5 or 4-8 be selected, as these were derived from the widest variety of chemicals.

- *Ranges.* In general, a regression equation should not be used for estimation if the value of either the input parameter (K_{ow}, S, P, BCF) or K_{oc} is outside the range covered by the data set from which the equation was obtained. (Ranges shown in Table 4-2.) Otherwise, the estimate may be subject to significant additional uncertainty.

Basic Steps for Estimating K_{oc}, K, and x/m

(1) Select from Table 4-1 the most appropriate equation(s) for estimating K_{oc}, using the criteria discussed in the subsection above.

(2) Calculate the value of K_{oc} using the selected equations. (Examples are given in the following subsection.) If all equations used appear equally applicable and the input

9. Estimation methods for K_{ow} are given in Chapter 1, and for S in Chapter 2. Estimation methods for P are given in Refs. 35 and 38. Simple tables of fragment constants for the estimation of P are given in Tables 12-3, 12-4 and 20-2.

data used for each equation have approximately the same uncertainty, an average value may be reported. In this case it is probably better to use the geometric mean than a simple average. To obtain the geometric mean, take the log of each estimate, average the logs, and find the antilog.

(3) If desired, an adsorption coefficient for a particular soil (K) with a known organic carbon content (% oc) may be calculated (cf. Eq. 4-3) from the expression $K = K_{oc}(\%\ oc)/100$.

(4) The amount of the chemical that would be adsorbed (x/m, in μg adsorbed per g of adsorbent) in a solution with a known equilibrium concentration (C, in μg/mL) is calculated as follows (cf. Eq. 4-2):

$$x/m = KC^{1/n}$$

The exponent 1/n may be taken as: (a) 1.0 if a linear isotherm is likely, (b) 0.87 (the average for 26 pesticides; see §4-1) if a nonlinear isotherm is likely, or (c) any other value that appears reasonable, considering values measured for similar compounds in equivalent concentration ranges.[10]

Example 4-1 Estimate K_{oc}, K, and x/m for hexachlorobenzene, given a water solubility (S) of 0.035 mg/L, a soil organic carbon content of 2%, and a solution concentration (C) of 0.01 mg/L. The molecular weight of hexachlorobenzene is 284.8.

(1a) From Eq. 4-5, with S in mg/L

$$\log K_{oc} = -0.55 \log (0.035) + 3.64 = 4.44$$

$$K_{oc} = 27{,}600$$

(1b) From Eq. 4-6, with S in mole fraction

$$\log K_{oc} = -0.54 \log \left(\frac{0.035 \times 10^{-3}}{284.8 \times 55.51} \right) + 0.44 = 5.11$$

$$K_{oc} = 130{,}000$$

(1c) From Eq. 4-7, with S in μ moles/L

$$\log K_{oc} = -0.557 \log \left(\frac{0.035 \times 10^{3}}{284.8} \right) + 4.277 = 4.78$$

10. The reader should be aware that the use of Eq. 4-2 outside the normal concentration range used for measurements of K, as well as the use of an assumed value for 1/n, will result in an additional uncertainty in the estimated value of x/m. This is discussed in a following subsection.

K_{oc} = 60,800

Note: The geometric mean of these three estimates, with the assumption of equal method error for each equation, is 60,200. However, based upon considerations of chemical class, Eq. 4-7 is probably the most applicable; Eqs. 4-6 and 4-5 are second and third choice respectively. A (subjective) weighted average estimate would thus be ~80,000 for K_{oc}. Recent measurements of K_{oc} for this chemical gave values in the range of 80,000-100,000, depending on whether the measurement was for a whole sediment or only the fines fraction [8]; thus, the value listed in Table 4-9 (~3,900) may be considered suspect.

(2) Using Eq. 4-3 and 80,000 for K_{oc}

$K = 80{,}000\ (2)/100 = 1{,}600$

(3) Using Eq. 4-2 with n=1 and C in μg/mL

$x/m = 1{,}600\ (0.01)^{1/1} = 16\ \mu g/g$

Example 4-2 Estimate K_{oc}, K, and x/m for trichloroethylene, given an octanol-water partition coefficient (K_{ow}) of 195, a soil organic carbon content of 5%, and a solution concentration of 10 mg/L.

(1a) From Eq. 4-8

$\log K_{oc} = 0.544 \log (195) + 1.377 = 2.62$

$K_{oc} = 420$

(1b) From Eq. 4-9

$\log K_{oc} = 0.937 \log (195) - 0.006 = 2.14$

$K_{oc} = 140$

(1c) Similarly, Eqs. 4-10 to 13 yield K_{oc} values of 120, 150, 150, and 110, respectively. The agreement is relatively good, considering that chlorinated hydrocarbons are poorly represented, if at all, in some of the equations.

(2) Using Eq. 4-3 and a geometric mean of 160 for K_{oc}

$K = 160\ (5)/100 = 8.0$

(3) Using Eq. 4-2 with n=1 and C in μg/mL

$x/m = 8\ (10)^{1/1} = 80\ \mu g/g$

Example 4-3 Estimate K_{oc} for methylphenylaminoacetone, given a parachor (P) of 382.9 [35].

(1) The number (N) of potential hydrogen bonding sites is 2 (1 amino and 1 ketone)

(2) Using Eq. 4-14

$$\log K_{oc} = 0.0067\ [382.9 - 45\ (2)] + 0.237 = 2.20$$

$$K_{oc} = 160$$

Example 4-4 Estimate K_{oc} for heptachlor, given BCF (f) = 17,400 and BCF (t) = 2,150 [26].

(1) Using Eq. 4-15

$$\log K_{oc} = 0.681 \log (17,400) + 1.963 = 4.85$$

$$K_{oc} = 71,000$$

(2) Using Eq. 16

$$\log K_{oc} = 0.681 \log (2,150) + 1.886 = 4.16$$

$$K_{oc} = 14,000$$

(3) The geometric mean is 31,500.

Uncertainty in Estimated Values. The uncertainty in values of K_{oc}, K, and x/m estimated from the equations given is related to a number of factors, including: (1) method errors, (2) uncertainty in the input data, (3) variability in environmental factors (e.g., temperature, pH, salinity), and (4) errors resulting from extrapolation based on assumptions of a linear isotherm and reversible adsorption. Method errors in the estimation of K_{oc} are typically less than one order of magnitude; a worst-case combination of the other factors can combine to make the real error in the estimated value of K_{oc}, K, or x/m over two orders of magnitude. However, an uncertainty of this extent should be relatively rare; even when it does occur, it is not completely unreasonable, as the values of K_{oc} can range over seven orders of magnitude. These error factors are discussed below in more detail.

- *Method error.* A good indication of method errors (i.e., those relating to the quality of fit of the various data sets to the associated regression equations) may be obtained from Figures 4-1, -2, and -3. Table 4-9 lists the method error (expressed as the ratio of the estimated to the measured value of K_{oc}) for a number of chemicals, using, where input data were available, four of the regression equations listed in Table 4-1. The chemicals in Table 4-9 are listed in order of increasing

TABLE 4-9

Comparison of Measured and Estimated Values of K_{oc} for Selected Chemicals

Chemical	Measured Values			Ratio of Estimated/Measured Value of K_{oc}[c]		
	K_{oc}[a]	% CV[b]	Reference	From S (Eq. 4-5)	From K_{ow} (Eq. 4-8)	From BCF (f) or (t) (Eq. 4-15 or -16)
Dicamba	2.2	74	[36]	19	18	
2,4-D	20	72	[36]	5.2	4.6	
Picloram	26	140	[36]	6.0	1.3	0.21 (t)
Carbofuran	29	30	[36]	6.1		
Acetophenone	43		[27]	0.90	4.1	
Ethylene dibromide	44		[26]	1.1		
Benzene	83		[25]	0.86	4.1	
Chlorthiamid	98	28	[36]	1.0		
Simazine	140	13	[36]	16	2.6	0.66 (f)
Atrazine	160	49	[36]	4.0	4.3	2.5 (t)
Fluometron	175		[26]	2.1	0.73	
Carbaryl	230		[26]	2.5	2.0	
p-Cresol	< 500		[40]	> 0.14	> 0.09	
Quinoline	570		[40]	0.06	0.53	
Linuron	860	72	[36]	0.47	0.43	
Nitralin	960		[26]	6.0		
Lindane	1,080	13	[36]	11	0.74	4.4 (f), 5.3 (t)
Disulfoton	1,600	140	[36]	0.46		

(continued)

TABLE 4-9 (Continued)

Chemical	Measured Values K_{oc}[a]	% CV[b]	Reference	Ratio of Estimated/Measured Values of K_{oc}[c] From S (Eq. 4-5)	From K_{ow} (Eq. 4-8)	From BCF (f) or (t) (Eq. 4-15 or -16)
Malathion	1,800	66	[36]	0.16	0.50	
Diallate	1.900		[26]	0.54		
Neburon	3,100	24	[36]	0.59		
Hexachlorobenzene	3,900		[26]	7.1	4.2	11 (f), 0.94 (t)
Parathion	10,600	75	[36]	0.07	0.26	0.38 (t)
Dibenzothiophene	11,200		[20]	0.32	0.51	
Trifluralin	13,700		[26]	0.42	1.4	2.1 (f), 0.59 (t)
2,2',4,5,5'-Pentachlorobiphenyl	42,500		[26]	1.3	1.5	3.2 (f), 1.1 (t)
Methoxychlor	80,000		[25]	1.3	0.10	0.04 (f), 0.14 (t)
DDT	243,000	65	[36]	0.60	0.18	0.69 (f), 0.72 (t)
7,12-Dimethylbenz[a] anthracene	476,000		[30]	0.07	0.09	
Benz[a] anthracene	1,380,000		[40]	0.04	0.03	
Mirex	24,000,000		[40]	0.04		0.0001 (t)

a. Values given are often the mean of measurements on a variety of soils and/or sediments. All values may be assumed to be uncertain by at least 10%. Units of K_{oc} are as shown in Eq. 4-1. In several cases the values of K_{oc} have been rounded off from those given in the original references.

b. % CV = % Coefficient of variation = (standard deviation/mean) x 100. Unlisted values are not available.

c. Input data (values for S, K_{ow}, BCF) obtained from Refs. 20, 25, 26, 30, 36, and 40. No estimates were made if measured values of these input parameters were not available.

K_{oc}; a listing by chemical class would not show any clear differences in uncertainty with chemical class.

It should be noted that data for many of the chemicals listed in Table 4-9 were used in one or more of the reported regression equations. This is because the number of independent values of K_{oc} available was too small and too limited in chemical class coverage to use as a test set. In addition, a regression equation was sometimes used outside the range of values covered by its data set.

As shown by the ratios of estimated to measured values in Table 4-9, 56 of the 71 estimated values (about 80% of the estimates) had errors of less than one order of magnitude; only one estimate (for mirex) was off by more than a factor of ± 35. It is also apparent that Eqs. 4-5 and -8 have a tendency to overestimate low values of K_{oc} and underestimate high values.

- *Uncertainty in input data.* Values of K_{ow}, S, and P can generally be measured with more accuracy than can BCF values. Also, the uncertainty in these parameters generally increases with decreasing S and P, and with increasing K_{ow} and BCF. The uncertainty in the input data used should, if known, be carried through and incorporated with the uncertainty in the reported estimate. The propagation of errors is discussed in Appendix C.

- *Environmental factors.* See "Factors Influencing the Values of K and K_{oc}" in §4-1.

- *Assumption of linear isotherm and reversible adsorption.* No method is available for estimating the exponential fraction in the Freundlich equation (Eq. 4-2). Thus, when values of x/m are calculated for specific soil-solution situations, some value of 1/n must be assumed. The magnitude of the associated error will depend not only on the difference between the real and assumed value of 1/n but also on how far one must extrapolate from the concentration range in which K was measured. Table 4-10 indicates the errors to be expected with the use of a linear isotherm (i.e., 1/n=1), assuming that the value of K is known at a concentration of 1 mg/L.

Errors associated with the assumption of reversible adsorption when irreversible adsorption is taking place have been discussed by Rao and Davidson [36]. Assuming that the value of 1/n found for the adsorption isotherm was 2.3 times the value of 1/n found for the desorption isotherm,

TABLE 4-10

Deviation from Linearity for the Freundlich Adsorption Isotherm (Eq. 4-2)

$$\frac{\text{(x/m) Freundlich}}{\text{(x/m) Linear Distribution}}$$

1/n	Equilibrium Concentration (μg/mL)						
	0.001	0.01	0.1	1	10	100	1000
0.95	1.41	1.26	1.12	1	0.891	0.794	0.708
0.90	2.00	1.59	1.26	1	0.794	0.631	0.501
0.85	2.82	2.00	1.41	1	0.708	0.501	0.355
0.80	3.98	2.51	1.59	1	0.631	0.398	0.251
0.75	5.62	3.16	1.78	1	0.562	0.316	0.178
0.70	7.94	3.98	2.00	1	0.501	0.251	0.126
0.65	11.2	5.01	2.24	1	0.447	0.200	0.089
0.60	15.9	6.31	2.51	1	0.398	0.159	0.063
0.55	22.4	7.94	2.82	1	0.355	0.126	0.045
0.50	31.6	10.0	3.16	1	0.316	0.100	0.032

Source: Hamaker and Thompson [16].

and that the desorption coefficient (K_d) was related to the maximum solution concentration prior to desorption (C_m), they found that the ratio of x/m for adsorption, $(x/m)_a$, and desorption, $(x/m)_d$, could be expressed as follows:

$$\frac{(x/m)_d}{(x/m)_a} \simeq C_m^{0.565(1/n)} \cdot C^{-0.565(1/n)} \qquad (4\text{-}19)$$

where 1/n is the value obtained from the *adsorption* isotherm and C is the equilibrium solution concentration.

Table 4-11 shows the values of $(x/m)_d/(x/m)_a$ obtained with different values of 1/n and C and an assumed concentration of 10 μg/mL for C_m. As the solution concentration decreases and as 1/n increases, an increasing degree of error is seen to result from assuming the isotherm to be reversible.

TABLE 4-11

Errors Associated with Assumption of Reversible Adsorption[a]

	$(x/m)_d/(x/m)_a$ Solution Concentration, C (μg/mL)		
1/n	1.0	0.1	0.01
1.1	4.19	17.5	73.3
1.0	3.67	13.5	49.6
0.9	3.23	10.4	33.6
0.8	2.83	8.01	22.7
0.7	2.49	6.20	15.4
0.6	2.18	4.77	10.4
0.5	1.92	3.68	7.07

a. Calculated from Eq. 4-19 using C_m = 10 μg/mL.

4-3 AVAILABLE DATA

Numerous compilations of K_{oc} values have been published. Most of them focus on pesticides and, to a lesser degree, on aromatic and polycyclic aromatic ("energy-related") compounds. The following references are recommended:

Chiou *et al.* [11] — Reported measurements for 15 chlorinated hydrocarbons.

Farmer, W.J. [13] — Data from a literature search on 49 pesticides.

Freed and Haque [14] — Data from the literature for 16 chemicals. Temperature effects shown.

Hamaker, J.W. and J.M. Thompson [16] — Data from the literature for about 36 pesticides.

Karickhoff, S.W. *et al.* [25] — Reported measurements for 10 chemicals, mostly polycyclic aromatic compounds.

Kenaga, E.E. and C.A.I. Goring [26] — Data from the literature for 109 chemicals, mostly pesticides and some polycyclic aromatics.

Rao, P.S.C. and J.M. Davidson [36] — Data from the literature for 44 pesticides.

Rao, P.S.C. and J.M. Davidson [37] — Data from a literature search on pesticides.

Reinbold *et al.* [39] — Data from a literature review of energy-related organic pollutants.

Smith *et al.* [40] — Reported measurements for nine aromatic or polycyclic aromatic compounds and two pesticides.

4-4 SYMBOLS USED

a	=	parameter in Eq. 4-4
b	=	parameter in Eq. 4-4
BCF	=	bioconcentration factor for aquatic life, obtained from tests in flowing water (f) or tests in model ecosystems (t)
C	=	concentration of chemical in solution at equilibrium (μg/mL)
C_m	=	maximum concentration of chemical in solution prior to desorption, Eq. 4-19 (μg/mL)
%CV	=	% coefficient of variation
K	=	Freundlich adsorption coefficient in Eq. 4-2 ((μg/g)/(μg/mL)); K_d = desorption coefficient
K_{oc}	=	adsorption coefficient based on organic carbon (oc) content of solid phase, Eq. 4-3 ((μg/g oc)/(μg/mL))
K_{om}	=	adsorption coefficient based on organic matter (om) content of a soil ((μg/g)/(μg/mL))
K_{ow}	=	octanol-water partition coefficient
M	=	molecular weight in Eqs. 4-17, -18 (g/mol)
m	=	mass of adsorbent in Eq. 4-2 (g)
N	=	number of potential hydrogen bonding sites on molecule, Eq. 4-14
n	=	parameter in Eq. 4-2
%oc	=	percentage of organic carbon in soil or sediment
P	=	parachor in Eqs. 4-17, -18 (($g^{¼} \cdot cm^3$)/($sec^{½} \cdot mol$))
pK	=	negative log of acid dissociation constant
r	=	correlation coefficient of regression equation (usually reported as r^2)
R_f	=	degree of retention of chemical in soil thin-layer chromatography tests
S	=	water solubility of chemical (mg/L for Eq. 4-5, mole fraction for Eq. 4-6, μ mol/L for Eq. 4-7)
V	=	molar volume in Eq. 4-18 (cm^3/mol)
x	=	amount of chemical adsorbed on soil or sediment, Eq. 4-2 (μg)

Greek

ρ	=	liquid density in Eqs. 4-17, -18 (g/cm^3)
ρ^o	=	vapor density in Eq. 4-17 (g/cm^3)
σ	=	surface tension in Eqs. 4-17, -18 ($g \cdot sec^{-2}$)

Subscripts

a	=	adsorption; used with x/m
d	=	desorption; used with x/m and K
m	=	maximum; used with C as indicated above
oc	=	organic carbon; used with K
om	=	organic matter; used with K
ow	=	octanol-water; used with K

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5

BIOCONCENTRATION FACTOR IN AQUATIC ORGANISMS

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5-1 INTRODUCTION

The accumulation of certain chemicals in aquatic organisms has become of increasing concern as an environmental hazard. Concentrations of some compounds that appear safe for organisms (according to bioassay criteria for acute or even chronic exposure) can accumulate to levels that are harmful to the consumers of such organisms or, ultimately, to the organisms themselves. A classic example is the accumulation of pesticide residues in fish, which has led to eventual decreases in the reproductive success of certain fish-eating birds. Further, when acute toxicity thresholds are high, chronic effects from residue-forming chemicals may not be noticed until after significant amounts have been released into the environment; this is especially true of organic compounds that are expensive to monitor. Reliable correlations between concentrations of chemicals in ambient media (e.g., water) and organisms can help to reduce monitoring requirements and provide early warning of potential contamination problems. Thus, it has become evident that methods are needed for screening chemical substances for potential hazard due to accumulation.

This chapter focuses on the use and limitations of methods for estimating the degree to which organic compounds may accumulate in aquatic species. The methods presented are similar, in that they are derived from observed correlations between the physical properties of

such organic compounds and their accumulation under laboratory test conditions. Estimates based on currently available regression equations must be assumed to have an uncertainty of about one order of magnitude.

The *bioconcentration factor* (BCF) indicates the degree to which a chemical residue may accumulate in aquatic organisms (usually fish), coincident with ambient concentrations of the chemical in water. Specifically, it is defined here as:

$$BCF = \frac{\text{Concentration of chemical at equilibrium in organism (wet weight)}}{\text{Mean concentration of chemical in water}} \qquad (5\text{-}1)$$

The units of both numerator and denominator must be the same (e.g., $\mu g/g$). Values of BCF range from about 1 to over 1,000,000.

To measure equilibrium residue concentrations in organisms, it is necessary to determine their uptake and depuration rates. Alternatively, measurements of the chemical residue concentration must be made over a sufficient period to ensure that equilibrium conditions exist [37].[1] Flow-through bioassay systems should be used, so that chemical concentrations remain relatively constant during the test.

The above "measurement-specific" definition of bioconcentration factor must be distinguished from other terms commonly used to describe increases in the concentration of chemicals in an organism, such as biomagnification, bioaccumulation, and ecological magnification. These other terms are associated with increasing concentrations of a chemical along a food chain, which could result in higher concentration factors in top-order consumers. They also imply that dietary uptake of contaminated food is additive to, or more significant than, direct exposure to the same contaminants in the water. The term bioconcentration is used in this chapter with the assumption that uptake across external membranous surfaces from water is the chief source of the material that is concentrated in the organism.

The primary significance of this water-to-organism pathway in bioconcentration is supported by numerous investigators [1,7,11,14,15,22]; however, there is also evidence that biomagnification via aquatic food chains can be important under certain environmental circumstances

1. In its technical guidelines, the Environmental Protection Agency states that a BCF should either be measured at equilibrium or in a test extending for more than 27 days [41].

[5,7]. Because many aspects of these phenomena are not yet fully understood, this chapter deals primarily with the nature of the estimation methods themselves and the limitations to their use.

The accumulation of organic chemicals in aquatic organisms can be predicted by several methods. This chapter focuses on techniques for estimation that are based on known relationships between bioconcentration factors and other, readily available properties of organic chemicals. Correlations between bioconcentration and octanol-water partition coefficients, water solubility, and soil adsorption coefficients in flow-through bioassays are highlighted in §5-3. In §5-4 the uses and limitations of the estimates are discussed. Correlations based on data from model ecosystems and from static bioassays are given in §5-5, which also describes some additional approaches to projecting the accumulation of organic material in the environment by aquatic organisms.

5-2 BASIC APPROACH

To obtain an estimated bioconcentration factor for a selected chemical, use the following procedure:

(1) Check the tables in §5-3 and any recent review articles to see if a BCF has already been measured by flow-through tests.

(2) If the BCF has not been measured or is not readily available, assess the existing physical and chemical data to see if the water solubility (S), octanol-water partition coefficient (K_{ow}), or soil adsorption coefficient (K_{oc}) is known. Any of these parameters can be used to estimate the BCF. Of the three, correlations for K_{ow} are currently based on the largest body of bioassay data; this parameter is relevant to the estimation of BCF because lipophilic organic chemicals are generally found to be more readily accumulated in organisms. Values of S, on the other hand, may be easier to obtain. Soil adsorption coefficients are likely to be the least available of the three.

(3) If measured values of K_{ow}, S, or K_{oc} are not available, they can be estimated by methods described in Chapters 1, 2, and 4 respectively. First preference should be given to K_{ow}, followed by S and K_{oc}, in that order.

(4) Use the appropriate regression equation in §5-3 to calculate the BCF for the chemical.

(5) See §5-4 for information on how estimated bioconcentration factors can be used, as well as the degree of uncertainty and sources of error associated with these estimates.

5-3 METHODS OF ESTIMATION

All methods described in this section for estimating bioconcentration factors in aquatic organisms are based on data from laboratory experiments that were designed to maintain relatively constant amounts of the chemical in the water environment, and where equilibrium concentrations of the chemical could be ascertained.

Tables 5-1 and 5-2 summarize some of the regression equations that have been developed. Lists of the chemical compounds from which these equations were derived accompany the descriptions of the individual methods.

Estimation from Octanol-Water Partition Coefficient. If the octanol-water partition coefficient (K_{ow}) for the organic chemical in question is available, the following equation is recommended for estimating the *bioconcentration factor:*

$$\log BCF = 0.76 \log K_{ow} - 0.23 \qquad (5\text{-}2)$$

This regression equation was derived by Veith *et al.* [39] from the results of laboratory experiments by several investigators with a variety of fish species and 84 different organic chemicals (see Table 5-3). To estimate the BCF with this equation, proceed as follows:

(1) Obtain a measured or estimated value for K_{ow} (see Chapter 1 for estimation techniques).

(2) Substitute this value in Eq. 5-2 and solve for log BCF.

(3) The antilog is the approximate degree to which a chemical will concentrate in aquatic organisms, relative to its ambient concentration in the water. No more than two significant figures should be reported for BCF.

TABLE 5-1

Recommended Regression Equations for Estimating log BCF, Based on Flow-through Laboratory Studies

Eq. No.	Equation[a]	N[b]	r^2[c]	Chemical Classes Represented	Range of Independent Variable	Species Used	Ref.
5-2[d]	$\log BCF = 0.76 \log K_{ow} - 0.23$	84	0.823	Wide (Table 5-3)	7.9 to 8.1×10^6	Fathead minnow Bluegill sunfish Rainbow trout Mosquitofish	[39]
5-3[e]	$\log BCF = 2.791 - 0.564 \log S$	36	0.49	Wide (Table 5-4)	0.001 to 50,000 ppm	Brook trout Rainbow trout Bluegill sunfish Fathead minnow Carp	[18]
5-4	$\log BCF = 1.119 \log K_{oc} - 1.579$	13	0.757	Wide (Table 5-5)	< 1 to 1.2×10^6	Various	[18]

a. BCF = bioconcentration factor; K_{ow} = octanol-water partition coefficient; S = water solubility (ppm); K_{oc} = soil (or sediment) adsorption coefficient.
b. N = number of chemicals used to obtain regression equation.
c. r = correlation coefficient for regression equation.
d. In the original equation, the octanol-water partition coefficient was represented by "P" instead of "K_{ow}."
e. The original equation used "WS" (water solubility) instead of "S."

TABLE 5-2

Additional Regression Equations for Estimating log BCF, Based on Flow-through Laboratory Studies

Eq. No.	Equation[a]	N[b]	r^2[c]	Chemical Classes Represented	Range of Independent Variable	Species Used to Approximate	Ref.
5-5[d]	$\log BCF = 0.542 \log K_{ow} + 0.124$	8	0.899	Table 5-5	437 to 41.6×10^6 (meas. or calc.)	Rainbow trout (muscle)	[29]
5-6[d]	$\log BCF = 0.85 \log K_{ow} - 0.70$	55	0.897	Table 5-6	7.9 to 87,000+	Bluegill Fathead minnow Rainbow trout Mosquitofish	[37]
5-7	$\log BCF = 0.935 \log K_{ow} - 1.495$	26	0.757	Table 5-4	436 to 3.7×10^6	Various	[18]
5-8[d,e]	$\log BCF = 0.819 \log K_{ow} - 1.146$	3	0.995	Table 5-7	66 to 28,100 (calc.)	*Daphnia pulex* (invertebrate)	[33]
5-9[d,e]	$\log BCF = 0.7520 \log K_{ow} - 0.4362$	7	0.85	Table 5-8	2000 to 1.5×10^6 (calc.)	*Daphnia pulex*	[34]
5-10[e]	$\log BCF = 3.41 - 0.508 \log S$	7	0.930	Table 5-9	437 to 41.6×10^6	Rainbow trout (muscle) Used data from Ref. 29	[6]

a. BCF = bioconcentration factor; K_{ow} = octanol-water partition coefficient; S = water solubility (μmoles/L)
b. N = number of chemicals used to obtain regression equation.
c. r^2 = correlation coefficient for regression equations.
d. Original equation used "P" rather than "K_{ow}" for the octanol-water partition coefficient.
e. Original equation used "CF" or "BF" instead of "BCF."

TABLE 5-3

Compounds Used to Derive Regression Equation 5-2

Compound	Species[a]	Exposure (days)	Bioconcentration Factor (BCF)[b]
Acenaphthene	BS	28	387
Acrolein	BS	28	344
Acrylonitrile	BS	28	48 (day 28)[d]
Aroclor 1016	FM	32	42,500
Aroclor 1248	FM	32	70,500
Aroclor 1254	FM	32	100,000
Aroclor 1260	FM	32	194,000
Atrazine	FM	276	<7.9
Benzene	--	--	12.6 (calc.)
Biphenyl	RT	4	437
p-Biphenyl phenyl ether	RT	4	550
Bis(2-chloroethyl)ether	BS	14	11
5-Bromoindole	FM	32	14
BSB[c]	BS	50	<2.1
Butylbenzylphthalate	BS	21	772
Carbon tetrachloride	BS	21	30
	RT	4	17.4
Chlordane	FM	32	37,800
Chlorinated ecosane	FM	32	49
Chlorobenzene	FM	28	450
Chloroform	BS	14	6
2-Chlorophenanthrene	FM	28	4270
2-Chlorophenol	BS	28	214
Chlorpyrifos	M	35	470
DASC-3[c]	BS	30	<2.1
DASC-4[c]	BS	30	<2.1
p,p'-DDT	FM	32	29,400
o,p'-DDT	FM	32	37,000
p,p'-DDE	FM	32	51,000
Dibenzoturon	FM	28	1,350
1,2-Dichlorobenzene	BS	14	89
1,3-Dichlorobenzene	BS	14	66
1,4-Dichlorobenzene	BS	14	60
	RT	4	215
1,2-Dichloroethane	BS	14	2
Diethylphthalate	BS	21	117
2,4-Dimethylphenol	BS	28	150

(Continued)

TABLE 5-3 (Continued)

Compound	Species[a]	Exposure (days)	Bioconcentration Factor (BCF)[b]
Dimethylphthalate	BS	21	57
Diphenylamine	FM	32	30
Diphenylether	RT	4	195
Endrin	FM	300	4,600
	M	35	1,480
2-Ethylhexylphthalate	FM	56	850
Fluorene	FM	28	1,300
FWA-2-A[c]	B	105	<2.1
FWA-3-A[c]	B	105	<2.1
FWA-4-A[c]	B	105	<2.1
Heptachlor	FM	276	20,000
		32	9,500
Heptachlor epoxide	FM	32	14,400
Heptachloronorbornene	FM	32	11,100
Hexabromobiphenyl	FM	32	18,100
Hexabromocyclododecane	FM	32	18,200
Hexachlorobenzene	RT	4	7,760
	FM	32	18,500
Hexachlorocyclopentadiene	FM	32	29
Hexachloroethane	BS	28	139
Hexachloronorbornadiene	FM	32	6,400
Isophorone	BS	14	7
Lindane	FM	304	470
		32	180
Methoxychlor	FM	32	8,300
2-Methylphenanthrene	FM	4	3,000
Mirex	FM	32	18,100
Naphthalene	FM	28	430
Nitrobenzene	FM	28	15
p-Nitrophenol	FM	28	126
N-Nitrosodiphenylamine	BS	14	217[d]
NTS-1[c]	BS	35	2.1-10
Octachlorostyrene	FM	32	33,000
Pentachlorobenzene	BS	28	3,400
Pentachloroethane	BS	14	67
Pentachlorophenol	FM	32	770
Phenanthrene	FM	4	2,630
N-Phenyl-2-naphthylamine	FM	32	147
1,2,3,5-Tetrachlorobenzene	BS	28	1,800 (days 21-28)[d]

(Continued)

TABLE 5-3 (Continued)

Compound	Species[a]	Exposure (days)	Bioconcentration Factor (BCF)[b]
1,1,2,2-Tetrachloroethane	BS	14	8
Tetrachloroethylene	BS	21	49
Toluene	—	—	15-70 (calc.)
Toluenediamine	FM	32	91
2,4,6-Tribromoanisole	FM	32	865
1,2,4-Trichlorobenzene	FM	32	2,800
1,1,1-Trichloroethane	BS	28	9
1,1,2-Trichloroethylene	RT	4	39
	BS	14	17
2,4,5-Trichlorophenol	FM	28	1,900
2,5,6-Trichloropyridinol	M	35	3.1
Tricresyl phosphate	FM	32	165
Tris(2,3-dibromopropyl)phosphate	FM	32	2.7

a. BS = bluegill sunfish, FM = fathead minnow, M = mosquitofish, RT = rainbow trout.
b. These values represent either those measured directly by the authors [39] or reported from sources where similar test conditions were used. In some cases, only log BCF was reported; these have been converted to BCF here for convenience.
c. Designations for sulfonated stilbene fluorescent whitening agents.
d. Maximum BCF value.

Source: Veith *et al.* [39].

Example 5-1 Estimate the bioconcentration factor for 4,4'-dichlorobiphenyl in fish, given an octanol-water partition coefficient (K_{ow}) of 380,000.

(1) From Eq. 5-2 and the given value for K_{ow},

$$\log BCF = 0.76 \log (380{,}000) - 0.23$$

(2) $\log BCF = 4.01$

(3) $BCF = 10{,}000$

A measured value reported for this compound is more than an order of magnitude lower than the above estimate (see Table 5-4).

Example 5-2 Estimate the bioconcentration factor for methoxychlor in fish, given a K_{ow} of 19,950.

(1) From Eq. 5-2 and the given K_{ow} value,

$$\log BCF = 0.76 \log (19{,}950) - 0.23$$

(2) log BCF = 3.04

(3) BCF = 1,100

A comparison of this estimate with laboratory measurements (see § 5-4) shows that Eq. 5-2 underestimated the measured BCF for methoxychlor by a factor of about 7.

Estimation from Water Solubility. If water solubility (S) in parts per million is available for the organic chemical in question, the following equation is recommended for estimating the BCF:

$$\log BCF = 2.791 - 0.564 \log S \qquad (5\text{-}3)$$

This regression equation was derived by Kenaga and Goring [18] from laboratory experiments by a number of investigators with a variety of fish species and 36 organic chemicals (see Table 5-4). Note the reciprocal nature of the relationship between water solubility and bioconcentration.

To estimate a bioconcentration factor from Eq. 5-3, the procedure is as described above for Eq. 5-2, except that the required physical/chemical parameter is S, which must be expressed in parts per million (ppm).

Example 5-3 Estimate the bioconcentration factor for diphenyl oxide in fish, given a water solubility of 21 ppm.

(1) From Eq. 5-3 and the given value of S,

$$\log BCF = 2.791 - 0.564 \log (21)$$

(2) log BCF = 2.04

(3) BCF = 110

This is reasonably close to the measured value (~ 196) reported in Ref. 18.

Example 5-4 Estimate the bioconcentration factor for heptachlor in fish, given a water solubility of 0.030 ppm.

(1) From Eq. 5-3 and the given value of S,

$$\log BCF = 2.791 - 0.564 \log (0.030)$$

(2) log BCF = 3.65

(3) BCF = 4,500

The measured value of BCF is 9,500 (see § 5-4).

TABLE 5-4

Compounds Used to Derive Regression Equations 5-3, 5-4, and 5-7

Compound	Water Solubility (S) for Eq. 5-3	Soil Adsorption Coefficient (K_{oc}) for Eq. 5-4	Octanol-water Partition Coefficient (K_{ow}) for Eq. 5-7[a]	Bioconcentration Factor (BCF)[b]
Halogenated Hydrocarbon Insecticides				
Chlordane	X			11,400
DDT	X	X	X	61,600
Dieldrin	X			5,800
Endrin	X		X	4,050
Heptachlor	X			17,400
Lindane	X	X		325
Methoxychlor	X	X	X	185
Toxaphene	X			26,400
Kepone®	X			8,400
Substituted Benzenes and Halobenzenes				
Chlorobenzene	X		X	12
p-Dichlorobenzene	X		X	215
Hexachlorobenzene	X	X	X	8,600
Pentachlorobenzene	X		X	~ 5,000
1,2,4,5-Tetrachlorobenzene	X		X	4,500
1,2,4-Trichlorobenzene	X		X	491
Halogenated Biphenyls and Diphenyl Oxides				
4-Chlorobiphenyl	X		X	490
4,4'-Dichlorobiphenyl	X		X	215
2,4,4' and 2,2',5-Trichlorobiphenyl (Aroclor 1016, 1242)	X		X	48,980
2,2',4,4' and 2,2',5,5'-Tetrachlorobiphenyl (Aroclor 1248)	X		X	72,950
2,2',4,5,5'-Pentachlorobiphenyl (Aroclor 1254)	X	X	X	45,600
2,2',4,4',5,5'-Hexachlorobiphenyl	X	X	X	46,000(est)

(Continued)

TABLE 5-4 (Continued)

Compound	Water Solubility (S) for Eq. 5-3	Soil Adsorption Coefficient (K_{oc}) for Eq. 5-4	Octanol-water Partition Coefficient (K_{ow}) for Eq. 5-7[a]	Bioconcentration Factor (BCF)[b]
Halogenated Biphenyls and Diphenyl Oxides (Cont'd.)				
Diphenyloxide	X		X	196
4-Chlorodiphenyloxide	X		X	736
X-sec-Butyl-4-chlorodiphenyl-oxide	X		X	298
X-Hexyl-*X'*-chlorodiphenyl-oxide	X		X	18,000
X-Dodeca-*X'*-chlorodiphenyl-oxide	X		X	12
Aromatic Hydrocarbons				
Biphenyl	X		X	340
***Phosphorus-containing* Insecticides**				
Diamidaphos	X	X		1
Chlorpyrifos	X	X	X	450
Liptophos	X	X	X	750
Diazinon	X			35
Carboxylic Acids and Esters				
Di-2-ethylhexylphthalate	X		X	380
Dinitroanilines				
Trifluralin	X	X	X	4,570
Symmetrical Triazines				
Atrazine	X	X	X	–
Simazine	X	X	X	1
Miscellaneous Nitrogen Heterocyclics				
3,5,6-Trichloro-2-pyridinol	X	X	X	3

a. Although the authors stated that 26 compounds were used in deriving Eq. 5-7, they listed the 28 compounds checked here. It is not clear which two were not used.

b. In many cases, the authors used more than one source, but they did not explain how they combined them to arrive at a single value.

Source: Kenaga and Goring [18]

Estimation from Soil Adsorption Coefficients. The relationship between soil adsorption coefficients (K_{oc}) and bioconcentration appears to be essentially empirical, although soil affinity for certain types of organic chemicals may, in fact, be related to the affinity of the same types of chemicals for certain parts of biological systems. Equation 5-4 was derived by Kenaga and Goring [18] from a relatively small number of measurements of soil adsorption coefficients (see Table 5-4). Nonetheless, the correlation between K_{oc} and measured values of BCF appears to be quite good; the derived regression equation could be utilized to estimate BCF if only soil adsorption information is available, or for comparison with estimates based on K_{ow} or S.

$$\log BCF = 1.119 \log K_{OC} - 1.579 \qquad (5\text{-}4)$$

The procedure for using this regression equation to estimate BCF is the same as described above for Eqs. 5-2 and 5-3.

Example 5-5 Estimate the bioconcentration factor for DDT in fish, given a soil adsorption coefficient of 238,000.

(1) From Eq. 5-4 and the given value for K_{oc},

$$\log BCF = 1.119 \log (238{,}000) - 1.579$$

(2) $\log BCF = 4.44$

(3) $BCF = 27{,}000$

This agrees closely with the measured value of 29,400 (see § 5-4).

Other Regression Equations. In addition to the above, various other correlations have been observed between bioconcentration in fish or certain aquatic invertebrates (i.e., *Daphnia*) and the physical/chemical characteristics of a more limited set of organic chemicals. The corresponding regression equations are listed in Table 5-2 and are used in the same way as described for Eqs. 5-2, -3, and -4.

Equation 5-5 is of particular interest, as it represents one of the earliest and most widely known uses of octanol-water partition coefficients for estimating bioconcentration potential in fish. This correlation, which was developed by Neely *et al.* [29], was based on a very small number of measured bioconcentration values in trout muscle (Table 5-5).

TABLE 5-5

Compounds Used to Derive Regression Equation 5-5[a,b]

2-Biphenyl phenyl ether
Carbon tetrachloride
p-Dichlorobenzene
Diphenyl
Diphenyl oxide
Hexachlorobenzene
2,2',4,4'-Tetrachlorodiphenyl oxide
1,1,2,2-Tetrachloroethylene

a. Table 5-3 lists log BCF values for these compounds.
b. Partition coefficients were calculated, not measured.

Source: Neely, Branson and Blau [29].

The correlation described by Eq. 5-2 is considered better, because it is based on a much larger number of measured values, including those used by Neely *et al.*

Similarly, Eq. 5-6 represents an earlier relationship observed by Veith, DeFoe and Bergstedt [37] among some of the organic compounds later used to derive Eq. 5-2. These compounds are listed in Table 5-6.

In addition to their regression equation based on solubility (Eq. 5-3), Kenaga and Goring [18] also developed a correlation with octanol-water coefficients (see Eq. 5-7). The compounds on which it is based are listed in Table 5-4.

Equations 5-8 and 5-9 were developed by Southworth *et al.* [33,34] to describe relationships between K_{ow} and bioconcentration in *Daphnia pulex*. The organic compounds that they used are listed in Tables 5-7 and 5-8 respectively.

The relationship between water solubility and bioconcentration described by Eq. 5-10 was developed by Chiou *et al.* [6], who used the uptake data reported by Neely *et al.* Table 5-9 lists the compounds used to derive this equation.

TABLE 5-6

Compounds Used to Derive Regression Equation 5-6[a]

Aroclor 1016	FWA-4-A
Aroclor 1248	Heptachlor
Aroclor 1254	Heptachlor epoxide
Aroclor 1260	Heptachloronorbornene
Atrazine	Hexabromobiphenyl
Biphenyl	Hexabromocyclododecane
p-Biphenyl phenyl ether	Hexachlorobenzene
5-Bromoindole	Hexachloronorbornadiene
BSB	Lindane
Carbon tetrachloride	Methoxychlor
Chlordane	Methylphenanthrene
Chlorobenzene	Mirex
2-Chlorophenanthrene	Naphthalene
Chloropyrifos	Nitrobenzene
DASC-3	p-Nitrophenol
DASC-4	NTS-1
p,p'-DDE	Octachlorostyrene
p,p'-DDT	Pentachlorophenol
o,p'-DDT	Phenanthrene
Dibenzoturon	N-Phenyl-2-naphthylamine
p-Dichlorobenzene	1,1,2,2-Tetrachloroethylene
Diphenylamine	Toluene diamine
Diphenylether	2,4,6-Tribromoanisol
Endrin	1,2,4-Trichlorobenzene
2-Ethylhexylphthalate	2,4,5-Trichlorophenol
Fluorene	2,5,6-Trichloropyridinol
FWA-2-A	Tricresyl phosphate
FWA-3-A	

a. Table 5-3 lists BCF values for these compounds.

Source: Veith, DeFoe and Bergstedt [37].

TABLE 5-7

Compounds Used to Derive Regression Equation 5-8

Compound	BCF in *Daphnia pulex*
Acridine	29.6
Benz(a)acridine	352
Isoquinoline	2.41

Source: Southworth, Beauchamp and Schmieder [33]

TABLE 5-8

Compounds Used to Derive Regression Equation 5-9

Compound	BCF in *Daphnia pulex*
Anthracene	917
Benz(a)anthracene	10,100
9-Methyl anthracene	4,580
Naphthalene	131
Perylene	7,190
Phenanthrene	325
Pyrene	2,700

Source: Southworth, Beauchamp and Schmieder [34]

TABLE 5-9

Compounds Used to Derive Regression Equation 5-10[a,b]

Biphenyl
Carbon tetrachloride
p-Dichlorobenzene
Diphenyl ether
Hexachlorobenzene
2,4,2',4'-PCB
Tetrachloroethylene

a. BCF values used were those of Neely *et al.* and are listed in Table 5-3.
b. Partition coefficients were calculated.

Source: Chiou *et al.* [6].

5-4 USES AND LIMITATIONS OF ESTIMATED VALUES

All of the estimation techniques described in the previous section are based on correlations between a measured or calculated physical/chemical property of an organic chemical and the observed bioconcentration, usually in fish. The accuracy of these estimates is limited by the accuracy of the measurement techniques used for the various correlation parameters. Although efforts to improve and standardize these techniques continue [39], the number of variables that affect the physical/chemical properties and bioconcentration factors make it unlikely that estimates of this kind will ever provide highly accurate projections, particularly with respect to the ambient environment. Accordingly, estimates of BCF based on relationships described in this chapter should be used *to gain understanding of the potential* for an organic chemical to be taken up and stored in aquatic biota and to indicate whether further research into its environmental fate may be warranted. An estimated bioconcentration factor for a compound can be compared with the BCFs for known problematic accumulators such as DDT or Aroclor, a mixture of polychlorbiphenyls, and with the BCFs for compounds like carbon tetrachloride that have *not* been implicated in residue formation in biological organisms. (See Table 5-10.)

It is also important to emphasize that, overall, bioconcentration factors can presently be estimated *only to within an order of magnitude* for most of the correlations listed (see correlation coefficients expressed as r^2 in Tables 5-1 and 5-2). Within this bound, estimates from Eqs. 5-2, 5-3, and 5-7 appear to have greater relative uncertainty. This is probably related to the broader range of chemical classes from which they were derived, in addition to the problems of measurement variability associated with all such correlations.

The so-called error sources that reduce the levels of confidence in BCF estimates are of several kinds. In the subsections that follow, a distinction is made between (1) those that create discrepancies between BCF estimates and laboratory measurements of bioconcentration and (2) those that affect bioconcentration in the ambient environment.

Sources of Discrepancies Between BCF Estimates and Laboratory Data. Table 5-10 compares values of BCF measured in the laboratory with estimates derived from correlations based on K_{ow}, S, and K_{oc}. It illustrates the degree of discrepancy that can be expected from such estimates. Both the variability inherent in biological responses and factors responsible for measurement inaccuracy contribute to the observed differences between estimated and measured values.

TABLE 5-10

Comparison of Estimated Values with Laboratory Measurements of BCF[a]

Compound	Physical/Chemical Parameter for Estimate			Estimated BCF			Laboratory Measurement	
	K_{ow} [37, 39]	S (ppm) [18]	K_{oc} [18]	From K_{ow} (Eq. 5-2)	From S (Eq. 5-3)	From K_{oc} (Eq. 5-4)	BCF	Ref.
Nitrobenzene	851	1,780	—	99	9.1	—	15.1	[37]
Carbon tetrachloride	437	800	—	17	14	—	30	[38]
p-Dichlorobenzene	2,400	79	—	220	53	—	215[b]	[29]
Atrazine	427	33	149	59	86	—	<7.94	[39]
1,2,4-Trichlorobenzene	17,000	30	—	970	91	—	2,800	[37]
Methoxychlor	20,000	0.003	80,000	1,100	16,000	8,100	8,300	[37]
Naphthalene	50,100	31.7	1,300	2,200	88	80	427	[39]
Pentachlorophenol	126,000	14	900	4,400	140	53	770	[37]
Hexachlorobenzene	170,000	0.035	3,910	5,600	4,100	280	18,500	[37]
Heptachlor	275,000	0.030	—	8,000	4,500	—	9,500	[37]
Biphenyl	5,750	7.5	—	420	71	—	437[b]	[29]
DDT	562,000	0.0017	23,800	14,000	23,000	27,000	29,400	[37]
Aroclor 1254	2,950,000	0.01	42,500	49,000	8,300	4,000	100,000	[37]
Chlordane	1,000,000	0.056	—	21,000	120	—	37,800	[37]

a. It is interesting to note that all the examples of estimates based on K_{ow} fall within an order of magnitude of the cited measured values. This is not true for all the examples based on K_{oc} or S. Caution should be exercised at this time in drawing any conclusions concerning the relative usefulness/accuracy of these three physical-chemical parameters for BCF estimates: much of the laboratory data cited, and that used to derive Eq. 5-2, were the result of somewhat standardized procedures. The same situation likely did not exist for the data generated to derive equations 5-3 and 5-4.

b. Muscle only.

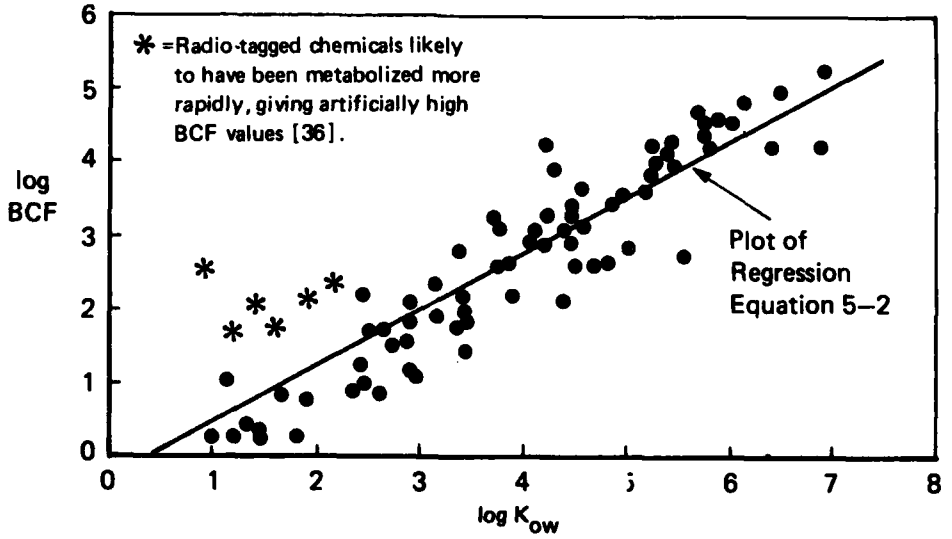
Errors in measuring the physical/chemical properties correlated with BCF are also responsible for some of the discrepancies observed. As discussed more thoroughly in Chapters 1, 2, and 4, several different methods can be used to measure K_{ow}, S, and K_{oc}. Although certain methods are becoming accepted as more reliable, the measurements of properties are limited by the accuracy and precision of the techniques and the way in which the results are interpreted. *Estimates* of these parameters, to the extent that they have been used (mostly for K_{ow}), represent an additional source of error for the relationships presented here. *Test conditions,* such as pH and temperature, have a marked effect on measurements of solubility and partition coefficient for some chemical species. Solubility is difficult to measure (and thus is subject to greater unreliability) for very insoluble compounds. K_{ow} is similarly less reliable for very soluble compounds. Because highly water-soluble compounds tend not to form problematic residues in fish, error associated with very soluble compounds is less important when used in BCF estimates [38]. (Such compounds may present other environmental hazards, such as acute toxicity.)

Errors in measurement of BCF itself under laboratory conditions are also a source of discrepancies. Although the regression relationships presented in §5-3 are reported to be based on BCFs measured by flow-through methods, various bioconcentration phenomena can affect the results:

- As stated at the beginning of this chapter, it is important that BCF be measured under equilibrium conditions between uptake and depuration. However, many compounds with high partition coefficients (log BCF > 6) move across membranes very slowly and may not reach equilibrium in 20 or even 30 days; as a result, their BCF measurements and predictions based on them may be too low [10].
- For some organic compounds, particularly those of high solubility, equilibrium can be reached in a few days or less. Highly soluble compounds are also more susceptible to degradation or excretion, both of which tend to cause artificially high BCF measurements in a study of short duration.
- Test temperatures, dissolved oxygen, and the size of test organisms also affect the time required for equilibrium to be established and, thus, the test duration that should be used for measurement of bioconcentration factors [39].

- The relative lipid content of fish species used in tests may well alter residue formation potential [7,17,19]. Even within a given species, lipid content can be affected by growth stage and position in the reproductive cycle [17,39]. Furthermore, measurements of residue concentrations in some specialized groups of tissues can easily produce different results from whole-organism analyses [13,26].

Thus, a number of significant variables can affect the accuracy of measurements from which the correlations are derived. The regression equations are based on straight-line correlations that have been developed from data with a fair degree of scatter. Figure 5-1, the plot of data points from which Eq. 5-2 was derived, illustrates this. It becomes obvious that the order-of-magnitude level of confidence associated with BCF estimates derived in this fashion represents a reasonable level of accuracy. While standardization of methods is likely to improve the reliability of BCF estimates under laboratory conditions (as in Eq. 5-6), there will always be some uncertainty because of the large number of variables. If estimates based on such data are used with an awareness of their limitations and only as a rapid means for identifying a potential for bioconcentration, the issue of absolute accuracy becomes less important.



Source: Adapted from Ref. 39.

FIGURE 5–1 Correlation Between Bioconcentration and Octanol-Water Partition Coefficient

Application of BCF Estimates to Field Situations. The BCF estimation techniques illustrated here could be used to identify environmental situations where further investigation of organic residue formation is warranted. However, attempts to define the fate of an organic compound *without field verification* are subject to many potentially significant errors. Some measures of reliability of correlations based on existing laboratory data have been calculated, but this is not yet possible for applications to field situations. Thus, while we can estimate the bioconcentration potential of an organic compound, it tells us little about the fate of that compound in the variety of potential environments. Table 5-11 compares some estimated BCFs with those measured in the ambient environment. Note that most of the estimates agree within an order of magnitude.

The factors that lead to discrepancies in measurements of bioconcentration under laboratory conditions also apply to ambient conditions, and there is likely to be a wider range of variability in the ambient exposure history of the organism. That exposure history is frequently unknown; for example, fish may move in and out of contact with varying concentrations of a contaminant, so that the bioconcentration depends not only on straightforward uptake and depuration rates, but also on the amount of time that the fish are in contact with the contamination source(s) before they are caught. The exposure of fish in the same body of water may vary with the strength, number, and location(s) of the source(s) and whether the species is pelagic or bottom dwelling, migratory, or remains in a relatively confined habitat. In addition, seasonal variations in major physical factors (e.g., temperature, salinity, dissolved oxygen) are usually uncontrolled in the ambient environment.

Laboratory studies have shown that the water is far more significant than food as a source of organic compounds for fish bioconcentration [1,7,11,14,15]. In the actual environment, however, this may not necessarily be the case. One explanation for the very high BCF observed in the Great Lakes for particularly persistent organics (see Table 5-11) may be that in situations where ambient concentrations are very low, as in the ng/L range illustrated, food may represent a more significant source than water; this would cause the values of BCF to be higher than water concentrations would indicate [37]. The range and significance of contamination from ingested sediment and the differences in feeding behavior between species are additional unquantified uncertainties in the field situation.

TABLE 5-11

Comparison of Estimated BCF with Observed BCF from Field Data

Compound and Location	Equation Used	Log K_{ow}	Log S (ppm)	Estimated BCF	Ambient Water Concentration	Concentration in Fish (Species, Duration)	Observed BCF	Ref.
Aroclor 1016 (Hudson River)	5-2	5.88 [37]	—	17,000	Mean of 0.17μg/L (may be closer to 0.10μg/L)	2.6μg/g (mean of 18 fish, 3 species of various sizes, 14 days' exposure)	15,000 (up to 26,000)	[32]
DDT (Hamilton, Lake Ontario)	5-2	5.75 [37]	—	14,000	4.5 ng/L	0.14μg/g (Alewife) 0.23μg/g (Smelt)	31,000 51,000	[40]
DDE (Hamilton, Lake Ontario)	5-2	5.69 [37]	—	12,000	37.4 ng/L	0.46μg/g (Alewife) 1.36μg/g (Smelt) 0.94μg/g (Sculpin)	12,000 36,000 25,000	[40]
Dieldrin (Hamilton, Lake Ontario)	5-3	—	−1.66 [18]	5,300	3.1 ng/L	0.04μg/g (Alewife)	13,000	[40]
PCB (Aroclor 1254) (Two lakes in South Dakota)	5-2	6.47 [37]	—	49,000	$<$ 0.5μg/L	0.11μg/g (one measurement for 10 carp)	$>$ 220	[9]
Lindane (Limestone quarry)	5-2	3.89 [37]	—	530	25-13 ng/L (over 235 days)	~ 27.3-13.3 ng/g (Trout, 3-7 fish per sample)	~ 1,090 to ~ 1,020	[12]
Trifluralin (Wabash River)	5-2	5.33 [35]	—	6,600	~ 1.8μg/L	10.46μg/g (237 Sauger) residue in fat	5,800	[35]

As a final caveat to extrapolation, it appears that estimates for BCF based on fish uptake may not be applicable to some other families of aquatic organisms. The work of Lu, Metcalf, and others [1,23,24,25] has revealed differences in the ability of aquatic organisms (e.g., fish vs. mollusk) to metabolize concentrated organic materials. These differences may be related to phylogenetic differences in enzyme systems. The question remains whether or not species differences can result in potential cumulative discrepancies of more than an order of magnitude between estimated and measured BCF values.

5-5 OTHER APPROACHES TO ESTIMATING THE ACCUMULATION OF ORGANIC COMPOUNDS

There is a significant body of data on bioconcentration measured in organisms in laboratory situations other than flow-through systems. These include data from model ecosystems (both aquatic and terrestrial/aquatic) and from other types of static tests. Table 5-12 lists some regression equations and correlation coefficients developed from such studies.[2] These estimates should be distinguished from those based on single-species flow-through tests, because model ecosystem test conditions do not always represent maximum bioconcentration potential. The reasons are as follows:

(1) The degree of variability in test compound concentrations is likely to be greater in model ecosystem water than in flow-through systems. Equilibrium may not be established at all, or it may exist at an inadequate exposure level. This could be the result of decomposition or other reactions that affect concentrations following a single dose [1,38] and/or the method by which such compounds are introduced.

(2) In a number of cases (e.g., Ref. 19), the duration of the ecosystem tests has been so brief that equilibrium conditions may not have been established for even a short time in the system. This situation would be more problematic with compounds of high BCF than with those at the other end of the spectrum. The relatively low coefficients of correlation given in Table 5-12 for Eqs. 5-15 and 5-19 may additionally be due to the methods used to measure K_{ow} [10,19,20].

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2. To indicate that model ecosystem rather than flow-through tests were used, the abbreviation "E.M." (for "ecological magnification") is often used instead of "BCF." Some authors prefer BCF(t).

TABLE 5-12

Regression Equations Derived from Model Ecosystem Tests and Static Bioassays[a]

Equation Number	Equation[b]	N[c]	r^2[d]	Chemical Classes	Ref.
5-11	log E.M. = 2.6204 − 0.3339 log S (ppm)	7	0.6744	Benzene derivatives	[19]
5-12	log E.M. = 0.2060 + 0.6669 log K_{ow}	7	0.6673		
5-13	log E.M. = 1.4578 + 0.4112 x	7	0.7302		
5-14	log E.M. = 2.5580 − 0.4275 log S (ppm)	19	0.6584	Benzene derivatives & others (a number of pesticides)	[19]
5-15[e]	log E.M. = 0.0300 + 0.7481 log K_{ow}	19	0.3659		
5-16	log E.M. = 0.1394 + 0.6308 log K_{ow}	4	0.8477	Veterinary drugs: Sulfamethazine, Clopidol, Diethylstilbestrol, Phenothiazine	[8]
5-17	log E.M. = 5.99 − 1.176 log S (ppb)	11	0.7569	Aldrin, Dieldrin, Endrin, Mirex, Lindane, DDT, DDE, DDD, Methoxychlor, Methylchlor, Ethoxychlor	[24]
5-18	log E.M. = 3.9950 − 0.3891 log S (ppb)	11	0.8516	Aldrin, DDT, Hexachlorobenzene, Chlorobenzene, Nitrobenzene, Benzoic acid, Aniline, Anisole, 2,6-Diethyl aniline, 3,5,6-Trichloro-2-pyridinol, Pentachlorophenol	[20]
5-19	log E.M. = 0.7285 + 0.6335 log K_{ow}	11	0.6208		

(Continued)

TABLE 5-12 (Continued)

Equation Number	Equation[b]	N[c]	r^2[d]	Chemical Classes	Ref.
5-20[f]	log E.M. = 5.328 − 1.059 log S (ppb)	13	0.4761	Three types of insecticides	[25]
5-21[f]	log E.M. = 4.529 − 0.627 log S (ppb)	16	0.6889	Range of chemicals	[25]
5-22	log BCF(t) = 2.183 − 0.629 log S (ppm)	50	0.4356	(PCBs, benzene	[18]
5-23	log BCF(t) = 1.225 log K_{oc} − 2.024	22	0.8281	derivatives, pesticides,	[18]
5-24	log BCF(t) = 0.767 log K_{ow} − 0.973	36	0.5776	others)	[18]

a. All correlations listed in this table were based on tests with mosquitofish.
b. E.M. = ecological magnification, as measured in a terrestrial/aquatic or aquatic model ecosystem; S = water solubility; K_{ow} = octanol-water partition coefficient; x= pi-constant from Fujita *et al.* 1964 (in Ref. 19); BCF(t) = bioconcentration factor, as measured in a model ecosystem or static bioassay; K_{oc} = soil adsorption coefficient. In several cases, the symbols "x" and "y" used in the original publication have been replaced by the "EM," "K_{ow}," or "S" symbols used throughout this text.
c. N = number of chemicals used to obtain regression equation.
d. r = correlation coefficient for regression equation.
e. Original source gave a minus sign for the log K_{ow} term. The data indicate, however, that the term should have a positive sign.
f. Original equations were expressed in terms of log S and are rearranged here.

(3) Although model ecosystems have been designed to represent more closely a total environmental system, they are still subject to the same potential sources of error as other laboratory tests — size and age of fish, temperature and specificity of dissolved oxygen, etc.

