

Chapter 1

Introductory Remarks

1.1 PERSPECTIVE

From the outset, let us make no mistakes about the purpose and content of this textbook. The main title—*Environmental Process Analysis*—suggests that we will analyze processes. The targeted processes are those operative homogeneously in aqueous solutions, involving the gas–water interface, and involving the water–solid interface. Understandings of the behavior of environmental systems can arise from examination of both natural or engineered processes under equilibrium or near-equilibrium conditions. The effects of perturbations on systems can be determined using the initial and predicted final equilibrium conditions. In addition, understandings can arise from examination of the progress of such processes under transient or near (quasi) steady-state conditions. Then, Environmental Process Analysis is the examination of the processes operative in conjunction with perturbations of environmental systems, either natural or engineered, arising mostly from actions of our society. Certain of these perturbations beget negative consequences associated with actions that, while well-intentioned, contribute to the detriment of an environmental system. Others are intended to positively affect a compromised natural system or to implement a desired outcome within the context of an engineered system. The subtitle—*Principles and Modeling*—suggests that we will employ appropriate principles, develop models in support of our analyses, and employ these models to predict the outcomes from intended or unintended perturbations. Modeling has three distinct levels. Conceptual modeling involves identifying, understanding, and interrelating processes operative

within targeted systems. Mathematical modeling involves coupling of relevant mathematical relations with processes identified by conceptual modeling efforts and assembling those mathematical relations into overall models describing behaviors of processes within systems. Lastly, numerical modeling involves work with the developed mathematical model to produce quantitative predictions of behavior.

We examine the scientific literature to understand processes and the means by which they may be mathematically described and consult resources assembled by the mathematicians to develop sets of or even single equations that might be used to describe the behavior of the system. It is not until we have collected these relations and devised means to use them to obtain quantitative answers that we have accomplished the process called modeling. A model can be as simple as a single linear relation or as complex as a set of coupled, higher-order, partial differential equations. The key is that, in either case, the conceptual, mathematical, and numerical aspects are employed. Even today, in the minds of many, numerical modeling is associated with the writing of lines and lines of structured programs that employ numerical methods in solution of sets of mathematical relations that defy closed-form analytic solution. We prefer the simpler idea that numerical modeling merely involves the production of numerical results using appropriate means to describe behaviors of processes in systems. Fortunately, with the development of the microchip, personal computers, and general computational software, the numerical part of modeling efforts has become much more conveniently accomplished. Then, in this text we illustrate and employ the modeling process to analyze effects of perturbations on both natural and engineered systems. We also illustrate the portability of key principles and concepts among the myriad contexts within which environmental engineering operates.

1.2 ORGANIZATION AND OBJECTIVES

Our prime objective with this textbook is the education of the student, interested faculty member, or practitioner in the means and methodologies to conceptually, mathematically, and numerically model processes operative in environmental systems. We begin with very basic processes and simple systems and progress to processes that are somewhat complex and to systems well beyond the simplistic. We have organized the text into 11 additional chapters beyond this introduction. Chapters 2–6 build upon each other in the general area of equilibrium aqueous chemistry. Chapters 7–9 are aligned along an alternative thread addressing reactions and reactors. Then Chapters 10–12 return to the aqueous equilibrium chemistry thread to address more advanced applications of the principles. In the following sections, we briefly describe the focus of each of the ensuing chapters.

1.2.1 Water

Although vital to environmental systems and perhaps of greatest importance relative to the future of the Earth and its inhabitants, water is somewhat ancillary to our analyses herein. We are mostly concerned about constituents within water and are

mostly interested in the properties of water that contribute to the behaviors of these constituents. We have thus included a short chapter addressing the properties of water that are important in examination of the behaviors of acids and bases, cations and anions, and specifically hydronium and hydroxide in aqueous solutions. For those wishing to delve more deeply into the mechanical or other properties of water, we suggest examination of the many texts written addressing fluid properties and physical chemistry of water.

1.2.2 Concentration Units

Each scientific and engineering discipline, and subdiscipline in many cases, has its own means to specify the abundances of constituents in gases, liquids, and solids. Since environmental engineering must embrace most of the natural sciences (e.g., chemistry, physics, biology, geology, limnology, etc.) and many of the engineering disciplines (e.g., chemical, civil, geological, metallurgical, mining, etc.), we environmental engineers must be conversant with the preferred means to describe species abundances by the many disciplines. To that end, we have included Chapter 3, in which we have assembled a database of concentration units used across these disciplines. Chapter 3 also contains a review of the means to interconvert units from one set to another using the basic chemical concepts of molecular mass and the ideal gas equation of state.

