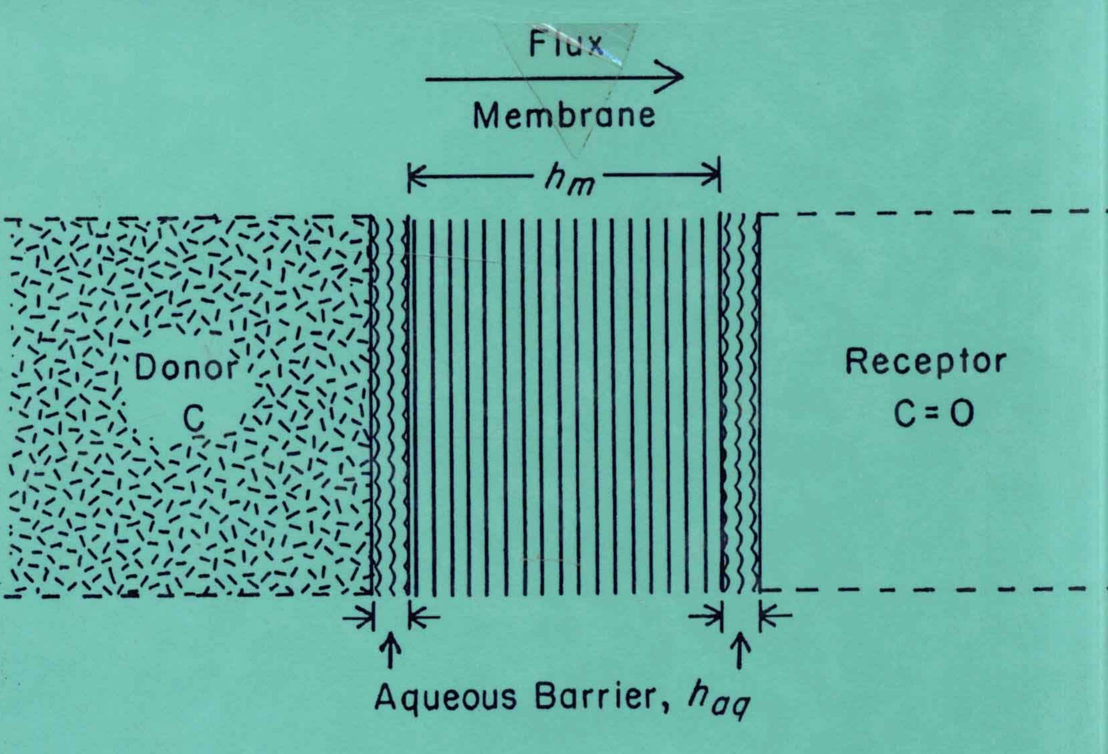
Chemical Concepts in Pollutant Behavior

Second Edition

Ian J. Tinsley


Flux
Membrane
h_m
Donor
C
Receptor
C = O
Aqueous Barrier, h_{aq}

CHEMICAL CONCEPTS IN POLLUTANT BEHAVIOR

SECOND EDITION

Ian J. Tinsley
Oregon State University

江苏工业学院图书馆
藏书章

WILEY-
INTERSCIENCE

A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:
Tinsley, Ian J., 1929–
Chemical concepts in pollutant behavior/Ian J. Tinsley.–2nd ed.
p. cm.
"A Wiley-Interscience publication."
Includes bibliographical references.
ISBN 0-471-09525-7 (cloth)
1. Agricultural chemicals—Environmental aspects. 2.
Pollution—Environmental aspects. I. Title.
QH545.A25 T56 2004
577.27--dc22
2003025152

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

CHEMICAL CONCEPTS IN POLLUTANT BEHAVIOR

PREFACE

Two developments in the early 1960s were major factors in the development of the field of environmental chemistry. The first was the introduction of the electron capture detector for the gas chromatograph (GC). This development provided a dramatic improvement in the level of sensitivity (several orders of magnitude) along with some improvement in selectivity. A direct consequence of the introduction of this technology was the demonstration of the widespread distribution of the polychlorinated biphenyls (PCBs) and organochlorine insecticides such as DDT and its metabolites. In her book, *Silent Spring*, Rachel Carson dramatized the potential biological consequences of chemicals in the environment and it was recognized that dilution could no longer be considered the answer to pollution. Research workers and government agencies realized that a systematic approach would be required to anticipate and manage the impact of compounds released into the environment.

