



SECOND EDITION

# ELEMENTS of ENVIRONMENTAL ENGINEERING

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*Thermodynamics  
and Kinetics*

**Kalliat T. Valsaraj**

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and Kinetics*

*Literacy is not the end of education, nor even the beginning*

— Mahatma Gandhi

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# Preface

Current environmental problems are related to increased population and the attendant competition for available resources to meet our everyday needs. Human endeavors are directed toward meeting these challenges, and improving the quality of life. Unfortunately, our attempts to combat these issues also contribute to pollution of the environment. The consequences of environmental pollution can be disastrous, and there are many examples that demonstrate the severity of the problem. Third-world industrialization and Earth's continual population growth (currently 1.5% per year) ensure that environmental protection will involve creative approaches to meet new and unforeseen challenges in the future.

To understand and combat environmental problems, we have to train students in the science and engineering of environmental protection. Only if an adequately informed group of professionals is in the forefront can scientific knowledge influence the formulation of public policy based on sound rational arguments. To this end, the present-day environmental professional should have a broad interdisciplinary training encompassing the disciplines of physics, chemistry, biology, and engineering.

Environmental engineering is a broad discipline that incorporates a number of specialties. Most universities now offer environmental degrees at the undergraduate level. It is a challenge to develop courses that will provide students a thorough, broad-based curriculum that includes every aspect of the environmental engineering profession. Traditionally environmental engineering has been a subdiscipline within civil engineering departments. Hence, most of the early curricula had a distinct civil engineering flavor and involved primarily water quality, air quality, municipal wastewater treatment, sewage treatment, and landfill management practices. Most of the activities within chemical engineering departments were confined to end-of-pipe treatment in chemical plants to control release of water, air, and solid wastes. With the realization that environmental problems are not confined to end-of-pipe treatment, chemical engineers began to move toward pollutant transport and transformation in the general environment, waste minimization, and pollution prevention activities within chemical plants. To impart these skills to graduating students, most chemical engineering departments began to embrace under their umbrella more and more courses in environmental processes. With the further realization that environmental engineering is interdisciplinary, stand-alone programs in environmental engineering began to appear in many universities. However, most of the programs still require courses to be taught out of both civil and chemical engineering departments.

Environmental engineers perform a variety of functions, the most critical of which are process designs for waste treatment, pollution prevention, fate and transport modeling, and risk assessment. Applied chemistry is an important component of environmental engineering. In particular, chemical thermodynamics and chemical kinetics, the two main pillars of physical chemistry, are paramount to

the understanding of environmental engineering. Unfortunately, these two topics are not covered at length in the environmental engineering curricula in most universities. Chemical engineers generally take two separate courses, one in thermodynamics and one in kinetics. They also take several prerequisites in chemistry, such as physical chemistry, organic chemistry, and analytical chemistry. Most environmental engineering programs, however, do not require such a broad spectrum of prerequisites. This means a single course has to be taught that introduces these subjects and lays the foundation for more-advanced courses in process design for waste separation, environmental transport modeling, and risk assessment. To accomplish this objective I embarked upon writing this textbook based on a course entitled "Chemical Thermodynamics and Kinetics for Environmental Processes" that I have been offering to environmental engineering majors. It is offered as a single semester required course for the ABET-accredited B.S. degree program in environmental engineering and is taught from the chemical engineering department at Louisiana State University.

This is an undergraduate textbook, but portions of it are also suitable for an introductory graduate level course. A basic understanding of physics, chemistry, and mathematics (especially differential calculus) is assumed. An introductory environmental engineering course followed by statics and dynamics should precede this course. Since physical chemistry and chemical engineering are the underlying principles in this book, two full chapters (Chapters 2 and 5) are devoted entirely to examining the fundamental aspects of thermodynamics and kinetics. Those with physical chemistry or chemical engineering background will find the treatment pedagogic, and they are encouraged to proceed directly to the applications (Chapters 3, 4, and 6). For the uninitiated, I strongly recommend following the worked examples and problems in the text. The examples are chosen to represent important applications and, since the choice is subjective, I do admit that some may be more relevant than others in illuminating the principles discussed. The problems are of varying levels of difficulty and they are ranked 1, 2, and 3, with 1 indicating the "least difficult" and 3 indicating the "most difficult" or "advanced." These are represented by subscripts beside the problem number. A solutions handbook is available from the publisher or can be obtained directly from me. My e-mail address is [valsaraj@che.lsu.edu](mailto:valsaraj@che.lsu.edu). Readers are encouraged to let me know directly any errors or omissions in the book as well as suggestions for improvement.