1.2.3 Chemical Equilibria and the Law of Mass Action

Over the past three plus centuries, the chemists have assembled a wonderful system with which to describe chemical processes. Tendencies for processes to proceed, rates at which they would proceed, and associated ending points (the equilibrium conditions) are all addressed within this very logical, quantitative system. In examination of perturbations of environmental systems, herein we choose to predict the final state of a system via close attention to the processes operative within. To that end, we employ chemical equilibria in combination with mass or molar accounting. Distinct styles for describing these equilibria arise from special applications of the law of mass action. Specifically, Henry's law, acid deprotonation, metal–ligand complex formation, solubility and dissolution, and oxidation/reduction half reactions all have their characteristic formulations of the law of mass action. These are reviewed in Chapter 4. For chemical equilibria, the change in standard-state Gibbs energy associated with a reaction as written is employed to define the equilibrium constant under standard conditions. The change in standard state enthalpy associated with a reaction as written is used in adjusting the magnitude of the equilibrium constant for varying temperature. We leave detailed discussions of these topics to the physical chemists and choose to employ two important results. Use of standard-state Gibbs energy changes to determine the magnitude of equilibrium constants is introduced in Chapter 10 and employed in detail in Chapter 12. Use of standard-state enthalpy changes to adjust equilibrium constants for alternative temperatures is employed in Chapter 10.

1.2.4 Henry's Law

Chapter 5 is devoted to developing understandings of the application of Henry's law to distributions of nonelectrolyte species between vapor and water. We employ Henry's law to predict abundances in the vapor from known abundances in water, and to predict abundances in water from known abundances in the vapor. We employ varying discipline-specific concentration units in these analyses. We begin our integrated modeling efforts by carrying Henry's law with us into a number of environmental contexts addressing air/water distributions in atmospheric, terrestrial, biogeochemical, and engineered systems. We showcase its portability.

1.2.5 Acids and Bases

In Chapter 6, we introduce the concept of water as an acid and a base and examine the interactions between water and the hydrogen ion (often simply called a proton) to form the hydronium ion, and begin the discussion of the hydration of cations in general, using the hydronium ion as an example. We introduce and solidify the concept that each acid has a conjugate base and that each base has a conjugate acid. Mono- and multiprotic acids are examined. Unlike many texts which focus on the carbonate system, the sulfur system, the nitrogen system, and the phosphorus system, we approach acid deprotonation from the standpoint of the general behavior of acids, employing a systematic approach to quantitate the behaviors of specific acids in defined systems. We stress that if any specie of an acid system is present in an aqueous solution, all must be present. We introduce the mole balance concept and strive toward an understanding of the idea of the *predominant specie or species* as dictated by the relation between the hydronium ion abundance within the system and the acid dissociation constant of the targeted acid system. We illustrate the connection between Henry's law and acid deprotonation equilibria. For a system that has attained the equilibrium condition, all equilibria must be simultaneously satisfied. We illustrate the prediction of aqueous speciation when the abundance of a vapor-phase specie and one critical condition of the aqueous solution are known. Similarly, from knowledge of at least two conditions relative to an acid system within an aqueous solution, we can predict the entire speciation within the aqueous solution as well as the abundance of the nonelectrolyte acid specie in vapor with which the water is in equilibrium. Employing the proton balance in the context of conjugate bases accepting protons and conjugate acids donating protons, we seek to develop beginning understandings of buffering capacity and the functional properties termed alkalinity and acidity. We make a beginning foray into the concepts of acid and base neutralizing capacity. We extend our integrated modeling efforts by carrying our understandings of acid deprotonation with us to join our understandings of Henry's law from Chapter 5 in contextual applications, again involving the atmospheric, terrestrial, biogeochemical, and engineered systems. In a manner similar to that employed in Chapter 5, we illustrate the portability of these principles and concepts.