Nevertheless, model ecosystems do provide useful reference data on the fate of doses of specific chemicals and their degradation products. They could be used, for example, to simulate uptake in the aftermath of a chemical spill in a small lake. In view of the present state of the art of estimating BCF for organic chemicals, however, estimates based on data from flow-through systems are generally more reliable, because these systems are more likely to achieve and maximize equilibrium accumulation. Accordingly, Eqs. 5-1 through 5-9 probably provide more safely conservative estimates than those based on static studies (Eqs. 5-10 through 5-24).

Some relatively simple models have been developed to describe bioconcentration in aquatic organisms under different environmental and/or exposure scenarios. (See, for example, Refs. 3-6, 29, and 30.) These models are not described here, primarily because they require more and different information than do the other estimation techniques, including measured uptake and depuration rates and measured or estimated values for organism metabolism, temperature, dissolved oxygen, sediment binding and release, and other environmental factors. Such models attempt to describe more accurately the various factors that affect the accumulation of organic residues in aquatic organisms. Because they are relatively new and untested, the underlying assumptions and their usefulness must be calibrated and/or validated by further laboratory and field experimentation.

5-6 AVAILABLE DATA

This chapter utilizes three major compilations of BCF values based on flow-through bioassay tests, namely, those by Kenaga and Goring [18], Veith, DeFoe, and Bergstedt [37], and Veith, Macek, Petrocelli, and Carroll [39].

5-7 SYMBOLS USED

BCF = bioconcentration factor for aquatic organisms obtained from flow-through bioassay tests

BCF(t) = bioconcentration factor for aquatic organisms obtained from static bioassay or model ecosystem tests

E.M. = ecological magnification for aquatic organisms based on model ecosystem tests

K_{oc} = soil (sediment) adsorption coefficient

K_{ow} = octanol-water partition coefficient

N = number of chemicals used to derive regression equation

r = correlation coefficient

S = solubility in water (ppm or ppb)

x = pi-constant, used in Eq. 5-13.

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6

ACID DISSOCIATION CONSTANT

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6-1 INTRODUCTION

The extent to which an organic chemical is partitioned among the gaseous, solid, and solution compartments of a given environment is determined by several physical and chemical properties of both the chemical and the environment. Among the chemical properties, those that determine acid-base interactions between the chemical and the aqueous or soil/sediment components of the environment exert a major influence on partitioning. An organic acid or base that is extensively ionized may be markedly different from the corresponding neutral molecule in solubility, adsorption, bioconcentration, and toxicity characteristics. For example, the ionized species of an organic acid is generally adsorbed by sediments to a much lesser degree than is the neutral form.

The significance of acid-base chemistry in this regard is most clearly reflected in the acid dissociation constant, K_a, of the chemical. For an organic chemical, HA, that is weakly acidic, K_a is defined as the equilibrium constant for the reaction:

$$HA + H_2O \rightarrow H_3O^+ + A^- \qquad (6\text{-}1)$$

A chemical, H_xA, that has more than one acidic proton undergoes successive dissociations as follows:

$$H_xA + H_2O \rightleftharpoons H_3O^+ + H_{x-1}\ A^- \qquad (6\text{-}1a)$$

$$H_{x-1}\ A^- + H_2O \rightleftharpoons H_3O^+ + H_{x-2}\ A^{-2} \qquad (6\text{-}1b)$$

$$\vdots$$

$$HA^{-(x-1)} + H_2O \rightleftharpoons H_3O^+ + A^{-x} \qquad (6\text{-}1c)$$

The equilibrium constants for the successive dissociation reactions are referred to as K_1 (Eq. 6-1a), K_2 (Eq. 6-1b) . . . K_x (Eq. 6-1c), respectively, of H_xA.

Thus,

$$K_a = \frac{a_{H_3O^+}\ a_{A^-}}{a_{HA}\ a_{H_2O}} \qquad (6\text{-}2)$$

where a_i is the activity of species i in an aqueous solution. It is conventional to assign unit activity to solvent water; this is equivalent to choosing pure water as the standard state and assuming that the solution is sufficiently dilute that the activity of the water is unaffected by the presence of solute(s). This assumption is generally true for solute concentrations in the millimolar range and below (i.e., < 0.1M). Equation 6-2 then reduces to

$$K_a = \frac{a_{H_3O^+}\ a_{A^-}}{a_{HA}} = \frac{\left(\gamma_{H_3O^+}\ M_{H_3O^+}\right)\left(\gamma_{A^-}\ M_{A^-}\right)}{\gamma_{HA}\ M_{HA}} \qquad (6\text{-}3)$$

in which γ_i is the molar activity coefficient and M_i is the molar concentration of species i. The value of K_a defined in terms of activities is referred to as the "true" or "thermodynamic" dissociation constant. Equation 6-3 is often further simplified by applying the approximation that all activity coefficients are unity, yielding the following equation:

$$K_a \approx \frac{M_{H^+}\ M_{A^-}}{M_{HA}} \qquad (6\text{-}4)$$

Note that K_a as defined in Eq. 6-4 has dimensions of concentration and units of mol/L. The concentration dissociation constant of Eq. 6-4 is generally a good approximation of the thermodynamic constant for solute concentrations below 0.01 M.

An alternative simplification is to retain the activity expression for H_3O^+ but to assume unit activity coefficients for A^- and HA. This yields the expression for the "mixed" or "Bjerrum" acid dissociation constant:

$$K_a \approx \frac{a_{H^+} M_{A^-}}{M_{HA}} \tag{6-5}$$

Taking the negative logarithm of both sides of Eq. 6-5 gives:

$$\left.\begin{aligned} -\log K_a &= -\log a_{H^+} - \log \frac{M_{A^-}}{M_{HA}} \\ \text{or} \\ pK_a &= pH - \log \frac{M_{A^-}}{M_{HA}} \end{aligned}\right\} \tag{6-6}$$

Rearranging Eq. 6-6 yields a form of the dissociation constant expression that is particularly useful in describing the aqueous solution behavior of the weak organic acid.

$$\log \frac{M_{A^-}}{M_{HA}} = pH - pK_a \tag{6-7}$$

According to Eq. 6-7, the concentrations of organic acid in the dissociated (A^-) and free (HA) forms are equal when $pH = pK_a$, and the ratio of A^- to HA increases by an order of magnitude for each unit of pH above pK_a. Thus, for example, acetic acid with $K_a = 1.8 \times 10^{-5}$ and $pK_a = 4.75$ is

1% dissociated at pH 2.75
10% dissociated at pH 3.75
50% dissociated at pH 4.75
90% dissociated at pH 5.75
99% dissociated at pH 6.75

A comparison of the pK_a of an organic acid with the pH of the aqueous system of concern quickly reveals the potential importance of acid dissociation of the organic compound in determining environmental distribution.

The acid-base behavior of weakly basic organic compounds could be treated in an exactly analogous fashion; the base dissociation constant (K_b) for a base, B, can be defined as follows:

$$B + H_2O \rightarrow BH^+ + HO^- \tag{6-8}$$

$$K_b = \frac{a_{HB^+}\, a_{OH^-}}{a_B\, a_{H_2O}} \tag{6-9}$$

For convenience and consistency, however, it seems preferable to address the behavior of weak bases in terms of the K_a or pK_a values of their respective conjugate acids, as in Eqs. 6-10 and 6-11.

$$BH^+ + H_2O \rightarrow H_3O^+ + B \tag{6-10}$$

$$K_a = \frac{a_{H_3O^+}\, a_B}{a_{BH^+}\, a_{H_2O}} \tag{6-11}$$

K_a for the conjugate acid, BH^+, and K_b for the base, B, are related by a constant — the autodissociation constant of water, K_w:

$$K_a = \frac{K_w}{K_b} \tag{6-12}$$

Thus, a decrease in K_a for BH^+ is automatically reflected in an increase in K_b for B; a stronger base corresponds to a weaker conjugate acid. If the pK_a of the conjugate acid is used as a measure of base strength, a uniform scale can be applied over the entire range of organic acid-base behavior in aqueous media.

Table 6-1, which lists pK_a values for various organic compounds, illustrates the wide range of acid and base strengths that can be encountered. Note that acid strength can vary over about 50 orders of magnitude. In aqueous media, however, the range of interest is restricted to acids with pK_a's of 0-14. Acids with $pK_a < 0$ will be completely dissociated to the corresponding conjugate base, while those with $pK_a > 14$ will be completely associated.

If the focus is further narrowed to aqueous media within the normal environmental pH range of 5-8, the range of acidities that are of concern is even more restricted. Equation 6-7 implies that the acidity range of principal interest corresponds to pK_a of 3 to 10. If an organic species has a pK_a outside these limits, it is expected to be either completely (>99%)

TABLE 6-1

Range of pK_a Values for Organic Acids

Conjugate Acid	pK_a	Conjugate Base
Methane	40	$CH_3:^-$
Toluene	35	$C_6H_5CH_2:^-$
Aniline	27	$C_6H_5NH:^-$
t-Butanol	19	$C_4H_9O:^-$
Water	15.7	$HO:^-$
Phenol	10	$C_6H_5O:^-$
RNH_3^+	~ 10	RNH_2
p-Nitrophenol	7.2	$p\text{-}NO_2\text{–}C_6H_4O:^-$
Pyridinium ion	5.2	Pyridine
Carboxylic acids	4.5 ± 0.5	Carboxylate anions
p-Nitroanilinium	1.0	*p*-Nitroaniline
$CH_3OH_2^+$	–2	Methanol
$C_6H_5OH_2^+$	–6.7	Phenol

Source: Hendrickson, Cram, and Hammond [3].

dissociated (pK_a of organic acid <3) or completely undissociated (pK_a of conjugate acid >10) in an aqueous environment.

6-2 EXPERIMENTAL MEASUREMENT OF K_a

Because acidity has long been recognized as an important property of organic compounds, methods for experimental measurement of pK_a values are well established. The principal procedures, which have been summarized by Kortüm *et al.* [6], are based on the determination of the pH and the concentrations (or ratio of concentrations) of the acid and conjugate base (Eq. 6-6). Dissociation constants are determined by conductance methods, electrometric methods, spectrophotometric methods, magnetic resonance, and measurements of catalytic effects on well-characterized reactions.

If the true thermodynamic K_a (Eq. 6-3) is sought, one must apply activity coefficient corrections to the measured concentrations of acid and conjugate base. This can be done by making measurements at a series of ionic strengths and extrapolating to zero ionic strength. Alternatively, activity coefficients may be calculated from relationships such as the Davies equation:

$$\log \gamma_i = -(Z_i)^2 \left(\frac{0.15\sqrt{I}}{1+\sqrt{I}} - 0.30\, I \right) \qquad (6\text{-}13)$$

in which Z_i is the charge on the *i*th species and I is the ionic strength [1].

Acid dissociation constants in the range of pK_a 3 to pK_a 11 can generally be measured with a high degree of accuracy and precision. The state of the art of these measurements is illustrated by the subjective description of uncertainties in tabulated values provided by the compendia of Kortüm *et al.* [6] and of Sergeant and Dempsey [10]:

"Very reliable"	± 0.0005 in pK_a
"Reliable"	± 0.005
"Approximate"	± 0.04
"Uncertain"	>0.04

The equilibrium constant for acid dissociation is affected by several parameters in addition to the structure of the organic acid. Increasing ionic strength of the aqueous medium influences pK_a by favoring the ionic form of the conjugate acid/base pair. The temperature of the medium also influences the magnitude of K_a. However, both of these effects are generally small compared with those related to molecular structure. For instance, K_a values for typical organic acids change by much less than an order of magnitude, typically less than 10%, between 5°C and 60°C [6,9,10]. In general, K_a decreases with increasing temperatures; some anomalous results in the 0-5°C range may reflect variations in properties of the solvent water within this range.

6-3 OVERVIEW OF ESTIMATION METHOD

The dissociation constant of an organic acid (or conjugate acid of an organic base) can be estimated by applying a linear free energy relationship (LFER). An LFER is an empirical correlation between the standard free energies of reaction (ΔF°) or activation ($\Delta F^\ddagger$) for two series of reactions, both subjected to the same variations in reactant structures or reaction conditions. Since $\Delta F^\circ = -RT \ln K$ for an equilibrium process and $\Delta F^\ddagger \propto -RT \ln k$ for a kinetic process, a linear free energy relationship is also a linear relationship between logarithms of equilibrium/rate constants. Wells [11] expressed the basic LFER for two reaction series, A and B, as

$$\log k_i^B = m \log k_i^A + C \qquad (6\text{-}14)$$

where k may stand for either a rate or an equilibrium constant. Several excellent treatments of both the theoretical aspects and the broad applicability of LFERs have been written [2,4,5,7,11], and no attempt will be made here to present a detailed explanation or derivation.

As applied to the estimation of acid dissociation constants, the LFER method is basically a substituent-effect approach. One member of the "A" series, typically an unsubstituted prototype with dissociation constant K_a^o (A), is taken as a reference point. The similarly unsubstituted member of the "B" series may be regarded as the parent compound of the acid whose dissociation constant, K_a^x(B), is to be determined. Equation 6-14 may then be written as:

$$\log \frac{K_a^x\,(B)}{K_a^o\,(B)} = m \log \frac{K_a^x\,(A)}{K_a^o\,(A)} \qquad (6\text{-}15)$$

where

K_a^o(A) = dissociation constant of reference acid in A series (e.g., benzoic acid)
K_a^x(A) = dissociation of substituted acid in A series (e.g., *p*-chlorobenzoic acid)
K_a^o(B) = dissociation constant of parent acid in B series (e.g., phenol)
K_a^x(B) = dissociation constant of substituted acid in B series (e.g., *p*-chlorophenol).

The proportionality constant, m, in Eq. 6-15 is a measure of the relative sensitivity of the B-series reactions to substituent changes, compared with the A series. The term $\log[K_a^x(A)/K_a^o\,(A)]$ may be considered an indication of the intrinsic effect of the substituent change. This concept of the separability of a "reaction parameter" and a "substituent effect" constitutes the major practical strength (and perhaps a theoretical weakness) of the LFER approach.

The choice of the "A" series used to define the substituent parameters is the principal difference between one LFER system and another. Table 6-2 summarizes four of the more familiar LFERs. Hansch and Leo [2] describe several additional systems that have been evolved for special purposes. The Hammett relationship for aromatic systems and the Taft relationship for aliphatics are the most generally applicable LFERs for estimating acid dissociation constants. Although one of the

TABLE 6-2

Commonly Encountered LFERs and Substituent Parameters

Name	Substituent Symbol	Parameter Defining Reaction Series	K or k Basis[a]	Special Feature(s)
Hammett	σ	Dissociation of benzoic acids	K	
Hammett	σ^-	Dissociation of anilinium ions	K	Accounts for "through resonance" between reaction center and electron-withdrawing substituents
Brown	σ^+	Hydrolysis of cumyl chlorides	k	Accounts for "through resonance" between reaction center and electron-donating substituents
Taft	σ^*	Hydrolysis of carboxylate esters – difference between base- and acid-catalyzed rates	k	Corrects for steric effects; inductive effects of substituent dominate σ^*

a. K indicates an equilibrium constant and k indicates a reaction rate constant as the basis for the LFER.

special-purpose equations might give somewhat better results in a particular instance, it is generally not possible to predict which LFER should be used. Moreover, the special-purpose LFERs do not expand the range of substituent types or acid types that can be considered. The Hammett and Taft correlations should provide estimates of dissociation constants that are adequately accurate for evaluation of probable environmental partitioning behavior.

6-4 ESTIMATION OF K_a FOR AROMATIC ACIDS — HAMMETT CORRELATION

The Hammett correlation is most commonly written as follows:

$$\log \frac{K_a^x}{K_a^o} = \sigma\rho \qquad (6\text{-}16)$$

where:

K_a^x = acid dissociation constant of substituted compound
K_a^o = acid dissociation constant of parent compound
σ = substituent constant, sigma
ρ = reaction constant, rho

The correlation can be rewritten for convenience in solving explicitly for K_a^x (Eq. 6-17) or pK_a^x (Eq. 6-18).

$$K_a^x = K_a^o \, 10^{\sigma\rho} \qquad (6\text{-}17)$$

$$pK_a^x = pK_a^o - \sigma\rho \qquad (6\text{-}18)$$

Three steps are involved in estimating the dissociation of a substituted acid:

(1) Selection of an appropriate parent compound for which K_a^o and ρ values are available,
(2) Selection of the substituent constant value(s), and
(3) Calculation of K_a^x or pK_a^x.

Both the complexity of the selection processes and the accuracy of the estimated dissociation constant vary, depending on the type of compound under consideration. The procedure is described in detail below.

The use of the Hammett correlation is simplest when estimating K_a for derivatives of benzoic acids containing only meta and para substituents, so this procedure is given first. The procedure used for more complex aromatic compounds is described in the following subsection.

Basic Steps for Substituted Benzoic Acids

(1) The parent compound of all species involved here is benzoic acid; its K_a is used as K_a^o ($pK_a^o = 4.203$, $K_a^o = 6.26 \times 10^{-5}$) [5], and the value of ρ is defined as 1.

(2) Find the value of σ as follows:

- If the compound is a monosubstituted benzoic acid, find the appropriate substituent constant in Table 6-3.
- If more than one substituent is present, see Table 6-4 for the appropriate multi-substituent σ value.
- If the correct combination is not found in Table 6-4, locate the individual substituents in Table 6-3 and sum their σ values. Use this sum (σ_T) in place of a single σ value to calculate K_a^x. If Table 6-3 does not list one or more of the substituents, find a default value of σ in Table 6-5.
- A substituent that is neither covered by the generalized categories of Table 6-5 nor found in Table 6-3 cannot be assigned a σ value; therefore, K_a^x for the corresponding acid cannot be calculated from the Hammett equation.

(3) Substitute the appropriate values into Eq. 6-17 and solve for K_a^x.

Example 6-1 Estimate the dissociation constant for *p-tert* butyl benzoic acid.

(1) As described above, K_a^o for benzoic acid is 6.26×10^{-5} and $\rho \equiv 1$.

(2) From Table 6-3, σ para for the *tert* butyl group, $C(CH_3)_3$, is -0.197.

(3) Substitute the above values in Eq. 6-17:

$$K_a^x = (6.26 \times 10^{-5})\, 10^{(-0.197)(1)}$$

$$= 3.98 \times 10^{-5}$$

This estimate is identical to the measured value as tabulated by Kortüm *et al.* [6].

TABLE 6-3

Hammett Substituent Constants

Substituent	σ Meta	σ Para	σ⁻ Para[a]	Ref.
Hydrocarbon Groups				
CH_3	−0.069	−0.170		[8]
CH_2CH_3	−0.07	−0.151		[8]
$CH_2CH_2CH_3$		−0.126		[5]
$CH_2(CH_2)_2CH_3$		−0.161		[5]
$CH_2CH(CH_3)_2$		−0.115		[5]
$CH(CH_3)CH_2CH_3$		−0.123		[5]
$CH_2CH_2CH(CH_3)_2$		−0.225		[5]
$C(CH_3)_2CH_2CH_3$		−0.190		[5]
$CH(CH_3)_2$		−0.151		[8]
$C(CH_3)_3$	−0.10	−0.197		[8]
C_6H_5	0.06	−0.01		[8]
$CH{=}CHC_6H_5$	0.141		0.619	[5]
$C{\equiv}CC_6H_5$	0.14	0.16		[11]
Carbonyl-Containing Groups				
$COCH_3$	0.376	0.502		[8]
$COOH$	0.355	0.265	0.728	[5]
$COOCH_3$	0.315		0.636	[5]
$COOCH_2CH_3$	0.398	0.522	0.678	[5]
$COO(CH_2)_3CH_3$			0.674	[5]
$COOCH_2C_6H_5$			0.667	[5]
$CONH_2$	0.280		0.267	[5]
CHO	0.35	0.22	1.126	[11]
COC_6H_5		0.459		[5]
COO^-	−0.1	0.0		[8]
$OCOCH_3$	0.39	0.31		[8]
CH_2CH_2COOH	−0.027	−0.066		[5]
Nitrogen-Containing Groups				
$N(CH_3)_2$		−0.83		[8]
$NHCOCH_3$	0.21	0.00		[8]
$NHCOC_6H_5$	0.217	0.078		[5]
$NHNH_2$	−0.1	−0.4		[11]
$NHOH$	−0.044	−0.339		[5]
NH_3^+	0.634			[5]
$NH_2CH_3^+$	0.958			[5]
$NH_2CH_2CH_3^+$	0.958			[5]
$N(CH_3)_3^+$	0.88	0.82		[8]
$N(CF_3)_2$	0.45	0.53		[11]
NO_2	0.710	0.778	1.270	[8]
CH_2CN		0.01		[11]
CN	0.56	0.660	1.00	[8,5]
$C_6H_4N{=}NC_6H_5$			1.088	[5]
$N{=}NC_6H_5$		0.64		[5]
N_2^+	1.76	1.91		[8]
NH_2	−0.16	−0.66		[8]
$NHCH_3$		−0.84		[8]
N_3	0.33	0.08		[11]
$NHCH_2CH_3$	−0.240			[5]
$NH(CH_2)_3CH_3$	−0.344			[5]

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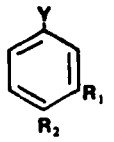
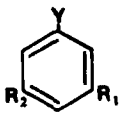
TABLE 6-3 (Continued)

Substituent	σ Meta	σ Para	σ⁻ Para[a]	Ref.
Halogens and Alkyl Halide Groups				
F	0.337	0.062		[8]
Cl	0.373	0.227		[8]
Br	0.391	0.232		[8]
I	0.352	0.18		[8]
IO_2	0.70	0.76		[8]
CF_3	0.43	0.54		[8]
CCl_3	0.40	0.46		[11]
CH_2Cl		0.184		[5]
Hydroxy and Alkoxy Groups				
OCH_3	0.115	−0.236		[8]
OCH_2CH_3	0.1	−0.24		[8]
$O(CH_2)_2CH_3$	0.1	−0.25		[8]
$OCH(CH_3)_2$	0.1	−0.45		[8]
$O(CH_2)_3CH_3$	0.1	−0.32		[8]
$O(CH_2)_4CH_3$	0.1	−0.34		[8]
$O(CH_2)_5CH(CH_3)_2$	—	−0.265		[5]
OC_6H_5	0.252	−0.320		[8]
$OCH_2C_6H_5$	—	−0.415		[5]
OCF_3	0.4	0.5		[11]
O^-	−0.71	−0.52		[11]
OH	0.121	−0.37		[8]
Sulfur-Containing Groups				
SCH_3	0.15	0.00		[8]
SCH_2CH_3		0.03		[8]
$SCH(CH_3)_2$		0.07		[8]
SH	0.25	0.15		[8]
$SCOCH_3$	0.39	0.31		[8]
SCN		0.52		[8]
$SOCH_3$	0.52	0.49		[8]
SO_2CH_3	0.60	0.72	1.049	[8,5]
SO_2NH_2	0.46	0.57		[8]
$S(CH_3)_2^+$	1.00	0.90		[8]
SO_3^-	0.05	0.09		[8]
SO_3H		0.5		[11]
SCF_3	0.44	0.57		[5]
SCF_5	0.6	0.7		[5]
Phosphorus-Containing Groups				
$P(CH_3)_2$	0.1	0.05		[11]
$P(CF_3)_2$	0.6	0.7		[11]
$P(CH_3)_3^+$	0.8	0.9		[11]
PO_3H^-	0.2	0.26		[11]
Miscellaneous Groups				
$CH_2Si(CH_3)_3$	−0.16	−0.21		[11]
$Si(CH_3)_3$	−0.04	−0.07		[8]
$Si(CH_2CH_3)_3$		0.0		[11]
$Ge(CH_3)_3$		0.0		[8]
$Ge(CH_2CH_3)_3$		0.0		[8]
$Sn(CH_3)_3$		0.0		[11]
$Sn(CH_2CH_3)_3$		0.0		[8]
AsO_3H^-		−0.02		[8]
$SeCH_3$	0.1	0.0		[8]
SeCN	0.6	0.664		[8]
$B(OH)_2$	0.006	0.454		[5]

a. See Table 6-2 for definition.

TABLE 6-4

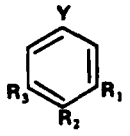
Values of σ for Multiple Substituents

R_1	R_2	$\Sigma\sigma_R$[a]	σ Measured[b]
	3,4-Disubstitution 		
Cl	Cl	0.600	0.525
Cl	OH	−0.016	−0.049
Cl	CH_3	0.203	0.235
Cl	OCH_3	0.105	0.268
CH_3	CH_3	−0.239	−0.303
CH_3	NO_2 (c)	0.709	0.694
CH_3	OCH_3	−0.337	−0.265
CH_3	$N(CH_3)_2$	−0.669	−0.302
CH_3	Cl	0.158	0.174
CH_3	NH_2	−0.720	−0.716
OCH_3	OCH_3	−0.153	−0.117
OCH_3	OH	−0.242	−0.329
OCH_3	Cl	0.342	0.338
NO_2	NO_2 (c)	1.488	1.379
NO_2	Cl	0.937	0.901
NO_2	Br	0.942	0.826
NO_2	OCH_3	0.442	0.414
NO_2	CH_3	0.540	0.505
NO_2	NO_2 (c)	1.980	2.036
OH	OH	−0.359	−0.278
NH_2	CH_3	−0.331	−0.209
$N(CH_3)_2$	CH_3	−0.381	−0.176
Br	CH_3	0.221	0.150
Br	OCH_3	0.123	0.088
	3,5-Disubstitution 		
NO_2	NO_2	1.420	1.395
NO_2	Cl	1.083	1.073
OCH_3	OCH_3	0.230	0.050
OCH_3	Cl	0.488	0.439
CH_3	CH_3	−0.138	−0.173
CH_3	Cl	0.304	0.347
Br	Br	0.782	0.720
Cl	Cl	0.746	0.746
OH	OH	0.242	0.162

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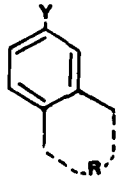
TABLE 6-4 (Continued)

Trisubstituted Compounds



R_1	R_2	R_3	$\Sigma\sigma_R$[a]	σ Measured[b]
OCH_3	OCH_3	OCH_3	−0.038	0.075
OCH_3	OH	NO_2	0.468	0.433
OH	OCH_3	NO_2	0.444	0.634

Fused Ring Systems



R	σ Measured[b]
3,4-$(CH_2)_3$	−0.259
3,4-$(CH_2)_4$	−0.477
3,4-(CH)$_4$	0.170
3,4-CH_2O_2	−0.159

a. The sums of the individual σ values from Table 6-3 are listed here to permit comparison with the measured σ for a multiple substitution, in order to demonstrate the magnitude of the uncertainty that may be incurred by assuming additivity of σ values.

b. To be used in calculations instead of $\Sigma\sigma$.

c. In calculating $\Sigma\sigma$, the σ^- value is used for the 4-nitro group.

Source: Jaffé [5]

TABLE 6-5

Default Values of σ for Substituents in Generalized Categories for Aromatic Acids

Substituent Category	Atom or Group Attached to Parent Acid (Ar)	Default Value[a] σ Meta	σ Para
Alkyl (C,H only)	Ar — C(—)(—)(—)	-0.08	-0.16
Alkyl with α Halogen	Ar — C(—)(—) — X	0.14[b]	0.18
Alkyl with α Carbonyl	Ar — C(=O) –	0.35	0.43
Amine[c]	Ar — N<	-0.30[c]	-0.83[c]
Aryl amide	Ar — N(—)–C(=O) — R	0.21	0.05
Ammonium	Ar — N^+(—)(—) — R	0.85	0.8
Ether	Ar — O — R	0.1	0.31
Mercaptan or Sulfide	Ar — S — R	0.15	0.03
Sulfoxy	Ar — S(=O) – R_2	0.6	0.7
Phosphorous	Ar — P (III) – R	0.1	0.05
Phosphoric	Ar — P (V) – R	0.2	0.26
Organo-Silicon	Ar — Si R_3	-0.04	-0.07
Organo-Germanium	Ar — Ge R_3	NA	0.0
Organo-Tin	Ar — Sn R_3	NA	0.0

a. Default values are arithmetic averages of values reported in Table 6-3 for each substituent category, except as noted.
b. Calculated as one third of the average of the Table 6-3 σ meta values for CCl_3 and CF_3.
c. Excluding $NOCOCH_3$, $NHCOC_6H_5$, and $N(CH_3)_2$.

Example 6-2 Estimate the dissociation constant for 4-methyl-3, 5-dinitrobenzoic acid.

(1) As above, K_a^o for benzoic acid is 6.26×10^{-5} and $\rho \equiv 1$.

(2) The exact desired substituent pattern is not included in Table 6-4, but the total σ value can be estimated by summing the value for 3,5-dinitro substitution (Table 6-4) and the value for 4-methyl substitution from Table 6-3.

		σ
m,m-diNO_2	=	1.395
p-CH_3	=	−0.170
σ_T	=	1.225

(3) Substitute the above values in Eq. 6-17:

$$K_a^X = (6.26 \times 10^{-5})\, 10^{(1.225)(1)} = 1.05 \times 10^{-3}$$

This estimate deviates −1.8% from the measured value of 1.07×10^{-3} [4].

Basic Steps for Other Aromatic Acids

(1) Locate in Table 6-6 the parent compound that is the most suitable model for the compound of interest and substitute the reaction constant (ρ) and dissociation constant (K_a^o) for that compound in Eq. 6-17. Use the measured value of K_a^o, not the calculated value, from Table 6-6. Use the following criteria in choosing the parent compound:

- Choose a parent compound that contains the same acid function (carboxylic acid, phenol) as the compound of interest.
- Choose a parent compound that contains any ortho substituents present in the compound of interest.
- Choose the parent so that substituent constants are available for the remaining substituents.
- If two comparable routes are available, calculate both and average the results.

(2) Search Tables 6-3 and 6-4, if necessary, for the substituents required to complete the structure of interest. For derivatives of phenol and aniline, use values of σ^-, if available. Obtain the value of σ for each substituent needed. If more than one is needed, sum the constants before substituting in the equation. If an exact substituent cannot be found, choose a default value from Table 6-5.

TABLE 6-6

Hammett Reaction Constants (ρ) for Equilibrium Reactions in Water

Parent Compound	pK_a^o (Measured)	T (°C)	ρ	n[a]	r[b]	pK_a^o (Calc.)[c]
Benzoic Acids						
Benzoic	4.205 [10]	25	1.000			
o-Nitrobenzoic	2.21 [10]	25	0.905	6	0.992	2.206
Toluic (*o*-methyl)	3.93 [10]	25	1.430	4	0.955	3.875
Salicylic (*o*-hydroxy)	3.08 [10]	25	1.103	6	0.978	3.997
o-Chlorobenzoic	2.900 [10]	25	0.855	4	0.970	3.693
o,o-Dimethylbenzoic	3.354 [10]	26	1.116[d]	4	0.999	3.974[d]
p-Phenylbenzoic[e]	—	25	0.482[e]	9	0.981	5.636[e]
Other Carboxylic Acids						
Phenylacetic	4.307 [10]	25	0.489	14	0.981	4.297
3-Phenylpropanoic	4.664 [10]	25	0.212	8	0.979	4.551
3-Phenylpropenoic *(trans)*	4.42 [10]	25	0.466	9	0.977	4.447
4-Phenyl-2-keto-but-3-enoic	—	25	−0.054	5	0.903	1.971
2-Furancarboxylic	3.16 [10]	24	1.396[f]	6	0.988	2.819
Other Acids						
Phenol	9.994 [10]	25	2.113[g]	17	0.990	9.847
Catechol (*o*-hydroxyphenol)	9.45 [10]	25	3.512[g,h,l]	8	0.991	11.012[h,l]
Anilinium ion	4.603 [9]	25	2.767[g]	14	0.995	4.557

(Continued)

TABLE 6-6 (Continued)

Parent Compound	pK_a^o (Measured)		T (°C)	ρ	n^a	r^b	pK_a^o (Calc.)[c]
Other Acids (Cont.)							
Dimethylanilinium ion	5.068	[9]	20	3.426[g,i,l]	5	0.986	3.285[i,l]
Benzylammonium ion	9.33	[9]	25	0.732	5	0.942	9.315
Thiophenol	6.615	[10]	20-22	2.236[j,l]	12	0.975	7.666[j,l]
Phenylboronic acid	8.84	[10]	25	2.146[k,l]	14	0.990	9.700[k,l]
Phenylphosphonic acid	1.83	[6] (pK_1)	25	0.755	10	0.995	1.836
	7.43	[10] (pK_2)	25	0.949	12	0.990	6.965
o-Chloro- or *o*-bromo-phenylphosphonic acid	1.63	[6] (pK_1)	25	0.995	4	0.998	2.942
	6.98	[6] (pK_2)	25	0.908[j,l]	6	0.964	6.901
Phenylarsonic acid	3.65	[10] (pK_1)	18-25	1.050	9	0.975	3.540
	8.77	[10] (pK_2)	22	0.874	11	0.965	8.491
Benzeneseleninic acid	4.70	[10]	25	0.905	16	0.906	4.740

a. Number of acids used in calculation of ρ.
b. Correlation coefficient.
c. Calculated pK_a for parent acid = intercept of regression line with the ordinate (σ=0).
d. Value for 20% dioxane/water solvent.
e. For substituents in the p-phenyl ring (not the aromatic ring bearing the –COOH). Values are for 50% butyl cellosolve/water solvent.
f. For substituents at the 5-position in the furan ring.
g. Use σ^- para values (Table 6-3), if available, for para substituents.
h. Value for 40% dioxane/water solvent.
i. Value for 30% ethanol/water solvent.
j. Value for 50% ethanol/water solvent.
k. Value for 25% ethanol/water solvent.
l. In general, ρ values are inversely related to dielectric constant of the medium; thus, ρ would be expected to be smaller for pure water than for mixed solvent. However, there are some known exceptions [5], and available data are insufficient for estimation of the magnitude of solvent effects on ρ values.

Source: Jaffé [5]

(3) Substitute the above data in Eq. 6-17 and solve for K_a. If K_b is needed, find K_a as above and calculate K_b from either of the alternative forms of Eq. 6-2:

$$K_b = 10^{-14}/K_a$$
$$pK_b = 14 - pK_a$$

Example 6-3 Estimate the dissociation constant for 3-chloro-4-methoxyphenylphosphonic acid.

(1) The most appropriate parent compound is phenylphosphonic acid. From Table 6-6

$\rho = 0.755$

$pK_a^o = 1.83$

$K_a^o = 1.46 \times 10^{-2}$

(2) From Table 6-4, the substituent constant for 3-chloro-4-methoxy is

σ found = 0.268

(3) Substitute the above values in Eq. 6-17 and solve:

$$K_a^x = K_a^o \, 10^{\sigma\rho}$$
$$= (1.46 \times 10^{-2}) \, 10^{(0.263)(0.755)}$$
$$= 2.32 \times 10^{-2}$$

This estimate deviates +314% from the experimentally measured value of 0.56×10^{-2} [4].

Example 6-4 Estimate the dissociation constant for 4-*t*-butylphenylacetic acid.

(1) The parent compound from Table 6-6 is phenylacetic acid.

$\rho = 0.489$

$pK_a^o = 4.307$

$K_a^o = 4.93 \times 10^{-5}$

(2) From Table 6-3, the substituent constant for the *para-tert* butyl group is $\sigma = -0.197$.

(3) Substitute the above values in Eq. 6-17.

$$K_a^x = (4.93 \times 10^{-5})\, 10^{(-0.197)(0.489)}$$

$$= 3.95 \times 10^{-5}$$

This estimate deviates +3.9% from the measured K_a of 3.8×10^{-5} [4].

Example 6-5 Estimate the dissociation constant for 3,4-dimethylaniline.

(1) The parent compound is aniline. From Table 6-6 (for anilinium ion)

$$\rho = 2.767$$

$$pK_a^o = 4.603$$

(2) From Table 6-4, the combined sigma constant is −0.303.

(3) Substitute the above values in Eq. 6-18.

$$pK_a^x = 4.603 - (-0.303)(2.767)$$

$$pK_a^x = 5.44$$

This estimate deviates −37% (in K_a) from the average measured value $pK_a = 5.24$ [5].

To calculate pK_b:

$$pK_b = 14 - 5.40 = 8.60$$

6-5 ESTIMATION OF K_a FOR ALIPHATIC ACIDS — TAFT CORRELATION

Correlation data have been collected, primarily from the work of Taft, for estimating the dissociation constants of aliphatic acids. The procedure used to estimate K_a parallels that for aromatic systems and uses the Taft equation, which, although derived differently, is similar to the Hammett equation. Any of the following three forms can be used:

$$\log \frac{K_a^x}{K_a^o} = \sigma^* \rho^* \tag{6-19}$$

$$K_a^x = K_a^o\, 10^{\sigma^* \rho^*} \tag{6-20}$$

$$pK_a^x = pK_a^o - \sigma^* \rho^* \tag{6-21}$$

Basic Steps

(1) Obtain from Table 6-7 the value of ρ^* and K_a^o for the parent compound corresponding to the species of interest.

TABLE 6-7

Reaction Parameters for Acid Dissociation

Acid	ρ^* [11]	pK_a^o
RCH_2COOH	1.75	4.76 [6]
$RCH_2PO_3H_2$	1.16	2.38 (pK_2 = 7.72) [6]
RCH_2OH	3.47	−2 [3]
RCH_2SH	3.73	
$RCH_2PH_3^+$	2.64	
$(RCH_2)_2PH_2^+$	2.61	
$(RCH_2)_3PH^+$	2.67	8.80 [9]
$RCH_2NH_3^+$	3.80	11.08 [9]
$(RCH_2)_2NH_2^+$	3.90	10.8 [9]
$(RCH_2)_3NH^+$	4.29	9.80 [9]

(2) Obtain from Table 6-8 the substituent constant σ^* for the group that completes the structure.

(3) Substitute the above values into the Taft equation (6-19, -20, or -21) and solve for K_a.

Example 6-6 Estimate the dissociation constant for isovaleric acid, $(CH_3)_2CHCH_2COOH$.

(1) The parent compound, from Table 6-7, is RCH_2COOH.

$$\rho^* = 1.75 \qquad pK_a^o = 4.76$$

(2) The substituent that completes the structure, from Table 6-8, is $i\text{-}C_3H_7$, which is $(CH_3)_2CH–$. The substituent constant is $\sigma^* = -0.13$.

(3) Substitute the above values into Eq. 6-21.

$$pK_a^X = 4.76 - (-0.13)(1.75) = 4.99$$

This estimate deviates −37% in K_a from the measured value of $pK_a = 4.79$.

TABLE 6-8

Substituent Constants for Taft Equation

R[a]	σ^*	R[a]	σ^*	R[a]	σ^*
$(CH_3)_3N^+$	2.00	$OCOCH_3$	0.89	$N(CH_3)_2$	0.22
NO_2	1.40	OCH_3	0.66	C_6H_5	0.22
CH_3SO_2	1.38	CO_2R	0.66	$CH{=}CH_2$	0.12
CH_3SO	1.33	$COCH_3$	0.62	$C_6H_4CH_2$	0.08
CN	1.25	$NHCCH_3$ (O)	0.60	H	0.00
F	1.10	OH	0.55	CH_3	−0.10
Cl	1.05	SH	0.47	C_2H_5	−0.12
Br	1.02	SCH_3	0.42	$i\text{-}C_3H_7$	−0.13
CF_3	0.92	NH_2	0.40	$i\text{-}C_4H_9$	−0.17
I	0.88	O^-	0.27	$Si(CH_3)_3$	−0.25

a. Substituent R in RCH_2

Source: Wells [11]

6-6 UNCERTAINTY IN ESTIMATED VALUES

It is difficult to gauge the probable uncertainties in values of K_a estimated by the methods described here. An indication of the inherent uncertainty in the LFER approach can be deduced from the data in Table 6-9. On the basis of observed ranges of standard deviations and correlation coefficients, Jaffé [5] has estimated that an average error of ±15% can be expected for a prediction based on a given LFER. Fundamental sources of error in predicted values include deviations from the basic LFER assumption of separability of substituent constants (σ values) and reaction constants (ρ values). These deviations, and hence the errors in the predicted values, are likely to be largest for strongly interacting substituents (large absolute value of σ). Some additional assumptions behind the LFER concept, such as the presumed constancy of the reaction mechanism, may safely be considered valid in the case of dissociation reactions. However, the uncertainty in the estimated K_a values using the procedures described in this chapter may be somewhat higher than the 15% indicated by Jaffé or that implied by Table 6-9.

The greater uncertainty is associated with difficulties in selecting an appropriate parent compound as well as in extending the correlations

TABLE 6-9

Some Correlation Data for Linear Free Energy Relationships of Hammett and Taft

Reaction Series	n[a]	ρ[b]	r[c]	s[d]
Hammett				
Dissociation of phenylacetic acids	5	0.56 ± 0.16	0.982	
Dissociation of phenylphosphonic acids	5	0.75 ± 0.00	1.000	
Dissociation of phenols	7	2.26 ± 0.07	0.997	
Dissociation of anilinium ions	7	2.94 ± 0.06	0.999	
Taft				
Dissociation of acetic acids	16	1.72 ± 0.03		0.06
Dissociation of alcohols	8	1.36 ± 0.09		0.09

a. Number of points in correlation
b. Reaction constant ± standard deviation
c. Correlation coefficient
d. Probable error of fit of single observation

Source: Wells [11]

beyond the range of substituents used in defining ρ for that parent. Additional uncertainty arises when value of pK_a^o measured for the parent acid differs substantially from that calculated from the intercept of the correlation equation. We have recommended use of the measured pK_a^o. Wolfe [12] has suggested that it seems more appropriate to use the pK_a^o value calculated from the regression equation. Our recommendation was made on the basis that the value of pK_a^o (calculated) depends on which particular compounds were used to develop the correlation, while pK_a^o (measured) is an intrinsic property of the parent acid. The recommended approach will give estimates that are more accurate for low absolute values of σ and less accurate for high values. Following Wolfe's suggestion will give more accurate estimates for large substituent changes and less accurate estimates for substituents with low values of σ.

A further source of uncertainty in estimated values results from the fact that the substituent and reaction constants given in Tables 6-3

through 6-7 are obtained from a variety of sources, rather than from one consistent set of measurements. Although the reliability of the estimated K_a's cannot be determined quantitatively, values estimated according to the procedures given in this chapter can confidently be regarded as reliable to within an order of magnitude. Most estimates are probably good to within a factor of 2 or 3 in K_a or ± 0.3-0.5 in pK_a.

Table 6-10 compares some measured and estimated values of K_a. It seems obvious from this small sample that errors are smallest for aromatic species with a single acid functionality. Errors are larger for aliphatic species and for compounds containing more than one acid functional group.

6-7 AVAILABLE DATA

There are a number of compilations of acid dissociation constants which cover a wide range of organic chemical compounds. The following are especially useful:

Kortüm, G., *et al.* [6] — Critical compilation of literature values of acid dissociation constants through 1955.

Perrin, D.D., [9] — Critical compilation of literature values of base dissociation constants through 1961.

Sergeant, E.P. and B. Dempsey, [10] — Critical compilation of literature values of acid dissociation constants through 1972.

6-8 SYMBOLS USED

a_i	=	activity of species i
A^-	=	conjugate anion of neutral organic acid
B	=	organic base
BH^+	=	conjugate acid of organic base
C	=	parameter in Eq. 6-14
ΔF°	=	standard free energy of reaction
$\Delta F^\ddagger$	=	standard free energy of activation
HA	=	organic acid
I	=	ionic strength
k_i	=	rate or equilibrium constant for reaction i
K_a	=	acid dissociation constant in Eq. 6-2
K_b	=	base dissociation constant in Eq. 6-9
K_w	=	autodissociation constant of water

TABLE 6-10

Comparison of Measured and Estimated Values of Dissociation Constants

Aromatic Compounds	K_a Measured	Ref.	K_a Estimated	Error in Estimated Value (%)
p-Aminobenzoic acid				
K_1 (NH_3^+ group)	5.13×10^{-3}	[6]	2.58×10^{-3}	− 49
K_2 (COOH group)	1.37×10^{-5}	[6]	1.36×10^{-5}	− 0.7
m-Aminobenzoic acid				
K_1 (NH_3^+ group)	8.51×10^{-4}	[6]	2.39×10^{-4}	− 72
K_2 (COOH group)	1.86×10^{-5}	[6]	4.32×10^{-5}	+132
p-Methoxybenzoic acid	3.38×10^{-5}	[6]	3.62×10^{-5}	+ 7
m-Phenoxybenzoic acid	1.12×10^{-4}	[6]	1.11×10^{-4}	− 0.9
m-Methylsulfonylbenzoic acid	3.02×10^{-4}	[6]	2.49×10^{-4}	− 17
p-Tolylacetic acid	4.27×10^{-5}	[6]	4.07×10^{-5}	− 5
p-Nitrophenylarsonic acid, K_1	1.27×10^{-3}	[6]	1.47×10^{-3}	+ 16
p-Cyanophenol	1.12×10^{-8}	[6]	1.31×10^{-8}	+ 17
Tetralol-2	3.31×10^{-11}	[6]	9.96×10^{-12}	− 70
1,3,5-Trihydroxybenzene, K_1	3.56×10^{-9}	[6]	2.23×10^{-10}	− 94[a]
m-Aminophenol, K_1 (NH_3^+ group)	6.76×10^{-5}	[9]	5.39×10^{-5}	− 20
m-Aminophenol, K_2 (OH group)	1.35×10^{-10}	[6]	4.66×10^{-11}	− 65
3-Bromo-4-methoxy anilinium ion	8.32×10^{-5}	[9]	4.37×10^{-5}	− 47
4-Chloro-3-nitroanilinium ion	1.26×10^{-2}	[9]	7.76×10^{-3}	− 39

(Continued)

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TABLE 6-10 (Continued)

Aliphatic Compounds	K_a Measured	Ref.	K_a Estimated	Error in Estimated Value (%)
Bromoacetic acid	1.25×10^{-3}	[6]	1.06×10^{-3}	− 15
Dichloroacetic acid	5.53×10^{-2}	[6]	8.22×10^{-2}	+ 49
Trifluoroacetic acid	0.59	[6]	10.35	+1600
Cyanoacetic acid	3.36×10^{-3}	[6]	2.68×10^{-3}	− 20
But-3-enoic acid	4.62×10^{-5}	[6]	2.82×10^{-5}	− 39
Chloromethylphosphonic acid	3.98×10^{-2}	[6]	6.89×10^{-2}	+ 73
Hydroxymethylphosphonic acid	1.23×10^{-2}	[6]	1.81×10^{-2}	+ 47
Glycine				
K_1	4.47×10^{-3}	[6]	8.7×10^{-5} (COOH group)	b
K_2	1.66×10^{-10}	[6]	2.6×10^{-9} (NH_3^+ group)	b
Aminocyanomethane	4.57×10^{-6}	[9]	4.67×10^{-7}	90

a. Estimated value not corrected for symmetry effects on K_a.
b. Estimation method fails seriously for amino acids; this is due, at least in part, to the existence of Zwitterions as the dominant form of the neutral molecule.

LFER	=	linear free energy relationship
m	=	proportionality constant in Eqs. 6-14 and 6-15
M_i	=	molar concentration of component i
pK_a	=	negative logarithm of acid dissociation constant
pK_a^o	=	pK_a of unsubstituted parent acid
pK_a^x	=	pK_a of substituted acid
r	=	correlation coefficient
R	=	gas constant
s	=	probable error of fit of single observation in Table 6-9
T	=	temperature
Z_i	=	charge on *i*th species in Eq. 6-13

Greek

γ_i	=	activity coefficient for *i*th species
ρ	=	reaction constant in Hammett correlation
ρ^*	=	reaction constant in Taft correlation
σ	=	substituent constant in Hammett correlation
σ^-	=	substituent constant in Hammett correlation especially for anilinium ions and phenols
σ^+	=	substituent constant in Brown correlation
σ^*	=	substituent constant in Taft correlation

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7. Leffler, J.E. and E. Grunwald, *Rates and Equilibria of Organic Reactions,* John Wiley and Sons, New York (1963).
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11. Wells, P.R., *Linear Free Energy Relationships*, Academic Press, New York (1968).

12. Wolfe, N.L., U.S. Environmental Protection Agency, Athens, GA, personal communication, September 23, 1980.

7

RATE OF HYDROLYSIS

Judith C. Harris

7-1 INTRODUCTION

Hydrolysis is a chemical transformation process in which an organic molecule, RX, reacts with water, forming a new carbon-oxygen bond and cleaving a carbon-X bond in the original molecule. The net reaction is most commonly a direct displacement of X by OH:

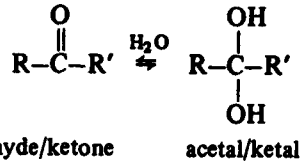
$$R{-}X \xrightarrow{H_2O} R{-}OH + X^- + H^+ \qquad (7\text{-}1)$$

This process can be distinguished from several other possible reactions between organic chemicals and water such as acid:base reactions (Eq. 7-2), hydration of carbonyls (Eq. 7-3), addition to carbon-carbon bonds (Eq. 7-4), and elimination (Eq. 7-5):

Acid: Base

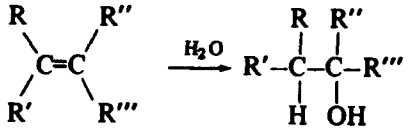
$$\left\{\begin{array}{l} \underset{\substack{\text{organic}\\\text{acid}}}{R{-}COOH} + H_2O \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{base}}}{RCOO^-} + H_3O^+ \\ \\ \underset{\substack{\text{organic}\\\text{base}}}{R{-}NH_2} + H_2O \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{RNH_3^+} + OH^- \end{array}\right\} \qquad (7\text{-}2)$$

Hydration



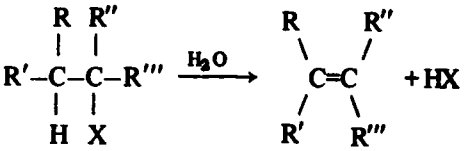
aldehyde/ketone acetal/ketal (7-3)

Addition



alkene alcohol (7-4)

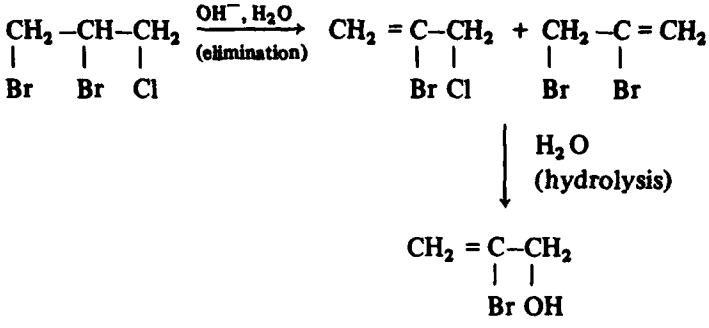
Elimination



alkyl halide alkene (7-5)

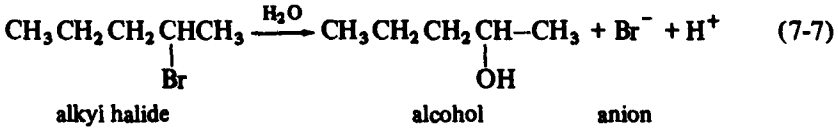
Acid-base equilibria of the type shown in Eq. 7-2 are discussed in Chapter 6. Hydration reactions as shown in Eq. 7-3 are reversible and therefore do not lead to a permanent chemical transformation of the organic species; these reactions are not considered further in this chapter. Addition reactions of the type shown in Eq. 7-4 are also excluded from further consideration, as they generally require reaction conditions that are unlikely to occur in the environment.

Detailed consideration of elimination reactions is also beyond the scope of this chapter. Reactions of this type are generally favored by higher temperatures and more strongly basic conditions than are commonly found in aqueous environments. However, elimination may be competitive with hydrolysis for organic compounds that contain good leaving groups (X of Eq. 7-5) such as a halide or sulfonate. For example, the hydrolysis of the nematocide 1,2-dibromo-3-chloropropane at 85°C and pH 9 has been reported [3b] to proceed via elimination of hydrogen bromide (major pathway) or hydrogen chloride (minor pathway) with subsequent further hydrolysis to 2-bromoallyl alcohol (Eq. 7-6). It is important that the possibility of competitive elimination be taken into account when one attempts to predict the hydrolytic behavior of organic chemicals in aqueous environments.

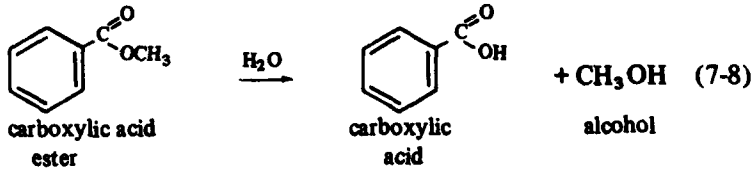


(7-6)

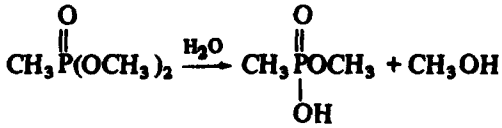
Hydrolysis (Eq. 7-1) is likely to be the most important reaction of organic compounds with water in aqueous environments and is a significant environmental fate process for many organic chemicals. It is actually not one reaction but a family of reactions involving compound types as diverse as alkyl halides, carboxylic acid esters, organophosphonates, carbamates, epoxides, and nitriles. Equations 7-7 through 7-12 illustrate some of these possible hydrolysis reactions and products.



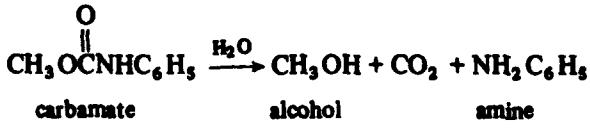
(7-7)



(7-8)

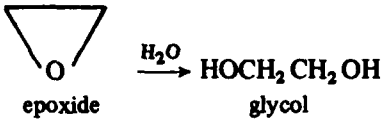


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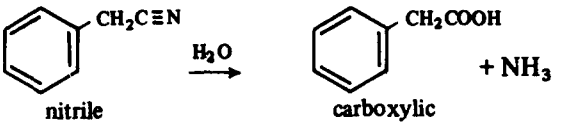


(7-10)

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epoxide — glycol (7-11)



nitrile — carboxylic acid (7-12)

Many organic functional groups (Table 7-1) are relatively or completely inert with respect to hydrolysis. Other functional groups that may hydrolyze under environmental conditions are listed in Table 7-2. Figure 7-1 gives examples of the range of hydrolysis half-lives that may be encountered for several categories of compounds.

TABLE 7-1

Types of Organic Functional Groups That Are Generally Resistant to Hydrolysis[a]

Alkanes	Aromatic nitro compounds
Alkenes	Aromatic amines
Alkynes	Alcohols
Benzenes/biphenyls	Phenols
Polycyclic aromatic hydrocarbons	Glycols
Heterocyclic polycyclic aromatic hydrocarbons	Ethers
	Aldehydes
Halogenated aromatics/PCBs	Ketones
Dieldrin/aldrin and related halogenated hydrocarbon pesticides	Carboxylic acids
	Sulfonic acids

a. Multifunctional organic compounds in these categories may, of course, be hydrolytically reactive if they contain a hydrolyzable functional group in addition to the alcohol, acid, etc., functionality.

7-2 CHARACTERISTICS OF HYDROLYSIS

Hydrolysis Mechanism. When an organic compound undergoes hydrolysis, a *nucleophile*[1] (water or hydroxide ion) attacks an *electrophile*[2] (carbon atom, phosphorus atom, etc.) and displaces a *leaving*

1. Nucleophile = nucleus-seeker
2. Electrophile = electron-seeker

TABLE 7-2

Types of Organic Functional Groups That Are Potentially Susceptible to Hydrolysis

Alkyl halides	Nitriles
Amides	Phosphonic acid esters
Amines	Phosphoric acid esters
Carbamates	Sulfonic acid esters
Carboxylic acid esters	Sulfuric acid esters
Epoxides	

group (chloride, phenoxide, etc.). As early as 1933, it was recognized that nucleophilic displacement reactions usually fit one of two distinct kinetic patterns, which were named S_N1 (Substitution, Nucleophilic, Unimolecular) and S_N2 (Substitution, Nucleophilic, Bimolecular) [11]. Although a detailed discussion of reaction mechanisms would be beyond the scope of this chapter, it is important to review briefly the important hydrolysis mechanisms. As Exner [5] has noted, "The fundamental condition for all correlations of rate data is a simple and constant reaction mechanism. . . . The condition of a constant reaction mechanism remains one of the most serious problems for correlation equations."

Kinetically, the "unimolecular" S_N1 process is characterized by a rate independent of the concentration and nature of the nucleophile, formation of racemic products from optically active material, and enhancement of rate by electron-donating substituents on the central atom. It is postulated that the rate-determining step is the ionization of RX to give a planar carbonium ion (Eq. 7-13a), which then undergoes a relatively rapid nucleophilic attack (Eq. 7-13b).

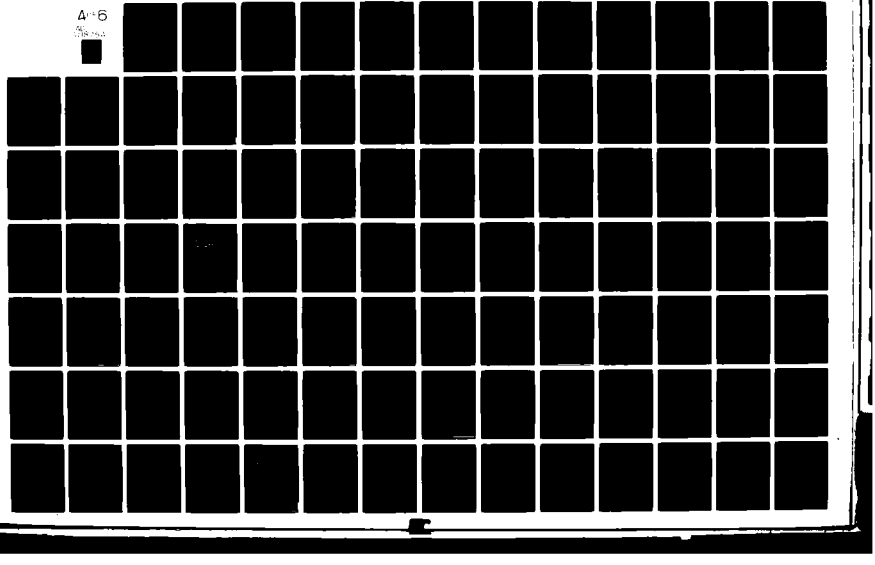
$$RX \xrightarrow{\text{slow}} R^{+} + X^{-} \qquad (7\text{-}13a)$$

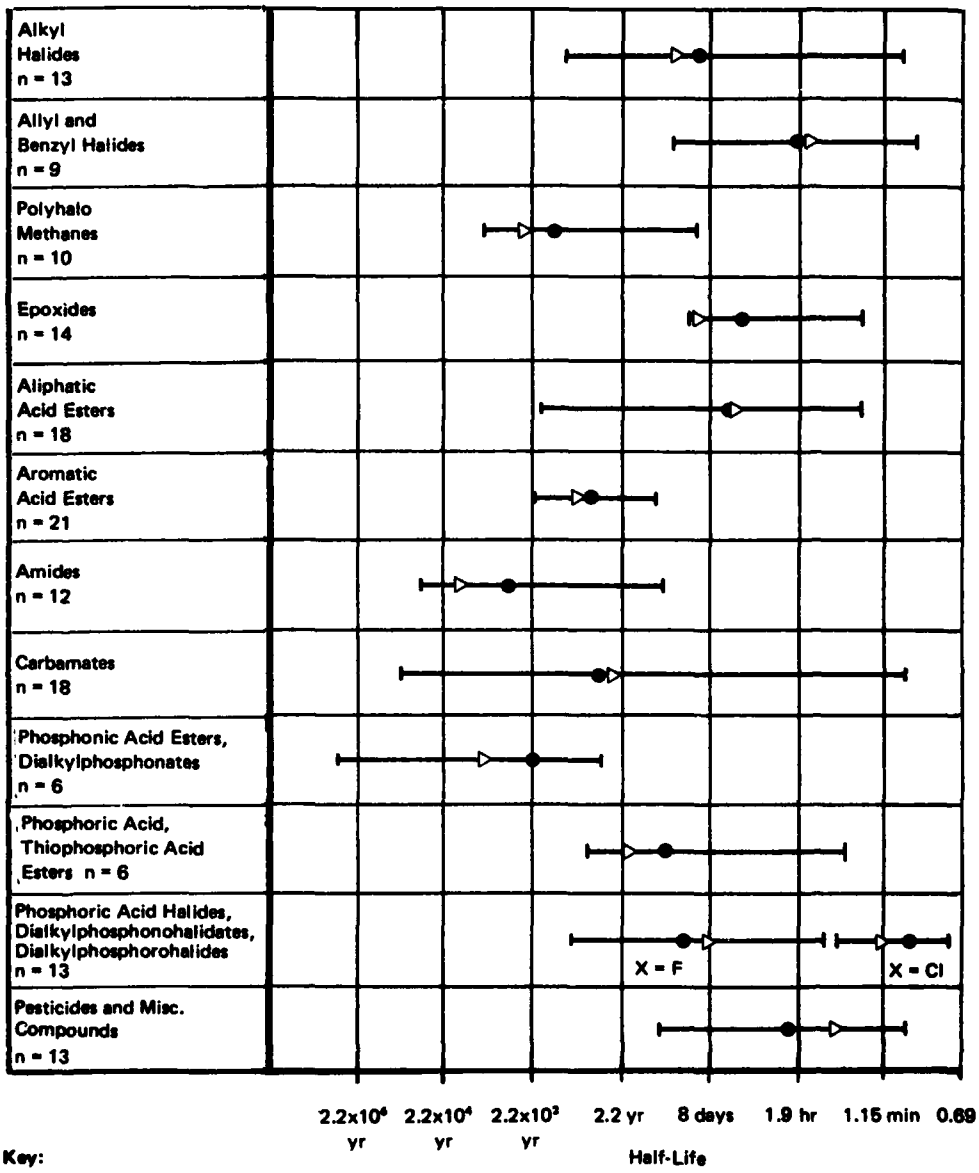
$$R^{+} + H_2O \xrightarrow{\text{fast}} ROH + H^{+} \qquad (7\text{-}13b)$$

In an S_N2 process, on the other hand, the rate depends on the concentration and identity of the nucleophile, and an optically active starting material gives a product of inverted configuration. This is postulated as a one-step bimolecular process involving nucleophilic attack on the central atom at the side opposite the leaving group:

$$H_2O + R{-}X \longrightarrow [H_2O\cdots R\cdots X] \longrightarrow H^{+} + HO{-}R + X^{-} \qquad (7\text{-}14)$$

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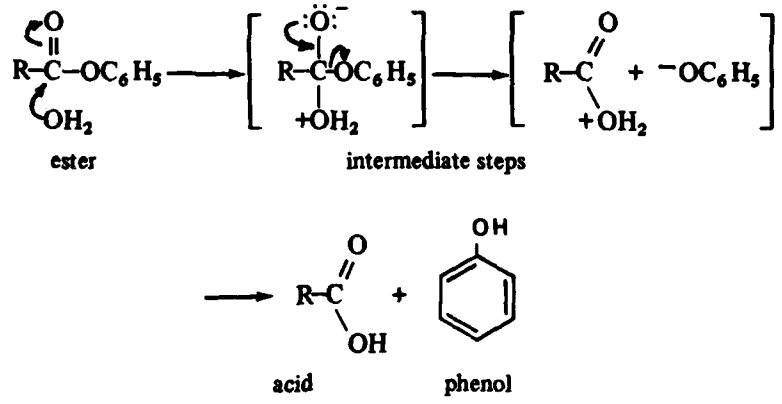
Key:

- ● Average
- ▷ Median
- n No. of Compounds Represented

Source: Adapted [7] from data of Mabey and Mill[16].

