

# Thermodynamic Basis of Equilibrium

## 3.1 INTRODUCTION

*thermodynamics*: the study of transformations of energy

### 3.1.1 Chapter overview

*Thermodynamics* (from the Greek *therme* heat – *dynamis* power) is the study of transformations of energy. Thermodynamics is a far-reaching and beautifully self-consistent field of study. Thermodynamics seeks to explain phenomena as diverse as high jumping (where kinetic energy is converted into potential energy) and thermonuclear weapons. This text is concerned with reactions between chemical species. Thus, the following discussion of thermodynamics will focus on chemical reactions. This is a slice of thermodynamics sometimes called *chemical thermodynamics*.

The intent of this chapter is to show that the concept of equilibrium has thermodynamic underpinnings. To accomplish this task, we must start with some basic thermodynamic principles and definitions. The thermodynamic functions Gibbs free energy and chemical potential will be introduced, along with their dependence on species concentrations. Equilibrium will be defined from these thermodynamic functions. Thus, you shall find that the equilibrium state of a chemical system is reflected in the concentrations of the species comprised in the system. The concept of an equilibrium constant will be developed. Further thermodynamic concepts will be introduced in Chapter 21.

### 3.1.2 Scope

As stated in section 3.1.1, the goal of this chapter is to develop expressions for the equilibrium state of a system based on thermodynamic concepts and the concentrations of chemical species. There are many ways to derive equilibrium expressions from thermodynamic laws. Which thermodynamic concepts should be employed?

In this chapter, the discussion will be guided by three principles. First, thermodynamic properties will be developed that are *convenient*. In some cases, this may mean combining simple properties into groupings to reach the chapter goal in an expedient fashion. Second, thermodynamic properties will be sought that are *reusable*. This means that we will take advantage of tabulated thermodynamic properties. Third, thermodynamic properties will be developed which describe the *system* of interest. Thus,

the focus will be on the properties of the *system*, not properties of the matter surrounding the system.

### 3.1.3 Motivation

Before diving into definitions and calculations, it is informative to step back and decide if a discussion of thermodynamics is really necessary. If your goal (from Chapter 1) is to be able to determine the concentrations of individual chemical species at equilibrium, then thermodynamics is absolutely required.

Thermodynamics will allow you to determine quickly whether certain chemical reactions will proceed as written. More significantly, thermodynamics will empower you to calculate species concentrations under specified conditions. You will find that thermodynamic properties of chemical reactions will let you determine, for example:

- The extent to which ammonia partitions between the atmosphere and a lake
- The effect of acid rain on national monuments
- The dose of soda ash required to neutralize an acid spill
- The effect of pH on the disinfection strength of chlorine
- The speciation of phosphorous in a drinking water reservoir

In short, thermodynamics is the key to many applications of aquatic chemistry.

## 3.2 THERMODYNAMIC PROPERTIES

### 3.2.1 Introduction

The state of a system can be defined by a number of *thermodynamic properties*. Thermodynamic properties sometimes are called *state variables* because their values depend on the state of the system and not on the manner in which the state was achieved. Thermodynamic properties are divided into two types: extensive and intensive properties. Property types are discussed in Sections 3.2.2 and 3.2.3. Some thermodynamic properties are *conserved*; that is, they are additive even after transformations of a system or when two systems are combined. Conservation of thermodynamic properties is discussed in Section 3.2.4. Finally, since the state of a system is defined by thermodynamic properties, it is useful to ask: how many thermodynamic properties does it take to define a system? This question is answered in Section 3.2.5.



**Key idea:** Thermodynamic systems are defined by thermodynamic properties (also called *state variables*)

*extensive property*: a thermodynamic property dependent on the amount of material in the system



**Key idea:** The values of a extensive thermodynamic property for each portion of a system add up to the value of the extensive thermodynamic property for the whole system

### 3.2.2 Extensive properties

As stated in Section 3.2.1, thermodynamic properties can be extensive properties or intensive properties. *Extensive properties* are *dependent on the amount of material in the system*. For example, mass is an extensive property because it is dependent on the amount of the substance present. Examples of extensive properties are listed with their common units in Table 3.1.

The extensive thermodynamic properties share a unique feature: the sum of the values of an extensive property for each portion of the system equals the value of the extensive property for the system as a whole. For example, if you empty a glass of water one drop at a time, the sum of the volumes (or masses) of each drop will be equal to the volume (or mass) of the original water in the glass.

**Table 3.1: Extensive and Intensive Properties**  
(common units in parentheses)

Type	Extensive Property	Intensive Property
Mass or mole	mass (g or kg)	concentration (mg/L) and density (kg/L)
	number of moles	concentration (mol/L)
Volume	volume (L)	specific volume (L/kg) and molar volume (L/mol)
Thermal	heat capacity (J/°K)	specific heat (J/g·°K)
	energy (kJ)	molar energy (kJ/mol)
	enthalpy (kJ)	molar enthalpy (kJ/mol)
	entropy (kJ/°K)	molar entropy (kJ/mol·°K)
	free energy (kJ)	molar free energy (kJ/mol)
Other		pressure (atm)
		temperature (°K)

*intensive property*: a thermodynamic property independent of the amount of material

### 3.2.3 Intensive properties

*Intensive properties* are *independent* of the amount of material. In other words, intensive properties are the same for each packet of material in the system. Temperature is an example of an intensive property. Concentration also is an intensive property since concentration is a mass (or number of moles) per unit volume (or mass). Examples of intensive properties are listed with their common units in Table 3.1.

\* This definition of extensive properties is valid for systems having constant thermodynamic properties at every point in space.



**Key idea:** Intensive thermodynamic properties are *not* additive within a system.

### Example 3.1: Balancing Thermodynamic Properties

What is the sodium ion concentration in a solution formed when one drop (0.05 mL) of seawater ( $[\text{Na}^+] = 10.8 \text{ g/L}$ ) at  $25^\circ\text{C}$  is added to 1 L of river water ( $[\text{Na}^+] = 6 \text{ mg/L}$ ) at  $25^\circ\text{C}$ ?

#### Solution:

Concentration is not an extensive property and therefore is not additive. Mass is additive and  $\text{mass} = m = VC$ , where  $V$  = volume and  $C$  = concentration.

$$\begin{aligned} m_s &= m_{sw} + m_{rw} \\ &= V_{sw}C_{sw} + V_{rw}C_{rw} \end{aligned}$$

(The subscripts  $s$ ,  $sw$ , and  $rw$  refer here to solution, seawater, and river water, respectively.)

$$\begin{aligned} m_s &= (5 \times 10^{-5} \text{ L})(10.8 \text{ g/L}) + \\ &\quad (1 \text{ L})(6 \times 10^{-3} \text{ g/L}) \\ &= 6.54 \times 10^{-3} \text{ g} \end{aligned}$$

$$\text{Also: } C_s = m_s/V_s$$

Since the density of the final solution is expected to be very close to the density of the river water, you can approximate:  $V_s = V_{sw} + V_{rw} = 1 \text{ L} + 5 \times 10^{-5} \text{ L} = 1.00005 \text{ L}$ . Thus:

$$\begin{aligned} C_s &= m_s/V_s \\ &= (6.54 \times 10^{-3} \text{ g})/(1.00005 \text{ L}) \\ &= 6.5 \text{ mg/L} \end{aligned}$$

Some intensive properties are formed from extensive properties by normalizing for the amount of material. In such cases, the intensive property is called a *specific* or *molar* property. For example, the specific volume is calculated as the volume divided by the mass, and the molar energy is the energy per mole. (Related intensive functions, the *partial molar* properties, will be discussed in Section 3.6.3.)

Recall that intensive properties are the same for each packet of material in the system. Thus, unlike extensive properties, *intensive properties are not additive within a system*. For example, the temperature of the water in a glass is *not* equal to the sum of the temperatures of each drop of water in the glass.

### 3.2.4 Conservation of some thermodynamic properties

Some thermodynamic properties are *conserved*; that is, they are additive even after transformations of a system or when two systems are combined. The general concept of the conservation laws will be explored in Section 3.4.1. In this section, the thermodynamic properties that are candidates for conservation will be identified.

#### Thoughtful Pause

Which thermodynamic properties are candidates for conservation: extensive or intensive properties?

You know that intensive properties are not conserved. Intensive properties are not additive even *inside* a system, so it does not make sense that they should be additive when systems are transformed or combined. Only the extensive properties are candidates for conservation.

Here you must tread carefully. Although only extensive properties are *candidates* for conservation, it does not follow that *every* extensive property is conserved. Hundreds of years of observation has led to the conclusion (see Section 3.4.1) that the extensive properties mass and energy (along with momentum) are conserved. Thus, you can balance mass, energy, and momentum as systems are transformed or combined.

It is very important to perform balances only on mass, energy, or momentum and *not* on intensive properties. One important implication in environmental engineering and science is that we must perform balances on the mass (or mass flux) of chemicals, not on chemical concentrations. This principle is illustrated in Example 3.1.

### 3.2.5 How many thermodynamic properties are enough?

Thermodynamic properties are used to define the state of a system. You need to know when to stop adding properties to your description of

**component:** a chemical species (or species fragment) that can be varied independently in a system

**Gibbs Phase Rule:** a system with  $P$  phases and  $C$  components requires  $C - P + 2$  thermodynamic properties

systems. In other words, we would like to know how many thermodynamic properties are required to define a system.

The number of thermodynamic properties required to define the state of a system depends on the complexity of the system. More specifically, the number of thermodynamic properties required depends on the number of phases and number of *components* of the system. The concept of the component is used throughout this text. A **component** is a chemical species (or fragment of a chemical species) that can be varied independently in a system. A system with  $P$  phases and  $C$  components requires  $C - P + 2$  thermodynamic properties. This is called the **Gibbs Phase Rule** (after J. Willard Gibbs, 1839-1903; see the *Historical Note* at the end of the chapter). The simplest possible aqueous system is a known volume of water. This is a one-phase, one-component system ( $P = C = 1$ ). Therefore, two thermodynamic properties ( $C - P + 2 = 1 - 1 + 2 = 2$ ) are required to define the system. In aqueous systems, it is convenient to use temperature and pressure as the two thermodynamic properties. Thus, a system of 1 L of pure water is completely and uniquely defined by specifying the temperature and pressure.