Colleagues in my department were involved in the analytical area while others such as the late Dr. Virgil Freed were focusing on research that would improve the understanding of the environmental behavior of agricultural chemicals. At the same time, Dr. Cary Chiou was making significant contributions to our understanding of sorption in soil and evaporation processes. The department decided to develop a course that would focus on those chemical concepts that influence the environmental behavior of organic compounds. This area became very important to the Civil Engineer who was responsible for water quality issues and solid waste management. Those in agriculture and forestry needed to improve their understanding of the chemicals used in pest management to maximize efficacy and minimize adverse effects. The curriculum for students in these fields provided a limited background in chemistry—freshman chemistry and perhaps a term of organic chemistry. I had been teaching freshman chemistry for a number of years and realized that although students were introduced to many of the needed concepts they were only interested in accumulating sufficient information to pass the course and really were in no position to understand how these concepts could be applied.

I have offered a one-term course every year for about 27 years that has become the basis for this text, a complete rewrite of my first effort published almost 25 years ago. The content of the course has changed dramatically over this time as the field matured, however, the objective to demonstrate chemical factors determining environmental behavior has remained the same. The student response has been gratifying. Students with limited background in chemistry were at times threatened by

此为试读，需要完整PDF请访问：www.ertongbook.com

the subject matter but developed a better understanding of the basic concepts as they were able to apply them to the definition of environmental behavior. Chemistry majors on the other hand were encouraged to find how much of the material they had studied was so directly applicable in the environmental area.

CONTENTS

Preface vii

1. Introduction 1

2. Physical Chemical Parameters 5

3. Sorption 75

4. Evaporation 123

5. Absorption and Bioconcentration 149

6. Photochemical Processes 193

7. Redox Processes 261

8. Hydroloysis 285

9. Metabolic Transformation 311

10. Synthesis 359

Appendix 387

Index 393

CHAPTER 1

Introduction

When a chemical is introduced into the environment, there is a certain probability that it can move from the point where it was released. The distribution of some compounds has been shown to be global in scope having been detected on mountain peaks and in polar regions. This discovery could involve their use over a broad geographical area or their ability to be transported over large distances. It is possible that problems associated with the widespread distribution of chemicals could have been avoided or at least reduced if the properties of the chemicals influencing their movement had been understood when they were first introduced. However, the recognition of these problems has provided the incentive to define the processes and outline the chemical concepts involved resulting in the development of a new focus of "environmental chemistry". This field has matured over the past 25 years to the point where predictions can be made concerning the fate and distribution of organic compounds.

Distribution pathways are summarized in Figure 1.1. First of all, there can be movement within a compartment; for example, any chemical introduced into an aquatic compartment can move to the extent that the water moves, whether or not the chemical is in solution or sorbed on a particle. This movement would be defined by the appropriate hydrological parameters. A chemical may find its way into the atmosphere where it may be transported in atmospheric currents: In this situation the appropriate meteorological phenomena will determine the rate and direction of movement. Distribution in a plant or animal will be controlled by the transport mechanisms in that organism; either the vascular system in an animal or the phloem in a plant. In a much broader context, the transport of a chemical in an ecosystem must have some relation to the overall mass flow in the system since the chemical moves with the food constituents of the various components in the ecosystem.

Soil particles may carry chemicals in the air or water, however, movement through the soil compartment is accomplished primarily through diffusion or mass transport in water that seeps through the soil. In the situation where chemicals move within a compartment, the transport processes of that compartment are controlling and the effects of the properties of the chemical are minimal.