FIGURE 7–1 Examples of the Range of Hydrolysis Half-Lives for Various Types of Organic Compounds in Water at pH 7 and 25°C

Hydrolysis of species such as carboxylic acid esters, amides, or organophosphorus compounds generally involves bimolecular nucleophilic attack. As the example in Eq. 7-15 indicates, such reactions are analogous to the S_N2 (rather than S_N1) mechanism of attack on saturated carbon.



(7-15)

Many reactions appear to involve either "pure S_N1" or "pure S_N2" mechanisms. The limiting S_N1 case is favored by R- systems that form stable carbonium ions (e.g., tributyl and triphenyl methyl systems), by X- systems that are good leaving groups (e.g., halide ions, *p*-toluenesulfonate ions), and by high-dielectric-constant solvents such as water. Conversely, the limiting S_N2 case is favored by R- systems with low steric hindrance and low carbonium ion stability (e.g., methyl and other primary alkyl systems), by X- systems that are poor leaving groups (e.g., NH_2^- or $CH_3CH_2O^-$), and by organic solvents such as acetone. However, there probably exists in nature a continuum of mechanisms between these two extremes [8]. In estimating rates of hydrolysis, it is important to consider whether the reaction of interest and the available "model reactions" involve similar mechanisms. Convincing evidence as to similarity of mechanism is available only from measured kinetic data — the form of the rate law, thermodynamic activation parameters, isotope effects, etc. — which are normally unavailable for the compound whose hydrolysis rate must be estimated. The only general guidance that can be provided is that one should select model reactions in which both R-and X- groups are as similar as possible to those of the compound whose hydrolysis rate is unknown.

Hydrolysis Rate Law. It is generally observed that hydrolysis of organic chemicals in water is first-order in the concentration of the organic species (Eq. 7-16) [1,6,16,17,30,31,33]; the rate of disappearance of RX, $-d[RX]/dt$, is directly proportional to the concentration of the compound, [RX]:

$$- d[RX]/dt = k_T [RX] \quad (7\text{-}16)$$

where k_T = hydrolysis rate constant. The first-order dependence is important, because it implies that the hydrolysis half-life of RX (Eq. 7-17) is independent of the RX concentration and, thus, that results obtained at relatively high RX concentration can be extrapolated to low concentrations of RX, assuming other reaction conditions (e.g., temperature, pH) are constant.

$$t_{1/2} = 0.693/k_T \quad (7\text{-}17)$$

The rate expression presented in Eq. 7-16 is an oversimplification for most organic hydrolysis reactions. The rate constant k_T is a pseudo first-order rate constant that may include contributions from acid- and base-catalyzed hydrolysis as well as nucleophilic attack by water. The following equation explicitly recognizes these possibilities:

$$k_T = k_H [H^+] + k_0 + k_{OH}[OH^-] + \sum_i k_{HA_i} [HA] + \sum_j k_{B_j} [B_j] \quad (7\text{-}18)$$

where:

k_T	=	total hydrolysis rate constant
k_H	=	rate constant for specific acid-catalyzed hydrolysis
k_0	=	rate constant for neutral hydrolysis
k_{OH}	=	rate constant for specific base-catalyzed hydrolysis
k_{HA}	=	rate constant for general acid-catalyzed hydrolysis
k_B	=	rate constant for general base-catalyzed hydrolysis
$[H^+]$	=	hydrogen ion concentration
$[OH^-]$	=	hydroxyl ion concentration
[HA]	=	general acid concentration
[B]	=	general base concentration
i,j	=	indices to identify different acids and bases that may be present

The first term in Eq. 7-18 represents specific acid catalysis by hydronium ion, H^+. Such catalysis is common in both S_N1 and S_N2 reactions of those compounds, RX, which can be protonated at a site that either makes X a better leaving group (as in the case of amine hydrolysis), or makes the central carbon in R more electrophilic (as in the case of ester hydrolysis), or both.

The second term, which corresponds to neutral hydrolysis, k_0, could be written in terms of a second-order rate constant:

$$k_0 = k_{H_2O}[H_2O] \qquad (7\text{-}19)$$

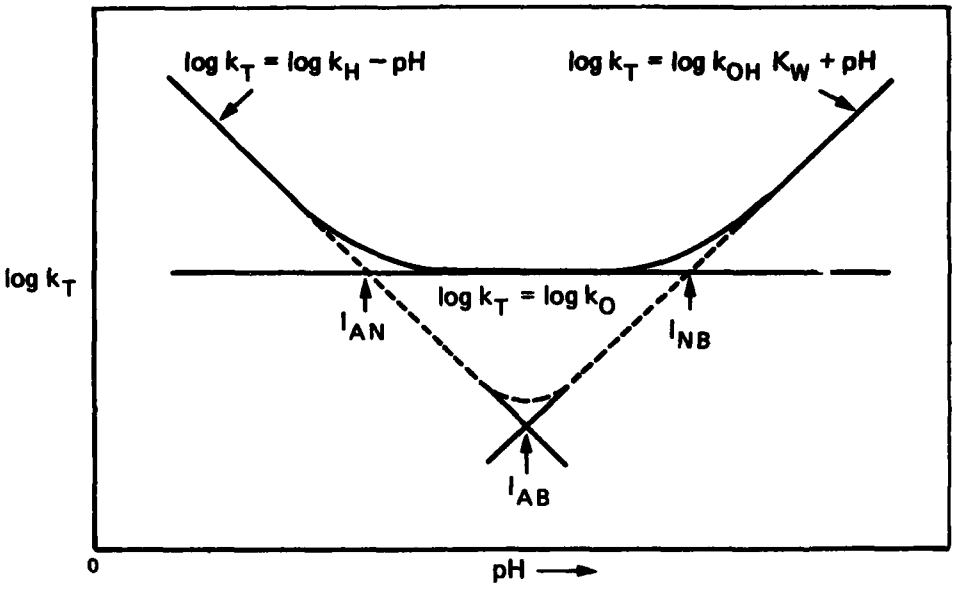
For S_N2 reactions, however, k_0 is more simply treated as pseudo first-order, since the concentration of water in aqueous systems is essentially constant at 55.5 M.

The third term in Eq. 7-18 represents specific base catalysis by hydroxide ion, OH^-. A contribution of this type to k_T is observed for virtually all substrates that undergo S_N2-type hydrolysis. The hydroxide ion "catalysis" reflects the fact that OH^- is a much stronger nucleophile (typically by a factor of about 10^4) than is water [22]. Specific base catalysis is not a feature of S_N1 reactions, because no nucleophile is involved in the rate-determining step (see Eq. 7-13a).

The two final terms in Eq. 7-18 reflect the possibility of general acid/base catalysis by acids/bases other than H^+ and OH^-. These processes can make significant contributions to values of k_T for some types and compounds when the hydrolysis rate constant is measured in aqueous buffer solutions. However, because it is impossible to predict the types and concentrations of acidic and basic species that may be present in aqueous environments, it is not possible to estimate the importance of general acid/base catalysis. Therefore, the two final terms of Eq. 7-18 are generally dropped [16,21], and the expression for k_T is written as:

$$k_T = k_H[H^+] + k_0 + k_{OH}[OH^-] \qquad (7\text{-}20)$$

Mabey and Mill [16] have neatly summarized the pH dependence of the hydrolysis rate implicit in Eq. 7-20 (Figure 7-2). They point out that pH-rate profiles for hydrolysis may be U-shaped (solid line) or V-shaped (dashed line), depending on the magnitude of the neutral hydrolysis rate constant compared with those of the specific acid/base-catalyzed process. The three transition points marked I_{AN}, I_{AB}, and I_{NB} in Figure 7-2 correspond to values of pH at which the acid- or base-catalyzed processes begin to make significant contributions to k_T. If such transition points fall within the aquatic environmental pH range of 5-8 for a particular organic compound or class, acid or base catalysis must be considered in predicting rates of aqueous hydrolysis. Table 7-3 summarizes Mabey and Mill's data for a number of categories of hydrolyzable organics.



Source: Mabey and Mill [16].

FIGURE 7–2 pH Dependence of k_T for Hydrolysis by Acid-, Water-, and Base-Promoted Processes

TABLE 7-3

pH Regimes in Which Specific Acid/Base Catalysis Is Significant for Organic Functional Groups

Category	Acid Catalysis	Base Catalysis
Organic halides	none	> 11
Epoxides	< 3-8[a]	> 10
Aliphatic acid esters	< 1.2-3.1	> 5.2-7.1[b]
Aromatic acid esters	< 3.9-5.2[a]	> 3.9-5.0[b]
Amides	< 4.9-7[a]	> 4.9-7[b]
Carbamates	< 2	> 6.2-9[b]
Phosphonic acid esters	< 2.8-3.6	> 2.8-3.6

a. Acid catalysis may be important within the typical aquatic-environment pH range of 5 < pH < 8.

b. Base catalysis may be important within the typical aquatic-environment pH range of 5 < pH < 8.

Source: Based on data of Mabey and Mill [16].

More complex pH-rate profiles may be observed for organic species, such as mono esters of phosphoric/phosphonic acids, that undergo acid/base dissociation in the environmental pH range. This possibility should be kept in mind when estimating hydrolysis rate constants.

Measurement of Hydrolysis Rate. Experimental measurement of the rate of hydrolysis should involve the determination of four conceptually distinct components:

- The form of the rate law,
- The magnitude of the rate constant(s),
- The products of reaction, and
- Temperature dependence (energy of activation).

Because of the simplicity of handling first-order kinetic data, experimental reaction conditions are usually selected so that the reaction is expected to be (pseudo) first-order in RX (Eq. 7-16). For a reaction that actually follows a rate law of the form shown by Eq. 7-21, the pseudo first-order condition is achieved by using dilute aqueous buffer to fix H^+ and OH^- at constant concentrations for the duration of the experiment.

$$-d[RX]/dt = k_H[H^+][RX] + k_0[RX] + k_{OH}[OH^-][RX] \qquad (7\text{-}21)$$

The decrease in concentration of RX as a function of time is then monitored by any convenient method, such as withdrawal of aliquots for extraction and chromatographic analysis of RX, measurement of visible or ultraviolet light absorbance at a frequency characteristic of RX, or determination of concentration of X released by the hydrolysis. The presumed first-order dependence of the reaction rate on [RX] is confirmed by plotting ln[RX] versus time; the plot should be linear with an intercept at the initial RX concentration. The slope is equal to $-k_T$, as shown below.

$$-d[RX]/dt = k_T[RT] \qquad (7\text{-}16)$$

$$-d[RX]/[RX] = k_T dt \qquad (7\text{-}22)$$

$$-\ln[RX] = k_T t + \text{constant} \qquad (7\text{-}23)$$

$$\ln[RX] = -k_T t - \ln[RX]_0 \qquad (7\text{-}24)$$

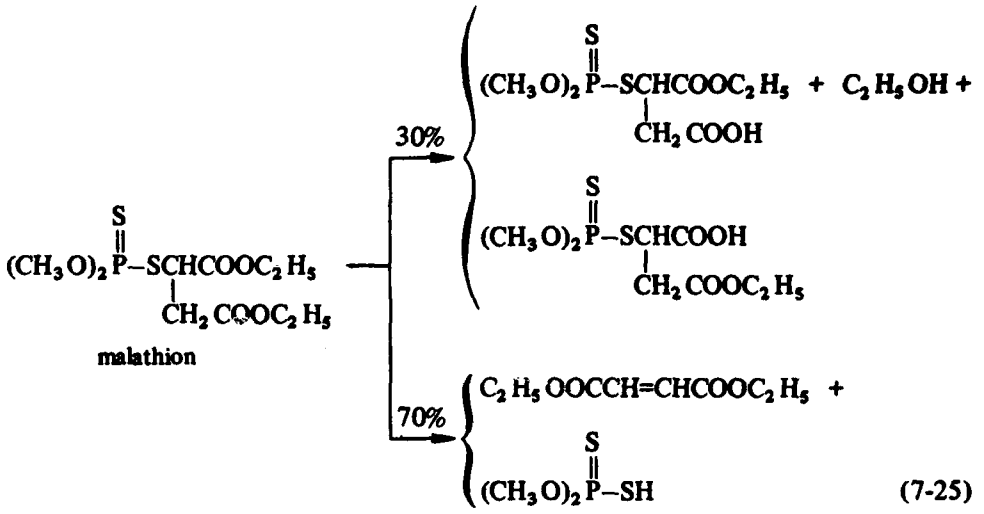
It is desirable that kinetic measurements be conducted over one or preferably two half-lives to ensure that any deviations from the presumed first-order linearity are detectable, but this may not be feasible for slow reactions.

Most kinetic studies are carried out at organic compound concentrations of at least 0.001 M, which is substantially higher than those typically encountered in the environment. The studies have therefore been criticized as unrealistic. Mabey and Mill [16] point out that such criticism is misplaced, since "it is axiomatic that rate processes found to be simple at high concentrations remain so at low concentrations [of the organic species]."

To determine whether Eq. 7-21 is the correct rate law and to determine the magnitude of k_H and/or k_{OH}, k_T is determined in separate experiments at various pH values. The k_H is determined from low-pH experiments, while k_{OH} is determined from results of high-pH experiments. It should be noted that uncertainties in the experimental measurement of pH may be a significant source of error in determination of the value of k_H or k_{OH}. For example, an uncertainty of ± 0.02 in the measured pH value corresponds to an uncertainty of about 5% in the concentration of H^+ (or OH^-) and thus in the value of k_H (or k_{OH}) calculated from k_T.

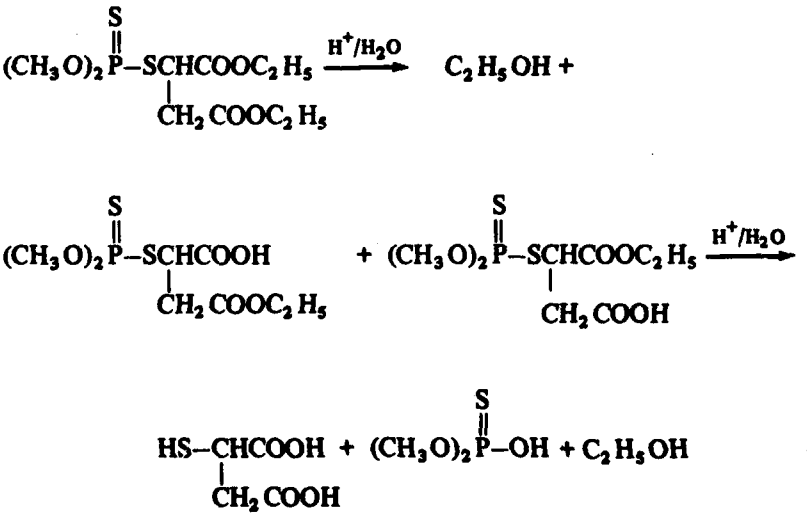
The identity of the product(s) of hydrolysis is important for confirming the mechanism and for selecting appropriate model reactions to estimate the rate of hydrolysis of additional organic chemicals of the type RX. Unfortunately, the products are frequently unknown, because many kinetic studies monitor only the disappearance of the starting material, RX, or appearance of one possible reaction product such as X^- (e.g., chloride ion). In such studies it is not possible to determine whether elimination reactions (Eq. 7-5) may be occurring instead of, or in addition to, the presumed hydrolysis.

An example of the complexities that can be encountered and that can be addressed only by careful examination of reaction products is provided by studies of the hydrolysis of malathion [6,30,31]. Wolfe and co-workers studied the pseudo first-order hydrolysis over a range of pHs and temperatures [30,31]. Under basic conditions at 27°C after one half-life, the relative product distribution was as shown in Eq. 7-25.



(7-25)

The relative importance of the two pathways — carboxylate ester cleavage versus phosphorodithioate ester cleavage — was found to be temperature-dependent. Furthermore, a different set of reaction pathways was found to be operative under acid conditions (Eq. 7-26).



(7-26)

Estimation of reaction rates for complex hydrolytic pathways such as these is well beyond the state of the art. Conversely, malathion hydrolysis is unlikely to provide a useful model for predicting reactivities of other organophosphorus compounds. ***The estimation of hydrolysis rates is feasible only when the hydrolysis pathway is reasonably simple and straightforward and the product(s) can be predicted.***

Temperature Dependence of k. The rate of hydrolysis of organic chemicals increases with temperature. The quantitative relationship between the rate constant and temperature is frequently expressed by the Arrhenius equation,

$$k = Ae^{-E_A/RT} \tag{7-27}$$

in which E_A is the Arrhenius activation energy (kcal/mol), R is the gas constant (1.987 cal/deg·mol), and T is the temperature (K) [15]. The pre-exponential factor, A, has the same units as the rate constant. According to Eq. 7-27, a plot of log k versus 1/T is linear, with slope equal to $-E_A/2.303R$ and intercept equal to log A:

$$\log k = \log A - \frac{E_A}{2.303RT} \tag{7-28}$$

An alternative form of temperature dependence derived from the Eyring reaction rate theory (transition state theory) is

$$k = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \tag{7-29}$$

in which k is Boltzmann's constant, h is Planck's constant, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are enthalpy of activation and entropy of activation, respectively [18]. According to Eq. 7-29, $\Delta H^{\ddagger}$ can be calculated from the slope of a plot of log k/T versus 1/T, and $\Delta S^{\ddagger}$ can be calculated from the intercept of the following equation:[3]

$$\log \frac{k}{T} = \log \frac{k}{h} - \frac{\Delta H^{\ddagger}}{2.303RT} + \frac{\Delta S^{\ddagger}}{R} \tag{7-30}$$

Some investigators [16] choose to fit the k,T data using a relationship of the following form:

$$\log k = -\frac{A}{T} + B \log T + C \tag{7-31}$$

In practice, Eqs. 7-28, -30 and -31 usually give equally good fit to experimental data because of the small number of data points (typically no more than 3 to 5) and the uncertainties in the individual measured values. In theory, the temperature dependence of k is more

3. The thermodynamic parameters of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, can be interpreted in terms of reaction mechanism as well as temperature dependence of k. Comparisons with ΔH° and ΔS° for equilibria and with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for other reactions are helpful. In particular, a change in sign of $\Delta S^{\ddagger}$ between one reaction and another is generally a reliable indicator that the two reactions involve different mechanisms.

complex than either equation would suggest, because E_A and A (Eq. 7-27), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Eq. 7-29), and constants B and C (Eq. 7-31) are themselves temperature-dependent. These second-order temperature dependencies can be accounted for (in the rare instances where it is warranted by the data) by incorporating heat capacity corrections to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for example [15].

Equations 7-28, -30 and -31 are appropriately applied to k_H, k_o and k_{OH} separately, rather than to the overall hydrolysis rate constant, k_T. Since the catalyzed and uncatalyzed reaction pathways generally show quite different temperature dependencies, plots based on k_T would probably be distinctly nonlinear. Furthermore, the slopes and intercepts of such plots would have no physical significance.

The values of E_A and $\Delta H^{\ddagger}$ for hydrolysis of organics in water usually fall in the range of 12-25 kcal/mol, with values of 17-20 kcal/mol most common. Some useful rules of thumb for temperatures in the vicinity of 300K (0-50°C) are that:

- a 1° change in temperature causes a 10% change in k,
- a 10° change in temperature causes a factor of 2.5 change in k, and
- a 25° change in temperature causes a factor of 10 change in k.

These rules are based on a 17-18 kcal/mol value of E_A or $\Delta H^{\ddagger}$.

The rather high sensitivity of k to changes in temperature has three important consequences:

(1) In the experimental measurement of k, the temperature must be controlled both accurately and precisely. For example, an uncertainty of ± 0.2°C in T corresponds to $\pm 2\%$ in k; ± 1° in T corresponds to $\pm 10\%$ in k.

(2) As pointed out by Mabey and Mill [16], $\pm 2\%$ in k leads to an uncertainty of $\pm 5\%$ in E_A ($\Delta H^{\ddagger}$), while $\pm 10\%$ in k leads to $\pm 100\%$ (factor of 2) uncertainty in E_A ($\Delta H^{\ddagger}$). The uncertainty in E_A ($\Delta H^{\ddagger}$) is magnified when laboratory rate data are extrapolated over 25° or larger intervals to estimate values of k under environmental conditions. For example, a 5% error in E_A ($\Delta H^{\ddagger}$) will give rise to a 30% error in the estimated k for an extrapolation from 50°C to 25°C. This inherent propagation of error (e.g., from 2% in

the laboratory rate data to 5% in E_A to 30% in the extrapolated k) is quite independent of the possibility that a typical small k-versus-T data set may contain at least one outlier. It is probably prudent to regard rate data obtained by extrapolation as order-of-magnitude estimates.

(3) A 10° seasonal temperature variation, a 1° diurnal variation, or a 5° spatial temperature gradient in an aquatic ecosystem would be associated with a corresponding 10% to 250% variation in hydrolysis rate for a compound with $\Delta H^{\ddagger} \approx 18$ kcal/mol. To adequately model the effects of these temperature variations on the hydrolysis rate, more accurate and precise kinetic data than are generally available would be required. On the other hand, the rough order-of-magnitude estimates of k that can be drawn from the available data are probably quite compatible with existing black-box, homogeneous-isothermal-compartment models of the environment.

Effect of Reaction Medium. Hydrolysis reactions, which frequently involve ionic species as reactants, intermediates, and/or products, are affected by changes in the solvating power of the reaction medium. Both changes in ionic strength and the presence of organic solvents can affect the solvating power and thus alter the hydrolysis rate. Specific medium effects due to general acid/base and trace-metal catalysis are also possible.

Freshwater environmental media are characterized by low organic content and by low (<0.01 M [16]) ionic strength. The dilute aqueous buffer solutions employed by most current workers for determining rate constants and developing empirical correlations may be adequate approximations of actual freshwater conditions. Wolfe *et al.* [31] have reported good agreement between laboratory data for distilled water solutions and results of hydrolysis in natural river water for malathion. Preliminary data suggest that this is also true for hydrolysis of hexachlorocyclopentadiene in three natural water samples [27].

Salt effects of buffer components will generally not alter k by more than 5-10% as long as the total ionic strength is ≤0.10 M [16]. However, the possibility of general acid or base catalysis (Eq. 7-18) by buffer components should be considered for reactions that show significant effects of specific acid (H^+) or base (OH^-) catalysis. Current practice is to use low (0.01-0.001 M) total buffer concentrations, which

are adequate when RX concentrations are in the range of 100-1000 ppm, but the general acid/base species are still substantially higher in concentration than the 10^{-5} to 10^{-8} H^+/OH^- concentrations of the environmental pH range. This effect would lead to overestimation of the rate of hydrolysis unless the laboratory data were corrected by extrapolation to zero buffer concentration. On the other hand, it is also possible that trace-metal species present in natural waters but not in the laboratory systems could catalyze hydrolysis and lead to reaction rates higher than predicted. An effect of this sort was postulated by Meikle and Youngson [17] to explain an observed rate enhancement of about 15 fold for hydrolysis of chlorpyrifos in canal water over that measured in phosphate buffer solutions in distilled water.

Sediment is another medium effect that may be important in comparing hydrolysis rates estimated from laboratory data with those for natural waters. Work is under way at EPA's Athens (Georgia) Environmental Research Laboratory [29] and elsewhere to develop a better understanding of the effect of sediment on chemical transformations of organics in aquatic environments. The literature gives little information on the possibility of significant effects beyond the removal of some fraction of the organic chemical by adsorption on sediment.

The present state of the art does not enable us to predict the influence of potential general acid/base catalysts, trace metal catalysts, or sediments present in natural water systems on the rate of hydrolysis of organic chemicals. The reader should, however, be aware of these potential complications in extrapolating estimated hydrolysis rates to aquatic environments.

The aqueous solvent influences the rate and mechanism of hydrolysis reactions in a number of ways: as a nucleophilic reagent, as a high-dielectric-constant continuum in which reaction takes place, and as a specific solvating agent for organic reactants and products (leaving groups). Therefore, it is highly desirable to base estimates of hydrolysis rates on kinetic data and empirical correlations developed from 100% aqueous solvent systems. Most present-day experimental programs approach this ideal; stock solutions of the organic are commonly prepared (for convenience) in a solvent such as methanol, acetone, or acetonitrile and then diluted with water to <1% organic solvent for kinetic runs.

Unfortunately, many of the rate-constant tabulations, such as those of Ref. 24, and empirical rate-constant correlations

[2,5,13,15,20,22,25] in the older literature refer to kinetic experiments in mixed organic-aqueous solvents. To achieve adequate solubility for determination of [RX] by the methods available at the time, solvent systems containing 50% to 90% of a polar organic solvent (such as methanol, ethanol, acetone, or dioxane) were commonly used. The influence of solvent composition on organic reactivity has been reviewed [13,25]. The subject is complex and only poorly understood in theory. Mabey and Mill [16] observed that "although extrapolation of rate data from mixed solvents to water can be done with moderate success using schemes like the Winstein-Grunwald relation [15], combined extrapolations of temperature and solvent composition together with the questionable meaning of pH in mixed solvents introduce sufficient error in the final estimate to make such effort of questionable value" for purposes of comparing rates of hydrolysis of organic compounds in water under environmental conditions.

We believe that this observation is equally true for purposes of this chapter and have therefore not discussed approaches to correcting for solvent effects. However, in the absence of any other data, it may be appropriate to apply an existing empirical correlation to estimate the rate constant for hydrolysis in a particular mixed organic-water solvent and treat this as an estimated *lower limit* of the hydrolysis rate constant in water. It has been noted that rate constants for hydrolysis in water may be 20 to 2500 times higher than in 50% organic solvent [16].

7-3 OVERVIEW OF ESTIMATION METHODS

Table 7-4 summarizes the estimation methods described in this chapter. These approaches are first discussed in general terms below; instructions are then given for: (1) initiating the estimation process, (2) calculating an overall hydrolysis rate, (3) correcting for temperature, and (4) calculating a hydrolysis half-life.

The fundamental approach for estimating the rate of hydrolysis of organic chemicals in water is the application of linear free energy relationships to the estimation of the hydrolysis rate constant(s). An LFER is an empirical correlation between the standard free energies of reaction (ΔF°) or activation ($\Delta F^{\ddagger}$) for two series of reactions, both subjected to the same variations in reactant structures or reaction conditions. Several excellent treatments of the theoretical aspects and the broad applicability of LFERs have been written [4,10,15,25], and no attempt will be made here to present a detailed explanation or

TABLE 7-4

Characteristics of Estimation Methods Described

Section	Estimate[a]	Basis	Chemical Classes Covered[b]
7-5	k_H	Hammett Correlation	Ring-substituted benzamides; ethyl benzoates
7-6	k_H	Taft Correlation	Ortho-substituted benzamides
7-7	k_0	Hammett Correlation	Benzyl halides; dimethyl benzyl halides; benzyl tosylates. (All in mixed organic/aqueous solvents.)
7-8	k_{OH}	Hammett Correlation	Benzene ring-substituted compounds based on $ArCOOCH_3$, $ArCOOCH_2CH_3$, $ArCH_2COOCH_2CH_3$, $ArCH{=}CHCOOCH_2CH_3$, $ArCONH_2$, $ArOCOCH_3$, $ArCH_2OCOCH_3$, $ArCON(CH_3)_2$, $ArCONHCH_3$, $ArCH_2Cl$, and $ArOSi(CH_2CH_3)_3$. (All in mixed organic/aqueous solvents.)
7-9	k_{OH}	Taft Correlation	Dialkyl phthalate esters
7-10	k_{OH}	Correlation with pK_a of leaving group	Aryl esters of methylphosphonic acid ($(CH_3)_2CHOP(O)(CH_3)OAr$); carbamates of the form: (1) $(C_6H_5)NHCOOAr$; (2) $CH_3N(C_6H_5)COOAr$; (3) $CH_3NHCOOAr$; or (4) $(CH_3)_2NCOOAr$.

a. k_H = rate constant for acid-catalyzed hydrolysis.
k_0 = rate constant for neutral hydrolysis.
k_{OH} = rate constant for base-catalyzed hydrolysis.

b. Ar = aromatic group.

derivation. The potential utility of LFERs in estimating environmental reaction rates has also been described by others [18,32].

Use of the LFER method to estimate hydrolysis reaction rates is basically a substituent-effect approach. It is essentially the same in

concept, though somewhat more complex in practice, as the approach to estimation of acid dissociation constants presented in Chapter 6. The reader who is not familiar with LFER concepts and approaches is urged to read through Chapter 6 and work out some simple acid dissociation constant examples before undertaking the estimation of hydrolysis rate constants.

Substituent changes in the hydrolyzable molecule, RX, may be made either in the central, R, portion of the molecule or in the leaving group, X. When substituent changes are made in R, and R is aromatic, the hydrolysis rate constant(s) may be correlated with the Hammett σ substituent constants as shown below (see also §6-4, Eq. 6-16 and Table 6-3).

$$\log k = \rho\sigma + \log k_0 \qquad (7\text{-}32)$$

As in the case of acid dissociation constants, ρ is a reaction constant that reflects the sensitivity of the particular reaction series to substituent effects.

If RX is aliphatic and substituent changes are made in the R group, the Taft $\rho^*\sigma^*$ is used in place of the Hammett equation (see §6-5). For estimation of hydrolysis reaction rate constants, it is recognized [20,25,30] that a single Taft substituent parameter, σ^*, sometimes does not give good correlations. Improved correlations are achieved by using a two-parameter Taft equation (Eq. 7-33) in which σ^* is a measure of the *polar* effects and E_s is a measure of the *steric* effects of the substituent.

$$\log k = \rho^*\sigma^* + \delta E_s + \log k_0 \qquad (7\text{-}33)$$

ρ^* and δ are reaction constants. Although there is a danger that the apparent improvement in correlation is simply an artifact due to inclusion of a second term in the equation, it is plausible that hydrolysis rates should be susceptible to both steric and polar effects of substituents and that these *might* be separable. In some cases, the steric effect is apparently dominant, so that $\rho = 0$ and Eq. 7-34 holds [20].

$$\log k = \delta E_s + \log k_0 \qquad (7\text{-}34)$$

If substituent changes are made in the leaving group, X, the Hammett and Taft correlations are potentially applicable to aromatic and aliphatic moieties, respectively. An alternative, conceptually equivalent to the Hammett relationship, is to attempt to apply a

correlation between the rate constant(s) and the pK_a of the leaving group [9,32].

The data base of established LFER correlations for prediction of hydrolysis rate constants is very limited. In fact, if one were to apply the criterion suggested by Exner [5] that "simple regressions with less than 10 points and multiple regressions with less than 20 may not be worthwhile," the data base would disappear altogether, save for one carbamate data set [32]. The correlations that have been published are described later in this chapter. The number of sample calculations provided is quite limited, because there are few independently measured rate constants with which estimated values can be compared. Essentially, all available data were used in developing the correlation equations.

The general procedure for estimating the rate of hydrolysis of an organic chemical is described below. Sections 7-5 through 7-10 describe the specific steps for estimating k_H, k_0, or k_{OH} from a particular correlation equation.

(1) Categorize the organic chemical in terms of functional groups present. Consult Tables 7-1 and 7-2 to identify hydrolyzable groups.

(2) Check Table 7-3 to determine whether k_H and/or k_{OH} in the hydrolyzable groups are potentially significant in the environmental pH range of 5-8.

(3) If k_H is required, estimate it from correlations in §7-5 or 7-6.

(4) Estimate k_0 from correlations in §7-7.

(5) If k_{OH} is required, estimate it from correlations in §7-8, 7-9 or 7-10.

(6) If k_H, k_0, and/or k_{OH} refers to a temperature, T_2, other than 298K (25°C), convert to 25°C as follows:

$$\log k_{25°C} = \log k_{T_2} - 3830\left(\frac{T_2 - 298}{298T_2}\right) \qquad (7\text{-}35)$$

in which T_2 is in K and an average $\Delta H^{\ddagger}$ or E_A value of 17.5 kcal/mol has been assumed.

(7) Calculate k_T for pH(s) of interest according to Eq. 7-36 (cf. Eq. 7-20):

$$k_T = (k_H \times 10^{-pH}) + k_0 + (k_{OH} \times 10^{pH-14}) \quad (7\text{-}36)$$

(8) Calculate the hydrolysis half-life ($t_{1/2}$) according to Eq. 7-37:

$$t_{1/2} = \frac{0.693}{k_T} \quad (7\text{-}37)$$

7-4 UNCERTAINTY IN ESTIMATING VALUES

Hydrolysis rate constants that are estimated by the methods described here are subject to the following major sources of uncertainty:

(1) The correlation equations are typically based on three to six data points. This reduces confidence in the validity of extrapolating to compounds outside the original data set.

(2) Substituent and reaction constants are obtained from a variety of sources and may refer to temperatures and reaction media that differ from those of the ambient aquatic environment.

(3) Changes in reaction mechanism across a series of related organic compounds is a real possibility.

(4) Correlation equations apply to k_H, k_0, and k_{OH} individually; it may be impossible to estimate all of the rate constants required for calculation of k_T and hence the hydrolysis half-life.

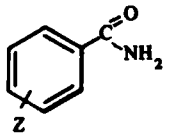
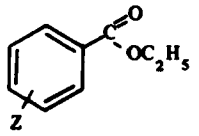
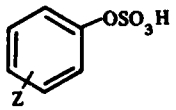
While it is not possible to quantify the probable uncertainties, a qualitative review would suggest that estimated k's be considered order-of-magnitude estimates. If an estimated k is within one or two orders of magnitude of the value considered critical in a given context, a sufficiently reliable value would probably be obtainable only by experimental measurement.

7-5 ESTIMATION OF k_H FROM THE HAMMETT CORRELATION

Data presently available limit the strict applicability of this method to two reaction series for which Hammett reaction constants for water solvent have been determined. These data (Table 7-5) are for hydrolysis of ring-substituted benzamides and ethyl benzoates. The tabulated ρ values (but *not* the tabulated rate constants) could be

TABLE 7-5

Data for Estimation of k_H from the Hammett Correlation

Compound	T (°C)	k_H^o ($M^{-1}s^{-1}$)[a]	Ref.	ρ	Ref.
	100	3.1×10^{-4}	[30]	0.12[b]	[25]
	25	1×10^{-7}	[12]	0.11[b]	[25]
	49	1.2×10^{-4}	[30]	0.60[c]	[12]

a. k_H for parent compound with Z=H.

b. For displacement of $-NH_2$ or $-OC_2H_5$.

c. For displacement of substituted phenoxide.

assumed to apply as well to closely related reaction series, such as acid-catalyzed hydrolysis of ring-substituted N-methylbenzamides or other alkyl benzoates. The range of applicability could thus be extended somewhat if values of the rate constants for parent compounds of interest (designated as k° in this chapter) were measured or found in the literature.

Basic Steps

(1) From Table 7-5 or other (literature) sources, obtain the value of k_H^o for an unsubstituted parent compound.

(2) From Table 7-5 or other literature source, obtain the value of ρ for the applicable reaction series.

(3) Find the value of σ as follows:

- If the compound of interest is a monosubstituted benzamide or benzoate ester, find the appropriate substituent constant in Table 6-3 of Chapter 6.
- If more than one substituent is present, see Table 6-4 (Chapter 6) for the appropriate multi-substituent σ value.

- If the correct combination is not found in Table 6-4, locate the individual substituents in Table 6-3 and sum their σ values. Use this sum (σ_T) in place of a single σ value to calculate k. If Table 6-3 does not list one or more of the substituents, find a default value of σ in Table 6-5.
- A substituent that is neither covered by the generalized categories of Table 6-5 nor found in Table 6-3 cannot be assigned a σ value; therefore, k for the corresponding organic compound cannot be calculated from the Hammett equation.

(4) Calculate k_H from Eq. 7-32.

(5) If k_H is for $T \neq 25°C$ and temperature coefficient data for k_H are available from the literature, calculate k_H (25°C) according to Eq. 7-27, -29, or -31. In lieu of these, use Eq. 7-35.

Example 7-1 Estimate k_H for ethyl *p*-nitrobenzoate. Also, estimate the hydrolysis half-life (considering only the acid-catalyzed reaction) at pH = 6.

(1) $k_H^0 = 1 \times 10^{-7}\ M^{-1}s^{-1}$ for ethyl benzoate in water at 25° (Table 7-5).

(2) From Table 7-5, $\rho = 0.11$ for ethyl benzoate hydrolysis.

(3) From Table 6-3, $\sigma = 0.778$ for a *p*-nitro substituent.

(4) From Eq. 7-32,

$$\log k_H = (0.11)(0.778) - 7.00$$

$$\log k_H = -6.92$$

$$k_H = 1.2 \times 10^{-7}\ M^{-1}s^{-1}$$

The literature value is $1.4 \times 10^{-7}\ M^{-1}s^{-1}$ [16], and the error is −14%.

(5) From Eq. 7-36 (assuming k_0 and $k_{OH} = 0$),

$$k_T = (1.2 \times 10^{-7})(10^{-6}) = 1.2 \times 10^{-13}\ s^{-1}$$

(6) From Eq. 7-37,

$$t_{1/2} = 0.693/(1.2 \times 10^{-13}\ s^{-1}) = 5.8 \times 10^{12}\ s$$

$$= 1.8 \times 10^5\ yr$$

7-6 ESTIMATION OF k_H FROM THE TAFT CORRELATION

Data presently available limit the strict applicability of this method to ortho-substituted benzamides. For this series of compounds, the rate constant was reported [20] to be correlated with the Taft steric substituent constant, E_s, according to Eq. 7-34. The published δ value (but not the rate constant) could be assumed to apply as well to closely related reactions, such as acid-catalyzed hydrolysis of N-methylbenzamides.

Basic Steps

(1) Set $k_H^\circ = 3.3 \times 10^{-5}$ (water, 100°C) [23] for *o*-methylbenzamide or use an appropriate literature value for some other (N-substituted) parent benzamide compound.

(2) Set $\delta = 0.81$ [20] for benzamide series, or use an appropriate literature value for some other (N-substituted) benzamide series.

(3) From Table 7-6, select the appropriate E_s value for the ortho-substituent.

TABLE 7-6

Taft, σ^*, and Steric, E_s, Substituent Constants for Taft Correlation[a]

Z	σ^*	E_s	Z	σ^*	E_s
F	1.10	−0.24	H	0.00	0.00
Cl	1.05	−0.24	CH_3	−0.10	−0.07
Br	1.00	−0.27	CH_2CH_3	−0.115	−0.36
I	0.85	−0.37	i-$CH(CH_3)_2$	−0.125	−0.93
			t-C_4H_9	−0.165	−1.74

a. Values are for Z substituent in ZCH_2-; therefore Z=H corresponds to a $-CH_3$ group.

Source: Calculated from data of Shorter [20].

(4) Calculate k_H at 100°C from Eq. 7-38 (cf. Eq. 7-34).

$$\log k_H = \log k_H^\circ + \delta E_s \qquad (7\text{-}38)$$

(5) If k_H is for $T \neq 25°C$ and temperature coefficient data for k_H are available from the literature, calculate k_H (25°C) by use of Eq. 7-27, -29, or -31. In lieu of such data, use Eq. 7-35.

7-7 ESTIMATION OF k_0 FROM THE HAMMETT EQUATION

Data presently available (Table 7-7) are based on rates of hydrolysis of benzyl and dimethyl benzyl halides and benzyl tosylates in mixed-organic aqueous solvents. This method is applicable only to these compound types. Furthermore, the estimated k_0 should be regarded as the lower limit of the value that might be observed in an aquatic environment.

Basic Steps

(1) Choose an appropriate value of k_0° from Table 7-7 (or from the literature).

(2) Find the appropriate value of the reaction parameter, ρ, from Table 7-7 (or from the literature).

(3) Find the value of σ from Table 6-3, -4, or -5 (in Chapter 6) as directed in §7-5.

(4) Calculate k_0 by the following equation (cf. Eq. 7-32):

$$\log k_0 = \rho\sigma + \log k_0^\circ \qquad (7\text{-}39)$$

(5) If k_0 is for $T \neq 25°C$ and temperature coefficient data for k_0 are available from the literature, calculate k_0 (25°C) according to Eq. 7-27, -29, or -31. In lieu of such data, use Eq. 7-35.

Example 7-2 Estimate k_0 for *p*-methylbenzyl chloride.

(1) $k_0^\circ = 6.2 \times 10^{-6}\ s^{-1}$ at 25°C (Table 7-7)

(2) $\rho = -1.31$ (Table 7-7)

(3) $\sigma = -0.170$ (Table 6-3)

(4) Substituting in Eq. 7-39, $\log k_0 = (-1.31)(-0.170) - 5.21$

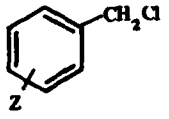
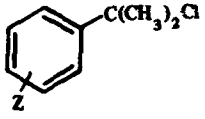
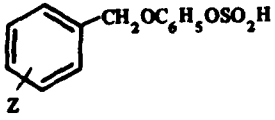
$$\log k_0 = -4.99$$

$$k_0 = 1.0 \times 10^{-5}\ s^{-1}$$

The literature value is $2.97 \times 10^{-5}\ s^{-1}$ at 30°C for water [16] indicating an error of about a factor of 300.

TABLE 7-7

Correlation of Neutral Hydrolysis Rate Constant With Hammett Substituent Constant

Compound/Conditions		n[a]	k_o^o (s^{-1})[b]	Correlation Equation[c] ($\log k_o = \rho\sigma + \log k_o^o$)
	25°C 50% Acetone	7	6.25×10^{-6}	$\log k_o = -1.31\ \sigma - 5.21$ r = 0.964
	25°C 90% Acetone	8	1.1×10^{-4}	$\log k_o = -4.48\ \sigma - 3.95$[d] r = 0.998
	25°C 50% Acetone	7	2.6×10^{-4}	$\log k_o = -2.32\ \sigma - 3.58$ r = 0.972

a. Number of compounds used to establish correlation.
b. Calculated from intercept of correlation equation.
c. Equation and correlation coefficient cited by Wells [25].
d. σ^+ values [25] used for electron-donating ρ substituents.

Source: Wells [25].

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7-8 ESTIMATION OF k_{OH} FROM THE HAMMETT EQUATION

A number of studies have established correlations between alkaline hydrolysis rates and Hammet σ constants. However, almost all of the data were obtained from systems containing mixtures of organic and aqueous solvents. A value of k_{OH} estimated from one of these correlations should be regarded as a lower limit of the value that might be observed in an aquatic environment.

Basic Steps

(1) Choose an appropriate value of k°_{OH} from Table 7-8 (or from the literature).

(2) Choose the appropriate value of ρ (coefficient of σ) from Table 7-8 (or from the literature).

(3) Find the value of σ from Table 6-3, 6-4 or 6-5, as directed in §7-5.

(4) Calculate k_{OH} as follows (cf. Eq. 7-32):

$$\log k_{OH} = \rho\sigma + \log k^{\circ}_{OH} \qquad (7\text{-}40)$$

(5) If k_{OH} is for $T \neq 25°C$ and temperature coefficient data for k_{OH} are available from the literature, calculate k_{OH} (25°C) by use of Eq. 7-27, -29, or -31. In lieu of such data, use Eq. 7-35.

Example 7-3 Estimate the rate constant for hydrolysis of methyl *p*-nitrobenzoate.

(1) k°_{OH} (60% acetone) = 7.2×10^{-3} $M^{-1}s^{-1}$ (Table 7-8)

(2) $\rho = 2.38$ (Table 7-8)

(3) $\sigma = 0.778$ (Table 6-3)

(4) Substituting in Eq. 7-40,

$$\log k_{OH} = (2.38)(0.778) + \log (7.2 \times 10^{-3})$$

$$= 1.85 - 2.14 = -0.29$$

$$k_{OH} = 5.1 \times 10^{-1}\ M^{-1}s^{-1} \text{ (60\% acetone)}$$

Literature vaues are 7.4×10^{-2} $M^{-1}s^{-1}$ in 55% methanol and 6.4×10^{-1} $M^{-1}s^{-1}$ in 56% acetone [16].

TABLE 7-8

Correlation of Alkaline Hydrolysis Rate Constant With Hammett Substituent Constant

Compound/Conditions	n[a]	k°_{OH} ($M^{-1}s^{-1}$)	Correlation Equation[b]
$ArCOOCH_3$ 60% Acetone, 25°	5	7.2×10^{-3} [c]	$\log k_{OH} = 2.38\,\sigma - 2.14$ $r = 0.991$
3% Ethanol, 25° [19a]	18	2.75	$\log k_{OH} = 1.17\,\sigma + 2.26$ $r = 0.996$
$ArCOOCH_2CH_3$ 60% Acetone, 25°	7	2.4×10^{-3} [c]	$\log k_{OH} = 2.47\,\sigma - 2.62$ $r = 0.996$
85% Ethanol, 25°	5	5.5×10^{-4} [c]	$\log k_{OH} = 2.61\,\sigma - 3.26$ $r = 0.999$
$ArCH_2COOCH_2CH_3$ 60% Acetone, 25°	8	4.4×10^{-2} [c]	$\log k_{OH} = 1.00\,\sigma - 1.36$
$ArCH{=}CHCOOCH_2CH_3$ 85% Ethanol, 25°C	5	1.4×10^{-3} [c]	$\log k_{OH} = 1.24\,\sigma - 2.86$ $r = 1.000$
$ArCONH_2$ 60% Ethanol, 53°C	4	7.6×10^{-6} [c]	$\log k_{OH} = 1.40\,\sigma - 5.12$ $r = 0.998$
$ArOCOCH_3$ 60% Acetone, 15°C	3	2.4×10^{-1} [c]	$\log k_{OH} = 1.51\,\sigma - 0.62$ $r = 1.000$

(continued)

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TABLE 7-8 (Continued)

Compound/Conditions	n[a]	k°_{OH} ($M^{-1}s^{-1}$)	Correlation Equation[b]
$ArCH_2OCOCH_3$ 60% Acetone, 25°C	4	6.6×10^{-2} [c]	$\log k_{OH} = 0.75\,\sigma - 1.18$ r = 0.996
$ArCON(CH_3)_2$ [19a] 10% Ethanol, 25°C	14	3.8×10^{-5}	$\log k_{OH} = 1.14\,\sigma - 2.59$ [d] r = 0.991
$ArCONHCH_3$ [19a] 10% Ethanol, 38°C	17	4.00	$\log k_{OH} = 2.69\,\sigma^{-} + 2.440$
$ArCH_2Cl$ [12]	6	3.3×10^{-6}	$\log k_{OH} = -0.333\,\sigma - 5.484$ [12]
$ArOSi(CH_2CH_3)_3$ 50% Ethanol, 25°C	3	1.4×10	$\log k_{OH} = 1.99\,\sigma + 0.15$ r = 0.999
$(ArO)_3P{=}O$ [26] Water, 30°C	4	2.7×10^{-1}	$\log k_{OH} = 1.4\,\Sigma\sigma - 0.47$ r = 0.995

a. Number of compounds used in establishing correlation.

b. $\log k_{OH} = \rho\sigma + \log k^{\circ}_{OH}$; units of k_{OH} are $M^{-1}s^{-1}$.

c. Calculated from correlation equation, σ=0.

d. Correlation used σ values tabulated by Exner [15].

Source: Wells [25] except as noted.

These figures cannot be directly compared with the estimated value because of variations in the solvent. Therefore, percentage deviations have not been calculated. It should be noted that the rate of hydrolysis in the aquatic environment will probably be considerably higher than the estimate based on the 60% acetone solvent. Compare the much higher rate constant reported for 95% water-5% ethanol in Table 7-8.

7-9 ESTIMATION OF k_{OH} FROM THE TAFT EQUATION

The applicability of this method has been described for only one compound class, the alkyl phthalate esters. Wolfe *et al.* [28] have presented a correlation between rates of alkaline hydrolysis of five phthalate esters and the Taft σ^* and E_s constants. The correlation equation, for water at 30°C, is (cf. Eq. 7-33):

$$\log k_{OH} = 4.59\,\sigma^* + 1.52E_s - 1.02 \qquad (7\text{-}41)$$

and $r^2 = 0.975$. Wolfe *et al.* make no claims of generality for this relationship, which was developed for a relatively narrow range of compounds (dialkyl phthalate esters). The number of data points available is also small for evaluation of a two-parameter correlation equation.

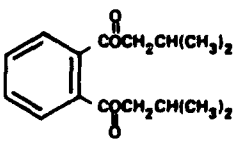
Basic Steps

(1) If the compound is a dialkyl phthalate ester, whose parent compound is dimethyl phthalate:

- Find σ^* and E_s from Table 7-6.
- Calculate k_{OH} according to Eq. 7-41. This is the rate constant at T = 30°C.
- If k_{OH} at 25°C is desired, substitute the above value of k_{OH} in Eq. 7-35, using $T_2 = 303$.

(2) For other compounds (or to find k_{OH} for dialkyl phthalate esters at a temperature other than 25°C or 30°C), use Eqs. 7-27, -29, or -31.

Example 7-4 Estimate k_{OH} for diisobutyl phthalate at 25°C.



(1) From Table 7-6, $\sigma^* = -0.13$ and $E_s = -0.93$. (Note that values in Table 7-6 are for Z in CH_2Z; therefore, the correct Z to use for an isobutyl ester is the value tabulated for i-$CH(CH_3)_2$.)

(2) Substituting in Eq. 7-41,

$$\log k_{OH} = 4.59\,(-0.13) + 1.52\,(-0.93) - 1.02$$

$$= -3.03$$

$$k_{OH} = 9.4 \times 10^{-4}\ M^{-1}s^{-1} \text{ at } 30°C$$

(3) Equation 7-35 is used to find k_{OH} at 25°C:

$$\log k_{OH} = -3.03 - 3830\left(\frac{303 - 298}{298 \times 303}\right)$$

$$= -3.24$$

$$k_{OH} = 5.7 \times 10^{-4}\ M^{-1}s^{-1}$$

The literature value is $1.4 \times 10^{-3}\ M^{-1}s^{-1}$ [28], indicating an error of approximately a factor of two.

7-10 ESTIMATION OF k_{OH} FROM THE pK_a OF THE LEAVING GROUP

This method is applicable, based on presently available data, to alkaline hydrolysis of a series of aryl esters of methylphosphonic acid and to four carbamate series. It is based upon correlations between log k_{OH} and the pK_a (negative log of the acid dissociation constant) of the phenol which is the conjugate acid of the leaving group. Table 7-9 presents the available correlation data. Figure 7-3 illustrates the fit of the correlation equations for two of the organophosphate ester series.

Basic Steps

(1) From the literature or Chapter 6, find pK_a for the phenol which is the conjugate acid of the leaving group, X.

(2) Choose the appropriate correlation equation from Table 7-9 (or from the literature).

(3) Calculate k_{OH} according to the correlation equation.

(4) If k_{OH} is for $T \neq 25°C$ and temperature coefficient data for k_{OH} are available from the literature, calculate k_{OH} (25°C) according to Eq. 7-27, -29, or -31. In lieu of these, use Eq. 7-35.

TABLE 7-9

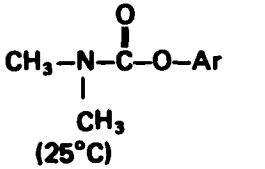
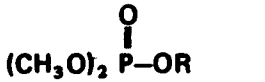
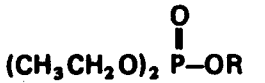
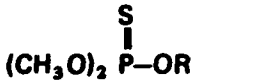
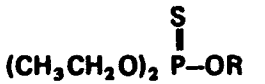
Correlations of Alkaline Hydrolysis Rate Constant with pK_a of Leaving Group

Compound/Conditions	n[a]	k°_{OH} $(M^{-1}s^{-1})$[b]	Correlation Equation[c]	Ref.
$(CH_3)_2CHO\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{\|}}{P}}-O-Ar$ (pH 10.2, 65°C)	4	3.5×10^{-2}	$\log k_{OH} = -0.68\ pK_a + 8.9$	9
$H-N(C_6H_5)-\overset{\overset{O}{\|}}{C}-O-Ar$ (25°C)	20	5.1×10^{1}	$\log k_{OH} = -1.15\ pK_a + 13.6$ $r = 0.994$	32
$CH_3-N(C_6H_5)-\overset{\overset{O}{\|}}{C}-O-Ar$ (25°C)	3	1.6×10^{-4}	$\log k_{OH} = -0.26\ pK_a - 1.3$ $r = 1.00$	32
$CH_3-N(H)-\overset{\overset{O}{\|}}{C}-O-Ar$ (25°C)	6	1.6×10^{0}	$\log k_{OH} = -0.91\ pK_a + 9.3$ $r = 0.994$	32

(Continued)

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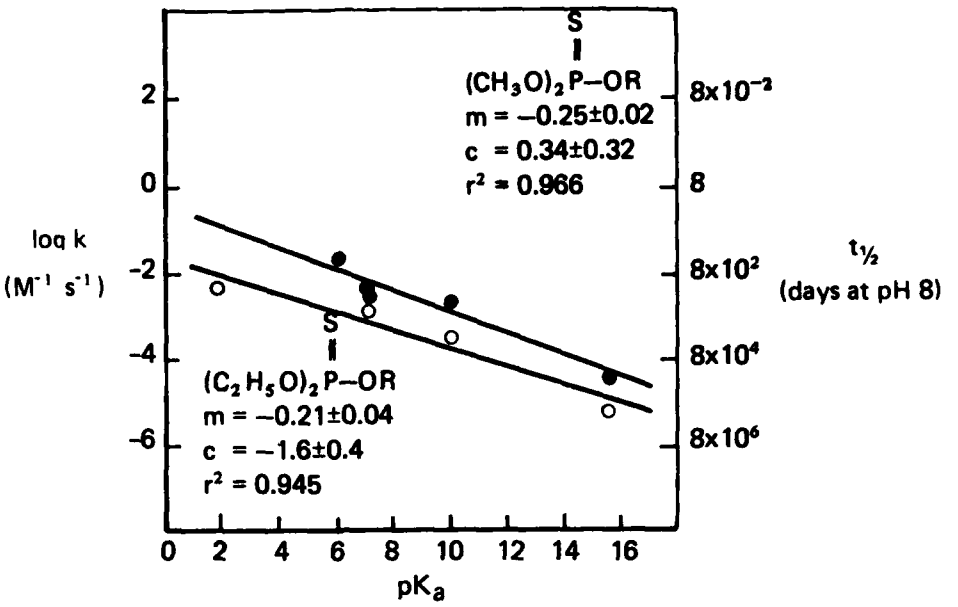
TABLE 7-9 (Continued)

Compound/Conditions	n[a]	k°_{OH} ($M^{-1}s^{-1}$)[b]	Correlation Equation[c]	Ref.
 (25°C)	7	7.9×10^{-5}	$\log k_{OH} = -0.17\ pK_a - 2.6$ $r = 0.89$	32
 (27°C)	3	N/A	$\log k_{OH} = -0.28\ pK_a + 0.50$ $r = 0.987$	26
 (27°C)	4	N/A	$\log k_{OH} = -0.28\ pK_a - 0.22$ $r = 0.962$	26
 (27°C)	5	N/A	$\log k_{OH} = -0.25\ pK_a + 0.34$ $r = 0.982$	26
 (27°C)	4	N/A	$\log k_{OH} = -0.21\ pK_a - 1.6$ $r = 0.972$	26

a. Number of compounds studied to establish correlation.

b. For aromatic carbamate series, k°_{OH} is tabulated for phenyl compound; for mixed alkyl/aryl phosphate ester series, no k°_{OH} value is tabulated.

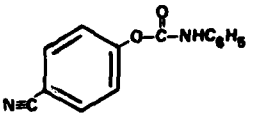
c. Equation presented in cited reference.



Source: Wolfe [26]

FIGURE 7–3 Linear Free Energy Relationships for the Alkaline Hydrolysis of O,O-Dimethyl and O,O-Diethyl-O-alkyl and Aryl Phosphorothioate in Water at 27°C

Example 7-5 Calculate the alkaline hydrolysis rate constant for *p*-cyanophenyl-N-phenylcarbamate.



(1) Conjugate acid of leaving group is *p*-cyanophenol.

$K_a = 1.12 \times 10^{-8}$ [14]; $pK_a = 7.95$

(2) From Table 7-9, the correlation equation for N-phenyl carbamates at 25°C is

$$\log k_{OH} = -1.15\ pK_a + 13.6$$

(3) $\log k_{OH} = (-1.15)(7.95) + 13.6$

$= 4.46$

$k_{OH} = 2.87 \times 10^4\ M^{-1}s^{-1}$

The literature value is $3.7 \times 10^4\ M^{-1}s^{-1}$ [32], indicating an error of –22%.

7-11 AVAILABLE DATA

Rate constant data are compiled in the sources listed below. The primary literature may provide additional, more recent values for particular compounds of interest. Tables 7-10 and -11 are compilations of some literature data for a variety of organic compound types.

National Bureau of Standards (1951) [24], *Tables of Chemical Kinetics: Homogeneous Reactions* — Older data, largely for organic solvent media. Supplements 1 (1956) and 3 (1961) provide additional data. Supplement 2 (1960) is an index.

Mabey and Mill (1977) [16], "Critical Review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions" —Data mostly for reactions in water, some in mixed solvents, which have been critically reviewed. Temperature and pH dependence of hydrolysis rates frequently noted.

Freed, V.H., "Solubility, Hydrolysis, Dissociation Constants and Other Constants of Benchmark Pesticides," Chap. 1 in *A Literature Survey of Benchmark Pesticides,* Department of Medical and Public Affairs, George Washington University Medical Center, Washington, DC, under Contract 68-01-2889 for Office of Pesticide Programs, U.S. Environmental Protection Agency (March 1976) — Primarily data on half-life and/or percent persistence after a specified time for one reaction condition.

Palm, V.A. (1975-1979) [19b], *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions,* Vols. 1-5. Volume 5, Part 2, is a table of correlation constants which may be useful.

