THERMODYNAMICS AND CHEMISTRY

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TABLE OF CONTENTS

11: Reactions and Other Chemical Processes

12: Equilibrium Conditions in Multicomponent Systems

13: The Phase Rule and Phase Diagrams

14: Galvanic Cells

15: Appendices

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A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

CHAPTER OVERVIEW

1: Introduction

Thermodynamics is a quantitative subject. It allows us to derive relations between the values of numerous physical quantities. Some physical quantities, such as a mole fraction, are dimensionless; the value of one of these quantities is a pure number. Most quantities, however, are not dimensionless and their values must include one or more *units*. This chapter reviews the SI system of units, which are the preferred units in science applications. The chapter then discusses some useful mathematical manipulations of physical quantities using quantity calculus, and certain general aspects of dimensional analysis.

1.1: Units

There is international agreement that the units used for physical quantities in science and technology should be those of the International System of Units, or SI (standing for the French **Système International d'Unités**). The Physical Chemistry Division of the International Union of Pure and Applied Chemistry, or IUPAC, produces a manual of recommended symbols and terminology for physical quantities and units based on the SI. The manual has become known as the Green Book (from the color of its cover) and is referred to here as the IUPAC Green Book. This e-book will, with a few exceptions, use symbols recommended in the third edition (2007) of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition. RSC Publishing, Cambridge, 2007). These symbols are listed for convenient reference in Appendices C and D.

Any of the symbols for units listed in Tables 1.1–1.3, except kg and $^\circ\mathrm{C}$, may be preceded by one of the prefix symbols of Table 1.4 to construct a decimal fraction or multiple of the unit. (The symbol g may be preceded by a prefix symbol to construct a fraction or multiple of the gram.) The combination of prefix symbol and unit symbol is taken as a new symbol that can be raised to a power without using parentheses, as in the following examples:

- The physical quantity formally called **amount of substance** is a counting quantity for particles, such as atoms or molecules, or for other chemical entities. The counting unit is invariably the **mole**, defined as the amount of substance containing as many particles as the number of atoms in exactly 12 grams of pure carbon-12 nuclide, $^{12}\mathrm{C}$. See Appendix A for the wording of the official IUPAC definition. This definition is such that one mole of $\mathrm{H_2O}$ molecules, for example, has a mass of 18.0153grams (where $18.0153$is the relative molecular mass of $\mathrm{H_2O}$) and contains 6.02214×10^{23}molecules (where $6.02214 \times 10^{23}\ \mathrm{mol}^{-1}$ is the *Avogadro constant* to six significant digits). The same statement can be made for any other substance if $18.0153$is replaced by the appropriate atomic mass or molecular mass value.

  The symbol for amount of substance is n. It is admittedly awkward to refer to $n(\mathrm{H_2O})$ as "the amount of substance of water." This e-book simply shortens "amount of substance" to **amount**. An alternative name suggested for n is "chemical amount." Thus, "the amount of water in the system" refers not to the mass or volume of water, but to the *number* of $\mathrm{H_2O}$ molecules in the system expressed in a counting unit such as the mole.

1.2: Quantity Calculus

This section gives examples of how we may manipulate physical quantities by the rules of algebra. The method is called *quantity calculus*, although a better term might be “quantity algebra.”

Quantity calculus is based on the concept that a physical quantity, unless it is dimensionless, has a value equal to the product of a *numerical value* (a pure number) and one or more *units*:

$$\text{physical quantity} = \text{numerical value} \times \text{units} \tag{1.2.1}$$

(If the quantity is dimensionless, it is equal to a pure number without units.) The physical property may be denoted by a symbol, but the symbol does *not* imply a particular choice of units. For instance, this e-book uses the symbol ρ for density, but ρ can be expressed in any units having the dimensions of mass divided by volume.

A simple example illustrates the use of quantity calculus. We may express the density of water at $25\,^{\circ}\mathrm{C}$ to four significant digits in SI base units by the equation

$$\rho = 9.970 \times 10^{2}\ \mathrm{kg\ m^{-3}} \tag{1.2.2}$$

and in different density units by the equation

$$\rho = 0.9970\ \mathrm{g\ cm^{-3}} \tag{1.2.3}$$

We may divide both sides of the last equation by 1 g $\mathrm{cm^{-3}}$ to obtain a new equation

$$\rho/\mathrm{g\ cm^{-3}} = 0.9970 \tag{1.2.4}$$

Now the pure number 0.9970 appearing in this equation is the number of grams in one cubic centimeter of water, so we may call the ratio $\rho/\mathrm{g\ cm^{-3}}$ “the number of grams per cubic centimeter.” By the same reasoning, $\rho/\mathrm{kg\ m^{-3}}$ is the number of kilograms per cubic meter. In general, a physical quantity divided by particular units for the physical quantity is a pure number representing the number of those units.

> Just as it would be incorrect to call ρ “the number of grams per cubic centimeter,” because that would refer to a particular choice of units for ρ, the common practice of calling n “the number of moles” is also strictly speaking not correct. It is actually the ratio n/mol that is the number of moles.

In a table, the ratio $\rho/\mathrm{g\ cm^{-3}}$ makes a convenient heading for a column of density values because the column can then show pure numbers. Likewise, it is convenient to use $\rho/\mathrm{g\ cm^{-3}}$ as the label of a graph axis and to show pure numbers at the grid marks of the axis. You will see many examples of this usage in the tables and figures in this e-book.

A major advantage of using SI base units and SI derived units is that they are *coherent*. That is, values of a physical quantity expressed in different combinations of these units have the same numerical value.

For example, suppose we wish to evaluate the pressure of a gas according to the ideal gas equation

$$p = \frac{nRT}{V} \tag{1.2.5}$$

(ideal gas)

This is the first equation that, like many others to follow, shows *conditions of validity* in parentheses immediately below the equation number at the right. Thus, Eq. 1.2.5 is valid for an ideal gas. In this equation, p, n, T, and V are the symbols for the physical quantities pressure, amount (amount of substance), thermodynamic temperature, and volume, respectively, and R is the gas constant.

The calculation of p for 5.000 moles of an ideal gas at a temperature of 298.15 kelvins, in a volume of 4.000 cubic meters, is

$$p = \frac{(5.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{4.000\ \mathrm{m^{3}}} = 3.099 \times 10^{3}\ \mathrm{J\ m^{-3}} \tag{1.2.6}$$

The mole and kelvin units cancel, and we are left with units of J $\mathrm{m^{-3}}$, a combination of an SI derived unit (the joule) and an SI base unit (the meter). The units J $\mathrm{m^{-3}}$ must have dimensions of pressure, but are not commonly used to express pressure.

To convert J $\mathrm{m^{-3}}$ to the SI derived unit of pressure, the pascal (Pa), we can use the following relations from Table 1.2:

$$1\,\mathrm{J} = 1\,\mathrm{N\,m} \qquad 1\,\mathrm{Pa} = 1\,\mathrm{N\,m^{-2}} \tag{1.2.7}$$

When we divide both sides of the first relation by $1\,\mathrm{J}$ and divide both sides of the second relation by $1\,\mathrm{N\,m^{-2}}$, we obtain the two new relations

$$1 = (1\,\mathrm{N\,m/J}) \qquad (1\,\mathrm{Pa/N\,m^{-2}}) = 1 \tag{1.2.8}$$

The ratios in parentheses are *conversion factors*. When a physical quantity is multiplied by a conversion factor that, like these, is equal to the pure number 1, the physical quantity changes its units but not its value. When we multiply Eq. 1.2.6 by both of these conversion factors, all units cancel except Pa:

$$p \; = (3.099 \times 10^3\,\mathrm{J\,m^{-3}}) \times (1\,\mathrm{N\,m/J}) \times (1\,\mathrm{Pa/N\,m^{-2}}) \; = 3.099 \times 10^3\,\mathrm{Pa} \tag{1.2.9}$$

This example illustrates the fact that to calculate a physical quantity, we can simply enter into a calculator numerical values expressed in SI units, and the result is the numerical value of the calculated quantity expressed in SI units. In other words, as long as we use only SI base units and SI derived units (without prefixes), *all conversion factors are unity*.

Of course we do not have to limit the calculation to SI units. Suppose we wish to express the calculated pressure in torrs, a non-SI unit. In this case, using a conversion factor obtained from the definition of the torr in Table 1.3, the calculation becomes

$$p = (3.099 \times 10^3\,\mathrm{Pa}) \times (760\,\mathrm{Torr}/101,325\,\mathrm{Pa}) = 23.24\,\mathrm{Torr} \tag{1.2.10}$$

1.3: Dimensional Analysis

Sometimes you can catch an error in the form of an equation or expression, or in the dimensions of a quantity used for a calculation, by checking for dimensional consistency. Here are some rules that must be satisfied:

- In this e-book the *differential* of a function, such as $\mathrm{d}f$, refers to an *infinitesimal* quantity. If one side of an equation is an infinitesimal quantity, the other side must also be. Thus, the equation $\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y$ (where ax and by have the same dimensions as f) makes mathematical sense, but $\mathrm{d}f = ax + b\,\mathrm{d}y$ does not.

  Derivatives, partial derivatives, and integrals have dimensions that we must take into account when determining the overall dimensions of an expression that includes them. For instance:

  - Some examples of applying these principles are given here using symbols described in Sec. 1.2.

    Example 1. Since the gas constant R may be expressed in units of J K^{-1} mol^{-1}, it has dimensions of energy divided by thermodynamic temperature and amount. Thus, RT has dimensions of energy divided by amount, and nRT has dimensions of energy. The products RT and nRT appear frequently in thermodynamic expressions.

    Example 3. Find the dimensions of the constants a and b in the van der Waals equation

    $$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \tag{1.3.1}$$

    Dimensional analysis tells us that, because nb is subtracted from V, nb has dimensions of volume and therefore b has dimensions of volume/amount. Furthermore, since the right side of the equation is a difference of two terms, these terms have the same dimensions as the left side, which is pressure. Therefore, the second term n^2a/V^2 has dimensions of pressure, and a has dimensions of pressure $\times$ volume^2 $\times$ amount^{-2}.

    Example 4. Consider an equation of the form

    $$\left(\frac{\partial \ln x}{\partial T}\right)_p = \frac{y}{R} \tag{1.3.2}$$

    What are the SI units of y? $\ln x$ is dimensionless, so the left side of the equation has the dimensions of $1/T$, and its SI units are K^{-1}. The SI units of the right side are therefore also K^{-1}. Since R has the units J K^{-1} mol^{-1}, the SI units of y are J K^{-2} mol^{-1}.

1.4: Chapter 1 Problem

1.1

Consider the following equations for the pressure of a real gas. For each equation, find the dimensions of the constants a and b and express these dimensions in SI units.

(a) The Dieterici equation:

$$p=\frac{RTe^{-(an/VRT)}}{(V/n)-b} \tag{1.4.1}$$

(b) The Redlich–Kwong equation:

$$p=\frac{RT}{(V/n)-b}-\frac{an^2}{T^{1/2}V(V+nb)} \tag{1.4.2}$$

CHAPTER OVERVIEW

2: Systems and Their Properties

This chapter begins by explaining some basic terminology of thermodynamics. It discusses macroscopic properties of matter in general and properties distinguishing different physical states of matter in particular. Virial equations of state of a pure gas are introduced. The chapter goes on to discuss some basic macroscopic properties and their measurement. Finally, several important concepts needed in later chapters are described: thermodynamic states and state functions, independent and dependent variables, processes, and internal energy.

2.1: The System, Surroundings, and Boundary

Chemists are interested in systems containing matter—that which has mass and occupies physical space. Classical thermodynamics looks at *macroscopic* aspects of matter. It deals with the properties of aggregates of vast numbers of microscopic particles (molecules, atoms, and ions). The macroscopic viewpoint, in fact, treats matter as a *continuous* material medium rather than as the collection of discrete microscopic particles we know are actually present. Although this e-book is an exposition of classical thermodynamics, at times it will point out connections between macroscopic properties and molecular structure and behavior.

A thermodynamic **system** is any three-dimensional region of physical space on which we wish to focus our attention. Usually we consider only one system at a time and call it simply “the system.” The rest of the physical universe constitutes the **surroundings** of the system.

The **boundary** is the closed three-dimensional surface that encloses the system and separates it from the surroundings. The boundary may (and usually does) coincide with real physical surfaces: the interface between two phases, the inner or outer surface of the wall of a flask or other vessel, and so on. Alternatively, part or all of the boundary may be an imagined intangible surface in space, unrelated to any physical structure. The size and shape of the system, as defined by its boundary, may change in time. In short, our choice of the three-dimensional region that constitutes the system is arbitrary—but it is essential that we know exactly what this choice is.

We usually think of the system as a part of the physical universe that we are able to influence only indirectly through its interaction with the surroundings, and the surroundings as the part of the universe that we are able to directly manipulate with various physical devices under our control. That is, we (the experimenters) are part of the surroundings, not the system.

For some purposes we may wish to treat the system as being divided into *subsystems*, or to treat the combination of two or more systems as a *supersystem*.

If over the course of time matter is transferred in either direction across the boundary, the system is **open**; otherwise it is **closed**. If the system is open, matter may pass through a stationary boundary, or the boundary may move through matter that is fixed in space.

If the boundary allows heat transfer between the system and surroundings, the boundary is **diathermal**. An **adiabatic** (Greek: *impassable*) boundary, on the other hand, is a boundary that does not allow heat transfer. We can, in principle, ensure that the boundary is adiabatic by surrounding the system with an adiabatic wall—one with perfect thermal insulation and a perfect radiation shield.

An **isolated** system is one that exchanges no matter, heat, or work with the surroundings, so that the mass and total energy of the system remain constant over time. (The energy in this definition of an isolated system is measured in a local reference frame, as will be explained in Sec. 2.6.2.) A closed system with an adiabatic boundary, constrained to do no work and to have no work done on it, is an isolated system.

> The constraints required to prevent work usually involve forces between the system and surroundings. In that sense a system may interact with the surroundings even though it is isolated. For instance, a gas contained within rigid, thermally-insulated walls is an isolated system; the gas exerts a force on each wall, and the wall exerts an equal and opposite force on the gas. An isolated system may also experience a constant external field, such as a gravitational field.

The term **body** usually implies a system, or part of a system, whose mass and chemical composition are constant over time.

2.1.1 Extensive and intensive properties

A quantitative *property* of a system describes some macroscopic feature that, although it may vary with time, has a particular value at any given instant of time.

Table 2.1 lists the symbols of some of the properties discussed in this chapter and the SI units in which they may be expressed. A much more complete table is found in Appendix C.

Most of the properties studied by thermodynamics may be classified as either extensive or intensive. We can distinguish these two types of properties by the following considerations.

If we imagine the system to be divided by an imaginary surface into two parts, any property of the system that is the sum of the property for the two parts is an **extensive property**. That is, an additive property is extensive. Examples are mass, volume, amount, energy, and the surface area of a solid.

> Sometimes a more restricted definition of an extensive property is used: The property must be not only additive, but also proportional to the mass or the amount when intensive properties remain constant. According to this definition, mass, volume, amount, and energy are extensive, but surface area is not.

If we imagine a homogeneous region of space to be divided into two or more parts of arbitrary size, any property that has the same value in each part and the whole is an **intensive property**; for example density, concentration, pressure (in a fluid), and temperature. The value of an intensive property is the same everywhere in a homogeneous region, but may vary from point to point in a heterogeneous region—it is a *local* property.

Since classical thermodynamics treats matter as a continuous medium, whereas matter actually contains discrete microscopic particles, the value of an intensive property at a point is a statistical average of the behavior of many particles. For instance, the density of a gas at one point in space is the average mass of a small volume element at that point, large enough to contain many molecules, divided by the volume of that element.

Some properties are defined as the ratio of two extensive quantities. If both extensive quantities refer to a homogeneous region of the system or to a small volume element, the ratio is an *intensive* property. For example concentration, defined as the ratio $\text{amount}/\text{volume}$, is intensive. A mathematical derivative of one such extensive quantity with respect to another is also intensive.

A special case is an extensive quantity divided by the mass, giving an intensive **specific quantity**; for example

$$\text{Specific volume} = \frac{V}{m} = \frac{1}{\rho} \tag{2.1.1}$$

If the symbol for the extensive quantity is a capital letter, it is customary to use the corresponding lower-case letter as the symbol for the specific quantity. Thus the symbol for specific volume is v.

Another special case encountered frequently in this e-book is an extensive property for a pure, homogeneous substance divided by the amount n. The resulting intensive property is called, in general, a **molar quantity** or molar property. To symbolize a molar quantity, this e-book follows the recommendation of the IUPAC: The symbol of the extensive quantity is followed by subscript m, and optionally the identity of the substance is indicated either by a subscript or a formula in parentheses. Examples are

$$\text{Molar volume} = \frac{V}{n} = V_{\text{m}} \tag{2.1.2}$$

$$\text{Molar volume of substance } i = \frac{V}{n_i} = V_{\text{m},i} \tag{2.1.3}$$

$$\text{Molar volume of H}_2\text{O } = V_{\text{m}}(\text{H}_2\text{O}) \tag{2.1.4}$$

In the past, especially in the United States, molar quantities were commonly denoted with an overbar (e.g., $\overline{V}_i$).