Chemical Concepts in Pollutant Behavior, Second Edition, by Ian Tinsley
ISBN 0-471-09525-7 © 2004 John Wiley & Sons, Inc.

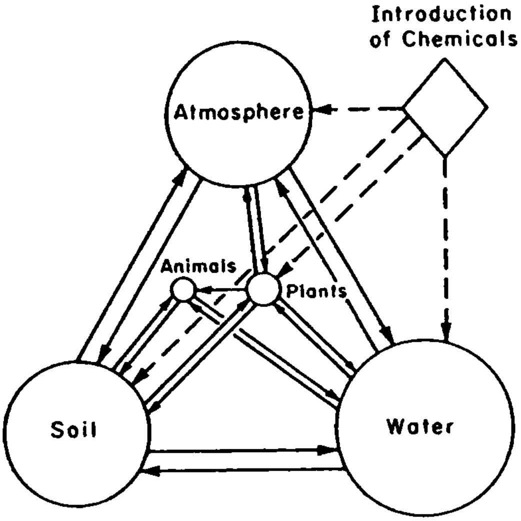


Figure 1.1 Processes by which chemicals distribute in the environment.

By contrast, the properties of the chemical become most significant in determining its tendency to move between compartments. Thermodynamic and kinetic factors influence distribution and although natural systems are rarely reversible, such an assumption can provide an indication of the trend for movement between compartments. The primary objective, then, will be to predict the environmental distribution of an organic compound as a function of its physical chemical properties using the following approach:

1. Define the process as concisely as possible: for example, what mechanisms may account for binding in soil, or how do compounds move through a biological membrane?
2. Demonstrate which properties of the chemical are controlling in each situation.
3. Develop quantitative treatment when possible.

This analysis will be applied to the following distribution processes:

1. Distribution between soil and water.
2. Evaporation from water and soil.
3. Absorption across a biological membrane into animals and plants.
4. Bioconcentration, a biological distribution process.

Having defined how an organic compound might distribute in the environment, the next question to address is, What is the potential for that compound to be transformed? This answer will involve the identification of processes that would be of significance. For any compound of interest, it will be necessary to identify which of these processes might be active, what products may be produced, and if possible assess the rate at which the transformations might occur under ambient conditions. In this analysis, the functional characteristics of the molecule, rather than the physical chemical parameters, will be determining.

Solar radiation represents a ubiquitous source of energy that can drive chemical reactions and, consequently, photochemical processes must be considered. Many oxidative processes are also photochemically induced. At low-oxygen tension, reductive reactions become important. The potential for organic compounds to react with water must be considered given the general distribution of this reactant in all compartments of the environment. Biochemical degradation processes in biota represent the most versatile since most are enzyme catalyzed and the organism can provide energy through cellular respiratory processes.

An understanding of transformation pathways will establish whether the compound is broken down to simple derivatives, such as carbon dioxide and water, and be incorporated into natural cycles or results in products that may be more toxic than the parent. A good example of the latter situation is photochemical smog. Automobile emissions, particularly the hydrocarbons and nitrogen oxides, are themselves undesirable; however, when these are acted upon by solar radiation a number of components are produced that are much more active and produce direct effects upon populace and plant life.

Reaction rates can be critical in determining the environmental impact of a compound. Those that are transformed at slower rates will be persistent and consequently result in more significant effects. Transformation rates will be influenced by distribution and site specific characteristics. For example, a compound that may be transformed by photochemical processes will persist if it is distributed primarily in the soil, and soil pH, which can vary with location, may have a marked influence on reactions with water.

In an environmental context, these processes are all occurring simultaneously, and it is not always apparent how they might interact. It is beyond the scope of this publication to provide a comprehensive analysis of this area, however, some discussion is given of how laboratory systems and mathematical models are being used to provide a more holistic analysis. These approaches are being used to predict levels of organics in different environmental compartments, which facilitate exposure assessment, one of the factors in defining the toxicological risk associated with a given site.