7-12 SYMBOLS USED

A	=	parameter in Eq. 7-27
B	=	a base
E_A	=	Arrhenius activation energy in Eq. 7-27 (kcal/mol)
E_s	=	steric effects constant in Taft equation, Eq. 7-33
ΔF°	=	standard free energy of reaction
$\Delta F^\ddagger$	=	free energy of activation
ΔH°	=	enthalpy of reaction for an equilibrium process
$\Delta H^\ddagger$	=	enthalpy of activation for a rate process in Eq. 7-29

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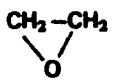
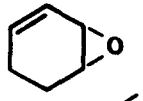
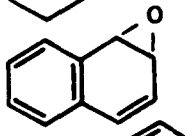
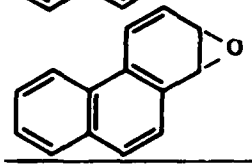
TABLE 7-10

Example Rate Data and Estimated Half-Lives (25°, pH 7) for Organic Compounds of Various Types in Aqueous Solution

	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	T (°C)	Temperature Dependence[b]	$t_{1/2}$[c]
Organohalides						
CH_3F	–	4.4×10^{-6}		100	$\Delta H^{\ddagger} = 25.6$; $\Delta S^{\ddagger} = -12.2$	30y
			9.0×10^{-4}	95	$E_A = 21.6$; log A = 9.607	
CH_3Cl	–	5.6×10^{-5}		90	$\Delta H^{\ddagger} = 25.3$; $\Delta S^{\ddagger} = -8.9$	0.9y
			2.4×10^{-2}	95	$E_A = 24.3$; log A = 12.614	
CH_3Br	–	1.1×10^{-4}		71	$\Delta H^{\ddagger} = 24.1$; $\Delta S^{\ddagger} = -6.6$	20d
			3.5×10^{-1}	95	$E_A = 23.0$; log A = 13.017	
CH_3I	–	8.2×10^{-5}		80	$\Delta H^{\ddagger} = 26.0$; $\Delta S^{\ddagger} = -5.2$	110d
			1.2×10^{-1}	95	$E_A = 22.2$; log A = 12.093	
$CH_3CH_2CH_2Br$	–	1.6×10^{-4}	–	80	$\Delta H^{\ddagger} = 23.3$; $\Delta S^{\ddagger} = -10.1$	26d
$(CH_3)_2CHCl$	–	1.0×10^{-3}	–	98	$\Delta H^{\ddagger} = 24.9$; $\Delta S^{\ddagger} = -5.3$	38d
$(CH_3)_3CF$	–	5.2×10^{-4}	–	90	$\Delta H^{\ddagger} = 22.6$; $\Delta S^{\ddagger} = -2.7$	50d
$CH_2=CHCH_2I$	–	4.1×10^{-6}	–	25		2d
$CHCl_3$	–	1.6×10^{-8}	6.0×10^{-5}	25	(See Ref. 12)	3500y
		7.3×10^{-8}		100		
$BrCHCl_2$	–	–	1.6×10^{-3}	25		140y
$C_6H_5CH_2Cl$	–	7.0×10^{-6}	–	20		15h
$C_6H_5CCl_3$	–	3.9×10^{-3}	–	5		19s

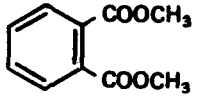
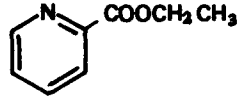
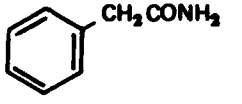
(continued)

TABLE 7-10 (Continued)

	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	T (°C)	Temperature Dependence[b]	$t_{1/2}$[c]
Epoxides						
	9.3×10^{-3}	6.8×10^{-7}	1.0×10^{-4}	25	For k_H, $\Delta H^{\ddagger} = 19.0$; $\Delta S^{\ddagger} = -6.1$ For k_0, $E_A = 19.0$; log $A = 7.726$ For k_{OH}, $E_A = 18.0$; log $A = 9.312$	12d
	1.6×10^{7}	2.2×10^{3}	1.5×10^{1}	25		6m
	4.7×10^{2} 1.4×10^{2} [3a]	3.0×10^{-3} 2.9×10^{-3}[f] [3a]	–	30 30		4m
	1.0×10^{3} [3a]	3.1×10^{-2} [3a]	–	30		22s[e]
Esters						
$HCOOCH_3$	–	–	3.7×10^{1}	25	$E_A = 40.0$; log $A = 8.57$	2d[e]
$CH_3COOCH_2CH_3$	1.1×10^{-4}	1.5×10^{-10}	1.1×10^{-1}	25		2y
$CH_3COOCH_2C_6H_5$	1.1×10^{-4}	–	2.0×10^{-1}	25		1.1y
$CH_3COOC_6H_5$	–	6.6×10^{-8}	–	25		38d
$Cl_2CHCOOC_6H_5$	–	1.8×10^{-3}	1.3×10^{4}	25		3.7m
$Cl_2CHCOOCH_3$	2.3×10^{-4}	1.5×10^{-5}	2.8×10^{3}	25		38m
$C_6H_5OCH_2COOCH_2CH_3$	–	–	3.0×10^{1}	28	$\Delta H^{\ddagger} = 20.1$; $\Delta S^{\ddagger} = 14.8$	2.4d[e]

(continued)

TABLE 7-10 (Continued)

	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	T (°C)	Temperature Dependence[b]	$t_{1/2}$[c]
$C_6H_5COOCH_3$	1.7×10^{-4}[d]	–		100	E_A = 17.7; log A = 6.57	118y
			1.9×10^{-3}[d]	25		
			9.0×10^{-3}[d]	25	E_A = 14.2; log A = 8.38	
	–	–	6.9×10^{-2} [28]	30		3.2y[e]
$C_6H_5COOCH_2C_6H_5$	–	–	5.9×10^{-3} to 1.2×10^{-2}[d]	30	E_A = 12.5 – 14.5; log A = 7.07 – 8.25	27y
	–	–	5.4×10^{-3}	25		41y[e]
Amides						
CH_3CONH_2	1.0×10^{-3}	–		75	$\Delta H^{\ddagger}$ = 19.2; $\Delta S^{\ddagger}$ = – 17.4	3950y
			1.4×10^{-3}	75	$\Delta H^{\ddagger}$ = 13.2; $\Delta S^{\ddagger}$ = – 33.9	
$CH_3CH_2CONH_2$	1.2×10^{-3}	–		75	$\Delta H^{\ddagger}$ = 18.1; $\Delta S^{\ddagger}$ = – 20.2	
			1.3×10^{-3}	75	$\Delta H^{\ddagger}$ = 14.7; $\Delta S^{\ddagger}$ = – 29.7	
	5.2×10^{-4}	–		75	$\Delta H^{\ddagger}$ = 18.0; $\Delta S^{\ddagger}$ = – 21.9	
			1.8×10^{-3}	75	$\Delta H^{\ddagger}$ = 11.8; $\Delta S^{\ddagger}$ = – 39.0	
$ClCH_2CONH_2$	1.2×10^{-3}	–		75	$\Delta H^{\ddagger}$ = 18.7; $\Delta S^{\ddagger}$ = – 18.8	1.46y
			1.4×10^{-1}	75		
Cl_3CCONH_2			1.4×10^{-1}	75		84d
$CH_3CONH(CH_3)$	5.8×10^{-5}	–		75	$\Delta H^{\ddagger}$ = 20.7; $\Delta S^{\ddagger}$ = – 18.6	38,000y
			3.6×10^{-4}	75	$\Delta H^{\ddagger}$ = 16.6; $\Delta S^{\ddagger}$ = – 29.1	
$CH_3CON(CH_2CH_3)_2$	2.3×10^{-6}	–		75		
			1.2×10^{-5}	75	$\Delta H^{\ddagger}$ = 18.0; $\Delta S^{\ddagger}$ = – 31.1	

(continued)

TABLE 7-10 (Continued)

	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	T (°C)	Temperature Dependence[b]	$t_{1/2}$[c]
Carbamates						
$CH_3CH_2OCNHC_6H_5$ (O)	–	–	3.3×10^{-5}	25	$\Delta H^{\ddagger} = 15.9$; $\Delta S^{\ddagger} = -25.5$	6,700y[e]
$CH_3CH_2OCN(CH_3)C_6H_5$ (O)	–	–	5.0×10^{-6}	25	$\Delta H^{\ddagger} = 12.9$; $\Delta S^{\ddagger} = -39.3$	44,000y
$C_6H_5OCNHC_6H_5$ (O)	–	–	4.7×10^{-1}		$\Delta H^{\ddagger} = 16.6$; $\Delta S^{\ddagger} = -28.0$	170d[e]
$C_{10}H_9OCNHCH_3$ (O) (α-naphthyl)	1.4×10^{-7}			25	$E_A = 12.7$; log A = 2.48	8.5d
		3.7×10^{-5}		80	$E_A = 15.0$; log A = 4.82	
			3.4×10^{0}	23	$E_A = 16.8$; log A = 11.95	
$CCl_3OCNHC_6H_5$ (O)	–	–	3.2×10^{-1}	25		250d
Organophosphorus Compounds						
$CH_3P(O)(OCH_3)_2$	1.1×10^{-5}	–		99	$E_A = 26.7$; log A = 10.7	89y
			1.5×10^{-3}	50	$E_A = 13.5$; log A = 7.3	
$CH_3P(O)(OC_6H_5)_2$	5.0×10^{-6}	–	–	110	$E_A = 26.6$; log A = 10.7	
$C_6H_5P(O)(OCH_2CH_3)_2$	1.0×10^{-5}	–	4.5×10^{-3}	59		440y
$(CH_3O)_3PO$	–	1.6×10^{-7}		45	$E_A = 22.7$; log A = 8.9	1.2y
			1.3×10^{-4}	25	$E_A = 16.2$; log A = 8.1	

(continued)

TABLE 7-10 (Continued)

	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	T (°C)	Temperature Dependence[b]	$t_{1/2}$[c]
$(CH_3CH_2S)_3PO$	–	7×10^{-7}[d]		82	E_A = 24.4; log A = 9.25	8.5y
			1.2×10^{-2}[d]	25	E_A = 15.0; log A = 7.94	
$(C_6H_5O)_3PO$	–	3×10^{-9}[d]		100		1.3y
			1.1×10^{-2}	25	E_A = 10.9; log A = 6.11	
$(p\text{-}NO_2C_6H_4O)_3PO$	–	1.0×10^{-3}[d]		25	E_A = 4.1; log A = 0.062	11m
			3.4×10^{1}[d]	25	E_A = 4.1; log A = 4.56	
$(p\text{-}NO_2C_6H_4O)_3PS$	–	2.1×10^{-1}	–	25		3.3s[e]
$(CH_3O)_2P(O)Cl$	–	2.9×10^{-5}	–	0	E_A = 10.6; log A = 5.7	1.3m
Miscellaneous						
	5.2×10^{-7}	–	–	25		154d
	–	3.3×10^{-3}	–	25		3.5m
$(CH_3O)_2SO_2$	–	1.7×10^{-4}	1.5×10^{-2}	25		1.2m
$ClCH_2OCH_2Cl$	–	1.8×10^{-2}	–	20		25s
C_6H_5COCl	–	4.2×10^{-2}	–	25		16s
$CH_3OSO_2\text{–}C_6H_5$	–	1.2×10^{-5}	8.8×10^{-4}	25		16h[e]
$CH_3CH_2OSO_2C_6H_5$	–	1.1×10^{-5} [22]	1.2×10^{-4} [22]	25 [22]		
$NaOSO_2(OCH_3)$	–	7.7×10^{-6}	4.6×10^{-4}	138		
$NaOSO_2(OCH_2CH_3)$	–	4.6×10^{-6}	9.2×10^{-5}	138		

(Footnotes are listed on the following page)

NOTES TO TABLE 7-10

a. Rate constant for acid (k_H), neutral (k_0) or basic (k_{OH}) hydrolysis. The overall hydrolysis rate in $M^{-1}s^{-1}$ is equal to k_T [O], where [O] is the molar concentration of the organic chemical and $k_T = k_H [H^+] + k_0 + k_{OH} [OH^-]$.

b. $\Delta H^{\ddagger}$ = enthalpy of activation in kcal/mol; E_A = Arrhenius activation energy in kcal/mol
$\Delta S^{\ddagger}$ = entropy of activation in entropy units (cal/deg K•mol). log A = Arrhenius pre-exponential factor; units of A same as for k

c. Estimated half-life of organic chemical in water at pH7 and 25°C according to Mabey and Mill [16]. y = years; d = days; h = hours; m = minutes; s = seconds. Note that $k_T = 0.693/t_{1/2}$.

d. Mixed organic, aqueous solvent; > 50% organic.

e. Calculated (this work) as $0.693/k_T$; k_T at pH 7 calculated from the tabulated rate constants as indicated in footnote a.

Source: Mabey and Mill [16] unless otherwise noted.

TABLE 7-11

Disappearance Rate Constants for Acid, Neutral and Alkaline Hydrolyses of Common Pesticides

Compound	T (°C)	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	Comments	Ref.
Organophosphates:						
Malathion	27	4.8×10^{-5}	7.7×10^{-9}	5.5×10^{0}	10^{-4} M in 1% acetonitrile: water; overall $\Delta H^{\ddagger}$ = 22.3 kcal/mol; $\Delta S^{\ddagger}$ = –4.1 eu	31
Parathion	20	—[b]	4.5×10^{-8}	2.3×10^{-2}	10^{-5} M in aqueous buffer	6

(Continued)

TABLE 7-11 (Continued)

Compound	T (°C)	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	Comments	Ref.
Paraoxon	20	–[b]	4.1×10^{-8}	1.3×10^{-1}	10^{-5} M in aqueous buffer	6
Diazinon	20	2.1×10^{-2}	4.3×10^{-8}	5.3×10^{-3}	10^{-5} M in aqueous buffer	6
Diazoxon	20	6.4×10^{-1}	2.8×10^{-7}	7.6×10^{-2}	10^{-5} M in aqueous buffer	6
Chlorpyrifos	25	–	1×10^{-7}	1×10^{-1}	10^{-7} to 10^{-9} M in aqueous buffer; E_A = 21.1kcal/mol	17
Carbamates:						
Sevin	20			7.7×10^{0}	10^{-5} M in aqueous buffer; E_A = 16.9 kcal/mol	6
	23			3.4×10^{0}	$2.5 \times 10^{-6} - 1 \times 10^{-4}$ M in water; E_A = 16.9 kcal/mol	1
Baygon	20			5.0×10^{-1}	$2.4 \times 10^{-6} - 9.7 \times 10^{-5}$ M in water; E_A = 15.8 kcal/mol	1
	20			4.6×10^{-1}	10^{-5} M in aqueous buffer; E_A = 15.8 kcal/mol	6
Pyrolam	20			1.1×10^{-2}	$2.0 \times 10^{-6} - 8.2 \times 10^{-5}$ M in water; E_A = 13.7 kcal/mol	1

(Continued)

TABLE 7-11 (Continued)

Compound	T (°C)	k_H[a] ($M^{-1}s^{-1}$)	k_0[a] (s^{-1})	k_{OH}[a] ($M^{-1}s^{-1}$)	Comments	Ref.
Dimetilan	20			5.7×10^{-5}	$2.1 \times 10^{-6} - 8.3 \times 10^{-5}$ M in water; E_A = 14.0 kcal/mol	1
p-Nitrophenyl-N-methyl carbamate	25		$< 4 \times 10^{-5}$	3.0×10^{3}	3×10^{-5} M in aqueous buffer	2
2,4-D Esters:						
n-Butoxyethyl	28	2.0×10^{-5}	2.0×10^{-5}	3.02×10^{1}	1×10^{-5} M in water. For k_H, $\Delta H^{\ddagger}$ = 17.6 kcal/mol and $\Delta S^{\ddagger}$ = 14.8 eu. For k_{OH}, $\Delta H^{\ddagger}$ = 20.1 kcal/mol, $\Delta S^{\ddagger}$ = −21.3 eu	34
	67	6.6×10^{-4}	2.7×10^{-7}	5.0×10^{3}		
Methyl	28			1.7×10^{1}		34
Methoxychlor	27	--	2.2×10^{-8}	3.8×10^{-4}	1×10^{-8} M in water	33
DDT	27	–	1.9×10^{-9}	9.9×10^{-3}	1×10^{-8} M in water	33

a. Rate constant for acid (k_H), neutral (k_0), or basic (k_{OH}) hydrolysis. Overall hydrolysis rate in $M^{-1}s^{-1} = k_T$ [O] where [O] = molar concentration of the organic chemical and $k_T = k_H$ [H+] + k_0 + k_{OH} [OH^-].

b. A dash in the k_H or k_{OH} column indicates that acid- or base-catalyzed hydrolysis is slow and may be insignificant. A blank simply indicates that no rate constant was reported.

c. Calculated from data presented in the cited reference on pH dependence of k_T.

h = Planck's constant in Eq. 7-29

HA = an acid

I_{AN}, I_{AB}, I_{NB} = transition points in Figure 7-2

k = Boltzmann's constant in Eq. 7-29

k = rate constant

k° = rate constant for parent compound in a class of compounds

k_0 = rate constant for neutral hydrolysis (s^{-1})

k_B = rate constant for general base-catalyzed hydrolysis in Eq. 7-18 ($M^{-1}s^{-1}$)

k_H = rate constant for specific acid-catalyzed hydrolysis ($M^{-1}s^{-1}$)

k_{HA} = rate constant for general acid-catalyzed hydrolysis in Eq. 7-18 ($M^{-1}s^{-1}$)

k_{H_2O} = rate constant for neutral hydrolysis in Eq. 7-18 ($M^{-1}s^{-1}$)

k_{OH} = rate constant for specific base-catalyzed hydrolysis ($M^{-1}s^{-1}$)

k_T = total, or overall, hydrolysis rate constant (s^{-1})

LFER = linear free energy relationship

n = number of compounds

pH = $-\log [H^+]$

pK_a = $-\log K_a$, where K_a = acid dissociation constant

R = gas constant (1.987 cal/mol·deg). Also used (in drawings of chemical structures) to represent an unspecified organic group

ΔS° = standard entropy of reaction for an equilibrium process

$\Delta S^\ddagger$ = entropy of activation for a rate process in Eq. 7-29

S_N1 = substitution, nucleophilic, unimolecular (see §7-2)

S_N2 = substitution, nucleophilic, bimolecular (see §7-2)

T = temperature (K)

$t_{1/2}$ = half-life due to hydrolysis in Eq. 7-37

t = time in Eqs. 7-16 and -21 to -24

X = leaving group on a molecule

Z = general designation for a substituent group on a compound

Greek

δ	=	reaction constant in Taft equation, Eq. 7-33
ρ	=	Hammett reaction constant in Eq. 7-32
ρ^*	=	Taft reaction constant in Eq. 7-33
σ	=	Hammett substituent constant in Eq. 7-32
σ^*	=	Taft substituent constant in Eq. 7-33
σ_T	=	total σ value (simple sum) due to presence of more than one substituent
σ^-	=	substituent constant in Hammett correlation especially for anilinium ions and phenols

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8

RATE OF AQUEOUS PHOTOLYSIS

Judith C. Harris

8-1 INTRODUCTION

It is increasingly recognized that photochemical processes may be important in determining the fate of organic pollutants in aqueous environments. Both *direct* photolysis, in which the pollutant itself absorbs solar radiation, and *sensitized* photolysis, in which energy is transferred from some other species in the aquatic solution, may occur. The rates of these processes in a natural water system depend both on the properties of the aquatic environment (intensity and spectrum of solar radiation, presence or absence of sensitizers, quenchers, etc.) and on the properties of the organic chemical (extent of absorption of light and inherent tendency to undergo photochemical reaction).

Existing models for predicting photochemical reactivity in the environment are essentially models for calculating the net rate at which an aqueous solution containing the organic chemical absorbs light. The basic approach is to evaluate the degree of overlap between the ultraviolet/visible absorption spectrum of the organic molecule and the solar radiation to which it is exposed. The necessary compound-specific data must usually be determined in the laboratory, since literature spectra do not contain this information in retrievable form.

The estimated rate of absorption of light by a solution of the molecule of interest is necessary but not sufficient for calculating the rate

constant for direct photochemical degradation. To estimate the latter quantity, which is a measure of the inherent photochemical reactivity of the organic chemical, one must also know its quantum yield for photolysis. There are, at present, no methods for estimating the quantum yield of an organic molecule from its chemical structure or from other physical/chemical properties.

Although the state of the art does not include any methods for estimation of photolytic reactivity in aquatic environments, there are some qualitative guidelines to indicate compounds that may be reactive and the types of reactions they may undergo. These guidelines apply to rates of direct photolysis only; the possibility for sensitized photolysis depends at least as much on the chemical characteristics of the aquatic system as on those of the organic chemical of concern and is not addressed in this chapter.

8-2 BASIC PRINCIPLES OF EXCITATION/DEACTIVATION

An organic molecule can undergo photochemical transformations if, and only if, both of the following conditions are met:

- Light energy is absorbed by the molecule to produce an electronically excited state of the molecule, and
- Chemical transformations of the excited state are competitive with deactivation processes.

Excitation. The necessity for light absorption is cited as the first law of photochemistry or the Grotthus-Draper Law [2,27]: *Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule.* It is well known that molecules absorb light in several regions of the electromagnetic spectrum, corresponding to different kinds of molecular transitions. Table 8-1 lists the types of transitions and summarizes the energy, wavelength, and frequency regimes for the respective absorption regions. If these data are compared with typical bond dissociation energies (Table 8-2), it becomes clear that only the electronic transitions, corresponding to UV/visible light absorption, are inherently energetic enough to lead to chemical reactions. The regime of importance for photochemical transformations is thus confined to UV/visible light with a wavelength of 110-750 nm.

When we focus on environmental photochemistry at or near the earth's surface, the wavelength regime of importance can be further

TABLE 8-1

Types of Molecular Transition and Associated Energy Levels

Type of Transition	Absorption Region	Energy Range E (kcal/mol)[a]	Energy Range λ (nm)	Time Scale (s)
Translational	(Thermal)			
Rotational	Microwave	0.01-0.1	1×10^6 - 1×10^7	10^{-10}
Vibrational	Infrared	1-10	10,000- 1,000	10^{-13}
Electronic	Visible-UV	38-250	750-110	10^{-15}

a. A "mol" of photons = 1 Einstein = 6.023×10^{23} photons of a specified wavelength.

Source: Calvert and Pitts [2], pp. 1-26.

TABLE 8-2

Some Approximate Bond Dissociation Energies

Bond Broken	ΔH_{298K} (kcal/mol)
C-H (alkanes)	91-99
C-H (benzene)	103
C-C (alkanes)	78-84
C-F	114-110
C-Cl	78-82
C-Br	67
C-I	53
O-H (alcohols)	100-102
C-O (alcohols)	89-90
C-N (amines)	79
O-O (peroxides)	35-51

Source: Calvert and Pitts [2], pp. 824-826.

narrowed, because the stratospheric ozone layer effectively prevents UV irradiation of less than 290 nm from reaching the ecosphere. Thus, the first law of [environmental] photochemistry may be restated: *Only the light of 290-750 nm wavelength absorbed by a molecule can potentially lead to photochemical transformations of that molecule in the environment.*

The excitation process is expressed as

$$P \xrightarrow{h\upsilon} P^* \qquad (8\text{-}1)$$

where P is the ground-state molecule, $h\upsilon$ is a quantum of light, and P* the excited-state molecule. In quantitative terms, the light absorbed in this process is given by the Beer-Lambert Law [5]:

$$A = \log \frac{I_0}{I} = \epsilon c \ell \qquad (8\text{-}2)$$

in which A is the absorbance, I_0 is the intensity of the incident light of specified wavelength, I is the intensity of transmitted light of the same wavelength, ϵ is the molar absorptivity (extinction coefficient) of the absorbing species, c is the concentration of the absorbing species, and ℓ is the depth of the absorbing medium. Deviations from Eq. 8-2, which can be derived by assuming a first-order absorption of light by species P, are generally not observed at values of $A < \sim 0.7$. Deviations due to second-order effects can occur at high concentrations of the absorbing species. Values of ϵ for compounds absorbing light above 290 nm wavelength are typically in the range from 10 to 100,000. Since environmental concentrations of pollutants in aqueous media are usually <10 ppm (w/v) or $<10^{-3}$ M, deviations from the Beer-Lambert Law are not likely under environmental conditions. However, materials that are opaque to UV/visible light (other than the pollutant) may be present in the environmental medium and may alter the effective value of I_0, thus effectively reducing the quantity of light absorbed by P.

Deactivation: Internal Conversion and Intersystem Crossing. The formation of a photochemically excited state, P* is a necessary but not a sufficient condition for producing a photochemical reaction of molecule P. The probability of accomplishing a net photochemical degradation (photolysis of P) depends on the competition among the primary photophysical processes of radiative (Eq. 8-3) and radiationless (Eq. 8-4) decay to the ground state and any primary photochemical processes (Eq. 8-5) that may occur.

$$P^* \longrightarrow P + h\nu' \quad (8\text{-}3)$$

$$P^* \longrightarrow P \quad (8\text{-}4)$$

$$P^* \longrightarrow \text{products} \quad (8\text{-}5)$$

The efficiency of each primary process, i, is conventionally expressed in terms of its quantum yield, ϕ_i, which may be defined as

$$\phi_i = \frac{\text{No. of P* excited states undergoing process i}}{\text{No. of quanta of light absorbed by P}} \quad (8\text{-}6)$$

The idea that the several deactivation and reaction pathways (Eqs. 8-3 through 8-5) are competitive is expressed in the second law of photochemistry, the Stark-Einstein-Bodenstein Law, which is stated by Calvert and Pitts [2] as: *The absorption of light by a molecule is a one-quantum process, so that the sum of the primary-process quantum yields (ϕ)* must be unity.

The quantum yields for disappearance of organic chemicals in water are generally <0.01. This implies that 90%, 99%, or more of the excited-state molecules undergo photophysical deactivation rather than photoreaction/photolysis.

One deactivation pathway involves a radiative process, *fluorescence,* in which a quantum of light is emitted during the transition to the ground electronic state and some residual vibrational excitation is rapidly lost via collision processes. This process is the inverse of the absorption process; in fact, fluorescence spectra are often mirror images of absorption spectra [11]. The "natural lifetime," τ, of the state can be estimated, assuming that fluorescence is the only important decay pathway, by Eq. 8-7 [11]:

$$\tau \approx 10^{-4}/\epsilon_{max} \quad (8\text{-}7)$$

where ϵ_{max} is the molar absorptivity at the wavelength of maximum absorption.[1] This fluorescence lifetime is on the order of 10^{-9} to 10^{-6} second [11]. Fluorescence quantum yields on the order of 0.3 are observed for simple aromatic hydrocarbons in solution at ordinary temperatures [2].

No other photophysical or photochemical primary process can compete with fluorescence unless it takes place within the brief fluorescence

1. τ is the time required for decay to 1/e of the original concentration of the excited state; it is about 44% longer than $t_{1/2}$ (the half-life) for a first-order decay process.

lifetime. One photophysical process that is sufficiently rapid is *internal conversion,* a non-radiative deactivation process in which the energy of the quantum of light originally absorbed is eventually dissipated as increased thermal energy of the reaction medium. The net effect of internal conversion and fluorescence photophysical processes is usually to regenerate the ground state of the organic molecule within 10^{-9} to 10^{-5} second.

It is empirically observed that the quantum yield for fluorescence, ϕ_f, is independent of the precise wavelength of light absorbed [11,28]. This generalization is called "Vavilov's Rule" by Turro *et al.* [28], who also discuss the relatively small number of exceptions known. However, this rule does not necessarily apply to the quantum yields for photochemical reaction when very large differences in the wavelength are involved. Quantum yields for photolysis in the vapor phase are normally wavelength dependent; irradiation with short-wavelength light (high energy quanta) may provide sufficient excitation energy to induce photochemical/physical transformations that are impossible when longer wavelength irradiation is applied. It is important to keep this point in mind when attempting to extrapolate results of laboratory photolysis experiments (usually at 254 nm UV irradiation) to environmental conditions (>290 nm irradiation). For wavelengths >300 nm, there may be little wavelength dependence of quantum yield in solution because relaxation to the lowest excited state is usually more rapid than reaction from the higher states.

An important additional photophysical process is the transition between singlet (all electron spins paired) and triplet (two unpaired electron spins) electronic states, known as *intersystem crossing.* Experimental evidence suggests that the quantum yield for intersystem crossing is on the order of 0.99 for aromatic ketones (acetophenone, benzophenone) and on the order of 0.2-0.6 for other aromatic species (benzene, naphthalene, quinoline, naphthol, naphthoic acid, and others) in organic solvents at ordinary temperatures.[2] The existence of the triplet state is important from the perspective of potential photochemical transformations, primarily because its natural lifetime is much longer than that of the corresponding singlet. Since triplet lifetimes are on the order of 10^{-6} to 10^{-3} s (vs. 10^{-9} to 10^{-5} s for singlets), relatively slow photochemical processes can compete with photophysical deactivation from this state. The latter process can occur by radiative *(phosphorescence)* or non-radiative (intersystem crossing) pathways. The quantum yield for

2. See Ref. 2, pp. 293-321.

phosphorescence, ϕ_p, from the lowest triplet excited state is highly sensitive to the medium in which irradiation occurs. Phosphorescence is normally observed only when organic molecules are frozen in a glassy matrix (such as a mixture of ether: pentane:alcohol at −196°C). In fluid media (solution or gas phase), radiationless deactivation occurs in time periods shorter than the natural phosphorescence lifetime of 10^{-6} to 10^{-3}s. The presence of other molecules such as oxygen can lead to enhanced rates of intersystem crossing [33]. Kan [11] suggests a time scale on the order of 10^{-6} s for intersystem crossing processes, such as radiationless deactivation from the triplet excited state to the ground singlet electronic state. Photochemical processes with first-order or pseudo first-order rate constants on the order of 10^6 s^{-1} or higher can therefore be expected to compete with photophysical deactivation in solution for systems which have high quantum yields for triplet formation.

Energy Transfer: Sensitization and Quenching. The preceding discussion focused on intramolecular photophysical processes. Triplet excited states, however, are sufficiently long-lived in solution to participate in intermolecular electronic energy transfer processes. (Singlet-singlet energy transfer resulting in enhanced fluorescence is quite possible in solid media but rare in solution or in gas phase reactions.) In such a process, energy is transferred from the triplet state of an excited donor molecule, S*, to the ground state of the acceptor molecule, P, yielding the P* triplet state. This process provides a means of populating an electronically excited state of P with no direct absorption of light by P ground-state molecules. This type of energy transfer can occur whenever the "triplet energy" (energy difference between the triplet excited state and singlet ground state) of S is greater than the corresponding energy difference in the P system. Table 8-3 lists triplet energies for some sample compounds. Energy transfer can either enhance (sensitize) or reduce (quench) the photochemical reactivity of an organic molecule in the aqueous environment.

Photochemical *sensitization* is said to occur when some species in solution, other than the target organic molecule, absorbs light and transfers its excitation energy to the target species. The donor species (the "sensitizer") undergoes no net reaction in the process but has an essentially catalytic effect. Photochemical sensitization is thus distinguished in principle from degradation of the target molecule by photoinitiated free radicals in solution. In practice, these two phenomena may be indistinguishable for complex situations, such as natural water systems. The importance of photochemical sensitization in the aquatic environment has not been well established.

TABLE 8-3

Triplet Energies for Selected Compounds

Compound	Triplet Energy (kcal/mol)
Acetophenone	73.6
Benzaldehyde	71.9
Carbazole	70.1
Triphenylamine	70.1
Benzophenone	68.5
Anthraquinone	62.4
Phenanthrene	62.2
Naphthalene	60.9
Biacetyl	54.9
Fluorenone	53.3
Pyrene	48.7

Source: Calvert and Pitts [2]

Quenching of a photochemical process is said to occur when excitation energy present in the target organic molecule is transferred to some other species in solution. This process is, in a sense, the inverse of sensitization, as it results in net *de*activation of the organic substance of concern via energy transfer. As noted above, energy can be transferred to any species with lower triplet energy. A very important and effective quencher (acceptor) is molecular oxygen, which has a triplet ground state. The second-order rate constant for oxygen quenching is on the order of 10^{10} L/mol-s [2]. At a dissolved oxygen concentration of 10 mg/L (0.31mM), this corresponds to a pseudo first-order quenching rate constant of 3×10^{6} s^{-1}, or a half-time for quenching of 2×10^{-7} s. This triplet energy transfer quenching is essentially a diffusion-controlled process in fluid solution [2] and is thus competitive with any potential bimolecular photochemical degradation processes. Non-photolytic deactivation of P* by oxygen quenching of the excited triplet may therefore be a significant and perhaps dominant fate process in aerobic aqueous environments.

Summary. The first law of photochemistry states that only light which is absorbed by a molecule can result in photochemical reaction. The extent of absorption of light, given by Beer's Law for each incident wavelength, can be calculated if the absorption spectrum of the organic

compound and the distribution of intensities/wavelengths of incident light are known. Photochemical excitation processes are thus rather straightforward, except for the potential complication of sensitized excitation by [unknown] sensitizer species in aqueous environments.

Deactivation processes include photophysical transitions among electronically excited and ground states, as well as photochemical degradation (photolysis). Within any particular broad absorption/excitation band, the relative importance of various deactivation processes is likely to be independent of excitation wavelength, since an "equilibrium" population of lowest excited singlet and triplet states is generally established. This is the basis for the common statement [24-36] that quantum yields are independent of wavelength. The generalization may frequently be invalid if large differences in wavelength (254 nm vs. >290 nm) are involved or if the excited states have different character (i.e., $n \rightarrow \pi^*$ vs. $\pi \rightarrow \pi^*$).

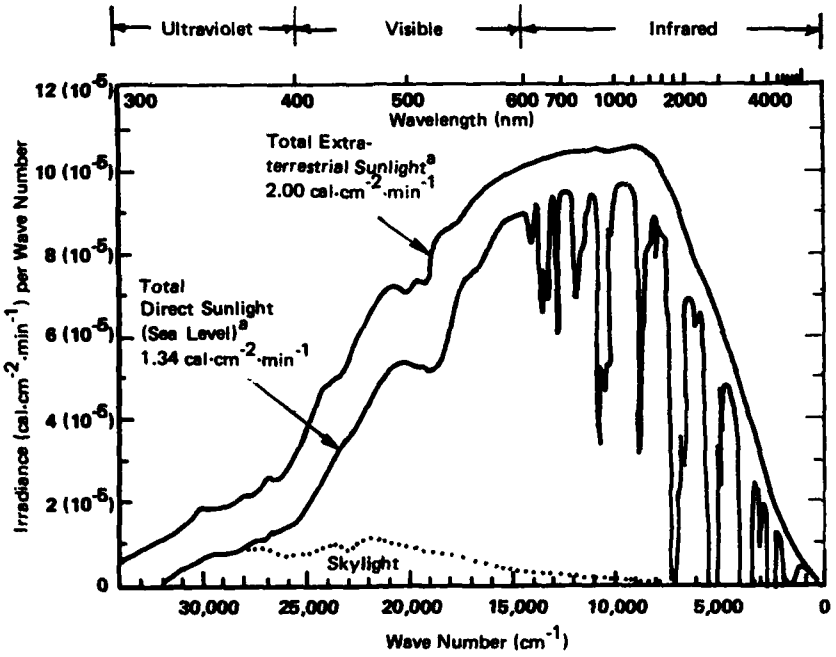
Photophysical deactivation processes include fluorescence, quenching, radiationless conversion to the ground state, and phosphorescence. The characteristic times for these processes, with which potential photolysis/photochemical transformations must compete, are on the order of: 10^{-9} to 10^{-5} s, 10^{-7} s, 10^{-6} s, and 10^{-5} to 10^{-3} s, respectively. Photolysis or other photochemical transformation processes must be rapid (pseudo first-order rate constants on the order of 10^5 to 10^9 s^{-1}) in order to compete with photophysical deactivation.

For reactions in fluid solutions, photophysical deactivation to the ground state, with no net chemical degradation, can generally be expected to account for more than 95% of the light energy absorbed.

8-3 ABSORPTION OF LIGHT

Chromophores and Characteristic Absorption Bands. As noted in the previous section, it is a necessary but not sufficient condition for photolysis that the organic species in question absorb light. A comparison of the spectrum of solar radiation with the characteristic absorption spectra of organic molecules will therefore provide a preliminary indication of the potential for photochemical reactivity.

Figure 8-1 represents the spectral distribution of solar energy incident on earth, or insolation [17]. Integration of the area under the curves of Figure 8-1 would show that about 10% of the incident light energy is in the ultraviolet region and 45% each in the visible and infrared



a. Curve represents energy incident on horizontal surface.

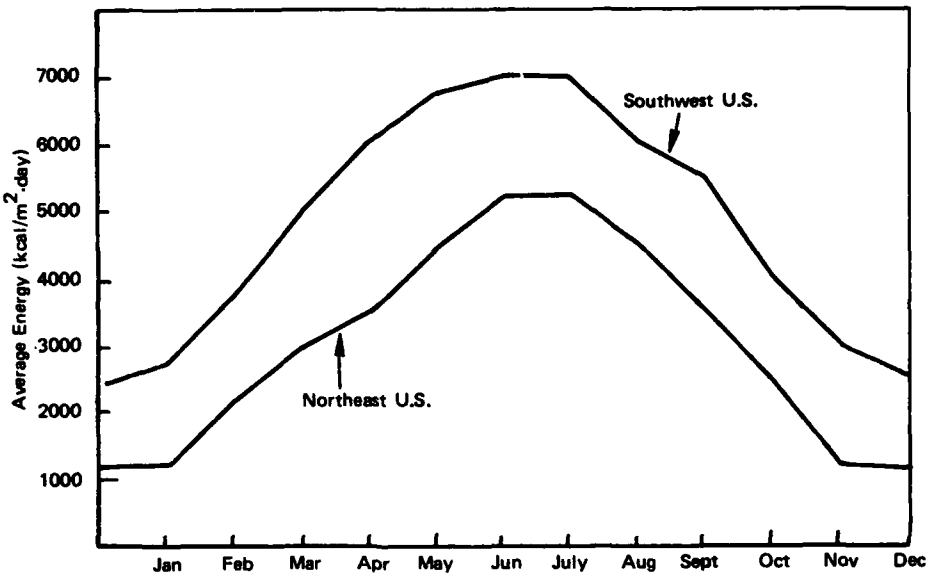
Source: Odum [17].

FIGURE 8–1 Spectral Distribution of Extraterrestrial Solar Radiation and of Solar Radiation at Sea Level on a Clear Day

regions [20]. Virtually all of the insolation is of wavelength >300 nm; shorter wavelengths are effectively filtered out by the stratospheric ozone layer.

At the earth's surface, light of < 290 nm wavelength has such a low intensity that direct photochemical activation at these wavelengths is improbable. On the other hand, UV/visible light of wavelength >290 nm (frequency 3.45×10^4 cm^{-1} or 100 kcal/Einstein) is available at moderate intensity. For a temperate zone such as the United States, it has been calculated [20] that the mean incident solar energy on a horizontal surface varies from about 3000 kcal/m^2-day (northeast) to about 5000 kcal/m^2-day (southwest). This energy input is not constant, of course, but varies diurnally and seasonally. Figure 8-2 indicates the seasonal fluctuations in the incident solar energy.

The solar energy incident on the surface of a natural water body is not uniformly transmitted through the aqueous medium. Figure 8-3 presents some examples showing the attenuation of solar irradiance with



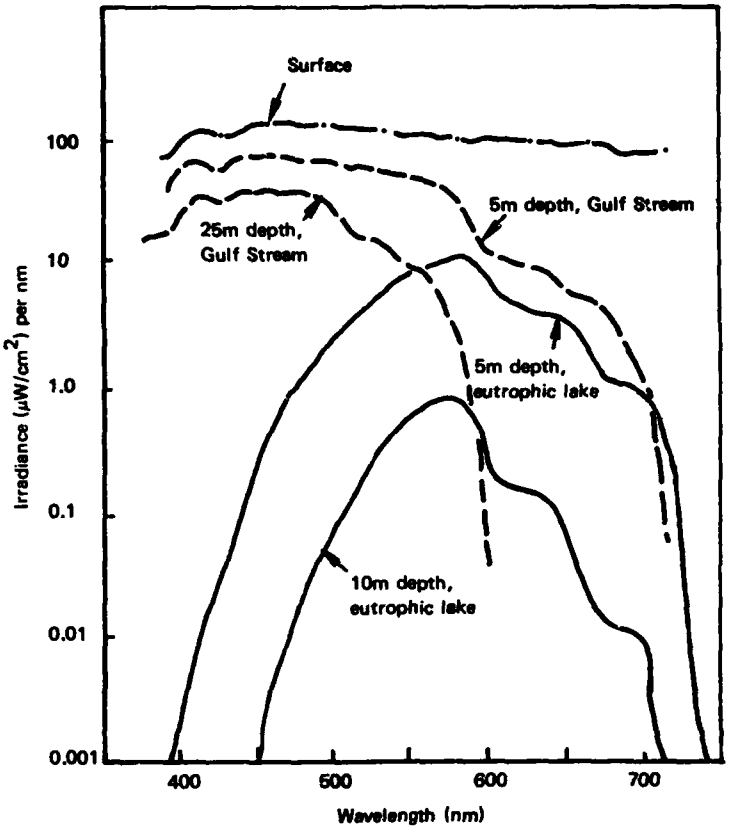
Source: Adapted from data of Reifsnyder and Lull [20].

FIGURE 8–2 Seasonal Variation in Solar Radiant Energy at the Earth's Surface

depth as a function of wavelength. Tyler [29] notes that the long-wavelength absorption of light is due to water itself, while the 400-500 nm absorption in the eutrophic lake can be attributed to phytoplankton and organic degradation products in the water column.

The absorption spectra of organic molecules can be compared with the solar spectra of Figures 8-1 and 8-3 to determine whether absorption of light energy in the environment is likely to be significant. A quantitative approach to such comparisons is presented in the following section of this chapter. Some qualitative rules of thumb that are useful in making preliminary assessments of potential photochemical reactivity are based on the characteristic absorption frequencies of various compounds.

As a first approximation, the electronic spectrum of an organic molecule can be attributed to the presence of one or more *chromophores*, which are functional groups that absorb UV/visible light. Table 8-4 lists typical frequencies of maximum absorption, λ_{max}, and molar absorptivities, ϵ, for particular chromophores in organic molecules that have λ_{max} above the 290-nm solar insolation cutoff. (Some molecules with



(For comparison with Fig. 8-2, note that 1 μW = 14.3×10^{-6} cal/min)

Source: Adapted from Tyler [29].

FIGURE 8–3 Attenuation of Solar Spectrum in Natural Waters

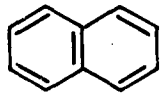
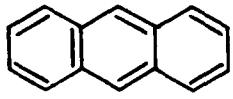
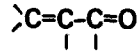
absorption maxima below 290 nm have been included, because the "tails" of such absorption peaks may lead to light absorption and subsequent photoreactivity.)

Table 8-5 presents comparable information for some specific organic compounds. Note that speciation of ionizable organics such as phenol can affect both the wavelength and the intensity of absorption maxima. In general, organic molecules that have moderate-to-strong absorption in the > 290 nm wavelength range contain either: (1) an extended conjugated hydrocarbon system (as in anthracene or larger fused-ring systems) or (2) a functional group with an unsaturated heteroatom (e.g., carbonyl, azo group, nitro group).

The exact position of the absorption maximum for a chromophore in a particular organic molecule depends on the details of the molecular

TABLE 8-4

Chromophoric Groups and Their Characteristic Absorption Maxima at $\lambda > 290$ nm

Group	λ_{max} (nm)	Molar Absorptivity, ϵ (L/mol-cm)
>C=O (aldehyde, ketone)	295	10
>C=S	460	weak
-N=N-	347	15
$-NO_2$	278	10
	311 270	250 5000
	360	6000
	440 300	20 1000
	330	20

Source: Calvert and Pitts [2], pp. 265-67

structure. Several compilations of UV/visible spectral data for organic compounds are available [7,9,10,21]. There are also several empirical correlations, such as the Woodward Rules [32] for calculating λ_{max} values for simple conjugated systems (dienes and α,β-unsaturated carbonyls); these involve addition of wavelength increments for each substituent on the simple system to the λ_{max} for the intense, short-wavelength absorption band of the unsubstituted system. In each instance, however, the base λ_{max} for the unsubstituted system is so low (217, 215, 209, 197 nm) [2] that wavelengths near the 290-nm solar cutoff are not achievable, even with extensive substitution. The Woodward type of empirical correlation is, therefore, not relevant to prediction of the environmental photochemical behavior of organic molecules.

TABLE 8-5

UV/Visible Absorption Maxima and Molar Absorptivities for Selected Organic Compounds

Compound	λ Below 290 nm		λ Above 290 nm	
	λ_{max}[a]	ϵ	λ_{max}[a]	ϵ
Hydrocarbons				
Ethylene	193	10,000		
1,3-Butadiene	217	20,900		
Benzene	255	215		
Styrene	244	12,000		
	282	450		
Biphenyl	246	20,000		
Naphthalene	221	100,000	311	250
	270	5,000		
Anthracene	250	150,000	360	6,000
Pyrene ($C_{16}H_{10}$)[b]	231	45,000	295	45,000
	241	83,000	305	11,000
	262	25,000	319	29,000
	272	50,000	335	47,000
			357	420
			362	360
			372	250
Benzo[a] pyrene ($C_{20}H_{10}$)[b]			347	13,000
			364	24,000
			384	29,000
β-Carotene[c]			452	139,000
			478	122,000
Substituted Aromatics				
Aniline	230	8,600		
	280	1,430		
Anilinium ion	203	7,500		
	254	160		
Acetophenone	240	13,000	319	50
	278	1,100		
Azobenzene			319	19,500
			445	300
Benzaldehyde	244	15,000	328	20
	280	1,500		
Benzoic acid	230	10,000		
	270	800		

(Continued)

TABLE 8-5 (Continued)

Compound	λ Below 290 nm		λ Above 290 nm	
	λ_{max}[a]	ϵ	λ_{max}[a]	ϵ
Substituted Aromatics				
Benzoquinone	250	15,000	300	1,000
			440	20
Chlorobenzene	210	7,500		
	257	170		
Nitrobenzene	252	10,000	330	125
	280	1,000		
Phenol	210	6,200		
	270	1,450		
Phenolate ion	235	9,400		
	287	2,600		
Benzonitrile	224	13,000		
	271	1,000		
Others				
Acetaldehyde			293	12
Acetone	272	19		
Acrolein	210	11,000	315	26
Furan	252	1		
Acridine	250	107,000	355	10,500
Amyl nitrite	218	1,120	356	56
Azomethane			347	4
Ethyl nitrate	270	12		
Nitrosobutane			300	100
			665	20
Pyridine	250	2,000		
Pyrrole	240	302		
Quinoline	275	3,700	313	2,700
Butanethiol	231	126		
Cyclohexyl methyl sulfoxide	210	1,500		
Di-n-butyl sulfide	210	1,200		
	229	145		
Thiophene	231	5,620		

(Continued)

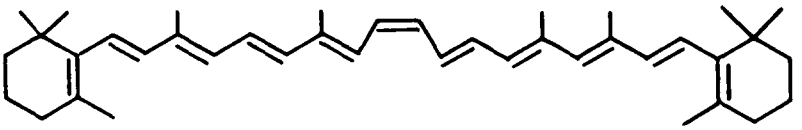
TABLE 8-5 (Continued)

Footnotes

a. Values generally refer to spectra in organic solvents and should be regarded as approximate absorption maxima for species in aqueous solution.

b. Data from Kamlet [10]

c. Trans-β-carotene, a plant pigment [5]:



Source: Refs. 2 and 23, except as noted in footnotes b and c.

Some insight into the inherent photochemical activity of organic target molecules can be obtained by considering the nature of the potential photochemical transitions. The majority of the photochemical activation processes that occur within the 290-750 nm wavelength range involve electronic transitions from non-bonding (n) orbitals — i.e., unshared electron pairs on covalently bonded N or O — or π-bonding (π) orbitals — i.e., electron pairs in double bonds or rings — to antibonding π^* orbitals. Table 8-6, compares some of the features of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In an α,β-unsaturated carbonyl compound, for example, the $\pi \rightarrow \pi^*$ transition is the intense, shorter wavelength band ($\lambda_{max} \approx 210$ nm, $\epsilon \approx 12{,}000$), while the $n \rightarrow \pi^*$ is the weak, longer wavelength band ($\lambda_{max} \approx 330$ nm, $\epsilon \approx 20$) [27]. The $n \rightarrow \pi^*$ transitions of carbonyls are particularly likely to generate excited states that undergo photochemical reaction (dissociation, hydrogen abstraction) as opposed to photophysical deactivation.

Quantitative Calculation of Absorption of Solar Energy. The qualitative consideration of chromophores and characteristic absorption bands described in the previous section is very useful for screening out compounds that have no potential for absorption of solar radiation in the environment. Such compounds cannot be active in direct photolysis. For compounds which do have absorption maxima near or above 290 nm, it is necessary to go beyond consideration of λ_{max} and ϵ_{max} to predict the extent and rate of absorption of solar energy.

A quantitative model for calculating the rate of absorption of light in aquatic environments has been developed and described in a series of

TABLE 8-6

Comparison of the Features of $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ Transitions

Property	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
Maximum ϵ	Less than 100	Greater than 1,000
Vibration band structure	Sharp in nonpolar solvents, broad in polar solvents. Possesses localized vibrational progression (e.g., C=O)	Moderately sharp in most solvents. Possesses C=C vibrational progression
τ_f and ϕ_f	$\tau_f > 10^{-6}$ s, $\phi_f < 0.01$	$\tau_f \sim 10^{-9}$–10^{-7} s $\phi_f \sim 0.5$–0.05
τ_p and ϕ_p	$\tau_p \sim 10^{-3}$ s, $\phi_p \sim 0.5$-0.05	$\tau_p \sim 0.1$–10 s $\phi_p \sim 0.5$–0.05
Direction of transition moment	Perpendicular to molecular plane for singlet-singlet transitions	Parallel to molecular plane for singlet-singlet transitions
Effect of increasing solvent polarity or electron-donating substituents	Transition shifts to shorter wavelengths	Transition shifts to longer wavelengths

Source: Turro [27], p. 46

papers [8,14,15,31,34-39] by Zepp and his colleagues at EPA's Environmental Research Laboratory in Athens, Georgia. Some similar procedures have also been proposed by others [12,13]. The essence of the Zepp approach is to evaluate the degree of overlap between the UV/visible absorption spectrum of an organic compound and the incident solar energy in an aquatic environment. In its simplest terms, this approach can be represented by

$$k_{a\lambda} = \frac{2.303}{j} \epsilon_\lambda I_\lambda \qquad (8\text{-}8)$$

in which $k_{a\lambda}$ is the rate constant for absorption of light of wavelength λ by the organic chemical, ϵ_λ is the molar absorptivity of the chemical at wavelength λ, I_λ represents the flux of solar energy of wavelength λ

incident on the chemical, and j is a conversion constant numerically equal to 6.023×10^{20}. Clearly, ϵ_λ is characteristic of the chemical, and I_λ is characteristic of the aquatic environment under consideration.

The rate constant for photochemical degradation, $k_{p\lambda}$, is related to the rate constant for absorption of light, $k_{a\lambda}$, by the quantum yield, ϕ_λ:

$$k_{p\lambda} = \phi_\lambda \, k_{a\lambda} \tag{8-9}$$

The overall first-order rate of photochemical degradation is then

$$-\frac{d[P]}{dt} = \int_\lambda k_{p\lambda} \, [P] \, d\lambda \tag{8-10}$$

$$= \int_\lambda \phi_\lambda \, k_{a\lambda} \, [P] \, d\lambda \tag{8-11}$$

where [P] is the molar concentration of the organic chemical. If it can be assumed that the quantum yield for photochemical reaction is independent of wavelength, Eq. 8-11 becomes

$$-\frac{d[P]}{dt} = \phi[P] \int_\lambda k_{a\lambda} \, d\lambda \tag{8-12}$$

$$= \phi[P] \int_\lambda \frac{2.303}{j} I_\lambda \, \epsilon_\lambda \, d\lambda \tag{8-13}$$

The assumption that ϕ_λ is invariant with λ has general validity for small changes in wavelength regime (e.g., for different irradiation wavelengths within the same absorption band). On the other hand, it is commonly observed that $\phi_{254\ nm} \neq \phi_{300\ nm}$ and, in fact, that entirely different photochemical processes and products are involved at the two wavelengths. Therefore, one should not attempt to estimate the rate of photolysis of P in the environment by using a literature value of ϕ that was measured using 254-nm irradiation (most common in photochemical literature) or any other irradiation wavelength that is not representative of insolation.

It may be valid to argue that the solar spectrum is sufficiently constant in its distribution of wavelengths that the quantum yield for disappearance of P is constant when one solar irradiation situation is

compared with another or with a simulated solar source. To emphasize this point, the ϕ's of Eqs. 8-12 and 8-13 are given a subscript:

$$-\frac{d[P]}{dt} = \phi_{solar}\,[P]\int_{\lambda} k_{a\lambda}\,d\lambda \qquad (8\text{-}14)$$

$$= \phi_{solar}\,[P]\,\frac{2.303}{j}\int_{\lambda} I_{\lambda}\,\epsilon_{\lambda}\,d\lambda \qquad (8\text{-}15)$$

To simplify data input requirements and computation of the rate of absorption of solar energy, the integral of Eq. 8-15 can be approximated as a sum:

$$-\frac{d[P]}{dt} = \phi_{solar}\,[P]\,\frac{2.303}{j}\sum_{\lambda} I_{\lambda}\,\epsilon_{\lambda} \qquad (8\text{-}16)$$

Thus, a finite number of pairs of I_a and ϵ values corresponding to a set of discrete wavelengths will suffice for calculation. In the Zepp model, a set of 39 individual wavelengths over the range 297.5 nm to 800 nm is specified [37]. These correspond to narrow wavelength intervals (2.5 nm) in the 295-320 nm region where organic molecules are more likely to absorb strongly and to wider intervals (10-50 nm) in the wavelength region above 330 nm. The use of Eq. 8-16 thus requires 39 compound-specific data inputs, the ϵ_{λ} values, and 39 ecosystem-specific data inputs, the $I_{a\lambda}$ values, as well as a value for the quantum yield, ϕ_{solar}.

- *Compound-specific Inputs* (ϵ_{λ} values). The molar absorptivities at the specified wavelengths are obtained experimentally by determination of the UV/visible spectrum of the compound. Smith *et al.* [24,25] have described a procedure for making the required measurements. They note that the spectra should be obtained with a high-quality UV/visible spectrophotometer (such as a Cary Model 14 or 15), using solutions of the compound at 10^{-2} to 10^{-4} M concentration in water. A water-acetonitrile solvent mixture can be used if necessary to achieve sufficiently high concentrations of water-insoluble species for accurate measurement of absorbances. The value of ϵ at a specified wavelength is calculated from the Beer-Lambert Law (Eq. 8-2) as

$$\epsilon_{\lambda} = \frac{A_{\lambda}}{\ell c} \qquad (8\text{-}17)$$

It is suggested [24] that the ϵ_λ value for each wavelength specified by Zepp be calculated as the mean of values for the upper and lower bounds of the appropriate interval, e.g.,

$$\epsilon_{297.5} = \frac{\epsilon_{295.0} + \epsilon_{300}}{2} \qquad (8\text{-}18)$$

Table 8-7 presents ϵ_λ data for eleven compounds investigated by Smith [25] and three pesticides studied by Hautala [8].

TABLE 8-7

Molar Absorptivities, ϵ_λ, of Selected Compounds as a Function of Wavelength

	ϵ_λ (L/mol-cm) at pH ≈ 7[a] (Data of Smith *et al.* [25])						
λ (nm)	p-Cresol	Benz[a] anthracene	Benzo[a] pyrene	Quinoline	Benzo[f] quinoline	9H-Carbazole	7H-Dibenzo[c,g] carbazole
297.5	18	7,930	46,600	2,910	3,960	5,540	16,500
300	7.2	7,070	27,700	3,050	3,910	3,100	15,900
302.5	3.8	5,880	13,900	2,740	2,140	2,440	12,300
305	2	3,790	6,670	2,480	1,500	2,270	8,760
307.5	2	3,200	4,840	2,050	1,240	2,390	6,480
310	2	3,480	3,970	2,440	1,180	2,530	4,990
312.5	1	3,900	3,890	2,920	1,430	2,600	4,340
315	0	4,200	3,650	1,680	1,670	2,700	4,070
317.5		4,170	3,730	622	1,480	2,920	3,930
320		4,120	3,570	269	1,380	3,190	3,960
323.1		4,800	3,650	119	1,490	3,170	4,260
330		5,450	5,400	26	3,020	2,900	5,830
340		5,390	8,330	9	1,680	1,520	9,220
350		4,850	12,300	0	1,530	166	11,000
360		3,350	18,100		250	23	12,700
370		1,560	19,680		185	13	7,890
380		662	21,910		96	12	770
390		417	15,160		37	2	10
400		17	2,100		0	0	0

(Continued)

TABLE 8-7 (Continued)

λ (nm)	ϵ_λ (L/mol-cm) at pH ≈ 7[a]						
	Data of Smith *et al.* [25]				Data of Hautala [8]		
	Benzo [b] thio-phene	Dibenzo-thio-phene	Methyl Para-thion	Mirex	2,4D Methyl Ester	Sevin	Para-thion
297.5	1,793	1,154	6,040	0[b]	236	1,410	4,800
300	395	1,224	5,460		78.7	930	4,500
302.5	130	1,327	4,930		52.5	737	4,250
305	30	1,499	4,310		39.4	529	3,750
307.5	13	1,782	3,700		39.4	409	3,250
310	7	2,025	3,210		26.2	351	2,750
312.5	3	2,080	2,760		26.2	378	2,350
315		1,939	2,290		13.1	259	2,000
317.5		1,892	1,920		13.1	236	1,600
320		2,119	1,630			112	1,550
323.1		2,394	1,310			29[c]	1,400[d]
330		526	933			13.2	950
340		13.1	568			3.2	550
350		7.5	374				400
360		0	244				
370			145				
380			82				
390			45				
400			9				

a. pH = 4.5 for 7H-dibenzo [c,g] carbazole.

b. $\epsilon_\lambda < 0.01$ for all $\lambda > 290$ nm [22].

c. λ = 325 nm.

d. λ = 322.5 nm.

The necessary ϵ_λ values for use in Eq. 8-16 generally cannot be obtained from the older compilations of UV/visible spectral information [7,9,10,21]. Most of these give only the values of λ and ϵ_λ corresponding to absorption maxima for a given compound rather than the complete spectrum. The Sadtler compilation [21] presents actual spectra and generally includes the concentration and pathlength information but does not always cover the >290 nm range at a sufficient sensitivity to allow calculation of ϵ_λ values for the solar spectral region. Also, most published UV/visible spectra of organics have been obtained with organic solvents (e.g., hexane, ethanol) rather than aqueous solutions. Solvent effects on spectra, both λ_{max} and ϵ_{max}, can significantly degrade the resolution implied in the Zepp approach. Thus, data suitable for use in Eq. 8-16 are not generally available for a large number of compounds beyond those in Table 8-7.

The stepwise procedure for application of Eq. 8-16 therefore begins in the laboratory, as follows:

Step 1: Prepare dilute solutions of the chemical at known concentration in water or water/acetonitrile.

Step 2: Determine the UV/visible spectrum at several concentrations over a tenfold concentration range using cells of 1-cm and 10-cm pathlength.

Step 3: Calculate ϵ_λ values from the measured spectra.

- *Ecosystem-specific Inputs* (I_λ Values). The principles and procedures for computation of I_λ have been described by Zepp and Cline [37], who developed a computer program to accomplish the task. Equation 8-19 describes the contributions to I_λ from direct radiation, I_d, and sky radiation, I_s

$$I_\lambda = \frac{I_{d\lambda}(1 - 10^{-\alpha_\lambda \ell_d}) + I_{s\lambda}(1 - 10^{-\alpha_\lambda \ell_s})}{D} \qquad (8\text{-}19)$$

where α_λ = attenuation coefficient for adsorption of light in the aquatic medium itself

ℓ_d = average pathlength for direct light in the water (cm)

ℓ_s = average pathlength for skylight in the water (cm)

D = depth in the water body (cm).

An explicit solution of Eq. 8-19 for a particular location, time of year/day, and body of water requires input information on [34]:

- Attenuation coefficients and refractive index of the aquatic medium,
- Solar declination, solar right ascension, and sidereal time,
- Latitude and longitude,
- Average ozone layer thickness, and
- Solar spectrum.