Now, thermodynamics would be pretty useless if it told you how to describe systems of only pure water. In fact, the Gibbs Phase Rule is very powerful. It will assist you in describing the equilibrium state of systems. In particular, it will assist in determining the species concentrations at equilibrium. For example, suppose you want to determine the equilibrium concentrations of every species in a system containing  $P$  phases and  $C$  components. The Gibbs Phase Rule tells you that you need to specify  $C - P + 2$  thermodynamic properties from Table 3.1. In most cases, those properties will be temperature, pressure, and  $C - P$  species concentrations (or combinations of species concentrations).

### 3.3 WHY DO WE NEED THERMODYNAMICS TO CALCULATE SPECIES CONCENTRATIONS?



**Key idea:** Thermodynamics can tell you which chemical reactions are possible (under a given set of conditions) and whether species concentrations are not time-dependent

We seek to determine the concentrations of each chemical species involved in a set of chemical reactions. To accomplish this, two features of chemical reactions must be determined. First, you must have a way of deciding *whether a chemical reaction will proceed as written*. If you can determine that a reaction will *not* occur under a given set of conditions (e.g., temperature, pressure, and species concentrations), then clearly it is of little interest to you.

Second, we would like to determine if the chemical species concentrations are changing with time. In particular, the goal for most of this text is confined to calculating species concentrations when they do **not** change with time. The time-dependent nature of species concentrations will be considered in Chapter 22.

How do you know whether a reaction proceeds as written or whether species concentrations are not time-dependent? We shall devise thermody-

dynamic properties specifically for determining whether reactions occur and whether species concentrations change with time. Before developing these thermodynamic properties, it is necessary to examine the concepts of whether reactions occur and the time-independence of species concentrations in more detail. To do so, we must introduce several related concepts, namely spontaneity, equilibrium, and reversibility.

### 3.3.1 Spontaneity

*spontaneous reaction*: a reaction occurring as written without energy added

A reaction that occurs as written without energy added is called a *spontaneous reaction*. Spontaneous reactions also are called *possible reactions*. In other words, reactions that are *not spontaneous* as written are said to be *not possible under the given set of thermodynamic conditions*. Identifying spontaneous reactions will allow the division of all reactions into two types: possible (i.e., spontaneous) reactions and impossible reactions.

It is important to remember that reactions are possible (spontaneous) or impossible under a *specific set of thermodynamic conditions*. In other words, you must specify the temperature, pressure, and chemical species concentrations when you determine whether or not a reaction is spontaneous. A reaction could occur spontaneously at, say, one temperature, but not occur spontaneously at another temperature. As an example, the evaporation of water to form water vapor is spontaneous at temperatures greater than 100°C (at 1 atm of pressure) but not spontaneous at temperatures less than 100°C (at 1 atm of pressure).

In addition, reactions may occur spontaneously at one set of species concentrations, but not spontaneously at another set of species concentrations. For example, the dissolution of sodium chloride to form sodium and chloride ions is spontaneous at 25°C and 1 atm if sodium chloride is the only source of Na<sup>+</sup> and Cl<sup>-</sup>. However, in a saturated brine solution, the dissolution of sodium chloride is not spontaneous.

### 3.3.2 Equilibrium

*equilibrium*: a state where the thermodynamic properties of the system do not change with time (for a system that does not have a net loss or gain of heat or mass with its surroundings)

Systems in which the species concentrations do not change with time are said to be at *equilibrium* (from the Latin *aequi* equal – *libra* weight). The formal thermodynamic definition of equilibrium is that *the thermodynamic properties of the system at equilibrium do not change with time and the system does not have a net loss or gain of heat or mass with its surroundings*.

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#### Thoughtful Pause

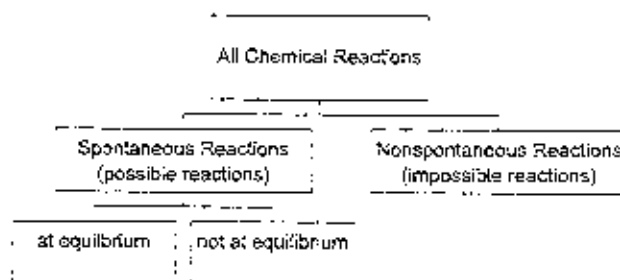
Is the formal definition of equilibrium more or less restrictive than the requirement that species concentrations be independent of time?

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Note that the formal definition of equilibrium is *very* restrictive. It says that *no* thermodynamic properties (not just the property of species con-

centration) change with time at equilibrium. A system at equilibrium also does not have a net loss or gain of heat or mass with its surroundings. In addition, the chemical composition of the system is independent of time. Why? At equilibrium, all thermodynamic properties (including the species concentrations) are independent of time. Identifying the equilibrium state will allow the division of all spontaneous reactions into two types: reactions at equilibrium and reactions not at equilibrium.

The definitions of spontaneity and equilibrium allow you to divide all chemical reactions into groups. One classification scheme is shown in Figure 3.1. Note that all reactions at equilibrium are spontaneous, but not all spontaneous reactions are at equilibrium.



**Figure 3.1: Classification of Chemical Reactions**  
(spontaneous reactions are possible and nonspontaneous reactions are impossible under a specified set of thermodynamic conditions)

### 3.3.3 Reversibility

The concept of equilibrium is closely aligned with the idea of *reversibility*. A reaction is said to be *reversible* if the reverse reaction (i.e., conversion of products into reactants) can occur spontaneously with an infinitesimal increase in the product concentration. Consider the reaction:  $\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}$ . The reaction is reversible if the reverse reaction ( $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ ) also occurs spontaneously when the HCl concentration is increased slightly. In general, a process is said to be reversible if it returns to its initial state when the mass, heat, and energy flows are reversed.

What is the relationship between equilibrium and reversibility? Reversible systems are said to be near equilibrium, whereas irreversible systems are far from the equilibrium state. *For a chemical reaction to be at equilibrium, the reaction must be reversible.*

### 3.3.4 Summary

The connection between spontaneity, equilibrium, and reversibility casts a new light on equilibrium. *For a reaction to be at equilibrium, the reaction*

*reversible reaction:* a reaction where the reverse reaction (i.e., conversion of products into reactants) can occur spontaneously with an infinitesimal increase in the product concentration



**Key idea:** For a reaction to be at equilibrium, both the reaction and its reverse reaction must be spontaneous

*must be both spontaneous and reversible.* In other words, both the reaction and its reverse reaction must be spontaneous. For example, it is known that hydrochloric acid equilibrates quickly with  $H^+$  and  $Cl^-$ . Thus, both the reactions  $HCl \rightarrow H^+ + Cl^-$  and  $H^+ + Cl^- \rightarrow HCl$  must be spontaneous. This leads to the expression of equilibrium as reactions that proceed in both directions, denoted  $HCl \rightleftharpoons H^+ + Cl^-$ , or more commonly in aquatic chemistry:  $HCl = H^+ + Cl^-$ .

At equilibrium, the concentrations of all chemical species do not change with time. This fact sometimes conjures up the image that no reactions are occurring at equilibrium. However, you now know that all chemical reactions and their reverse reactions proceed spontaneously at equilibrium. Overall, the species concentrations are not changing with time. However, reactants are converted to products and products to reactants continuously at equilibrium in such a way that the reactant and product concentrations do not change over time. In the hydrochloric acid example,  $HCl$  is being formed continuously from reaction of  $H^+$  and  $Cl^-$ . In addition,  $HCl$  is continuously dissociating to form  $H^+$  and  $Cl^-$ . The system is not static at equilibrium, but no net change in species concentration occurs.

An analogy may make this clearer. At many college campuses and shopping malls, parking space is at a premium.\* During the day, the number of empty parking spaces remains nearly constant (at some very small number), and the number of filled parking spaces remains nearly constant as well. In spite of this observation, the actual cars parked in the parking spaces change throughout the day. Parking is reversible. The processes of parking and vacating a parking space (analogous to a reaction and its reverse reaction) are spontaneous. The number of empty and full spaces (analogous to species concentrations) does not change much over time, even though new empty parking spaces are becoming available and being filled continuously. As with chemical systems at equilibrium, the system is not static, but no net change in the number of empty parking spaces occurs.

\* This leads to the cynical definition of a university as a place where faculty, students, and staff gather together to complain about parking.



### 3.9 CHEMICAL EQUILIBRIUM AND THE EQUILIBRIUM CONSTANT

#### 3.9.1 Equilibrium constants

From Section 3.7.4, you know that  $\Delta G_{rxn} = 0$  at equilibrium. This means that there must be some set of species activities that allows  $\Delta G_{rxn}$  to be zero. At equilibrium, these activities are called the *equilibrium activities* (denoted with a subscript eq), so that eq. 3.17 becomes:

$$0 = \Delta G_{rxn}^{\circ} + RT \ln \left( \frac{\{C\}_{eq}^c \{D\}_{eq}^d}{\{A\}_{eq}^a \{B\}_{eq}^b} \right) \quad \text{eq. 3.23}$$

Since  $\Delta G_{rxn}^{\circ}$  is a constant for a given reaction, it follows that the term in parentheses in eq. 3.23 must be constant at equilibrium. The term in parentheses is called the *equilibrium constant* and is denoted  $K$  or  $K_{eq}$ . For the reaction  $aA + bB = cC + dD$ , the equilibrium constant is:

$$K = \frac{\{C\}_{eq}^c \{D\}_{eq}^d}{\{A\}_{eq}^a \{B\}_{eq}^b}$$



**Key idea:** The equilibrium constant is the product of the reactant activities divided by the product of the product activities, each raised to the power of their reaction stoichiometric coefficient

This text is focused on chemical reactions at equilibrium. Therefore, the subscript eq will be understood and generally not written. The activity of species A,  $\{A\}$ , will be assumed to be the equilibrium activity unless otherwise indicated.