In writing this book, I have received help and encouragement from a number of people. Special thanks to friends and colleagues of mine at LSU: Louis Thibodeaux, Danny Reible, and David Constant. Louis has collaborated with me for over a decade in environmental engineering research, and he also planted in me the idea of writing a book. I extend special thanks to David Wilson for being a great role model as an educator and researcher, especially for his infectious enthusiasm for teaching. My sincere thanks to Carl Knopf, the current chairman of the department of chemical engineering at LSU, and Art Sterling, the immediate past chairman of the department, for their encouragement and support. My present and past graduate students (R. Ravikrishna, J.S. Smith, G. de Seze, and G.J. Thoma) have contributed in many ways by working out problems and pointing out errors in the first edition, and I owe a debt of gratitude to them all.

Of course, without the love and support from my family (my wife Nisha and my two children Viveca and Vinay), none of this would have been possible.

This book is dedicated to my beloved father who was always there for me when I needed him, but did not live to see his son's achievements, and to my dear mother who is a source of inspiration to me in my life.

**Kalliat T. Valsaraj**



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# Author

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# List of Notations

$a$	area per unit volume in a reactor ( $\text{m}^2 \cdot \text{m}^{-3}$ )
$a_i$	activity of solute $i$ ( $\text{mol} \cdot \text{l}^{-1}$ )
$a_{mn}$	interaction constant in UNIFAC
$a_\sigma$	activity of solute $i$ on the surface or at an interface
$A$	Helmholtz free energy (J); it also denotes the Hamaker constant in Chapter 4
$A_s$	surface area of a liquid or solid. $A_{\text{int}}$ , $A_{\text{ext}}$ are used to represent the internal and external surface area, respectively, of a solid ( $\text{m}^2$ )
$A_c$	cross-sectional area of a reactor ( $\text{m}^2$ ), cavity surface area in water ( $\text{nm}^2 \cdot \text{mol}^{-1}$ )
$A_{ij}$	interaction energy between $i$ and $j$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$A_m$	molar surface area of a solute ( $\text{nm}^2 \cdot \text{mol}^{-1}$ )
$[A]_a$	concentration of $A$ in air ( $\text{mol} \cdot \text{l}^{-1}$ )
$[A]_w$	concentration of $A$ in water ( $\text{mol} \cdot \text{l}^{-1}$ )
$[A]_o$	initial concentration of $A$ ( $\text{mol} \cdot \text{l}^{-1}$ )
$[A]_{\text{org}}^i$	concentration of $A$ in an organism; also denoted as $C_B^i$ ( $\text{mol} \cdot \text{kg}^{-1}$ )
$b_j$	fragment constant for the $j$ th group in octanol–water partition constant estimation
$b_{\text{si}}$	stream availability function ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$B(T)$	virial constant
$B_k$	structural factor for the $k$ th group in octanol–water partition constant estimation
[BOD]	biochemical oxygen demand; also denoted as $L$ ( $\text{mol} \cdot \text{l}^{-1}$ )
$C_i$ , $[C]_i$ , $C_i^w$	molar concentration of $i$ in water ( $\text{mol} \cdot \text{l}^{-1}$ ).
$C_i^g$	molar concentration of $i$ in air or gas phase ( $\text{mol} \cdot \text{l}^{-1}$ )
$C_i^o$	initial concentration of a pollutant in a reactor ( $\text{mol} \cdot \text{l}^{-1}$ ), molar concentration of $i$ in octanol ( $\text{mol} \cdot \text{l}^{-1}$ )
$C_i^{\text{ss}}$	steady state concentration in a reactor ( $\text{mol} \cdot \text{l}^{-1}$ ).
$C_s$	total suspended particulates in the atmosphere ( $\mu\text{g} \cdot \text{m}^{-3}$ )
$C_v$	molar heat capacity at constant volume ( $\text{J/mol} \cdot \text{K}$ )
$C_p$	molar heat capacity at constant pressure ( $\text{J/mol} \cdot \text{K}$ )
$C_c$	concentration of dissolved organic carbon (DOC) in water ( $\text{mol} \cdot \text{l}^{-1}$ )