Zepp and Cline [37] describe two limiting cases in which Eq. 8-19 can be simplified. When both of the $\alpha\ell$ exponents exceed 2, essentially all sunlight is absorbed within the water column. Equation 8-19 then becomes

$$I_\lambda = \frac{I_{d\lambda} + I_{s\lambda}}{D} \approx \frac{W_\lambda}{D} \qquad (8\text{-}20)$$

Table 8-8 lists values of W_λ, the solar radiation intensity, calculated by Zepp and Cline for a body of water at a hypothetical 40°N latitude location at midday and midseason.

The other limiting case described by Zepp and Cline is that in which the water column under consideration absorbs very little of the incident light, which is true for a sufficiently shallow surface layer of any natural water body. Equation 8-19 then becomes

$$I_\lambda = 2.303\, Z_\lambda \qquad (8\text{-}21)$$

where $Z_\lambda = I_{d\lambda} \sec\theta + 1.2\, I_{s\lambda}$

θ = angle of refraction

Values of Z_λ from Zepp and Cline's work are presented in Table 8-9, again for a hypothetical 40°N latitude location at midday.

Once a phytolysis rate, -d[P]/dt, has been calculated (e.g., from Eq. 8-16), a photolysis half-life, $t_{1/2}$, may be calculated as follows:

$$t_{1/2} = 0.693[P]\,(-d[P]/dt)^{-1}\ s \qquad (8\text{-}22)$$

The examples of ecosystem-dependent parameters presented in Tables 8-8 and 8-9 are not intended to represent values for a "typical" ecosystem, although they might be used as such. To a considerable extent, the elegance of the Zepp approach to aqueous photolysis lies in the fact that it is almost as easy to model a real situation of interest as it is to compute the behavior of a hypothetical case. The tables have been included here partly because they provide some quantitative information on the distribution of solar energy as a function of wavelength and complement the more qualitative picture provided by Figures 8-1 and 8-3.

Another reason for presenting sample values of W_λ and Z_λ is to show the seasonal variation in solar intensity. This is also illustrated in Figure 8-4, where seasonal variations in log W_λ and log Z_λ are plotted as a function of wavelength. Note that the high (summer) and low (winter) intensities differ by no more than a factor of four for the longer wavelengths (≥320 nm). Within the 295-320 nm range, however, the summer intensity is up to 36 times the winter intensity. Light with a wavelength

TABLE 8-8

Solar Irradiation Intensity, W_λ, from Eq. 8-20[a]

Wavelength (nm)	Spring	Summer	Fall	Winter
	Photons (cm^{-2} s^{-1} per 2.5 nm interval)			
297.5	0.240E + 12	0.648E + 12	0.786E + 11	b
300.0	0.105E + 13	0.219E + 13	0.434E + 12	0.601E + 11
302.5	0.369E + 13	0.657E + 13	0.185E + 13	0.300E + 12
305.0	0.106E + 14	0.163E + 14	0.555E + 13	0.139E + 13
307.5	0.195E + 14	0.274E + 14	0.112E + 14	0.369E + 13
310.0	0.325E + 14	0.444E + 14	0.173E + 14	0.698E + 13
312.5	0.510E + 14	0.643E + 14	0.308E + 14	0.145E + 14
315.0	0.683E + 14	0.836E + 14	0.410E + 14	0.222E + 14
317.5	0.867E + 14	0.103E + 15	0.532E + 14	0.296E + 14
320.0	0.103E + 15	0.121E + 15	0.663E + 14	0.408E + 14
	Photons (cm^{-2} s^{-1} per 3.75 nm interval)			
323.1	0.193E + 15	0.226E + 15	0.119E + 15	0.740E + 14
	Photons (cm^{-2} s^{-1} per 10 nm interval)			
330.0	0.669E + 15	0.762E + 15	0.421E + 15	0.279E + 15
340.0	0.778E + 15	0.875E + 15	0.500E + 15	0.341E + 15
350.0	0.835E + 15	0.938E + 15	0.533E + 15	0.363E + 15
360.0	0.895E + 15	0.100E + 16	0.568E + 15	0.383E + 15
370.0	0.997E + 15	0.112E + 16	0.623E + 15	0.418E + 15
380.0	0.110E + 16	0.124E + 16	0.679E + 15	0.450E + 15
390.0	0.133E + 16	0.148E + 16	0.895E + 15	0.646E + 15
400.0	0.191E + 16	0.212E + 16	0.129E + 16	0.931E + 15
410.0	0.251E + 16	0.279E + 16	0.170E + 16	0.123E + 16
420.0	0.258E + 16	0.287E + 16	0.175E + 16	0.127E + 16
430.0	0.249E + 16	0.277E + 16	0.170E + 16	0.123E + 16
440.0	0.295E + 16	0.327E + 16	0.201E + 16	0.146E + 16
450.0	0.332E + 16	0.368E + 16	0.227E + 16	0.164E + 16
460.0	0.335E + 16	0.372E + 16	0.230E + 16	0.167E + 16
470.0	0.347E + 16	0.384E + 16	0.238E + 16	0.172E + 16
480.0	0.355E + 16	0.394E + 16	0.244E + 16	0.177E + 16
490.0	0.336E + 16	0.372E + 16	0.231E + 16	0.168E + 16

(continued)

TABLE 8-8 (Continued)

Wavelength (nm)	Spring	Summer	Fall	Winter
	Photons (cm^{-2} s^{-1} per 10 nm interval)			
500.0	0.343E + 16	0.380E + 16	0.236E + 16	0.171E + 16
525.0	0.362E + 16	0.401E + 16	0.251E + 16	0.181E + 16
550.0	0.377E + 16	0.418E + 16	0.262E + 16	0.188E + 16
575.0	0.380E + 16	0.423E + 16	0.265E + 16	0.190E + 16
600.0	0.385E + 16	0.427E + 16	0.268E + 16	0.192E + 16
625.0	0.387E + 16	0.428E + 16	0.271E + 16	0.196E + 16
650.0	0.389E + 16	0.429E + 16	0.273E + 16	0.199E + 16
675.0	0.388E + 16	0.427E + 16	0.273E + 16	0.200E + 16
700.0	0.384E + 16	0.422E + 16	0.272E + 16	0.200E + 16
750.0	0.369E + 16	0.404E + 16	0.261E + 16	0.193E + 16
800.0	0.354E + 16	0.387E + 16	0.252E + 16	0.187E + 16

a. 1.0E + 12 = 1.0 X 10^{12} etc.
b. Irradiation intensity below detection limit.

Source: Zepp and Cline [37].

of <320 nm is most likely to overlap the absorption spectra of organic molecules. A tenfold or greater seasonal variation in photolysis half-lives can thus be expected due to variations in insolation intensity. This effect is likely to be comparable to or larger than the effects of seasonal temperature variation.

Finally, the fact that the relative intensities within the solar spectrum, as well as the total intensity of insolation, vary with the season has relevance to a key assumption made in deriving Eq. 8-16. The assumption that the quantum yield, ϕ_λ, of Eq. 8-11 can be factored out of the integral (sum) and treated as a constant, ϕ_{solar}, is less likely to be valid when substantial shifts in the distribution of solar energy are considered.

Because the emphasis of this handbook is on the properties of organic chemicals, rather than on the properties of environments, detailed procedures for calculating I_λ values are not discussed here. A computer program is the most convenient way to compute I_λ values and the I_λ e_λ products of Eq. 8-16. Such a program, accepting as input the 39 compound-specific ϵ_λ values, is incorporated into the EPA's Exposure Analysis Modelling System (EXAMS), which is widely available [6].

TABLE 8-9

Solar Irradiation Intensity, Z_λ, from Eq. 8-21[a]

Wavelength (nm)	Spring	Summer	Fall	Winter
	Photons (cm^{-2} s^{-1} per 2.5 nm interval)			
297.5	0.274E + 12	0.716E + 12	0.949E + 11	b
300.0	0.120E + 13	0.240E + 13	0.524E + 12	0.733E + 11
302.5	0.419E + 13	0.723E + 13	0.223E + 13	0.368E + 12
305.0	0.121E + 14	0.181E + 14	0.670E + 13	0.170E + 13
307.5	0.223E + 14	0.305E + 14	0.135E + 14	0.450E + 13
310.0	0.372E + 14	0.495E + 14	0.208E + 14	0.854E + 13
312.5	0.584E + 14	0.717E + 14	0.371E + 14	0.177E + 14
315.0	0.780E + 14	0.933E + 14	0.494E + 14	0.271E + 14
317.5	0.992E + 14	0.115E + 15	0.641E + 14	0.362E + 14
320.0	0.117E + 15	0.135E + 15	0.800E + 14	0.498E + 14
	Photons (cm^{-2} s^{-1} per 3.75 nm interval)			
323.1	0.221E + 15	0.252E + 15	0.144E + 15	0.906E + 14
	Photons (cm^{-2} s^{-1} per 10 nm interval)			
330.0	0.761E + 15	0.846E + 15	0.508E + 15	0.342E + 15
340.0	0.880E + 15	0.963E + 15	0.604E + 15	0.420E + 15
350.0	0.942E + 15	0.103E + 16	0.645E + 15	0.449E + 15
360.0	0.101E + 16	0.110E + 16	0.687E + 15	0.479E + 15
370.0	0.112E + 16	0.122E + 16	0.754E + 15	0.520E + 15
380.0	0.124E + 16	0.135E + 16	0.822E + 15	0.562E + 15
390.0	0.149E + 16	0.161E + 16	0.108E + 16	0.805E + 15
400.0	0.213E + 16	0.231E + 16	0.156E + 16	0.116E + 16
410.0	0.280E + 16	0.302E + 16	0.206E + 16	0.154E + 16
420.0	0.288E + 16	0.310E + 16	0.212E + 16	0.159E + 16
430.0	0.277E + 16	0.298E + 16	0.205E + 16	0.154E + 16
440.0	0.327E + 16	0.351E + 16	0.244E + 16	0.184E + 16
450.0	0.368E + 16	0.394E + 16	0.275E + 16	0.208E + 16
460.0	0.371E + 16	0.398E + 16	0.279E + 16	0.211E + 16
470.0	0.384E + 16	0.411E + 16	0.289E + 16	0.219E + 16
480.0	0.392E + 16	0.420E + 16	0.296E + 16	0.225E + 16
490.0	0.371E + 16	0.396E + 16	0.281E + 16	0.213E + 16

(continued)

TABLE 8-9 (Continued)

Wavelength (nm)	Spring	Summer	Fall	Winter
	Photons (cm^{-2} s^{-1} per 10 nm interval)			
500.0	0.378E + 16	0.404E + 16	0.287E + 16	0.218E + 16
525.0	0.398E + 16	0.426E + 16	0.305E + 16	0.232E + 16
550.0	0.413E + 16	0.442E + 16	0.318E + 16	0.241E + 16
575.0	0.417E + 16	0.446E + 16	0.322E + 16	0.243E + 16
600.0	0.421E + 16	0.450E + 16	0.326E + 16	0.247E + 16
625.0	0.422E + 16	0.450E + 16	0.329E + 16	0.252E + 16
650.0	0.424E + 16	0.451E + 16	0.332E + 16	0.256E + 16
675.0	0.423E + 16	0.448E + 16	0.333E + 16	0.259E + 16
700.0	0.419E + 16	0.443E + 16	0.330E + 16	0.258E + 16
750.0	0.401E + 16	0.423E + 16	0.318E + 16	0.250E + 16
800.0	0.385E + 16	0.405E + 16	0.306E + 16	0.242E + 16

a. 1.0 E + 12 = 1.0×10^{12} etc.
b. Irradiation intensity below detection limit.

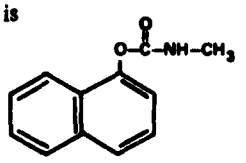
Source: Zepp and Cline [37].

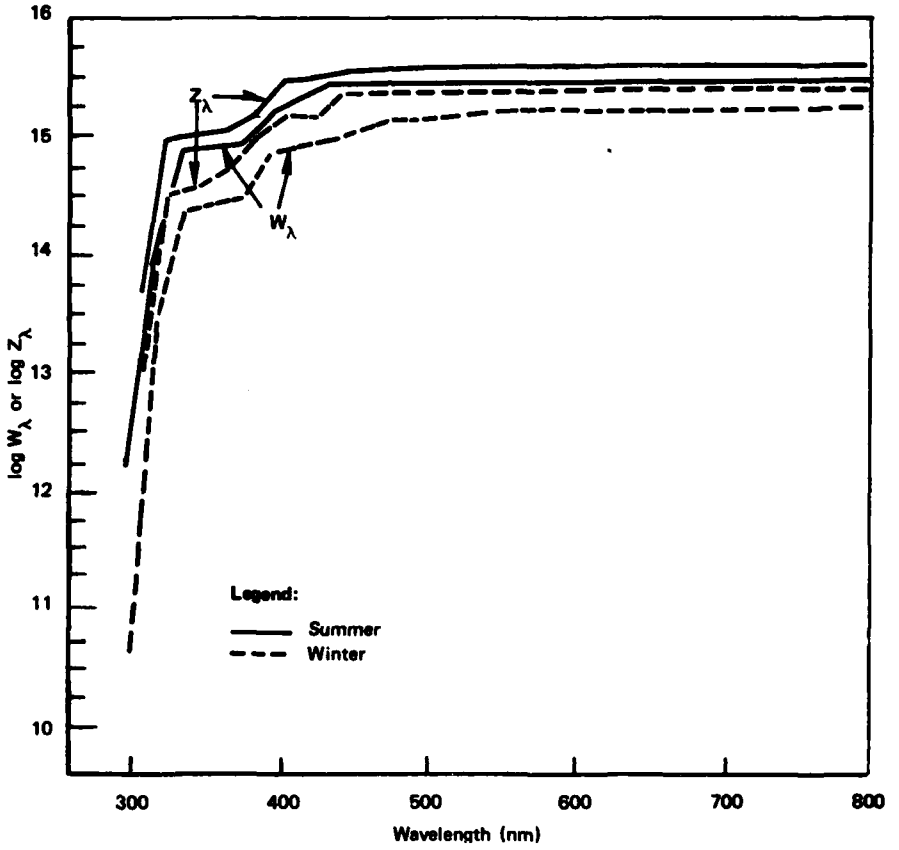
Example 8-1 illustrates the calculation of the rate of photolysis according to the Zepp procedure.

Example 8-1 Estimate the rate of photolysis for Sevin® (Carbaryl®) in a clear, deep lake. Assume that:

- All sunlight is absorbed in the water column. (Thus, Eq. 8-20 may be used.)
- The lake is 5 m deep. (Thus, $D = 5 \times 10^2$ cm.)
- The pollutant concentration, [P], is 5×10^{-5} M (≈10 mg/L)
- The lake is at 40°N latitude and the time is midday and midsummer. (Thus, values of W_λ in Table 8-8 may be used.)

(1) The structure of Sevin® is





Source: Data from Zepp and Cline [37].

FIGURE 8–4 Seasonal Variations in log Z_λ and log W_λ

Note that this structure contains two components (a $\rangle$C=O group and the naphthalene ring system) that are identified in Table 8-4 as chromophoric groups with $\lambda_{max} > 290$ nm. Thus, direct photolysis can take place.

(2) Equation 8-16 provides the basic expression for the rate of photolysis. When Eq. 8-20 ($I_\lambda = W_\lambda/D$) is substituted in Eq. 8-16, the result is:

$$-\frac{d[P]}{dt} = \phi_{solar}\ [P]\ \frac{2.303}{jD} \sum_\lambda W_\lambda \epsilon_\lambda \qquad (8\text{-}23)$$

(3) Using values of W_λ from Table 8-8 (summer) and ϵ_λ from Table 8-7:

$$\sum_\lambda W_\lambda \epsilon_\lambda = (1410 \times 0.648 \times 10^{12}) + (930 \times 0.219 \times 10^{13}) +$$
$$(737 \times 0.657 \times 10^{13}) + \ldots . \text{(next 10 terms of sum not shown)}$$
$$= 1.39 \times 10^{17}\ \frac{\text{L·photons}}{\text{mol·cm}^3\text{·s}}$$

(4) Then with $\phi_{solar} = 0.01$ (Table 8-11), $D = 5 \times 10^2$ cm, $[P] = 5 \times 10^{-5}$ M, and $j = 6.023 \times 10^{20}$, Eq. 8-23 is evaluated as:

$$-\frac{d[P]}{dt} = (0.01)(5 \times 10^{-5}) \frac{2.303}{(6.023 \times 10^{20})(5 \times 10^2)} (1.39 \times 10^{17})$$

$$= 5.3 \times 10^{-13} \text{ mol} \cdot L^{-1} \cdot s^{-1}$$

$$= 1.7 \times 10^{-5} \text{ mol} \cdot L^{-1} \cdot yr^{-1}$$

(5) From Eq. 8-22, the half-life for photolysis in this lake is

$$t_{1/2} = 0.693 (5 \times 10^{-5})/(1.7 \times 10^{-5})$$

$$= 2 \text{ yr}$$

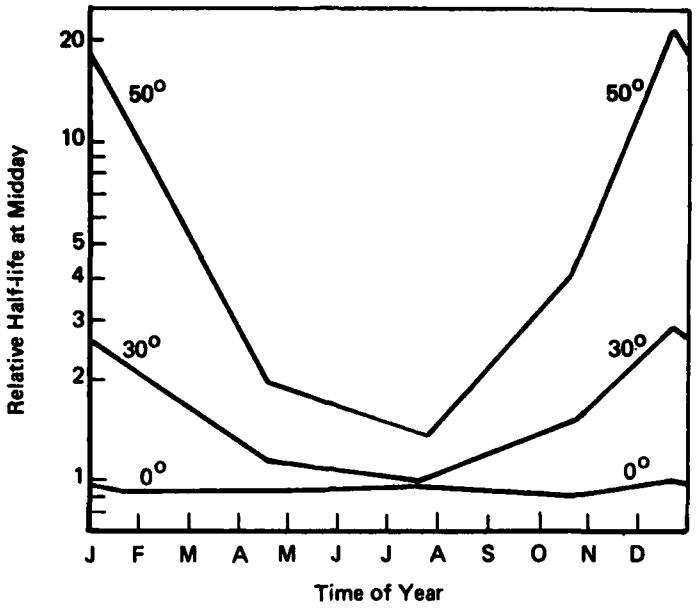
An assessment of the relative importance of photolysis as a removal mechanism in this lake would also require consideration of other degradation processes (e.g., hydrolysis, biodegradation), other removal processes (e.g., volatilization, sedimentation), and the residence time of the water in the lake. Note that if we had considered only the top 5 cm of the lake, the photolysis half-life in this layer would be about 7 days, which is close to the 11-day half-life given by Hautala [8] (see Table 8-12).

(6) Zepp and Cline [37] have carried out additional calculations for Sevin® to show the effects of time (of day and of year) and latitude on the photolysis rate. Their results are shown in Figures 8-5 and -6. The depth dependence of direct photolysis, for pure water and average river water, is shown in Figure 8-7.

8-4 PHOTOCHEMICAL REACTIONS

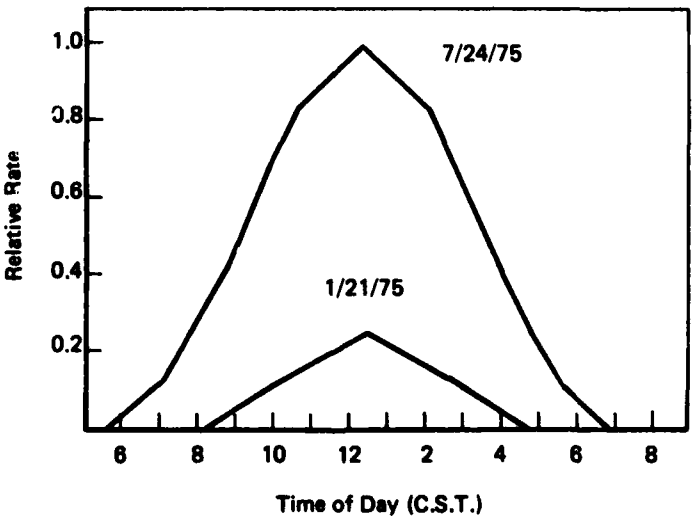
General Considerations. Our present understanding of photochemical reaction mechanisms does not allow prediction of either the qualitative product distribution or the quantitative reaction efficiency of chemical transformations that may occur as a result of light absorption by an organic molecule. This is not surprising; photochemical degradation generally competes poorly with the photophysical deactivation processes described in §8-2, so overall quantum yields for photolytic degradation of organics in solution are typically much less than 0.1. Furthermore, those photochemical processes that do take place involve rapid transformations of the short-lived excited states and are, therefore, more difficult to study systematically than the slower thermal processes.

Despite the fact that it is not feasible to develop reliable predictions of the nature and extent of photochemical transformations that may occur under specified conditions, it is useful to review briefly the broad



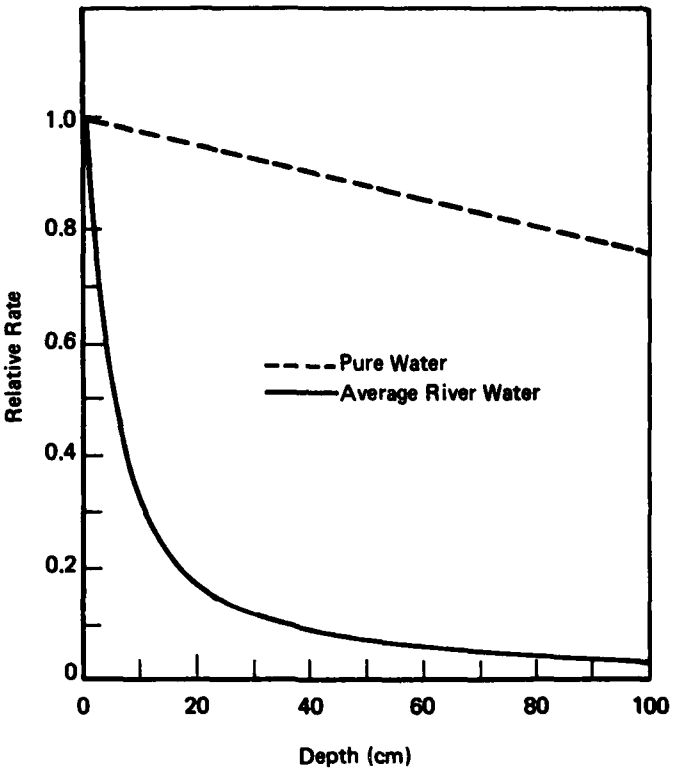
Source: Zepp and Cline [37]

FIGURE 8–5 Relative Midday Half-life for Direct Photolysis of Sevin® at Midseason for Northern Latitudes



Source: Zepp and Cline [37]

FIGURE 8–6 Diurnal Variation of Direct Photolysis Rate of Sevin® at Latitude 40°N



Source: Zepp and Cline [37]

FIGURE 8–7 Computed Depth Dependence of Direct Photolysis of Sevin® at Midday and Midsummer, Latitude 40°N

categories of reaction types and product types that have been observed. More detailed treatments of these subjects can be found in the excellent texts of Calvert and Pitts [2], Kan [11] and Turro [27].

Primary photochemical processes in organic molecules include fragmentation into free radicals or neutral molecules, rearrangement and isomerization reactions, photoreduction by hydrogen atom abstraction from other molecules, dimerization and related addition reactions, photoionization, and electron transfer reactions. Table 8-10 summarizes primary photochemical reaction processes that are typical of various organic compound categories. This summary has been abstracted from Calvert and Pitts' review [2] of the photochemistry of polyatomic molecules. The entries have been selected to emphasize reactions that are considered important at irradiation wavelengths >290 nm and/or ones that are known to occur in fluid solutions. The

(continued on p. 8-36)

TABLE 8-10

Primary Photochemical Reaction Modes Typical of Various Organic Compound Categories

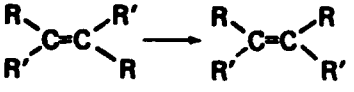
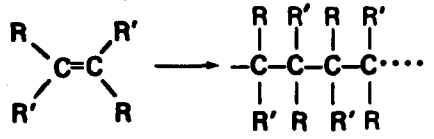
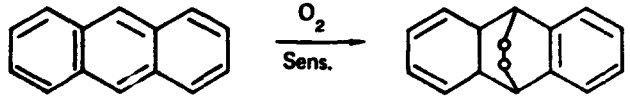
Reaction Process	Comments
1. Aldehydes, Ketones	
a. $RCHO \longrightarrow R\cdot + HCO\cdot$ $RCOR' \longrightarrow R\cdot + R'CO\cdot$	"Norrish Type I" fragmentation; typical with 313-nm irradiation
b. $RCHO^* \longrightarrow RH + CO$	Fragmentation with 254-nm irradiation
c. $R_2\underset{\displaystyle H}{\underset{\vert}{C}}CR_2CR_2CHO \longrightarrow R_2C{=}CR_2 + HCR_2\overset{\displaystyle O}{\overset{\Vert}{C}}H$	"Norrish Type II" split of aldehydes and ketones; requires γ-hydrogen
d. $RCOR' + SH \longrightarrow R\dot{C}R'OH + S\cdot$ (solvent)	Photoreduction; hydrogen atom abstraction by triplet state of aldehyde or ketone
e. $R_2\underset{\displaystyle H}{\underset{\vert}{C}}CR_2CR_2COR' \longrightarrow CR_2(\overset{\displaystyle OH}{\overset{\vert}{C}}R')CR_2CR_2$	Intramolecular photoreduction of ketones
f. 	Decarbonylation and ring contraction of cyclic ketones
2. Hydrocarbons	
a. 	Cis-trans isomerization. Occurs at $\lambda > 290$ nm only if R and/or R' aromatic

TABLE 8-10 (Continued)

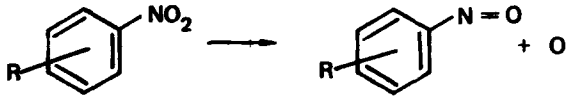
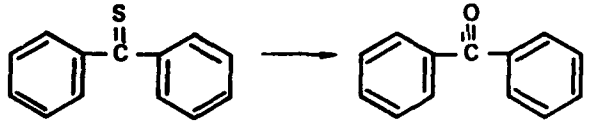
Reaction Process	Comments
2. Hydrocarbons (cont'd.)	
b. 	Polymerization. Occurs at $\lambda > 290$ nm only if R and/or R' aromatic
c. $CHR{=}CR{-}CR{=}CHR \longrightarrow R{-}C{=}C{-}CHR$ (R on the second C)	Cyclization
d. 	Isomerization at 254 nm. Fluorescence at longer wavelength.
e. 	Photosensitized oxidation. Not a direct photolysis of the aromatic.
3. Organo Halides	
a. $RX \longrightarrow R\cdot + X\cdot$	Photodissociation. For X=I, can occur at $\lambda > 290$ nm.
b. $R_2CHCH_2X \longrightarrow R_2C{=}CH_2 + HX$	Dehydrohalogenation. $\lambda < 200$ nm
4. Carboxylic Acids	
a. $RCO_2H \longrightarrow R\cdot + \cdot CO_2H$	Primarily for $\lambda < 254$ nm
b. $RCO_2H \longrightarrow RCO_2\cdot + H\cdot$	Primarily for $\lambda < 254$ nm

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TABLE 8-10 (Continued)

Reaction Process	Comments
4. Carboxylic Acids (cont'd.)	
c. $RCO_2H \longrightarrow RH + CO_2$	Decarboxylation; dominant photodecomposition mode in water at 366 nm irradiation
d. $RCCO_2H \longrightarrow R{-}C(COOH){-}C(OH){-}R$	*Photoreduction + dimerization of α-keto acids*
5. Carboxylate Esters	
a. $RCOR' \longrightarrow RCO_2\cdot + R'\cdot$ $\longrightarrow R\cdot + \cdot CO_2R'$	*Analogs of Norrish Type I splits in carbonyls. Type II splits also occur*
b. $RCOR' \longrightarrow R\cdot + \cdot OR' + CO$	*Decarbonylation. Radicals may recombine within solvent cage*
6. Peroxides	
a. $ROOR' \longrightarrow RO\cdot + R'O\cdot$	Photodissociation
b. $ROOR' \longrightarrow RO_2\cdot + R'\cdot$	Photodissociation mode found only for < 230 nm irradiation
7. Azo Compounds	
a. $RN{=}NR \longrightarrow 2R\cdot + N_2$	Common, efficient procedure for production of R·. Occurs at > 366 nm, but only for aliphatic R.

TABLE 8-10 (Continued)

Reaction Process	Comments
7. Azo Compounds (cont'd.)	
b. $R_2C{=}\bar{N}{=}\overset{+}{N} \longrightarrow R_2C: + N_2$	Efficient photoprocess at $\lambda > 300$ nm, but diazo compounds not stable in water
8. Nitroso Compounds	
a. $R{-}N{=}O \longrightarrow R\cdot + NO\cdot$	Photodissociation important even at 750-500 nm
9. Nitro Compounds	
a. $R_2CHCH_2NO_2 \longrightarrow R_2CHCH_2\cdot + NO_2\cdot$	Photodissociation of nitroalkane can occur at $\lambda > 300$ nm
b. $R_2CHCH_2NO_2 \longrightarrow R_2C{=}CH_2 + HONO$	Photoelimination of nitroalkane with β-hydrogen. Can occur at $\lambda > 300$ nm
c. 	Principal fragmentation route of nitroarenes.
10. Organic Nitrites/Nitrates	
a. $RONO \longrightarrow RO\cdot + NO\cdot$	Dominant process in solution
b. $RCH_2O{\cdot}NO_2 \longrightarrow RCH_2O\cdot + NO_2\cdot$	Dominant photodissociation mode
11. Organosulfur compounds	
a. $RSSR \longrightarrow 2\ RS\cdot$	Photodissociation. Can occur at 365 nm
b. 	Photooxidation by direct photolysis in presence of oxygen. 588 nm irradiation effective.

Source: Calvert and Pitts [2], pp. 366-579.

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latter is a rather severe limitation, since much of the classical literature of organic chemistry refers to gas-phase or frozen-solution (77K) matrices. Because of the selection criteria, Table 8-10 excludes such categories as alcohols, ethers, amines, and nitriles, which do not absorb light in the solar spectral region.

The reactions indicated in Table 8-10 are *primary* photochemical processes. Keep in mind that more than one of these processes can occur on direct photolysis of an organic chemical in water and that they compete with each other and with photophysical deactivation processes in determining the fate of the excited state. Furthermore, the intermediate species produced in the primary photochemical processes, such as free radicals, undergo various secondary chemical reactions until thermally stable products are formed. When the considerable variations in composition of aquatic media are also taken into consideration, it becomes clear that predicting the course of a direct photolysis reaction is generally impractical and frequently not feasible.

Because of the complex network of possible pathways for an excited-state molecule, the photochemical fate of organic compounds in the environment is usually treated simply in terms of disappearance of the pollutant, P. The rate constant, k, and half-life, $t_{1/2}$, are derived for assumed first-order or pseudo first-order degradation of P, and the quantum yield is, similarly, a disappearance quantum yield. Thus, k, $t_{1/2}$, and ϕ reflect the combined effects of all processes other than deactivation of the excited state.

The complexity of the network of possible reaction pathways also makes development of structure/reactivity correlations a formidable task. To date, such correlations have not been derived, even for relatively restricted sets of organic chemicals.

Some Specific Examples. Within the past five years, numerous experimental investigations have been made of the photolysis of organic chemicals in aqueous media. (See, for example, Refs. 1, 3, 4, 8, 14, 19, 22, 25, 26, 30, and 34-39.) The compounds studied have been primarily pesticides and polycyclic aromatic hydrocarbons, although a few other compound categories have been included.

Tables 8-11 and 8-12 present the quantum yield data and photolysis half-life, respectively, for a representative subset of the available data. These were selected primarily from the results of systematic investigations conducted and/or sponsored by the EPA's Environmental

TABLE 8-11

Disappearance Quantum Yield, ϕ, for Photolysis in Aqueous Media

Compound	λ^a (nm)	ϕ	Ref.
Pesticides			
Carbaryl	313	0.005	31
2,4-D, butoxyethyl ester	313	0.05	31
2,4-D, methyl ester	290	0.06	8
DDE	b	0.30	36
Methoxychlor	>288	0.30	31
Methyl parathion	313	0.00017	25
N-nitrosoatrazine	b	0.30	36
Parathion	313	0.0002	8
	>280	< 0.001	31
	b	0.00015	36
Sevin	290	0.01	8
Trifluralin	b	0.0020	36
Polycyclic Aromatic Hydrocarbons (PAH)			
Anthracene	366	0.003	39
Benzo[a] anthracene	313,366	0.0033	25
Benzo[a] pyrene	313	0.00089	25
Chrysene	313	0.003	39
9,10-Dimethylanthracene	366	0.004	39
Fluoranthene	313	0.0002	39
Naphthalene	313	0.015	39
Phenanthrene	313	0.010	39
Pyrene	313,366	0.002	39
Miscellaneous			
Benzo[f] quinoline	313	0.014	25
Benzophenone	>300	0.02	27
p-Cresol	313	0.079	25
3,4-Dichloroaniline	313	0.052	14
9H-Dibenzocarbazole	366	0.0028	25
Dibenzothiophene	313	0.00050	25
Quinoline	313	0.00033	25

a. Wavelength for which ϕ was determined
b. Sunlight

TABLE 8-12

Half-Life for Disappearance via Direct Photolysis in Aqueous Media

Compound	λ^a (nm)	$t_{1/2}$	Ref.
Pesticides			
Carbaryl	b	50 h	31
2,4-D, butoxyethyl ester	b	12 d	31
2,4-D, methyl ester	b	62 d	8
DDE	b	22 h (calc)	36
Malathion	b	15 h	31
Methoxychlor	b	29 d	31
Methyl parathion	b	30 d	25
Mirex	b	1 y	25
N-Nitrosoatrazine	b	0.22 h (calc)	36
Parathion	b	10 d (calc)	36
	b	9.2 d	8
Sevin	b	11 d	8
Trifluralin	b	0.94 h (calc)	36
Polycyclic Aromatic Hydrocarbons (PAH)			
Anthracene	366	0.75 h	39
Benz[a]anthracene	b	3.3 h	25
Benzo[a]pyrene	b	1 h	25
Chrysene	313	4.4 h	39
9,10-Dimethylanthracene	366	0.35 h	39
Fluoranthene	313	21 h	39
Naphthalene	313	70 h	39
Phenanthrene	313	8.4 h	39
Pyrene	313,366	0.68 h	39
Miscellaneous			
Benzo[f]quinoline	b	1 h	25
9H-Carbazole	b	3 h	25
p-Cresol	b	35 d	25
9H-Dibenzocarbazole	b	0.3 h	25
Dibenzothiophene	b	4-8 h	25
Quinoline	b	5-21 d	25

a. Wavelength(s) at which photolysis rate was measured
b. Sunlight

Research Laboratory. These studies provide a fairly consistent data base and include all of the types of compounds for which quantitative experimental data are available.

Examination of the data presented in Tables 8-11 and 8-12 confirms the difficulty of predicting photochemical reactivities from molecular structure. Even within a restricted series of similar compounds, such as the polycyclic aromatic hydrocarbons, there is no apparent correlation between $t_{1/2}$ and ϕ. Furthermore, neither $t_{1/2}$ nor ϕ shows a monotonic trend across the series of compounds.

Again, this complex pattern of photochemical reactivities is not unexpected: the data inevitably reflect the influence of a number of interacting properties of the compound and the aqueous system under consideration. Given the present state of the art, the photochemical reactivity of an organic chemical can be "predicted from its chemical structure" only to the extent that direct photolysis can be ruled out for those compounds with no or extremely low absorbance of light at wavelengths of less than 290 nm. For compounds that do absorb at the wavelengths of terrestrial surface solar radiation, the photochemical reactivity can be estimated from the measured UV/visible spectral data and the measured quantum yield, using the approach of Zepp and coworkers as described above. At present, however, there are no known procedures for estimating the compound-specific inputs required by the Zepp model.

Real-World Complications. In the preceding sections of this chapter, it has been assumed implicitly that the photoreactivity of organic molecules is independent of the nature of the aquatic medium. This assumption is not inappropriate in qualitative considerations of potential photochemical reactivity, but any attempts at quantitative prediction of photolysis rates will require more detailed consideration of the medium. There is evidence to suggest that both the rate and the products of photochemical degradation may be influenced by such factors in the environment as suspended sediment [15,16,18], surfactants [8], and sensitizers [40]. Quenchers, such as molecular oxygen, may also influence the rate of photolysis, although one study [39] reported no apparent effect of oxygen on the rate of aqueous photolysis of polycyclic aromatic hydrocarbons. Detailed discussion of ecosystem-specific effects is beyond the scope of this handbook. However, the user should be aware that such effects may complicate attempts to extrapolate data for photolysis rates from one aquatic medium (e.g., distilled water) to a very different medium (e.g., seawater, a eutrophic lake, or a turbid river).

8-5 SYMBOLS USED

A	=	absorbance
c	=	concentration (mol/L)
D	=	depth of water body in Eq. 8-19 (cm)
h	=	Planck constant = 6.6256×10^{-27} erg-s
ΔH_{298K}	=	bond dissociation energy in Table 8-2 (cal/mol)
I	=	intensity of light
$I_{d\lambda}$	=	intensity of direct solar radiation in Eq. 8-19
I_o	=	intensity of incident light
I_λ	=	intensity of monochromatic light of wavelength λ
$I_{s\lambda}$	=	intensity of sky radiation in Eq. 8-19
j	=	conversion constant in Eq. 8-8
$k_{a\lambda}$	=	rate constant for absorption of light of wavelength λ (s^{-1})
$k_{p\lambda}$	=	rate constant for degradation of organic species P by light of wavelength λ (s^{-1})
ℓ_d	=	pathlength of direct light in water
ℓ_s	=	pathlength of skylight in water
P	=	ground-state organic (pollutant) molecule
P*	=	electronically-excited-state organic (pollutant) molecule
[P]	=	pollutant concentration (mol/L)
S*	=	electronically-excited-state sensitizer molecule
$t_{1/2}$	=	half-life for reaction in Table 8-12 and Eq. 8-22
W_λ	=	measure of solar irradiation intensity in Eq. 8-20
Z_λ	=	measure of solar irradiation intensity in Eq. 8-21

Greek

α_λ	=	attenuation coefficient for light in aqueous medium in Eq. 8-19 (cm^{-1})
ϵ	=	molar absorptivity (formerly called extinction coefficient) in Eq. 8-2 (L/mol-cm) (wavelength-dependent)
ϵ_{max}	=	molar absorptivity at a wavelength of maximum absorption
θ	=	angle of refraction in Eq. 8-21
$h\upsilon$	=	quantum of light of frequency υ
λ	=	wavelength of light (nm)
λ_{max}	=	wavelength corresponding to a maximum in the absorption spectrum (nm)
$n \rightarrow \pi^*$	=	electronic transition from non-bonding to π-antibonding orbital
υ	=	frequency of light (s^{-1})

$\pi \rightarrow \pi^*$	=	electronic transition from π-bonding to π-antibonding orbital
ϕ	=	quantum yield in Eq. 8-6
ϕ_λ	=	quantum yield for irradiation with light of wavelength λ
ϕ_f	=	quantum yield for fluorescence in Table 8-6
ϕ_p	=	quantum yield for phosphorescence in Table 8-6
ϕ_{solar}	=	quantum yield for disappearance of P by photolysis under solar irradiation in Eq. 8-14
τ	=	natural radiative lifetime of an excited state in Eq. 8-7 (s)
τ_f	=	radiative lifetime for fluorescence in Table 8-6
τ_p	=	radiative lifetime for phosphorescence in Table 8-6
ω	=	wavenumber of light (cm^{-1})

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9

RATE OF BIODEGRADATION

Kate M. Scow

9-1 INTRODUCTION

Biodegradation is one of the most important environmental processes that cause the breakdown of organic compounds. It is a significant loss mechanism in soil and aquatic systems and plays an essential role in wastewater treatment. The eventual *mineralization* of organic compounds — i.e., their conversion to inorganic substances — can be attributed almost entirely to biodegradation [6].

This chapter does not provide a procedure for estimating the rate of biodegradation of organic compounds, because investigations of this complex process are still in the early stages. Most research is descriptive, focusing on identification of the organisms responsible for degradation of specific substances, the metabolic products of such degradation, and classification of metabolic pathways. Quantitative data are scarce and have generally not been compiled in secondary sources to facilitate correlation with other chemical properties. Because experimental methods for measuring biodegradation rates are not standardized, the results are not comparable and apply only to a particular set of experimental conditions. The variables that control rates are not well understood, as they have not been examined across different classes of chemicals. New areas must be explored and existing data must be extensively organized before it will be possible to predict rates of biodegradation.

As an aid in judging the potential for biodegradation of a particular organic compound, this chapter presents background information about the process of biodegradation, standard test procedures, chemical rules of thumb for biodegradability, and attempts by various investigators to estimate rates. Sources of additional information are noted, and suggestions are given for methods of generating necessary data. Despite all this, only qualitative judgments are possible.

9-2 PRINCIPLES OF BIODEGRADATION

Definition: Several definitions of biodegradation have been proposed [53];

- *Primary biodegradation* — any biologically induced structural transformation in the parent compound that changes its molecular integrity;
- *Ultimate biodegradation* — biologically mediated conversion of an organic compound to inorganic compounds and products associated with normal metabolic processes;
- *Acceptable biodegradation* — biological degradation to the extent that toxicity or other undesirable characteristics of a compound are removed.

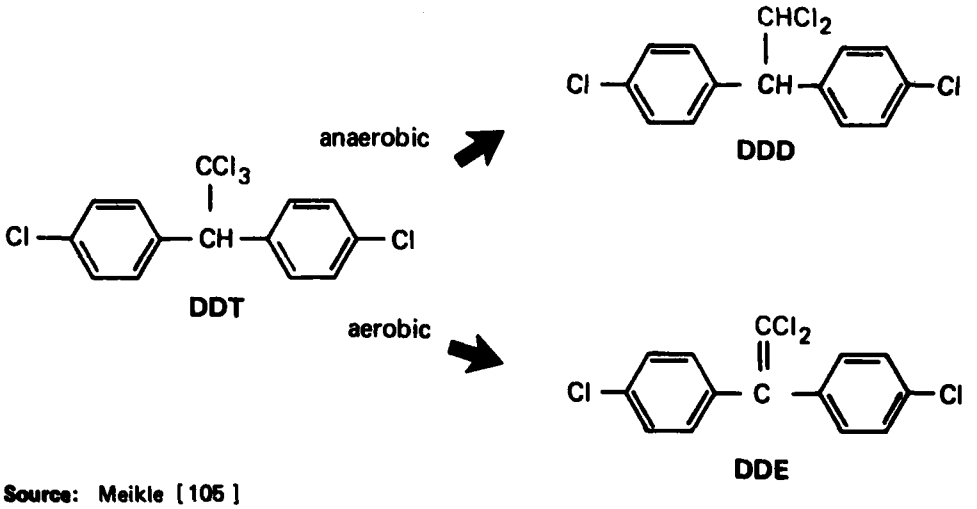
Other definitions are related to specific test methods or analytical techniques and are therefore not as widely applicable [72].

The rate of reaction varies with the type of biodegradation. For example, a complex compound will undergo a long chain of separate and different reactions to reach ultimate biodegradation, while a simple compound may require only one or two reactions to break it down completely.

Biodegradation is most commonly defined in this chapter as the *primary biodegradation* of organic compounds. Therefore, any structural change in the parent compound falls into this definition if the compound no longer responds to the analytical techniques developed for its identification [155]. Although it is important to identify and follow the breakdown of the products of primary biodegradation, which are sometimes more toxic or biologically accessible than the original compound, many biodegradation studies are concerned only with the first step in degradation. Rules of thumb and correlation of biodegradation rates with other chemical properties are usually derived from primary biodegradation results.

Only microbial degradation is covered in this chapter; higher organisms also metabolize compounds, but they play a less significant role in biodegradation in environmental systems.

Almost all of the reactions involved in biodegradation can be classified as oxidative, reductive, hydrolytic, or conjugative [66]. Examples of the first three kinds of reactions are shown in Table 9-1. At least 26 oxidative, 7 reductive, and 14 hydrolytic transformations of pesticides had been identified as of 1975 [50]. Conjugative reactions such as methylation and acetylation have also been observed in the presence of microorganisms [53]. Reactions take place both in the presence and in the absence of oxygen. Some compounds, such as DDT, are transformed under both aerobic and anaerobic conditions (see Figure 9-1).



Source: Meikle [105]

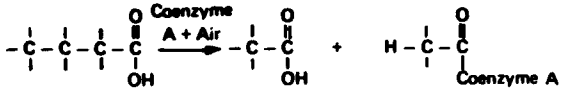
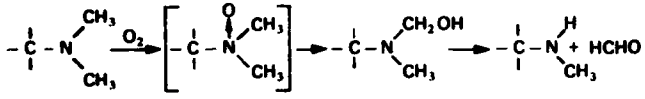
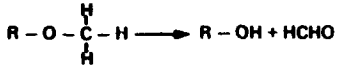
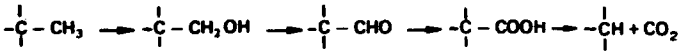
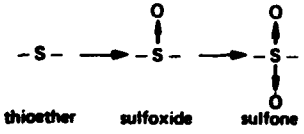
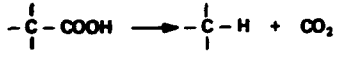
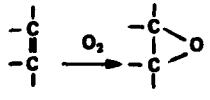
FIGURE 9–1 Anaerobic and Aerobic Biodegradation of DDT

Characterization of the Biological System

• *Organisms Responsible for Biodegradation.* Microorganisms are the most significant group of organisms involved in biodegradation. Although higher organisms, both plant and animal, are capable of metabolizing numerous compounds, microorganisms convert to inorganic substances (H_2O, CO_2, mineral salts) many complex organic molecules that higher organisms are unable to metabolize [3,72]. Furthermore, microorganisms may be the first agents in biodegradation, converting compounds into the simpler forms required by higher organisms [32].

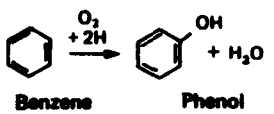
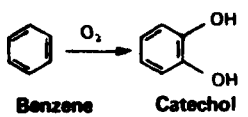
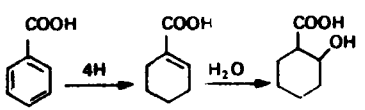
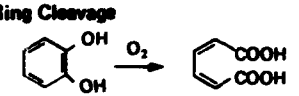
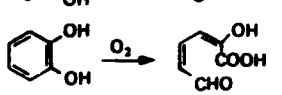
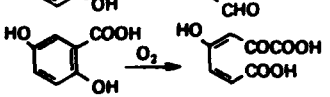
TABLE 9-1

EXAMPLES OF BIODEGRADATION REACTIONS

Type of Reaction		Examples of Chemicals Subject to Reaction
β-Oxidation		Aliphatic fatty acids, some ω-phenoxyalkanoate herbicides
Oxidative Dealkylation		
N-dealkylation:		Alkylcarbamates, phenyl ureas, s-triazines
O-dealkylation:		Vanillic acid, many organophosphorus insecticides and phenoxyalkanoate herbicides
C-dealkylation:		Xylene, toluene, diazinon, methoxychlor
Thioether Oxidation		Carbophenothion, prometryne, aldicarb
Decarboxylation		Nicotinic acid, o-pyrocatechuic acid
Epoxidation		Aldrin, heptachlor

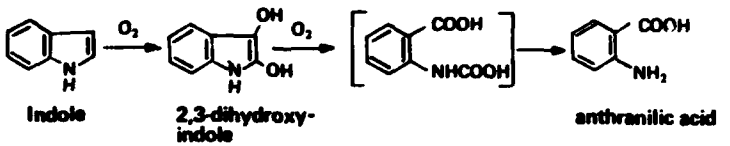
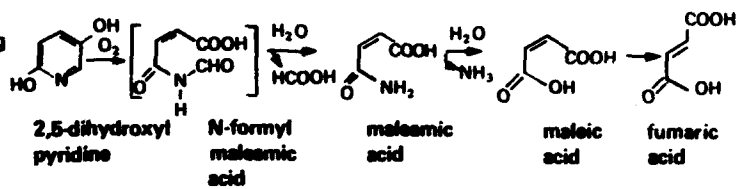
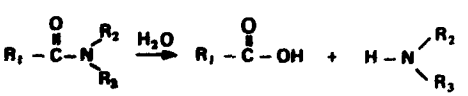
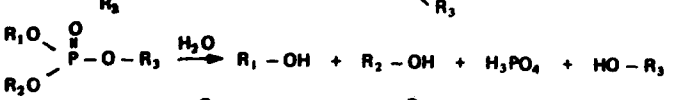
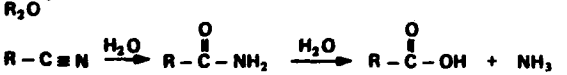
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TABLE 9-1 (Continued)

Type of Reaction	Examples of Chemicals Subject to Reaction
Aromatic Hydroxylation	
1) Aerobic:  Benzene Phenol	Pyridine, nicotinic acid, 2,4-D, some phenylalkanes, benzoic acid
 Benzene Catechol	
2) Anaerobic:  Benzoic acid; Cyclohex-1-ene-1-carboxylate; 1-Hydroxycyclohexane-carboxylate	Benzoate
Aromatic, Non-heterocyclic Ring Cleavage	
Ortho fission 	Many catechols and phenols, gentisic acid, hydroxycyclohexanecarboxylate, many phenoxyalkanoate herbicides, carbaryl
Meta fission 	
"Gentisate" fission 	Only first step in degradation pathway is shown.

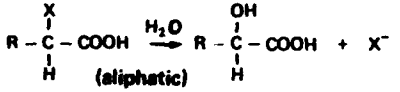
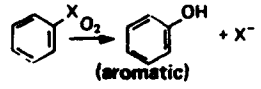
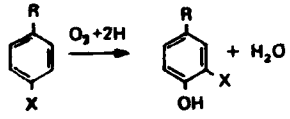
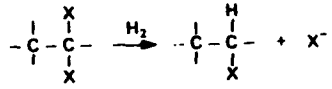
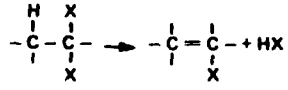
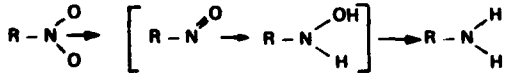
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TABLE 9-1 (Continued)

Type of Reaction	Examples of Chemicals Subject to Reaction
Aromatic, Heterocyclic Ring Cleavage	
1) 5-membered ring 	Many heterocyclic pesticides (e.g. paraquat, picloram, amitrole)
2) 6-membered ring 	Pyridines, pyrimidines, triazines
Hydrolysis	
Ester hydrolysis 	Carbamates, organophosphates, many urea and anilide herbicides
Amide hydrolysis 	
Phosphorus ester hydrolysis 	
Nitrile hydrolysis 	

(Continued)

TABLE 9-1 (Continued)

Type of Reaction		Examples of Chemicals Subject to Reaction
Halogen Reactions		
Hydrolytic dehalogenation	 	TCA, dalapon, halogenated phenoxyacetates, chlorobenzoates
Halogen migration		Alkylbenzenes, tryptophan, halobenzenes, anisoles, 2, 4-D
Reductive dehalogenation		p,p'-DDT, BHC
Dehydrohalogenation		p,p'-DDT, γ-BHC (lindane)
Nitro-reduction		Parathion and other aromatic nitro compounds

Source: Adapted from Hill [68].

Arthur D Little Inc

Bacterial metabolism alone can account for 65% of the total metabolism of a soil community because of high bacterial biomass and metabolic rates [98]. Bacteria and fungi utilize energy more efficiently than do higher organisms [100]. The high rates of reproduction and mutation in microorganisms contribute to the considerable diversity of species and adapted strains and, hence, enzyme systems; numerous biochemical pathways for degradation are present in microorganisms as a group [72].

Other lower organisms, such as algae and certain invertebrates, exhibit some of the preceding characteristics. Although they have not been as thoroughly investigated as other microorganisms and higher organisms, their potential as significant degraders of pollutants cannot be discounted. There is some evidence that algal species contribute significantly to biodegradation of substances in the surface layer of water [175].

The microorganisms predominantly responsible for biodegradation in natural systems are heterotrophic bacteria, including the actinomycetes, some autotrophic bacteria, fungi including the basidiomycetes and yeasts, and certain protozoa [2]. A number of detailed reviews describe the biology and ecology of these groups [2,5,53,135,151]. Different conditions favor each group; for example, fungi and *Thiobacillus* are common in acid soils, while most bacteria thrive and apparently have a competitive edge in less acid soils and in alkaline soils (pH >5.5) [2,151]. Fungi are not as important in aquatic systems as in soil [134]. Not only different classes but different genera within classes react to an organic compound with responses ranging from sensitivity to degradation, so it is not possible to categorize the biodegradative ability of microorganisms according to their taxonomic classification.

Anaerobic microorganisms are either obligate anaerobes to which oxygen is toxic (*oxylabile*) or facultative anaerobes that can live with or without oxygen or prefer a reduced oxygen atmosphere (*oxyduric*) [166]. Some species specialize in reducing nitrates or sulfates, and others in reducing various alcohols to methane and other alkanes. As a group, anaerobic organisms are more sensitive and susceptible to inhibition (in sewage treatment, for example) than are aerobic organisms [160].

- *Habitats of Microorganisms.* Soil, water and wastewater treatment systems provide the most important microbial habitats for the

biodegradation of pollutants. In all environments, microorganisms are essentially aquatic organisms [151], and certain characteristics are shared by all species. The organisms' habitat has a greater influence on biodegradation than does the similarity of the species [79].

In all three habitats both aerobic and anaerobic conditions exist. Although only one fifth as much free energy is obtained from one electron-mole of a methane-forming reaction as from a complete oxidation reaction, reductive reactions may play a significant role in the environment. The anaerobic habitats of interest in this chapter include some soils, sediments, and certain sewage treatment systems and sludges.

The diversity of microbial populations in soil is attributable to the large variety of food sources and habitats found there [55]. The mobility of microorganisms is decreased in soil, however, because of physical barriers (such as clay aggregates) and patchy distribution of supportive microhabitats. Usually aquatic systems have less diverse microbial populations and support a greater homogeneity in distribution [154], partly because the concentration of nutrients is diluted in the water column. Bottom sediments tend to have high nutrient levels from deposition of decaying organic matter. Growth substrates are potentially more accessible in aquatic than in soil systems, except where removal by adsorption and concentration in bottom sediment occurs [37].

As they are interconnected, soil, freshwater systems and wastewater treatment systems are inhabited by the same major species groups. Populations in the media are related, because the population characteristics of the surrounding soil help define the species make-up of an aquatic system and sewage populations through seeding by soil erosion and runoff [124,173]. Runoff from storm water and sewage overflows also contributes to the mix of species found in natural waters [174].

Air serves primarily as a transport medium for microorganisms rather than as a support system [53]. Organisms are found at low densities in the atmosphere, usually in such non-metabolizing forms as spores. Water availability is low, and extreme fluctuations in temperature and solar radiation discourage growth and activity of populations.

Aquatic systems that support microorganisms vary considerably, encompassing habitats as diverse as streams, small ponds, lakes, estuaries, and open ocean. Although aquatic microbial populations differ by system, they have some common characteristics. An aquatic system

can be roughly divided into a sediment fraction, which is suspended or settled in a bottom layer, and a liquid fraction.

Vertical zonation of the liquid fraction (including its suspended sediment) is found in most standing freshwater bodies deeper than two meters with well-distinguished layers differing in temperature, oxygen content, and nutrient distribution. Figure 9-2 shows the microhabitat distribution in a freshwater aquatic system. The stratification of the layers fluctuates seasonally, as the upper layers mix with deeper waters and the sediment layer. The sediment layer is stratified into an upper oxidized zone and a lower reduced zone, each having distinctive bacterial flora (aerobic and anaerobic, respectively).

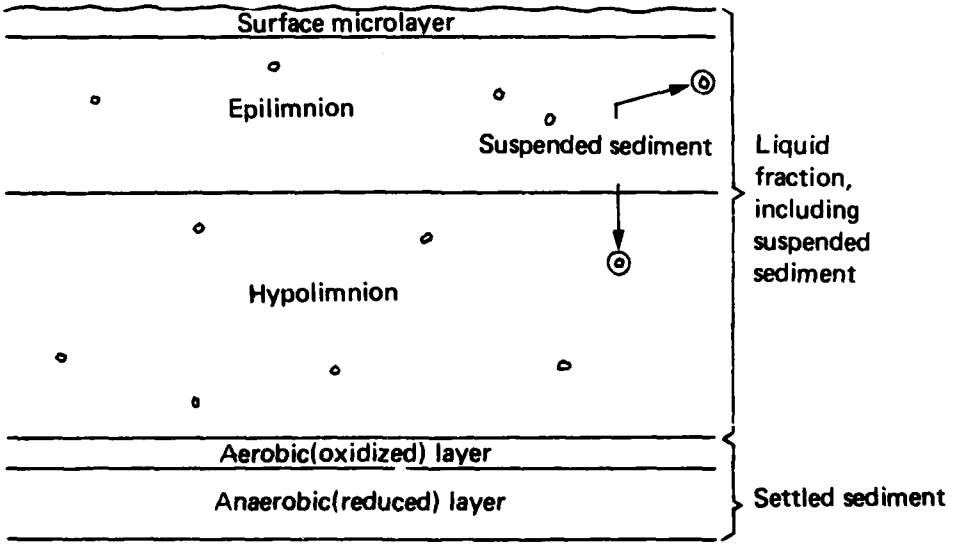
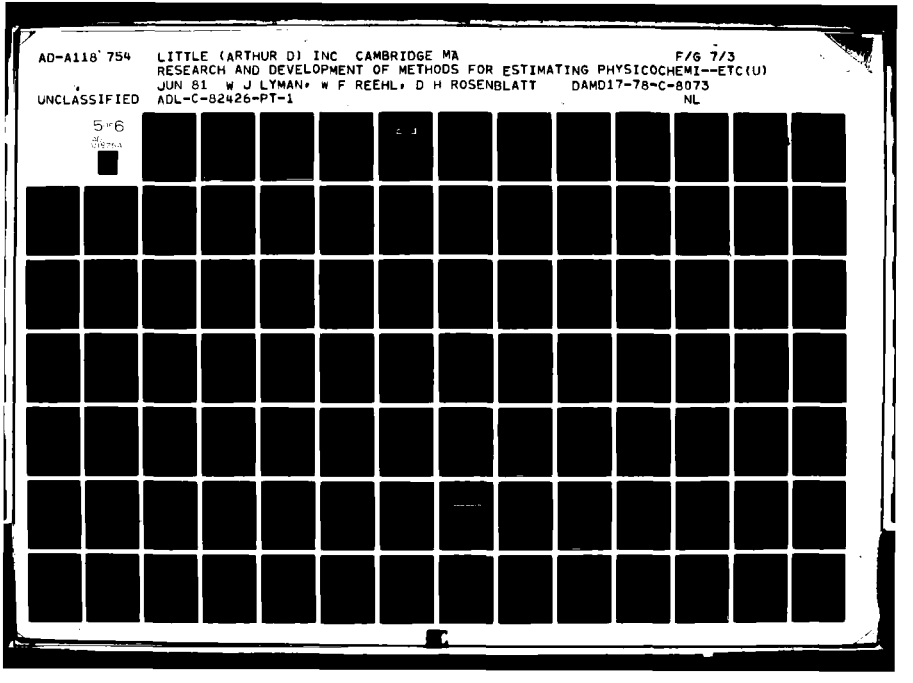


FIGURE 9–2 Microbial Microhabitats in a Generalized Freshwater System

In marine habitats, increased productivity and biological activity are associated with coastal regions because of upwelling from nutrient-rich deeper waters and the contribution from estuaries [53]. Shore habitats, such as intertidal zones with highly organic muds, support large microbial populations. The continental shelf area (neritic zone) and the open ocean (oceanic or pelagic zone) can be divided into three layers: euphotic, aphotic, and benthic (Figure 9-3). The euphotic layer extends to approximately the point where the light intensity is 1% of that at the surface; the aphotic layer is the deeper water that extends to the benthos, which is the bottom or sediment layer. As in freshwater systems, the sediment contains aerobic and anaerobic zones, which shift according to the availability of oxygen.