此为试读，需要完整PDF请访问：www.ertongbook.com

CHAPTER 2

Physical Chemical Parameters

The potential for an organic compound to distribute among environmental compartments is determined by its physical chemical properties. Thus it is necessary to review these parameters in this context. For example, environmental conditions impose temperature constraints of 10–40°C, which are often considerably lower than those used under laboratory conditions or in other processes. Observations at 20–25°C are usually acceptable. The only solvent of consequence is water; not a very effective solvent for many nonpolar organic compounds and determining aqueous solubilities at ambient temperatures can present significant experimental challenges. This chapter will address equilibrium vapor pressure, aqueous solubility, Henry's law constant, octanol–water partition coefficient, and acid–base dissociation constants (pK_a). The objective will be to develop a theoretical background, provide some perspective on how these quantities are determined, and if possible some basis for determining their validity—in some cases values reported in the literature for a given compound can vary by orders of magnitude. Useful data references will be summarized along with procedures for predicting values that may not have been reported.

2.1 EQUILIBRIUM VAPOR PRESSURE

When a pure liquid or solid is held at a constant temperature in a closed system some molecules at the surface will achieve sufficient energy to escape to the gas phase. In time, molecules in the gas phase will begin to return to the solid or liquid ultimately achieving a steady state with the evaporation rate balancing the condensation rate. The equilibrium vapor pressure, P^0, is thus defined as the pressure of the vapor that is in equilibrium with its pure condensed phase.

Pressure is force per unit area and although the Pascal, Pa ($N \cdot m^{-2}$ or $kg \cdot m^{-1} s^{-2}$) is the accepted SI unit, older terms found in the literature are listed in Table 2.1. Equilibrium vapor pressures for selected compounds of environmental interest are tabulated in Table 2.2. Equilibrium vapor pressure is considered to be an index of volatility, but this refers only to the pure compound. It will be seen that

Chemical Concepts in Pollutant Behavior, Second Edition, by Ian Tinsley
ISBN 0-471-09525-7 © 2004 John Wiley & Sons, Inc.

TABLE 2.1 Units of Pressure

Unit	Symbol	SI Equivalent
Pascal	Pa	
Atmosphere	atm	101,325 Pa
Torr	Torr	101,325/760 = 133.32 Pa
mm Mercury	mmHg	101,325/760 = 133.32 Pa

some of the more highly chlorinated PCBs can evaporate from water at significant rates despite having low vapor pressures. This process is defined by the Henry's law constant, which involves water solubility as well as vapor pressure.

2.1.1 Vapor Density and Concentration Terms

It is often useful to convert equilibrium vapor pressures to vapor densities using the ideal gas law

$$PV = nRT \qquad PV = \frac{m}{\mathrm{MW}}RT$$

where MW = molecular weight and the vapor density in $\mathrm{g \cdot L^{-1}}$ would be given by

$$\frac{m}{V} = \frac{P \cdot \mathrm{MW}}{RT}$$

where P is expressed in atmospheres (atm), V in liters (L), MW is in $\mathrm{g \cdot mol^{-1}}$, and the gas constant $R = 0.082\ \mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}}$. For example, P^0 (25°C) for 4,4′-(DCB) is 0.0050 Pa and

$$\text{vap density} = \frac{0.0050/101325(\text{atm}) \times 223(\mathrm{g \cdot mol^{-1}})}{0.082(\mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}}) \times 298\ \mathrm{K}}$$

$$= 0.451\ \mathrm{\mu g \cdot L^{-1}} = 451\ \mathrm{\mu g \cdot m^{-3}}$$

In the vapor phase, the concentration term, parts per million, (ppm), is defined as molecules per million molecules of air, and since the gas laws tell us that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, this is a volume-to-volume relation. The number of moles in a liter of air at 25°C and 1 atm would be

$$n/V(\text{air}) = 1\ \text{atm}/[0.082(\mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}}) \times 298\ \mathrm{K}] = 0.0409\ \mathrm{mol \cdot L^{-1}}$$

