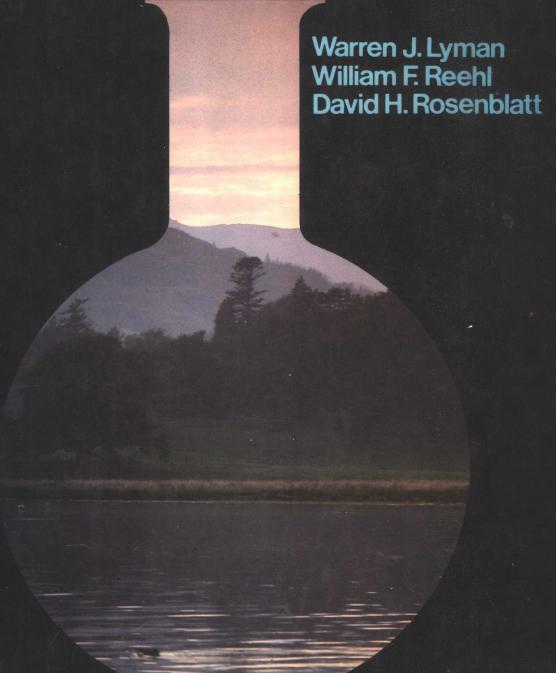
Handbook of
CHEMICAL PROPERTY
ESTIMATION METHODS
Environmental Behavior of Organic Compounds

Warren J. Lyman
William F. Rookl



54,155 1986

HANDBOOK OF CHEMICAL PROPERTY ESTIMATION METHODS

Environmental Behavior of Organic Compounds

Warren J. Lyman, Ph.D. William F. Reehl

Arthur D. Little, Inc., Cambridge, Massachusetts

David H. Rosenblatt, Ph.D.

U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Maryland

McGraw-Hill Book Company

New York St. Louis San Francisco Auckland Bogotá Hamburg Johannesburg London Madrid Mexico Montreal New Delhi Panama Paris São Paulo Singapore Sydney Tokyo Toronto Library of Congress Cataloging in Publication Data Lyman, Warren J.

Handbook of chemical property estimation methods.

Includes index.

1. Organic compounds—Analysis. I. Reehl, William F. II. Rosenblatt, David Hirsh. III. Title. QD271.L95 547.3 81-23662 ISBN 0-07-039175-0 AACR2

Copyright © 1982 by McGraw-Hill, Inc. This copyright applies only to the material (listed on the pages following the Index) reproduced by permission of the original copyright owners. The remainder of the book is a reprint of U.S. Army Report C-82426, "Research and Development of Methods for Estimating Physicochemical Properties of Organic Compounds of Environmental Concern, Final Report, Phase II," U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD 21701, June 1981.

1234567890 KPKP 898765432

ISBN 0-07-039175-0

ACKNOWLEDGMENTS

This book is the result of a project undertaken by Arthur D. Little, Inc., under contract to the U.S. Army Medical Research and Development Command. A project report exists which does not differ substantially from the material in this publication.¹

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.

The U.S. Army Medical Bioengineering Research and Development Laboratory funded both Phase I of this program, a preliminary problem definition study, and a major portion of Phase II, the writing of the handbook. Financial support for Phase II was also provided by the U.S. Army Toxic and Hazardous Materials Agency (Aberdeen Proving Ground, MD) and the U.S. Environmental Protection Agency's Office of Pesticides and Toxic Substances (Washington, DC).

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 each chapter.

All of the chapters in this handbook were rigorously reviewed by individuals in the U.S. Army, the U.S. Environmental Protection Agency, Arthur D. Little, Inc., and various universities and other organizations. These reviewers provided many helpful comments and pointed out several errors in our initial drafts. The authors are, however, responsible for any errors that may remain. The extramural reviewers who assisted us are listed below; special mention must be made of Dr. Robert Reid's contribution in the review of eleven chapters.

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt (eds.), "Research and Development of Methods for Estimating Physicochemical Properties of Organic Chemicals of Environmental Concern, Final Report, Phase II," U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD (June 1981). (Available from N.T.I.S.)