2.2: Phases and Physical States of Matter

A **phase** is a region of the system in which each intensive property (such as temperature and pressure) has at each instant either the same value throughout (a *uniform* or *homogeneous* phase), or else a value that varies continuously from one point to another. Whenever this e-book mentions a phase, it is a *uniform* phase unless otherwise stated. Two different phases meet at an **interface surface**, where intensive properties have a discontinuity or change over a small distance.

Some intensive properties (e.g., refractive index and polarizability) can have directional characteristics. A uniform phase may be either *isotropic*, exhibiting the same values of these properties in all directions, or *anisotropic*, as in the case of some solids and liquid crystals. A vacuum is a uniform phase of zero density.

Suppose we have to deal with a *nonuniform* region in which intensive properties vary continuously in space along one or more directions—for example, a tall column of gas in a gravitational field whose density decreases with increasing altitude. There are two ways we may treat such a nonuniform, continuous region: either as a single nonuniform phase, or else as an infinite number of uniform phases, each of infinitesimal size in one or more dimensions.

2.2.1 Physical states of matter

We are used to labeling phases by physical state, or state of aggregation. It is common to say that a phase is a *solid* if it is relatively rigid, a *liquid* if it is easily deformed and relatively incompressible, and a *gas* if it is easily deformed and easily compressed. Since these descriptions of responses to external forces differ only in degree, they are inadequate to classify intermediate cases.

The way in which Z varies with p at different temperatures is shown for the case of carbon dioxide in Fig. 2.3(a).

A temperature at which the initial slope is zero is called the **Boyle temperature**, which for CO_2 is $710\,\mathrm{K}$. Both B and B_p must be zero at the Boyle temperature. At lower temperatures B and B_p are negative, and at higher temperatures they are positive—see Fig. 2.3(b). This kind of temperature dependence is typical for other gases. Experimentally, and also according to statistical mechanical theory, B and B_p for a gas can be zero only at a single Boyle temperature.

> The fact that at any temperature other than the Boyle temperature B is nonzero is significant since it means that in the limit as p approaches zero at constant T and the gas approaches ideal-gas behavior, the *difference* between the actual molar volume V_{m} and the ideal-gas molar volume RT/p does not approach zero. Instead, $V_{\mathrm{m}} - RT/p$ approaches the nonzero value B (see Eq. 2.2.8). However, the *ratio* of the actual and ideal molar volumes, $V_{\mathrm{m}}/(RT/p)$, approaches unity in this limit.

Virial equations of gas *mixtures* will be discussed in Sec. 9.3.4.

2.2.6 Solids

A solid phase responds to a small applied stress by undergoing a small *elastic deformation*. When the stress is removed, the solid returns to its initial shape and the properties return to those of the unstressed solid. Under these conditions of small stress, the solid has an equation of state just as a fluid does, in which p is the pressure of a fluid surrounding the solid (the hydrostatic pressure) as explained in Sec. 2.3.4. The stress is an additional independent variable. For example, the length of a metal spring that is elastically deformed is a unique function of the temperature, the pressure of the surrounding air, and the stretching force.

If, however, the stress applied to the solid exceeds its elastic limit, the response is *plastic deformation*. This deformation persists when the stress is removed, and the unstressed solid no longer has its original properties. Plastic deformation is a kind of hysteresis, and is caused by such microscopic behavior as the slipping of crystal planes past one another in a crystal subjected to shear stress, and conformational rearrangements about single bonds in a stretched macromolecular fiber. Properties of a solid under plastic deformation depend on its past history and are not unique functions of a set of independent variables; an equation of state does not exist.

2.3: Some Basic Properties and Their Measurement

2.4: The State of the System

The thermodynamic **state** of the system is an important and subtle concept. At each instant of time, the system is in some definite state that we may describe with values of the macroscopic properties we consider to be relevant for our purposes. The values of these properties at any given instant define the state at that instant. Whenever the value of any of these properties changes, the state has changed. If we subsequently find that each of the relevant properties has the value it had at a certain previous instant, then the system has returned to its previous state.

> Do not confuse the *state* of the system with the kind of *physical state* or state of aggregation of a phase discussed in Sec. 2.2.1. A *change of state* refers to a change in the state of the system, not necessarily to a phase transition.

2.4.1 State functions and independent variables

The properties whose values at each instant depend only on the state of the system at that instant, and not on the past or future history of the system, are called **state functions** (or state variables or state parameters). There may be other system properties that we consider to be irrelevant to the state, such as the shape of the system, and these are *not* state functions.

Various conditions determine what states of a system are physically possible. If a uniform phase has an equation of state, property values must be consistent with this equation. The system may have certain built-in or externally-imposed conditions or constraints that keep some properties from changing with time. For instance, a closed system has constant mass; a system with a rigid boundary has constant volume. We may know about other conditions that affect the properties during the time the system is under observation.

We can define the state of the system with the values of a certain minimum number of state functions which we treat as the **independent variables**. Once we have selected a set of independent variables, consistent with the physical nature of the system and any conditions or constraints, we can treat all other state functions as **dependent variables** whose values depend on the independent variables.

Whenever we adjust the independent variables to particular values, every other state function is a dependent variable that can have only one definite, reproducible value. For example, in a single-phase system of a pure substance with T, p, and n as the independent variables, the volume is determined by an equation of state in terms of T, p, and n; the mass is equal to nM; the molar volume is given by $V_{\mathrm{m}} = V/n$; and the density is given by $\rho = nM/V$.

2.4.2 An example: state functions of a mixture

The heat-conducting metal rod shown in Fig. 2.8 is a system in such a steady state. Each end of the rod is in thermal contact with a **heat reservoir** (or **thermal reservoir**), which is a body or external system whose temperature remains constant and uniform when there is heat transfer to or from it.

A heat reservoir can be a body that is so large that its temperature changes only imperceptibly during heat transfer; a thermostat bath whose temperature can be controlled; or an external system of coexisting phases of a pure substance (e.g., ice and water) at constant pressure.

The two heat reservoirs in the figure have different temperatures, causing a temperature gradient to form along the length of the rod and energy to be transferred by heat from the warmer reservoir to the rod and from the rod to the cooler reservoir. Although the properties of the steady state of the rod remain constant, the rod is clearly not in an equilibrium state because the temperature gradient will quickly disappear when we isolate the rod by removing it from contact with the heat reservoirs.

2.5: Processes and Paths

A **process** is a change in the state of the system over time, starting with a definite initial state and ending with a definite final state. The process is defined by a **path**, which is the continuous sequence of consecutive states through which the system passes, including the initial state, the intermediate states, and the final state. The process has a direction along the path. The path could be described by a curve in an N-dimensional space in which each coordinate axis represents one of the N independent variables.

This e-book takes the view that a thermodynamic process is defined by what happens *within* the system, in the three-dimensional region up to and including the boundary, and by the forces exerted on the system by the surroundings and any external field. Conditions and changes in the surroundings are not part of the process except insofar as they affect these forces. For example, consider a process in which the system temperature decreases from $300\,\mathrm{K}$ to $273\,\mathrm{K}$. We could accomplish this temperature change by placing the system in thermal contact with either a refrigerated thermostat bath or a mixture of ice and water. The process is the same in both cases, but the surroundings are different.

Expansion is a process in which the system volume increases; in **compression**, the volume decreases.

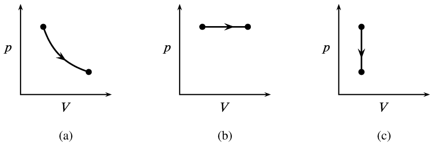


Figure 2.9 Paths of three processes of a closed ideal-gas system with p and V as the independent variables. (a) Isothermal expansion. (b) Isobaric expansion. (c) Isochoric pressure reduction.

Paths for these processes of an ideal gas are shown in Fig. 2.9. An **isothermal** process is one in which the temperature of the system remains uniform and constant. An **isobaric** or **isopiestic** process refers to uniform constant pressure, and an **isochoric** process refers to constant volume.

An **adiabatic** process is one in which there is no heat transfer across any portion of the boundary. We may ensure that a process is adiabatic either by using an adiabatic boundary or, if the boundary is diathermal, by continuously adjusting the external temperature to eliminate a temperature gradient at the boundary.

Recall that a state function is a property whose value at each instant depends only on the state of the system at that instant. The finite change of a state function X in a process is written ΔX. The notation ΔX always has the meaning $X_2 - X_1$, where X_1 is the value in the initial state and X_2 is the value in the final state. Therefore, the value of ΔX depends only on the values of X_1 and X_2. *The change of a state function during a process depends only on the initial and final states of the system, not on the path of the process.*

An infinitesimal change of the state function X is written $\mathrm{d}X$. The mathematical operation of summing an infinite number of infinitesimal changes is integration, and the sum is an integral (see the brief calculus review in Appendix E). The sum of the infinitesimal changes of X along a path is a definite integral equal to ΔX:

$$\int_{X_1}^{X_2} \mathrm{d}X = X_2 - X_1 = \Delta X \tag{2.5.1}$$

If $\mathrm{d}X$ obeys this relation—that is, if its integral for given limits has the same value regardless of the path—it is called an **exact differential**. The differential of a state function is always an exact differential.

A **cyclic process** is a process in which the state of the system changes and then returns to the initial state. In this case the integral of $\mathrm{d}X$ is written with a cyclic integral sign: $\oint \mathrm{d}X$. Since a state function X has the same initial and final values in a cyclic process, X_2 is equal to X_1 and the cyclic integral of $\mathrm{d}X$ is zero:

$$\oint \mathrm{d}X = 0 \tag{2.5.2}$$

Heat (q) and work (w) are examples of quantities that are *not* state functions. They are not even properties of the system; instead they are quantities of energy transferred across the boundary over a period of time. It would therefore be incorrect to write "Δq" or "Δw." Instead, the values of q and w depend in general on the path and are called **path functions**.

This e-book uses the symbol đ (the letter "d" with a bar through the stem) for an infinitesimal quantity of a path function. Thus, $đq$ and $đw$ are infinitesimal quantities of heat and work. The sum of many infinitesimal quantities of a path function is not the difference of two values of the path function; instead, the sum is the *net* quantity:

$$\int đq = q \qquad \int đw = w \tag{2.5.3}$$

The infinitesimal quantities $đq$ and $đw$, because the values of their integrals depend on the path, are **inexact differentials**.

> Chemical thermodynamicists often write these quantities as $\mathrm{d}q$ and $\mathrm{d}w$. Mathematicians, however, frown on using the same notation for inexact and exact differentials. Other notations sometimes used to indicate that heat and work are path functions are $\mathrm{D}q$ and $\mathrm{D}w$, and also δq and δw.

There is a fundamental difference between a state function (such as temperature or volume) and a path function (such as heat or work): *The value of a state function refers to one instant of time; the value of a path function refers to an interval of time*.

> The difference between a state function and a path function in thermodynamics is analogous to the difference between elevation and trail length in hiking up a mountain. Suppose a trailhead at the base of the mountain has several trails to the summit. The hiker at each instant is at a definite elevation above sea level. During a climb from the trailhead to the summit, the hiker's change of elevation is independent of the trail used, but the trail length from base to summit depends on the trail.

2.6: The Energy of the System

A large part of classical thermodynamics is concerned with the energy of the system. The total energy of a system is an extensive property whose value at any one instant cannot be measured in any practical way, but whose change is the focus of the first law of thermodynamics (Chap. 3).

2.6.1 Energy and reference frames

Classical thermodynamics ignores microscopic properties such as the behavior of individual atoms and molecules. Nevertheless, a consideration of the classical mechanics of particles will help us to understand the sources of the potential and kinetic energy of a thermodynamic system.

In classical mechanics, the energy of a collection of interacting point particles is the sum of the kinetic energy $\frac{1}{2}mv^2$ of each particle (where m is the particle's mass and v is its velocity), and of various kinds of potential energies. The potential energies are defined in such a way that if the particles are isolated from the rest of the universe, as the particles move and interact with one another the total energy (kinetic plus potential) is constant over time. This principle of the conservation of energy also holds for real atoms and molecules whose electronic, vibrational, and rotational energies, absent in point particles, are additional contributions to the total energy.

The positions and velocities of particles must be measured in a specified system of coordinates called a *reference frame*. This e-book will use reference frames with *Cartesian* axes. Since the kinetic energy of a particle is a function of velocity, the kinetic energy depends on the choice of the reference frame. A particularly important kind is an *inertial* frame, one in which Newton's laws of motion are obeyed (see Sec. G.1 in Appendix G).

A reference frame whose axes are fixed relative to the earth's surface is what this e-book will call a *lab frame*. A lab frame for all practical purposes is inertial (Sec. G.10). It is in this kind of stationary frame that the laws of thermodynamics have been found by experiment to be valid.

The energy E of a thermodynamic system is the sum of the energies of the particles contained in it and the potential energies of interaction between these particles. Just as for an individual particle, the energy of the system depends on the reference frame in which it is measured. The energy of the system may change during a process, but the principle of the conservation of energy ensures that the sum of the energy of the system, the energy of the surroundings, and any energy shared by both, all measured in the same reference frame, remains constant over time.

This e-book uses the symbol E_{sys} for the energy of the system measured in a specified inertial frame. The system could be located in a weightless environment in outer space, and the inertial frame could be one that is either fixed or moving at constant velocity relative to local stars. Usually, however, the system is located in the earth's gravitational field, and the appropriate inertial frame is then an earth-fixed lab frame.

If during a process the system as a whole undergoes motion or rotation relative to the inertial frame, then E_{sys} depends in part on coordinates that are not properties of the system. In such situations E_{sys} is not a state function, and we need the concept of internal energy.

2.6.2 Internal energy

The **internal energy**, U, is the energy of the system measured in a reference frame that allows U to be a state function—that is, at each instant the value of U depends only on the state of the system. This e-book will call a reference frame with this property a *local frame*. A local frame may also be, but is not necessarily, an earth-fixed lab frame.

Here is a simple illustration of the distinction between the energy E_{sys} of a system measured in a lab frame and the internal energy U measured in a local frame. Let the *system* be a fixed amount of water contained in a glass beaker. (The glass material of the beaker is part of the surroundings.) We can define the state of this system by two independent variables: the temperature, T, and pressure, p, of the water. The most convenient local frame in which to measure U in this case is a frame fixed with respect to the beaker.

- Section 3.1.1 will show that the relation between changes of the system energy and the internal energy in this example is $\Delta E_{\text{sys}} = \Delta E_{\text{k}} + \Delta E_{\text{p}} + \Delta U$, where E_{k} and E_{p} are the kinetic and potential energies of the system as a whole measured in the lab frame.

Our choice of the local frame used to define the internal energy U of any particular system during a given process is to some extent arbitrary. Three possible choices are as follows.

- Is it possible to determine a numerical *value* for the internal energy of a system? The total energy of a body of mass m when it is at rest is given by the Einstein relation $E = mc_0^2$, where c_0 is the speed of light in vacuum. In principle, then, we could calculate the internal energy U of a system at rest from its mass, and we could determine ΔU for a process from the change in mass. In practice, however, an absolute value of U calculated from a measured mass has too much uncertainty to be of any practical use. For example, the typical uncertainty of the mass of an object measured with a microbalance, about $0.1\ \mu$g (Table 2.2), would introduce the enormous uncertainty in energy of about 10^{10} joules. Only values of the *change* ΔU are useful, and these values cannot be calculated from Δm because the change in mass during an ordinary chemical process is much too small to be detected.

2.7: Chapter 2 Problems

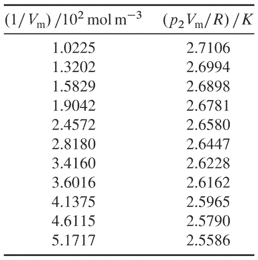
2.1

Let X represent the quantity V^2 with dimensions $(\mathrm{length})^6$. Give a reason that X is or is not an extensive property. Give a reason that X is or is not an intensive property.

2.2

Calculate the *relative uncertainty* (the uncertainty divided by the value) for each of the measurement methods listed in Table 2.2, using the typical values shown. For each of the five physical quantities listed, which measurement method has the smallest relative uncertainty?

Table 2.5 Helium at a fixed temperature



$(1/V_\mathrm{m})\,/10^2\,\mathrm{mol\,m^{-3}}$	$(p_2V_\mathrm{m}/R)\,/K$
1.0225	2.7106
1.3202	2.6994
1.5829	2.6898
1.9042	2.6781
2.4572	2.6580
2.8180	2.6447
3.4160	2.6228
3.6016	2.6162
4.1375	2.5965
4.6115	2.5790
5.1717	2.5586

2.3

Table 2.5 lists data obtained from a constant-volume gas thermometer containing samples of varying amounts of helium maintained at a certain fixed temperature T_2 in the gas bulb (K. H. Berry, *Metrologia*, **15**, 89–115, 1979). The molar volume V_m of each sample was evaluated from its pressure in the bulb at a reference temperature of $T_1 = 7.1992\,\mathrm{K}$, corrected for gas nonideality with the known value of the second virial coefficient at that temperature.

Use these data and Eq. 2.2.2 to evaluate T_2 and the second virial coefficient of helium at temperature T_2. (You can assume the third and higher virial coefficients are negligible.)