So far, activity has not been defined very precisely. Activity is an idealized concentration. As a thermodynamic property, activity depends on the temperature, pressure, and number of moles of material in the system. The dependence of activity on the temperature, pressure, and number of moles of material in the system will be examined in Chapter 21. For now, assume you are working with dilute solutions (i.e., the number of moles of material in the system is small) at standard and constant temperature and pressure. The dilute solution assumption is valid for many freshwaters. Under these conditions, the concentration of a chemical species is nearly equal to its activity. Thus, the activity of species A,  $\{A\}$ , can be replaced

with the concentration of species A,  $[A]$ . You can write  $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ .



**Key idea:** In dilute solution, the equilibrium constant is approximately equal to the product of the reactant concentrations divided by the product of the product concentrations, each raised to the power of their reaction stoichiometric coefficient

Again, the concentrations are assumed here to be equilibrium concentrations unless otherwise noted. In words, *the equilibrium constant in dilute solution is the product of the reactant concentrations divided by the product of the product concentrations, each raised to the power of their reaction stoichiometric coefficient.*

### 3.9.2 Properties of the equilibrium constant

All equilibrium constants show some important properties. First, equilibrium constants are thermodynamic functions. As such, they may depend on the temperature, pressure, and concentrations of other species in the system. These relationships will be quantified in Chapter 21.

Second, equilibrium constants can be calculated from  $\Delta G_{rxn}^\circ$ . From eq. 3.18 and the definition of the equilibrium constant:

$$K = e^{-\frac{\Delta G_{rxn}^\circ}{RT}}$$

Thus, you can calculate  $K$  if you know  $\Delta G_{rxn}^\circ$ . As an example, the value of  $\Delta G_{rxn}^\circ = -8.7$  kJ/mol was calculated for the reaction  $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$  in Example 3.5. For this reaction at 25°C (= 298°K):

$$K = \exp\left[-(8.7 \text{ kJ/mol}) / (8.314 \times 10^{-3} \text{ kJ/mol}^\circ\text{K})(298^\circ\text{K})\right] \\ = 4.35 \times 10^{-2}$$

You also can calculate  $\Delta G_{rxn}^\circ$  if you know  $K$  (see Example 3.6).

Third, it is necessary to think carefully about the units of equilibrium constants. In reality, equilibrium constants have no units. Each term is a concentration (or activity) divided by the concentration (or activity) of the standard state (see Section 3.8.2). Thus, all  $K$  values are unitless, and you should have no qualms about taking the natural logarithm of  $K$  in calculating  $\Delta G_{rxn}^\circ$ . However, as discussed in Section 4.3, it is common to associate units with equilibrium constants to indicate the concentration units of the species involved in the equilibrium.

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#### Example 3.6: Calculation of $\Delta G_{rxn}^\circ$ from $K$

Calculate  $\Delta G_{rxn}^\circ$  for the reaction  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{OH}^-(\text{aq}) + \text{H}^+(\text{aq})$  if  $K = 1.0 \times 10^{-14}$  M at 25°C

#### Solution:

$$\Delta G_{rxn}^\circ = -RT \ln K = (8.314 \times 10^{-3} \text{ kJ/mol}^\circ\text{K})(298^\circ\text{K}) \ln(1.0 \times 10^{-14}) \\ = +79.9 \text{ kJ}$$

You can verify this value using:

$$\Delta G_{rxn}^\circ = \sum \nu_i \Delta \bar{G}_{f,i}^\circ, \text{ where the } \Delta \bar{G}_{f,i}^\circ \text{ values for } \text{H}_2\text{O}(\text{l}), \text{OH}^-(\text{aq}), \text{ and } \text{H}^+(\text{aq}) \text{ are } -237.2, 0, \text{ and } -157.3 \text{ kJ/mol}, \text{ respectively.}$$


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## 3.10 SUMMARY

This chapter provided a brief review of the thermodynamic basis of chemical equilibrium. Equilibrium is defined as the state in which the thermodynamic functions of the system (such as temperature, pressure, and species concentrations) do not change with time. Three links were made in this chapter to allow for calculation of species concentrations at equilibrium. First, the concept of equilibrium was related to the change in one particular thermodynamic function, Gibbs free energy. Gibbs free energy combines internal energy, pressure-volume work, and entropy (a measure of disorder in the system). The change in the Gibbs free energy of a reaction is zero at equilibrium.

Second, Gibbs free energy was related to chemical potential. Differences in chemical potential drive chemical reactions, just as differences in potential energy (i.e., elevation) drive some mechanical processes.

Third, the chemical potential (and thus the change in Gibbs free energy for a reaction) was related to species activities. Activity is an idealized concentration, which takes into account the effects of temperature,

pressure, and other species concentrations on the behavior of a given species.

Also in this chapter, the concept of the equilibrium constant was introduced. The equilibrium constant is a thermodynamic function, related to both the standard Gibbs free energy of a reaction and to species activities. The equilibrium constant in dilute solutions is the product of the reactant concentrations divided by the product of the product concentrations, each raised to the power of their reaction stoichiometric coefficient.

# Acids and Bases

## 11.1 INTRODUCTION

As stated in section 1.3, pH is a master variable in aquatic systems. Why the emphasis on pH? We choose pH as a master variable of interest because  $H^+$  has such a strong influence on aquatic chemistry and toxicity endpoints and because pH is easily measured. In this chapter, you shall begin to explore the equilibria in which protons,  $H^+$ , are transferred between chemical species. These equilibria constitute equilibrium acid-base chemistry.

The chapter begins by examining the formal definitions of the words *acid* and *base*. The definitions of acid and base have changed over time. This history will be followed to arrive at definitions that are both consistent and useful. Acids and bases will be defined by equilibria, as well as words. The thermodynamic concepts of acid and base strength will be quantified by the equilibrium constants of the defining equilibria.

Next, the discussion of acids and bases will be extended to polyprotic species - those acids and bases that donate or accept more than one proton. The solution techniques from Part II will be applied to polyprotic acid and base systems. In particular, the shortcut graphical method for monoprotic acids developed in Chapter 8 will be broadened and applied to systems containing polyprotic acids.

Finally, compact equations called *alpha values* will be developed. Alpha values show concisely the effects of pH on the percentage contributions of acidic and basic forms to the total mass.



**Key idea:** Acid-base chemistry (and pH) are important because  $H^+$  is transferred in many reactions that influence the water quality of aquatic systems

## 11.2 DEFINITIONS OF ACIDS AND BASES

### 11.2.1 The early history of acids and bases

You will notice that the title of section 11.2 refers to more than one definition of acids and bases. The concept of acids and bases has evolved over the last 200 years or so<sup>1</sup>. In several cases, an old definition of acid or base had to be replaced when exceptions were found.

<sup>1</sup> The progression of acid-base concepts presented here was influenced by material at the ChemTeam web site ([dbhs.wvusd.k12.ca.us/ChemTeamIndex.htm](http://dbhs.wvusd.k12.ca.us/ChemTeamIndex.htm)).



**Key idea:** Lavoisier thought, incorrectly, that all acids contained oxygen

In the early days of modern chemistry (mid-eighteenth century), acids were thought to be acids because they contained some common substance. The substance made liquids containing acids taste sour, hence the name acid (from the Latin *acere* sour). Antoine Laurent Lavoisier (1743-1794) concluded that the common substance was oxygen. His commitment to this idea is shown in the name he selected for oxygen - *principe oxygene*, meaning acidifying principle.

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### Thoughtful Pause

Can you think of a substance that is categorized as an acid today but that does not fit Lavoisier's definition of an acid?

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Lavoisier was wrong, of course. Many acids do not contain oxygen, including common acids (e.g., HCl), less common acids (HCN and HSCN), and some compounds that may not look like acids at first glance (e.g.,  $\text{NH}_3$ ). One of the troublesome compounds of the day that did not fit Lavoisier's definition was chlorine. Chlorine was originally named oxymuriatic acid (after muriatic acid, HCl, named from the Latin *muria* brine), with the prefix *oxy-* because all acids were supposed to contain oxygen. Humphry Davy (1778-1829) showed that molecular chlorine did not contain oxygen. He suggested, based on acids such as HCl and  $\text{H}_2\text{S}$ , that perhaps hydrogen was the common substance among acids. To explain why some hydrogen-containing substances were not acids, Justus von Liebig (1803-1873) proposed that an acid was a hydrogen-containing substance in which the hydrogen could be replaced by a metal. Thus, HCl is an acid, according to this definition, because the hydrogen can be replaced by, say, sodium to form NaCl. On the other hand, methane ( $\text{CH}_4$ ) is not an acid because  $\text{CH}_3\text{Na}$  does not exist in nature.

All was well for 50 years. Then, in his Ph.D. dissertation of 1884, Svante August Arrhenius (1859-1927) shocked his dissertation committee with the idea that molecules could break apart in a solvent (such as water) to form charged species called *ions*. Arrhenius received the Nobel Prize in Chemistry in 1903 for this work, later called the ionic theory. Arrhenius extended his ionic theory to acids and bases. The Arrhenius definitions of acids and bases are as follows:

**Arrhenius acid:** a substance that produces  $\text{H}^+$  in aqueous solution

**Arrhenius base:** a substance that produces  $\text{OH}^-$  in aqueous solution

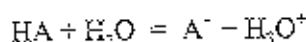
**Arrhenius acids** are substances that produce  $\text{H}^+$  in aqueous solution, and **Arrhenius bases** are substances that produce  $\text{OH}^-$  in aqueous solution

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<sup>†</sup> To see why molecular chlorine was considered an acid, recall that chlorine undergoes the following equilibrium in water:  $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^-$ . HOCl is hypochlorous acid.

### 11.2.2 Brønsted-Lowry definitions

Arrhenius had taken a giant leap forward in linking  $H^+$  to acids. He also provided a definition for a base that was consistent with the observations that bases neutralize acids. However, the Arrhenius definitions did not describe the behavior of some common bases, such as ammonia and sodium carbonate. The next step in the evolution of acids and bases was provided independently and nearly simultaneously by the Danish chemist Johannes Nicolaus Brønsted (1879-1947) and the English chemist Thomas Martin Lowry (1874-1936). Brønsted postulated that acids donated a proton ( $H^+$ ) to the solvent and bases accepted a proton from the solvent. Lowry used the following formalization:



Together, the Brønsted-Lowry definitions are as follows:

**Brønsted-Lowry acids** are substances that *donate*  $H^+$  to water<sup>2</sup> (to produce  $H_3O^+$ ), and **Brønsted-Lowry bases** are substances that *accept* a proton from water (to leave  $OH^-$ )

These concepts of acids and bases as, respectively, *proton donors* and *proton acceptors* are very powerful. The definitions link acids and bases very tightly. They are consistent with Arrhenius's idea that bases are somehow connected with  $OH^-$ .