1.2.6 Mixing

The mixing of two or more continuous streams is an important environmental process often given but cursory treatment in environmental engineering texts. While “zero volume mixing” is simple in concept, the nuances regarding when, how, and to what systems we can employ this principle often smudge the understandings of its applicability. In Chapter 7, we use continuous mixing of flows to begin our examination of the differences between transient and steady-state processes. Understandings of mixing phenomena are employed in developing beginning understandings of ideal reactors. The principles behind residence time distribution analyses are addressed and used in the definitions of completely mixed flow and plug flow reactors (CMFRs and PFRs). Impulse and step input stimuli are introduced, and exit responses for CMFRs and PFRs are examined. We introduce the process mass balance: the rate of accumulation within a control volume is the sum of the rates of input, output, and generation of a targeted substance. We employ the process mass balance to model the behavior of CMFRs receiving impulse and step input stimuli. We carry these zero-volume and transient mixing principles into environmental contexts, using them to model responses of selected natural and engineered systems to perturbations involving substances that are assumed to be nonreactive. In this manner, we illustrate the portability of these principles.

1.2.7 Reactions in Ideal Reactors

Although chemical stoichiometry is examined in preuniversity courses as well as in general chemistry courses completed by environmental engineers, the ability to employ these principles in specific environmental applications is not assured. Therefore, in Chapter 8 we begin with a review of the use of stoichiometry to determine reactant requirements and production of products using a number of common environmental engineering contexts. With these we illustrate quantitatively the conversions of one substance to another, without the complication associated with examination of the rates of transformation. We include mass–volume–porosity relations so that both the requirements for reactants and creation of products, for example, from water treatment operations can be expressed using molar, mass, and volume units. Mass–volume–porosity relations are also useful in quantitating rates of a process in natural systems considered as reactors (either ideal as examined in Chapter 8 or non-ideal as examined in Chapter 9).

We introduce two formulations of the reaction rate law: pseudo-first-order and saturation (arising from enzyme-limited microbial processes). Beyond radioactive decay, few processes rates are directly and linearly dependent only upon the abundance of the reactant. The pseudo-first-order rate law arises when certain of the reactants, aside from a target reactant, upon which the reaction rate is truly dependent, are maintained at constant abundance. If we can quantitate the abundances of these non-target reactants, we can mathematically treat the overall reaction as if it were a first-order reaction, greatly simplifying the resultant mathematics. Microbial reactions are

said to be first-order in biomass abundance while, relative to a targeted substrate, they are enzyme-limited. Then, for saturation-type reactions, whose rate laws are described by Monod or Michaelis–Menton kinetics, we include the biomass abundance term in the rate law. Initially we examine systems in which the biomass abundance is considered constant in order that we can illustrate modeling of processes using closed-form analytic solutions. Then, we couple substrate utilization with microbial growth to illustrate the necessary numeric solution of such a system. We employ ideal reactor–reaction principles in multiple contexts, spanning both natural and engineered systems, thereby illustrating the portability of the principles and concepts in modeling efforts.

While not necessarily a reaction, we examine the transfer of oxygen to and from aqueous solutions, employing the concept of the mass transfer coefficient. We examine this mass transfer process in contexts appropriate for implementation of ideal reactor principles, providing a beginning understanding of the broad applicability of mass-transfer phenomena. We model transfer of oxygen across vapor–liquid interfaces of natural systems and in aeration of wastewaters. Extension of mass transfer principles to modeling of subsurface contaminant remediation systems or to modeling of gas–liquid, gas–solid, and liquid–solid contactors would be relevant and perhaps interesting to the student. These advanced systems become special cases of ideal reactors, best left to the more focused texts in which they are currently addressed. We hope the student can gain phenomenological understandings upon which competency in modeling of the more complex systems can be built later, if desired.

1.2.8 Nonideal Reactors

The ideal flow reactors mentioned in Chapter 8 comprise the extremes relative to the real reactors encountered in environmental engineering. No reactor can truly be perfectly plug flow or completely mixed flow. The engineering literature addresses three models for use in analyses of real (nonideal) reactors: CMFRs (Tanks) in series (TiS), plug-flow with dispersion (PFD), and segregated flow (SF). In Chapter 9, we examine the development and analyses of exit responses to input stimuli, useful in quantitatively describing the residence time distributions of real reactors. We employ the three nonideal reactor models to predict performance of a plug-flow like reactor and compare results with those predicted using the ideal plug-flow reactor model. The analyses and applications of the nonideal reactor models included in Chapter 9, especially for the PFD and SF models, are well beyond those included in any alternative texts known to this author.