2.4

Discuss the proposition that, to a certain degree of approximation, a living organism is a steady-state system.

2.5

The value of ΔU for the formation of one mole of crystalline potassium iodide from its elements at $25\,^\circ\mathrm{C}$ and 1 bar is $-327.9\,\mathrm{kJ}$. Calculate Δm for this process. Comment on the feasibility of measuring this mass change.

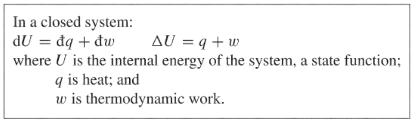
CHAPTER OVERVIEW

3: The First Law

In science, a **law** is a statement or mathematical relation that concisely describes reproducible experimental observations. Classical thermodynamics is built on a foundation of three laws, none of which can be derived from principles that are any more fundamental. This chapter discusses theoretical aspects of the first law; gives examples of *reversible* and *irreversible* processes and the heat and work that occur in them; and introduces the extensive state function *heat capacity*.

3.1: Heat, Work, and the First Law

The box below gives two forms of the **first law of thermodynamics**.



In a closed system:
$\mathrm{d}U = \text{đ}q + \text{đ}w \qquad \Delta U = q + w$
where U is the internal energy of the system, a state function;
q is heat; and
w is thermodynamic work.

The equation $\mathrm{d}U = \text{đ}q + \text{đ}w$ is the *differential* form of the first law, and $\Delta U = q + w$ is the *integrated* form.

The heat and work appearing in the first law are two different modes of energy transfer. They can be defined in a general way as follows.

- An infinitesimal quantity of energy transferred as heat at a surface element of the boundary is written $\text{đ}q$, and a finite quantity is written q (Sec. 2.5). To obtain the total finite heat for a process from $q = \int \text{đ}q$ (Eq. 2.5.3), we must integrate over the total boundary surface and the entire path of the process.

  An infinitesimal quantity of work is $\text{đ}w$, and a finite quantity is $w = \int \text{đ}w$. To obtain w for a process, we integrate all kinds of work over the entire path of the process.

  The first-law equation $\Delta U = q + w$ sets up a balance sheet for the energy of the system, measured in the local frame, by equating its change during a process to the net quantity of energy transferred by means of heat and work. Note that the equation applies only to a *closed* system. If the system is open, energy can also be brought across the boundary by the transport of matter.

  An important part of the first law is the idea that heat and work are *quantitative* energy transfers. That is, when a certain quantity of energy enters the system in the form of heat, the same quantity leaves the surroundings. When the surroundings perform work on the system, the increase in the energy of the system is equal in magnitude to the decrease in the energy of the surroundings. The principle of conservation of energy is obeyed: the total energy (the sum of the energies of the system and surroundings) remains constant over time.

  > Strictly speaking, it is the sum of the energies of the system, the surroundings, and any potential energy shared by both that is constant. The shared potential energy is usually negligible or essentially constant (Sec. G.5).

  Heat transfer may occur by conduction, convection, or radiation. (Some thermodynamicists treat radiation as a separate contribution to ΔU, in addition to q and w.) We can reduce conduction with good thermal insulation at the boundary, we can eliminate conduction and convection with a vacuum gap, and we can minimize radiation with highly reflective surfaces at both sides of the vacuum gap. The only way to completely prevent heat during a process is to arrange conditions in the surroundings so there is no temperature gradient at any part of the boundary. Under these conditions the process is adiabatic, and any energy transfer in a closed system is then solely by means of work.

3.1.1 The concept of thermodynamic work

Appendix G gives a detailed analysis of energy and work based on the behavior of a collection of interacting particles moving according to the principles of classical mechanics. The analysis shows how we should evaluate mechanical thermodynamic work. Suppose the displacement responsible for the work comes from linear motion of a portion of the boundary in the $+x$ or $-x$ direction of the local frame. The differential and integrated forms of the work are then given by

$$\text{đ}w = F_x^{\mathrm{sur}}\,\mathrm{d}x \qquad w = \int_{x_1}^{x_2} F_x^{\mathrm{sur}}\,\mathrm{d}x \tag{3.1.1}$$

(These equations are Eq. G.6.11 with a change of notation.) Here F_x^{sur} is the component in the $+x$ direction of the force exerted by the surroundings on the system at the moving portion of the boundary, and $\mathrm{d}x$ is the infinitesimal displacement of the boundary in the local frame. If the displacement is in the same direction as the force, $\text{đ}w$ is positive; if the displacement is in the opposite direction, $\text{đ}w$ is negative.

The kind of force represented by F_x^{sur} is a short-range contact force. Appendix G shows that the force exerted by a conservative time-independent external field, such as a gravitational force, should not be included as part of F_x^{sur}. This is because the work done by this kind of force causes changes of potential and kinetic energies that are equal and opposite in sign, with no net effect on the internal energy (see Sec. 3.6).

Newton's third law of action and reaction says that a force exerted by the surroundings on the system is opposed by a force of equal magnitude exerted in the opposite direction by the system on the surroundings. Thus the expressions in Eq. 3.1.1 can be replaced by

$$\text{đ}w = -F_x^{\text{sys}}\,\mathrm{d}x \qquad w = -\int_{x_1}^{x_2} F_x^{\text{sys}}\,\mathrm{d}x \tag{3.1.2}$$

where F_x^{sys} is the component in the $+x$ direction of the contact force exerted by the *system* on the surroundings at the moving portion of the boundary.

> An alternative to using the expressions in Eqs. 3.1.1 or 3.1.2 for evaluating w is to imagine that the only effect of the work on the system's surroundings is a change in the elevation of a weight in the surroundings. The weight must be one that is linked mechanically to the source of the force F_x^{sur}. Then, provided the local frame is a stationary lab frame, the work is equal in magnitude and opposite in sign to the change in the weight's potential energy: $w = -mg\Delta h$ where m is the weight's mass, g is the acceleration of free fall, and h is the weight's elevation in the lab frame. This interpretation of work can be helpful for seeing whether work occurs and for deciding on its sign, but of course cannot be used to determine its *value* if the actual surroundings include no such weight.
>
> The procedure of evaluating w from the change of an external weight's potential energy requires that this change be the only mechanical effect of the process on the surroundings, a condition that in practice is met only approximately. For example, Joule's paddle-wheel experiment using two weights linked to the system by strings and pulleys, described latter in Sec. 3.7.2, required corrections for (1) the kinetic energy gained by the weights as they sank, (2) friction in the pulley bearings, and (3) elasticity of the strings (see Prob. 3.10).

In the first-law relation $\Delta U = q + w$, the quantities ΔU, q, and w are all measured in an arbitrary *local* frame. We can write an analogous relation for measurements in a stationary *lab* frame:

$$\Delta E_{\text{sys}} = q_{\text{lab}} + w_{\text{lab}} \tag{3.1.3}$$

Suppose the chosen local frame is not a lab frame, and we find it more convenient to measure the heat q_{lab} and the work w_{lab} in a lab frame than to measure q and w in the local frame. What corrections are needed to find q and w in this case?

If the Cartesian axes of the local frame do not rotate relative to the lab frame, then the heat is the same in both frames: $q = q_{\text{lab}}$ (Sec. G.7).

The expressions for $\text{đ}w_{\text{lab}}$ and w_{lab} are the same as those for $\text{đ}w$ and w in Eqs. 3.1.1 and 3.1.2, with $\mathrm{d}x$ interpreted as the displacement in the *lab* frame. There is an especially simple relation between w and w_{lab} when the local frame is a center-of-mass frame—one whose origin moves with the system's center of mass and whose axes do not rotate relative to the lab frame (Eq. G.8.12):

$$w = w_{\text{lab}} - \tfrac{1}{2}m\Delta\left(v_{\text{cm}}^2\right) - mg\Delta z_{\text{cm}} \tag{3.1.4}$$

In this equation m is the mass of the system, v_{cm} is the velocity of its center of mass in the lab frame, g is the acceleration of free fall, and z_{cm} is the height of the center of mass above an arbitrary zero of elevation in the lab frame. In typical thermodynamic processes the quantities v_{cm} and z_{cm} change to only a negligible extent, if at all, so that usually to a good approximation w is equal to w_{lab}.

When the local frame is a center-of-mass frame, we can combine the relations $\Delta U = q + w$ and $q = q_{\text{lab}}$ with Eqs. 3.1.3 and 3.1.4 to obtain

$$\Delta E_{\text{sys}} = \Delta E_{\text{k}} + \Delta E_{\text{p}} + \Delta U \tag{3.1.5}$$

where $E_{\text{k}} = \frac{1}{2}mv_{\text{cm}}^2$ and $E_{\text{p}} = mgz_{\text{cm}}$ are the kinetic and potential energies of the system as a whole in the lab frame.

A more general relation for w can be written for any local frame that has no rotational motion and whose origin has negligible acceleration in the lab frame (Eq. G.7.3):

$$w = w_{\text{lab}} - mg\Delta z_{\text{loc}} \tag{3.1.6}$$

Here z_{loc} is the elevation in the lab frame of the origin of the local frame. Δz_{loc} is usually small or zero, so again w is approximately equal to w_{lab}. The only kinds of processes for which we may need to use Eq. 3.1.4 or 3.1.6 to calculate a non-negligible difference between w and w_{lab} are those in which massive parts of the system undergo substantial changes in elevation in the lab frame.

Simple relations such as these between q and q_{lab}, and between w and w_{lab}, do not exist if the local frame has rotational motion relative to a lab frame.

Hereafter in this e-book, thermodynamic work w will be called simply *work*. For all practical purposes you can assume the local frames for most of the processes to be described are stationary lab frames. The discussion above shows that the values of heat and work measured in these frames are usually the same, or practically the same, as if they were measured in a local frame moving with the system's center of mass. A notable exception is the local frame needed to treat the thermodynamic properties of a liquid solution in a centrifuge cell. In this case the local frame is fixed in the spinning rotor of the centrifuge and has rotational motion. This special case will be discussed in Sec. 9.8.2.

3.1.2 Work coefficients and work coordinates

If a process has only one kind of work, it can be expressed in the form

$$đw = Y\,\mathrm{d}X \qquad \text{or} \qquad w = \int_{X_1}^{X_2} Y\,\mathrm{d}X \tag{3.1.7}$$

where Y is a generalized force called a **work coefficient** and X is a generalized displacement called a **work coordinate**. The work coefficient and work coordinate are *conjugate* variables. They are not necessarily actual forces and displacements. For example, we shall see in Sec. 3.4.2 that reversible expansion work is given by $đw = -p\,\mathrm{d}V$; in this case, the work coefficient is $-p$ and the work coordinate is V.

A process may have more than one kind of work, each with its own work coefficient and conjugate work coordinate. In this case the work can be expressed as a sum over the different kinds labeled by the index i:

$$đw = \sum_i Y_i\,\mathrm{d}X_i \qquad \text{or} \qquad w = \sum_i \int_{X_{i,1}}^{X_{i,2}} Y_i\,\mathrm{d}X_i \tag{3.1.8}$$

3.1.3 Heat and work as path functions

Consider the apparatus shown in Fig. 3.1. The *system* consists of the water together with the immersed parts: stirring paddles attached to a shaft (a paddle wheel) and an electrical resistor attached to wires. In equilibrium states of this system, the temperature and pressure are uniform and the paddle wheel is stationary. The system is open to the atmosphere, so the pressure is constrained to be constant. We may describe the equilibrium states of this system by a single independent variable, the temperature T. (The angular position of the shaft is irrelevant to the state and is not a state function for equilibrium states of this system.)

Here are three experiments with different processes. Each process has the same initial state defined by $T_1 = 300.0\,\mathrm{K}$, and each has the same final state.

- Although the paths in the three experiments are entirely different, the overall change of state is the same. In fact, a person who observes only the initial and final states and has no knowledge of the intermediate states or the changes in the surroundings will be ignorant of the path. Did the paddle wheel turn? Did an electric current pass through the resistor? How much energy was transferred by work and how much by heat? The observer cannot tell from the change of state, because heat and work are not state functions. The change of state depends on the *sum* of heat and work. This sum is the change in the state function U, as expressed by the integrated form of the first law, $\Delta U = q + w$.

  It follows from this discussion that neither heat nor work are quantities possessed by the system. A system at a given instant does not *have* or *contain* a particular quantity of heat or a particular quantity of work. Instead, heat and work depend on the path of a process occurring over a period of time. They are *path* functions.

3.1.4 Heat and heating

In everyday speech the noun *heat* is often used somewhat differently. Here are three statements with similar meanings that could be misleading:

"Heat is transferred from a laboratory hot plate to a beaker of water."

"Heat flows from a warmer body to a cooler body."

"To remove heat from a hot body, place it in cold water."

Statements such as these may give the false impression that heat is like a substance that retains its identity as it moves from one body to another. Actually heat, like work, does not exist as an entity once a process is completed. Nevertheless, the wording of statements such as these is embedded in our everyday language, and no harm is done if we interpret them correctly. This e-book, for conciseness, often refers to "heat transfer" and "heat flow," instead of using the technically more correct phrase "energy transfer by means of heat."

Another common problem is failure to distinguish between thermodynamic "heat" and the process of "heating." To *heat* a system is to cause its temperature to increase. A *heated* system is one that has become warmer. This process of *heating* does not necessarily involve thermodynamic heat; it can also be carried out with work as illustrated by experiments 1 and 2 of the preceding section.

The notion of heat as an indestructible substance was the essence of the caloric theory. This theory was finally disproved by the cannon-boring experiments of Benjamin Thompson (Count Rumford) in the late eighteenth century, and in a more quantitative way by the measurement of the mechanical equivalent of heat by James Joule in the 1840s (see Sec. 3.7.2).

3.1.5 Heat capacity

The **heat capacity** of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change:

$$\text{heat capacity} \overset{\text{def}}{=} \frac{đq}{\mathrm{d}T} \tag{3.1.9}$$

(closed system)

Since q is a path function, the value of the heat capacity depends on the specified conditions, usually either constant volume or constant pressure. C_V is the *heat capacity at constant volume* and C_p is the *heat capacity at constant pressure*. These are extensive state functions that will be discussed more fully in Sec. 5.6.

3.1.6 Thermal energy

It is sometimes useful to use the concept of **thermal energy**. It can be defined as the kinetic energy of random translational motions of atoms and molecules relative to the local frame, plus the vibrational and rotational energies of molecules. The thermal energy of a body or phase depends on its temperature, and increases when the temperature increases. The thermal energy of a system is a contribution to the internal energy.

It is important to understand that a change of the system's thermal energy during a process is not necessarily the same as energy transferred across the system boundary as heat. The two quantities are equal only if the system is closed and there is no work, volume change, phase change, or chemical reaction. This is illustrated by the three experiments described in Sec. 3.1.3: the thermal energy change is the same in each experiment, but only in experiment 3 is the work negligible and the thermal energy change equal to the heat.

3.2: Spontaneous, Reversible, and Irreversible Processes

A **spontaneous process** is a process that can actually occur in a finite time period under the existing conditions. Any change over time in the state of a system that we observe experimentally is a spontaneous process.

A spontaneous process is sometimes called a natural process, feasible process, possible process, allowed process, or real process.

3.2.1 Reversible processes

A **reversible process** is an important concept in thermodynamics. This concept is needed for the chain of reasoning that will allow us to define entropy changes in the next chapter, and will then lead on to the establishment of criteria for spontaneity and for various kinds of equilibria.

Before reversible processes can be discussed, it is necessary to explain the meaning of the *reverse* of a process. If a particular process takes the system from an initial state A through a continuous sequence of intermediate states to a final state B, then the reverse of this process is a change over time from state B to state A with the same intermediate states occurring in the reverse time sequence. To visualize the reverse of any process, imagine making a movie film of the events of the process. Each frame of the film is a “snapshot” picture of the state at one instant. If you run the film backward through a movie projector, you see the reverse process: the values of system properties such as p and V appear to change in reverse chronological order, and each velocity changes sign.

The concept of a reversible process is not easy to describe or to grasp. Perhaps the most confusing aspect is that a reversible process is not a process that ever actually occurs, but is only approached as a hypothetical limit. During a reversible process the system passes through a continuous sequence of equilibrium states. These states are ones that can be approached, as closely as desired, by the states of a spontaneous process carried out sufficiently slowly. As the spontaneous process is carried out more and more slowly, it approaches the reversible limit. Thus, a reversible process is an *idealized* process with a sequence of equilibrium states that are those of a spontaneous process in the *limit* of infinite slowness.

This e-book has many equations expressing relations among heat, work, and state functions during various kinds of reversible processes. What is the use of an equation for a process that can never actually occur? The point is that the equation can describe a spontaneous process to a high degree of accuracy, if the process is carried out slowly enough for the intermediate states to depart only slightly from exact equilibrium states. For example, for many important spontaneous processes we will assume the temperature and pressure are uniform throughout the system, which strictly speaking is an approximation.