---

#### Thoughtful Pause

How are the Brønsted-Lowry definitions consistent with Arrhenius' ideas about bases?

---

With the Brønsted-Lowry definitions, you can see that the  $OH^-$  comes from *water*, not necessarily from the base itself.

We shall pause in our romp through history here, although the definition of acids and bases will undergo one more major change in Chapter 14. For the majority of this text, the Brønsted-Lowry definitions will be used: acids are proton donors and bases are proton acceptors. In other words, *acid-base chemistry (in the Brønsted-Lowry sense) means proton transfer chemistry.*

---

<sup>2</sup> The focus here is on water because this is a text on aquatic chemistry. However, one of the strengths of the Brønsted-Lowry definitions is that they can be applied to proton-donating and proton-accepting solvents other than water (e.g., ethanol).

**Brønsted-Lowry acid:** a substance that donates  $H^+$  (to water)

**Brønsted-Lowry base:** a substance that accepts a proton (from water)



**Key idea:** The Brønsted-Lowry definitions link

acids and bases by relating them both to proton transfer



libria

**Key idea:** Acid-base equilibria are proton-transfer equilibria



**Key idea:** Brønsted-Lowry acids and bases also can be

defined by acid dissociation reactions and base association reactions

**monoprotic acid:** an acid that donates one proton (to water)

**polyprotic acid:** an acid that donates more than one proton (to water)

**acid dissociation reaction:** a reaction of the form of eq. 11.1 or 11.2

**acid dissociation constant ( $K_a$ ):** the equilibrium constant for an acid dissociation reaction

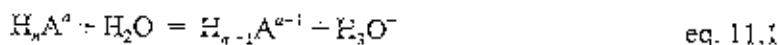
**base association reaction:** a reaction of the form of eq. 11.3

**base association constant ( $K_b$ ):** the equilibrium constant for a base association reaction

**ampholyte:** a species that can both donate and accept a proton

### 11.2.3 Acid dissociation reactions and base association reactions

Following the approach of Brønsted and Lowry, you also can define acids and bases by chemical equilibria. (This material was presented briefly in Section 8.2.2 but will be developed in more detail here.) For acids, you can write:



A **monoprotic acid** is acid that donates one proton:  $n = 1$  in eq. 11.1. If  $n > 1$ , the acid is called a **polyprotic acid**. For example, diprotic acids and triprotic acids can donate two and three protons, respectively.

For an uncharged, monoprotic acid:



Equations 11.1 and 11.2 are called **acid dissociation reactions**. Any substance for which you can write an equilibrium in the form of eq. 11.1 or 11.2 is called an acid (formally, a Brønsted-Lowry acid). The equilibrium constant for the equilibria in eqs. 11.1 and 11.2 is given a special name. The equilibrium constants are called **acid dissociation constants** and are given the special symbol  $K_a$ . Remember:  $K_a$  is just an equilibrium constant. It is the equilibrium constant for equilibria of the form of eq. 11.1 or 11.2.

You can develop a similar system for bases. For bases, you can write:



Equation 11.3 is called a **base association reaction**. Any substance for which you can write an equilibrium in the form of eq. 11.3 is called a base (again, formally, a Brønsted-Lowry base). The equilibrium constant for the equilibrium in eq. 11.3 is given a special name. The equilibrium constants are called **base association constants** and are abbreviated  $K_b$ . Again,  $K_b$  is just an equilibrium constant. It is the equilibrium constant for equilibria of the form of eq. 11.3.

### 11.2.4 Ampholytes

Some species can both donate a proton to water and accept a proton from water. Such compounds are both acids and bases. They are given special names and are called **amphoteric species** (from the Greek *ampho* both) or **ampholytes** (short for *amphoteric electrolytes*).

---

#### Thoughtful Pause

Can you name the most common ampholyte in aqueous systems?

---



**Key idea:** Water is amphoteric (acts as both an acid and a

base)

The most common ampholyte in aquatic systems is water itself. As eq. 11.4 shows, water can both *donate* a proton to water (and hence is an acid) and *accept* a proton from water (and thus is a base):

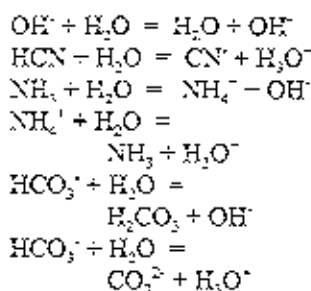


### Example 11.1: Identification of Acids, Bases, and Ampholytes

Identify the following as an acid, base, or ampholyte, using the Brønsted-Lowry definitions:  $\text{OH}^-$ ,  $\text{HCN}$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{HCO}_3^-$ .

#### Solution:

You can write the following equilibria, analogous to eqs. 11.1 and 11.3:



Thus, you would classify the species as follows:  $\text{OH}^-$  is a base,  $\text{HCN}$  is an acid,  $\text{NH}_3$  is a base,  $\text{NH}_4^+$  is an acid, and  $\text{HCO}_3^-$  is amphoteric.

Other common ampholytes include species with intermediate degrees of protonation (i.e., species that are neither completely protonated nor completely deprotonated). For example, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a triprotic acid. It dissociates in water to form three other species:  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  (phosphate).

### Thoughtful Pause

Are  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  acids, bases, or ampholytes?

Phosphoric acid is called an acid (can only donate protons to water) and phosphate a base (can only accept protons from water).  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are ampholytes. For example,  $\text{H}_2\text{PO}_4^-$  can donate a proton to water to form  $\text{HPO}_4^{2-}$  or accept a proton from water to form  $\text{H}_3\text{PO}_4$ . For more practice in identifying acids, bases, and ampholytes, see Example 11.1.

The example of phosphoric acid shows ampholytes formed from partially protonated species that are part of a polyprotic acid family. Sometimes, ampholytes can be formed when more than one acidic groups are found on the same molecule. For example, ethanedioic acid (commonly, oxalic acid:  $\text{HOOC-COOH}$ ) and 1,2-benzenedicarboxylic acid (commonly, *o*-phthalic acid) each have two acidic functional groups. The partially protonated species (e.g., the monoanionic species  $\text{HOOC-COO}^-$ ) are ampholytes. A good example of complex systems exhibiting ampholytic behavior are the macromolecules that contribute color to natural waters, called humic and fulvic acids.

Another type of ampholyte has both acidic and basic functional groups on the same backbone. Examples include the amino acids (see Problem 11.10) and some types of polymers.

## 11.3 ACID AND BASE STRENGTH

### 11.3.1 Introduction

How should you compare the relative strengths of acids and bases? Acids donate protons to water, so it makes sense to develop an acid strength scale that measures the tendency of a compound to donate a proton to water. There are several ways to construct such a scale. The most common



approach is to compare the *thermodynamic tendency* of an acid to donate protons to water.

### Thoughtful Pause

What is an appropriate quantitative measure of the thermodynamic tendency of an acid to donate protons to water?

**acid strength:** thermodynamic tendency of an acid to donate a proton to water

**base strength:** thermodynamic tendency of a base to accept a proton from water



**Key idea:** Acid and base strength are thermodynamic properties

#### Example 11.2: Acid and Base Strength

Rank the following acids by their acid strength:  $\text{H}_2\text{S}$  (hydrogen sulfide;  $\text{p}K_a = 7.1$ ),  $\text{HNO}_3$  (nitric acid;  $K_a = 10^{-2}$ ), and  $\text{H}_2\text{O}_2$  (hydrogen peroxide;  $\text{p}K_a = 11.7$ ). Rank the following bases by their base strength:  $\text{NH}_3$  (ammonia;  $K_b = 10^{-4.7}$ ),  $\text{CN}^-$  (cyanide;  $\text{p}K_b = 4.8$ ), and  $\text{CO}_3^{2-}$  (carbonate;  $\text{p}K_b = 3.7$ ).

#### Solution:

To compare, express the acid strength for all acids (or bases) in terms of either  $K_a$  ( $K_b$  for bases) or  $\text{p}K_a$  values ( $\text{p}K_b$  for bases). The choice is arbitrary, but  $\text{p}K_a$  and  $\text{p}K_b$  values are more convenient. Thus:

A reasonable quantitative measure is  $K_a$  (or  $\text{p}K_a$ ). Thus, **acid strength** is defined as the thermodynamic tendency of an acid to donate a proton to water. Acid strength is quantified by  $K_a$  or  $\text{p}K_a$ . Similarly, you can define **base strength** as the thermodynamic tendency of a base to accept a proton from water and quantify base strength by  $K_b$  or  $\text{p}K_b$ .

### 11.3.2 Properties of acid and base strength

The concepts of acid and base strength have a number of important properties. First, since acid and base strength are quantified by an equilibrium constant, acid and base strength are thermodynamic properties. This means that acid and base strength (as with all thermodynamic properties) may change as a function of temperature, pressure, and the concentrations of other species.

Second, acid and base strength are defined for *one-proton transfer equilibria* (eqs. 11.2 and 11.3). For example, in considering the acid strength of carbonic acid ( $\text{H}_2\text{CO}_3$ ), use the equilibrium constant for the transfer of *one* proton (i.e.,  $K$  for  $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}_3\text{O}^+$ ), **not** the equilibrium constant for the transfer of two protons (i.e., not  $K$  for  $\text{H}_2\text{CO}_3 + 2\text{H}_2\text{O} = \text{CO}_3^{2-} + 2\text{H}_3\text{O}^+$ ).