- Dr. George Armstrong, U.S. EPA and National Bureau of Standards, Washington, DC
- Mr. Sami Atallah, Gas Research Institute, Chicago, IL
- Mr. George Baughman, U.S. EPA, Athens, GA
- Dr. Howard Bausum, U.S. Army, Fort Detrick, Frederick, MD
- Dr. Robert Boething, U.S. EPA, Washington, DC
- Dr. Robert Brink, U.S. EPA, Washington, DC
- Dr. David Brown, U.S. EPA, Athens, GA
- Dr. Joseph Bufalini, U.S. EPA, Research Triangle Park, NC
- Dr. William D. Burrows, U.S. Army, Fort Detrick, Frederick, MD
- Dr. John Carey, National Water Research Institute, Burlington, Ontario
- Dr. James Davidson, University of Florida, Gainesville, FL
- Dr. James Dragun, U.S. EPA, Washington, DC
- Dr. Walter Farmer, University of California, Riverside, CA
- Dr. Lewis Gevantman, National Bureau of Standards, Washington, DC
- Dr. Corwin Hansch, Pomona College, Claremont, CA
- Dr. Albert Leo, Pomona College, Claremont, CA
- Dr. Donald Mackay, University of Toronto, Toronto, Ontario
- Dr. Doris Paris, U.S. EPA, Athens, GA
- Dr. Kenneth Partymiller, U.S. EPA, Washington, DC
- Dr. John Prausnitz, University of California, Berkeley, CA
- Dr. Robert Reid, Massachusetts Institute of Technology, Cambridge, MA
- Mr. David Renard, U.S. Army, Aberdeen Proving Ground, MD
- Dr. Ivan Simon (independent consultant), Cambridge, MA
- Dr. Arthur Stern, U.S. EPA, Washington, DC
- Dr. Gilman Veith, U.S. EPA, Duluth, MN
- Dr. John Walker, U.S. EPA, Washington, DC
- Dr. N. Lee Wolfe, U.S. EPA, Athens, GA
- Dr. Richard Zepp, U.S. EPA, Athens, GA
- Dr. Gunter Zweig, U.S. EPA, Washington, DC

xxiii

In addition to the above, special thanks are due to Dr. Joan Berkowitz, Dr. George Harris, Dr. John Ketteringham and Dr. Philip Levins, all of Arthur D. Little, Inc., who served as program reviewers.

Warren J. Lyman Program Manager Arthur D. Little, Inc.

Disclaimer

This handbook describes a variety of methods for obtaining estimates of chemical property values for organic chemicals. All estimation methods are subject to some limitations and involve some range of method errors (i.e., deviations of the estimates from the real values). It is incumbent upon the user to determine what estimation methods might be appropriate for each property and chemical, and to make a careful assessment of the possible errors in the predicted values. Neither the authors nor McGraw-Hill Book Co. provide any guarantee, express or implied, with regard to the general or specific applicability of any method, the range of errors that may be associated with any estimation routine, or the appropriateness of using an estimated property value in any subsequent calculation, design, or decision process. The authors and McGraw-Hill Book Co. accept no responsibility for damages, if any, suffered by any reader/user of this handbook as a result of decisions made or actions taken based on information contained herein.

HANDBOOK OF CHEMICAL PROPERTY ESTIMATION METHODS

SUMMARY OF CONTENTS

Table of Contents	V
Acknowledgments	xxi
List of Figures	XXV
List of Tables	XXi
Introduction	1
1 — Octanol/Water Partition Coefficient	1-1
2 — Solubility in Water	2-1
3 — Solubility in Various Solvents	3-1
4 — Adsorption Coefficient for Soils and Sediments	4-1
5 — Bioconcentration Factor in Aquatic Organisms	5-1
6 — Acid Dissociation Constant	6-1
7 — Rate of Hydrolysis	7-1
8 — Rate of Aqueous Photolysis	8-1
9 — Rate of Biodegradation	9-1
10 — Atmospheric Residence Time	10-1
11 — Activity Coefficient	11-1
12 — Boiling Point	12-1
13 — Heat of Vaporization	13-1
14 — Vapor Pressure	14-1
15 — Volatilization from Water	15-1
16 — Volatilization from Soil	16-1
17 — Diffusion Coefficients in Air and Water	17-1
18 — Flash Points of Pure Substances	18-1
19 — Densities of Vapors, Liquids and Solids	19-1
20 — Surface Tension	20-1
21 — Interfacial Tension with Water	21-1
22 — Liquid Viscosity	22-1
23 — Heat Capacity	23-1
24 — Thermal Conductivity	24-1
25 — Dipole Moment	25-1
26 — Index of Refraction	26-1
Appendices	
A — Bibliography of Standard Chemical Property	
Data Sources	A-1
B — Simple Linear Regression	B-1
C — Evaluating Propagated and Total Error in	
Chemical Property Estimates	C-1