$C_{C,i}$	concentration of $i$ on DOC in water ( $\text{mol} \cdot \text{kg}^{-1}$ )
$[\text{CMC}], C_{\text{mic}}$	critical micellar concentration of a surfactant in water ( $\text{mmol} \cdot \text{l}^{-1}$ )
$C_i^*, C_i^\infty$	saturation solubility of $i$ in water ( $\text{mol} \cdot \text{l}^{-1}$ )
$C(t)$	concentration as a function of time in a reactor
$d, d_p$	diameter (m); in Chapter 4, $d$ also represents the distance between two colloids (m)
$D_i^w, D_i^a$	diffusivity of $i$ in water and air respectively ( $\text{m}^2 \cdot \text{s}^{-1}$ )
$D_e^*, D_s^*$	effective diffusivity in soils, sediments, and atmospheric particles ( $\text{m}^2 \cdot \text{s}^{-1}$ )
$D_s$	surface diffusivity ( $\text{m}^2 \cdot \text{s}^{-1}$ )
$D_{\text{ow}}$	distribution constant for $i$ between octanol and water ( $\text{mol} \cdot \text{l}^{-1} / (\text{mol} \cdot \text{l}^{-1})$ )
$e$	electron charge (C)
$[e]$	electron activity
$E$	emission rate ( $\text{mol} \cdot \text{h}^{-1}$ ); also denotes enrichment ratio for air–water partitioning in atmospheric moisture
$E_a$	activation energy of a chemical reaction ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$E_0$	zero point energy of a molecule (J)
$f_i, f_i^g, f_i^l$	fugacity (Pa); $g$ and $l$ represent gas and liquid phases
$f_i^\ominus$	standard state fugacity (Pa)
$f_i^\sigma$	fugacity of $i$ at an interface (Pa)
$f_{\text{om}}$	fractional organic matter in soils and sediments
$f_{\text{oc}}$	fractional organic carbon in soils and sediments
$F$	Faraday constant ( $\text{C} \cdot \text{mol}^{-1}$ ); also denotes the filter-retained solute concentration in air–particulate partitioning ( $\mu\text{g} \cdot \text{m}^{-3}$ )
$g$	acceleration due to gravity ( $\text{m} \cdot \text{s}^{-2}$ )
$g^E$	excess partial molar Gibbs free energy for $i$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$G$	Gibbs free energy (J); also denotes molar gas flow rate in a reactor ( $\text{mol} \cdot \text{s}^{-1}$ )
$G_c, G_t$	cavity forming free energy and solute–solvent interaction free energy, respectively ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$\Delta G^\ominus, \Delta G_r^\ominus$	standard free energy of reaction ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$\Delta G_{\text{ads}}$	adsorption free energy ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$\Delta G^\ddagger$	Gibbs activation energy for a reaction ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$h$	Planck's constant ( $\text{J} \cdot \text{s}$ )
$h_s$	height (m)
$h^E$	excess molar enthalpy ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$H$	enthalpy (J)
HSA	area of the hydrophobic part of a molecule ( $\text{nm}^2$ )