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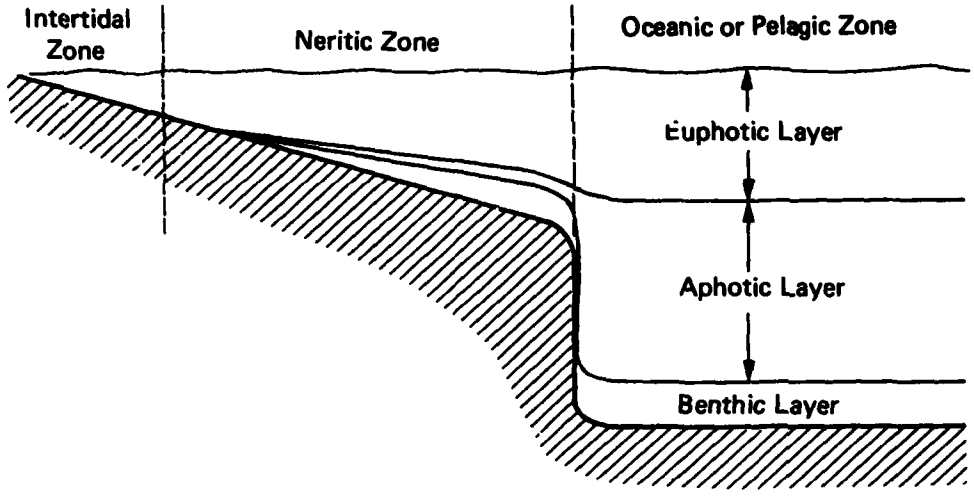


FIGURE 9–3 Microbial Habitats in a Generalized Marine System

Estuaries are among the most productive aquatic systems and are extremely variable because of differences in surrounding topography (which contribute to the degree of silting), ratio of salt to freshwater, tidal activity, and other factors [116]. The sediment layer, stratified into aerobic and anaerobic zones, is well developed biologically with abundant microbial populations [53].

Benthic sediments of both marine and freshwater systems below the surface layer-water interface are usually anaerobic and support microorganisms [42]. Many lakes and some marine areas also have anaerobic bottom waters [41]. Little is known about these environments and their associated species, especially in marine systems [74]. No more than 1% of bacteria observed in these systems will grow under laboratory conditions [166]. Many sediment microorganisms may remain in a dormant stage or at a low rate of activity for long periods because of low temperatures.

Microbial populations are distributed at different densities throughout these various microhabitats. Table 9-2 describes their distribution in the horizontal layers of aquatic systems.

Soil is not as uniform or continuous an environment as most aquatic systems. It consists of discrete compartments, only some of which are suitable as microbial habitats. The majority of the microbial population is located in the top layer of soil (approximately upper 14 cm [19]; see Table 9-3), because nutrient levels and oxygen availability are high

TABLE 9-2

Presence of Microbial Populations in Various Aquatic Systems

	Upper Layer of Water	Lower Layer of Water	Sediment Layer
Fresh Water			
Lotic (running water)	Microbial population very dependent on stream flow, usually higher in slower streams and rivers.	–	Presence of sediment layer and microbial population dependent on stream flow, surrounding substrate characteristics, and sediment load. Generally higher in slower flowing than in rapid streams.
Lentic (standing water)	*Epilimnion:* Microbial populations primarily associated with this layer, although sediment populations higher under some conditions. Organisms associated with surface area of detritus [41]	*Hypolimnion:* Anaerobic microorganisms may be high in nutrient-rich eutrophic lakes.	Microbial populations vary greatly, depending on depth, bottom substrate, and other factors. In most lakes, populations high near surface of sediment, although sediment investigations are few [53]
Estuary	Biological activity highest in lower bay (from river mouth upstream), in upper basins, and especially in tidal salt marshes and mud flats. Salinity shifts in the headwaters (area of mixing of fresh and salt waters) may be too extreme to support much life.		Microbial populations high, especially in highly organic muds.
Marine Waters			
Intertidal (Littoral)	–	–	Microbial populations dependent on substrate: high on organic substrates, low on cobble and shingle beaches.
Neritic	*Euphotic layer:* biological activity high. Organisms associated with surface area of detritus [41]	Most neritic waters fall within the euphotic zone.	Benthic layer: microbial activity high.
Oceanic	*Euphotic layer:* area of greatest microbial activity [70,71,76]	*Aphotic layer:* microbial activity generally lower than in euphotic layer, although specific depths may have higher populations.	Benthic layer: microbial activity low because of cold temperatures and low nutrient levels.

Sources: [53, 116, 134]

TABLE 9-3

Distribution of Microorganisms in Various Soil Horizons

Depth (cm)	No. Organisms/g soil (x 10^5)	Percentage of Total Organisms Counted
3-8	119.7	79
20-25	24.8	16
35-40	6.3	4
65-75	0.22	<1
135-145	0.04	<1

Source: *Adapted from Alexander [5]; podzol soil.*

there [36]. The plant rhizosphere (the area including and surrounding a plant's roots) supports high densities of microorganisms, because root exudates, dead root material, and adhering organic matter provide nutrients for growth (Figure 9-4). Increased microbial activity extends for 1 or 2 millimeters beyond the root surface and is not associated with all locations on the roots [53]. Other nutrient sources, primarily in the form of decomposing organic matter, are scattered throughout the soil in different stages of availability. Some are adsorbed to the mineral fraction or are blocked from access in a clay structure [151]. Although they may represent as little as 15% of the colonizable surface area in soil, organic particles can be populated by 60% (by mass) of the soil bacteria, while mineral particles are only minimally colonized [52]. Microorganisms comprise a large fraction of the living biomass in soil — up to 80% when soil algae are included [116] — although not all organisms are metabolically active at the same time. As would be expected, microbial density is strongly influenced by organic matter content, which can vary from a minimum of 1% in mineral soils to more than 90% in rich, organic soil [151]; the usual range is from 3% to 6% [5]. The density of microorganisms is much lower in the soil water fraction than at soil-water interfaces [2].

In soils submerged in water, oxygen levels and diffusion rates are too low to support aerobic microorganisms. Furthermore, localized anaerobic pockets may be distributed throughout a generally aerobic soil [95,166]. During periods of high microbial activity, such as the early stage of plant residue decomposition, temporary anaerobic conditions may be created when the oxygen demand exceeds the supply [125,166].

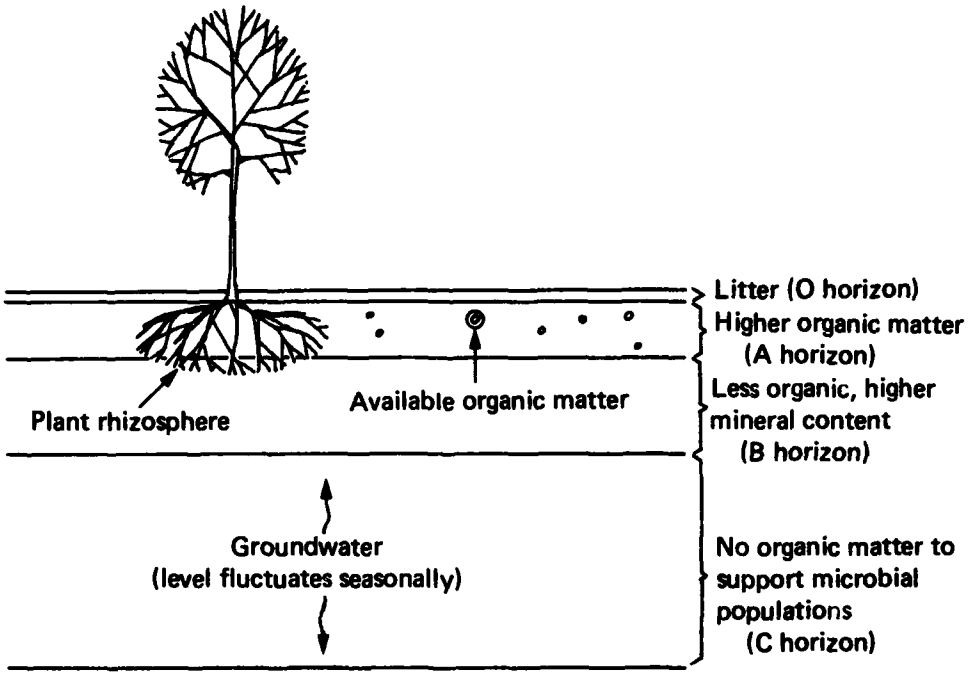
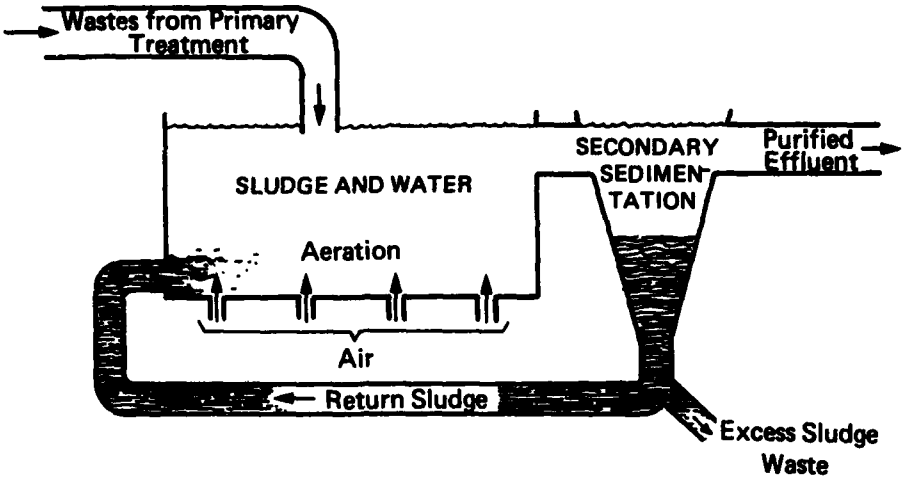


FIGURE 9–4 Microbial Microhabitats in a Generalized Soil System

Wastewater treatment provides a third major system. In the municipal and industrial treatment of organic wastes, two approaches are commonly used, often in combination: aerobic mineralization and anaerobic digestion. The latter takes the form of fermentation to methane and CO_2. Activated sludge treatment and filtration through trickling and/or sand filters are aerobic processes.

Activated sludge is a well-mixed, stirred (for aeration), single-stage process in which organic waste is mixed in a reactor with mixed-species microbial populations that are either growing in flocs or freely suspended in the supernatant liquid. Figure 9-5 depicts the process. Less than 10% of the floc is made up of active organisms; the rest is mostly insoluble organic matter made up of polymeric material [90]. Floc sizes, ranging from 0.02 to 0.2 mm [113], may be rate-limiting because the transport of nutrients to microorganisms in the center of the floc slows the reaction [40]. The activated sludge process has many variations, which differ in degree of aeration, mixing, container size, and procedure.

Slow sand filters (SSF) and trickling filters (TF) are, respectively, two- and three-phase processes in which dissolved organic wastes are passed through a biologically active film colonized by microorganisms. The SSF is slower than the TF and provides no aeration [90].



Source: Manahan [100]

FIGURE 9–5 A Conventional Activated Sludge System for Secondary Biological Waste Treatment

Most municipal sewage treatment plants use anaerobic digestion for sludge stabilization [133]. After the settleable matter and supernatant liquid are separated, the process has two stages, starting with an "acid phase" followed by a "methane phase" (Figure 9-6). In the first phase, complex organic solids in the settled material are degraded to acid form, transforming cellulose, starches, proteins, and carbohydrates to simple sugars, amino acids, and volatile acids (formic, acetic, butyric, etc.). During the second phase the acids produced, along with any original long-chain fatty acids, are reduced to methane and carbon dioxide [133].

- *Significant Species.* The microbial species found in natural ecosystems are diverse, but certain groups appear to play prominent roles in biodegradation and are encountered again and again in microbial cultures from natural sources. These genera are able to metabolize a variety of organic substrates. Specificity to certain compounds is more commonly found at the species level, although some species such as *E. coli* are generalists. Table 9-4 lists some genera commonly found in soil, aquatic, sludge, and anaerobic habitats. These are typical only; the table is not intended as a compilation of each system's most prominent genera.

The microorganisms involved in anaerobic digestion are primarily bacteria, both facultative (able to live under aerobic and anaerobic conditions) and obligate (able to live only under anaerobic conditions)

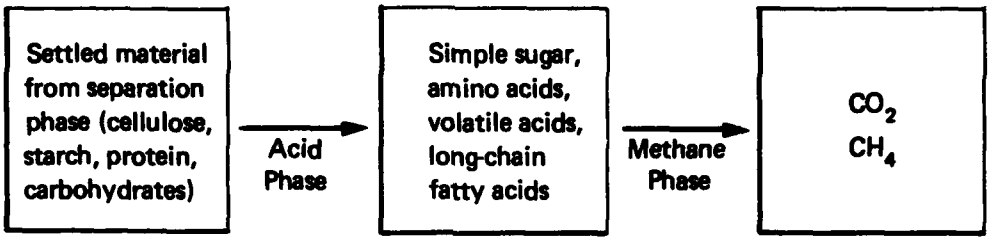


FIGURE 9–6 Anaerobic Wastewater Treatment Process

TABLE 9-4

Representative Microbial and Protozoan Genera Found in Different Environments

Environment	Genera	Source
Freshwater Aquatic and Soil Systems	*Arthrobacter, Aspergillus, Bacillus, Corynebacterium, Flavobacterium, Fusarium, Nocardia, Penicillium, Pseudomonas, Thiobacillus, Torulopris, Trichoderma, Micromonospora, Streptomyces*	[37,50,51, 53,134]
Marine Aquatic System	*Achromobacter, Flavobacterium, Pseudomonas, Vibrio*	[53]
Sludge and Anaerobic Systems	Acid formers: *Pseudomonas, Flavobacterium, Alcaligenes, Escherichia, Aerobacter, Aeromonas Clostridium, Leptospira, Micrococcus, Sarcina*	[133,161]
	Methane formers: *Methanobacterium, Methanobacillus, Methanococcus, Methanosarcina*	[100,133]
	Activated Sludge: *Achromobacter, Alcaligenes, Arthrobacter, Bacillus, Bacterium, Bdellovibrio, Comomonas, Flavobacterium, Microbacterium, Nitrosomonas; Pseudomonas, Sphaerotilus*	[127,161]
	Others: *Aspergillus, Fusarium, Rhizopus, Penicillium, Cladosporium*	[84,88,133,142, 144,161,167]

anaerobes. The acid-forming bacteria have higher rates of reproduction and tolerate a pH as low as 5.0. Methane-forming bacteria are inhibited at a pH below 6.5 and are generally more sensitive to temperature and substrate concentration [133].

- *Biodegradation Reactions.* For any one microorganism, organic compounds can be divided into three groups according to their biodegradability: (1) usable immediately as an energy or nutrient source, (2) usable following acclimation by microorganisms, and (3) degraded slowly or not at all [155,17]. Some investigators believe that a fourth group also exists, consisting of compounds subject to cometabolic degradation. Figure 9-7 depicts a generalized disappearance curve for each of the first three groups. A chemical may be classified in more than one category, depending on the response of the microorganisms to which it is exposed; different species may react differently to the same compound.

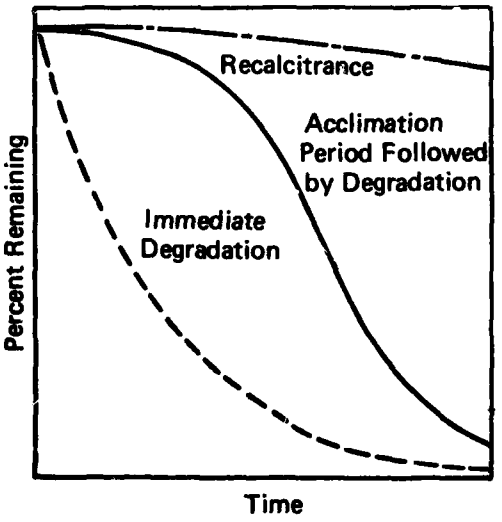


FIGURE 9–7 Degradation of Organic Compounds

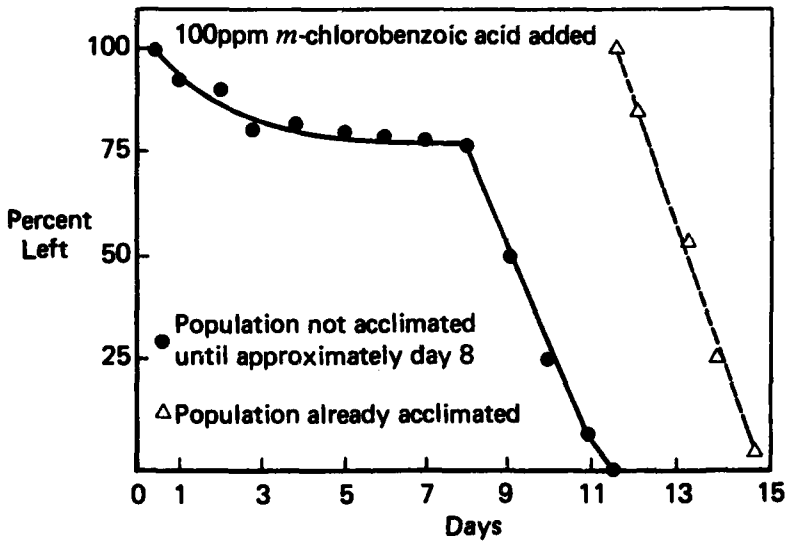
The first group includes certain simple sugars, amino and fatty acids, and compounds in the proper form to enter typical metabolic pathways. The enzymes necessary for taking up or degrading these compounds are constitutive or immediately inducible and thus minimal acclimation is required [26].

The second group requires acclimation, a lag period during which little or no degradation takes place. The delay is usually caused by the following processes which are somewhat interrelated:

(a) Selection of those species in a mixed population that are capable of assimilating the substance, in which case the lag is due to the initial phase of exponential population growth of the favored organism, and

(b) Adaptation of existing microorganisms through induction of enzymes that catalyze degradation.

Lag periods vary from a few hours to days or even weeks, depending on the chemical, the organism, and the medium (see Figure 9-8). A period of more than 50 days has been observed for pyrazon in garden soil [38]. Thus, laboratory experiments conducted over a prescribed period of time, rather than until degradation commences, may not establish whether a substance is biodegradable if the chemical requires a long acclimation period.



Source: Adapted from DiGeronimo *et al.* [33]

FIGURE 9–8 Lag Period in Biodegradation of *m*-Chlorobenzoic Acid

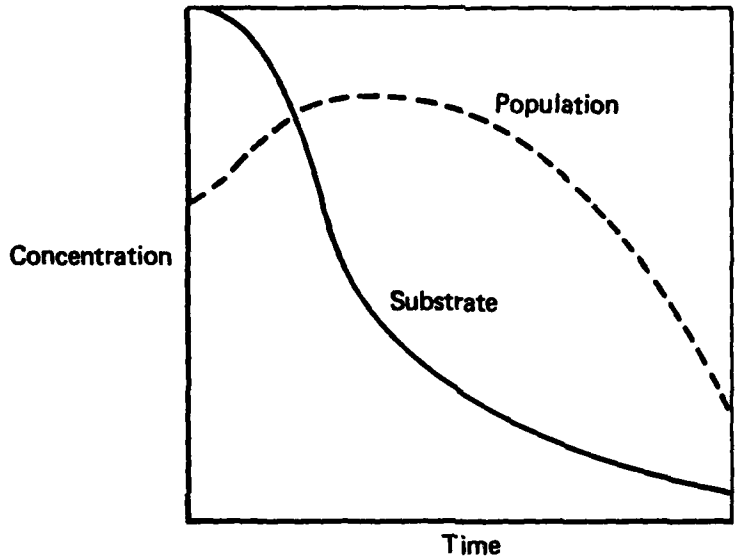
Once acclimation is achieved, the degradation reaction begins. Intensive activity occurs first with primary alteration of the introduced substance; this is usually followed by slower activity as the intermediate products are digested [155]. The microbial population increases at first, levels off, and declines once the substrate has disappeared or has been converted either to non-metabolizable catabolites or to inorganic compounds. The disappearance curve for the parent compound can follow one of several forms, depending upon the kinetics of the reaction. Biodegradation reaction kinetics are discussed in §9-4.

The third group of organic compounds includes such naturally occurring substances as humus and lignin, as well as such anthropogenic substances as some of the organochlorine pesticides [1]. These substances degrade at very slow rates or not at all. Furthermore, they may not be degradable due to factors other than chemical structure — e.g., physical inaccessibility or environmental influences (low O_2, pH, etc.). Alexander [1,3,4] has written extensively on the subject of recalcitrance. Some of the factors responsible for the failure of biodegradation are discussed later in this chapter.

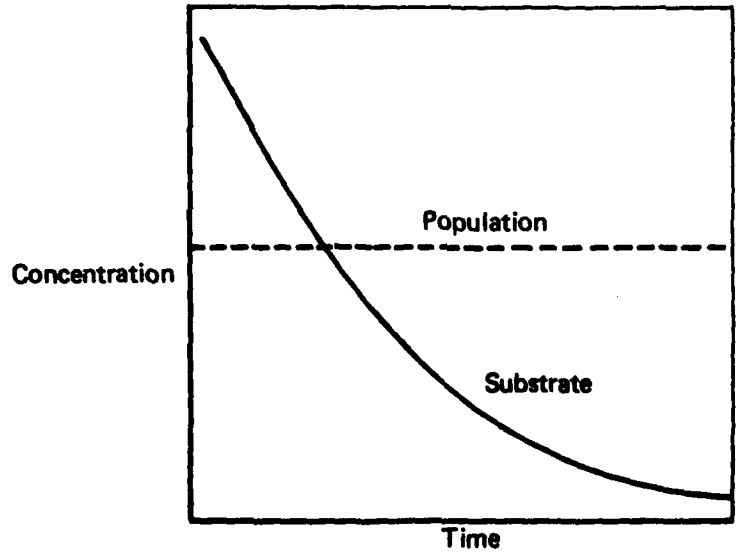
Cometabolism is thought to play a role in the degradation of certain chemicals, although little research has been done on the process. It is defined as the degradation of a compound that does not provide a nutrient or energy source for the degrading organisms but is broken down during the degradation of other substances [7]. Figure 9-9 compares metabolic and cometabolic rate curves. Because cometabolism does not provide a growth substrate, the population increase characteristic of metabolic degradation reactions does not take place [7] and the rate of degradation is often slower. Compounds with chlorine, nitro, or other substituents are sometimes susceptible to cometabolism [7].

- *Microbial Population Densities and Biomasses.* Counting the number of individuals in a population overestimates the significance of microorganisms in a community; measurement of biomass, on the other hand, underestimates their significance [116]. For example, in the benthic community of a small lake, bacteria accounted for 30% of the community respiration but less than 1% of the total biomass [116]. Nevertheless, an actual count is necessary when one is investigating the biodegradation of specific compounds by microorganisms with variable metabolic activity.

Measurement of microbial populations is subject to considerable error because of the characteristics of the organisms and deficiencies in measurement techniques. The problem is greater in soil and activated sludge than in more homogeneous media such as water [151,155]. A population of microorganisms is unlikely to be uniformly active; this is due to species specialization on substrates that are not all equally or consistently available. Furthermore, because of their adaptability and short regeneration time, microbial populations are quite variable and dependent on the conditions at the moment of sampling [116]. It is virtually impossible to distinguish between active and dormant or dead organisms without using respirometry or similar measures of activity such as acridine orange staining and epifluoresence microscopy.



a. Metabolic Biodegradation



b. Cometabolic Biodegradation

FIGURE 9–9 Population and Substrate Concentrations During Biodegradation

Several techniques have been developed to estimate microbial population; each has its own set of disadvantages (see Table 9-5). Numbers determined by direct microscopic count are usually higher than those determined by plate counts, because any one plate culture medium cannot satisfy the requirements of most bacterial species in natural habitats [153]. Differences of the order of 10^3 are often seen between these two most commonly used techniques [53]. A combination of two or more methods is the best approach, although it may be expensive and time-consuming in some cases.

Microbial population densities reported in the literature for aquatic, soil, anaerobic, and sludge systems are compiled in Table 9-6. In Table 9-7 microbial biomasses for soil and water are presented. In all systems, population densities varied more than several orders of magnitude, probably because of environmental factors and differences in sampling techniques.

Variables in Biodegradation. The variables that influence the rate of biodegradation fall into two general categories: (1) those that determine the availability and concentration of the compound to be degraded (e.g., propensity for adsorption) or that affect the microbial population size and activity (e.g., population interactions) and (2) those that directly control the reaction rate itself (e.g., population size, temperature). Both direct and indirect variables can be classified as substrate-related, organism-related, or environment-related. Table 9-8 lists all the variables discussed in this section. Most of the information is presently qualitative, primarily as observations of variable influences on degradation by specific species. Because of considerable variation in species, habitat, and chemical environment, not all variables will influence all situations in the same way. For example, low pH is likely to decrease metabolic activity in most bacteria, but it favors activity in fungi [21].

An important characteristic of environmental variables is their degree of interrelation. For example: (1) temperature and moisture content in soil are interdependent; (2) where there are high levels of organic matter, the pH is usually low; and (3) pH affects adsorption [55]. In this section, each variable is considered separately. Both direct and indirect variables are discussed under each of the three main categories.

- *Substrate-Related.* Certain properties of a compound that serves as a substrate for biodegradation affect microbial reactivity. Correlations between various physicochemical properties and biodegradability of organic compounds have been reported. These observations are discussed in §9-5.

TABLE 9-5

Methods for Estimating Microbial Populations and Biomass

Type	Method	Problems
Viable Counts • Pour plates • Spread plates • Membrane filter plates	Cells to be counted are cultured on a growth-supporting medium; each cell divides, forming a colony that indicates presence of a cell.	No one medium will support all species; organisms tend to clump together around detritus, making separation difficult.
Direct Microscopic Count	Visual counting of cells under a microscope	Does not differentiate between dead/inactive and living cells; dye concentration difficult to maintain; cells clump together; difficult to detect individuals at low concentrations ($<10^6$ cells/mL)
Turbidity	Measurement of light transmitted through bacterial suspension	Interference of shape of cell with passage of light; only works in dilute microbial concentrations; mass of microorganism can change while number of cells remains constant.
Measurement of Cell Constituent	Content of ATP (adenosine triphosphate) or DNA is measured to indicate total biomass.	Concentrations of many indicator consitituents are too low to measure. Method requires that: (1) concentration of constituent being measured is constant in relation to biomass; and (2) constituent is rapidly degraded when released outside of cell wall. Turnover time and concentration of ATP per cell varies by cell and species (50-fold range of ATP per unit weight for variety of organisms).
Respirometry	Oxygen uptake or CO_2 generation	Some CO_2 may be non-biological in origin. Oxygen removed may be adsorbed or consumed by chemical reaction.
	Electron transport (tetrazolium salts)	Reaction can interfere with normal electron transport process.

Source: Adapted from Refs. 2, 75, 116, and 151.

TABLE 9-6

Microbial Population Density in Various Environments

System	Population Density	Comments	Source
Aquatic	10^3-10^6/mL	Surface water	[92]
	$< 10^{-3}$-10^8/mL	Oceanic waters (from open water to inshore respectively)	[177]
	10^{13}-10^{14}/m^2	Open pond water	[116]
	10^9-10^{10}/mL	Laboratory culture	[2]
	10^6 (10^5 active)[a]/mL	Bacteria –pond	[12]
	10^5 (10^4 active)/mL	Bacteria –stream	[12]
	10^6 (10^5 active)/mL	Bacteria –eutrophic lake	[12]
	10^2 (10 active)/mL	Bacteria –oligotrophic lake	[12]
	10^5-10^{10}/mL	Natural waters	[2]
Soil	10^8/g	Bacteria only	[52]
	10^5/g	Actinomycete spores	[52]
	5m/g[b]	Fungal mycelium	[52]
	10^7/g	Upper 3-8 cm of soil	[5]
	10^{14}-10^{15}/m^2	Meadow or old field	[116]
Anaerobic	10^1-10^8/g	Marine sediment	[177]
	10^3-10^6/g	Gram-negative motile bacilli –marine sediment	[167]
	10^9/g	Feedlot waste	[137]
Activated Sludge	10^{10}-10^{12}/g dry wt	In floc	[127]
Sewage Treatment	10^7/mL	Sewage entering	[172]
	10^8/mL	Mixed liquor	[172]
	10^6-10^7/mL	Effluent	[172]
	10^6-10^7/mL	Supernatant	[92]
Anaerobic Treatment	10^8-10^{10}/mL	Nonmethanogenic obligate anaerobes	[162, 30]
	10^5-10^{10}/mL	Methanogenic bacteria	[91]
	10^4-10^9/mL	Sulfur-reducing bacteria	[129, 167]

a. "Active" = bacteria not in dormant stage

b. Length of mycelium (m) is measured

TABLE 9-7

Microbial Biomass in Various Environments

System	Biomass	Comment	Source
Aquatic	1-10g/m^2[a]	Open pond water	[116]
Soil	100-1000 kg/ha[a]	Meadow or old field	[116]
	6.0×10^4 g/g	0.06% of soil mass	[52]
	300-3000 kg/ha	0.015-0.05% of soil mass	[2]
	37 kg/ha (living)	Bacteria in woodland soil	[53]
	9113 kg/ha (dead)	Bacteria in woodland soil	[53]
	110 kg/ha (living)	Fungi in woodland soil	[53]
	566 kg/ha (dead)	Fungi in woodland soil	[53]

a. Dry weight; other measures are assumed to be wet weight.

Another influential factor is the substrate concentration. If it is too low, biodegradation may be limited, possibly from lack of sufficient stimulus to initiate enzymatic response [3]. There is some evidence that compounds that are usually easily degradable are persistent at very low concentrations [33,74]. On the other hand, high concentrations may be toxic or inhibitory to metabolism. The optimum concentration is chemical- and species-specific. Several discussions of the deleterious effects of introduced chemicals on microbial populations have been published [11,35,124]. Concentrations greater than a compound's solubility in water may result in a lower rate constant than concentrations below the solubility limit, as observed for chlorodiphenyl oxide [20]. Reaction kinetics may shift in order and rate as the substrate is depleted and its concentration decreases during the biodegradation process [92].

- *Organism-Related.* Biological influences include the species composition of the microbial population, their concentration and distribution, their past history, and intra- and interspecies interactions among population members. Another significant factor is the ability of the species to synthesize the enzyme systems required for the breakdown of organic compounds.

Species variability is exhibited in the metabolic response of a microbial population to a newly introduced organic compound. Some of the

TABLE 9-8

Variables Potentially Affecting Rate of Biodegradation

Substrate-Related
• Physico-chemical properties
• Concentration
Organism-Related
• Species composition of population
• Spatial distribution
• Population density (concentration)
• Previous history
• Interspecies interactions
• Intraspecies interactions
• Enzymatic make-up and activity
Environment-Related
• Temperature
• pH
• Moisture
• Oxygen availability
• Salinity
• Other substances

simpler molecules, such as glucose, are immediately degradable and support growth of numerous species [155]. Complex organics requiring more extensive metabolic pathways are likely to support fewer species — specifically, only those that have evolved mechanisms for induction of adaptive enzymes matched to the chemical. Therefore, glucose is rapidly metabolized in most biologically active environments, but many hydrocarbons support few microbial species (e.g., *Nocardia, Pseudomonas, Mycobacterium*) and often require acclimation periods before degradation proceeds [21].

The distribution of microorganisms in the medium in which a potential substrate is contained is an important factor in biodegradation. Either environmental parameters (see below) or the presence of toxic substances may limit microbial colonization of the site. Soil is such a heterogeneous environment that the distribution of microorganisms is patchy. Soil microhabitats immediately adjacent to one another commonly differ in numbers of microorganisms because of a wide temporal and spatial distribution of organic matter available for microbial diges-

tion, variations as high as three units in pH around growth sites, differences in moisture retention ability, and other factors [53].

Over long periods of time, microbial concentration is not as important as the other factors described because of the rapid response of, and numerical increase in, populations of a species capable of metabolizing the substrate. If short time periods are of concern, however, microbial concentration can have a significant effect. For example, the time for complete metabolic oxidation of glucose (including intermediates) may range from a few hours in a concentrated bacterial culture (100 to 1000 ppm in activated sludge, assuming 10% of mass by weight is active) to days in a dilute culture (10^9 to 10^6 cells/mL)[1] [155].

The previous history of microorganisms in relation to the particular compound undergoing degradation may be reflected in the reaction rate. If a compound is continually introduced into a system, as are some agricultural pesticides, often the microorganisms soon acclimate to the substance and begin degradation immediately, without a lag period. The difference is noticeable even in regard to simple, readily degradable substances. A glucose-adapted laboratory culture was found to degrade sugar at a rate three times higher than a culture of fresh-water isolates [154]. For more complex compounds the significance of prior acclimation on biodegradation rates is well known (e.g., see Figure 9-8).

Inter- and intraspecific interactions among species may indirectly affect the rate of biodegradation in the initial period through their effects on microbial activity in general. These effects can be positive or negative and are quite specific to each population mix. Processes common to all mixed-species groups, such as competition and predation, determine which species will succeed in growing on a substrate compound. The presence of other species, such as protozoa and rotifers, can increase the degradation rate of a population through selective predation on weak or inactive members [24]. The metabolic activity of a microbial population is not necessarily equal to the additive effects of each species; metabolism may be cooperative, with successive species degrading the initial substrate in sequential steps [153]. Extracellular enzymes of one organism may break down a compound such as polysaccharide sufficiently for uptake and metabolism by another organism [3]. Dissimilar species may have to attack different sites on a branched compound, such as melanin, before degradation can take place [3]. *Arthrobacter* and *Streptomyces* can degrade the pesticide diazinon together but are unable to do so independently [54].

1. Equivalent to 2-200 mg/L by mass, assuming one cell = 2×10^{-13} g [44].

Enzymes are so substrate-specific that a compound subjected to structural alteration may require a different enzyme catalyst. Specialization is so precise that enzymes can distinguish between amino acid stereoisomers and between such geometrical isomers as fumaric and maleic acid [3]. Microorganisms without the enzymatic make-up required by a compound will be unable to degrade it. In some cases the necessary enzymes can be induced during a period of acclimation following contact with a substance.

Once enzymes are activated, other factors may prevent their catalyzing a degradation reaction. Inhibition of the enzyme or repression of its synthesis by a substrate or its catabolites can complicate initiation or continuation of a degradation reaction [153]. Extracellular enzymes, such as hydrolytic enzymes, can be inhibited or inactivated by clay or other colloids, humic acids, and other substances [3]. Because of cross linkages, coiling, folding, etc., enzymes may be unable to complement a compound's particular steric configuration and reach the activation site [3]. The absence of appropriate enzymes and physical interference are responsible for the recalcitrance of various compounds, such as some of the synthetic high-molecular-weight polymers and certain proteins [3].

- *Environment-Related.* Environmental variables control microbial metabolic activity in general rather than biodegradation specifically. The significance of particular parameters varies with each ecosystem. Also, as expected from the considerable genetic variability in microorganisms as a group, certain species have evolved to function in extreme environmental conditions.

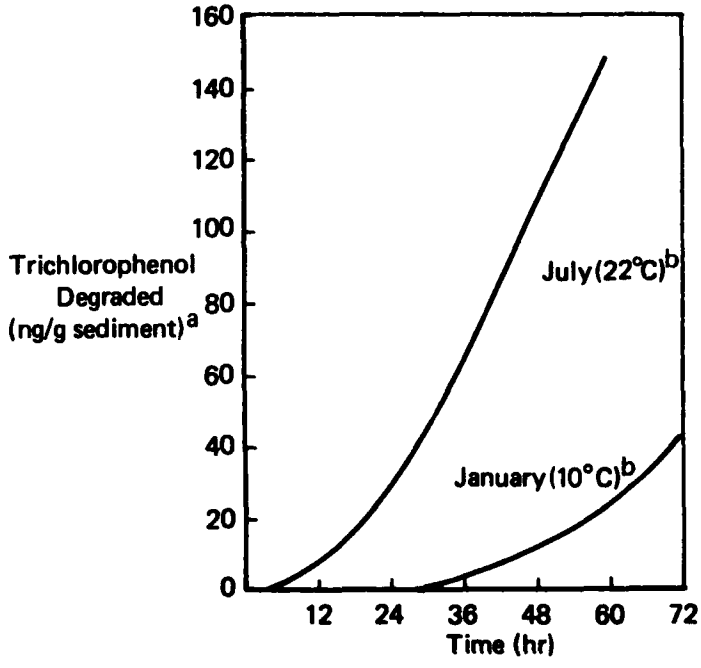
Microbial growth has been observed in environmental temperatures ranging from −12 to 100°C [21]. Individual species are usually adapted to a 30-40 degree range somewhere between these extremes. Depending on the temperature in which microorganisms have a competitive advantage over other species, they are commonly classified in one of three groups: psychrophiles (< 25°C), mesophiles (between 25° and 40°C), and thermophiles (above 40°C) [21]. Organisms that degrade chitin in tropical soils (ranging from 28° to 30°C) are primarily actinomycetes, protozoa, and higher organisms, while in temperate soils, fungi and *eubacteria* are responsible [117]. Temperatures outside a microorganism's range are not necessarily lethal; many species (e.g., sporeformers) have a dormant state that permits survival until conditions supportive of growth return.

Rates of biological reactions increase with increasing temperature within the range tolerated by the organism. This is illustrated in Figure 9-10, which is a plot of the degradation of a chemical at two temperatures. The relationship can be described by the Arrhenius equation:

$$Y = Ae^{-E_a/RT} \qquad (9\text{-}1)$$

where

Y	=	temperature-corrected rate of reaction
A	=	initial rate of reaction
E_a	=	activation energy
R	=	gas constant
T	=	absolute temperature



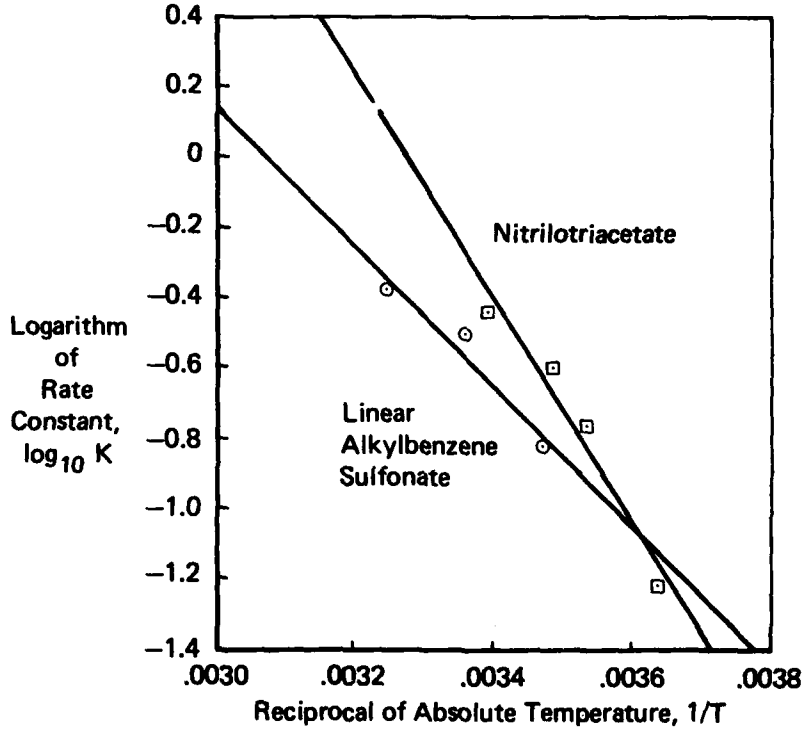
a. Initial concentration at both temperatures = 2.5 µg/g sediment

b. Incubation temperature

Source: Lee and Ryan [93]

FIGURE 9–10 Amount of ^{14}C–trichlorophenol Degraded with Time at Two Temperatures

Reduced bacterial activity was observed in several river-water tests when the incubation temperature was decreased: a 75% reduction in maximum breakdown rate of 2,4-D occurred in a river die-away test when the temperature was reduced from 25°C to 15°C [163]. The Arrhenius plots in Figure 9-11 show the relationship between temperature and biodegradation.

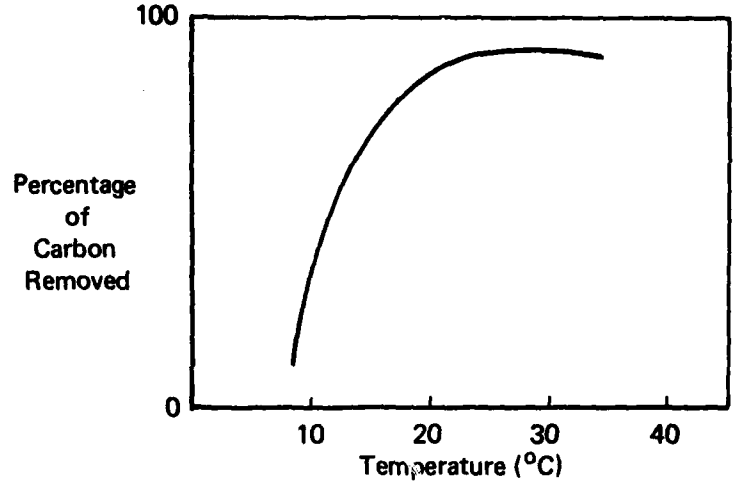


Source: Larson [92]

FIGURE 9–11 Arrhenius Temperature Plots for Biodegradation in Water

Wastewater biological treatment processes are dependent on temperature, functioning optimally between approximately 20°C and 35°C [27]. Figure 9-12 shows the relationship between temperature and efficiency of carbon removal in an activated sludge system. Degradation took place at both the low and high temperatures tested.

Populations that are adapted to temperature extremes may deviate from rates predicted by Eq. 9-1 — e.g., psychrophilic populations may show increased efficiency during winter [92]. The relationship between reaction rate and temperature may also be complicated by



Source: Collins [27]

FIGURE 9–12 Effect of Temperature on Efficiency of Biological Processes for an Activated Sludge System

other factors. For example, although temperatures are lower in winter, upwelling or lower water flow rates may increase microbial population density and, therefore, the rate of degradation [174].

Temperature is interrelated with other environmental parameters, especially in soil. Moist soils conduct heat more efficiently and thus have a smaller temperature gradient over a given depth than do dry soils [130]. Adsorption of some pesticides on clay particles increases with decreasing temperature, while the reverse is expected for organic matter [147].

Microorganisms as a group have adapted to the entire pH range normally encountered in natural systems. Optimal growth for fungi usually occurs under slightly acidic conditions, between pH 5 and 6, but activity continues at a pH less than 3. Bacterial growth is favored by slightly alkaline conditions and, except in acidophilic species, is inhibited when the pH drops to approximately 5 [21,53]. Microbial oxidation is most rapid between pH 6 and 8 [72].

Moisture is an important variable in the soil habitat. First, moisture controls soil oxygen levels by competing with oxygen for soil pore spaces. Second, most microorganisms require water because of their relatively permeable cell membranes and large surface-to-volume ratio. Many do

not survive drying, although some wait for more favorable conditions in such dormant forms as endospores [52,106]. Some filamentous fungi can tolerate dry soil conditions by extracting moisture from air, but their activity increases if water is present [21]. The measure of soil moisture that is most relevant to microorganisms is not moisture content but "water potential." This is the difference between the energy state of soil water and of free water and represents the total contributions of gravity, soil matrix, and osmotic pressure. Water potential levels tolerated by various microbial groups are listed in Table 9-9.

TABLE 9-9

Effect of Soil Water Potential on Microorganisms

Aspergillus penicillium (fungus)	Predominates at less than -145 bar[a]
Most other fungi	Lower limit approximately -40 bar
Most bacteria	Lower limit -80 bar, upper limit approximately -5 bar.

a. 1 bar = 10^6 dynes/cm^2 = 0.987 atm.

Source: Gray [53]

Biodegradation can occur in both aerobic and anaerobic environments; the type and rate of the reaction is affected by the amount of oxygen present. In aerobic environments, oxygen is used as a terminal electron acceptor for many degradation reactions (e.g., for many aliphatic hydrocarbons). Some organisms also need oxygen for the dissimilative process [1]. Lack of air commonly limits the growth of bacteria in laboratory cultures in closed systems [21], but it does not become rate-limiting until the concentration of dissolved oxygen drops below about 1 mg/L [92]. Oxygen levels are reduced by microbial depletion of non-replaceable oxygen during metabolism or, in soil, by encroachment of water into pore spaces containing oxygen, which can reduce oxygen diffusion rates by as much as two thirds [55]. When the gas-filled pore spaces represent less than approximately 10-20% of the total pore space, conditions shift from aerobic to anaerobic [136]; in this environment, even small amounts of oxygen inhibit microbial activity [21].

The effects of salt vary with the species of microorganism. Salt in a concentrated solution causes dehydration of living cells, but some species, such as those adapted to marine or other saline environments,

require salt at typical seawater concentrations (approximately 3.5%) for membrane stability and enzyme activation [21]. Organisms in freshwater or non-saline soil environments, on the other hand, have not required evolution of salt tolerance, so their activity may be limited or temporarily repressed under saline conditions.

The presence or absence of substances other than the substrate can influence the rate of biodegradation. Some metabolic reactions require compounds in addition to the substrate for the induction of enzymes necessary for degradation or as nutrient sources. The lack of an essential nutrient can retard or limit biodegradation [3,114b,115a]; for example, insufficient nitrogen and phosphorus in certain estuarine systems retards the degradation of glucose at concentrations above 1 mg/L [92]. Marine, oligotrophic (low productivity) lake, and some soil systems may show similar limitations. The importance of oxygen for aerobic biodegradation has already been mentioned.

Another controlling parameter is the presence and concentration of substances onto which the substrate can be adsorbed or with which it can form complexes, making the substrate inaccessible to biological activity. Adsorption may be the primary factor preventing, or significantly delaying, the degradation in soil of some usually metabolizable compounds [1]. Some compounds are physically trapped within the lattice structure of clay in pores too small for penetration by microorganisms; alternatively, by combining with clay or other material, a compound may become unable to penetrate cell membranes [3]. New, recalcitrant compounds may appear when the substrate forms complexes with resistant organic compounds such as lignins, melanins, and tannins [3]. In aquatic systems, similar interactions between a compound and particulate matter can occur. Adsorption onto suspended solids and biological matter in sludge may significantly reduce the concentration of substrate available for biodegradation [155]. Rate equations have been adapted to account for adsorption in natural waters. An increase in the sediment-water ratio by 100 was associated with an equivalent decrease in the second-order rate contant for biodegradation of chlorpropham and di-n-butyl phthalate [149].

The importance of sediment in aquatic systems as a source of nutrients and microhabitats for microbial populations has also been indicated [114b,115a]. In a biodegradation study of 2,4-D in river water, 50% was degraded at 40 days in samples with sediment added as compared with only 10% degraded at the same time in unadulterated samples [115a]. The mechanisms responsible for this phenomenon were not isolated in this study.

9-3 STANDARD TEST METHODS

Principles of Use. To estimate biodegradability and to generate a usable measure of the loss rate of an organic compound in the environment, it is necessary to conduct experiments under controlled conditions. Such experiments are especially important in biodegradation studies because so many variables may influence the process, as described in the preceding section. The three biological habitats of interest in this chapter are aquatic, soil, and wastewater treatment systems. In addition, anaerobic conditions exist within these habitats (in soil, sediment, and sludge). A particular set of biological, physical, and chemical properties is associated with each system, and the testing procedures must replicate these controlling parameters. The text that follows describes, first, biodegradation tests in general and then specific tests that best simulate each of the environments.

Tests for measuring biodegradation generally follow a standard procedure:

(1) A microbial population is collected from an environmental source (e.g., river water, agricultural soil) or is isolated through use of an enrichment culture. The substrate may be introduced early as a carbon source, to ensure the presence of a population capable of biodegradation before the experiment begins.

(2) The population is incubated with the substrate in some medium (e.g., water, soil), with or without additional nutrient or energy supply.

(3) The rate of disappearance of the substrate is monitored through indirect or direct analytical techniques.

A standard reference compound should be tested under the same conditions concurrently [163], but this is not always possible.

The time required for a given test depends on the nature of the chemical being tested, the source of the microbial inoculum, and the procedures used. Tests can take from a few days (river die-away) to 14 weeks (trickling filter) [72,163]. The assimilation of organic compounds by microorganisms may depend on acclimation of the cells to the test compound, which requires varying amounts of time for different organisms (3-30 days) [72,163] until synthesis of the necessary enzymes for species selection takes place. Acclimation time also depends on the temperature and the source of seed.

The quantity of chemical compound required per test varies from 5 to 200 mg total organic carbon/L for many tests. Lower concentrations may simulate the natural environment more accurately, but they can also make it more difficult to obtain conclusive results. Biodegradation should be measured in several separate runs, each with a different initial concentration.

Many biodegradation experiments employ sterilized or poisoned controls to compare with biologically active samples; this is essential for differentiating between chemical and biological reactions. The drawback to sterilization by chemicals, heat or radiation is that this may alter the system chemically or trigger other reactions [50]. Filtration is an alternative.

Mixed-species microbial cultures are preferable to single-species cultures, because they better reflect the microbial diversity found in nature. The main disadvantage is the difficulty in replicating results; different species may play dominant roles in different runs, or dominance may shift during a single run.

Several analytical techniques are available to monitor changes in chemical concentration over time. Both direct and nonspecific (for the parent compound) methods are used in biodegradation experiments. Table 9-10 lists analytical techniques commonly used in biodegradation tests and their main disadvantages.

Nonspecific methods include bioassays, O_2 uptake, measure of a constituent of the compound that becomes available during degradation (such as chlorine), CO_2 evolution, and increases in bacterial populations. There are arguments against all of these methods; each assumes a consistent relationship between the effect measured and the compound concentration. CO_2 evolution assumes that all carbon liberated originates from the test compound and not from the death of the original organisms. Bacterial counts assume that the substrate is the only growth-supporting medium; furthermore, it is difficult to measure microbial population accurately.

Direct methods are analytical procedures sensitive to the parent compound, including chromatography, spectrophotometry, and radiolabeling with carbon-14. The latter is the most accurate method; by permitting a total mass balance of the parent compound and its metabolites, it accounts for all losses due to biodegradation [72]. Also, lower initial concentrations can be used. Radio-labelled material should be checked by GLC or TLC (see Table 9-10) for impurities. The primary drawback to ^{14}C-labelling is expense.

TABLE 9-10

Analytical Techniques Commonly Used in Biodegradation Tests

Technique	Direct (D) or Indirect (I)	Potential for Metabolite Identification	Problems
Chromatography • Paper • Thin-layer (TLC) • Column • Gas (GC or GLC)	D	Yes (with co-chromatography)	Analytical techniques must be developed specifically for a chemical or chemical group; only volatile substances can be measured with GLC.
Radiotracers • Assay for loss of ^{14}C in parent compound	D	Yes	Expensive; label must be attached to site of rate-determining step unless $^{14}CO_2$ evolution is measured; complex equipment required; lack of $^{14}CO_2$ evolution may only mean incomplete mineralization; must be combined with TLC or GLC as analytical tools.
Colorimetry	D	Poor	Interference from other compounds in medium; not very sensitive.
Spectrometry • UV absorption • Infra-red (IR)	D	Yes	Not as sensitive as GLC & TLC; potential for interference from other substances; fails to reveal minor modifications in parent compound; UV requires large amount of compound to be measured.
CO_2 Evolution	I	No	Not all released carbon goes to CO_2, so results not precise; used to measure ultimate biodegradation (i.e. mineralization).

(Continued)

TABLE 9-10 (Continued)

Technique	Direct (D) or Indirect (I)	Potential for Metabolite Identification	Problems
O_2 Consumption • BOD • Respirometer	I	No	Reaction must be oxidation; O_2 may be utilized for other reasons than oxidation of substrate.
Total Carbon determination • Chemical Oxygen Demand (COD) determination • Combustion • Dissolved Organic Carbon (DOC) removal	I	No	Substrate must be sole carbon source; differences in susceptibility of different chemicals to analytical technique (combustion); interference by other impurities.

Source: Howard [72] and Swisher [155].

Many tests use relatively inexpensive nonspecific analytical techniques that do not measure changes in concentration of the parent compound or identify degradation products. Nonspecific tests do not yield any quantifiable data on the biodegradation reaction rate of the substance's disappearance *per se*. Some quantification of biodegradation can be obtained, however, by measuring the rate of CO_2 evolution or by other processes. Such data cannot substitute directly for a measured biodegradation rate. In many cases more than one analytical technique can be chosen for a given test procedure: any of five different techniques might be used in a soil perfusion test, for example. The following section summarizes the test methods commonly used to screen for biodegradability of organic compounds and discusses how the choice of test and analytical technique can affect the results.

The type of test selected can greatly influence the biodegradation measurements, as shown in Table 9-11. Some methods, such as semicontinuous sludge and trickling filters, may provide better conditions for biodegradation than others.

Table 9-12 lists methods that have been recommended by various groups for screening organic compounds for biodegradability.

TABLE 9-11

Comparison of Biodegradation Test Methods
(Percent removal of MBAS[a] after 15 days)

	Surfactant[b]			
	A	B	C	D
Continuous sludge	61 ± 5.2	66 ± 2.9	75 ± 5.0	34 ± 5.5
Slope culture[c]	74 ± 8.8	89 ± 1.6	0–66	20 ± 7.3
River water	88 ± 0.9	93 ± 0.6	96 ± 0.3	29 ± 1.9
Shake culture	88	96	91	34
Semicontinuous sludge	89 ± 0.4	96 ± 0.3	98 ± 0.3	70 ± 4.0
Recycle trickling filter	92 ± 1.6	96 ± 0.7	97 ± 0.4	83 ± 1.5

a. MBAS = methylene blue active substances, which include anionic surfactants and/or certain natural materials detected by this method.
b. A=Dobane JNX, B=Dobane JNQ, C=Dobane 055, D=ABS.
c. Die-away test using activated sludge inoculum in aerated BOD dilution water.

Source: Swisher [155].

Characteristics of Typical Tests. Table 9-13 lists some biodegradation tests that are commonly used for each of the four environments described above. Table 9-14 describes in greater detail each of these test methods for each environment. The tests were selected for the table on the basis of EPA recommendations under the Toxic Substances Control Act (TSCA) [162]. Additional information was obtained from reviews of biodegradation testing procedures [72,155].

- *Surface Water.* Several tests are commonly used to estimate biodegradation in surface water. The TSCA guidelines [162] recommend the shake flask, CO_2 evolution, and BOD dilution tests. Howard *et al.* [72] described the river die-away and BOD respirometer tests. Many different seed sources can be used for the shake flask test, and more complete information about biodegradation can be obtained if both acclimated and unacclimated seed is used [72]. The shake flask test has better reproducibility than the river die-away. The BOD_5 (with dilution technique) is used most frequently in testing surface water, but there are a number of problems with this method [72].

- *Soils.* Three test methods are used to simulate the aerobic soil environment. The $^{14}CO_2$ evolution test recommended by the EPA un-

TABLE 9-12

Biodegradation Tests Recommended for Screening Organic Compounds

Recommended by	Test Methods	Ref.
Task Group on Methodological Criteria for Biodegradation	• Activated sludge method (batch and continuous) • River die-away	[132]
EPA under TSCA[a]	• Shake flask method • Activated sludge method • Methane and CO_2 production in anaerobic digestion • CO_2 evolution[b] • BOD method No soil tests recommended	[162]
Monsanto[a]	• River die-away • Semi-continuous activated sludge • CO_2 evolution[b] • Anaerobic	[47]

a. Recommended tests are meant for screening purposes; quantification of rates of disappearance applicable to environmental conditions requires radiolabeling or other direct techniques.
b. Measures ultimate biodegradation.

TABLE 9-13

Summary List of Standard Tests for Measuring Biodegradation

Aquatic	Soil	Anaerobic	Activated Sludge
• Shake Flask	• Soil perfusion	• Anaerobic digestion	• Semi-continuous activated sludge
• River die-away	• Soil incubation	• Closed river die-away	• Trickling filter
• BOD respirometer	• Soil suspended in aqueous solution		• Recirculating filter

der TSCA [162] is considered better than the aqueous solution or perfusion test [72]. The recommended test can be used for sediments, and the transformation products of the test compound can be quantified by thin layer chromatography of acetone extracts [141].

Most of the analytical techniques listed in Table 9-14 for the aqueous solution test method can be used for the other two test methods as well. The O_2 consumption and CO_2 production tests are usually not used for natural soils because of the high endogenous rates of soil respiration [72].

Tests for biodegradability in soil are affected by soil type and amount. Using a soil with a high proportion of organic matter should give higher degradation rates. On the other hand, it might produce a lower rate because cells and enzymes could be adsorbed onto the organic matter. Also, the organic matter present may be degraded by the microbial population in preference to an added substrate, delaying the rate of biodegradation for the compound. Therefore, the type (or degradability) of organic matter present, as well as the concentration, may be an important factor in biodegradation tests. In one study [84], the $^{14}CO_2$ evolved from five soil types receiving ^{14}C-carbaryl varied from 5% to 35% [72]. The high microbial content of most soils allows them to be used as microbial inoculum in degradation studies without adding nutrient amendment or other microorganisms, thus achieving a closer simulation of natural conditions.

- *Anaerobic Soils or Sludge.* The EPA under TSCA [162] recommends the anaerobic digestion test to assess biodegradation potential in anaerobic sludge. Anaerobic soil and water conditions can be simulated by flooding natural soils or by preventing air from contacting a river die-away system.

- *Activated Sludge Waste Treatment Plant.* The activated sludge test is most frequently used to simulate an activated sludge waste treatment plant. Acclimation of seed can be an unpredictable parameter in this test. Many attempts have been made to standardize it by using freeze-dried or air-dried sludge [72]. Temperature has a strong effect on the degree of biodegradation [72].

Although a BOD test could be used, it provides less insight into biodegradability under treatment plant conditions than does the continuous activated sludge or trickling filter test. The river die-away test might also be used, seeded with a much lower bacterial concentration than the activated sludge [72].

TABLE 9-14

Environment and Ref.	Test Method	Analytical Technique	Time for Test	Quantity or Conc. of Test Compound	Procedure (pH, nutrient, source, temp., culture)
Surface Water [72, 132, 155, 162]	River Die-Away	1. TLC (chromatography) 2. Spectrophotometry 3. Radiolabeling (^{14}C) 4. GC-MS 5. Colorimetry	Few days to 8 weeks	Varies according to test compound & analytical technique. Concentrations reported from 1-200 mg/L. [72]	Monitor disappearance of compound after it is placed in natural water sample and incubated until degradation ceases.
	BOD (Biochemical Oxygen Demand)	O_2 Dilution	1. 5 days 2. 10 days, or 3. long term (~42 days)	0.2 mg/mL to 4.8 mg/mL	Same as CO_2 Evolution Test with acclimated culture (13 days). Measure D.O. (dissolved oxygen).
	BOD Respirometer	1. Warburg differential manometer 2. O_2 electrolytic respirometer.	Varies	Varies according to test compound & analytical technique. Concentrations reported from 1-320 mg/L [72]	Measure O_2 consumption. High microorganism concentration required. Allows continual introduction of substrate and oxygen.
	Shake flask	Loss of DOC (Dissolved organic carbon)	13 day adaptation & 21 days of testing = 34 days	Relatively low (Supply 10 mg organic carbon per L of basal medium.)	Microorganisms inoculated in flasks with basal compound & test compound & aerated after 4 adaptive transfers; biodegradation is measured by reduction in DOC

Standard Laboratory Test Methods for Measuring Biodegradation

Results Indicate	Calculations and Information Recorded	Problems
Disappearance of parent compound over time.	Plot rate of parent compound disappearance.	Variation in bacterial count & composition of different rivers. Populations from industrial rivers may be acclimated. Small size of inoculum. [132]
O_2 uptake >60% of theoretical maximum suggests substantial degradation.	Subtract daily D.O from D.O. on day zero (= depletion value). Subtract depletion value of blanks. Multiply by inverse of dilution factor to get BOD. Use molecular structure of test compound to calculate O_2 needed to oxidize it to CO_2, H_2O, & inorganic molecules. $\%\ \text{theoretical} = 100\left(\frac{BOD_T - BOD_M}{BOD_T}\right)$ where T = theoretical M = measured	1. No information on nature of degradation products. 2. O_2 also used to make new cell material etc., so unless extremes are noted (0 or 100%) cannot assume biodegradation. 3. Ignores possibility that normal O_2 is ↑ or ↓ by chemical means. 4. If outside carbon source is used, could confuse results. 5. O_2 could be consumed by nitrification & misrepresent results; so determine NO_3 formed. 6. All oxygen required for degradation must be dissolved in water at start of experiment, thus limiting concentration of substrate. 7. Not very accurate
Same as BOD	Same as BOD	See above (except #6 and #7). Also, CO_2 must be continually removed to prevent interference.
Degradation of compound, but not complete conversion to CO_2.	% removal of organic C at time t. Express DOC as mgC/L.	Loss of DOC could be due to cellular uptake, sorption, or loss by evaporation. Use of high concentration of microorganisms permits relatively short test period but makes conditions more favorable for degradation than those encountered in nature.