Index follows Appendix C

TABLE OF CONTENTS

ACKNO\	WLEDGMENTS	xxi	
LIST OF	FIGURES	xxv	
LIST OF	TABLES	xxix	
INTROD	UCTION	1	
Overv	iew	1	
Apper	ndices	4	
Objec		4	
	its of Estimation	6	
	nts of Each Chapter	7	
	tions of this Handbook	8	
	Associated with Chemical Property Estimates	8	
Docur	nentation and Reporting of Estimated Values	9	
1 OC	OCTANOL/WATER PARTITION COEFFICIENT		
1-1	Introduction	1-1	
	Definition and Measurement	1-1	
	Environmental Significance	1-2	
	Estimation Methods Described in This Handbook	1-3	
1-2	Overview of Available Estimation Methods	1-5	
1-3	Leo's Fragment Constant Method	1-10	
	Principles of Use	1-10	
	Method Error	1-12	
	Fragments and Factors	1-16	
	Basic Steps	1-29	
1-4	Estimation with Solvent Regression Equations	1-39	
	Principles of Use	1-39	
	Solvent Regression Equations	1-39	
	Method Errors	1-42	
	Basic Steps	1-42	
1-5	Estimation from (Estimated) Activity Coefficients	1-47	
	Introduction	1-47	

vi Contents

		Relating K_{ow} to γ	1-47
		Estimating γ^{w} and γ°	1-49
	1-6	Available Data	1-49
	1-7	Symbols Used	1-50
	1-8	References	1-51
2	SOL	JBILITY IN WATER	
	2-1	Introduction	2-1
		Definition	2-1
		Units and Range of Values Estimation Methods Provided	2-2 2-2
	2-2	Overview of Available Estimation Methods	2-4
	2-3	Factors Influencing Solubility	2-11
		Method of Measurement	2-11
		Temperature	2-11
		Salinity	2-12
		Dissolved Organic Matter pH	2-12 2-13
	2-4	Estimation of S from K _{ow}	2-13
		Equations Available	2-13
		Basis for Estimation Method	2-24
		Method Errors	2-25 2 - 33
		Selection of Appropriate Equation(s) Basic Steps	2-35 2-35
	2-5	Estimation of S from Structure (Method of Irmann)	2-39
		Method Errors	2-39
		Basic Steps	2-41
	2-6	Available Data	2-46
	2-7	Symbols Used	2-46
	2-8	References	2-48
3	SOL	UBILITY IN VARIOUS SOLVENTS	
	3-1	Introduction	3-1
		Liquid-Liquid Systems	3-1
		Solid-Liquid Systems	3-2
		Gas-Liquid Systems	3-2

vii

Contents

		Estimation from Octanol-Water Partition Coefficient	5-4		
		Estimation from Water Solubility	5-10		
		Estimation from Soil Adsorption Coefficients Other Regression Equations	5-13 5-13		
	5-4	Uses and Limitations of Estimated Values	5-17		
	0 4	Sources of Discrepancies between BCF	•		
		Estimates and Laboratory Data	5-17		
		Application of BCF Estimates to Field Situations	5-21		
	5-5	Other Approaches to Estimating the			
		Accumulation of Organic Compounds	5-23		
	5-6	Available Data	5-26		
	5-7	Symbols Used	5-26		
	5-8	References	5-27		
6	ACID DISSOCIATION CONSTANT				
	6-1	Introduction	6-1		
	6-2	Experimental Measurement of K _a	6-5		
	6-3	Overview of Estimation Method	6-6		
	6-4	Estimation of K _a for Aromatic Acids —			
		Hammett Correlation	6-9		
		Basic Steps for Substituted Benzoic Acids	6-10		
		Basic Steps for Other Aromatic Acids	6-16		
	6-5	Estimation of K _a for Aliphatic Acids —	0.00		
		Taft Correlation	6-20		
		Basic Steps	6-21		
	6-6	Uncertainty in Estimated Values	6-22		
	6-7	Available Data	6-24		
	6-8	Symbols Used	6-24		
	6-9	References	6-27		
7	RAT	RATE OF HYDROLYSIS			
	7-1	Introduction	7-1		
	7-2	Characteristics of Hydrolysis	7-4		
		Hydrolysis Mechanism	7-4		
		Hydrolysis Rate Law	7-7		

		Measurement of Hydrolysis Rate Temperature Dependence of k	7-11 7-14		
		Effect of Reaction Medium	7-16		
	7-3	Overview of Estimation Methods	7-18		
	7-4	Uncertainty in Estimating Values	7-22		
	7-5	Estimation of $k_{\rm H}$ from the Hammett Correlation	7-22		
		Basic Steps	7-23		
	7-6	Estimation of k _H from the Taft Correlation	7-25		
		Basic Steps	7-25		
	7-7	Estimation of k₀ from the Hammett Equation	7-26		
		Basic Steps	7-26		
	7-8	Estimation of k _{OH} from the Hammett Equation	7-28		
		Basic Steps	7-28		
	7-9	Estimation of k _{oh} from the Taft Equation	7-31		
		Basic Steps	7-31		
	7-10	Estimation of k _{OH} from the pK _a of the Leaving Group	7-32		
		Basic Steps	7-32		
	7-11	Available Data	7-36		
	7-12	Symbols Used	7-36		
	7-13	References	7-46		
8	RATE OF AQUEOUS PHOTOLYSIS				
	8-1	Introduction	8-1		
	8-2	Basic Principles of Excitation/Deactivation	8-2		
		Excitation	8-2		
		Deactivation: Internal Conversion and	0.4		
		Intersystem Crossing Energy Transfer: Sensitization and Quenching	8-4 8-7		
		Summary	8-8		
	8-3	Absorption of Light	8-9		
		Chromophores and Characteristic Absorption Bands	8-9		
		Quantitative Calculation of Absorption of Solar Energy	8-16		
		Compound-specific Inputs $(\epsilon_{\lambda} \text{ values})$	8-19		
		Ecosystem-specific Inputs $(I_{\lambda} \text{ values})$	8-22		