$H_i$	Henry's constant (atm or kPa); also represented as $H_v$ (dimensionless mole fraction ratio), $H_c$ (dimensionless, molar concentration ratio), and $H_a$ (atm · m <sup>3</sup> /mol or kPa · m <sup>3</sup> /mol)
$\Delta H_f^\ominus, \Delta H_r^\ominus, \Delta H_c^\ominus$	standard heat of formation, reaction, and combustion, respectively (kJ · mol <sup>-1</sup> )
$\Delta H_v$	molar enthalpy of vaporization (kJ · mol <sup>-1</sup> )
$I$	ionic strength of an electrolyte solution (mol · l <sup>-1</sup> ); also used to represent intensity of absorbed radiation in Chapter 6
$I_o$	intensity of incident radiation (W · m <sup>-2</sup> ).
$k_B$	Boltzmann constant (J · K <sup>-1</sup> )
$k_a, k_w, k_c$	individual phase mass transfer coefficient for a solute $i$ (m · s <sup>-1</sup> )
$k_j, k_s$	salting-out parameter
$k_d$	deoxygenation rate constant (s <sup>-1</sup> )
$k_r$	reaeration rate constant (s <sup>-1</sup> )
$k_{dec}$	decay constant for microorganisms (s <sup>-1</sup> )
$k_E^*$	complexation rate constant (l/mol · s)
$k_f$	rate of a forward reaction (s <sup>-1</sup> )
$k_b$	rate of a backward reaction (s <sup>-1</sup> )
$k_i$	rate constant for an $i$ th-order reaction
$k_A^s$	surface reaction constant for $A$ (m · s <sup>-1</sup> )
$k^\ddagger$	rate constant from activated complex theory (l/mol · s)
$k_{AB}$	rate constant for electron transfer between $A$ and $B$ (l/mol · s)
$k^*$	overall rate constant for a reaction (s <sup>-1</sup> )
$K_H$	linear (Henry's) adsorption constant
$K_L$	Langmuir adsorption constant
$K_F$	Freundlich adsorption constant
$K_{sw}, K_{ads}$	linear adsorption constant for a solute between solid and water (l · kg <sup>-1</sup> )
$K_B$	BET adsorption constant
$K_l, K_w$	overall liquid-phase mass transfer coefficient between air and water (m · s <sup>-1</sup> )
$K_C$	DOC–water partition constant for a solute (l · kg <sup>-1</sup> )
$K_{aw}$	air–water partition constant (dimensionless)
$K_{aw}^\sigma$	partition constant between the air–water interface and bulk water (m)
$K_{oc}$	linear adsorption constant between soil or sediment and water based on organic carbon content (l · kg <sup>-1</sup> )
$K_{Bw}$	bioconcentration factor (l · kg <sup>-1</sup> )
$K_{PA}$	air–particulate partition constant (ng · m <sup>-3</sup> )

$K_{BA}$	partition constant for a solute between solvents $B$ and $A$
$K_{AS}$	air–soil partition constant ( $\text{l} \cdot \text{kg}^{-1}$ )
$K_{VA}$	vegetation–air partition constant ( $\text{l} \cdot \text{kg}^{-1}$ )
$K_{\text{ion}}$	ion-exchange separation factor
$K_c^*$	equilibrium constant for an ion-exchange reaction
$K_{\text{eq}}$	equilibrium constant for a chemical reaction (dimensions depend on the order of the reaction)
$K^\ddagger$	equilibrium constant for a chemical reaction from the activated complex theory
$K_m$	Michaelis–Menten kinetics parameter ( $\text{kg} \cdot \text{l}^{-1}$ )
$K_s$	Monod kinetics parameter ( $\text{kg} \cdot \text{l}^{-1}$ )
$K_a, K_b$	ionization constant for acid and base, respectively; note that additional subscripts 1, 2, etc. denote first, second, etc. ionization constants
$K_{\text{ow}}$	partition constant for a solute between octanol and water
$K_{BA}^x$	partition constant for $i$ between two liquid phases based on mole fractions
$l$	liquid phase when used as a subscript
$\text{l}$	unit liter
$L_o$	ultimate biochemical oxygen demand in a natural stream ( $\text{mol} \cdot \text{l}^{-1}$ )
$m_i$	molarity of species $i$ in solution ( $\text{mol} \cdot \text{l}^{-1}$ )
$m_o$	molality of solvent ( $\text{mol} \cdot \text{kg}^{-1}$ )
$m$	mass (kg)
$M$	molar mass
$n, n_i$	number of moles
$n_i^\sigma$	moles of solute at an interface
$N_A$	Avogadro's number; in Chapter 6, denotes the total number of moles of solute $A$ in a reactor at any given time, $t$
$N_c$	capillary number
$N_{A,\text{in}}, N_{A,\text{out}}$	influent and effluent rates in a reactor ( $\text{mol} \cdot \text{s}^{-1}$ )
$p, P, P_T$	pressure (external), total pressure (Pa)
$p_i, P_i$	partial pressure of component $i$ (Pa); in Chapter 6, $p_i$ also represents the photolysis rate constant ( $\text{s}^{-1}$ )
$P^*, P_s^*, P_l^*$	saturation vapor pressure of $i$ in the solid or liquid forms (kPa)
$P^\ominus$	standard state pressure ( $1 \text{ atm} = 101.325 \text{ kPa}$ )
$P_{s(l)}^*$	subcooled liquid vapor pressure (kPa)
$\text{Pe}$	Peclet number
$\Delta p_\sigma$	Laplace pressure (kPa)
$q$	heat absorbed by a system ( $\text{J} \cdot \text{mol}^{-1}$ )