(Continued)

Environment and Ref.	Test Method	Analytical Technique	Time for Test	Quantity or Conc. of Test Compound	Procedure (pH, nutrient source, temp., culture)
Surface Water (Continued)	CO_2 Evolution	Evolution of CO_2	13 day acclimation + 1 day aeration + 28 day test = 42 days	5-10 mgC/L	In presence of O_2, microorganisms degrade organic compound to CO_2 & inorganic salts. Calculate theoretical maximum evolution of CO_2 & use of O_2 if all C atoms in compound are oxidized to CO_2. CO_2 evolution values >60% of theoretical max. indicate degradation.
Aerobic Soils [72]	1. Soil perfusion 2. Soil incubation 3. Soils suspended in aqueous solution	1. Chromatographic TLC 2. Spectrophotometric 3. Radiolabeling (^{14}C) 4. GC-MS 5. Colorimetry 6. Oxygen consumption methods usually not used because of high endogenous rates of soil respiration.	Continue until rate of disappearance levels off.	5-100 ppm	In general, obtain natural soil and mix with chemical with (Methods 1 and 3) or without (Method 2) addition of water. Many different apparatus used, usually liquid reservoir with soil column and tube to deliver solution and air. Stationary containers aerated for Method 1, not for Methods 2 and 3.

(Continued)

Results Indicate	Calculations and Information Recorded	Problems
Ultimate biodegradability potential. Use this test or BOD (this test preferred). CO_2 evolution >60% of theoretical maximum indicates substantial degradation.	mg CO_2 produced from substrate = $\frac{(T_b - T_x)\ 220}{V}$ where T_b = ml of 0.1 N HCl required to titrate aliquot from blank absorber; T_x = ml of 0.1 N HCl required to titrate aliquot from test compound absorber; V = ml of aliquot used in titration. Calculate % of theoretical CO_2 = $\frac{100 \sum_{1}^{n} [CO_2]}{110}$ where $\Sigma [CO_2]$ = sum of CO_2 production values from the absorber samples taken on day 1 through last day (n).	See Table 9-11.
Disappearance of parent compound over time, either in soil (Method 2) or by a soil inoculum (Methods 1 and 3).	Plot rate of disappearance of parent compound.	1. Method 1 has high biodegradability potential so does not simulate most natural environments. 2. In Method 2 analytical techniques more difficult to use; additional extraction and clean-up steps required because of adsorption of chemical onto soil; less uniformity in distribution of compound in soil. 3. When soil used as medium (in Method 2), difficult to replicate results because of high degree of variability. 4. In Methods 1 and 3, moisture content too high to simulate natural soils. 5. Difficulty in handling multi-units of Method 1.

(Continued)

Environment and Ref.	Test Method	Analytical Technique	Time for Test	Quantity or Conc. of Test Compound	Procedure (pH, nutrient, source, temp., culture)
Anaerobic Soils or Sludge or Aquatic [72, 155]	Anaerobic digestion	Compare production of methane & CO_2 by anaerobic bacteria in samples with & without test material.	At least: 3 days to equilibrate & 28 days to test = 31 days	10-200 mg/L	Obtain anaerobic sludge from municipal plant and allow to equilibrate. Put test compound in some containers. Periodically measure gas production and analyze for methane and CO_2 content. Methane production in units receiving test compound compared with controls will provide information on the biodegradability of the substrate under anaerobic conditions.
	Die-away	Same as aerobic river die-away test.	14-60 days (for surfactant).	10-100 ppm (for surfactant)	Initial dissolved O_2 is consumed by aerobic biooxidation processes and system becomes anaerobic; air prevented from contacting the river die-away type system. Different studies put surfactant with sewage in closed jars for 2 weeks, 40 days, & 60 days. Measure test compound left at end.
Activated Sludge Waste Treatment Plant [60, 72, 128, 155, 162]	1. One-batch die-away 2. Semi-continuous activated sludge 3. Trickling filter 4. Recirculating filter	1. GLC 2. Colorimetry 3. Radiolabeling 4. DOC removal	Maximum of: 1. See river die-away 2. 30 days acclimation + 19 days testing = 49 days 3. 4-8 weeks acclimation + 14 weeks to develop mature film 4. 7 days for recirculating filter	1. Moderate to heavy concentration test: 50-100 mg/L as DOC. 2. Low concentration test: 100 mg of compound as DOC. 3. High concentration test: 200 mg of compound as DOC.	After activated sludge has adapted to synthetic sewage & increasing concentrations of test compound, it is: 1. Like river die-away using sludge inoculum (see river die-away test). 2. Exposed to mineral salts medium plus compound in aerated chamber for up to 20 days. Process involves: aeration, settling of sludge, removal of supernatant liquor, filling with fresh sludge and substrate, repeat. Biodegradation is followed by comparing DOC at start with DOC mixed liquor on last day. 3. Passed once through packing medium, on which bacterial populations develop over time. Once population is established, solutes may be adsorbed onto film for long exposure times. 4. Similar to trickling, except that water recirculates throughout test procedures.

(Continued)

Results Indicate	Calculations and Information Recorded	Problems
Excess gas production in units receiving test compound (compared to control) may be related to anaerobic digestion of test compound. Excess CH_4 & CO_2 (as mg of C) produced is compared with theoretical maximum & % theoretical production can be calculated.	Record total gas as well as CH_4 & CO_2 content. % of theoretical $= \frac{(G_T - G_M)\,100}{G_T}$ where G_T = total mg organic C in sample G_M = mg of C in excess ($CH_4 + CO_2$).	
Disappearance of parent compound over time.	Plot rate of disappearance of parent compound.	Same as aerobic die-away test.
Depending on analytical technique, either disappearance of parent compound over time or removal of organic carbon (DOC).	% removal of DOC during acclimation & test period or plot rate of disappearance of parent compound.	Difficult to maintain continuous circulation of sludge; long test time; fly nuisance; lack of easy accommodation in constant temp. room or bath; operational conditions are not readily adjusted; large amounts of substrate required; long acclimation period required for Methods 3 and 4.

The activated sludge test recommended by TSCA [162] is semi-continuous. Each cycle is a batch run on a particular unit of feed solution, but the cycle is repeated over and over with fresh feed, which provides an opportunity for acclimation and attainment of a "steady state" [155]. This semi-continuous process is also called fill-and-draw, because after aeration of sludge and feed solution, the sludge settles and the supernatant liquor is drawn off. Continuous systems generally require a much greater investment of time, space, and money than do semi-continuous systems [155].

Effect of Method and Analytical Technique on Measured Rates. In addition to the general variables affecting biodegradation discussed in §9-2, specific variables that characterize each test methodology influence the measured rate of biodegradation. The variables are related to the choice of:

- Chemical (concentration used, position of radiolabels);
- Microorganisms (source, concentration, acclimation time);
- Medium (amount of adsorbing soil or sediment);
- Procedure (pH, temperature, use of agitation); and
- Analytical technique.

The measured biodegradability of a given compound can vary significantly from one test method to another, because some tests may provide a better environment for biodegradation than others. Table 9-11 presents rates of degradation obtained for a chemical using different measuring techniques. Methods with optimum conditions for biodegradation support high microbial activity. Methods with the lowest potential usually have a low bacterial concentration in a synthetic medium (for example, the shake culture test). The higher bacterial concentration and thus high activity rates of the activated sludge test provide a higher potential for biodegradation. Even though bacterial concentrations in the river water test are relatively low, the use of naturally occurring water and microbial species often results in a high potential for biodegradation. Soil systems with unsaturated flow conditions exhibit the highest biodegradation potential [155].

Both continuous and semi-continuous systems can be used to simulate an activated sludge waste treatment plant. Biodegradation of surfactants has been shown to vary greatly in continuous systems, compared with the inherently more stable semi-continuous system. This variation is due to the wide variation from one sludge microbial culture to another and even within a single sludge culture at different times [155].

9-4 BIODEGRADATION RATE CONSTANTS

Derivation. Before the rate of biodegradation can be quantified and a rate constant can be calculated, a kinetic expression must be derived to describe the pattern of loss over time. Two general rate laws have been proposed to describe biodegradation: the power rate law and the hyperbolic rate law. Both are described below.

Depending on whether a chemical is degraded cometabolically or metabolically, is strongly adsorbed or not, is subject to competing reactions simultaneously, and other factors, different rate equations are applicable in deriving the rate constant [50]. One rate law may not adequately describe a chemical over its total degradation curve because of changes in its concentration-dependency and availability over time; in most cases, however, one rate order is assumed to be in effect over the entire biodegradation curve.

The *power rate law* states that the rate is proportional to some power of the substrate concentration [55]:

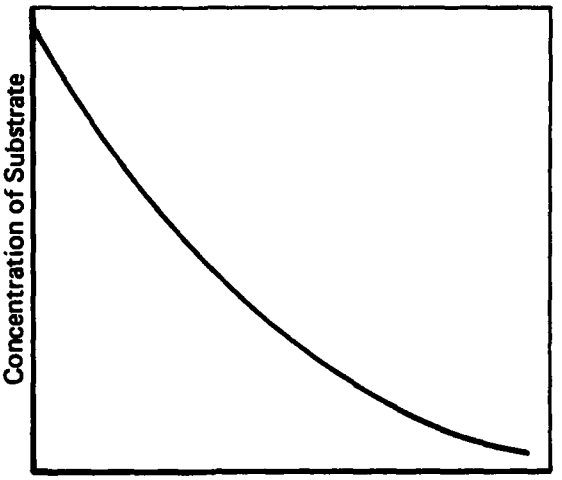
$$\frac{-d[C]}{dt} = k\,[C]^n \qquad (9\text{-}2)$$

where

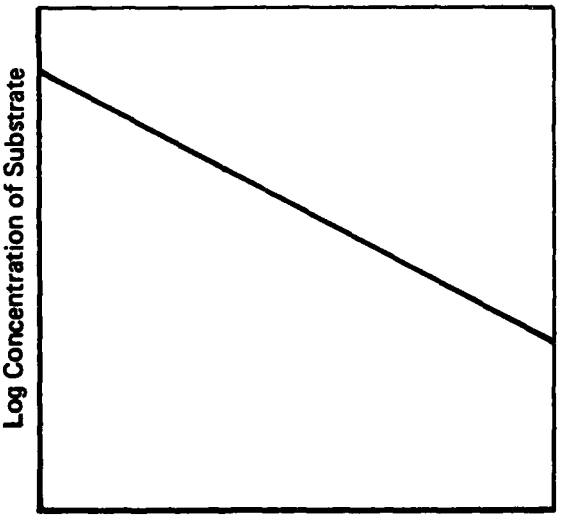
n = the order of the reaction
[C] = concentration of substrate
k = biodegradation rate constant

If first-order kinetics are assumed (i.e., n = 1), the rate is simply the product of the rate constant and the substrate concentration. The assumption of first order is most common in homogeneous media [55] or as a first approximation when the relationship between concentration and the variables affecting it are not understood. It can be used to calculate the half-life ($t_{1/2}$) of a chemical subjected to biodegradation ($t_{1/2} = 0.693/k$). Figure 9-13 depicts a typical first-order decay curve due to biodegradation; when the log of the concentration is plotted against time, the curve becomes a straight line.

At low pollutant concentrations, the assumption of first-order kinetics for biodegradation is reasonable [36,55]. For a system as variable and complex as soil, however, there are likely to be many exceptions to this assumption. The measured rate of disappearance of pollutants from soil under natural conditions is commonly lower than would be expected



a. Measured Substrate Concentration vs. Time



b. Logarithm of Substrate Concentration vs. Time

FIGURE 9–13 First-order Disappearance Curve of a Chemical

based on laboratory results [58,59]. This discrepancy may be partly due to:

- Lower availability of pollutant because of increasing adsorption over time;
- Changes in the microbial population over time; and
- Shut-down of reactive sites because of toxic effects of metabolic products [55].

Further investigation of the influence of these factors on the rate of degradation is needed before they can be expressed as terms in a rate equation.

The *hyperbolic rate law* is commonly used to quantify the growth of microbial populations. Based on Monod kinetics, this law expresses the rate as a hyperbolic saturation function of the substrate concentration [111,112]. Although the measured rate refers to population growth, it can be converted to a term to describe the disappearance of the substrate supporting the growth. The equation is a reasonable first approximation for biodegradation in aquatic systems [12] and in soil [55].

The Monod kinetics rate equation states that the growth rate of a single-species population of microorganisms on a single carbon substrate is dependent on the substrate concentration and, at higher concentrations, on the sum of concentration and other terms (comprising a single constant):

$$U = \frac{U_{max}\,[C]}{K_c + [C]} \qquad (9\text{-}3)$$

where:

U = specific growth rate of microorganism
U_{max} = maximum growth rate of microorganism
$[C]$ = concentration of substrate
K_c = concentration of substrate in water supporting a half-maximum growth rate ($U_{max}/2$) (pseudoequilibrium constant).

Equation 9-3 is also applicable to mixed-species populations [101], and it can be modified [13] to a die-away expression through use of a yield coefficient describing the conversion efficiency of substrate to microorganism mass:

$$Y_d = -\frac{d[B]}{d[C]} \tag{9-4}$$

where:

Y_d = yield coefficient
[B] = microbial population concentration
[C] = substrate concentration

The expression describing substrate disappearance is written:

$$\frac{-d[C]}{dT} = \frac{U_{max}\,[B]\,[C]}{Y_d\,(K_c + [C])} \tag{9-5}$$

Further simplification is possible with the following assumptions:

- K_c values commonly range from 0.1 to 10 mg/L, which is higher than most environmental concentrations of substrates [13]; therefore, [C] in the denominator can be ignored.
- U_{max}/Y_dK_c is equivalent to a second-order constant K [120].

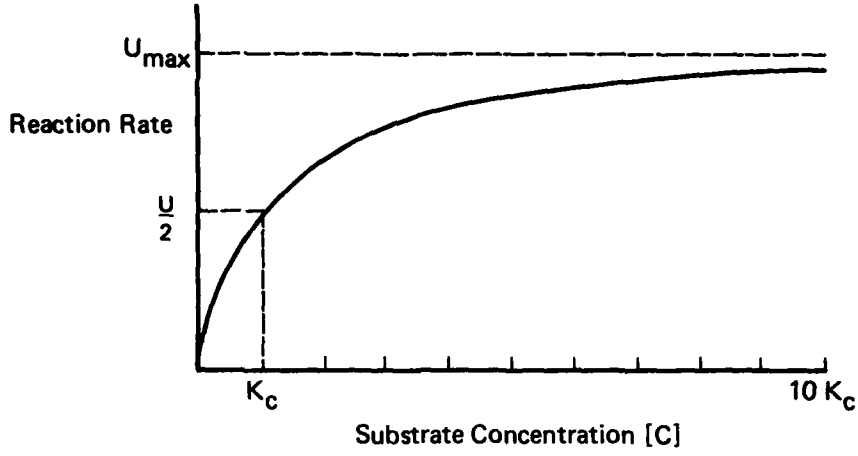
The simplified form becomes a second-order rate expression,

$$\frac{-d[C]}{dt} = K[B]\,[C] \tag{9-6}$$

which is a function of both population and substrate concentration. Figure 9-14 depicts the concentration dependence of a second-order decay rate, using the full form of Eq. 9-3.

The use of Monod kinetics to describe biodegradation rates requires that biodegradation be directly measurable in terms of all microbial growth that occurs during the course of the experiment. Although this may be true in cases where the substrate of concern is the sole source of energy or nutrient, the population increase may be partly dependent on other available substrates, which can be controlled in an experiment but not in the field. Larson discusses the following assumptions of Monod kinetics which may not be applicable to environmental conditions [92]:

- *The growth yield is a constant, equal to 50% of the substrate.* This assumption is not applicable to many of the dilute systems found in the environment, where a significant



Source: Larson [92]

FIGURE 9–14 Second-order Reaction Rate as a Function of Substrate Concentration Following Eq. 9–2

amount of the energy derived from the substrate may be used for maintenance rather than for growth.

- *The biomass of microorganisms can be accurately measured by plate counts.* Measurement can be very difficult in natural systems. Even at a substrate concentration of 10 mg/L, the density of microorganisms would reach no higher than 10^6 cells/mL, assuming a growth yield of 50% and dry cell weights of 10^{-12} to 10^{-13} g/cell.

The most accurate analytical technique for monitoring the disappearance of a chemical and collecting data for use in rate equations is one that measures the concentration over time directly and keeps track of the distribution and quantity of the degradation products. A method that employs carbon-14 labeling, while expensive, is the best because it allows subtraction of other losses from the biodegradation rate. Other direct analytical techniques can be used, however, as described in §9-3.

Rate Constants for Various Organic Compounds. The following section tabulates some biodegradation rate constants reported in the literature. These values were measured in laboratory experiments simulating aquatic, soil, activated sludge and anaerobic environments. The constants are both first- and second-order; Table 9-15 lists the units in which each rate order constant is expressed. For some chemicals, half-lives are reported if the authors stated that first-order kinetics were observed.

TABLE 9-15

Units for Biodegradation Rate Constants

Form Reported In	Rate Order	Definition
day^{-1}	1st	Per day
$t_{½}$ = ( ) days	1st	$t_{½}$ is half-life, i.e., time required for 50% of chemical to be biodegraded
mL $(gVS)^{-1}$ day^{-1}	2nd	Milliliters of substrate per gram of volatile solids (including microorganisms) per day
mg (g sludge)$^{-1}$ day^{-1}	2nd	Milligrams of substrate per gram of sludge (dry weight) per day
mg (g bacteria)$^{-1}$ day^{-1}	2nd	Milligrams of substrate per gram of bacteria (dry weight) per day
mL $(cell)^{-1}$ day^{-1}	2nd	Milliliters of substrate per bacterial cell (determined by counts or estimation) per day
mg COD (g biomass)$^{-1}$ hr^{-1}	2nd	Milligrams of COD per gram of initial biomass (dry weight) of inoculum per hour (for Table 9-22)

Although all rate constants describe the disappearance of the chemical over time, only results measured by direct analytical techniques or $^{14}CO_2$ evolution (in the case of soil) are presented. Information on test conditions (pH, temperature) is not given in this compilation, but the test method is stated wherever possible. An assortment of organic compounds is included, to represent the maximum number of chemical groups; for many chemicals, however, there were no data for certain conditions, and very few data were available for anaerobic systems.

Tables 9-16 through 9-19 are not intended to be a compilation of all the rate constants cited in the literature. At best, they provide an assortment of rate constants representative of each environment and illustrate typical ranges of constants.

Extrapolation of Laboratory Results to Field Conditions. The use of laboratory-derived rate constants to predict the persistence of a chemical in the environment must be done cautiously. As discussed in §9-2, many

TABLE 9-16

Biodegradation Rate Constants for Organic Compounds in Aquatic Systems

Compound	Rate Constant[a]	See Note	Ref.
Anthracene	0.007-0.055 day^{-1}	b	[46]
Atrazine (N-phosphorylated)	$t_{1/2}$ 3.21 days	c	[39]
Benzo[*a*] anthracene	0		[146]
Benzene	0.11 day^{-1}		[93]
Benzo[*a*] pyrene	0		[146]
Benzo[*f*] quinoline	8.6×10^{-7} $mL(cell)^{-1}$ day^{-1}		[146]
Bis(2-ethylhexyl)phthalate	1.0×10^{-9} $mL(cell)^{-1}$ day^{-1}		[168]
Carbaryl	2.4×10^{-10} $mL(cell)^{-1}$ day^{-1}		[167]
Carbazole (9H)	1.2×10^{1} $mL(cell)^{-1}$ day^{-1}		[146]
Chlorobenzene	0.0045 day^{-1}		[93]
	0.0092 day^{-1}	d	[93]
Chlorodiphenyl oxide	7.2×10^{-3} $mL(gVS)^{-1}$ day^{-1}		[20]
p-Chlorophenol	0.23 day^{-1}	d	[93]
Chlorpropham	$1.6\text{-}1.8 \times 10^{-8}$ $mL(cell)^{-1}$ day^{-1}	e	[149]
	$3.6\text{-}6.7 \times 10^{-10}$ $mL(cell)^{-1}$ day^{-1}	e,f	[123]
Crotoxyphos	$t_{1/2}$ = 7.5 days (pH 9)		[86]
	= 22.5 days (pH 2)		[86]
2,4-D (Butoxyethyl ester)	$6.24\text{-}24.0 \times 10^{-6}$ $mL(cell)^{-1}$ day^{-1}	e,f	[123]
	6.2×10^{-5} $mL(cell)^{-1}$ day^{-1}	g	[121]
	9.6×10^{-7} $mL(cell)^{-1}$ day^{-1}	h	[121]
p,p'-DDE	0.0006 day^{-1}	d	[93]
Diazinon	$t_{1/2}$ = 4.91 days (pH 3.1)		[48]
	= 185 days (pH 7.4)		[48]
Diazoxon	$t_{1/2}$ = 0.016 days (pH 3.1)		[48]
	= 27.9 days (pH 7.4)		[48]
Dibenzo[*c,g*] carbazole	0		[146]
Dibenzothiophene	1.27×10^{-5} $mL(cell)^{-1}$ day^{-1}		[146]
Dimethyl phthalate	1.2×10^{-4} $mL(cell)^{-1}$ day^{-1}		[168]
Di-*n*-butyl phthalate	7.4×10^{-7} $mL(cell)^{-1}$ day^{-1}		[149]
Di-*n*-octyl phthalate	7.4×10^{-9} $mL(cell)^{-1}$ day^{-1}		[168]

(Continued)

TABLE 9-16 (Continued)

Compound	Rate Constant[a]	See Note	Ref.
Galactose	1.2-10 x 10^3 mg(g bacteria)$^{-1}$ day^{-1}	i	[153]
	1.4 x 10^3 mg(g bacteria)$^{-1}$ day^{-1}	j	[153]
Glucose	0.24 day^{-1}		[92]
	1.1-1.6 x 10^4 mg(g bacteria)$^{-1}$ day^{-1}	i	[153]
	5.2 x 10^3 mg(g bacteria)$^{-1}$ day^{-1}	j	[153]
Hexachlorophene	0.0024 day^{-1}	d	[93]
Malathion	2.6-16.1 x 10^{-7} mL(cell)$^{-1}$ day^{-1}	e,f	[123]
	6.2 x 10^{-8} mL(cell)$^{-1}$ day^{-1}		[120]
	5.0 x 10^{-8} mL(cell)$^{-1}$ day^{-1}		[12]
	1.9 x 10^{-1} mg(g fungi)$^{-1}$ day^{-1}		[94]
Methyl anisate	1.3 x 10^{-8} mL(cell)$^{-1}$ day^{-1}		[168]
Methyl benzoate	1.7 x 10^{-8} mL(cell)$^{-1}$ day^{-1}		[168]
Mirex	0		[146]
Nitrilotriacetate (NTA)	0.05-0.23 day^{-1}	k	[92]
Parathion	$t_{1/2}$ = >4250 days		[166]
Paraoxon	$t_{1/2}$ = >4250 days		[166]
p-Cresol	1.24 x 10^{-5} mL(cell)$^{-1}$ day^{-1}		[146]
Phenol	0.079 day^{-1}		[93]
Propham (IPC)	0.003-2.1 mg(g bacteria)$^{-1}$ day^{-1}		[167]
Quinoline	7.4 x 10^{-5} mL(cell)$^{-1}$ day^{-1}		[146]
Triallate	$t_{1/2}$ ≈ 680 days 0pH 6,8)		[145]
	≈ 1170 days (pH 7)		[145]
2,4,5-T	0.001 day^{-1}		[93]
	0.01-0.03 day^{-1}	d,l	[93]
1,4,5-Trichlorophenoxy-acetic acid	0.0005 day^{-1}		[93]
	0.0012-0.012 day^{-1}	d,l	[93]

a. All tests assumed to be river die-away.
b. First value is mean for days 0-15; second is for days 20-65.
c. First-order half-life in aqueous solution.
d. In sediment (slurry).
e. Range due to measurement in different samples of river water.
f. Rate constant does not account for lag period.
g. Degradation by yeast culture (*Rhodotorula glutinis*).
h. Degradation by bacterial culture (*Bacillus subtilus*).
i. First value from unacclimated microbial population, second from acclimated population.
j. River water bacterial culture.
k. Dissolved concentrations ranging from 0.2 mg/L to saturation.
l. Temperature range 9-21°C.

TABLE 9-17

Biodegradation Rate Constants for Organic Compounds in Soil[a] (day^{-1})

Compound	Test Method	
	Die-Away	$^{14}CO_2$ Evolution
Aldrin, Dieldrin	0.013	
Atrazine	0.019	0.0001
Bromacil	0.0077	0.0024
Carbaryl	0.037	0.0063
Carbofuran	0.047	0.0013
Dalapon	0.047	
DDT	0.00013	
Diazinon	0.023	0.022
Dicamba	0.022	0.0022
Diphenamid		0.123[b]
Fonofos	0.012	
Glyphosate	0.1	0.0086
Heptachlor	0.011	
Lindane	0.0026	
Linuron	0.0096	
Malathion	1.4	
Methyl parathion	0.16	
Paraquat	0.0016	
Parathion	0.029	
Phorate	0.0084	
Picloram	0.0073	0.0008
Simazine	0.014	
TCA	0.059	
Terbacil	0.015	0.0045
Trifluralin	0.008	0.0013
2,4-D	0.066	0.051
2,4,5-T	0.035	0.029

a. All constants are from soil incubation studies. Except where noted, source is Rao and Davidson [131], a compilation of first-order rate constants derived from data published from other studies.

b. Optimum degradation rate, from Donigan *et al.* [36]. Test method not specified.

TABLE 9-18

Biodegradation Rate Constants for Organic Compounds in Anaerobic Systems (day^{-1})

Compound	In Soil[a]		In Sewage Sludge[b]
	Die-Away	$^{14}CO_2$ Evolution	
Carbofuran	0.026		
DDT	0.0035		
Endrin	0.03		
Lindane		0.0046	
PCP		0.07	
Trifluralin	0.025		
Mirex			0.0192
Methoxychlor			9.6
2,3,5,6-Tetrachlorobenzene			12.72
Bifenox			6.27

a. *Flooded soil incubation studies as reported in Rao and Davidson [131], a compilation of* first-order rate constants derived from data published from other sources.

b. As reported by Geer [45]. Test method not specified.

variables influence biodegradation rates. In a laboratory experiment, most of the variables are controlled, and results derived under the same conditions can be compared; natural habitats, on the other hand, have numerous unpredictable elements, and at least one of these elements is likely to cause the biodegradation rate to differ from the value obtained in the laboratory.

Besides the differences in the control of variables between laboratory and field conditions, certain basic, unavoidable differences caused by the constraints of the laboratory further complicate the extrapolation process:

- The microbial population isolated for an experiment cannot truly reflect the diversity of the environment it represents.
- To save time in the laboratory, experimental nutrient conditions are often better than those found in the environment. Organic matter concentrations are commonly 1-10 g/L in culture media but only 1-10 mg/L in nature [21]
- High substrate and microbial concentrations must be used in most experiments to generate quick results.

TABLE 9-19

Rate Constants for Biodegradation of Organic Compounds by Activated Sludge Cultures

Compound	Rate Constant	Reference
Chlorodiphenyl oxide	8.9×10^2 mL $(gVS)^{-1}$ day^{-1}	[20]
Linear alkyl benzene sulfonate (LAS)	0.10 day^{-1}	[92]
Glucose	0.20 day^{-1}	[92]
	0.36 day^{-1} [a]	[153]
	6.6×10^3 mg (g bacteria)$^{-1}$ day^{-1} [a]	[153]
	$1.7\text{-}9.1 \times 10^3$ mg (g sludge)$^{-1}$ day^{-1}	[119]
Galactose	2.6×10^3 mg (g bacteria)$^{-1}$ day^{-1} [a]	[153]
Fructose	$1.6\text{-}4.4 \times 10^3$ mg (g sludge)$^{-1}$ day^{-1}	[119]
Sucrose	$3.8\text{-}16.8 \times 10^3$ mg (g sludge)$^{-1}$ day^{-1}	[119]
2,4-D	6.9×10^{-2} mL (g bacteria)$^{-1}$ day^{-1}	[64]

a. Specific substrate utilization rate.

Biodegradation rate constants have several applications. One is the comparison of disappearance rates for a series of compounds; another is the comparison with rates measured for other loss processes, such as hydrolysis, for the same chemical. In situations where the conditions of a specific habitat have quantified or are well understood and their effect has been observed in the laboratory, a meaningful extrapolation is possible. Ideally, investigations will continue from this point, analyzing the persistence of a chemical in field conditions under various climatic and habitat regimes, such as was done by Hamaker *et al.* [56] for picloram in soil.

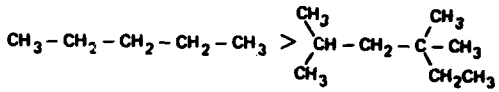
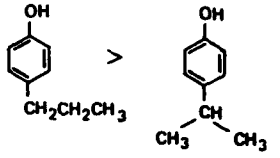
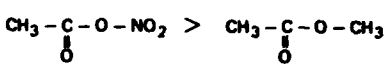
9-5 ESTIMATION OF BIODEGRADATION RATES

Two general methods of estimation are covered in this section:

(1) Rules of thumb for obtaining a qualitative and relative estimate of biodegradation based on structural factors and on chemical class (Table 9-20). These generalizations are applicable only to the specific groups of chemicals in which

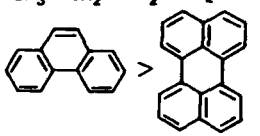
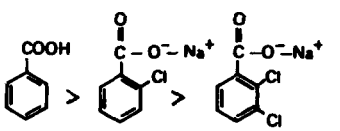
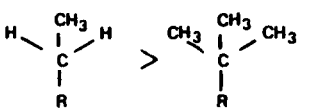
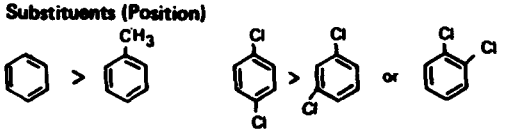
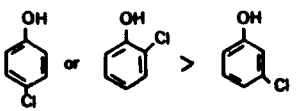
TABLE 9-20

RULES OF THUMB FOR BIODEGRADABILITY

Factors	Schematic Example[a]
Branching — Highly branched compounds are more resistant to biodegradation. 1) Unbranched side chains on phenolic and phenoxy compounds are more easily metabolized than branch alkyl moieties [164]. 2) 2,4-Dichlorophenoxyalkanates with side chains of 4 or more carbons degraded easily, the propionate more slowly, and the dichlorophenoxyacetate not at all by a *Flavobacterium* sp. [99]. 3) Branched alkyl benzene sulfonates degrade more slowly than straight-chain [156].	**Branching**  
Chain Length — Short chains are not as quickly degraded as long chains. 1) Rate of oxidation of straight-chain aliphatic hydrocarbons is correlated to length of chain [89]. 2) Soil micros attack long-chain mononuclear aromatics faster than short-chain [152]. 3) Micros grow on normal alkanes from n-octane to n-eicosane but not on n-heptane to methane [43]. 4) Sulfate-reducing bacteria more rapidly degrade long-length carbon chains (decane to hentriacontane) than short-length carbon chains [22]. 5) ABS detergents increase in degradability with increase in chain length from C_6 to C_{12} but not $> C_{12}$ [73, 156]. 6) Rate of mineralization of N in urea-formaldehyde complexes declines with increasing ureaform chain [96].	**Chain Length** 
Oxidation — Highly oxidized compounds, like halogenated compounds, may resist further oxidation under aerobic conditions but may be more rapidly degraded under anaerobic conditions [50, 55, 63, 67].	
Polarity and Ionization — Non-ionic compounds with active halogens are likely to be degraded by nucleophilic displacement reactions like hydrolysis. Same is true of linkages separating highly polar groups [50].	**Polarity** 
Saturation — Unsaturated aliphatics are more readily attacked than corresponding saturated hydrocarbons, perhaps because of presence of many ethylene reducing enzyme systems and few ethane ones.	**Saturation**

(Continued)

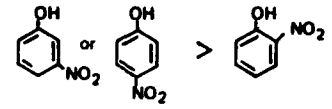
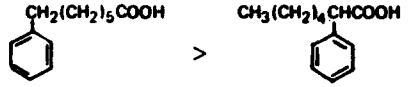
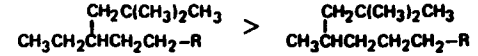
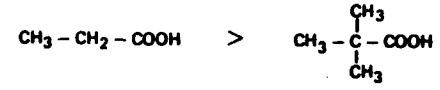
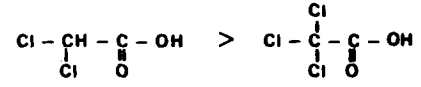
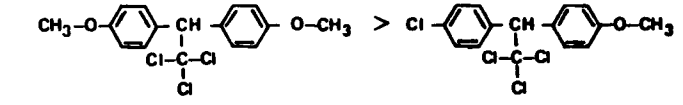
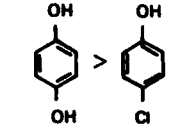
TABLE 9-20 (Continued)

Factors	Schematic Example[a]
Substituents (Number of) on Simple Organic Molecules	**Substituents (Number of)**
1) Alcohols, aldehydes, acids, esters, amides, and amino acids are more susceptible to biodegradation than the corresponding alkanes, olefins, ketones, dicarboxylic acids, nitriles, amines, and chloroalkanes [118].	(1) $CH_2OH-CH_2-CH_3 > CH_3-CH_2-CH_3$; $NH_2-CH_2-COOH > NH_2-CH_3$; $CH_3-\overset{\overset{O}{\|}}{C}H > CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
2) Increased substitution hinders oxidation responsible for breakdown of alkyl chains [57].	(2) $CH_3-CH_2-CH_2-CH_2-R > CH_3-\underset{OH}{CH}-\underset{Cl}{CH}-\underset{NH_2}{CH}-R$
3) No significant oxidation of polycyclic aromatic hydrocarbons containing more than three rings [104].	(3) 
4) Longer persistence of chloroacetic acids, α-substituted propionic acids, isopropyl N-phenylcarbamates, and isopropyl phenylcarbamates with greater number of chlorines [81].	
5) Diaminobenzenes show less availability than monoaminobenzenes [9].	
6) On aromatic ring: benzoic acid quickly degraded; monochloro- and monofluoro benzoates are more resistant but can be degraded; di-, tri- and tetra- are quite resistant. The more chlorines, the more resistant the compound [99].	(6) 
7) Presence of more than one methyl group attached to a carbon strongly inhibits alkane utilization [100].	(7) 
Substituents (Position of) on Simple Organic Molecules	**Substituents (Position)**
1) Aromatics with methyl, chloro, nitro, or amino are generally not available to bacteria which are active on unsubstituted molecules, or they are decomposed more slowly. But para is more utilized than ortho or meta. [10, 15, 25, 65, 87, 99, 158a].	(1) 
2) Meta-disubstituted phenols and phenoxys more resistant than ortho or para isomers [8].	
3) Mono-, di-, and tri-chlorophenols with halogen meta to hydroxyl, phenoxyalkanoic acids with chlorine meta to ether oxygen, and benzoic acids with meta-amino, nitro, or methoxy groups are less readily degraded than corresponding isomers with substituents in ortho or para positions [8, 9, 23, 85, 99].	(3) 

(Continued)

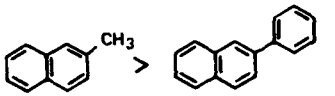
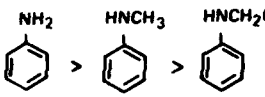
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TABLE 9-20 (Continued)

Factors	Schematic Example[a]
Substituents (Position of) (Cont.)	
4) On the other hand, ortho isomers of nitrophenols, methylanilines, sulfonates of 1-phenyldodecane, and chlorine-containing isopropyl phenylcarbonates are most persistent [9, 31, 157].	(4) 
5) In fatty acids, introduction of halogen or phenyl group on alpha carbon reduces rate of degradation as opposed to same group on omega carbon [23, 34].	(5) 
6) Parahydroxybenzoate degrades more rapidly than ortho or meta (fewer micros degrade these) [148].	
7) For ABS, para sulfonates are more readily degraded than ortho sulfonates of phenyldodecane and phenyltetradecane. In diheptylbenzene sulfonates the meta is more susceptible than the *para* substituent [156, 157].	
8) Neo-pentyl group addition inhibits alkane utilization if carbon atom bonded is next to last on the chain [100].	(8) 
Substituents (Type of) on Simple Organic Molecules	Substituent (Type)
1) Mono- and dicarboxylic acids, aliphatic alcohols, and ABS are decreasingly degraded when hydrogen is replaced by methyl groups [34, 57, 155].	(1) 
2) Aliphatic acids are less easily degraded when chlorine replaces a hydrogen [34].	(2) 
3) Triazines or methoxychlor is less easily degraded when methoxy groups are replaced by chlorines [61].	(3) 
4) Degradation of disubstituted benzenes is less when carboxyl or hydroxyl is replaced by nitro, sulfonate or chloro group [9].	(4) 

(Continued)

TABLE 9-20 (Continued)

Factors	Schematic Example[a]
Substituents (Type of) (Cont.)	
5) Successive replacement of hydroxyls of cyanuric acid with amino groups makes compounds less degradable [61].	
6) For naphthalene compounds, nuclei bearing single small alkyl groups (methyl, ethyl or vinyl) oxidize at more rapid rate than those with a phenyl substituent [104].	(6) 
7) 3-phenyl -1,1-dimethylurea (fenuron) is more rapidly degraded than 3-(p-chlorophenyl)... (monuron), or 3-(3,4-dichlorophenyl)... (diuron) [143].	
8) *N*-substituent *methyl and ethyl groups in anilines are* harder to oxidize [1].	(8) 
9) Dehalogenation may be specific for the halide substituent (e.g., 3-chloro-propionate, not 3-bromo-; tribromoacetate, *not trifluoro*) [69].	(9) $Cl_3CCOOCH_3$ > $Br_3CCOOCH_3$
Miscellaneous	
1) Ether functions are sometimes particularly resistant to biodegradation [140].	
2) Alkyl and quaternary groups attached via oxygen to phosphorus atoms increase stability, possibly through steric blocking of ester bond [115].	

a. ">" implies "more easily degradable than"

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they have been observed. They are also dependent on test method, on the species responsible for biodegradation, on the definition of biodegradation, and other variables.

(2) Correlations observed between the biodegradability of certain chemical groups and fundamental properties that have been investigated in a relatively systematic way.

No attempt is made here to correlate the results of these estimation techniques with biodegradation rate constants measured under standard conditions. The reason is the lack of a data base to support quantification of these relationships.

None of the following estimation techniques is recommended for use in predicting biodegradation rates, because (1) it is not consistently valid, being based on gross assumptions (such as that BOD represents biodegradation), or (2) it has not been tested for more than a few chemicals or chemical groups.

Some empirical relationships between biodegradability and molecular characteristics are listed in Table 9-20. Correlations with other chemical properties are described below.

Solubility. Water-insoluble compounds are thought to persist longer than those that are water-soluble [1,3]. Little quantitative work has been done on microbial degradation of the former compounds, but Alexander [3] suggests the following possible reasons for this behavior:

(1) Inability of the compound to reach the reaction site in the microbial cell;

(2) A reduced rate of reaction when biodegradation is regulated by the rate of solubilization; and

(3) The inaccessibility of insoluble compounds because of increased adsorption or trapping in inert material due to insolubility.

A correlation between solubility and the biodegradability index (B.I.) was found [80] for DDT analogs in osquito fish (*Gambusia affinis*). However, as the focus of this chapter is on microbial biodegradation, this relationship will not be discussed here.

BOD/COD. Several methods have been proposed for estimating the biodegradability of organic compounds, two of which are described below. The limitations of such approaches have been described in the

discussion of analytical techniques in §9-3; briefly stated, the concepts of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) assume that all carbon is assimilated into new biomass and that the transformation from substrate to biomass is not inhibited by the compound under investigation or by any other substances in the test medium. COD and BOD may involve different sites of reaction and degrees of reactivity. Moreover, the reactivity of a site in COD depends on the reagent used. The results, with the exception of Pitter's approach [128], provide only an index of degradability, not the rate of degradation.

Several approaches for estimating biodegradability of organic compounds are based on the ratio between BOD and either COD or UOD (ultimate oxygen demand). Lyman [97] classified a number of chemicals into categories of biodegradability based on the BOD/COD ratio. Compounds with a ratio less than 0.01 were classified as relatively undegradable, between 0.01 and 0.1 as moderately degradable, and greater than 0.1 as relatively degradable. Table 9-21 presents BOD_5/COD ratios for various compounds.[2]

In Czechoslovakia, the Department of Water Technology and Environmental Engineering has developed a standard test, based on measurement of COD decrease, to compare the biodegradability of organic compounds [128]. Using activated sludge inoculum with 20 days of adaptation to the substrate, the decrease in the COD of a substance is calculated until no further decrease is observed. The percentage decrease of total COD is calculated as well as the rate, expressed in units of mg COD removed per gram of initial biomass (dry weight) of inoculum per hour. Pitter [128] tabulated these data for 94 aromatic, 15 cycloaliphatic, and 14 aliphatic compounds. Removal rates ranged over two orders of magnitude from 0 (e.g., nitroanilines and dinitrobenzenes) to 180 mg COD/g-hr (for glucose). Table 9-22 lists percentage removal and rate of biodegradation for 123 organic compounds. Pitter considered rates greater than 15 mg COD/g-hr as "readily decomposable" (defined as 90% of initial COD removed in 120 hours of incubation). Rates may be overestimated for some compounds, especially aromatics, due to a lack of control for volatilization.

The refractory index (RI) was developed to indicate the degradability of organic compounds [14,60] and to predict the persistence of a compound and its degradation products after discharge into receiving waters. It is the ratio of ultimate biochemical oxygen demand (BOD_u) to

2. BOD_5 refers to the results of a 5-day BOD test.

TABLE 9-21

BOD_5 /COD Ratios for Various Organic Compounds[a]

Compound	Ratio	Compound	Ratio
Relatively Undegradable		**Moderately Degradable (cont'd.)**	
Butane	~ 0	Mineral spirits	~ 0.02
Butylene	~ 0	Cyclohexanol	0.03
Carbon tetrachloride	~ 0	Acrylonitrile	0.031
Chloroform	~ 0	Nonanol	> 0.033
1,4-Dioxane	~ 0	Undecanol	⩽ 0.04
Ethane	~ 0	Methylethylpyridine	0.04-0.75
Heptane	~ 0	1-Hexene	< 0.044
Hexane	~ 0	Methyl isobutyl ketone	⩽ 0.044
Isobutane	~ 0	Diethanolamine	⩽ 0.049
Isobutylene	~ 0	Formic acid	0.05
Liquefied natural gas	~ 0	Styrene	> 0.06
Liquefied petroleum gas	~ 0	Heptanol	⩽ 0.07
Methane	~ 0	*sec*-Butyl acetate	0.07-0.23
Methyl bromide	~ 0	*n*-Butyl acetate	0,07-0.24
Methyl chloride	~ 0	Methyl alcohol	0.07-0.73
Monochlorodifluoromethane	~ 0	Acetonitrile	0.079
Nitrobenzene	~ 0	Ethylene glycol	0.081
Propane	~ 0	Ethylene glycol monoethyl ether	< 0.09
Propylene	~ 0	Sodium cyanide	⩽ 0.09
Propylene oxide	~ 0	Linear alcohols (12-15 carbons)	> 0.09
Tetrachloroethylene	~ 0	Allyl alcohol	0.09
Tetrahydronaphthalene	~ 0	Dodecanol	0.097
1-Pentene	< 0.002	**Relatively Degradable**	
Ethylene dichloride	0.002	Valeraldehyde	⩽ 0.10
1-Octene	> 0.003	*n*-Decyl alcohol	> 0.10
Morpholine	⩽ 0.004	*p*-Xylene	< 0.11
Ethylenediaminetetracetic acid	0.005	Urea	0.11
Triethanolamine	⩽ 0.006	Toluene	< 0.12
o-Xylene	< 0.008	Potassium cyanide	0.12
m-Xylene	< 0.008	Isopropyl acetate	⩽ 0.13
Ethylbenzene	< 0.009	Amyl acetate	0.13-0.34
Moderately Degradable		Chlorobenzene	0.15
Ethyl ether	0.012	Jet fuels (various)	~ 0.15
Sodium alkylbenzenesulfonates	~ 0.017	Kerosene	~ 0.15
Monoisopropanolamine	⩽ 0.02	Range oil	~ 0.15
Gas oil (cracked)	~ 0.02	Glycerine	⩽ 0.16
Gasolines (various)	~ 0.02	Adiponitrile	0.17

(continued)

TABLE 9-21 (Continued)

Compound	Ratio	Compound	Ratio
Relatively Degradable (cont'd.)		**Relatively Degradable (cont'd.)**	
Furfural	0.17-0.46	Ethyleneimine	0.46
2-Ethyl-3-propylacrolein	<0.19	Monoethanolamine	0.46
Methylethylpyridine	<0.20	Pyridine	0.46-0.58
Vinyl acetate	<0.20	Dimethylformamide	0.48
Diethylene glycol monomethyl ether	≤ 0.20	Dextrose solution	0.50
Naphthalene (molten)	≤ 0.20	Corn syrup	~ 0.50
Dibutyl phthalate	0.20	Maleic anhydride	≥ 0.51
Hexanol	~ 0.20	Propionic acid	0.52
Soybean oil	~ 0.20	Acetone	0.55
Paraformaldehyde	0.20	Aniline	0.56
n-Propyl alcohol	0.20-0.63	Isopropyl alcohol	0.56
Methyl methacrylate	<0.24	*n*-Amyl alcohol	0.57
Acrylic acid	0.26	Isoamyl alcohol	0.57
Sodium alkyl sulfates	~ 0.30	Cresols	0.57-0.68
Triethylene glycol	0.31	Crotonaldehyde	<0.58
Acetic acid	0.31-0.37	Phthalic anhydride	0.58
Acetic anhydride	≥ 0.32	Benzaldehyde	0.62
Ethylenediamine	≤ 0.35	Isobutyl alcohol	0.63
Formaldehyde solution	0.35	2,4-Dichlorophenol	0.78
Ethyl acetate	≤ 0.36	Tallow	~ 0.80
Octanol	0.37	Phenol	0.81
Sorbitol	≤ 0.38	Benzoic acid	0.84
Benzene	<0.39	Carbolic acid	0.84
n-Butyl alcohol	0.42-0.74	Methyl ethyl ketone	0.88
Propionaldehyde	<0.43	Benzoyl chloride	0.94
n-Butyraldehyde	≤ 0.43	Hydrazine	1.0
		Oxalic acid	1.1

a. BOD_5 values were not measured under the same conditions for all chemicals.

Source: Lyman [97].

TABLE 9-22

COD Removal and Rate of Removal for Various Compounds

Compound	Percent Removed[a] (based upon COD)	Average Rate of Biodegradation (mg COD g^{-1} hr^{-1})
Aliphatic Compounds		
Ammonium oxalate	92.5	9.3
n-Butanol	98.8	84.0
sec-Butanol	98.5	55.0
tert-Butanol	98.5	30.0
1,4-Butanediol	98.7	40.0
Diethylene glycol	95.0	13.7
Diethanolamine	97.0	19.5
Ethylene diamine	97.5	9.8
Ethylene glycol	96.8	41.7
Glycerol	98.7	85.0
Glucose	98.5	180.0
n-Propanol	98.8	71.0
Isopropanol	99.0	52.0
Triethylene glycol	97.7	27.5
Cycloaliphatic Compounds		
Borneol	90.3	8.9
Caprolactam	94.3	16.0
Cyclohexanol	96.0	28.0
Cyclopentanol	97.0	55.0
Cyclohexanone	96.0	30.0
Cyclopentanone	95.4	57.0
Cyclohexanolone	92.4	51.5
1,2-Cyclohexanediol	95.0	66.0
Dimethylcyclohexanol	92.3	21.6
4-Methylcyclohexanol	94.0	40.0
4-Methylcyclohexanone	96.7	62.5
Menthol	95.1	17.7
Tetrahydrofurfuryl alcohol	96.1	40.0
Tetrahydrophthalimide	0	–
Tetrahydrophthalic acid	0	–
Aromatic Compounds		
Aniline	94.5	19.0
Aminophenolsulfonic acid	64.6	7.1
Acetanilide	94.5	14.7

(continued)

TABLE 9-22 (Continued)

Compound	Percent Removed[a] (based upon COD)	Average Rate of Biodegradation (mg COD g^{-1} hr^{-1})
Aromatic Compounds (cont'd.)		
p-Aminoacetanilide	93.0	11.3
o-Aminotoluene	97.7	15.1
m-Aminotoluene	97.7	30.0
p-Aminotoluene	97.7	20.0
o-Aminobenzoic acid	97.5	27.1
m-Aminobenzoic acid	97.5	7.0
p-Aminobenzoic acid	96.2	12.5
o-Aminophenol	95.0	21.1
m-Aminophenol	90.5	10.6
p-Aminophenol	87.0	16.7
Benzenesulfonic acid	98.5	10.6
m-Benzenedisulfonic acid	63.5	3.4
Benzaldehyde	99.0	119.0
Benzoic acid	99.0	88.5
o-Cresol	95.0	54.0
m-Cresol	95.5	55.0
p-Cresol	96.0	55.0
d-Chlorampnenicol	86.2	3.3
o-Chlorophenol	95.6	25.0
p-Chlorophenol	96.0	11.0
o-Chloroaniline	98.0	16.7
m-Chloroaniline	97.2	6.2
p-Chloroaniline	96.5	5.7
2-Chloro-4-nitrophenol	71.5	5.3
2,4-Dichlorophenol	98.0	10.5
1,3-Dinitrobenzene	0	–
1,4-Dinitrobenzene	0	–
2,3-Dimethylphenol	95.5	35.0
2,4-Dimethylphenol	94.5	28.2
3,4-Dimethylphenol	97.5	13.4
3,5-Dimethylphenol	89.3	11.1
2,5-Dimethylphenol	94.5	10.6
2,6-Dimethylphenol	94.3	9.0
3,4-Dimethylaniline	76.0	30.0
2,3-Dimethylaniline	96.5	12.7
2,5-Dimethylaniline	96.5	3.6
2,4-Diaminophenol	83.0	12.0
2,4-Dinitrophenol	85.0	6.0

(continued)

TABLE 9-22 (Continued)

Compound	Percent Removed[a] (based upon COD)	Average Rate of Biodegradation (mg COD g^{-1} hr^{-1})
Aromatic Compounds (cont'd.)		
3,5-Dinitrobenzoic acid	50.0	–
3,5-Dinitrosalicylic acid	0	–
Furfuryl alcohol	97.3	41.0
Furfurylaldehyde	96.3	37.0
Gallic acid	90.5	20.0
Gentisic acid	97.6	80.0
p-Hydroxybenzoic acid	98.7	100.0
Hydroquinone	90.0	54.2
Isophthalic acid	95.0	76.0
Metol	59.4	0.8
Naphthoic acid	90.2	15.5
1-Naphthol	92.1	38.4
1-Naphthylamine	0	0
1-Naphthalenesulfonic acid	90.5	18.0
1-Naphthol-2-sulfonic acid	91.0	18.0
1-Naphthylamine-6-sulfonic acid	0	0
2-Naphthol	89.0	39.2
p-Nitroacetophenone	98.8	5.2
Nitrobenzene	98.0	14.0
o-Nitrophenol	97.0	14.0
m-Nitrophenol	95.0	17.5
p-Nitrophenol	95.0	17.5
o-Nitrotoluene	98.0	32.5
m-Nitrotoluene	98.5	21.0
p-Nitrotoluene	98.0	32.5
o-Nitrobenzaldehyde	97.0	13.8
m-Nitrobenzaldehyde	94.0	10.0
p-Nitrobenzaldehyde	97.0	13.8
o-Nitrobenzoic acid	93.4	20.0
m-Nitrobenzoic acid	93.4	7.0
p-Nitrobenzoic acid	92.0	19.7
o-Nitroaniline	0	–
m-Nitroaniline	0	–
p-Nitroaniline	0	–
Phthalimide	96.2	20.8
Phthalic acid	96.8	78.4
Phenol	98.5	80.0
Phloroglucinol	92.5	22.1

(continued)

TABLE 9-22 (Continued)

Compound	Percent Removed[a] (based upon COD)	Average Rate of Biodegradation (mg COD g^{-1} hr^{-1})
Aromatic Compounds (cont'd.)		
N-Phenylanthranilic acid	28.0	–
o-Phenylendiamine	33.0	–
m-Phenylendiamine	60.0	–
p-Phenylendiamine	80.0	–
Pyrocatechol	96.0	55.5
Pyrogallol	40.0	–
Resorcinol	90.0	57.5
Salicylic acid	98.8	95.0
Sulfosalicylic acid	98.5	11.3
Sulfanilic acid	95.0	4.0
Thymol	94.6	15.6
p-Toluenesulphonic acid	98.7	8.4
2,4,6-Trinitrophenol	0	–

a. "Percent Removed" represents to what extent the reaction goes before stopping.

Source: Pitter [128].

UOD, indicating the proportion of the theoretical total oxidation of an organic compound that is attributed to bacterial action. An RI approaching 1.0 indicates that a substance is readily degraded to the point of mineralization. An error factor of approximately 13% is associated with the RI because of interactions with microorganisms. Refractory indices for 25 compounds are listed in Table 9-23.

Hydrolysis. Structure-activity relationships between second-order alkaline hydrolysis rate constants (k_{OH}) and microbial degradation rate constants (k_b) have been reported for two groups of esters [13,168]. Figure 9-15 is a plot of the correlation between hydrolysis and biodegradation for the two groups of chemicals. The curve is described by the equation:

$$\log k_b = m \log k_{OH} + c \qquad (9\text{-}7)$$

The specific compounds which were tested are listed in Figure 9-15. The authors discussed similar relationships found by analyzing data for substituted phenols [158a]. Although further study on other chemical groups is needed, these correlations comprise a significant step forward in relating the biodegradation of some substances to other

TABLE 9-23

Refractory Indices for Various Organic Compounds

Compound	RI	Compound	RI
High Degradability		**Low Degradability**	
Biphenyl	1.14	Benzene	0.23
Antifreeze	1.12	Gasoline	0.21
Sevin	1.0	Adenine	0.14, 0.12
d-Glutamic acid	1.00	Vinyl chloride	0
d-Glucose	0.93	Carboxymethyl cellulose	0
l-Valine	0.93	Humics	0
Acetone	0.93, 0.71	DDT with carrier	0
Phenol	0.87	*p*-Chlorophenol	0
Sodium butyrate	0.84	Dichlorophenol	<0
l-Aspartic acid	0.81	DDT	<0
Sodium propionate	0.80	Bipyridine	<0
Propylene glycol	0.78, 0.52	Chloroform	<0
Ethylene glycol	0.76	Cyanuric Acid	<0
Medium-High Degradability			
Potato Starch	0.72, 0.64		
l-Arginine	0.65		
Acetic acid	0.61		
Aniline	0.58		
Soluble starch	0.54		
l-Histidine	0.52		
l-Lysine	0.52		
Hydroquinone	0.41		

Source: Bedard [14] and Helfgott *et al.* [62].

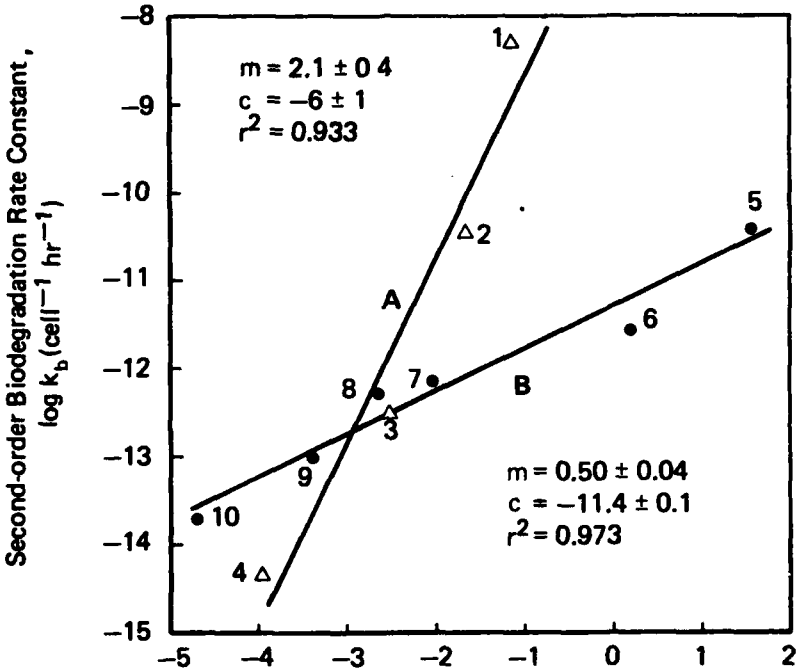
chemical properties. The relationship may not be applicable to all classes of chemicals.

9-6 AVAILABLE DATA

Degradability and Degradation Pathways of Organic Compounds

Chapman, P.J. [26] — Classification of common metabolic pathways associated with biodegradation of organics.

Menzie, C.M. [107,108] — Extensive review of the metabolism of pesticides by microorganisms and higher organisms in all systems.



Curve A compounds:

1 – Dimethyl phthalate
2 – Di–n–butyl phthalate
3 – Di–*n*–octyl phthalate
4 – Di–(2–ethylhexyl) phthalate

Curve B compounds:

5 – n–Butoxyethyl ester of 2,4–D
6 – Malathion
7 – Methyl benzoate
8 – Methyl anisate
9 – Methoxychlor
10 – Chlorpropham

k_B *measured in natural water samples at* 25°C
k_{OH} measured in distilled water at 30°C(A) and 27°C(B)

Source: Wolfe et al. [168]

FIGURE 9–15 Correlation of Second-order Alkaline Hydrolysis Rate Constants with Second-order Biodegradation Rate Constants for Two Groups of Compounds

Goring, C.A.I., *et al.* [50] — Review of biodegradation pathways.

Matsumara, F. [102] — Review of degradation of pesticides in soil.

Kaufman, D.D. [82] — Review of degradation of pesticides in soil.

Kaufman, D.D. [83] — Review of degradation of pesticides in soil, including tables of half-lives.

Meikle, R.W. [105] — Review of degradation of organic compounds in soil.

NAS [114a] — Collection of papers on the degradation of synthetic organic molecules in the environment.

Miller, M.W. [109] — Handbook compiling all known microbial metabolites, organized by chemical group.

Rao, P.S.C. and J.M. Davidson [131] — Compilation of biodegradation rate constants measured in soil.

Pfister, R.M. [126] — Review of biodegradation of halogenated pesticides.

Sanborn, J.R. *et al.* [139] — Extensive literature review of degradation reactions and metabolites of selected pesticides in soil.

Williams, P.P. [166] — Review of anaerobic metabolic pathways for various pesticides.

Bollag, J.M. [16] — Review of degradation of pesticides by soil fungi.

Swisher, R.D. [155] — Book on biodegradation of surfactants.

Hill, I.R. and S.J.L. Wright [68] — Collection of review articles on microbial degradation of pesticides in all environments.

Matsumara, F. and H.J. Benezet [103] — Review of degradation of insecticides.

Cripps, R.E. and T.R. Roberts [29] — Review of degradation of herbicides.

Woodcock, D. [171] — Microbial degradation of fungicides, fumigants, and nematocides by chemical group and discussion of how application method affects degradation.

Biology and Ecology of Microorganisms

Alexander, M. [2] — Textbook on microbial ecology.

Brock, T.D. [21] — Textbook on microbial biology.

Stotzky, G. [151] — Article on microorganisms in soil environment.

Gaudy, A. and E. Gaudy [44] — Text on environmental microbiology and applications to wastewater treatment.

Gray, T.R.G. *et al.* [53] — Article on microorganisms in soil, aquatic and air environments in biota.

Alexander, M. [5] — Text on soil microorganisms and ecology.

Mitchell, R. [110] — Collection of articles on water pollution microbiology.

Jones, J.G. [77,78] — Ecology of freshwater microorganisms.

Bourquin, A.W. and P.H. Pritchard [18] — Collection of articles on aquatic microbial degradation of pollutants in marine environments.

Colwell, R.R. and R.Y. Morita [28] — Textbook on marine microbiology.

Wood, E.J.F. [169] — Textbook on marine microbiology.

Wood, E.J.F. [170] — Textbook on marine and estuarine microbiology.