1.2.9 Acids and Bases: Advanced Principles

In Chapter 10, we build upon the foundational principles addressed in Chapters 5 and 6. We address the hydration of cations and anions in the context of developing understandings regarding the behavior of electrolytes in nondilute solutions. Relative to these nondilute solutions, we introduce the relation between chemical activity

and abundance and present a number of equations used for computing activity coefficients. We incorporate activity coefficients into our accounting system of mole balances, while preserving the unique relation among the chemical activities of reactants and products expressed by the law of mass action. Mole balances account for total abundances while chemical equilibria relate activities and the equilibrium constant. We address use of enthalpy in adjusting equilibrium constants for varying temperature and, along the way, provide an introduction to use of Gibbs energy in determination of equilibrium constants. We reserve significant application of Gibbs energy concepts for Chapter 12 in conjunction with redox half reactions that we write. We introduce the proton balance, equating evidence of protons accepted with corresponding evidence of protons donated as a consequence of proton-transfer reactions. Our treatment of the proton balance is well beyond that of any alternative text known to this author. The proton balance is a powerful tool in modeling changes in speciation as a consequence of a perturbation involving addition of an acid or base to an environmental system. The proton balance also is a critical tool in modeling acid- and base-neutralizing capacity of aqueous solutions. We present a step-wise approach to the visualization of proton-transfer reactions, leading to critical ability to define the initial conditions, upon mixing two or more solutions, prior to the occurrence of any proton transfers. We carry the proton balance along with the law of mass action and our mole balance accounting equations into a variety of environmental contexts specific to atmospheric, terrestrial, biogeochemical, and engineered systems. We complete our work in Chapter 10 by examining the behavior of water in solutions of high salt content.

1.2.10 Metal Complexation and Solubility

Many texts address coordination chemistry (metal complexation) before and separately from the solubility and dissolution of metals. Others address solubility and dissolution prior to metal complexation. We believe that the two topics are so closely related that simultaneous treatment is highly warranted. Hence, in Chapter 11 from the outset we couple formation of metal–ligand complexes and formation/dissolution of inorganic solids containing metals and ligands. We illustrate the hydrolysis of hydrated metal ions and present the correlations between cation hydrolysis and the process the chemists have termed complexation. Most importantly, in Chapter 11, we quantitatively address speciation of metals and ligands in aqueous systems, beginning with hydrolysis-dominated systems and then addressing multiple ligand systems. We illustrate the coupling of processes within mixed metal–ligand systems and provide means to quantitatively model such systems. We include metal solubility equilibria in the context of the mixed ligand systems. We illustrate the concept of solid-phase control of metal solubility and showcase multiple systems in which dual control of metal solubility, and hence control of ligand solubility is operative. We extend the concepts of acid- and base-neutralizing capacity to systems involving soluble metals and their metal–ligand solid phases. We carry these sets of principles into selected environmental systems to illustrate their portability.

1.2.11 Oxidation and Reduction

We begin our treatment of oxidation and reduction processes by writing half reactions: determining oxidation states of the element to which the reduction from the oxidized condition is ascribed, and employing the chemists' algorithm for balancing such reactions. We employ Gibbs energy to determine the equilibrium constant, in the context that much of the geochemical literature shuns equilibrium constants in the favor of tabulated values of Gibbs energy of formation. Most of the acid deprotonation and complex formation equilibrium constants have been measured or estimated and are tabulated. Similar data for redox half reactions is not so readily available. We thus waited until we really needed Gibbs energy concepts to illustrate their application. We review the addition of half reactions to produce overall oxidation–reduction reactions. The geochemical literature is rife with pE (or E_H) versus pH speciation predominance diagrams. In order that these can be fully appreciated, we illustrate the process of construction: first the lines separating predominance regions and then entire diagrams. We then examine the dependence of speciation on electron availability at constant pH before investigating the determination of speciation abundances in the near vicinity of predominance boundary lines. Finally, we illustrate means by which assays of the abundance of key redox species in combination with modeling of the system can provide accurate estimates of electron availability of environmental systems.

1.3 APPROACH

For this text, we did not perform exhaustive searches of the literature to uncover the detailed specific knowledge of targeted phenomena. Many fine texts have been assembled in that vein. Rather, we collected basic principles from the scientific literature, mostly chemistry-based texts, for implementation in environmental contexts. We call these first principles. Some of these principles are the detailed chemical stoichiometry and equilibria, mass (or mole) accounting, reaction rate laws, theory of ideal and nonideal reactors, thermodynamic fundamentals, and various special definitions associated with chemical systems.