A reversible process of a closed system, as used in this e-book, has all of the following characteristics:

- We must imagine the reversible process to proceed at a finite rate, otherwise there would be no change of state over time. The precise rate of the change is not important. Imagine a gas whose volume, temperature, and pressure are changing at some finite rate while the temperature and pressure magically stay perfectly uniform throughout the system. This is an entirely imaginary process, because there is no temperature or pressure gradient—no physical “driving force”—that would make the change tend to occur in a particular direction. This imaginary process is a reversible process—one whose states of uniform temperature and pressure are approached by the states of a real process as the real process takes place more and more slowly.

  It is a good idea, whenever you see the word “reversible,” to think “in the reversible limit.” Thus a *reversible process* is a process in the reversible limit, *reversible work* is work in the reversible limit, and so on.

3.2.2 Irreversible processes

An **irreversible** process is a spontaneous process whose reverse is neither spontaneous nor reversible. That is, the reverse of an irreversible process can never actually occur and is *impossible*. If a movie is made of a spontaneous process, and the time sequence of the events depicted by the film when it is run backward could not occur in reality, the spontaneous process is irreversible.

A good example of a spontaneous, irreversible process is experiment 1 in Section 3.1.3, in which the sinking of an external weight immersed in water causes a paddle wheel to rotate and the temperature of the water to increase. During this experiment mechanical energy is dissipated into thermal energy. Suppose you insert a thermometer in the water and make a movie film of the experiment. Then when you run the film backward in a projector, you will see the paddle wheel rotating in the direction that raises the weight, and the water becoming cooler according to the thermometer. Clearly, this reverse process is impossible in the real physical world, and the process occurring during the experiment is irreversible. It is not difficult to understand why it is irreversible when we consider events on the microscopic level: it is extremely unlikely that the H_2O molecules next to the paddles would happen to move simultaneously over a period of time in the concerted motion needed to raise the weight.

3.2.3 Purely mechanical processes

There is a class of spontaneous processes that are also spontaneous in reverse; that is, spontaneous but not irreversible. These are *purely mechanical* processes involving the motion of perfectly-elastic macroscopic bodies without friction, temperature gradients, viscous flow, or other irreversible changes.

A simple example of a purely mechanical process and its reverse is shown in Fig. 3.2. The ball can move spontaneously in either direction. Another example is a flywheel with frictionless bearings rotating in a vacuum.

A purely mechanical process proceeding at a finite rate is not reversible, for its states are not equilibrium states. Such a process is an idealization, of a different kind than a reversible process, and is of little interest in chemistry. Later chapters of this e-book will ignore such processes and will treat the terms *spontaneous* and *irreversible* as synonyms.

3.3: Heat Transfer

This section describes irreversible and reversible heat transfer. Keep in mind that when this e-book refers to *heat transfer* or *heat flow*, energy is being transferred across the boundary on account of a temperature gradient at the boundary. The transfer is always in the direction of decreasing temperature.

We may sometimes wish to treat the temperature as if it is discontinuous at the boundary, with different values on either side. The transfer of energy is then from the warmer side to the cooler side. The temperature is not actually discontinuous; instead there is a thin zone with a temperature gradient.

3.3.1 Heating and cooling

As an illustration of irreversible heat transfer, consider a system that is a solid metal sphere. This spherical body is immersed in a well-stirred water bath whose temperature we can control. The bath and the metal sphere are initially equilibrated at temperature $T_1 = 300.0\,\mathrm{K}$, and we wish to raise the temperature of the sphere by one kelvin to a final uniform temperature $T_2 = 301.0\,\mathrm{K}$.

One way to do this is to rapidly increase the external bath temperature to $301.0\,\mathrm{K}$ and keep it at that temperature. The temperature difference across the surface of the immersed sphere then causes a spontaneous flow of heat through the system boundary into the sphere. It takes time for all parts of the sphere to reach the higher temperature, so a temporary internal temperature gradient is established. Thermal energy flows spontaneously from the higher temperature at the boundary to the lower temperature in the interior. Eventually the temperature in the sphere becomes uniform and equal to the bath temperature of $301.0\,\mathrm{K}$.

Figure 3.3(a) graphically depicts temperatures within the sphere at different times during the heating process. Note the temperature gradient in the intermediate states. Because of the gradient, these states cannot be characterized by a single value of the temperature. If we were to suddenly isolate the system (the sphere) with a thermally-insulated jacket while it is in one of these states, the state would change as the temperature gradient rapidly disappears. Thus, the intermediate states of the spontaneous heating process are not equilibrium states, and the rapid heating process is not reversible.

To make the intermediate states more nearly uniform in temperature, with smaller temperature gradients, we can raise the temperature of the bath at a slower rate. The sequence of states approached in the limit of infinite slowness is indicated in Fig. 3.3(b). In each intermediate state of this limiting sequence, the temperature is perfectly uniform throughout the sphere and is equal to the external bath temperature. That is, each state has thermal equilibrium both internally and with respect to the surroundings. A single temperature now suffices to define the state at each instant. Each state is an *equilibrium* state because it would have no tendency to change if we isolated the system with thermal insulation. This limiting sequence of states is a *reversible* heating process.

The reverse of the reversible heating process is a reversible cooling process in which the temperature is again uniform in each state. The sequence of states of this reverse process is the limit of the spontaneous cooling process depicted in Fig. 3.3(c) as we decrease the bath temperature more and more slowly.

In any real heating process occurring at a finite rate, the sphere's temperature could not be perfectly uniform in intermediate states. If we raise the bath temperature very slowly, however, the temperature in all parts of the sphere will be very close to that of the bath. At any point in this very slow heating process, it would then take only a small decrease in the bath temperature to start a *cooling* process; that is, the practically-reversible heating process would be reversed.

The important thing to note about the temperature gradients shown in Fig. 3.3(c) for the spontaneous cooling process is that none resemble the gradients in Fig. 3.3(a) for the spontaneous heating process—the gradients are in opposite directions. It is physically impossible for the sequence of states of either process to occur in the reverse chronological order, for that would have thermal energy flowing in the wrong direction along the temperature gradient. These considerations show that a spontaneous heat transfer is irreversible. Only in the reversible limits do the heating and cooling processes have the same intermediate states; these states have no temperature gradients.

Although the spontaneous heating and cooling processes are irreversible, the energy transferred into the system during heating can be fully recovered as energy transferred back to the surroundings during cooling, provided there is no irreversible work. This recoverability of irreversible heat is in distinct contrast to the behavior of irreversible work.

3.3.2 Spontaneous phase transitions

Consider a different kind of system, one consisting of the liquid and solid phases of a pure substance. At a given pressure, this kind of system can be in transfer equilibrium at only one temperature: for example, water and ice at $1.01\ \text{bar}$ and $273.15\ \text{K}$ Suppose the system is initially at this pressure and temperature. Heat transfer into the system will then cause a phase transition from solid to liquid (Sec. 2.2.2). We can carry out the heat transfer by placing the system in thermal contact with an external water bath at a higher temperature than the equilibrium temperature, which will cause a temperature gradient in the system and the melting of an amount of solid proportional to the quantity of energy transferred.

The closer the external temperature is to the equilibrium temperature, the smaller are the temperature gradients and the closer are the states of the system to equilibrium states. In the limit as the temperature difference approaches zero, the system passes through a sequence of equilibrium states in which the temperature is uniform and constant, energy is transferred into the system by heat, and the substance is transformed from solid to liquid. This idealized process is an *equilibrium* phase transition, and it is a reversible process.

3.4: Deformation Work

3.5: Applications of Expansion Work

3.6: Work in a Gravitational Field

Figure 3.9 depicts a spherical body, such as a glass marble, immersed in a liquid or gas in the presence of an external gravitational field. The vessel is stationary on a lab bench, and the local reference frame for work is a stationary lab frame. The variable z is the body's elevation above the bottom of the vessel. All displacements are parallel to the vertical z axis. From Eq. 3.1.1, the work is given by $đw = F_z^{\text{sur}}\,\mathrm{d}z$ where F_z^{sur} is the upward component of the net contact force exerted by the surroundings on the system at the moving portion of the boundary. There is also a downward gravitational force on the body, but as explained in Sec. 3.1.1, this force does not contribute to F_z^{sur}.

Consider first the simple process in Fig. 3.9(a) in which the body falls freely through the fluid. This process is clearly spontaneous. Here are two choices for the definition of the system:

- The buoyant force is a consequence of the pressure gradient that exists in the fluid in a gravitational field (see Sec. 8.1.4). We ignore this gradient when we treat the fluid as a uniform phase.

  Next, consider the arrangement in Fig. 3.9(b) in which the body is suspended by a thin string. The string is in the surroundings and provides a means for the surroundings to exert an upward contact force on the system. As before, there are two appropriate choices for the system:

  - When we compare Eqs. 3.6.3 and 3.6.5, we see that the work when the system is the body is greater by the quantity $(F_{\text{buoy}} + F_{\text{fric}})\,\mathrm{d}z$ than the work when the system is the combination of body and fluid, just as in the case of the freely-falling body. The difference in the quantity of work is due to the different choices of the system boundary where contact forces are exerted by the surroundings.

3.7: Shaft Work

Shaft work refers to energy transferred across the boundary by a rotating shaft.

The complete apparatus is depicted in Fig. 3.13. In use, two lead weights sank and caused the paddle wheel to rotate. Joule evaluated the stirring work done on the system (the vessel, its contents, and the lid) from the change of the vertical position h of the weights. To a first approximation, this work is the negative of the change of the weights’ potential energy: $w = -mg\Delta h$ where m is the combined mass of the two weights. Joule made corrections for the kinetic energy gained by the weights, the friction in the connecting strings and pulley bearings, the elasticity of the strings, and the heat gain from the air surrounding the system.

A typical experiment performed by Joule is described in Prob. 3.10. His results for the mechanical equivalent of heat, based on 40 such experiments at average temperatures in the range $13\,^{\circ}\mathrm{C}$–$16\,^{\circ}\mathrm{C}$ and expressed as the work needed to increase the temperature of one gram of water by one kelvin, was $4.165\,\mathrm{J}$. This value is close to the modern value of $4.1855\,\mathrm{J}$ for the “$15\,^{\circ}\mathrm{C}$ calorie,” the energy needed to raise the temperature of one gram of water from $14.5\,^{\circ}\mathrm{C}$ to $15.5\,^{\circ}\mathrm{C}$.

The thermochemical calorie (cal), often used as an energy unit in the older literature, is defined as $4.184\,\mathrm{J}$. Thus $1\,\mathrm{kcal} = 4.184\,\mathrm{kJ}$.

3.8: Electrical Work

3.9: Irreversible Work and Internal Friction

Consider an irreversible adiabatic process of a closed system in which a work coordinate X changes at a finite rate along the path, starting and ending with equilibrium states. For a given initial state and a given change ΔX, the work is found to be less positive or more negative the more slowly is the rate of change of X. The work is least positive or most negative in the reversible limit—that is, the least work needs to be done on the system, or the most work can be done by the system on the surroundings. This *minimal work principle* has already been illustrated in the sections of this chapter describing expansion work, work in a gravitational field, and electrical work with a galvanic cell.

Let the work during an irreversible adiabatic process be w_{irr}, and the reversible adiabatic work for the same initial state and the same value of ΔX be w_{rev}. w_{irr} is algebraically greater than w_{rev}, and we can treat the difference $w_{\text{irr}} - w_{\text{rev}}$ as *excess work* w_{ex} that is positive for an irreversible process and zero for a reversible process.

Conceptually, we can attribute the excess work of an irreversible adiabatic process to *internal friction* that dissipates other forms of energy into thermal energy within the system. Internal friction occurs only during a process with work that is irreversible . Internal friction is not involved when, for example, a temperature gradient causes heat to flow spontaneously across the system boundary, or an irreversible chemical reaction takes place spontaneously in a homogeneous phase. Nor is internal friction necessarily involved when positive work increases the thermal energy: during an infinitely slow adiabatic compression of a gas, the temperature and thermal energy increase but internal friction is absent—the process is reversible.

During a process with irreversible work, energy dissipation can be either partial or complete. *Dissipative work*, such as the stirring work and electrical heating described in previous sections, is irreversible work with complete energy dissipation. The final equilibrium state of an adiabatic process with dissipative work can also be reached by a path in which positive heat replaces the dissipative work. This is a special case of the minimal work principle.

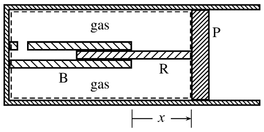


Figure 3.18 Cylinder and piston with internal sliding friction. The dashed rectangle indicates the system boundary. P—piston; R—internal rod attached to the piston; B—lubricated bushing fixed inside the cylinder. A fixed amount of an ideal gas fills the remaining space inside the cylinder.

As a model for work with partial energy dissipation, consider the gas-filled cylinder-and-piston device depicted in Fig. 3.18. This device has an obvious source of internal friction in the form of a rod sliding through a bushing. The contact between the rod and bushing is assumed to be lubricated to allow the piston to move at velocities infinitesimally close to zero. The *system* consists of the contents of the cylinder to the left of the piston, including the gas, the rod, and the bushing; the piston and cylinder wall are in the surroundings.

From Eq. 3.1.2, the energy transferred as work across the boundary of this system is

$$w = -\int_{x_1}^{x_2} F^{\text{sys}}\,\mathrm{d}x \tag{3.9.1}$$

where x is the piston position and F^{sys} is the component in the direction of increasing x of the force exerted by the system on the surroundings at the moving boundary.

For convenience, we let V be the volume of the gas rather than that of the entire system. The relation between changes of V and x is $\mathrm{d}V = A_{\text{s}}\,\mathrm{d}x$ where A_{s} is the cross-section area of the cylinder. With V replacing x as the work coordinate, Eq. 3.9.1 becomes

$$w = -\int_{V_1}^{V_2} (F^{\text{sys}}/A_{\text{s}})\,\text{d}V \tag{3.9.2}$$

Equation 3.9.2 shows that a plot of $F^{\text{sys}}/A_{\text{s}}$ as a function of V is an indicator diagram (Sec. 3.5.4), and that the work is equal to the negative of the area under the curve of this plot.

We can write the force F^{sys} as the sum of two contributions:

$$F^{\text{sys}} = pA_{\text{s}} + F_{\text{fric}}^{\text{int}} \tag{3.9.3}$$

(This equation assumes that the gas pressure is uniform, and that a term for the acceleration of the rod is negligible.) Here p is the gas pressure, and $F_{\text{fric}}^{\text{int}}$ is the force on the rod due to internal friction with sign opposite to that of the piston velocity $\text{d}x/\text{d}t$. Substitution of this expression for F^{sys} in Eq. 3.9.2 gives

$$w = -\int_{V_1}^{V_2} p\,\text{d}V - \int_{V_1}^{V_2} (F_{\text{fric}}^{\text{int}}/A_{\text{s}})\,\text{d}V \tag{3.9.4}$$

The first term on the right is the work of expanding or compressing the gas. The second term is the frictional work: $w_{\text{fric}} = -\int (F_{\text{fric}}^{\text{int}}/A_{\text{s}})\,\text{d}V$. The frictional work is positive or zero, and represents the energy dissipated within the system by internal sliding friction.

Consider the situation when the piston moves very slowly in one direction or the other. In the limit of infinite slowness $F_{\text{fric}}^{\text{int}}$ and w_{fric} vanish, and the process is reversible with expansion work given by $w = -\int p\,\text{d}V$.

The situation is different when the piston moves at an appreciable finite rate. The frictional work w_{fric} is then positive. As a result, the irreversible work of expansion is less negative than the reversible work for the same volume increase, and the irreversible work of compression is more positive than the reversible work for the same volume decrease. These effects of piston velocity on the work are consistent with the minimal work principle.

> The piston velocity, besides affecting the frictional force on the rod, has an effect on the force exerted by the gas on the piston as described in Sec. 3.4.1. At large finite velocities, this latter effect tends to further decrease F^{sys} during expansion and increase it during compression, and so is an additional contribution to internal friction. If turbulent flow is present within the system, that would also be a contribution.

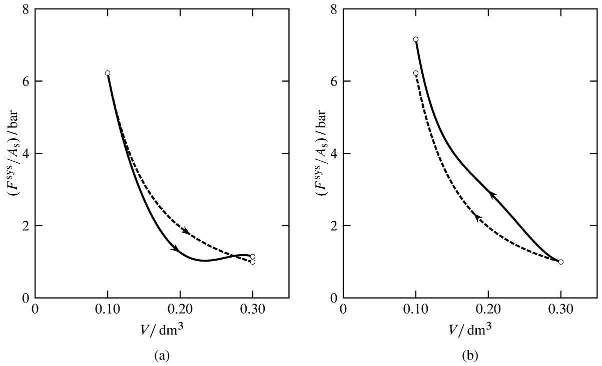


Figure 3.19 Indicator diagrams for the system of Fig. 3.18.
Solid curves: $F^{\text{sys}}/A_{\text{s}}$ for irreversible adiabatic volume changes at finite rates in the directions indicated by the arrows.
Dashed curves: $F^{\text{sys}}/A_{\text{s}} = p$ along a reversible adiabat.
Open circles: initial and final equilibrium states.
(a) Adiabatic expansion.
(b) Adiabatic compression.

Figure 3.19 shows indicator diagrams for adiabatic expansion and compression with internal friction. The solid curves are for irreversible processes at finite rates, and the dashed curves are for reversible processes with the same initial states as the irreversible processes. The areas under the curves confirm that the work for expansion is less negative along the irreversible path than along the reversible path, and that for compression the work is more positive along the irreversible path than along the reversible path.