Rodina, R.G. [138] — Textbook on aquatic microbiology.

Stevenson, L.H. and R.R. Colwell [150] — Textbook on estuarine microbiology.

Curds, C.R. and H.A. Hawkes [31] — Article on waste water microbiology.

Biodegradation Test Methods

Howard, P.H. *et al.* [72]

Swisher, R.D. [155]

TSCA [162]

Kinetics of Microbial Degradation

Hamaker, J.W. [55] — Discussion of degradation kinetics, degradation in soil, variables affecting degradation, application to field environment.

Larson, R.J. [92] — Discussion of degradation kinetics.

Rules of Thumb

Kearney, P.C. and J.R. Plimmer [85] — Discussion of relation of chemical structure to degradation in pesticides.

Alexander, M. [1,3] — Discussion of factors (environmental, biological, and physico-chemical) responsible for recalcitrance of chemicals in natural systems.

Kaufman, D.D. [81] — Discussion of relation of structure to degradation of pesticides.

Other Sources

Thom, N.S. and A.R. Agg [160] — Classification of over 200 synthetic organic compounds into 3 categories of degradability by biological sewage treatment.

Helfgott, T.B. *et al.* [62] — Review of laboratory techniques to derive refractory index (BOD/UOD ratio) and compilation of indices for 38 organic compounds.

Bedard, R.G. [14] — Compilation of refractory indices for organic compounds.

Tabak, H.H. [158b] — Compilation of results from static flask die-away experiments on 96 organic compounds.

9-7 SYMBOLS AND ABBREVIATIONS

A	=	initial rate of reaction in Eq. 9-1
ABS	=	alkyl benzene sulfonate
[B]	=	microbial population concentration in Eq. 9-4
BI	=	biodegradability index
BOD	=	biological (or biochemical) oxygen demand
[C]	=	substrate concentration
c	=	parameter in Eq. 9-7
COD	=	chemical oxygen demand
DO	=	dissolved oxygen
DOC	=	dissolved organic carbon
E_a	=	activation energy in Eq. 9-1
k	=	biodegradation rate constant in Eq. 9-2
K_c	=	concentration of substrate supporting a half-maximum growth rate
k_b	=	second-order biodegradation rate constant in Eq. 9-7
k_{OH}	=	second-order hydrolysis rate constant in Eq. 9-7
m	=	parameter in Eq. 9-7
n	=	order of reaction in Eq. 9-2
PAH	=	polycyclic aromatic hydrocarbon
R	=	gas constant
RI	=	refractory index
T	=	temperature (absolute)

t	=	time
U	=	microorganism specific growth rate in Eq. 9-3
U_{max}	=	microorganism maximum growth rate in Eq. 9-3
UOD	=	ultimate oxygen demand
Y	=	rate of reaction (after Arrhenius temperature correction) in Eq. 9-1
Y_d	=	yield coefficient in Eq. 9-4

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10

ATMOSPHERIC RESIDENCE TIME

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10-1 INTRODUCTION

The residence time of a chemical in a specified atmospheric compartment (total atmosphere, troposphere, stratosphere, etc.) is well defined only under steady-state conditions, i.e., when the total mass and the statistical distribution in the compartment do not vary with time. In such cases the residence time, τ, may be simply defined as the ratio of the total mass in the compartment (Q) to the total emission rate (E) or removal rate (R):

$$\tau \equiv Q/E = Q/R \qquad (10\text{-}1)$$

In this equation, E is the sum of all land, fresh water and ocean emissions to the atmosphere plus any other inputs, such as in-situ generation in the atmosphere. Similarly, R is the sum of all losses from the compartment, not only by outflow to land, ocean, and space but also by in-situ degradation. More formal definitions of atmospheric residence time (also called "turn-over time" or "average transit time") are given by Bolin and Rodhe [3] and Slinn [31].

Note that τ is *not* the same as the "average age" of a pollutant molecule in the compartment, nor is it equal to the "half-life" of the pollutant. When the removal rate (R) for a chemical is due solely to some first-order loss process, then the half-life ($t_{1/2}$) and τ are related as follows:

$$t_{1/2} = 0.693\,\tau \qquad (10\text{-}2)$$

Atmospheric residence time, unlike the other properties discussed in this handbook, cannot be directly measured.[1] It must be calculated or inferred on the basis of a simplified model of the atmosphere. When very simple models are chosen (steady-state, well-mixed atmosphere, uniform distribution of sources and sinks, etc.), the only requisite chemical-specific data may be such numbers as total emission rates, atmospheric concentrations, and/or reactivities.

Since residence time cannot be directly measured, this chapter can give no "measured values" with which estimated values can be compared. In the few cases where adequate data are available, an estimate may be compared with others obtained by different methods, but there are no firm rules for deciding which is the most reliable.

The number of ways by which atmospheric residence times can be estimated is limited only by the imagination of the modeler, the available data, and the computation facilities available. The five methods described in this chapter, which are listed below, can be solved without a computer and do not require voluminous data in the computations.

- Steady-state model [3,31]
- Nonsteady-state model, one compartment [25,30]
- Nonsteady-state model for two compartments [26,30]
- Use of chemical reactivity data [4,31]
- Correlation with mean standard deviation (Junge's correlation) [17]

These methods are intended only for calculating tropospheric residence times,[2] although residence times in other compartments (total atmosphere, stratosphere, portions of the troposphere, etc.) may be calculated if the appropriate data are available. The above methods are applicable to both organic and inorganic chemicals, although reactivity of inorganic chemicals is not addressed here.

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1. It is possible, if wall interference is negligible, to measure the rate of disappearance of a chemical in a small test chamber designed to simulate atmospheric conditions. This can yield valuable information on losses to be expected via chemical or photochemical reactions, but it may not give a true indication of the residence time of relatively unreactive chemicals.

2. The troposphere, which extends up to about 8-12 km, is a well-mixed compartment (for most pollutants) and contains a large fraction of the atmospheric mass; the overlying stratosphere is not well mixed. The lower part of the troposphere (the earth's boundary layer), which extends from the earth's surface up to approximately one kilometer, generally contains higher levels of some components such as carbon dioxide, water, and suspended particulate matter.

Estimation of the tropospheric residence time for a chemical can yield valuable insights into its atmospheric fate and the effectiveness of the processes by which it is removed. If, for example, a chemical has a residence time of ten years or more, appreciable quantities may enter the stratosphere, where special reactions (e.g., ozone depletion) may be a concern. Such a residence time also indicates that tropospheric degradation (by direct photolysis, reaction with hydroxyl radical or ozone, etc.) and removal via wet and dry fallout occur very slowly relative to the input rate.

However, atmospheric residence time is not an intrinsic property of a chemical, nor is it even well defined for a given chemical in a specified compartment. It is a rough measure, averaged over both space and time, of the input fluxes and removal processes acting on the chemical in a somewhat arbitrarily defined atmospheric compartment.

The residence time of a pollutant is affected by many factors, such as latitude, input flux, and various atmospheric phenomena. Most of the latter are associated with characteristic time scales. For example, precipitation and the temperature and density of the atmosphere are subject to seasonal cycles; the prevalence of OH radicals follows both diurnal and seasonal cycles, because the formation of these radicals is light-induced. Some other time scales are listed in Table 10-1.

10-2 SELECTION OF APPROPRIATE METHOD

Method selection should be based on several considerations, including:

(1) the appropriateness of the method and the assumptions implied,

(2) the nature and quality of the available data,

(3) the value of τ, and, to a lesser degree,

(4) the complexity of the calculations.

For each of the five methods described in this chapter, Table 10-2 lists information on data requirements, most applicable ranges, and advantages and limitations. The data requirements are more explicitly described in Table 10-3. Table 10-2 should be used to make a preliminary selection of the most appropriate methods; a value of τ should be calculated by each of these and the results reviewed before one value is chosen.

TABLE 10-1

Time Scales for Atmospheric Phenomena

Process	Typical Time Scale	Ref.
Precipitation or nucleation scavenging	1 week	[18,31]
Vertical mixing time of troposphere	1 week	[31]
Horizontal mixing time of troposphere	1 year	[31]
Mixing between northern and southern hemispheres	1 year	[26,29]
Movement from troposphere to lower stratosphere	4 years[a]	[18]
Movement from lower stratosphere to troposphere	1 year[a]	[18]

a. Time required for exchange of air between the specified compartments. Movement from the troposphere to the lower stratosphere takes longer than the reverse process because the troposphere contains about four times as much air as the stratosphere.

In addition to the disadvantages listed in Table 10-2, all of the methods except the one based on chemical reactivity data require fairly accurate and extensive measurements of atmospheric concentrations so that a valid average value can be obtained. This average is then used to calculate the atmospheric (or tropospheric) burden, Q, for the chemical.

As previously mentioned, it is not possible to determine the absolute error associated with the estimation of atmospheric residence times, since they cannot be directly measured. Nonetheless, some aspects of the likely errors are suggested by (1) the accuracy of the input data used, (2) the appropriateness of the method selected, and (3) the values of τ obtained from the different methods used. The uncertainty associated with the accuracy of the input data should always be calculated by evaluating the propagation of errors in the equations involved. The uncertainty associated with items (2) and (3) may be assessed with the help of the information in Tables 10-2 and 10-4.

TABLE 10-2

Estimation Methods Considered

Section	Method [Ref.]	Information Required[a]	Most Applicable Range for τ	Advantages	Disadvantages and Limitations
10-3	Steady-state model [3,31]	Q, E (or R)	> 1 yr[b]	– Minimal data requirements – Simple calculation	– Valid only for steady-state conditions – E and R difficult to estimate accurately – Q uncertain, since it derives from a somewhat arbitrarily chosen tropospheric mass
10-4	Nonsteady-state, one-compartment model [25,30]	Q, A, b	> 1 yr[b]	– Allows consideration of non-steady-state conditions – Simple calculation	– Q, A, and b difficult to estimate accurately – Limited to cases where emissions increase exponentially with time
10-5	Nonsteady-state, two-compartment model [26,30]	Q_N, Q_S, A, b, τ_e	> 1 yr[b]	– Allows consideration of non-steady-state conditions – Allows northern and southern hemispheres to be considered as separate compartments	– Data requirements large – Q_N, Q_S, A, and b difficult to estimate accurately – Limited to cases where emissions increase exponentially with time – Calculations relatively difficult; may be no solution for some sets of input data

(Continued)

TABLE 10-2 (Continued)

Section	Method [Ref.]	Information Required[a]	Most Applicable Range for τ	Advantages	Disadvantages and Limitations
10-6	Use of chemical reactivity data [4,31]	k_{OH}, k_{O_3}, etc. [OH], [O_3], etc.	< 1 yr	– Minimal data requirements – Simple calculation – Only method that does not require data on concentrations in atmosphere – Only method for reactive chemicals (*i.e., when τ is on the order of hours to a* few days)	– Calculated τ must be considered a maximum, since other reactions (for which no rate constant is available) may be important – Rate constants (k) and reactant concentrations may have large uncertainties; k, if measured at high temperature, must be extrapolated to ambient temperature
10-7	Correlation with mean standard deviation (Junge's Correlation) [17]	C, σ	$3 - 10^3$ yr	– Minimum data requirements – Simple calculation	– Probably valid only when steady state conditions are at least approximately fulfilled and when sources and sinks are evenly distributed – Measurements of C must be accurate enough so that σ reflects natural variability and not sampling and analysis errors

a. See Table 10-3 for details.

b. *This value assumes* the whole troposphere is being considered; the method is appropriate for smaller values of τ if smaller compartments are being considered.

TABLE 10-3

Data Required for Estimation

Section	Method	Required Data
10-3	Steady-state model	(1) Average concentration of chemical in troposphere (C); this is used to estimate total mass of chemical in troposphere (Q).
		(2) Rate of emission of chemical into troposphere (E) or Rate of removal of chemical from troposphere (R).
10-4	Nonsteady-state, one-compartment model	(1) Average concentration of chemical in troposphere (C); this is used to estimate total mass of chemical in troposphere (Q).
		(2) Year-by-year emissions inventory for chemical; this is used to obtain cumulative emissions (A) and the parameter (b) in the exponential expression for the rate of emission in recent years.
10-5	Nonsteady-state, two-compartment model	(1) Average concentrations of chemical in both northern and southern hemispheres; these are used to estimate the total mass of chemical in the northern (Q_N) and southern (Q_S) hemispheres.
		(2) Year-by-year emissions inventory for chemical; this is used to obtain cumulative emissions (A) and the parameter (b) in the exponential expression for the rate of emission in recent years.
		(3) Interhemispheric exchange rate (τ_e); this may be taken as $\sim$ 1.2 years.
10-6	Use of chemical reactivity data	(1) Rate constants for reaction of chemical with hydroxyl radical (k_{OH}), ozone (k_{O_3}), and other reactants, if any. (Tables of measured values of k_{OH} and k_{O_3} are given from which appropriate surrogates may be selected for some chemicals.)
		(2) Concentration of hydroxyl radical, [OH·], ozone [O_3], and any other reactant being considered. (A table of default values is given for [OH·] and [O_3] and may be used if site-specific data are not available.)
10-7	Correlation with mean standard deviation (Junge's correlation)	(1) Average concentration of chemical in troposphere (C).
		(2) Standard deviation (σ) associated with average concentration.

TABLE 10-4

Estimated Atmospheric Residence Times for Selected Chemicals

Compound	Residence Time (τ)	Compartment	Basis for Calculation	Ref.
Methane	3.1 yr	N. Troposphere	Junge's correlation with data from [29]	a
	3.8 yr	S. Troposphere		
	4 yr	Troposphere	Best estimate (used by Junge [17]) after considering data from several sources. Estimate uncertain by factor of 3	[17]
Gaseous non-methane hydrocarbons:				
(a) Considering only anthropogenic sources	2-3 yr	Troposphere	Q/E (Q = 1.02×10^{11} kg, E = 4.5×10^{10} kg/yr)	[11]
(b) Considering anthropogenic plus natural sources	0.5 yr	Troposphere	Q/E (Q = 1.02×10^{11} kg, E = 1.95×10^{11} kg/yr)	[11]
Ethene	3 hr[b]	Troposphere	Reaction with OH radical in polluted atmospheres ($[OH\cdot] = 10^7$ cm^{-3}); data from [7]	a
Formaldehyde	~ 60d	Troposphere	Junge's correlation with data from [19]	a
Phenol	~ 50 d	Troposphere	Junge's correlation with data from [19]	a

(continued)

TABLE 10-4 (Continued)

Compound	Residence Time (τ)	Compartment	Basis for Calculation	Ref.
Methyl Chloride	1 yr	N. Troposphere	Junge's correlation with data from [29]	a
	0.8 yr	S. Troposphere	Junge's correlation with data from [29]	a
	0.37 yr[c]	Troposphere	Reaction with OH radical	[6]
	2.3 yr	Troposphere	Reaction with OH radical ($[OH\cdot] = 3 \times 10^5 - 5 \times 10^5$ cm^{-3})	[29]
	~ 2 yr	Troposphere	Q/E with oceans assumed to be major source of the chemical	[29]
Methyl Iodide	6 d	Troposphere	Junge's correlation with data from [20]	a
	50 hr	Atmosphere	Photolysis assumed to be sole destructive process	[12]
Methylene Chloride	< ~ 20 – ~ 150 d	Troposphere	Q/E (with concentration < 5 – ~ 35 ppt)	[9]
	~ 40 – 230 d	Troposphere	Reaction with OH radical ($[OH\cdot] = 10^6$ cm^{-3})	[9]
	~ 12 hr – ~ 1 yr	Troposphere	Rate of disappearance in simulated tropospheric reaction chamber	[9]
	110 d[c]	Troposphere	Reaction with OH radical	[6]
	~ 160 d	N. Troposphere	Junge's correlation with data from [29]	a
	~ 250 d	S. Troposphere		
Chloroform	100 d	N. Troposphere	Junge's correlation with data from [29]	a
	1.7 yr	Troposphere	One-compartment, nonsteady-state model	[30]

(continued)

TABLE 10-4 (Continued)

Compound	Residence Time (τ)	Compartment	Basis for Calculation	Ref.
Carbon Tetrachloride	~ 1.4 yr	Troposphere	Junge's correlation	[20]
	3.5 yr	N. Troposphere	Junge's correlation with data from [29]	[a]
	4.2 yr	S. Troposphere	Junge's correlation with data from [29]	[a]
	~ 20 yr	Troposphere	Q/E with data from [1]	[a]
	~ 10 – 20 yr	Troposphere	Q/E with data from [27]	[a]
	> 330 yr[c]	Troposphere	Reaction with OH radical	[6]
	30 – 50 yr[d]	Troposphere and Stratosphere	Q/E, where Q calculated with consideration of photodissociation in stratosphere	[21]
	100 yr	Troposphere	Q/R, where R calculated from consideration of oceans as sink	[29]
Dichlorodifluoromethane	1.2 yr	Troposphere	Junge's correlation with data from [29]	[a]
	67 – 70 yr	Troposphere	Two-compartment, nonsteady-state model	[29]
	50 yr	N. Troposphere	One-compartment, nonsteady-state model	[30]
Trichlorofluoromethane	1 yr	Troposphere	Junge's correlation with data from [20]	[a]
	1.4 yr	Troposphere	Junge's correlation with data from [29]	[a]
	6 yr	Troposphere	Q/E with data from [23]	[a]
	1000 yr[c]	Troposphere	Reaction with OH radical	[6]
	40 – 45 yr	Troposphere	Two-compartment, nonsteady-state model	[29]

(continued)

TABLE 10-4 (Continued)

Compound	Residence Time (τ)	Compartment	Basis for Calculation	Ref.
Trichlorofluoromethane (cont.)	36 yr	N. Troposphere	One-compartment, nonsteady-state model	[30]
	15 – 20 yr	Troposphere	More complex mathematical model of troposphere and stratosphere	[16]
	8 – 10 yr	Troposphere	Two-compartment, nonsteady-state model	[25,29]
Methyl Chloroform	7.2 yr	N. Troposphere	One-compartment, nonsteady-state model	[30]
	1.1 yr[c]	Troposphere	Reaction with OH radical	[6]
	4 d	Troposphere	Q/E	[22]
	~ 200 d	Troposphere	Junge's correlation with data from [29]	a
	150 d	N. Troposphere	One-compartment, nonsteady-state model	[30]
Tetrachloroethylene	150 – 390 d	N. Troposphere	Reaction with OH radical using annual average of $3 - 8 \times 10^{-19}$ moles/cm^3 for [OH·] (Table 10-7). $k_{OH} = 1.0 \times 10^{11}$ cm^3 · mole^{-1} · sec^{-1} (Table 10-5)	a
	1 – 7 d	Polluted atmosphere in lower troposphere with constant sunlight	Reaction with OH radical using $1.7 - 17 \times 10^{-17}$ moles/cm^3 for [OH·] (Table 10-7). $k_{OH} = 1.0 \times 10^{11}$ cm^3 · mole^{-1} · sec^{-1} (Table 10-5)	a

(continued)

TABLE 10-4 (Continued)

Compound	Residence Time (τ)	Compartment	Basis for Calculation	Ref.
Chloracetyl chlorides:				
$CClH_2COCl$	13,000 yr[b,e]	Atmosphere (T = 298 K, P_{H_2O} = 10 mm Hg)	Hydrolysis rate constant measured at T = 470-620 K	[5]
CCl_3COCl	450 yr[b,e]			
$COCl_2$	110 yr[b,e]			
DDT	3.3 yr	Troposphere	Q/R, where R based on assumption that rainfall is dominant mechanism for removal from air	[37]
	50 d	Troposphere (over Sargasso Sea)	Q/R, where R based on assumption that major source of DDT input to oceans is via the atmosphere	[2]
Polychlorinated biphenyls	40 d	Troposphere (over Sargasso Sea)	Q/R, where R based on assumption that major source of PCB input to oceans is via the atmosphere	[2]

a. The value listed was calculated by the author of this chapter. In many cases these calculations were carried out even though it was known that the method of calculation might not be applicable. Thus, these numbers should be considered more as examples of the estimation method than as valid estimates of τ.

b. The value listed is the half-life.

c. Other information given in Ref. 6 indicates that the values of τ listed here may be low by as much as a factor of 3 for some chemicals.

d. The estimate of 30-50 years may be too low, according to Ref. 27. The rate of photodissociation assumed in the calculations is considered to be too high.

e. Butler and Snelson [5] concluded from their data that homogeneous gas-phase hydrolysis is not an efficient conversion process. They suggested that heterogeneous hydrolysis by water droplets would be a more efficient scavenging process for these compounds. This could involve typical residence times as short as one week (see Table 10-1).

Table 10-4 lists the calculated residence times for a number of chemicals by one or more methods. For purposes of illustration, some methods of calculation (primarily Junge's correlation) are used in situations where they might not be appropriate. *Thus, the estimates given in this table should not be taken as the best estimates of* τ. Note that Junge's correlation gives values of τ on the order of one year ($\pm$ a factor of 3) for most of the halocarbons; this suggests that the reported values of standard deviation (σ) are dominated more by sampling and analysis errors than by the natural fluctuations in atmospheric concentration.

The possibility that misleading values of τ will be calculated from chemical reactivity data is exemplified in the estimates given for trichlorofluoromethane and carbon tetrachloride in Table 10-4. If one had calculated τ on the assumption that reaction with OH radicals was the only tropospheric loss mechanism, erroneously high values of τ would be predicted. The steady-state model (using Q/E) appears to give lower values for τ than the two nonequilibrium models, which are presumably more accurate; this is seen for trichlorofluoromethane, carbon tetrachloride, and tetrachloroethylene. It is not clear, however, if this result should be generally expected or whether it is unique to these cases.

10-3 STEADY-STATE MODEL

Principles of Use. The use of a steady-state model for estimating tropospheric residence time is limited to those cases where the total "growth" rate of the chemical in the troposphere (caused by emissions from land and oceans plus input, if any, from the stratosphere) may be assumed to equal the total "removal" rate of the chemical in the same compartment via outflow plus chemical degradation. This assumption of steady state will generally be appropriate when the residence time is large compared with the time scale for atmospheric fluctuations. If emissions of the chemical to the atmosphere have been relatively constant for a number of years and τ is expected to be about a year or more, the method is probably appropriate to use for the whole troposphere.

The residence time may be calculated with Eq. 10-3 or 10-4.

$$\tau = Q/E \qquad (10\text{-}3)$$

$$\tau = Q/R \qquad (10\text{-}4)$$

where Q is the total mass of the pollutant in the troposphere, E is the total emissions rate, and R is the total removal rate. Consistent units of mass must be used for Q, E and R (Q has units of mass and E and R units

of mass/time), and the data used to obtain these values should come from the same time period.

The value of Q (in grams) may be obtained from

$$Q = C\,(4 \times 10^{21})/10^{9} \qquad (10\text{-}5)$$

where C is the global average tropospheric concentration (in parts per billion by weight)[3] and 4×10^{21} is the assumed mass [31] of the troposphere in grams. The concentration of man-made pollutants is generally greater in the northern hemisphere than in the southern hemisphere (see, for example, Refs. 28 and 29); therefore, values of Q calculated from northern hemispheric data only may be too large, especially for chemicals with short residence times. Even some naturally occurring chemicals may have different concentrations in the northern and southern hemispheres. Methane, for example, which is presumed to be emitted primarily from land masses, would have a higher concentration in the northern hemisphere, since the ratio of land masses in the northern and southern hemispheres is about 2.4:1.

Equation 10-3 (τ = Q/E) is used more frequently than Eq. 10-4 (τ = Q/R). The value of E must be obtained from as accurate an emissions inventory as possible for the whole earth. There are no easy shortcuts or firm guidelines for estimating E; the user must evaluate all known sources and use the best available emissions data for each. (Some guidance in the basic methodology used to estimate emission rates is given in Appendices A and B of Ref. 4.) Values of R are no easier to estimate. One mechanism that can be considered for calculating a value of R is rainout. (See examples for DDT and PCBs in Table 10-4.) If rainfall is expected to be the major atmospheric loss mechanism, R (in grams per year) may be obtained from

$$R = C_p(4.2 \times 10^{20})/10^{9} = C_p(4.2 \times 10^{11}) \qquad (10\text{-}6)$$

where C_p is the global average concentration of the pollutant in the precipitation (in parts per billion by weight) and 4.2×10^{20} is the assumed [34] annual precipitation (grams/year) for the earth.[4]

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3. Atmospheric concentrations are often reported on a volume per volume basis (v/v), e.g., 50 ppb(v/v). To convert to a weight per weight basis (w/w) for C, multiply this number by the molecular weight of the pollutant and divide by the molecular weight of air (~28.9). If measurements are reported on a weight per volume basis (e.g., 50 ng/m^3), convert this to a w/w basis by using 1205 g/m^3 (20°C, 76 cm Hg) or 1293 g/m^3 (0°C, 76 cm Hg) as the density of air and adjust the scale of the units so that C is expressed in ppb by weight.

4. This is equivalent to an annual rainfall of 81 cm (32 inches).

For unreactive gases, if the average concentration in precipitation is not known, it may be estimated from

$$C_{(precipitation)} \simeq C_{(air)} / H \qquad (10\text{-}7)$$

where H is Henry's law constant in the appropriate units [32]. Equation 10-7 should be used to estimate concentrations in rain only; snow scavenging of gases can generally be ignored [32]. Estimation methods for H are given in Chapter 15. (See especially §15-6.)

Basic Steps

(1) Estimate the mass (Q) of the chemical in the compartment of interest. If the whole troposphere is being considered, Eq. 10-5 may be used.

(2) If the emission rate (E) can be estimated, use Eq. 10-3 to estimate τ.

(3) If the removal rate (R) can be estimated, use Eq. 10-4 to estimate τ. If rainfall is expected to be the principal removal mechanism, Eqs. 10-6 and 10-7 may be used in situations where the concentration in rain is not known.

Example 10-1 Estimate the tropospheric residence time for methylene chloride, given an estimated global anthropogenic emission rate of 3.5×10^{11} g/yr and a mean tropospheric concentration of 30 ppt (by weight).

(1) From Eq. 10-5, $Q = .03\,(4 \times 10^{21})/10^9 = 1.2 \times 10^{11}$ g.

(2) Then, with Eq. 10-3,

$$\tau = (1.2 \times 10^{11}\ g)/(3.5 \times 10^{11}\ g/yr)$$
$$= 0.34\ yr$$

Example 10-2 Estimate the tropospheric residence time for methane based on the assumption that rainfall is the principal removal mechanism. (This assumption is not valid but is used for purposes of the example.) The concentration of methane in air is about 1.4 ppm (v/v), and the (dimensionless) value of Henry's law constant is 25.7 at 15°C [32].

(1) Convert air concentration to weight/weight basis.
$C = 1.4$ (molecular wt. of CH_4/molecular weight of air)
$= 1.4\,(16/28.9)$
$= 0.78$ ppm (w/w) or 780 ppb (w/w)

(2) From Eq. 10-7, $C_{(precipitation)} = 0.78$ ppm/25.7 = 30 ppb (w/w)

(3) Equation 10-6 gives $R = 30(4.2 \times 10^{20})/10^9 = 1.3 \times 10^{13}$ g/yr for the removal rate.

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(4) The tropospheric burden is obtained from Eq. 10-5 as
$Q = 780\,(4 \times 10^{21})/10^{9} = 3.1 \times 10^{15}$ g.

(5) Finally with Eq. 10-4,

$\tau = (3.1 \times 10^{15}\ g)/(1.3 \times 10^{13}\ g/yr)$
$= 240$ yr

Since this estimate is much larger than Junge's estimate of ~ 4 yrs [17], one can conclude that rainfall is not an important removal mechanism for methane.

10-4 NONSTEADY-STATE, ONE-COMPARTMENT MODEL

Principles of Use. Nonsteady-state methods are appropriate for anthropogenic pollutants for which recent emissions have been increasing exponentially. The one-compartment model considers the whole troposphere as the compartment of interest, making no distinction between the northern and southern hemispheres. The calculation is simpler than with the two-compartment model described in the following section, but the estimates of τ may be less reliable if pollutant concentrations and removal rates differ significantly between the two hemispheres.

With this model the tropospheric residence time is given [25,30] by

$$\tau = \frac{\theta}{b\,(1-\theta)} \qquad (10\text{-}8)$$

where b is the coefficient in the exponential expression for the emission rate (E) as a function of time (t)

$$E = ae^{bt} \qquad (10\text{-}9)$$

and θ is the ratio, calculated at a specified time, of the tropospheric burden (Q) to the cumulative emissions (A) of the chemical since it was first produced; i.e.

$$\theta = Q/A \qquad (10\text{-}10)$$

Basic Steps

(1) Prepare a year-to-year emissions inventory for the chemical, listing the total emissions in each year since substantial amounts were produced.

(2) Determine the cumulative emissions, A, by summing the numbers.

(3) Estimate the tropospheric burden, Q, from the global average tropospheric concentration (C) with Eq. 10-5. Note that Q must be calculated for the same time up to which A was obtained.

(4) Calculate θ with Eq. 10-10.

(5) Plot the emissions vs. time as ln E vs. t, and obtain b from the slope of the line. Note that b has units of time^{-1}.

(6) Calculate τ with Eq. 10-8.

Example 10-3 Estimate the tropospheric residence time for dichlorodifluoromethane (mol. wt. = 120.93), given a measured tropospheric concentration of 0.19 ppb (v/v) and the year-by-year emissions inventory (synthesized for this example) given below.

Year	Emissions (E) g/yr x 10^{-11}	ln E
1961	1.0	25.3
1962	1.4	25.7
1963	1.8	25.9
1964	2.0	26.0
1965	2.2	26.1
1966	2.3	26.2
1967	2.6	26.3
1968	2.7	26.3
1969	3.2	26.5
1970	3.4	26.6
1971	3.6	26.6
1972	4.3	26.8
1973	4.6	26.8
1974	5.0	26.9
1975	5.5	27.0
Total	45.6	

(1) The cumulative emissions (A) of 45.6 x 10^{11} g is the sum of the yearly emissions. Emissions prior to 1961 are assumed to be small compared with this total.

(2) Convert the measured atmospheric concentration to units of ppb by weight (see footnote 3).

$$C = 0.19 \text{ ppb (v/v)} (120.93/28.9) = 0.80 \text{ ppb (w/w)}$$

(3) From Eq. 10-5, the tropospheric burden is

$$Q = 0.80 (4 \times 10^{21})/10^{9} = 3.2 \times 10^{12} \text{g}$$

(4) From Eq. 10-10, $\theta = 3.2 \times 10^{12} \text{g}/4.56 \times 10^{12} \text{ g} = 0.70$

(5) Plot ln E (values given above) as shown in Figure 10-1. The slope, b, of the best-fit line through the points (drawn by eye) is found to be 0.10 yr^{-1}.

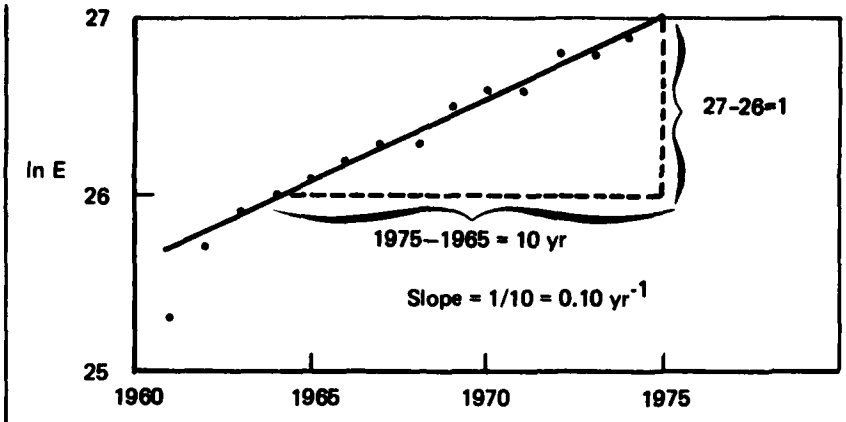


FIGURE 10-1 Plot of Yearly Emissions for Example 10-3

(6) Then, with Eq. 10-8,

$$\tau = \frac{0.70}{0.10\,(1-0.70)} = 23 \text{ yr}$$

10-5 NONSTEADY-STATE, TWO-COMPARTMENT MODEL

Principles of Use. The two-compartment model is appropriate for anthropogenic pollutants for which tropospheric burdens and removal rates in the northern and southern hemispheres are expected to differ. Since tropospheric burdens must be estimated for each hemisphere (Q_N and Q_S), concentration data are required for both. The inter-hemispheric exchange rate (τ_e) is also required; various estimates put τ_e in the range of 1 to 1.4 years, with 1.2 years being an acceptable value for most calculations [23,26,29]. The method allows the estimation of a chemical's residence time in both the northern (τ_N) and southern (τ_S) hemispheres as well as a global average residence time (τ). All of the emissions are assumed to be in the northern hemisphere.

With this model [26,30], the global average residence time (τ) is obtained from

$$\tau = \frac{1 + Q_N/Q_S}{1/\tau_S + (1/\tau_N)\,(Q_N/Q_S)} \qquad (10\text{-}11)$$

τ_S is obtained from

$$\tau_S = \frac{1}{\frac{1}{\tau_e}\left(\frac{Q_N}{Q_S} - 1\right) - b} \qquad (10\text{-}12)$$

where, as in Eq. 10-9, b is the coefficient in the exponential expression for the emissions growth rate. The value of a parameter, D, is next calculated as follows:

$$D = \frac{\theta}{b\,(1 + Q_N/Q_S)} \qquad (10\text{-}13)$$

where $\theta = (Q_N + Q_S)/A$ and A is the cumulative emissions of the chemical since it was first produced. The value of τ_N is then obtained from the following two equations:

$$D = 1/[\tau_e\,(b-\alpha)\,(b-\beta)] \qquad (10\text{-}14)$$

where α and β are the roots[5] of the equation

$$p^2 + p\left(\frac{2}{\tau_e} + \frac{1}{\tau_S} + \frac{1}{\tau_N}\right) + \frac{1}{\tau_e\,\tau_N} + \frac{1}{\tau_e\,\tau_S} + \frac{1}{\tau_N\,\tau_S} = 0 \qquad (10\text{-}15)$$

The calculation of τ from Eq. 10-11, τ_S from Eq. 10-12 and D from Eq. 10-13 is straightforward. However, once the value of D is known, Eqs. 10-14 and -15 must be solved by trial and error; various values of τ_N are used until a matching value of D (calculated with Eq. 10-14) is found. It can be shown that the values of α and β will always be real numbers; i.e., the solution of Eq. 10-15 does not involve complex numbers. The value of τ_N obtained from Eqs. 10-14 and -15 may be quite sensitive to the values of both θ and τ_e; τ_S is somewhat less sensitive, and τ (the global average) is quite insensitive to these parameters. For some values of θ it is possible that no value of D obtained from Eq. 10-14 will match that obtained from Eq. 10-13. In this case the method must be abandoned.

For most chemicals, especially those subject to reaction with OH radicals, τ_N should be greater than τ_S, as the concentration of OH radicals in the southern hemisphere is about twice that in the northern hemisphere. (See Table 10-7 in the following section.) Thus, a reason-

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5. For a quadratic equation of the form $p^2 + mp + n = 0$, the roots are given by:

$$\alpha = \frac{-m + \sqrt{m^2 - 4n}}{2} \quad \text{and} \quad \beta = \frac{-m - \sqrt{m^2 - 4n}}{2}$$

able first guess for τ_N when solving Eqs. 10-14 and -15 by trial and error is $2\tau_S$. If the first guess for τ_N gives a value of D from Eq. 10-14 larger than that from Eq. 10-13, use a smaller value of τ_N for the second guess. If desired, the values of D from these first two guesses may be plotted against τ_N; the third guess for τ_N can then be taken off the straight line through these two points, since the "correct" value of D (from Eq. 10-13) is known. This iterative procedure should require only a few trial-and-error solutions and should not be taken beyond the point where two significant figures for τ_N have been obtained.

Basic Steps

(1) Prepare a year-by-year emissions inventory for the chemical, listing the total emissions in each year since substantial amounts were produced.

(2) Determine the cumulative emissions, A, by summing the numbers.

(3) Plot emissions vs. time as ln E vs. t and obtain b from the slope of the line.

(4) Calculate the total mass of the chemical in the troposphere ($Q_N + Q_S$) using the global average tropospheric concentration and Eq. 10-5. Note that Q must be calculated for the same time up to which A was calculated.

(5) Use Eq. 10-12 to calculate τ_S. A value of 1.2 years may be used for τ_e. Q_N/Q_S may simply be obtained from the ratio of the average atmospheric concentrations in the two hemispheres.

(6) Use Eq. 10-13 to calculate D.

(7) Using the values of τ_e and τ_S from above, try different values of τ_N in Eq. 10-15 until the value of D obtained from Eq. 10-14 matches that obtained in step (6). A value of $\tau_N = 2\tau_S$ should provide a reasonable first guess for τ_N. Use a lower value of τ_N for the second (and subsequent) guess(es) if D from Eq. 10-14 is greater than D from Eq. 10-13.

(8) Calculate the global average residence time (τ) from Eq. 10-11.

Example 10-4 Estimate τ_S, τ_N, and τ for methyl chloroform, given b = 0.17 yr^{-1}, τ_e = 1.2 yr, Q_N/Q_S = 1.47, and θ = 0.59

(1) With Eq. 10-12,

$$\tau_S = \frac{1}{\frac{1}{1.2}(1.47-1) - 0.17}$$

$$= 4.5 \text{ yr}$$

(2) From Eq. 10-13,

$$D = \frac{0.59}{0.17\,(1 + 1.47)}$$

$$= 1.41$$

(3) Using Eq. 10-15 and, subsequently, Eq. 10-14 for various values of τ_N shows $\tau_N \simeq 20$ yr. Values of α, β and D for three values of τ_N are as follows:

τ_N	α	β	D
9 yr	−0.16	−1.84	1.24
15 yr	−0.14	−1.83	1.34
20 yr	−0.13	−1.82	1.40
∞	−0.11	−1.80	1.51

(4) Then, from Eq. 10-11, the global average residence time is

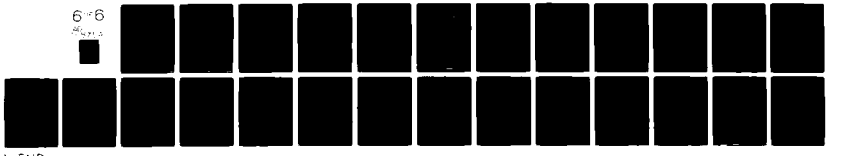
$$\tau = \frac{1 + 1.47}{1/4.5 + (1/20)\,1.47} = 8 \text{ yr}$$

10-6 USE OF CHEMICAL REACTIVITY DATA

Principles of Use. The residence time of a chemical in the atmosphere may be estimated if the rate constants for one or more destruction or removal processes are known. The reactions most frequently considered are those with hydroxyl radicals and with ozone. Rate constants for reactions with such species are relatively easy to measure in the laboratory, although the experiments must sometimes be carried out at elevated temperatures. The value of τ estimated from such data should be viewed as a maximum, since other reactions for which no data are available (e.g., direct or sensitized photolysis, reaction with other radicals) may proceed more rapidly than the ones considered.

For reactions with such species as ozone and the hydroxyl radical, a reaction that is first-order with respect to the pollutant is generally found (and thus is usually presumed for other chemicals), and the rate constant reported, k, is usually the bimolecular rate constant. Thus, the rate of decrease in the concentration (C) of the chemical is given by:

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RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEMI--ETC(U)
JUN 81 W J LYMAN, W F REEHL, D H ROSENBLATT DAMD17-78-C-8073
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$$\frac{-dC}{dt} = k_{OH}\,[OH\cdot]\,[C] \qquad (10\text{-}16)$$

or

$$\frac{-dC}{dt} = k_{O_3}\,[O_3]\,[C] \qquad (10\text{-}17)$$

Similar equations could be written for other reactions. The rate constant is frequently given in liters·mole^{-1}·sec^{-1}; in such cases [OH·] and [O_3] must be expressed in units of moles/liter. Other units encountered include cm^3·mole^{-1}· sec^{-1} and cm^3·sec^{-1}; concentrations of [OH·] and [O_3] then must be expressed in moles/cm^3 and number/cm^3, respectively.

To calculate a residence time by this method, a value of τ is first calculated for each reaction of interest. Equations 10-18 and 10-19 show the formulas for reaction with OH· or O_3; an identical form may be used for any other reaction that follows similar kinetics.

$$\tau_{OH\cdot} = \frac{1}{k_{OH}\,[OH\cdot]} \qquad (10\text{-}18)$$

$$\tau_{O_3} = \frac{1}{k_{O_3}\,[O_3]} \qquad (10\text{-}19)$$

An overall value of τ is then obtained as follows [31]:

$$\frac{1}{\tau} = \frac{1}{\tau_{OH\cdot}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_x} + \cdots \qquad (10\text{-}20)$$

where τ_x refers to the residence time associated with any other reaction for which data are available.

If reaction with OH· or O_3 is considered to be likely for a chemical but values of k_{OH} and k_{O_3} are not available, approximate values may be found for a similar chemical or class of chemicals in Table 10-5 (for k_{OH}) or Table 10-6 (for k_{O_3}). Additional assistance in the selection of a surrogate k_{OH} value may be found in Ref. 15 or in the relative (atmospheric) reactivity scales given in Refs. 7 and 33.

Since reaction rate constants are a function of temperature, it is desirable to use values of k that relate to the mean temperature in the compartment and the time scale of concern. Mean temperatures in the

TABLE 10-5

Rate Constants[a] for Reaction of Organic Chemicals with OH Radical at 300K

Compound	k_{OH} ($cm^3 \cdot mol^{-1} \cdot sec^{-1}$)	Compound	k_{OH} ($cm^3 \cdot mol^{-1} \cdot sec^{-1}$)
Alkanes		**Alcohols**	
Methane	4.8×10^9	Methanol	5.7×10^{11}
Ethane	1.7×10^{11}	Ethanol	1.8×10^{12}
Propane	1.3×10^{12}	Propanol	2.3×10^{12}
Methyl-	1.3×10^{12}	2-Propanol	4.3×10^{12}
Dimethyl-	4.8×10^{11}	Butanol	4.1×10^{12}
n-Butane	1.6×10^{12}	4-Methyl-2-pentanol	4.3×10^{11}
Methyl-	7.8×10^{11}	**O,N,S Substituted Alkanes**	
2,3-Dimethyl-	3.1×10^{12}	Methyl ether	2.1×10^{12}
2,2,3-Trimethyl-	2.3×10^{12}	Ethyl ether	5.4×10^{12}
2,2,3,3-Tetramethyl-	6.6×10^{11}	n-Propyl ether	1.0×10^{13}
n-Pentane	3.9×10^{12}	Tetrahydrofuran	8.8×10^{12}
2-Methyl-	3.2×10^{12}	1-Propylacetate	2.7×10^{12}
3-Methyl-	4.3×10^{12}	2-Butylacetate	3.4×10^{12}
2,2,4-Trimethyl-	2.3×10^{12}	Methylamine	1.3×10^{13}
n-Hexane	3.6×10^{12}	Methyl sulfide	2.0×10^{13}
n-Octane	5.1×10^{12}	Formaldehyde	9.0×10^{12}
Cycloalkanes		Acetaldehyde	9.6×10^{12}
c-Butane	7.2×10^{12}	Propionaldehyde	1.3×10^{13}
c-Pentane	3.7×10^{12}	Benzaldehyde	7.8×10^{12}
Haloalkanes		**Alkenes**	
Methane		Ethene	4.7×10^{12}
Fluoro-	9.6×10^{9}	Propene	1.5×10^{13}
Difluoro-	4.7×10^{9}	Methyl-	3.0×10^{13}
Trifluoro-	1.2×10^{8}	1-Butene	2.1×10^{13}
Tetrafluoro-	$< 2.4 \times 10^{8}$	2-Methyl-	3.5×10^{13}
Chloro-	2.4×10^{10}	3,3-Dimethyl-	1.7×10^{13}
Dichloro-	8.4×10^{10}	2-Butene	
Trichloro-	6.6×10^{10}	cis-	3.2×10^{13}
Tetrachloro-	$< 2.4 \times 10^{8}$	trans-	4.2×10^{13}
Bromo-	2.4×10^{10}	2-Methyl-	4.8×10^{13}
Ethane		2,3-Dimethyl-	9.2×10^{13}
Chloro-	2.3×10^{11}	1-Pentene	1.8×10^{13}
1,1-Dichloro-	1.6×10^{11}	cis-2-Pentene	3.9×10^{13}
1,2-Dichloro-	1.3×10^{11}	1-Hexene	1.9×10^{13}
1,1,1-Trichloro-	9.0×10^{9}	1-Heptene	2.2×10^{13}
1,1,1-Trifluoro-2-chloro-	6.0×10^{9}	**Cycloalkenes**	
1,1,1-Trifluoro-2,2-dichloro-	1.7×10^{10}	c-Cyclohexene	4.3×10^{13}
1,1,1,2-Tetrafluoro-2-chloro-	7.2×10^{9}	1-Methyl-	5.8×10^{13}
1,2-Dibromo-	1.5×10^{11}	**Haloalkenes**	
Alkanones		Ethene	
Butanone	2.0×10^{12}	Fluoro-	3.4×10^{12}
2-Methylpentanone	9.0×10^{12}	1,1-Difluoro-	1.2×10^{12}
2,6-Dimethylheptanone	1.5×10^{13}	Chloro-	3.9×10^{12}

(Continued)

TABLE 10-5 (Continued)

Compound	k_{OH} ($cm^3 \cdot mol^{-1} \cdot sec^{-1}$)	Compound	k_{OH} ($cm^3 \cdot mol^{-1} \cdot sec^{-1}$)
Ethene (Cont.)		**Arenes**	
Trichloro-	1.2×10^{12}	Benzene	8.4×10^{11}
Tetrachloro-	1.0×10^{11}	Methyl-	3.5×10^{12}
Chlorotrifluoro-	4.2×10^{12}	1,2-Dimethyl-	7.8×10^{12}
Bromo-	4.1×10^{12}	1,3-Dimethyl-	1.2×10^{13}
O-Substituted Alkene		1,4-Dimethyl-	6.0×10^{12}
Methoxy	2.0×10^{13}	1,2,3-Trimethyl-	1.5×10^{13}
Alkadienes		1,2,4-Trimethyl-	2.0×10^{13}
Propadiene	2.7×10^{12}	1,3,5-Trimethyl-	3.0×10^{13}
1,3-Butadiene	4.6×10^{13}	Ethyl-	4.5×10^{12}
2-Methyl-	4.7×10^{13}	1,2-Ethylmethyl-	8.2×10^{12}
Terpenes		1,3-Ethylmethyl-	1.2×10^{13}
p-Menthane	4.0×10^{12}	1,4-Ethylmethyl-	7.7×10^{12}
α-Pinene	1.5×10^{13}	Propyl-	3.6×10^{12}
β-Pinene	1.3×10^{13}	2-Propyl-	4.7×10^{12}
3-Carene	1.7×10^{13}	1,4-Methylpropyl-2-	9.1×10^{12}
Carvomenthane	2.5×10^{13}	Hexafluoro-	1.3×10^{11}
β-Phellandrone	2.3×10^{13}	Propylpentafluoro-	1.8×10^{12}
d-Limonene	2.9×10^{13}	**Substituted Arenes**	
Dihydromyrcene	3.6×10^{13}	Methoxybenzene	1.2×10^{13}
Myrcene	4.5×10^{13}	o-Cresol	2.0×10^{13}
cis-Ocimene	6.3×10^{13}		
Alkynes			
Ethyne	9.6×10^{10}		
Methyl	5.7×10^{11}		

a. $k\ (L\ mol^{-1}\ sec^{-1}) = 10^{-3}\ k\ (cm^3 \cdot mol^{-1} \cdot sec^{-1})$

Source: Hendry and Kenley [15].

TABLE 10-6

Rate Constants for Reaction of Organic Chemicals with Ozone at 300K

Compound	k_{O_3} ($cm^3 \cdot mole^{-1} \cdot sec^{-1}$)
Alkanes	
Methane	0.84
Ethane	0.72
Propane	4.1
Methyl-	1.2
n-Butane	5.9
Alkenes	
Ethene	1.1×10^{6}
Propene	7.8×10^{6}
Methyl-	9.1×10^{6}
1-Butene	7.4×10^{6}
2-Butene	
cis-	9.7×10^{7}
trans-	1.6×10^{8}
2-Methyl-	3.0×10^{8}
2,3-Dimethyl-	9.1×10^{8}
1-Pentene	6.4×10^{6}
2-Pentene	
cis-	2.7×10^{8}
trans-	3.4×10^{8}
1-Hexene	6.7×10^{6}
1-Heptene	4.9×10^{6}
1-Octene	4.9×10^{6}
1-Decene	6.5×10^{6}
Cyclohexene	1.0×10^{8}
Conjugated Alkenes	
1,3-Butadiene	5.0×10^{6}
Phenylethene	1.0×10^{8}
Halogenated Alkenes	
Ethene	
Chloro-	1.2×10^{6}
1,1-Dichloro-	2.2×10^{4}
1,2-Dichloro-	
cis-	3.7×10^{4}
trans-	2.3×10^{5}
Trichloro-	3.6×10^{3}
Tetrachloro-	10.0×10^{2}
Tetrafluoro-	8.1×10^{7}
Propene	
3-Chloro-	1.1×10^{7}
Hexafluoro-	1.3×10^{7}
Terpenes	
α-Pinene	9.9×10^{7}
Alkynes	
Ethyne	4.7×10^{4}
Aromatic Hydrocarbons	
Benzene	2.8×10^{1}
Methyl-	1.6×10^{2}
1,2-Dimethyl-	9.5×10^{2}
1,3-Dimethyl-	7.8×10^{2}
1,4-Dimethyl-	9.5×10^{2}
1,3,4-Trimethyl-	2.8×10^{3}
1,3,5-Trimethyl-	4.2×10^{3}
1,2,4,5-Tetramethyl-	1.1×10^{4}
Pentamethyl-	5.0×10^{4}
Hexamethyl-	2.4×10^{5}
Ethyl-	3.4×10^{2}
1,3-Diethyl-	1.1×10^{3}
1,3,5-Triethyl-	3.4×10^{3}
Pentaethyl-	1.0×10^{4}
Hexaethyl-	3.4×10^{3}
2-Propyl-	3.5×10^{2}
t-Butyl-	6.9×10^{1}

troposphere are about 17°C near the earth's surface and drop to −40°C to −60°C at an altitude of 10-12 km. Daily and seasonal cycles should obviously be considered; a tropospheric temperature of about −10°C might be appropriate for a mean residence time of months to years, but a value of 20°C would be appropriate for a highly reactive chemical ($\tau \leq 1$ day) being emitted into the atmosphere in a warm climate. The Arrhenius equation[6] may be used to find a temperature-adjusted value of k if laboratory data for two or more temperatures are available or if the energy of activation for the reaction is known. The change in k may be as much as one order of magnitude for a temperature change of about 50°C.

If the concentrations of OH· and/or O_3 are now known for the time period and compartment of interest, appropriate default values may be selected from those listed in Table 10-7.

Basic Steps

(1) Obtain literature values for k_{OH}, k_{O_3}, etc. and, if necessary, correct these rate constants for the temperature of the compartment being considered. If literature values are not available, surrogate values may be selected on the basis of information given in Tables 10-5 and -6 or, preferably, Ref. 15.

(2) Determine the appropriate values to use for [OH·], [O_3], etc. Default values may be selected from Table 10-7.

(3) For each reaction being considered, calculate a residence time as shown by Eqs. 10-18 and -19 for reaction with OH· and O_3.

(4) Use Eq. 10-20 to estimate an overall (maximum) residence time.

Example 10-5 Estimate the atmospheric residence time for 1,3,5-trimethylbenzene, given $k_{OH} = 31 \times 10^9$ liters · mole^{-1} · sec^{-1} [10], $k_{O_3} = 4.2 \times 10^3$ cm^3 · mole^{-1} · sec^{-1} (Table 10-6), [OH ·] = 1×10^{-15} moles/liter, and [O_3] = 1.6×10^{-12} mole/cm^3.

(1) Using Eq. 10-18, we obtain

$$\tau_{OH} = \frac{1}{(31 \times 10^9)(1 \times 10^{-15})} \text{ sec} = 3.2 \times 10^4 \text{ sec} = 9 \text{ hr}$$

6. $k = A \exp(-E_A/RT)$, where k is the rate constant, A a constant, E_A the energy of activation, R the gas constant, and T the temperature. E_A is typically on the order of 10^3 to 10^4 cal/mole for reactions with OH·; with E_A in these units, R is 1.987 cal/mole·K and T must be in K.

TABLE 10-7

Typical Concentrations of OH· and O_3 in the Atmosphere

Situation	Concentration			Ref.
	Moles/cm³	Moles/Liter	Number/cm³	
Ozone:				
Annual average	1.6×10^{-12}	1.6×10^{-9}	9.6×10^{11}	[15]
Urban	5.0×10^{-12}	5.0×10^{-9}	3.0×10^{12}	[13]
Rural	1.6×10^{-12}	1.6×10^{-9}	9.6×10^{11}	[13]
Hydroxyl Radical:				
Global annual average	1.8×10^{-18}	1.8×10^{-15}	1.1×10^{6}	[24]
	6.8×10^{-19}	6.8×10^{-16}	4.1×10^{5}	[26]
Northern hemisphere (annual average)	8.0×10^{-19}	8.0×10^{-16}	4.8×10^{5}	[24]
	$3\text{-}5 \times 10^{-19}$	$3\text{-}5 \times 10^{-16}$	$2\text{-}3 \times 10^{5}$	[26]
Southern hemisphere (annual average)	3.0×10^{-18}	3.0×10^{-15}	1.8×10^{6}	[24]
	$8\text{-}10 \times 10^{-19}$	$8\text{-}10 \times 10^{-16}$	$5\text{-}6 \times 10^{5}$	[26]
Atmospheric above boundary layer in N.H. (daytime)	$5.8\text{-}14 \times 10^{-18}$	$5.8\text{-}14 \times 10^{-15}$	$3.5\text{-}8.1 \times 10^{6}$	[8]
Polluted atmospheres (daytime, ground level, with full sunlight)	$1.7\text{-}17 \times 10^{-17}$	$1.7\text{-}17 \times 10^{-14}$	$10^{7}\text{-}10^{8}$	[7,35,36]

(2) Using Eq. 10-19, we obtain

$$\tau_{O_3} = \frac{1}{(4.2 \times 10^{3})(1.6 \times 10^{-12})} \text{ sec} = 1.5 \times 10^{8} \text{ sec} = 4.7 \text{ yr}$$

(3) Finally, Eq. 10-20 is used to calculate an overall value of τ; since in this example $1/\tau_{OH} > 1/\tau_{O_3}$, $\tau \simeq \tau_{OH} = 9$ hr

10-7 CORRELATION WITH MEAN STANDARD DEVIATION (JUNGE'S CORRELATION)

Principles of Use. While this method is enticingly simple, more care must be exercised in determining its appropriateness than with any of the other methods. The only data requirements are an adequate number of

measurements of the atmospheric concentration (over appropriate space and time scales) so that an accurate average, C, and standard deviation, σ, can be obtained. Using such data, mostly for trace inorganic gases, Junge has shown [17] that a correlation exists between the mean standard deviation (σ/C) and the tropospheric residence time. Using the data shown in Table 10-8, Junge obtained the following correlation:

$$\tau = \frac{0.14}{\sigma/C} \text{ years} \qquad (10\text{-}21)$$

TABLE 10-8

Data Used in Junge's Correlation

	Residence Time		Standard Spatial Variation	
Gas	τ (yr)	Uncertainty Factor	σ/C	Uncertainty Factor
O_2	5×10^3	3.0	$< 2.4 \times 10^{-5}$	[a]
CO_2	15.0	1.5	5.0×10^{-3}	1.5
N_2O	8.0	2.0	8.0×10^{-2}	1.5
H_2	6.5	2.0	8.0×10^{-2}	1.4
CH_4	4.0	3.0	1.0×10^{-1}	2.0
CO	6×10^{-1}	2.0	5.0×10^{-1}	1.3
O_3	2.5×10^{-1}	1.5	4.0×10^{-1}	1.5
H_2O	2.2×10^{-2}	1.3	5.0×10^{1}	1.2
Rn	1.4×10^{-2}	1.1	1.0×10^{1}	4.0

a. Only upper limits can be given.

Source: Junge [17].

The standard deviation of a set of measured C_i values is given by

$$\sigma = \left[\frac{1}{n-1}\left(\sum_{i=1}^{n} C_i^2 - nC^2\right)\right]^{1/2} \qquad (10\text{-}22)$$

where C is the average value of the individual C_i values and n is the number of data points (i.e., number of C_i values). Sample calculations of standard deviations are shown in Appendix B.

If the data used to obtain C and σ are obtained from a large number of geographically separated stations over a suitable time period, the

correlation is probably appropriate as long as the precision of the measurements is high enough so that σ represents the real variability in C rather than measurement errors. In addition, the sources and sinks for the pollutant must be evenly distributed. Even when the above-mentioned requirements are met, Table 10-8 shows that the value of τ estimated from Junge's correlation will have an uncertainty factor of about 2.

Although Eq. 10-21 was obtained as a correlation with existing data, the form of the equation has been validated on a theoretical basis. Junge showed [17] that for 5 days $\leq \tau \leq$ 1.5 years a correlation of the following form would be expected:

$$\tau^{0.95} = \frac{0.0216}{\sigma/C} \quad \text{years} \tag{10-23}$$

Another model evaluated by Gibbs and Slinn [14] indicated that $\tau^{0.5}$ would be inversely proportional to σ/C.

Basic Steps

(1) Determine appropriateness of method (see text) on the basis of the precision of the measurements, the number and geographic location of the measurement sites, and the time interval of the sampling.

(2) Obtain the average (C) and standard deviation (σ) from the available data on atmospheric concentrations. Use Eq. 10-22 to calculate σ if it is not known.

(3) Solve for τ using Eq. 10-21.

Example 10-6 Estimate τ for methyl chloride, given C = 610 ppt and σ = 90 ppt. (We will assume the method is appropriate.)

Substituting these values in Eq. 10-21, we obtain

$$\tau = \frac{0.14}{90/610} = \frac{0.14}{0.15} = 0.95 \text{ yr}$$

10-8 SYMBOLS USED

Note: The dimensions of the important parameters are indicated in parentheses. The actual units used in calculations can vary as long as they are self-consistent.

A = cumulative emissions of a chemical, Eqs. 10-10, -13 (mass)

a = parameter in Eq. 10-9

b = parameter in Eq. 10-9 (time^{-1})

C = average concentration of chemical in compartment (mass/mass, or mass/volume)

D = parameter in Eqs. 10-13, -14

E = total emission rate, as in Eq. 10-1 (mass/time)

H = Henry's law constant, used in Eq. 10-7 (conc/conc)

k, k_{OH}, k_{O_3} = rate constant for bimolecular reaction; see §10-6 (volume · mass^{-1} · time^{-1} or volume · number^{-1} · time^{-1})

n = number of points in data set, used in Eq. 10-22

P_{H_2O} = partial pressure of water in atmosphere (not used in any equation)

p = parameter in Eq. 10-15

Q = total mass of chemical in compartment, as in Eq. 10-1 (mass)

R = total removal rate, as in Eq. 10-1 (mass/time)

T = temperature

t = time

$t_{1/2}$ = half-life; in Eq. 10-2 (time)

Greek

α = parameter in Eq. 10-14

β = parameter in Eq. 10-14

σ = standard deviation of measured atmospheric concentration, Eq. 10-21 (mass/mass or mass/volume)

τ = residence time (time)

θ = ratio of current atmospheric burden to cumulative emissions, Eq. 10-10 (dimensionless)

Subscripts

e = used with τ (τ_e) to denote exchange rate for air between northern and southern hemispheres

i = individual value, used with C in Eq. 10-22

N = northern hemisphere

p = precipitation, used with C in Eq. 10-6

S = southern hemisphere

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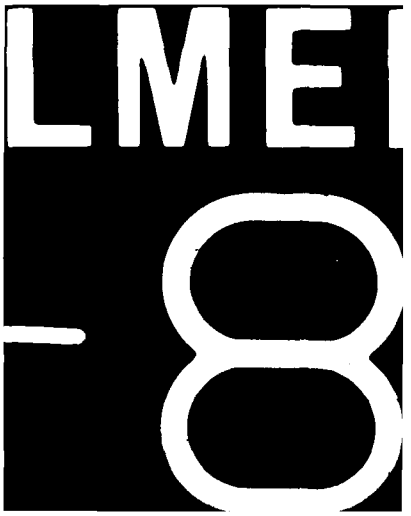
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