Third, one acid is said to be stronger than another acid if it dissociates more completely to donate a proton to water. Thus, from eqs. 11.1 and 11.2, a stronger acid has a *larger*  $K_a$ . This means that a stronger acid has a *smaller*  $\text{p}K_a$ . Thus,  $\text{HOCl}$  (hypochlorous acid), with a  $\text{p}K_a$  of 7.54, is a stronger acid than ammonium ( $\text{p}K_a = 9.3$ , both values at  $25^\circ\text{C}$ ). Very strong acids have very small (and even negative)  $\text{p}K_a$  values: the  $\text{p}K_a$  of  $\text{HCl}$  is about  $-3$ . Similarly, stronger bases have larger  $K_b$  values (and thus smaller  $\text{p}K_b$  values). Other examples of ranking acids and bases by their strengths are given in Example 11.2.

### 11.3.3 Acid strength of $\text{H}^+$

What is the acid strength of  $\text{H}^+$ ? To determine its acid strength, write an equilibrium similar to eq. 11.1 with  $\text{H}^+$  as a reactant:



What is  $K_a$  for  $\text{H}^+$ ? Formally, the standard Gibbs free energy of reaction for this equilibrium is defined to be zero, and thus  $K_a = 1$ . Why was the

$\text{H}_2\text{S}$	$\text{p}K_a = 7.1$
$\text{HNO}_3$	$\text{p}K_a = -3$
$\text{H}_2\text{O}_2$	$\text{p}K_a = 11.7$
$\text{NH}_3$	$\text{p}K_b = 4.7$
$\text{CN}^-$	$\text{p}K_b = 4.8$
$\text{CO}_3^{2-}$	$\text{p}K_b = 3.7$

The acid strength order is given by  $\text{HNO}_3$  (a strong acid)  $\gg$   $\text{H}_2\text{S} > \text{H}_2\text{O}_2$ . The base strength order is given by  $\text{CO}_3^{2-} > \text{NH}_3 > \text{CN}^-$ .



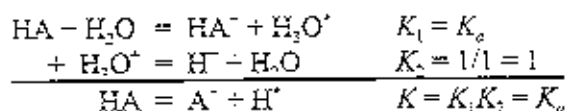
**Key idea:** Since the equilibrium  $\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$  has  $K = 1$ , then the equilibria  $\text{HA} + \text{H}_2\text{O} = \text{HA}^- + \text{H}_3\text{O}^+$  and  $\text{HA} = \text{HA}^- + \text{H}^+$  have the same equilibrium constant.

**conjugate base:** the base formed when an acid dissociates

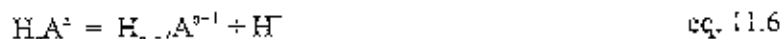
**conjugate acid:** the acid formed when a base accepts a proton

standard Gibbs free energy of reaction defined to be zero? Recall from Section 1.4.3 that  $\text{H}^-$  is really an abbreviation for  $\text{H}^-(\text{H}_2\text{O})_n$ . Thus, it makes sense that the free energy required to convert  $\text{H}^-$  to  $\text{H}_3\text{O}^-$  will be zero.

There are several important ramifications of the fact that  $K_a = 1$  for the equilibrium in eq. 11.5. First, it means that  $\text{H}^-$  is a strong acid with  $\text{p}K_a = 0$ . (You can show that the  $\text{p}K_a$  of  $\text{H}_3\text{O}^+$  also is zero; see Problem 11.2.) Second, it means that you can save some ink when you write the  $K_a$  expressions in eqs. 11.1 and 11.2. For example, adding eq. 11.2 and the reverse of eq. 11.5 (see Chapter 4 for a review of the rules of adding and reversing equilibria) results in:



This little exercise shows that the equilibrium  $\text{HA} + \text{H}_2\text{O} = \text{A}^- + \text{H}_3\text{O}^+$  and the equilibrium  $\text{HA} = \text{A}^- + \text{H}^+$  have the *same equilibrium constant*. Thus, you can stop writing acid dissociation reactions in the form of eqs. 11.1 and 11.2 and write them as eqs. 11.6 and 11.7:



The equilibria in eqs. 11.1 and 11.6 have the same equilibrium constant, as do the equilibria in eqs. 11.2 and 11.7. This text will use equilibria in the form of eqs. 11.6 and 11.7 in most instances and use the equilibrium forms in eqs. 11.1 and 11.2 only when the transfer of protons to water needs to be emphasized.

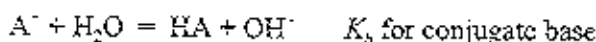
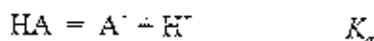
### 11.3.4 Conjugate bases and acids

When an acid donates a proton to water, it produces  $\text{H}_3\text{O}^+$  and another species. The other species is called the *conjugate base* of the acid. Thus, from Example 11.1, you can see that  $\text{CN}^-$  is the conjugate base of  $\text{HCN}$  and ammonia is the conjugate base of ammonium ion. Similarly, when a base accepts a proton from water, it produces  $\text{OH}^-$  and the *conjugate acid* of the starting base.

#### Thoughtful Pause

How are the acid strength of an acid and the base strength of its conjugate base related?

You can write the acid dissociation equilibrium and  $K_a$  equilibrium for the conjugate base of an uncharged, monoprotic acid as follows:



Adding:



To summarize in words: the product of the  $K_a$  of an acid and the  $K_b$  of its conjugate base is  $K_w$ . An equivalent statement is this: *the sum of the  $\text{p}K_a$  of an acid and the  $\text{p}K_b$  of its conjugate base is  $\text{p}K_w$* . At 25°C, where  $\text{p}K_w = 14$ :

$$\text{p}K_a + \text{p}K_b \text{ (of the conjugate base)} = 14 \quad \text{eq. 11.8}$$

Equation 11.8 is very useful. It gives you a lot of information from the knowledge of just one equilibrium constant. If you know the  $\text{p}K_a$  of an acid, then you can calculate easily the  $\text{p}K_b$  of its conjugate base (from  $\text{p}K_b = 14 - \text{p}K_a$ ). Equation 11.8 implies a truism in aquatic chemistry - namely, *the conjugate base of a strong acid is a weak base* (and, conversely, the conjugate base of a weak acid is a strong base). For example, HCl is a strong acid. Its  $\text{p}K_a$  is about -3.



**Key idea:** The  $\text{p}K_a$  of an acid and the  $\text{p}K_b$  of its conjugate base sum to  $\text{p}K_w$  (= 14 at 25°C)



**Key idea:** The conjugate base of a strong acid is a weak base

### Example 11.3: Conjugate Acids and Bases

The  $K_a$  for phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is  $10^{-2.1}$ . What can you say about the acid strength of phosphoric acid? What can you say about the base and acid strengths of  $\text{H}_2\text{PO}_4^-$ ?

#### Solution:

The  $\text{p}K_a$  of phosphoric acid (= 2.1) is fairly small, so **phosphoric acid is a relatively strong acid**. The conjugate base of  $\text{H}_3\text{PO}_4$  is  $\text{H}_2\text{PO}_4^-$  (since  $\text{H}_3\text{PO}_4 = \text{H}_2\text{PO}_4^- + \text{H}^+$ ). Thus,  $\text{H}_2\text{PO}_4^-$  is a **relatively weak base**, with  $\text{p}K_b = 14 - 2.1 = 11.9$ . With the information provided, **you can make no comment about the acid strength of  $\text{H}_2\text{PO}_4^-$** . Its acid strength is quantified by the equilibrium constant of  $\text{H}_2\text{PO}_4^- = \text{HPO}_4^{2-} + \text{H}^+$ .

### Thoughtful Pause

What can you say about the base strength of chloride ( $\text{Cl}^-$ )?

Chloride must be a very weak base since it is the conjugate base of a very strong acid. In fact,  $\text{p}K_b$  for chloride is 14 minus the  $\text{p}K_a$  for HCl =  $14 - (-3) = 17$ . The implication is that chloride will *not* accept a proton appreciably from water to form HCl. As your common experiences tell you, dumping table salt (NaCl) into a glass of water does not lead to the formation of appreciable quantities of hydrochloric acid. The relationship between conjugate acids and bases is explored further in Example 11.3.

### 11.3.5 Limits to acid and base strength

Are there limits to the strengths of acids and bases? For all practical purposes, you can put limits on the strengths of acids and bases in aqueous systems. Fluids with  $\text{pH} < 0$  or  $\text{pH} > 14$  generally are considered to be nonaqueous (that is, the solvent is no longer water). Very strong acids (i.e., acids with  $\text{p}K_a < 0$ ) are essentially completely deprotonated (i.e., donate at least one proton completely to water) at all pH values in water. Thus, you should not expect to see appreciable concentrations of the most protonated forms of strong acids such as HCl or  $\text{H}_2\text{SO}_4$  in water. Only the conjugate bases of these acids ( $\text{Cl}^-$  and  $\text{HSO}_4^-$ , along with its conjugate base,  $\text{SO}_4^{2-}$ )

are expected to be found in water at reasonable concentrations. In the same vein, you should not expect to see appreciable concentrations of strong bases such as  $\text{NH}_2^-$  or  $\text{S}^{2-}$  in water. Only their conjugate acids will be present (e.g.,  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$ , and  $\text{HS}^-$  along with  $\text{H}_2\text{S}$ ).

### 11.3.6 A brief review of equilibrium calculations with monoprotic acids and bases

You have been exposed to equilibrium calculations with monoprotic acids and bases in Chapters 7 through 9. In this section, the key points in the equilibrium calculations will be reviewed. Recall that to perform algebraic equilibrium calculations with monoprotic acids, you should write the species list, equilibria (one acid dissociation equilibrium for each acid plus the self-ionization of water), mass balance equation(s) (one mass balance equation for each acid family), and the charge balance or proton condition. As a shortcut for the graphical method, draw the lines for the  $\text{H}^+$  and  $\text{OH}^-$  concentrations, identify the system point (the point where  $\text{pC} = \text{p}(\text{total acid}) = \text{p}A_T$  and  $\text{pH} = \text{p}K_a$ ), and draw lines for the acid and conjugate base. The line for the acid (HA) concentration is about equal to  $A_T$  at  $\text{pH} \ll \text{p}K_a$ , and the line for the conjugate base ( $\text{A}^-$ ) concentration is about equal to  $A_T$  at  $\text{pH} \gg \text{p}K_a$ . The [HA] and [ $\text{A}^-$ ] lines cross at  $\text{pH} = \text{p}K_a$  and  $\text{pC} \approx \text{p}A_T + 0.3$  (i.e., 0.3 log units below the system point). The equilibrium position of the system is the single point on the pC-pH diagram where the charge balance or proton condition is satisfied. The proton condition is more useful in systems having a large concentration of a species with constant concentration, such as when the salt of an acid (e.g., NaA) is added to water.