Because of these differences in work, the final states of the irreversible processes have greater internal energies and higher temperatures and pressures than the final states of the reversible processes with the same volume change, as can be seen from the positions on the indicator diagrams of the points for the final equilibrium states. The overall change of state during the irreversible expansion or compression is the same for a path in which the reversible adiabatic volume change is followed by positive heat at constant volume. Since ΔU must be the same for both paths, the heat has the same value as the excess work $w_{\text{ex}} = w_{\text{irr}} - w_{\text{rev}}$. The excess work and frictional work are not equal, because the thermal energy released by frictional work increases the gas pressure, making w_{ex} less than w_{fric} for expansion and greater than w_{fric} for compression. There seems to be no general method by which the energy dissipated by internal friction can be evaluated, and it would be even more difficult for an irreversible process with both work and heat.

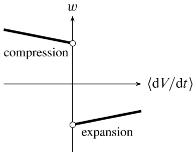


Figure 3.20 Adiabatic expansion work with internal friction for a fixed magnitude of ΔV, as a function of the average rate of volume change. The open circles indicate the reversible limits.

Figure 3.20 shows the effect of the rate of change of the volume on the adiabatic work for a fixed magnitude of the volume change. Note that the work of expansion and the work of compression have opposite signs, and that it is only in the reversible limit that they have the same *magnitude*. The figure resembles Fig. 3.17 for electrical work of a galvanic cell with the horizontal axis reversed, and is typical of irreversible work with partial energy dissipation.

3.10: Reversible and Irreversible Processes- Generalities

This section summarizes some general characteristics of processes in closed systems. Some of these statements will be needed to develop aspects of the second law in Chap. 4.

- Table 3.1 lists general formulas for various kinds of work, including those that were described in detail in Secs. 3.4–3.8.

3.11: Chapter 3 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

3.1 Assume you have a metal spring that obeys Hooke's law: $F = c(l - l_0)$, where F is the force exerted on the spring of length l, l_0 is the length of the unstressed spring, and c is the spring constant. Find an expression for the work done on the spring when you reversibly compress it from length l_0 to a shorter length l'.

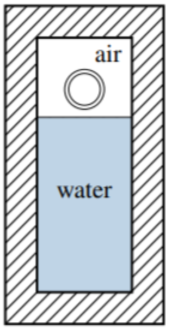


Figure 3.22

3.2 The apparatus shown in Fig. 3.22 consists of fixed amounts of water and air and an incompressible solid glass sphere (a marble), all enclosed in a rigid vessel resting on a lab bench. Assume the marble has an adiabatic outer layer so that its temperature cannot change, and that the walls of the vessel are also adiabatic.

Initially the marble is suspended above the water. When released, it falls through the air into the water and comes to rest at the bottom of the vessel, causing the water and air (but not the marble) to become slightly warmer. The process is complete when the system returns to an equilibrium state. The system energy change during this process depends on the frame of reference and on how the system is defined. ΔE_{sys} is the energy change in a lab frame, and ΔU is the energy change in a specified local frame.
For each of the following definitions of the system, give the sign (positive, negative, or zero) of both ΔE_{sys} and ΔU, and state your reasoning. Take the local frame for each system to be a center-of-mass frame.
(a) The system is the marble.
(b) The system is the combination of water and air.
(c) The system is the combination of water, air, and marble.

3.3 Figure 3.23 shows the initial state of an apparatus consisting of an ideal gas in a bulb, a stopcock, a porous plug, and a cylinder containing a frictionless piston. The walls are diathermal, and the surroundings are at a constant temperature of $300.0\ \mathrm{K}$ and a constant pressure of $1.00\mathrm{bar}$.

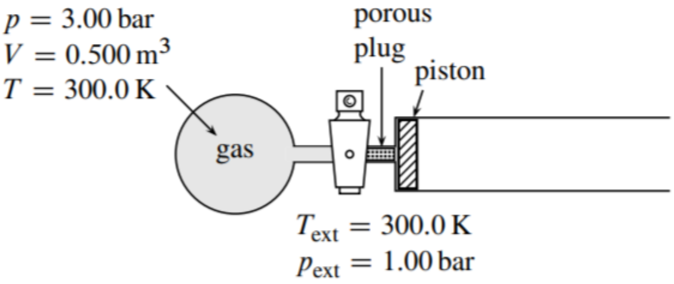


Figure 3.23

When the stopcock is opened, the gas diffuses slowly through the porous plug, and the piston moves slowly to the right. The process ends when the pressures are equalized and the piston stops moving. The system is the gas. Assume that during the process the temperature throughout the system differs only infinitesimally from $300.0\ \mathrm{K}$ and the pressure on both sides of the piston differs only infinitesimally from 1.00 bar.

(a) Which of these terms correctly describes the process: isothermal, isobaric, isochoric, reversible, irreversible?
(b) Calculate q and w.

3.4 Consider a horizontal cylinder-and-piston device similar to the one shown in Fig. 3.5 on page 72. The piston has mass m. The cylinder wall is diathermal and is in thermal contact with a heat reservoir of temperature T_{ext} . The system is an amount n of an ideal gas confined in the cylinder by the piston.

The initial state of the system is an equilibrium state described by p_1 and $T = T_{\text{ext}}$. There is a constant external pressure p_{ext} , equal to twice p_1, that supplies a constant external force on the piston. When the piston is released, it begins to move to the left to compress the gas. Make the idealized assumptions that (1) the piston moves with negligible friction; and (2) the gas remains practically uniform (because the piston is massive and its motion is slow) and has a practically constant temperature $T = T_{\text{ext}}$ (because temperature equilibration is rapid).
(a) Describe the resulting process.
(b) Describe how you could calculate w and q during the period needed for the piston velocity to become zero again.
(c) Calculate w and q during this period for 0.500 molgas at 300 K.

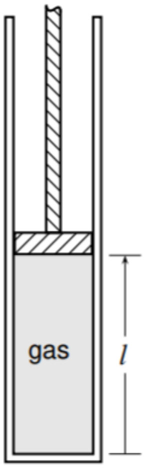


Figure 3.24

3.5 This problem is designed to test the assertion on page 60 that for typical thermodynamic processes in which the elevation of the center of mass changes, it is usually a good approximation to set w equal to $w_{\text{lab.}}$. The cylinder shown in Fig. 3.24 on the preceding page has a vertical orientation, so the elevation of the center of mass of the gas confined by the piston changes as the piston slides up or down. The system is the gas. Assume the gas is nitrogen $\left(M = 28.0 \text{ g mol}^{1}\right)$ at 300 K, and initially the vertical length l of the gas column is one meter. Treat the nitrogen as an ideal gas, use a center-of-mass local frame, and take the center of mass to be at the midpoint of the gas column. Find the difference between the values of w and w_{lab} , expressed as a percentage of w, when the gas is expanded reversibly and isothermally to twice its initial volume.

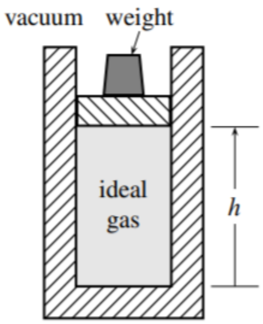


Figure 3.25

3.6 Figure 3.25 shows an ideal gas confined by a frictionless piston in a vertical cylinder. The system is the gas, and the boundary is adiabatic. The downward force on the piston can be varied by changing the weight on top of it.

(a) Show that when the system is in an equilibrium state, the gas pressure is given by $p = mgh/V$ where m is the combined mass of the piston and weight, g is the acceleration of free fall, and h is the elevation of the piston shown in the figure.

(b) Initially the combined mass of the piston and weight is m_1, the piston is at height h_1, and the system is in an equilibrium state with conditions p_1 and V_1. The initial temperature is $T_1 = p_1 V_1 / nR$. Suppose that an additional weight is suddenly placed on the piston, so that m increases from m_1 to m_2, causing the piston to sink and the gas to be compressed adiabatically and spontaneously. Pressure gradients in the gas, a form of friction, eventually cause the piston to come to rest at a final position h_2. Find the final volume, V_2, as a function of p_1, p_2, V_1, and C_V. (Assume that the heat capacity of the gas, C_V, is independent of temperature.) Hint: The potential energy of the surroundings changes by $m_2 g \Delta h$; since the kinetic energy of the piston and weights is zero at the beginning and end of the process, and the boundary is adiabatic, the internal energy of the gas must change by $-m_2 g \Delta h = -m_2 g \Delta V / A_\mathrm{s} = -p_2 \Delta V$.

(c) It might seem that by making the weight placed on the piston sufficiently large, V_2 could be made as close to zero as desired. Actually, however, this is not the case. Find expressions for V_2 and T_2 in the limit as m_2 approaches infinity, and evaluate V_2 / V_1 in this limit if the heat capacity is $C_V = (3/2) nR$ (the value for an ideal monatomic gas at room temperature).

3.7 The solid curve in Fig. 3.7 shows the path of a reversible adiabatic expansion or compression of a fixed amount of an ideal gas. Information about the gas is given in the figure caption. For compression along this path, starting at $V = 0.3000 \mathrm{dm}^3$ and $T = 300.0$ K and ending at $V = 0.1000 \mathrm{dm}^3$, find the final temperature to 0.1 K and the work.

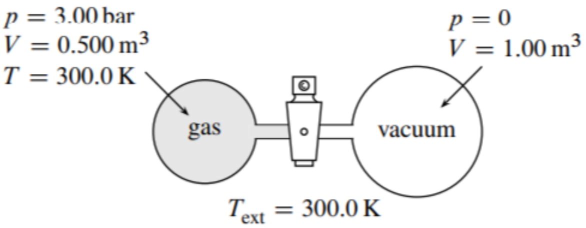


Figure 3.26

3.8 Figure 3.26 shows the initial state of an apparatus containing an ideal gas. When the stopcock is opened, gas passes into the evacuated vessel. The system is the gas. Find q, w, and ΔU under the following conditions.
(a) The vessels have adiabatic walls.
(b) The vessels have diathermal walls in thermal contact with a water bath maintained at $300.$ K, and the final temperature in both vessels is $T = 300.$ K.

3.9 Consider a reversible process in which the shaft of system A in Fig. 3.11 makes one revolution in the direction of increasing ϑ. Show that the gravitational work of the weight is the same as the shaft work given by $w = mgr\Delta\vartheta$.
Table 3.2 Data for Problem 3.10. The values are from Joule's 1850 paper [a] and have been converted to SI units.
[a] Ref. [91], p. 67, experiment 5.
[b] Calculated from the masses and specific heat capacities of the materials.

3.10 This problem guides you through a calculation of the mechanical equivalent of heat using data from one of James Joule's experiments with a paddle wheel apparatus (see Sec. 3.7.2). The experimental data are collected in Table 3.2.

In each of his experiments, Joule allowed the weights of the apparatus to sink to the floor twenty times from a height of about 1.6 m, using a crank to raise the weights before each descent (see Fig. 3.14 on page 89). The paddle wheel was engaged to the weights through the roller and strings only while the weights descended. Each descent took about 26 seconds, and the entire experiment lasted 35 minutes. Joule measured the water temperature with a sensitive mercury-in-glass thermometer at both the start and finish of the experiment.

For the purposes of the calculations, define the system to be the combination of the vessel, its contents (including the paddle wheel and water), and its lid. All energies are measured in a lab frame. Ignore the small quantity of expansion work occurring in the experiment. It helps conceptually to think of the cellar room in which Joule set up his apparatus as being effectively isolated from the rest of the universe; then the only surroundings you need to consider for the calculations are the part of the room outside the system.

(a) Calculate the change of the gravitational potential energy E_p of the lead weights during each of the descents. For the acceleration of free fall at Manchester, England (where Joule carried out the experiment) use the value $g = 9.813\ \mathrm{m\,s^{-2}}$. This energy change represents a decrease in the energy of the surroundings, and would be equal in magnitude and opposite in sign to the stirring work done on the system if there were no other changes in the surroundings.

(b) Calculate the kinetic energy E_{k} of the descending weights just before they reached the floor. This represents an increase in the energy of the surroundings. (This energy was dissipated into thermal energy in the surroundings when the weights came to rest on the floor.)

(c) Joule found that during each descent of the weights, friction in the strings and pulleys decreased the quantity of work performed on the system by $2.87\ \mathrm{J}$. This quantity represents an increase in the thermal energy of the surroundings. Joule also considered the slight stretching of the strings while the weights were suspended from them: when the weights came to rest on the floor, the tension was relieved and the potential energy of the strings changed by $-1.15\ \mathrm{J}$. Find the total change in the energy of the surroundings during the entire experiment from all the effects described to this point. Keep in mind that the weights descended 20 times during the experiment.

(d) Data in Table 3.2 show that change of the temperature of the system during the experiment was

$$\Delta T=(289.148-288.829)\mathrm{K}=+0.319\ \mathrm{K} \tag{3.11.1}$$

The paddle wheel vessel had no thermal insulation, and the air temperature was slighter warmer, so during the experiment there was a transfer of some heat into the system. From a correction procedure described by Joule, the temperature change that would have occurred if the vessel had been insulated is estimated to be $+0.317\ \mathrm{K}$.
Use this information together with your results from part (c) to evaluate the work needed to increase the temperature of one gram of water by one kelvin. This is the "mechanical equivalent of heat" at the average temperature of the system during the experiment. (As mentioned on p. 87 , Joule obtained the value $4.165\ \mathrm{J}$ based on all 40 of his experiments.)

3.11 Refer to the apparatus depicted in Fig. 3.1 on page 61. Suppose the mass of the external weight is $m=1.50\ \mathrm{kg}$, the resistance of the electrical resistor is $R_{\mathrm{el}}=5.50\mathrm{k}\Omega$, and the acceleration of free fall is $g=9.81\ \mathrm{m\ s}^{-2}$. For how long a period of time will the external cell need to operate, providing an electric potential difference $|\Delta\phi|=1.30\ \mathrm{V}$, to cause the same change in the state of the system as the change when the weight sinks $20.0\ \mathrm{cm}$ without electrical work? Assume both processes occur adiabatically.

CHAPTER OVERVIEW

4: The Second Law

The second law of thermodynamics concerns entropy and the spontaneity of processes. This chapter discusses theoretical aspects and practical applications.

We have seen that the first law allows us to set up a balance sheet for energy changes during a process, but says nothing about why some processes occur spontaneously and others are impossible. The laws of physics explain some spontaneous changes. For instance, unbalanced forces on a body cause acceleration, and a temperature gradient at a diathermal boundary causes heat transfer. But how can we predict whether a phase change, a transfer of solute from one solution phase to another, or a chemical reaction will occur spontaneously under the existing conditions? The second law provides the principle we need to answer these and other questions—a general criterion for spontaneity in a closed system.

4.1: Types of Processes

Any conceivable process is either spontaneous, reversible, or impossible. These three possibilities were discussed in Sec. 3.2 and are summarized below.

- A *spontaneous* process is a real process that can actually take place in a finite time period.
- A *reversible* process is an imaginary, idealized process in which the system passes through a continuous sequence of equilibrium states. This sequence of states can be approached by a spontaneous process in the limit of infinite slowness, and so also can the reverse sequence of states.
- An *impossible* process is a change that cannot occur under the existing conditions, even in a limiting sense. It is also known as an unnatural or disallowed process. Sometimes it is useful to describe a hypothetical impossible process that we can imagine but that does not occur in reality. The second law of thermodynamics will presently be introduced with two such impossible processes.

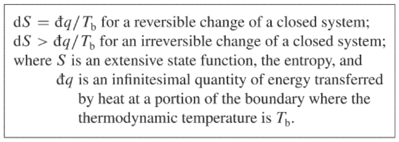
The spontaneous processes relevant to chemistry are *irreversible*. An irreversible process is a spontaneous process whose reverse is an impossible process.

There is also the special category, of little interest to chemists, of purely mechanical processes. A purely mechanical process is a spontaneous process whose reverse is also spontaneous.

It is true that reversible processes and purely mechanical processes are idealized processes that cannot occur in practice, but a spontaneous process can be *practically* reversible if carried out sufficiently slowly, or *practically* purely mechanical if friction and temperature gradients are negligible. In that sense, they are not impossible processes. This e-book will reserve the term “impossible” for a process that cannot be approached by any spontaneous process, no matter how slowly or how carefully it is carried out.

4.2: Statements of the Second Law

A description of the **mathematical statement of the second law** is given in the box below.



$\mathrm{d}S = đq/T_\mathrm{b}$ for a reversible change of a closed system;
$\mathrm{d}S > đq/T_\mathrm{b}$ for an irreversible change of a closed system;
where S is an extensive state function, the entropy, and
$đq$ is an infinitesimal quantity of energy transferred
by heat at a portion of the boundary where the
thermodynamic temperature is T_b.

The box includes three distinct parts. First, there is the assertion that a property called **entropy**, S, is an extensive state function.

Second, there is an equation for calculating the entropy change of a closed system during a reversible change of state: $\mathrm{d}S$ is equal to $đq/T_\mathrm{b}$. During a reversible process, the temperature usually has the same value T throughout the system, in which case we can simply write $\mathrm{d}S = đq/T$. The equation $\mathrm{d}S = đq/T_\mathrm{b}$ allows for the possibility that in an equilibrium state the system has phases of different temperatures separated by internal adiabatic partitions.