Under equilibrium conditions at 25 K the number of mol of 4,4′-DCB per liter would be

$$n/V(\text{4,4-DCB}) = [0.0050/101325](\text{atm})/[0.082(\mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}}) \times 298\ \mathrm{K}]$$

$$= 2.019 \times 10^{-9}\ \mathrm{mol \cdot L^{-1}}$$

TABLE 2.2 Equilibrium Vapor Pressures

Compound	P, 25°C (Pa)	Log P(Pa) = $f(1/T)$ 5–50°C	Compound	P, 25°C (Pa)	Log P(Pa) = $f(1/T)$ 5–50°C
Chlorobenzenes[a]			*Chlorinated Dibenzofurans*[a]		
1,2-DCB[b]	170	$\log P^c = 19.40 - 6013/T$	2,8-	3.9×10^{-4}	$\log P = 14.30669 - 5281.67/T$
1,4-DCB[b]	130	$\log P = 1.63209 - 2829.32/T$	Octo-	5.0×10^{-10}	$\log P = 16.88937 - 7808.74/T$
1,3,5-TCB[d]	25	$\log P^c = 8.301 - 2956/T$	*Aromatic Hydrocarbons*[e]		
PentaCB	0.22	$\log P = 15.6174 - 4138.4/T$	Benzene	12,700	$\log P^c = 6.02994 - 1211.003/(T - 52.)$
HCB	0.0023	$\log P = 10.83 - 4044/T$	Toluene	3800	$\log P^c = 6.16273 - 1391.005/(T - 48.97)$
Chlorinated Biphenyls[b]			1,2,4-Trimethylbenzene	270	$\log P^c = 6.16866 - 1573.267/(T - 64.586)$
3-	1.0	$\log P = 11.64178 - 3515.0/T$	Styrene	880	$\log P^c = 7.3945 - 2221.3/T$
4,4′-	0.0050	$\log P = 14.10 - 4977/T$	Naphthalene	10.4	$\log P = 13.59 - 3742/T$
2,4,5-	0.132	NA[b]	Biphenyl	1.30	$\log P^c = 14.840 - 4402.1/T$
2,2′.5.5′-	0.0049	NA[b]	Acenaphthene	0.30	$\log P^c = 10.883 - 4290.5/T$
2,3,4,5-	0.00037	$\log P = 12.10 - 4632/T$	Fluorene	0.09	$\log P = 14.385 - 4616.07/T$
2,2′4,4′6,6′	0.0005	$\log P = 14.84 - 5399/T$	Anthracene	0.001	$\log P = 12.977 - 4791.89/T$
2,2′3,3′5,5′,6.6′	2.7×10^{-5}	$\log P = 14.84 - 5399/T$	Phenanthrene	0.020	$\log P = 14.852 - 4962.77/T$
Chlorinated Dibenzodioxins[b]			Pyrene	6.0×10^{-4}	$\log P = 12.748 - 4760.73/T$
1-	0.012	$\log P = 15.35327 - 5150.4/T$	Chrysene	5.7×10^{-7}	$\log P = 14.848 - 6189/T$
2,7-	1.2×10^{-4}	$\log P = 14.6083 - 5523.34/T$	Benzo[*a*]pyrene	7.0×10^{-7}	$\log P = 11.6067 - 6181/T$
2,3,7,8-	2.0×10^{-7}	$\log P = 15.0391 - 6482.7/T$	Dibenzodioxin	0.055	$\log P = 14.91018 - 4820.43/T$
1,2,3,4,7-	8.8×10^{-8}	$\log P = 17.0221 - 7179.05/T$	Dibenzofuran	0.30	$\log P = 13.17192 - 4083/T$

[a] From Ref. 1.
[b] Dichlorobiphenyl = PCB
[c] P = kPa.
[d] Trichlorobiphenyl = TCB
[e] From Ref. 2.
[f] Not available = NA.