x Contents

	8-4	Photochemical Reactions	8-29	
		General Considerations	8-29	
		Some Specific Examples	8-36	
		Real-World Complications	8-39	
	8-5	Symbols Used	8-40	
	8-6	References	8-41	
9	RATE	OF BIODEGRADATION		
	9-1	Introduction	9-1	
	9-2	Principles of Biodegradation	9-2	
		Definition	9-2	
		Characterization of the Biological System	9-3	
		Variables in Biodegradation	9-21	
	9-3	Standard Test Methods	9-33	
		Principles of Use	9-33	
		Characteristics of Typical Tests	9-37	
		Effect of Method and Analytical		
		Technique on Measured Rates	9-46	
	9-4	Biodegradation Rate Constants	9-47	
		Derivation	9-47	
		Rate Constants for Various Organic Compounds	9-51	
		Extrapolation of Laboratory Results to Field Conditions	9-52	
	9-5	Estimation of Biodegradation Rates	9-57	
		Solubility	9-62	
		BOD/COD	9-62	
		Hydrolysis	9-69	
	9-6	Available Data	9-70	
	9-7	Symbols and Abbreviations	9-74	
	9-8	References	9-75	
10	ATMOSPHERIC RESIDENCE TIME			
	10-1	Introduction	10-1	
	10-2	Selection of Appropriate Method	10-3	
	10-3	Steady-State Model	10-13	
		Principles of Use	10-13	
		Basic Steps	10-15	

	10-4	Nonsteady-State, One-Compartment Model	10-16	
		Principles of Use	10-16	
		Basic Steps	10-16	
	10-5	Nonsteady-State, Two-Compartment Model	10-18	
		Principles of Use Basic Steps	10-18 10-20	
	10-6	Use of Chemical Reactivity Data	10-21	
		Principles of Use Basic Steps	10-21 10-26	
	10-7	Correlation with Mean Standard Deviation (Junge's Correlation)	10-27	
		Principles of Use Basic Steps	10-27 10-29	
	10-8	Symbols Used	10-29	
		References	10-31	
11	ACTIVITY COEFFICIENT			
	11-1	Introduction	11-1	
	11-2	Available Methods	11-2	
	11-3	Method Errors	11-7	
	11-4	Method 1 — Infinite Dilution Activity Coefficients	11-10	
		Basic Steps	11-14	
	11-5	Method 2 — UNIFAC	11-20	
		Basic Steps	11-25	
	11-6	Available Data	11-49	
	11-7	Symbols Used	11-49	
	11-8	References	11-51	
12	BOILING POINT			
	12-1	Introduction	12-1	
	12-2	Selection of Appropriate Method	12-3	
	12-3	Meissner's Method	12-8	
		Principles of Use Basic Steps	12-8 12-13	

xli Contents

13

12-4	Lydersen-Forman-Thodos Method	12-16
	Principles of Use	12-16
	Calculation of Temperature Ratio, $ heta$	12-17
	Estimation of Critical Temperature	12-17
	Basic Steps	12-28
12-5	Miller's Method	12-33
	Basic Steps	12-34
12-6	Method of Ogata and Tsuchida	12-39
	Principles of Use	12-39
	Basic Steps	12-40
12-7	Method of Somayajulu and Palit	12-42
	Principles of Use	12-42
	Basic Steps	12-42
12-8	Kinney's Method	12-44
	Principles of Use	12-44
	Basic Steps	12-46
12-9	Method of Stiel and Thodos	12-47
	Principles of Use	12-47
	Basic Steps	12-48
12-10	Factors Affecting Boiling Point	12-50
12-11	Available Data	12-52
12-12	Symbols Used	12-52
12-13	References	12-54
HEAT	OF VAPORIZATION	
13-1	Introduction	13-1
13-2	Available Estimation Methods	13-2
13-3	Selection of Appropriate Method	13-4
13-4	Estimation of ΔH_{vb} from Critical Constants	13-4
	Principles of Use	13-4
	Basic Steps	13-9
13-5	Estimation of ΔH _{vb} from Vapor Pressure Data	13-12
	Principles of Use	13-12
	Basic Steps	13-15