Third, there is a criterion for spontaneity: $\mathrm{d}S$ is greater than $đq/T_\mathrm{b}$ during an irreversible change of state. The temperature T_b is a thermodynamic temperature, which will be defined in Sec. 4.3.4.

Each of the three parts is an essential component of the second law, but is somewhat abstract. What fundamental principle, based on experimental observation, may we take as the starting point to obtain them? Two principles are available, one associated with Clausius and the other with Kelvin and Planck. Both principles are equivalent statements of the second law. Each asserts that a certain kind of process is impossible, in agreement with common experience.

Next consider the impossible process shown in Fig. 4.2(a). A Joule paddle wheel rotates in a container of water as a weight rises. As the weight gains potential energy, the water loses thermal energy and its temperature decreases. Energy is conserved, so there is no violation of the first law. This process is just the reverse of the Joule paddle-wheel experiment (Sec. 3.7.2) and its impossibility has already been discussed.

We might again attempt to use some sort of device operating in a cycle to accomplish the same overall process, as in Fig. 4.2(b). A closed system that operates in a cycle and does net work on the surroundings is called a **heat engine**. The heat engine shown in Fig. 4.2(b) is a special one. During one cycle, a quantity of energy is transferred by heat from a heat reservoir to the engine, and the engine performs an *equal* quantity of work on a weight, causing it to rise. At the end of the cycle, the engine has returned to its initial state. This would be a very desirable engine, because it could convert thermal energy into an equal quantity of useful mechanical work with no other effect on the surroundings. (This hypothetical process is called “perpetual motion of the second kind.”) The engine could power a ship; it would use the ocean as a heat reservoir and require no fuel. Unfortunately, *it is impossible to construct such a heat engine*!

The principle was expressed by William Thomson (Lord Kelvin) in 1852 as follows: “It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.” Max Planck in 1922 gave this statement: “It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir.” For the purposes of this chapter, the principle can be reworded as follows.

- Both the Clausius statement and the Kelvin–Planck statement assert that certain processes, although they do not violate the first law, are nevertheless *impossible*.

> These processes would not be impossible if we could control the trajectories of large numbers of individual particles. Newton’s laws of motion are invariant to time reversal. Suppose we could measure the position and velocity of each molecule of a macroscopic system in the final state of an irreversible process. Then, if we could somehow arrange at one instant to place each molecule in the same position with its velocity reversed, and if the molecules behaved classically, they would retrace their trajectories in reverse and we would observe the reverse “impossible” process.
>
> Carnot engines and Carnot cycles are admittedly outside the normal experience of chemists, and using them to derive the mathematical statement of the second law may seem arcane. G. N. Lewis and M. Randall, in their classic 1923 book *Thermodynamics and the Free Energy of Chemical Substances*, complained of the presentation of “cyclical processes limping about eccentric and not quite completed cycles.” There seems, however, to be no way to carry out a rigorous *general* derivation without invoking thermodynamic cycles. You

may avoid the details by skipping Secs. 4.3–4.5. (Incidently, the cycles described in these sections are complete!)

4.3: Concepts Developed with Carnot Engines

4.3.1 Carnot engines and Carnot cycles

Could the efficiency of the Carnot engine be different from the efficiency the heat pump would have when run in reverse as a Carnot engine? If so, either the supersystem is an impossible Clausius device as shown in Fig. 4.7(b), or the supersystem operated in reverse (with the engine and heat pump switching roles) is an impossible Clausius device as shown in Fig. 4.7(d). We conclude that *all Carnot engines operating between the same two temperatures have the same efficiency*.

> This is a good place to pause and think about the meaning of this statement in light of the fact that the steps of a Carnot engine, being reversible changes, cannot take place in a real system (Sec. 3.2). How can an engine operate that is not real? The statement is an example of a common kind of thermodynamic shorthand. To express the same idea more accurately, one could say that all heat engines (real systems) operating between the same two temperatures have the same *limiting* efficiency, where the limit is the reversible limit approached as the steps of the cycle are carried out more and more slowly. You should interpret any statement involving a reversible process in a similar fashion: a reversible process is an idealized *limiting* process that can be approached but never quite reached by a real system.

Thus, the efficiency of a Carnot engine must depend only on the values of T_{c} and T_{h} and not on the properties of the working substance. Since the efficiency is given by $\epsilon = 1 + q_{\text{c}}/q_{\text{h}}$, the ratio $q_{\text{c}}/q_{\text{h}}$ must be a unique function of T_{c} and T_{h} only. To find this function for temperatures on the ideal-gas temperature scale, it is simplest to choose as the working substance an ideal gas.

An ideal gas has the equation of state $pV = nRT$. Its internal energy change in a closed system is given by $\text{d}U = C_V\,\text{d}T$ (Eq. 3.5.3), where C_V (a function only of T) is the heat capacity at constant volume. Reversible expansion work is given by $đw = -p\,\text{d}V$, which for an ideal gas becomes $đw = -(nRT/V)\,\text{d}V$. Substituting these expressions for $\text{d}U$ and $đw$ in the first law, $\text{d}U = đq + đw$, and solving for $đq$, we obtain

$$đq = C_V\,\text{d}T + \frac{nRT}{V}\,\text{d}V \tag{4.3.4}$$

(ideal gas, reversible expansion work only)

Dividing both sides by T gives

$$\frac{đq}{T} = \frac{C_V\,\text{d}T}{T} + nR\frac{\text{d}V}{V} \tag{4.3.5}$$

(ideal gas, reversible expansion work only)

In the two adiabatic steps of the Carnot cycle, $đq$ is zero. We obtain a relation among the volumes of the four labeled states shown in Fig. 4.3 by integrating Eq. 4.3.5 over these steps and setting the integrals equal to zero:

$$\text{Path B}\rightarrow\text{C:}\qquad \int\frac{đq}{T} = \int_{T_{\text{h}}}^{T_{\text{c}}}\frac{C_V\,\text{d}T}{T} + nR\ln\frac{V_{\text{C}}}{V_{\text{B}}} = 0 \tag{4.3.6}$$

$$\text{Path D}\rightarrow\text{A:}\qquad \int\frac{đq}{T} = \int_{T_{\text{c}}}^{T_{\text{h}}}\frac{C_V\,\text{d}T}{T} + nR\ln\frac{V_{\text{A}}}{V_{\text{D}}} = 0 \tag{4.3.7}$$

} Adding these two equations (the integrals shown with limits cancel) gives the relation

$$nR\ln\frac{V_{\text{A}}V_{\text{C}}}{V_{\text{B}}V_{\text{D}}} = 0 \tag{4.3.8}$$

which we can rearrange to

$$\ln(V_{\text{B}}/V_{\text{A}}) = -\ln(V_{\text{D}}/V_{\text{C}}) \tag{4.3.9}$$

(ideal gas, Carnot cycle)

We obtain expressions for the heat in the two isothermal steps by integrating Eq. 4.3.4 with $\text{d}T$ set equal to 0.

$$\text{Path A}\rightarrow\text{B}: \qquad q_{\text{h}} = nRT_{\text{h}}\ln(V_{\text{B}}/V_{\text{A}}) \tag{4.3.10}$$

$$\text{Path C}\rightarrow\text{D}: \qquad q_{\text{c}} = nRT_{\text{c}}\ln(V_{\text{D}}/V_{\text{C}}) \tag{4.3.11}$$

The ratio of q_{c} and q_{h} obtained from these expressions is

$$\frac{q_{\mathrm{c}}}{q_{\mathrm{h}}}=\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}}\times\frac{\ln(V_{\mathrm{D}}/V_{\mathrm{C}})}{\ln(V_{\mathrm{B}}/V_{\mathrm{A}})} \tag{4.3.12}$$

By means of Eq. 4.3.9, this ratio becomes

$$\frac{q_{\mathrm{c}}}{q_{\mathrm{h}}}=-\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}} \tag{4.3.13}$$

(Carnot cycle)

Accordingly, the unique function of T_{c} and T_{h} we seek that is equal to $q_{\mathrm{c}}/q_{\mathrm{h}}$ is the ratio $-T_{\mathrm{c}}/T_{\mathrm{h}}$. The efficiency, from Eq. 4.3.3, is then given by

$$\epsilon=1-\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}} \tag{4.3.14}$$

(Carnot engine)

In Eqs. 4.3.13 and 4.3.14, T_{c} and T_{h} are temperatures on the ideal-gas scale. As we have seen, these equations must be valid for *any* working substance; it is not necessary to specify as a condition of validity that the system is an ideal gas.

The ratio $T_{\mathrm{c}}/T_{\mathrm{h}}$ is positive but less than one, so the efficiency is less than one as deduced earlier. This conclusion is an illustration of the Kelvin–Planck statement of the second law: A heat engine cannot have an efficiency of unity—that is, it cannot in one cycle convert all of the energy transferred by heat from a single heat reservoir into work. The example shown in Fig. 4.5, with $\epsilon=1/4$, must have $T_{\mathrm{c}}/T_{\mathrm{h}}=3/4$ (e.g., $T_{\mathrm{c}}=300\,\mathrm{K}$ and $T_{\mathrm{h}}=400\,\mathrm{K}$).

Keep in mind that a Carnot engine operates *reversibly* between two heat reservoirs. The expression of Eq. 4.3.14 gives the efficiency of this kind of idealized heat engine only. If any part of the cycle is carried out irreversibly, dissipation of mechanical energy will cause the efficiency to be *lower* than the theoretical value given by Eq. 4.3.14.

4.3.4 Thermodynamic temperature

The negative ratio $q_{\mathrm{c}}/q_{\mathrm{h}}$ for a Carnot cycle depends only on the temperatures of the two heat reservoirs. Kelvin (1848) proposed that this ratio be used to establish an “absolute” temperature scale. The physical quantity now called **thermodynamic temperature** is defined by the relation

$$\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}}=-\frac{q_{\mathrm{c}}}{q_{\mathrm{h}}} \tag{4.3.15}$$

(Carnot cycle)

That is, the ratio of the thermodynamic temperatures of two heat reservoirs is equal, by definition, to the ratio of the absolute quantities of heat transferred in the isothermal steps of a Carnot cycle operating between these two temperatures. In principle, a measurement of $q_{\mathrm{c}}/q_{\mathrm{h}}$ during a Carnot cycle, combined with a defined value of the thermodynamic temperature of one of the heat reservoirs, can establish the thermodynamic temperature of the other heat reservoir. This defined value is provided by the triple point of $\mathrm{H_2O}$; its thermodynamic temperature is defined as exactly 273.16 kelvins.

Just as measurements with a gas thermometer in the limit of zero pressure establish the ideal-gas temperature scale (Sec. 2.3.5), the behavior of a heat engine in the reversible limit establishes the thermodynamic temperature scale. Note, however, that a reversible Carnot engine used as a “thermometer” to measure thermodynamic temperature is only a theoretical concept and not a practical instrument, since a completely-reversible process cannot occur in practice.

It is now possible to justify the statement in Sec. 2.3.5 that the ideal-gas temperature scale is proportional to the thermodynamic temperature scale. Both Eq. 4.3.13 and Eq. 4.3.15 equate the ratio $T_{\mathrm{c}}/T_{\mathrm{h}}$ to $-q_{\mathrm{c}}/q_{\mathrm{h}}$; but whereas T_{c} and T_{h} refer in Eq. 4.3.13 to the *ideal-gas* temperatures of the heat reservoirs, in Eq. 4.3.15 they refer to the *thermodynamic* temperatures. This means that the ratio of the ideal-gas temperatures of two bodies is equal to the ratio of the thermodynamic temperatures of the same bodies, and therefore the two scales are proportional to one another. The proportionality factor is arbitrary, but must be unity if the same unit (e.g., kelvins) is used in both scales. Thus, as stated in Sec. 2.3.5, the two scales expressed in kelvins are identical.

4.4: Derivation of the Mathematical Statement of the Second Law

4.4.1 The existence of the entropy function

This section derives the existence and properties of the state function called entropy.

Consider an arbitrary cyclic process of a closed system. To avoid confusion, this system will be the “experimental system” and the process will be the “experimental process” or “experimental cycle.” There are no restrictions on the contents of the experimental system—it may have any degree of complexity whatsoever. The experimental process may involve more than one kind of work, phase changes and reactions may occur, there may be temperature and pressure gradients, constraints and external fields may be present, and so on. All parts of the process must be either irreversible or reversible, but not impossible.

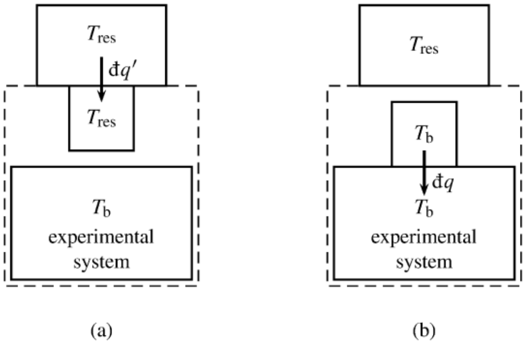


Figure 4.8 Experimental system, Carnot engine (represented by a small square box), and heat reservoir. The dashed lines indicate the boundary of the supersystem.
(a) Reversible heat transfer between heat reservoir and Carnot engine.
(b) Heat transfer between Carnot engine and experimental system.
The infinitesimal quantities $đq'$ and $đq$ are positive for transfer in the directions indicated by the arrows.

We imagine that the experimental cycle is carried out in a special way that allows us to apply the Kelvin–Planck statement of the second law. The heat transferred across the boundary of the experimental system in each infinitesimal path element of the cycle is exchanged with a hypothetical Carnot engine. The combination of the experimental system and the Carnot engine is a closed *supersystem* (see Fig. 4.8). In the surroundings of the supersystem is a heat reservoir of arbitrary constant temperature T_{res}. By allowing the supersystem to exchange heat with only this single heat reservoir, we will be able to apply the Kelvin–Planck statement to a cycle of the supersystem.

> This procedure is similar to ones described by A. B. Pippard (*Elements of Classical Thermodynamics for Advanced Students of Physics*, Cambridge University Press, Cambridge, 1966, Chap. 4); C. J. Adkins (*Equilibrium Thermodynamics*, 3rd edition, Cambridge University Press, Cambridge, 1983, Chap. 5); and Peter T. Landsberg (*Thermodynamics and Statistical Mechanics*, Dover Publications, Inc., New York, 1990, p. 53).

We assume that we are able to control changes of the work coordinates of the experimental system from the surroundings of the supersystem. We are also able to control the Carnot engine from these surroundings, for example by moving the piston of a cylinder-and-piston device containing the working substance. Thus the energy transferred by *work* across the boundary of the experimental system, and the work required to operate the Carnot engine, is exchanged with the surroundings of the supersystem.

During each stage of the experimental process with nonzero heat, we allow the Carnot engine to undergo many infinitesimal Carnot cycles with infinitesimal quantities of heat and work. In one of the isothermal steps of each Carnot cycle, the Carnot engine is in thermal contact with the heat reservoir, as depicted in Fig. 4.8(a). In this step the Carnot engine has the same temperature as the heat reservoir, and reversibly exchanges heat $đq'$ with it. The sign convention is that $đq'$ is positive if heat is transferred in the direction of the arrow, from the heat reservoir to the Carnot engine.

In the other isothermal step of the Carnot cycle, the Carnot engine is in thermal contact with the experimental system at a portion of the system's boundary. as depicted in Fig. 4.8(b). The Carnot engine now has the same temperature, T_{b}, as the experimental system at this part of the boundary, and exchanges heat with it. The heat $đq$ is positive if the transfer is into the experimental system.

The relation between temperatures and heats in the isothermal steps of a Carnot cycle is given by Eq. 4.3.15. From this relation we obtain, for one infinitesimal Carnot cycle, the relation $T_{\mathrm{b}}/T_{\mathrm{res}} = đq/\,đq'$, or

$$đq' = T_{\mathrm{res}} \frac{đq}{T_{\mathrm{b}}} \tag{4.4.1}$$

After many infinitesimal Carnot cycles, the experimental cycle is complete, the experimental system has returned to its initial state, and the Carnot engine has returned to its initial state in thermal contact with the heat reservoir. Integration of Eq. 4.4.1 around the experimental cycle gives the net heat entering the supersystem during the process:

$$q' = T_{\mathrm{res}} \oint \frac{đq}{T_{\mathrm{b}}} \tag{4.4.2}$$

The integration here is over each path element of the experimental process and over each surface element of the boundary of the experimental system.

Keep in mind that the value of the cyclic integral $\oint đq/T_{\mathrm{b}}$ depends only on the path of the experimental cycle, that this process can be reversible or irreversible, and that T_{res} is a positive constant.