$q_{\text{ads}}$	heat of adsorption ( $\text{J} \cdot \text{mol}^{-1}$ )
$Q_l, Q_g$	volumetric liquid and gas flow rate ( $\text{m}^3 \cdot \text{s}^{-1}$ )
$Q_i, Q_o$	influent and effluent volumetric flow rates in a reactor ( $\text{l} \cdot \text{s}^{-1}$ )
$r$	radius of a spherical particle or drop or bubble (m)
$-r_A$	rate of a reaction ( $\text{mol/l} \cdot \text{s}$ ); also denoted as $R_A$
$r_c$	radius of a column (m)
$\bar{R}$	average rainfall intensity (m)
$R$	gas constant ( $\text{J/K} \cdot \text{mol}$ ); also used to represent the radius of a sphere (m)
$R_B$	Revelle buffer factor
$R_{\text{ei}}$	rate of respiration by an organism ( $\text{g/g} \cdot \text{day}$ )
$s$	represents the solid phase when used as the subscript
$S$	entropy ( $\text{J} \cdot \text{K}^{-1}$ ); also used to represent the separation factor
$S^E$	excess molar entropy ( $\text{kJ} \cdot \text{mol}^{-1}$ )
$S_a$	surface area of an adsorbent ( $\text{m}^2 \cdot \text{kg}^{-1}$ )
$S_T$	surface area of particles per unit volume of air ( $\text{m}^2 \cdot \text{m}^{-3}$ )
$\Delta \bar{S}_v, \Delta \bar{S}_m$	molar entropy of vaporization and fusion, respectively ( $\text{J/K} \cdot \text{mol}$ )
$t_m$	melting point in degrees centigrade
$t_b$	boiling point in degrees centigrade.
$T_M$	melting point in Kelvin
$T_b$	boiling point in Kelvin
$t_{1/2}$	half-life of a chemical reaction (s)
$T$	temperature in Kelvin
$u, u_g$	gas velocity or superficial velocity ( $\text{m} \cdot \text{s}^{-1}$ )
$U$	internal energy (J)
$u_D$	Darcy velocity ( $\text{m} \cdot \text{s}^{-1}$ )
$V$	volume, total volume of a reactor (l)
$V_H$	partial molar volume of a hydrocarbon in water ( $\text{l} \cdot \text{mol}^{-1}$ )
$\bar{v}_i$	partial molar volume of $i$ in a gas mixture ( $\text{l} \cdot \text{mol}^{-1}$ )
$\bar{v}_w, \bar{v}_o$	molar volume of water and octanol, respectively ( $\text{l} \cdot \text{mol}^{-1}$ )
$v_{\text{set}}$	settling velocity of particles in water ( $\text{m} \cdot \text{s}^{-1}$ )
$V_T$	total volume of particles per unit volume of air ( $\text{m}^3 \cdot \text{m}^{-3}$ )
$V_{\text{atm}}$	total volume of the atmosphere ( $\text{m}^3$ )
$V_{\text{max}}$	Michaelis–Menten kinetics parameter ( $\text{s}^{-1}$ ).
$w$	work done on the system (J); in Chapters 4 and 6, also denotes the total mass of solute on a solid (mg or kg); when used as a subscript, denotes water
$w_{\text{ads}}$	mass of solute adsorbed per mass of soil or sediment ( $\text{mg} \cdot \text{kg}^{-1}$ or $\text{kg} \cdot \text{kg}^{-1}$ ); sometimes represented simply as $w_d$
$w_p$	aerosol washout ratio

$w_v, w_g$	washout ratio of vapor or gas
$W_{s w}$	work of coupling a solute with solvent (J)
$W_{cav w}$	work of forming a cavity in water to accommodate a solute (J)
$x_A$	fractional surface coverage of a solute A
$x_i^w, x_i$	mole fraction of component $i$ in water
$x_i^*$	saturation aqueous mole fraction solubility
$x_i^\sigma$	mole fraction of $i$ at an interface
$X_s$	length (m)
$[X]$	concentration of microorganisms in the aqueous phase ( $g \cdot l^{-1}$ )
$y_i$	mole fraction of $i$ in the gas phase
$Y_s$	width (m)
$Z_i$	charge of an ion in the aqueous phase
$Z_s$	total height (m)
$Z, Z_j$	fugacity capacity in an environmental compartment $j$