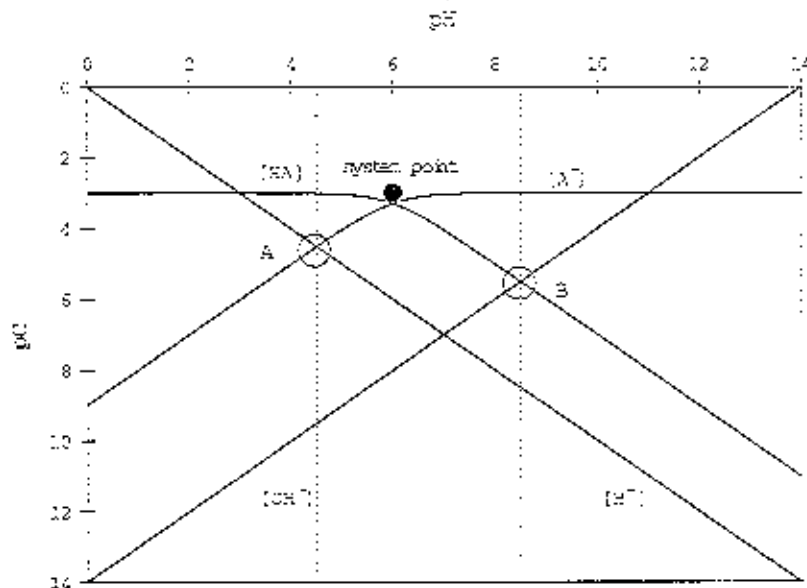
A typical pC-pH diagram for a monoprotic acid is shown in Figure 11.1. The charge balance (and proton condition) for the addition of HA to water is:  $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$ . This is satisfied near point A in Figure 11.1, where  $[\text{H}^+] \approx [\text{A}^-]$  and  $[\text{OH}^-]$  is small enough to be ignored. The proton condition for the addition of NaA to water is:  $[\text{H}^+] + [\text{HA}] = [\text{OH}^-]$ . This is satisfied near point B in Figure 11.1, where  $[\text{HA}] \approx [\text{OH}^-]$  and  $[\text{H}^+]$  is small enough to be ignored.

Several results from the algebraic and graphical solutions are important to remember. First, the HA and  $\text{A}^-$  concentrations depend on  $A_T$ , pH, and  $\text{p}K_a$ . Specifically, from eqs. 8.3 and 8.4:

$$\begin{aligned} [\text{A}^-] &= A_T K_a / (K_a + [\text{H}^+]) \text{ and} \\ [\text{HA}] &= A_T [\text{H}^+] / (K_a + [\text{H}^+]) \end{aligned}$$

<sup>7</sup> Acids stronger than about the strength of 100% sulfuric acid are called *superacids*. An example of a superacid is fluorosulfonic acid,  $\text{HSO}_3\text{F}$ . Fluorosulfonic acid is about 40 times stronger than 100% sulfuric acid and, of course, completely deprotonated in water. The acid strength of superacids cannot be measured by their  $\text{p}K_a$  values. In fact, the concept of a  $\text{p}K_a$  is meaningless, since all superacids are completely deprotonated in water. Instead, their acid strengths are quantified by *acidity functions*. Acidity functions are based on equilibria where the superacids are allowed to protonate bases other than water.

Thus, the concentration of HA is greater than  $[A^-]$  at  $\text{pH} < \text{p}K_a$ . Conversely, the concentration of  $A^-$  is greater than  $[HA]$  at  $\text{pH} > \text{p}K_a$ . Second, at  $\text{pH} = \text{p}K_a$ , the HA and  $A^-$  concentrations are equal. You may wish to verify these conclusions for the monoprotic acid in Figure 11.1.



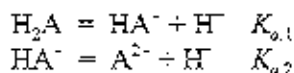
**Figure 11.1: pC-pH Diagram for a Monoprotic Acid with  $\text{p}K_a = 6$  and  $\text{p}A_T = 3$**

[dotted lines indicate the approximate equilibrium pH for an HA solution (left line, point A) and a NaA solution (right line, point B)]

## 11.4 POLYPROTIC ACIDS

### 11.4.1 Definitions

As stated in Section 11.2.3, a polyprotic acid can donate more than one proton to water. Common examples of diprotic acids (which can donate two protons to water) in the aquatic environment include  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{SO}_3$ . The donation of protons to water from polyprotic acids usually is written as a stepwise process.<sup>†</sup> For a general diprotic acid,  $\text{H}_2\text{A}$ :



**Key idea:** Since  $K_a$  is defined for a one-proton transfer, the dissociation of polyprotic acids usually is written as a stepwise process

<sup>†</sup> It is not required to write polyprotic acid dissociation as a stepwise process. Usually, the equilibria are written as one-proton transfers because  $K_a$  is defined for one-proton transfers. You could write any consistent set of equilibria to express the relationships among  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ , and  $\text{A}^{2-}$ ; for example,  $\text{H}_2\text{A} = \text{A}^{2-} + 2\text{H}^+$  and  $\text{HA}^- = \text{A}^{2-} + \text{H}^+$ .

Because of the stepwise nature of proton transfer,  $K_{a1}$  is always greater than  $K_{a2}$  and thus  $pK_{a1} < pK_{a2}$ .

For diprotic acids, the amphoteric form ( $HA^-$  in the equilibria above) is given the name of the most basic form with the prefix *bi-*. Examples include the carbonate family  $H_2CO_3$  (carbonic acid),  $HCO_3^-$  (bicarbonate), and  $CO_3^{2-}$  (carbonate), as well as the sulfide family  $H_2S$  (hydrogen sulfide),  $HS^-$  (bisulfide), and  $S^{2-}$  (sulfide).

### 11.4.2 Solving equilibrium systems with polyprotic acids

You can use the algebraic, graphical, and computer methods discussed in Part II to solve equilibrium systems containing polyprotic acids. The example of a  $10^{-3}$  M  $H_2CO_3$  solution (closed system) will be solved by each method in this section. We must pause for a moment and introduce one new symbol. Recall from Section 1.4.3 that  $H^+$ ,  $(H_2O)H^+$ ,  $(H_2O)_2H^+$ , and so on are almost indistinguishable. Thus, the symbol  $[H^+]$  is used to represent the sum  $[H^+] + [(H_2O)H^+] + [(H_2O)_2H^+] + \text{other similar species}$ . Similarly, the species  $H_2CO_3(aq)$  and  $CO_2(aq)$  are nearly indistinguishable, and it is common to represent the sum of their concentrations by one symbol:  $[H_2CO_3^*] = [H_2CO_3(aq)] + [CO_2(aq)]$ . The system is as follows (if activity and concentration are interchangeable):

#### Example 11.4: Salt of a Diprotic Acid

Following the example in the text with the  $H_2CO_3^*$  system, find the equilibrium concentrations for a  $1 \times 10^{-3}$  M sodium bicarbonate solution.

#### Solution:

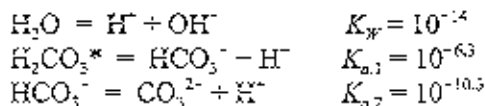
If  $NaHCO_3$  ( $-Na^+ + HCO_3^-$ ) was added to water instead of carbonic acid, the following changes would be made to the in the text

- (1) Add  $Na^+$  as a species
- (2) Change starting materials to  $NaHCO_3$ ,  $-Na^+$ ,  $HCO_3^-$  and  $H_2O$
- (3) Add a new mass balance equation:  $Na_T = 10^{-3} \text{ M} = [Na^+]$
- (4) Include  $Na^+$  as a cation in the charge balance
- (5) Change the proton condition to:  $[H^+] + [H_2CO_3^*] = [CO_3^{2-}] + [OH^-]$ .

Unknowns:  $[H_2O]$ ,  $[H^+]$ ,  $[OH^-]$ ,  $[H_2CO_3^*]$ ,  $[HCO_3^-]$ , and  $[CO_3^{2-}]$

Starting materials:  $H_2O$  and  $H_2CO_3^*$

Equilibria:



Equations:

Equilibria:

$$\begin{aligned} K_w &= [H^+][OH^-]/[H_2O] \\ K_{a1} &= [HCO_3^-][H^+]/[H_2CO_3^*] \\ K_{a2} &= [CO_3^{2-}][H^+]/[HCO_3^-] \end{aligned}$$

Mass balance:

$$C_T = 1 \times 10^{-3} \text{ M} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

Charge balance:

$$\begin{aligned} [H^+] &= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \\ (\text{or you can use the proton condition, also: } [H^+] &= [HCO_3^-] \\ &+ 2[CO_3^{2-}] + [OH^-]) \end{aligned}$$

Other:

$$\begin{aligned} \text{Activity of } H_2O &= 1 \\ \text{All species concentrations} &> 0 \end{aligned}$$

(Remember that any two of the mass balance, charge balance, and proton condition can be combined to generate the third equation.) This system can be solved by the algebraic, graphical, and computer methods. Examples of each solution technique will be presented.