In this experimental cycle, could the net heat q' transferred to the supersystem be positive? If so, the net work would be negative (to make the internal energy change zero) and the supersystem would have converted heat from a single heat reservoir completely into work, a process the Kelvin–Planck statement of the second law says is impossible. Therefore it is impossible for q' to be positive, and from Eq. 4.4.2 we obtain the relation

$$\oint \frac{đq}{T_{\mathrm{b}}} \leq 0 \tag{4.4.3}$$

(cyclic process of a closed system)

This relation is known as the **Clausius inequality**. It is valid only if the integration is taken around a cyclic path in a direction with nothing but reversible and irreversible changes—the path must not include an impossible change, such as the reverse of an irreversible change. The Clausius inequality says that if a cyclic path meets this specification, it is impossible for the cyclic integral $\oint(đq/T_{\mathrm{b}})$ to be positive.

If the entire experimental cycle is adiabatic (which is only possible if the process is reversible), the Carnot engine is not needed and Eq. 4.4.3 can be replaced by $\oint(đq/T_{\mathrm{b}}) = 0$.

Next let us investigate a *reversible* nonadiabatic process of the closed experimental system. Starting with a particular equilibrium state A, we carry out a reversible process in which there is a net flow of heat into the system, and in which $đq$ is either positive or zero in each path element. The final state of this process is equilibrium state B. If each infinitesimal quantity of heat $đq$ is positive or zero during the process, then the integral $\int_{\mathrm{A}}^{\mathrm{B}}(đq/T_{\mathrm{b}})$ must be positive. In this case the Clausius inequality tells us that if the system completes a cycle by returning from state B back to state A by a different path, the integral $\int_{\mathrm{B}}^{\mathrm{A}}(đq/T_{\mathrm{b}})$ for this second path must be negative. Therefore the change B→A cannot be carried out by any *adiabatic* process.

Any reversible process can be carried out in reverse. Thus, by reversing the reversible nonadiabatic process, it is possible to change the state from B to A by a reversible process with a net flow of heat out of the system and with $đq$ either negative or zero in each element of the reverse path. In contrast, the absence of an adiabatic path from B to A means that it is impossible to carry out the change A→B by a reversible adiabatic process.

The general rule, then, is that whenever equilibrium state A of a closed system can be changed to equilibrium state B by a reversible process with finite "one-way" heat (i.e., the flow of heat is either entirely into the system or else entirely out of it), it is impossible for the system to change from either of these states to the other by a reversible adiabatic process.

> A simple example will relate this rule to experience. We can increase the temperature of a liquid by allowing heat to flow reversibly into the liquid. It is impossible to duplicate this change of state by a reversible process without heat—that is, by using some kind of reversible work. The reason is that reversible work involves the change of a work

coordinate that brings the system to a different final state. There is nothing in the rule that says we can’t increase the temperature *irreversibly* without heat, as we can for instance with stirring work.

States A and B can be arbitrarily close. We conclude that *every equilibrium state of a closed system has other equilibrium states infinitesimally close to it that are inaccessible by a reversible adiabatic process*. This is Carathéodory’s principle of adiabatic inaccessibility. (Constantin Carathéodory in 1909 combined this principle with a mathematical theorem—Carathéodory’s theorem—to deduce the existence of the entropy function. The derivation outlined here avoids the complexities of that mathematical treatment and leads to the same results.)

Next let us consider the reversible adiabatic processes that *are* possible. To carry out a reversible adiabatic process, starting at an initial equilibrium state, we use an adiabatic boundary and slowly vary one or more of the work coordinates. A certain final temperature will result. It is helpful in visualizing this process to think of an N-dimensional space in which each axis represents one of the N independent variables needed to describe an equilibrium state. A point in this space represents an equilibrium state, and the path of a reversible process can be represented as a curve in this space.

A suitable set of independent variables for equilibrium states of a closed system of uniform temperature consists of the temperature T and each of the work coordinates (Sec. 3.10). We can vary the work coordinates independently while keeping the boundary adiabatic, so the paths for possible reversible adiabatic processes can connect any arbitrary combinations of work coordinate values.

There is, however, the additional dimension of temperature in the N-dimensional space. Do the paths for possible reversible adiabatic processes, starting from a common initial point, lie in a *volume* in the N-dimensional space? Or do they fall on a *surface* described by T as a function of the work coordinates? If the paths lie in a volume, then every point in a volume element surrounding the initial point must be accessible from the initial point by a reversible adiabatic path. This accessibility is precisely what Carathéodory’s principle of adiabatic inaccessibility denies. Therefore, the paths for all possible reversible adiabatic processes with a common initial state must lie on a unique *surface*. This is an $(N-1)$-dimensional hypersurface in the N-dimensional space, or a curve if N is 2. One of these surfaces or curves will be referred to as a **reversible adiabatic surface**.

Now consider the initial and final states of a reversible process with one-way heat (i.e., each nonzero infinitesimal quantity of heat $đq$ has the same sign). Since we have seen that it is impossible for there to be a reversible *adiabatic* path between these states, the points for these states must lie on different reversible adiabatic surfaces that do not intersect anywhere in the N-dimensional space. Consequently, there is an infinite number of nonintersecting reversible adiabatic surfaces filling the N-dimensional space. (To visualize this for $N=3$, think of a flexed stack of paper sheets; each sheet represents a different reversible adiabatic surface in three-dimensional space.) A reversible, nonadiabatic process with one-way heat is represented by a path beginning at a point on one reversible adiabatic surface and ending at a point on a different surface. If q is positive, the final surface lies on one side of the initial surface, and if q is negative, the final surface is on the opposite side.

4.4.2 Using reversible processes to define the entropy

The existence of reversible adiabatic surfaces is the justification for defining a new state function S, the **entropy**. S is specified to have the same value everywhere on one of these surfaces, and a different, unique value on each different surface. In other words, the reversible adiabatic surfaces are surfaces of *constant entropy* in the N-dimensional space. The fact that the surfaces fill this space without intersecting ensures that S is a state function for equilibrium states, because any point in this space represents an equilibrium state and also lies on a single reversible adiabatic surface with a definite value of S.

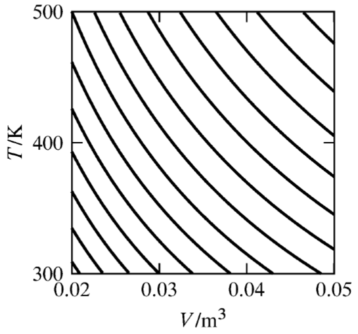


Figure 4.9 A family of reversible adiabatic curves (two-dimensional reversible adiabatic surfaces) for an ideal gas with V and T as independent variables. A reversible adiabatic process moves the state of the system along a curve, whereas a reversible process with positive heat moves the state from one curve to another above and to the right. The curves are calculated for $n = 1\,\mathrm{mol}$ and $C_{V,\mathrm{m}} = (3/2)R$. Adjacent curves differ in entropy by $1\ \mathrm{J\,K^{-1}}$.

We know the entropy function must exist, because the reversible adiabatic surfaces exist. For instance, Fig. 4.9 shows a family of these surfaces for a closed system of a pure substance in a single phase. In this system, N is equal to 2, and the surfaces are two-dimensional curves. Each curve is a contour of constant S. At this stage in the derivation, our assignment of values of S to the different curves is entirely arbitrary.

How can we assign a unique value of S to each reversible adiabatic surface? We can order the values by letting a reversible process with *positive* one-way heat, which moves the point for the state to a new surface, correspond to an *increase* in the value of S. Negative one-way heat will then correspond to decreasing S. We can assign an arbitrary value to the entropy on one particular reversible adiabatic surface. (The third law of thermodynamics is used for this purpose—see Sec. 6.1.) Then all that is needed to assign a value of S to each equilibrium state is a formula for evaluating the *difference* in the entropies of any two surfaces.

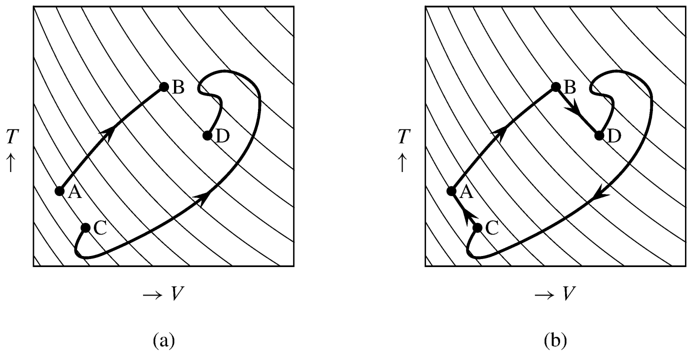


Figure 4.10 Reversible paths in V–T space. The thin curves are reversible adiabatic surfaces.
(a) Two paths connecting the same pair of reversible adiabatic surfaces.
(b) A cyclic path.

Consider a reversible process with *positive* one-way heat that changes the system from state A to state B. The path for this process must move the system from a reversible adiabatic surface of a certain entropy to a different surface of greater entropy. An example is the path A→B in Fig. 4.10(a). (The adiabatic surfaces in this figure are actually two-dimensional curves.) As before, we combine the experimental system with a Carnot engine to form a supersystem that exchanges heat with a single heat reservoir of constant temperature T_{res}. The net heat entering the supersystem, found by integrating Eq. 4.4.1, is

$$q' = T_{\mathrm{res}} \int_{\mathrm{A}}^{\mathrm{B}} \frac{đq}{T_{\mathrm{b}}} \tag{4.4.4}$$

and it is positive.

Suppose the same experimental system undergoes a second reversible process, not necessarily with one-way heat, along a different path connecting the same pair of reversible adiabatic surfaces. This could be path C→D in Fig. 4.10(a). The net heat entering the supersystem during this second process is q'':

$$q'' = T_{\text{res}} \int_{\text{C}}^{\text{D}} \frac{đq}{T_{\text{b}}} \tag{4.4.5}$$

We can then devise a *cycle* of the supersystem in which the experimental system undergoes the reversible path A→B→D→C→A, as shown in Fig. 4.10(b). Step A→B is the first process described above, step D→C is the reverse of the second process described above, and steps B→D and C→A are reversible and adiabatic. The net heat entering the supersystem in the cycle is $q' - q''$. In the reverse cycle the net heat is $q'' - q'$. In both of these cycles the heat is exchanged with a single heat reservoir; therefore, according to the Kelvin–Planck statement, neither cycle can have positive net heat. Therefore q' and q'' must be equal, and Eqs. 4.4.4 and 4.4.5 then show the integral $\int(đq/T_{\text{b}})$ has the same value when evaluated along either of the reversible paths from the lower to the higher entropy surface.

Note that since the second path (C→D) does not necessarily have one-way heat, it can take the experimental system through any sequence of intermediate entropy values, provided it starts at the lower entropy surface and ends at the higher. Furthermore, since the path is reversible, it can be carried out in reverse resulting in reversal of the signs of ΔS and $\int(đq/T_{\text{b}})$.

It should now be apparent that a satisfactory formula for defining the entropy change of a reversible process in a closed system is

$$\Delta S = \int \frac{đq}{T_{\text{b}}} \tag{4.4.6}$$
(reversible process, closed system)

This formula satisfies the necessary requirements: it makes the value of ΔS positive if the process has positive one-way heat, negative if the process has negative one-way heat, and zero if the process is adiabatic. It gives the same value of ΔS for any reversible change between the same two reversible adiabatic surfaces, and it makes the sum of the ΔS values of several consecutive reversible processes equal to ΔS for the overall process.

In Eq. 4.4.6, ΔS is the entropy change when the system changes from one arbitrary equilibrium state to another. If the change is an infinitesimal path element of a reversible process, the equation becomes

$$\text{d}S = \frac{đq}{T_{\text{b}}} \tag{4.4.7}$$
(reversible process, closed system)

It is common to see this equation written in the form $\text{d}S = đq_{\text{rev}}/T$, where $đq_{\text{rev}}$ denotes an infinitesimal quantity of heat in a reversible process.

> In Eq. 4.4.7, the quantity $1/T_{\text{b}}$ is called an *integrating factor* for $đq$, a factor that makes the product $(1/T_{\text{b}})\,đq$ be the infinitesimal change of a state function. The quantity c/T_{b}, where c is any nonzero constant, would also be a satisfactory integrating factor; so the definition of entropy, using c=1, is actually one of an infinite number of possible choices for assigning values to the reversible adiabatic surfaces.

4.4.3 Some properties of the entropy

It is not difficult to show that the entropy of a closed system in an equilibrium state is an *extensive* property. Suppose a system of uniform temperature T is divided into two closed subsystems A and B. When a reversible infinitesimal change occurs, the entropy changes of the subsystems are $\text{d}S_{\text{A}} = đq_{\text{A}}/T$ and $\text{d}S_{\text{B}} = đq_{\text{B}}/T$ and of the system $\text{d}S = đq/T$. But $đq$ is the sum of $đq_{\text{A}}$ and $đq_{\text{B}}$, which gives $\text{d}S = \text{d}S_{\text{A}} + \text{d}S_{\text{B}}$. Thus, the entropy changes are additive, so that entropy must be extensive: $S = S_{\text{A}} + S_{\text{B}}$. (The argument is not quite complete, because we have not shown that when each subsystem has an entropy of zero, so does the entire system. The zero of entropy will be discussed in Sec. 6.1.)

How can we evaluate the entropy of a particular equilibrium state of the system? We must assign an arbitrary value to one state and then evaluate the entropy change along a reversible path from this state to the state of interest using $\Delta S = \int(đq/T_{\text{b}})$.

We may need to evaluate the entropy of a *non*equilibrium state. To do this, we imagine imposing hypothetical internal constraints that change the nonequilibrium state to a constrained equilibrium state with the same internal structure. Some examples of such internal constraints were given in Sec. 2.4.4, and include rigid adiabatic partitions between phases of different temperature and pressure, semipermeable membranes to prevent transfer of certain species between adjacent phases, and inhibitors to prevent chemical reactions.

We assume that we can, in principle, impose or remove such constraints reversibly without heat, so there is no entropy change. If the nonequilibrium state includes macroscopic internal motion, the imposition of internal constraints involves negative reversible work to bring moving regions of the system to rest. This concept amounts to defining the entropy of a state with macroscopic internal motion to be the same as the entropy of a state with the same internal structure but without the motion, i.e., the same state frozen in time. By this definition, ΔS for a purely mechanical process (Sec. 3.2.3) is zero.

If the system is nonuniform over its extent, the internal constraints will partition it into practically-uniform regions whose entropy is additive. The entropy of the nonequilibrium state is then found from $\Delta S = \int (đq/T_{\text{b}})$ using a reversible path that changes the system from an equilibrium state of known entropy to the constrained equilibrium state with the same entropy as the state of interest. This procedure allows every possible state (at least conceptually) to have a definite value of S.

4.5: Irreversible Processes

We know that during a reversible process of a closed system, each infinitesimal entropy change $\mathrm{d}S$ is equal to $đq/T_\mathrm{b}$ and the finite change ΔS is equal to the integral $\int(đq/T_\mathrm{b})$—but what can we say about $\mathrm{d}S$ and ΔS for an *irreversible* process?

The derivation of this section will show that for an infinitesimal irreversible change of a closed system, $\mathrm{d}S$ is greater than $đq/T_\mathrm{b}$, and for an entire process ΔS is greater than $\int(đq/T_\mathrm{b})$. That is, the *equalities* that apply to a reversible process are replaced, for an irreversible process, by *inequalities*.

The derivation begins with irreversible processes that are adiabatic, and is then extended to irreversible processes in general.

4.5.1 Irreversible adiabatic processes

Consider an arbitrary irreversible adiabatic process of a closed system starting with a particular initial state A. The final state B depends on the path of this process. We wish to investigate the sign of the entropy change $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$. Our reasoning will depend on whether or not there is work during the process.

If there is work along any infinitesimal path element of the irreversible adiabatic process ($đw \neq 0$), we know from experience that this work would be different if the work coordinate or coordinates were changing at a different rate, because energy dissipation from internal friction would then be different. In the limit of infinite slowness, an adiabatic process with initial state A and the same change of work coordinates would become reversible, and the net work and final internal energy would differ from those of the irreversible process. Because the final state of the reversible adiabatic process is different from B, there is no reversible adiabatic path with work between states A and B.

> All states of a reversible process, including the initial and final states, must be equilibrium states. There is therefore a conceptual difficulty in considering reversible paths between two states if either of these states are nonequilibrium states. In such a case we will assume that the state has been replaced by a constrained equilibrium state of the same entropy as described in Sec. 4.4.3.

If, on the other hand, there is no work along any infinitesimal path element of the irreversible adiabatic process ($đw$=0), the process is taking place at constant internal energy U in an *isolated* system. A reversible limit cannot be reached without heat or work (Sec. 3.2.1). Thus any reversible adiabatic change from state A would require work, causing a change of U and preventing the system from reaching state B by any reversible adiabatic path.

So regardless of whether or not an irreversible adiabatic process A→B involves work, there is no *reversible* adiabatic path between A and B. The only reversible paths between these states must be *non*adiabatic. It follows that the entropy change $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$, given by the value of $đq/T_\mathrm{b}$ integrated over a reversible path from A to B, cannot be zero.

Next we ask whether $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$ could be negative. In each infinitesimal path element of the irreversible adiabatic process A→B, $đq$ is zero and the integral $\int_\mathrm{A}^\mathrm{B}(đq/T_\mathrm{b})$ along the path of this process is zero. Suppose the system completes a cycle by returning along a different, reversible path from state B back to state A. The Clausius inequality (Eq. 4.4.3) tells us that in this case the integral $\int_\mathrm{B}^\mathrm{A}(đq/T_\mathrm{b})$ along the reversible path cannot be positive. But this integral for the reversible path is equal to $-\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$, so $\Delta S_{\mathrm{A}\rightarrow\mathrm{B}}$ cannot be negative.