Thus, the vapor density of this biphenyl can be expressed in ppm

$$\begin{aligned}\text{vap density} &= (2.019 \times 10^{-9} \times N \times 1 \times 10^{6})/(0.0409 \times N)\\ &= 0.0494\,\text{ppm} = 49.4\,\text{ppb (parts per billion)}\end{aligned}$$

N is Avogadro's number, 6.022×10^{23} molecules · mol^{-1}

Air quality standards are often expressed in ppm and it can be useful to convert these values to mass per unit volume, usually $\mu g \cdot m^{-3}$. If a liter of air contains 0.0409 mol, a concentration of 1 ppm of say ozone, would thus contain 4.09×10^{-8} mol · L^{-1} which would convert to 4.09×10^{-5} mol per cubic metre or $4.09 \times 10^{-5}(\text{mol} \cdot \text{m}^{-3}) \times \text{MW}(\text{g} \cdot \text{mol}^{-1}) \times 1 \times 10^{6}\ (\mu\text{g} \cdot \text{g}^{-1})$. Thus

$$\mu\text{g} \cdot \text{m}^{-3} = \text{ppm} \times 40.9 \times \text{MW}$$

A background concentration of 0.03 ppm of ozone would correspond to

$$\mu\text{g} \cdot \text{m}^{-3} = 0.03 \times 40.9 \times 48 = 59\,\mu\text{g} \cdot \text{m}^{-3}$$

2.1.2 Procedures for Measuring Vapor Pressure

Different procedures can be used to determine equilibrium vapor pressure.[3] When a compound is sufficiently volatile, one can simply use head-space analysis of a closed system. Boiling points can be measured as a function of pressure down to ~10 mmHg, defining the liquid–vapor equilibrium of the phase diagram (Fig. 2.1). The Knudson effusion method[4] measures the rate of loss of vapor through a small aperture into a vacuum, which is accomplished using a Knudsen cell and monitoring, over time, the weight loss of the container or trapping and measuring the mass of vapor effusing. The weight loss, W, over time, t, is defined by the Knudsen equation developed from the kinetic theory of gases

$$W = PA(\text{MW}/[2\pi RT])^{1/2}t$$

where P is the vapor pressure, A is the area of the orifice, and MW is the molecular weight. This procedure can provide accurate data but is very sensitive to the presence of impurities, particularly those more volatile than the compound under investigation.

The gas saturation or transpiration method[3] can measure vapor pressures as low as 10^{-8} mmHg and involves the saturation of a slowly moving stream of carrier gas with the chemical and trapping and analysis of the chemical in the vapor phase. The vapor pressure is derived from the concentration of the vapor in the carrier gas. The accuracy of this method is predicated on achieving equilibrium between the liquid or solid and the vapor phase. This accuracy is accomplished by passing the carrier gas through a column containing quartz sand coated with the compound under study (Fig. 2.2) and providing sufficient residence time in the column (30–40 min) either