*Algebraic solution:*

The system has the same equilibria as in the text, so eqs. 11.9-11.11 are still valid. Since  $[\text{Na}^+]$  is present, it is easier to use the proton condition than the charge balance. Plugging eqs. 11.9-11.11 into the charge balance yields a variation of eq. 11.12:

$$[\text{H}^+] + C_T[\text{H}^+]^2/\Delta = C_T K_{a1} K_{a2} / \Delta + K_w / [\text{H}^+] \quad (*)$$

$$\text{where } \Delta = [\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}$$

Solving:

$$[\text{H}^+] = 5.28 \times 10^{-9} \text{ M} \\ (\text{pH } 8.28)$$

$$[\text{OH}^-] = 1.89 \times 10^{-6} \text{ M}$$

$$[\text{H}_2\text{CO}_3^*] = 1.03 \times 10^{-5} \text{ M}$$

$$[\text{HCO}_3^-] = 9.80 \times 10^{-5} \text{ M}$$

$$[\text{CO}_3^{2-}] = 9.30 \times 10^{-6} \text{ M}$$

*Approximation method:*

You expect the pH to be closer to neutral pH than in the case of  $\text{H}_2\text{CO}_3^*$  addition. Thus,  $\Delta$  is about equal to  $K_{a1}[\text{H}^+]$  and you might try ignoring  $[\text{OH}^-]$  relative to  $[\text{CO}_3^{2-}]$  in the proton condition. Thus, (\*) becomes:

$$[\text{H}^+] - C_T[\text{H}^+]/K_{a1} = C_T K_{a2} / [\text{H}^+]$$

$$\text{Or: } [\text{H}^+]^2(1 + C_T/K_{a1}) = C_T K_{a2}$$

$$\text{Since } C_T/K_{a1} \gg 1: [\text{H}^+] = \\ [(C_T K_{a2}) / (C_T/K_{a1})]^{1/2} = (K_{a1} K_{a2})^{1/2} \\ = 10^{-8.27} = 10^{-8.3} \text{ or pH } 8.3.$$

Checking the assumptions, you can show that at pH 8.26,  $\Delta = 2.6 \times 10^{-13} \approx K_{a1}[\text{H}^+] = 2.5 \times 10^{-13}$ . Also:  $[\text{OH}^-] = 10^{-5.7} \text{ M}$  and  $[\text{CO}_3^{2-}] = C_T K_{a2} / [\text{H}^+] = 10^{-5} \text{ M}$ . The assumption that  $[\text{OH}^-]$  can be ignored relative to  $[\text{CO}_3^{2-}]$  is of questionable validity.

In the brute force algebraic method, express each species concentration in terms of the concentration of one species (usually  $[\text{H}^+]$ ). From the equilibria and mass balances (after a little algebra, which you should confirm):

$$[\text{OH}^-] = K_w / [\text{H}^+] \\ [\text{H}_2\text{CO}_3^*] = C_T [\text{H}^+]^2 / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad \text{eq. 11.9}$$

$$[\text{HCO}_3^-] = C_T K_{a1} [\text{H}^+] / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad \text{eq. 11.10}$$

$$[\text{CO}_3^{2-}] = C_T K_{a1} K_{a2} / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \quad \text{eq. 11.11}$$

Substituting into the charge balance (or proton condition) yields:

$$[\text{H}^+] = \frac{C_T K_{a1} K_{a2} / [\text{H}^+] + 2C_T K_{a1} K_{a2} + K_w}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad \text{eq. 11.12}$$

Solving (see Appendix A for hints on solving this equation):

$$[\text{H}^+] = 2.22 \times 10^{-5} \text{ M (pH } 4.65)$$

$$[\text{OH}^-] = 4.51 \times 10^{-10} \text{ M}$$

$$[\text{H}_2\text{CO}_3^*] = 9.78 \times 10^{-4} \text{ M}$$

$$[\text{HCO}_3^-] = 2.21 \times 10^{-5} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.99 \times 10^{-11} \text{ M}$$

Using the method of approximation, you might guess that the solution is mildly acidic since a relatively weak acid ( $\text{p}K_{a1}$  of  $\text{H}_2\text{CO}_3^*$  is 6.3) is being added to water. Thus, the righthand side of the charge balance should be dominated by the weaker bases.

**Thoughtful Pause**

Why is the charge balance dominated by the weaker bases?

The weaker bases generally are higher in concentration because the stronger bases will be more protonated at an acidic pH. Therefore, from the charge balance:  $[\text{H}^+] \approx [\text{HCO}_3^-]$  or, using eq. 11.9:

$$[\text{H}^+] \approx C_T K_{a1} [\text{H}^+] / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})$$

The denominator of the expression for  $[\text{HCO}_3^-]$  (eq. 11.10) is about equal to  $[\text{H}^+]^2$  under acidic conditions.<sup>†</sup> Thus:  $[\text{H}^+] \approx C_T K_{a1} / [\text{H}^+]$  or  $[\text{H}^+]^2 \approx C_T K_{a1}$  or  $\text{pH} = (\text{p}C_T + \text{p}K_{a1})/2 = (3 + 6.3)/2 = 4.65$ .

<sup>†</sup> Why is the denominator in eq. 11.9 about equal to  $[\text{H}^+]^2$  under acidic conditions? The term  $[\text{H}^+]^2$  is larger than  $K_{a1}[\text{H}^+] = 10^{-6.3}[\text{H}^+]$  if the pH is less than 6.3. Also,  $[\text{H}^+]^2$  is larger than  $K_{a1}K_{a2} = 10^{-12.6}$  if the pH is less than  $12.6/2 = 6.3$ . Thus,  $[\text{H}^+]^2$  is the largest term in the denominator if the pH is less than 6.3.

*Graphical method:*

Figure 11.2 is still valid. We seek the point where the proton condition is satisfied, i.e., where

$$[\text{H}^+] + [\text{H}_2\text{CO}_3^*] = [\text{CO}_3^{2-}] + [\text{OH}^-]$$

Near neutral pH, you expect  $[\text{H}^+]$  and  $[\text{OH}^-]$  to be small, so the proton condition becomes  $[\text{H}_2\text{CO}_3^*] \approx [\text{CO}_3^{2-}]$ . From Figure 11.2, the  $[\text{H}_2\text{CO}_3^*]$  and  $[\text{CO}_3^{2-}]$  lines cross at about pH 8.2-8.3.

You may wish to check that the assumptions are valid. The assumptions were:

$$\begin{aligned} \text{In the charge balance: } & [\text{HCO}_3^-] \gg 2[\text{CO}_3^{2-}] \text{ and } [\text{HCO}_3^-] \gg [\text{OH}^-] \\ \text{In the denominator: } & [\text{H}^+]^2 \gg K_{a1}[\text{H}^+] + K_{a1}K_{a2} \end{aligned}$$

This example points out the value of chemical intuition in selecting the approximation. The wise assumption of mildly acidic conditions here converted a fourth-order polynomial equation in  $[\text{H}^+]$  to the arithmetic of  $\text{pH} \approx (3 - 6.3)/2 = 4.65$ . Working problems like this is one of the best ways to strengthen your chemical intuition and save you work in the long run.

To use the graphical method, merely plot the expressions in eqs. 11.9-11.11 and find where the charge balance (or proton condition) is satisfied. A pC-pH diagram for the carbonic acid system is shown in Figure 11.2. The equilibrium pH is again approximated from the charge balance at the pH where  $[\text{H}^+] = [\text{HCO}_3^-]$  (about where the lines for  $[\text{H}^+]$  and  $[\text{HCO}_3^-]$  cross). This occurs at about pH 4.6-4.7 (dotted line in Figure 11.2). The approximations in the charge balance ( $[\text{HCO}_3^-] \gg 2[\text{CO}_3^{2-}]$  and  $[\text{HCO}_3^-] \gg [\text{OH}^-]$ ) can be checked easily in the pC-pH diagram. A shortcut to the graphical method with polyprotic acids will be discussed in Section 11.4.3.

#### 11.4.3 A shortcut to the graphical method for polyprotic acids

You can develop a shortcut method for graphical solutions to polyprotic acid systems similar to the shortcut method developed for monoprotic acids in Section 8.4. For a diprotic acid, consider three pH ranges:  $\text{pH} < \text{p}K_{a1}$ ,  $\text{p}K_{a1} < \text{pH} < \text{p}K_{a2}$ , and  $\text{pH} > \text{p}K_{a2}$ . In the lowest pH range, the denominator in eqs. 11.9-11.11 is about equal to  $[\text{H}^+]^2$ . Thus:

$$[\text{H}_2\text{CO}_3^*] = C_T[\text{H}^+]^2 / ([\text{H}^+]^2 - K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \approx C_T$$

$$[\text{HCO}_3^-] = C_T K_{a1}[\text{H}^+] / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \approx C_T K_{a1} / [\text{H}^+]$$

$$[\text{CO}_3^{2-}] = C_T K_{a1}K_{a2} / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \approx C_T K_{a1}K_{a2} / [\text{H}^+]^2$$

Therefore, where  $\text{pH} < \text{p}K_{a1}$ , you expect:

1. The  $[\text{H}_2\text{CO}_3^*]$  line should have a slope of zero and be about equal to  $C_T$ .



- The  $[\text{HCO}_3^-]$  line should be downward sloping to the left with a slope equal to -1 (parallel to the  $[\text{OH}^-]$  line, where  $[\text{OH}^-] = K_{a2}/[\text{H}^+]$ ).
- The  $[\text{CO}_3^{2-}]$  line should be downward sloping to the left with a slope equal to -2. Also note that  $[\text{CO}_3^{2-}]$  is much smaller than either  $[\text{H}_2\text{CO}_3^*]$  or  $[\text{HCO}_3^-]$  since  $[\text{H}^+] \gg K_{a2}$  ( $\text{pH} < \text{p}K_{a2} = 10.3$ ) in this pH range.

Be sure to work with the above equations until these conclusions make sense to you.