We combine these fundamental principles with companion mathematical relations to quantitatively describe processes operative within environmental systems. In many cases, we have combined sets of first principles applicable to general contexts and derived usable relations. We might refer to these as second principles. These second principles relate the important parameters characteristic to the general contexts in which they would be applied. Typically, these relations have been designated as numbered equations. Intermediate results necessary to the understandings of the relations among the first principles and the general contexts in which they are applied, while important, are not intended for direct use in analysis/modeling efforts. These then are not assigned equation numbers. When we illustrate the applications of principles via an example, without fail, we begin either with first or second principles.

In this text, through the many detailed examples, we address many real processes operative in real contexts. Our process with examples is carried well beyond that traditionally employed: pose a question, with some associated reasoning select an equation for implementation, show how the numbers fit into the equation, and state the result. We wanted our examples to go much deeper, illustrating the true complexity of the mathematical/numerical methodologies necessary to obtaining quantitative results for questions posed in conjunction with complex systems. For computations, beginning with the simple linear relations associated with application of Henry's law, we have employed MathCAD as a computational tool. Then, with its "what you see is what you get" user interface, each MathCAD worksheet becomes an absolutely complete and accurate record of the mathematical/numerical processes employed. MathCAD programmers have developed a set of toolbars: arithmetic operators, graphing, vector and matrix operations, evaluation, calculus operations, Boolean operations, programming operations, Greek symbols, and symbolic operations. Then, with a click of the mouse, the user has at his or her command this entire broad and deep array of mathematical operations. A symbolic operations feature allows the user to set up integrals and derivatives and symbolically solve them. Approximately 450 intrinsic functions are available for use either by entering the function name or selecting desired functions from a drop-down list. MathCAD's help section explains each of these functions and provides examples of their use in computational efforts. Beyond these intrinsic functions, the user can define his or her own functions that employ many of the operations from the toolbars as well as employing user-defined functions and programs developed by the user. Among the intrinsic functions are several which can be employed to obtain numeric solutions of systems of (both linear and nonlinear) algebraic equations, systems of ordinary differential equations, and selected partial differential equations. The capability of solving systems of nonlinear algebraic equations is key to developing convenient models, employing chemical equilibria, mole balances, and the proton balance in examination of environmental systems. Of great utility is the fact that the aforementioned capability can be conveniently programmed using loops and logic to conveniently develop complex user-defined programs. In fact, each entire worksheet can become a program useful for analyzing the "what ifs" to predict system behavior. Huge sections of the work sheet can be "hidden," allowing the user to directly view results corresponding to manipulation of selected forcing parameters.

At this point we could go on and on about the numerical and mathematical capabilities programmed into MathCAD. Indeed, this author has moved well below the surface of MathCAD's sea of capabilities, but still has much to learn. Then, given that each MathCAD worksheet is a perfect visual record of the mathematical and numerical operations employed, we determine that for most of our examples, we would use "snippets" from our MathCAD worksheets to illustrate both the mathematics and the numerics employed in our examples. Our examples are intended to be complete logical and mathematical records of our solutions to the posed questions. It is our intent that the reader be able to follow all the mathematical and numerical operations embedded in our examples and translate them for use with mathematical/numerical modeling software alternative to MathCAD. We urge readers to adopt

a favorite such software and employ that software in quantitatively understanding the processes and procedures of our examples. Perhaps 95% of the work addressed in Chapters 3 and 5–8 can be accomplished using a pencil, paper, and a calculator. In Chapter 7 we use some programming capability to conveniently generate some of our plots. In Chapter 8 we employ a root-finder in several examples and for the modeling of the rise of an air bubble emitted from an aeration diffuser, we employ the nonlinear equation solver in a looping program. In Chapter 9, we employ numerical integration techniques for large sets of data that do beg for solution using a computer. Also in Chapter 9, we write a number of short programs. Seemingly quite straightforward within the MathCAD worksheet, several of these involve the use of a root-finding process within a set of nested loops. Such a program, coded in a structured language, would require many lines of code. Then, in Chapters 10–12 we employ the nonlinear equation solver to provide numeric solutions to systems of nonlinear equations. In one example we illustrate a worksheet assembled in MS Excel that accomplishes the same solution as is performed in the immediately previous example using MathCAD. We much prefer the transparent structure of the MathCAD worksheet. This author is not well-versed in any other modern general mathematical/numerical modeling software (beyond MathCAD and Excel). Given the time demands of assembling a textbook of this nature, a decision was made to rely nearly exclusively upon the capabilities available from MathCAD for illustration of the mathematical/numerical techniques employed in *Environmental Process Analysis: Principles and Modeling*.