### Greek alphabets

$\alpha$	degree of acid or base ionization in water
$\gamma_i$	activity coefficient of $i$
$\gamma_c$	activity coefficient based on molar concentration
$\gamma_m$	activity coefficient based on molality
$\gamma_i^w$	activity coefficient of $i$ in water
$\gamma_i^o$	activity coefficient of $i$ in octanol
$\gamma_{\pm}$	mean ionic activity coefficient of an electrolyte solution
$\gamma_i^*, \gamma_i^\infty$	activity coefficient of $i$ in water at saturation solubility and infinite dilution, respectively
$\Gamma_i, \Gamma_{i(j)}$	surface excess of $i$ ( $mol \cdot m^{-2}$ )
$\Gamma_{max}, \Gamma_i^{max}$	maximum surface concentration ( $mol \cdot m^{-2}$ )
*	thickness of an interface, or the boundary layer thickness (m)
$\Delta, \Delta_o, \Delta_c$	oxygen deficit in a natural stream ( $mol \cdot l^{-1}$ )
$\epsilon$	porosity; also represents dielectric permittivity in electrostatics
$\epsilon_g$	gas holdup in a bubble column, gas fraction in soil pores
$\epsilon_v$	molar absorptivity ( $m^2 \cdot mol^{-1}$ )
$\kappa$	reciprocal Debye length ( $m^{-1}$ ); also represents the transmission coefficient for a reaction
$\lambda$	wavelength of radiation ( $m^{-1}$ )
$\Lambda$	dimensionless radius
$\mu_s^s, \mu_l^l, \mu_g^g$	chemical potential of solid, liquid, and gas, respectively

$\mu_i$	growth rate of an organism $i$ ( $\text{g} \cdot \text{day}^{-1}$ )
$\mu^\ominus, \mu_i^\ominus$	standard state chemical potential
$\mu_i^*$	chemical potential of pure liquid
$\mu_{\max}$	Monod kinetics parameter ( $\text{day}^{-1}$ or $\text{s}^{-1}$ )
$\nu$	viscosity of solution (Poise); also used to represent the frequency of vibration of a molecule
$\nu_i$	stoichiometry of species $i$ in a reaction
$\zeta$	compressibility factor ( $\text{Pa}^{-1}$ ), extent of a reaction ( $\text{mol} \cdot \text{s}^{-1}$ ) and effectiveness factor
$\Pi$	osmotic pressure (Pa)
$\pi$	surface pressure (Pa)
$\rho$	density ( $\text{kg} \cdot \text{l}^{-1}$ ); also represents an LFER constant
$\rho_s$	concentration of sorbent in solution ( $\text{kg} \cdot \text{l}^{-1}$ )
$\rho_p$	particle density ( $\text{kg} \cdot \text{l}^{-1}$ )
$\rho_c, \rho_T$	concentration of suspended particles in solution ( $\text{kg} \cdot \text{l}^{-1}$ )
$\rho_b$	bulk density ( $\text{kg} \cdot \text{l}^{-1}$ )
$\sigma$	surface tension of a liquid ( $\text{mN} \cdot \text{m}^{-1}$ ); also denotes surface charge density on a solid ( $\text{C} \cdot \text{g}^{-1}$ ); also used to represent an LFER constant
$\sigma_{s/w}, \sigma_{l/w}$	interfacial tension between solid and water or liquid and water ( $\text{mN} \cdot \text{m}^{-1}$ )
$\tau$	residence time for an air bubble in water (s); also represents the tortuosity factor in soils, sediments, and atmospheric particles
$\tau_d$	detention time or contact time in a reactor (s)
$\tau_r$	time constant for a photochemical transient ( $\text{s}^{-1}$ )
$\phi$	molar osmotic coefficient
$\phi_c$	cosolvent volume fraction in a mixture of water and organic solvent
$\phi_\lambda$	quantum efficiency
$\phi_i^w, \phi_i^p$	fractional mass of $i$ in water or on particles in the atmosphere
$\Phi_n$	Thiele modulus
$\chi_i$	fugacity coefficient of $i$
$\psi$	electrostatic potential of an ion
$\theta$	contact angle
$\theta_i$	surface coverage by molecule $i$
$\theta_w$	volumetric water content in soils
$\theta_l$	liquid water content in atmospheric particles.
$\Theta$	Damkohler number



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### Chapter 2

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