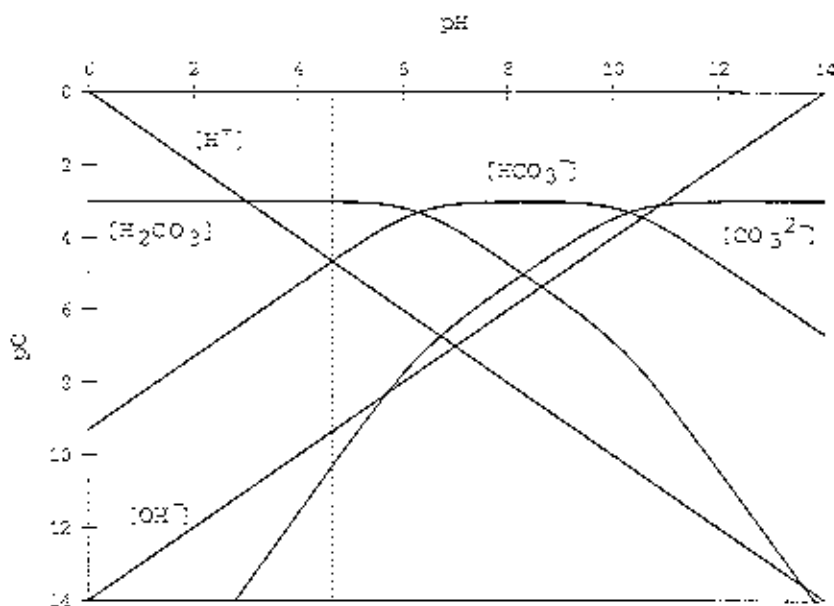


Figure 11.2: pC-pH Diagram for the Addition of  $10^{-3} \text{ M H}_2\text{CO}_3^*$  to Water

(dotted line represents the equilibrium pH - where the charge balance and proton condition are satisfied)

In the middle pH range, the denominator in eqs. 11.9-11.11 is about equal to  $K_{a1}[\text{H}^+]$ . Thus:

$$[\text{H}_2\text{CO}_3^*] = C_T[\text{H}^+]^2 / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] - K_{a1}K_{a2}) \approx C_T[\text{H}^+] / K_{a1}$$

$$[\text{HCO}_3^-] = C_T K_{a1}[\text{H}^+] / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \approx C_T$$

$$[\text{CO}_3^{2-}] = C_T K_{a1}K_{a2} / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) \approx C_T K_{a2} / [\text{H}^+]$$

Therefore, where  $pK_{a1} < pH < pK_{a2}$  you expect:

1. The  $[H_2CO_3^*]$  line should be downward sloping to the right with a slope equal to +1 (parallel to the  $[H^+]$  line).
2. The  $[HCO_3^-]$  line should have a slope of zero and be about equal to  $C_T$ .
3. The  $[CO_3^{2-}]$  line should be downward sloping to the left with a slope equal to -1.

Finally, in the highest pH range ( $pH > pK_{a2}$ ), the denominator in eqs. 11.9-11.11 is about equal to the product of the  $K_a$  values ( $= K_{a1}K_{a2}$ ). Thus:

$$[H_2CO_3^*] = C_T [H^+]^2 / ([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \approx C_T [H^+]^2 / (K_{a1}K_{a2})$$

$$[HCO_3^-] = C_T K_{a1} [H^+] / ([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \approx C_T [H^+] / K_{a2}$$

$$[CO_3^{2-}] = C_T K_{a1} K_{a2} / ([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \approx C_T$$

Therefore, where  $pH > pK_{a2}$  you expect:

1. The  $[H_2CO_3^*]$  line should be downward sloping to the right with slope = -2. Also note that  $[H_2CO_3^*]$  is much smaller than either  $[HCO_3^-]$  or  $[CO_3^{2-}]$  since  $[H^+] \ll K_{a2}$  ( $pH > pK_{a2} = 10.3$ ) in this pH range.
2. The  $[HCO_3^-]$  line should be downward sloping to the right with a slope equal to +1 (parallel to the  $[H^+]$  line).
3. The  $[CO_3^{2-}]$  line should have a slope of zero and be about equal to  $C_T$ .

The graphical shortcut method takes advantage of the two system points for a diprotic acid. The first system point occurs at  $pH = pK_{a1}$  and  $pC = pC_T$ . The second system point occurs at  $pH = pK_{a2}$  and  $pC = pC_T$ .

The behavior of the species in the diprotic acid system with respect to pH can be summarized. The p(concentration) of the most protonated form of the diprotic acid ( $H_2CO_3^*$  in the example) is about equal to  $C_T$  at pH values less than  $pK_{a1}$  (i.e., to the left of the first system point), increases in a 1:1 ratio with increasing pH at pH values between the two  $pK_a$  values (i.e., between the system points), and increases in a 2:1 ratio with increasing pH at pH values greater than  $pK_{a2}$  values (i.e., to the right of the second system point).

Similarly, the p(concentration) of the next most protonated form of the diprotic acid ( $HCO_3^-$  in the example) decreases in a 1:1 ratio with pH at



**Key idea:** pC-pH diagrams for diprotic acids have two system points (corresponding to the two  $pK_a$  values), with the slope of the pC lines changing at the system points

increasing pH values less than  $pK_{a,1}$  (i.e., to the left of the first system point), is about equal to  $C_T$  at pH values between the two  $pK_a$  values (i.e., between the system points), and increases in a 1:1 ratio with increasing pH at pH values greater than  $pK_{a,2}$  (i.e., to the right of the second system point).

Finally, the p(concentration) of the least protonated form of the diprotic acid ( $\text{CO}_3^{2-}$  in the example) decreases in a 2:1 ratio with pH at increasing pH values less than  $pK_{a,1}$  (i.e., to the left of the first system point), decreases in a 1:1 ratio with increasing pH at pH values between the two  $pK_a$  values (i.e., between the system points), and is about equal to  $C_T$  at pH values greater than  $pK_{a,2}$  (i.e., to the right of the second system point). As with monoprotic acids, it is quite easy to sketch the pC-pH diagram for a polyprotic acid.

The extension of the shortcut method of Section 8.4 to  $n$ -protic acids is fairly straightforward. Consider an  $n$ -protic acid,  $\text{H}_n\text{A}$ , which dissociates in water to form  $n$  other species:  $\text{H}_{n-1}\text{A}^-$ ,  $\text{H}_{n-2}\text{A}^{2-}$ , ...,  $\text{A}^{n-}$ . Each species is of the form  $\text{H}_i\text{A}$ . The sum of the concentrations of the  $n$  species containing the fragment  $-\text{A}$  is  $A_T$ . To sketch the pC-pH diagram (see also Appendix C, Section C.4.3), use the following approach:

#### Step 1: Locate system points

Prepare a pC-pH diagram with lines representing the  $\text{H}^+$  and  $\text{OH}^-$  concentrations. Locate the  $n$  system points. These occur where  $\text{pH} = \text{p}K_{a,1}$  and  $\text{pC} = \text{p}A_T$ ,  $\text{pH} = \text{p}K_{a,2}$  and  $\text{pC} = \text{p}A_T$ , ..., and  $\text{pH} = \text{p}K_{a,n}$  and  $\text{pC} = \text{p}A_T$ .

#### Step 2: Draw species lines

Draw the lines for the p(concentration) of each species at least 1.5 pH units away from each system point. The p(concentration) line of species  $\text{H}_i\text{A}$  has the following slopes:  $i - n$  at pH values less than the first system point,  $i - n + j$  between the  $j^{\text{th}}$  and  $(j + 1)^{\text{th}}$  system point, and  $-i$  at pH values greater than the final ( $n^{\text{th}}$ ) system point. (Recall that a negative slope means that the pC decreases with increasing pH and thus the line is upward sloping to the right.) Make sure that the lines, if extended, would go through the system points.

#### Step 3: Make species lines intersect below the system points

Curve the lines so that they intersect about 0.3 log units below the system points.

#### Step 4: Find the equilibria pH



**Key idea:** To apply the graphical shortcut to polyprotic

acids, locate system points (at  $\text{pC} = \text{p}A_T$  and  $\text{pH} = \text{p}K_{a,i}$ ), draw species lines (making sure that species lines intersect below the system points), and find the equilibrium pH where the proton condition is satisfied.

To find the equilibria pH (and equilibrium concentrations of all plotted species), find the pH where the charge balance or proton condition is satisfied. Check any assumptions made in the charge balance and iterate if necessary.

With this shortcut, a pC-pH diagram for any acid can be sketched quickly and the equilibrium pH estimated with little fuss.



**Key idea:** The proton condition is valuable in working with the salts of polyprotic acids

#### 11.4.4 The power of the proton condition

The real value of the proton condition shows itself with polyprotic acids. Once you have solved the system formed by adding  $H_nA$  to water, you can easily calculate the equilibrium conditions for adding various salts to water (generalized as  $Na_mH_pA$ , where  $m + p = n$ ). For example, after putting in the work on the  $H_2CO_3^*$  system, you can find the equilibrium pH for systems where  $NaHCO_3$  (sodium bicarbonate) and  $Na_2CO_3$  (sodium carbonate) are added to water. The three systems (adding  $H_2CO_3^*$ ,  $NaHCO_3$ , or  $Na_2CO_3$  to water) have the same set of equilibria and differ only in their mass balance on the sodium ion and thus differ in their proton condition.

Example 11.4 demonstrated the ease in extending the  $H_2CO_3^*$  system to  $NaHCO_3$  solutions. You also can apply the previous work to  $Na_2CO_3$  solutions. Begin by writing the proton condition for a  $Na_2CO_3$  solution (starting materials are  $Na_2CO_3 + 2Na^+ + CO_3^{2-}$  and  $H_2O$ ):

$$[H^+] + [HCO_3^-] - 2[H_2CO_3^*] = [OH^-]$$

(Note the factor of 2 in front of the carbonic acid concentration, because  $H_2CO_3^*$  has two more protons than its source in the starting materials, namely  $CO_3^{2-}$ .) You might expect the pH to be high.

---

#### Thoughtful Pause

Why should the pH be high for a sodium carbonate solution?

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The righthand side of the proton condition contains only  $[OH^-]$ . Thus,  $[OH^-]$  must be much larger than  $[H^+]$ . At high pH,  $[H^+]$  and  $[H_2CO_3^*]$  are expected to be small and the proton condition becomes:  $[HCO_3^-] = [OH^-]$ . From Figure 11.2, this occurs at about pH 10.5-10.6 (exact solution: pH 10.56).

---

† The same conclusion can be reached from the charge balance:  $[H^+] + [Na^+] = [HCO_3^-] - 2[CO_3^{2-}] + [OH^-]$ . Since  $[Na^+] = 2 \times 10^{-3} M$  is large, the species concentrations on the righthand side also must be large and  $[OH^-]$  is expected to be much larger than  $[H^+]$ .

5

4'

6

3'