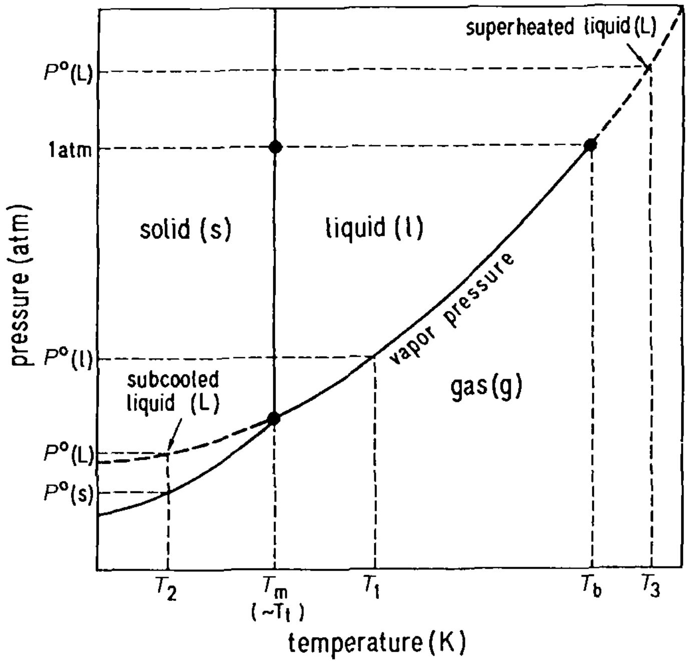

superheated liquid (L)
$P^o(L)$
1atm
pressure (atm)
solid (s)
liquid (l)
vapor pressure
$P^o(l)$
subcooled liquid (L)
gas (g)
$P^o(L)$
$P^o(s)$
T_2
T_m
$(\sim T_t)$
T_1
T_b
T_3
temperature (K)

Figure 2.1 Phase diagram for an organic compound indicating temperature–pressure relations between the phases.

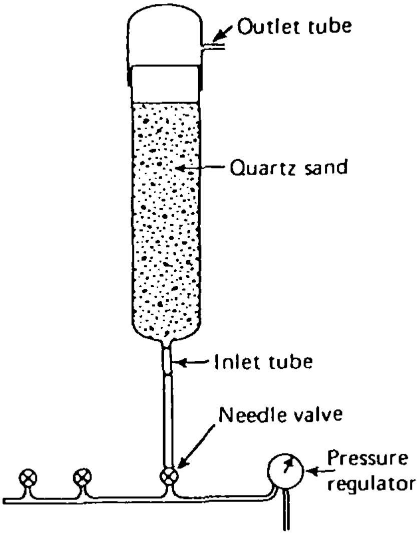

Outlet tube
Quartz sand
Inlet tube
Needle valve
Pressure regulator

Figure 2.2 A vapor saturator.

by using low flow rates or a large column. If the analytical method is specific, this method is not affected by impurities and, in fact, the vapor pressures of several compounds can be determined simultaneously providing there are no interactions between compounds in the vapor phase (Table 2.3). These data illustrate the effect of impurities on vapor composition. The technical product contains <1% of the *o, p*′-DDE, which contributes 27% of the vapor density.

2.1.3 Temperature Relations

Many organic compounds of environmental interest are solids at ambient temperatures and have low vapor pressures. Consequently, it has been expedient to measure vapor pressures at elevated temperatures to provide a response that is easier to detect. These data may be useful to a process engineer who might be managing these compounds at elevated temperatures, but the environmental chemist is put in the position of extrapolating from these observations to ambient conditions.

Phase diagrams (Fig. 2.1) summarize the pressure and temperature relations defining the equilibria between different phases. From an environmental perspective, the more important processes are the solid–vapor and liquid–vapor equilibria. The effect of temperature on the vapor pressure of the solid and the liquid are defined by the lines separating the two phases and, of course, the boiling point is the temperature at which the vapor pressure is 1 atm. Also note that a liquid can be cooled below its melting point providing a super-cooled liquid and in this state the vapor pressure is higher than the solid at the same temperature. It will be demonstrated that, in some situations there are advantages in considering the response of compounds in this state.

Thermodynamic analysis of the equilibrium between a condensed phase (solid or liquid) and the vapor is summarized by the Clausius–Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

TABLE 2.3 Composition at 30°C of 1–2% Technical DDT on Silica Sand

	Vapor Density			Conc. in
Compound	($ng \cdot L^{-1}$)	% of Total	P^0 (Pa)	Tech. DDT (%)
p,p′-DDT	13.6	8.0	9.66×10^{-5}	74.6
o,p′-DDT	104	61.7	7.39×10^{-4}	21.1
p,p′-DDE	24.1	14.3	1.91×10^{-4}	0.81
o,p′-DDE	26.9	16.0	2.13×10^{-4}	0.07

此为试读，需要完整PDF请访问：www.ertongbook.com