We conclude that because the entropy change of the irreversible adiabatic process A→B cannot be zero, and it cannot be negative, it must be *positive*.

In this derivation, the initial state A is arbitrary and the final state B is reached by an irreversible adiabatic process. If the two states are only infinitesimally different, then the change is infinitesimal. Thus for an infinitesimal change that is irreversible and adiabatic, $\mathrm{d}S$ must be *positive*.

4.5.2 Irreversible processes in general

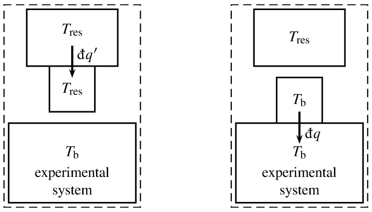


Figure 4.11 Supersystem including the experimental system, a Carnot engine (square box), and a heat reservoir. The dashed rectangle indicates the boundary of the supersystem.

To treat an irreversible process of a closed system that is nonadiabatic, we proceed as follows. As in Sec. 4.4.1, we use a Carnot engine for heat transfer across the boundary of the experimental system. We move the boundary of the supersystem of Fig. 4.8 so that the supersystem now includes the experimental system, the Carnot engine, and a heat reservoir of constant temperature T_{res}, as depicted in Fig. 4.11. During an irreversible change of the experimental system, the Carnot engine undergoes many infinitesimal cycles. During each cycle, the Carnot engine exchanges heat $\text{đ}q'$ at temperature T_{res} with the heat reservoir and heat $\text{đ}q$ at temperature T_{b} with the experimental system, as indicated in the figure. We use the sign convention that $\text{đ}q'$ is positive if heat is transferred to the Carnot engine, and $\text{đ}q$ is positive if heat is transferred to the experimental system, in the directions of the arrows in the figure.

The supersystem exchanges work, but not heat, with its surroundings. During one infinitesimal cycle of the Carnot engine, the net entropy change of the Carnot engine is zero, the entropy change of the experimental system is $\text{d}S$, the heat transferred between the Carnot engine and the experimental system is $\text{đ}q$, and the heat transferred between the heat reservoir and the Carnot engine is given by $\text{đ}q' = T_{\text{res}}\,\text{đ}q/T_{\text{b}}$ (Eq. 4.4.1). The heat transfer between the heat reservoir and Carnot engine is reversible, so the entropy change of the heat reservoir is

$$\text{d}S_{\text{res}} = -\frac{\text{đ}q'}{T_{\text{res}}} = -\frac{\text{đ}q}{T_{\text{b}}} \tag{4.5.1}$$

The entropy change of the supersystem is the sum of the entropy changes of its parts:

$$\text{d}S_{\text{ss}} = \text{d}S + \text{d}S_{\text{res}} = \text{d}S - \frac{\text{đ}q}{T_{\text{b}}} \tag{4.5.2}$$

The process within the supersystem is adiabatic and includes an irreversible change within the experimental system, so according to the conclusions of Sec. 4.5.1, $\text{d}S_{\text{ss}}$ is positive. Equation 4.5.2 then shows that $\text{d}S$, the infinitesimal entropy change during the irreversible change of the experimental system, must be greater than $\text{đ}q/T_{\text{b}}$:

$$\text{d}S > \frac{\text{đ}q}{T_{\text{b}}} \tag{4.5.3}$$

(irreversible change, closed system)

This relation includes the case of an irreversible *adiabatic* change, because it shows that if $\text{đ}q$ is zero, $\text{d}S$ is greater than zero.

By integrating both sides of Eq. 4.5.3 between the initial and final states of the irreversible process, we obtain a relation for the finite entropy change corresponding to many infinitesimal cycles of the Carnot engine:

$$\Delta S > \int \frac{\text{đ}q}{T_{\text{b}}} \tag{4.5.4}$$

(irreversible process, closed system)

4.6: Applications

The lengthy derivation in Secs. 4.3–4.5 is based on the Kelvin–Planck statement describing the impossibility of converting completely into work the energy transferred into the system by heat from a single heat reservoir. The derivation has now given us all parts of the mathematical statement of the second law shown in the box in Sec. 4.2. The mathematical statement includes an equality, $\mathrm{d}S = đq/T_\mathrm{b}$, that applies to an infinitesimal *reversible* change, and an inequality, $\mathrm{d}S > đq/T_\mathrm{b}$, that applies to an infinitesimal *irreversible* change. It is convenient to combine the equality and inequality in a single relation that is a general mathematical statement of the second law:

$$\mathrm{d}S \geq \frac{đq}{T_\mathrm{b}} \tag{4.6.1}$$

$\left(\substack{\text{irrev}\\\text{rev}}, \text{closed system}\right)$

The inequality refers to an irreversible change and the equality to a reversible change, as indicated by the notation $\substack{\text{irrev}\\\text{rev}}$ in the conditions of validity. The integrated form of this relation is

$$\Delta S \geq \int \frac{đq}{T_\mathrm{b}} \tag{4.6.2}$$

$\left(\substack{\text{irrev}\\\text{rev}}, \text{closed system}\right)$

During a reversible process, the states are equilibrium states and the temperature is usually uniform throughout the system. The only exception is if the system happens to have internal adiabatic partitions that allow phases of different temperatures in an equilibrium state. When the process is reversible and the temperature is uniform, we can replace $\mathrm{d}S = đq/T_\mathrm{b}$ by $\mathrm{d}S = đq/T$.

The rest of Sec. 4.6 will apply Eqs. 4.6.1 and 4.6.2 to various reversible and irreversible processes.

4.6.1 Reversible heating

The definition of the heat capacity C of a closed system is given by Eq. 3.1.9: $C \overset{\text{def}}{=} đq/\mathrm{d}T$. For reversible heating or cooling of a homogeneous phase, $đq$ is equal to $T\,\mathrm{d}S$ and we can write

$$\Delta S = \int_{T_1}^{T_2} \frac{C}{T}\,\mathrm{d}T \tag{4.6.3}$$

where C should be replaced by C_V if the volume is constant, or by C_p if the pressure is constant (Sec. 3.1.5). If the heat capacity has a constant value over the temperature range from T_1 to T_2, the equation becomes

$$\Delta S = C \ln \frac{T_2}{T_1} \tag{4.6.4}$$

Heating increases the entropy, and cooling decreases it.

4.6.2 Reversible expansion of an ideal gas

When the volume of an ideal gas, or of any other fluid, is changed reversibly and *adiabatically*, there is of course no entropy change.

When the volume of an ideal gas is changed reversibly and *isothermally*, there is expansion work given by $w = -nRT \ln(V_2/V_1)$ (Eq. 3.5.1). Since the internal energy of an ideal gas is constant at constant temperature, there must be heat of equal magnitude and opposite sign: $q = nRT \ln(V_2/V_1)$. The entropy change is therefore

$$\Delta S = nR \ln \frac{V_2}{V_1} \tag{4.6.5}$$

(reversible isothermal volume
change of an ideal gas)

Isothermal expansion increases the entropy, and isothermal compression decreases it.

Since the change of a state function depends only on the initial and final states, Eq. 4.6.5 gives a valid expression for ΔS of an ideal gas under the less stringent condition $T_2 = T_1$; it is not necessary for the intermediate states to be equilibrium states of the same temperature.

4.6.3 Spontaneous changes in an isolated system

An isolated system is one that exchanges no matter or energy with its surroundings. Any change of state of an isolated system that actually occurs is spontaneous, and arises solely from conditions within the system, uninfluenced by changes in the surroundings—the process occurs by itself, of its own accord. The initial state and the intermediate states of the process must be nonequilibrium states, because by definition an equilibrium state would not change over time in the isolated system.

Unless the spontaneous change is purely mechanical, it is irreversible. According to the second law, during an infinitesimal change that is irreversible and adiabatic, the entropy increases. For the isolated system, we can therefore write

$$\mathrm{d}S > 0 \tag{4.6.6}$$
$$\text{(irreversible change, isolated system)}$$

In later chapters, the inequality of Eq. 4.6.6 will turn out to be one of the most useful for deriving conditions for spontaneity and equilibrium in chemical systems: *The entropy of an isolated system continuously increases during a spontaneous, irreversible process until it reaches a maximum value at equilibrium*.

If we treat the universe as an isolated system (although cosmology provides no assurance that this is a valid concept), we can say that as spontaneous changes occur in the universe, its entropy continuously increases. Clausius summarized the first and second laws in a famous statement: *Die Energie der Welt ist constant; die Entropie der Welt strebt einem Maximum zu* (the energy of the universe is constant; the entropy of the universe strives toward a maximum).

4.6.4 Internal heat flow in an isolated system

Suppose the system is a solid body whose temperature initially is nonuniform. Provided there are no internal adiabatic partitions, the initial state is a nonequilibrium state lacking internal thermal equilibrium. If the system is surrounded by thermal insulation, and volume changes are negligible, this is an isolated system. There will be a spontaneous, irreversible internal redistribution of thermal energy that eventually brings the system to a final equilibrium state of uniform temperature.

In order to be able to specify internal temperatures at any instant, we treat the system as an assembly of phases, each having a uniform temperature that can vary with time. To describe a region that has a continuous temperature gradient, we approximate the region with a very large number of very small phases or parcels, each having a temperature infinitesimally different from its neighbors.

We use Greek letters to label the phases. The temperature of phase α at any given instant is T^α. We can treat each phase as a subsystem with a boundary across which there can be energy transfer in the form of heat. Let $đq_{\alpha\beta}$ represent an infinitesimal quantity of heat transferred during an infinitesimal interval of time to phase α from phase β. The heat transfer, if any, is to the cooler from the warmer phase. If phases α and β are in thermal contact and T^α is less than T^β, then $đq_{\alpha\beta}$ is positive; if the phases are in thermal contact and T^α is greater than T^β, $đq_{\alpha\beta}$ is negative; and if neither of these conditions is satisfied, $đq_{\alpha\beta}$ is zero.

To evaluate the entropy change, we need a reversible path from the initial to the final state. The net quantity of heat transferred to phase α during an infinitesimal time interval is $đq^\alpha = \sum_{\beta\neq\alpha} đq_{\alpha\beta}$. The entropy change of phase α is the same as it would be for the reversible transfer of this heat from a heat reservoir of temperature T^α: $\mathrm{d}S^\alpha = đq^\alpha / T^\alpha$. The entropy change of the entire system along the reversible path is found by summing over all phases:

$$\mathrm{d}S = \sum_\alpha \mathrm{d}S^\alpha = \sum_\alpha \frac{đq^\alpha}{T^\alpha} = \sum_\alpha \sum_{\beta\neq\alpha} \frac{đq_{\alpha\beta}}{T^\alpha} = \sum_\alpha \sum_{\beta>\alpha} \left(\frac{đq_{\alpha\beta}}{T^\alpha} + \frac{đq_{\beta\alpha}}{T^\beta} \right) \tag{4.6.7}$$

There is also the condition of quantitative energy transfer, $đq_{\beta\alpha} = -đq_{\alpha\beta}$, which we use to rewrite Eq. 4.6.7 in the form

$$\mathrm{d}S = \sum_\alpha \sum_{\beta>\alpha} \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) đq_{\alpha\beta} \tag{4.6.8}$$

Consider an individual term of the sum on the right side of Eq. 4.6.8 that has a nonzero value of $đq_{\alpha\beta}$ due to finite heat transfer between phases α and β. If T^α is less than T^β, then both $đq_{\alpha\beta}$ and $(1/T^\alpha - 1/T^\beta)$ are positive. If, on the other hand, T^α is greater than T^β, both $đq_{\alpha\beta}$ and $(1/T^\alpha - 1/T^\beta)$ are negative. Thus each term of the sum is either zero or positive, and as long as phases of different temperature are present, $\mathrm{d}S$ is positive.

This derivation shows that during a spontaneous thermal equilibration process in an isolated system, starting with any initial distribution of the internal temperatures, the entropy continuously increases until the system reaches a state of thermal equilibrium with a single uniform temperature throughout. The result agrees with Eq. 4.6.6. Harvey S. Leff (*Am. J. Phys.*, **45**, 252–254, 1977) obtains the same result by a more complicated derivation.

4.6.5 Free expansion of a gas

Consider the free expansion of a gas shown in Fig. 3.8. The *system* is the gas. Assume that the vessel walls are rigid and adiabatic, so that the system is isolated. When the stopcock between the two vessels is opened, the gas expands irreversibly into the vacuum without heat or work and at constant internal energy. To carry out the same change of state reversibly, we confine the gas at its initial volume and temperature in a cylinder-and-piston device and use the piston to expand the gas adiabatically with negative work. Positive heat is then needed to return the internal energy reversibly to its initial value. Because the reversible path has positive heat, the entropy change is positive.

This is an example of an irreversible process in an isolated system for which a reversible path between the initial and final states has both heat and work.

4.6.6 Adiabatic process with work

In general (Sec. 3.10), an adiabatic process with a given initial equilibrium state and a given change of a work coordinate has the least positive or most negative work in the reversible limit. Consider an irreversible adiabatic process with work w_{irr}. The same change of state can be accomplished reversibly by the following two steps: (1) a reversible adiabatic change of the work coordinate with work w_{rev}, followed by (2) reversible transfer of heat q_{rev} with no further change of the work coordinate. Since w_{rev} is algebraically less than w_{irr}, q_{rev} must be positive in order to make ΔU the same in the irreversible and reversible paths. The positive heat increases the entropy along the reversible path, and consequently the irreversible adiabatic process has a positive entropy change. This conclusion agrees with the second-law inequality of Eq. 4.6.1.

4.7: Summary

Some of the important terms and definitions discussed in this chapter are as follows.

- The derivation of the mathematical statement of the second law shows that during a reversible process of a closed system, the infinitesimal quantity $đq/T_{\mathrm{b}}$ equals the infinitesimal change of a state function called the entropy, S. Here $đq$ is heat transferred at the boundary where the temperature is T_{b}.

  In each infinitesimal path element of a process of a closed system, $\mathrm{d}S$ is equal to $đq/T_{\mathrm{b}}$ if the process is reversible, and is greater than $đq/T_{\mathrm{b}}$ if the process is irreversible, as summarized by the relation $\mathrm{d}S \geq đq/T_{\mathrm{b}}$.

  The second law establishes no general relation between entropy changes and heat in an open system, or for an impossible process. The entropy of an open system may increase or decrease depending on whether matter enters or leaves. It is possible to imagine different impossible processes in which $\mathrm{d}S$ is less than, equal to, and greater than $đq/T_{\mathrm{b}}$.

4.8: The Statistical Interpretation of Entropy

Because entropy is such an important state function, it is natural to seek a description of its meaning on the microscopic level.

Entropy is sometimes said to be a measure of “disorder.” According to this idea, the entropy increases whenever a closed system becomes more disordered on a microscopic scale. This description of entropy as a measure of disorder is highly misleading. It does not explain why entropy is increased by reversible heating at constant volume or pressure, or why it increases during the reversible isothermal expansion of an ideal gas. Nor does it seem to agree with the freezing of a supercooled liquid or the formation of crystalline solute in a supersaturated solution; these processes can take place spontaneously in an isolated system, yet are accompanied by an apparent *decrease* of disorder.

> Thus we should not interpret entropy as a measure of disorder. We must look elsewhere for a satisfactory microscopic interpretation of entropy.

A rigorous interpretation is provided by the discipline of *statistical mechanics*, which derives a precise expression for entropy based on the behavior of macroscopic amounts of microscopic particles. Suppose we focus our attention on a particular macroscopic equilibrium state. Over a period of time, while the system is in this equilibrium state, the system at each instant is in a *microstate*, or stationary quantum state, with a definite energy. The microstate is one that is *accessible* to the system—that is, one whose wave function is compatible with the system’s volume and with any other conditions and constraints imposed on the system. The system, while in the equilibrium state, continually jumps from one accessible microstate to another, and the macroscopic state functions described by classical thermodynamics are time averages of these microstates.

The fundamental assumption of statistical mechanics is that accessible microstates of equal energy are equally probable, so that the system while in an equilibrium state spends an equal fraction of its time in each such microstate. The statistical entropy of the equilibrium state then turns out to be given by the equation

$$S_{\text{stat}} = k \ln W + C \tag{4.8.1}$$

where k is the Boltzmann constant $k = R/N_{\text{A}}$, W is the number of accessible microstates, and C is a constant.

In the case of an equilibrium state of a perfectly-isolated system of constant internal energy U, the accessible microstates are the ones that are compatible with the constraints and whose energies all have the same value, equal to the value of U.

It is more realistic to treat an equilibrium state with the assumption the system is in thermal equilibrium with an external constant-temperature heat reservoir. The internal energy then fluctuates over time with extremely small deviations from the average value U, and the accessible microstates are the ones with energies close to this average value. In the language of statistical mechanics, the results for an isolated system are derived with a microcanonical ensemble, and for a system of constant temperature with a canonical ensemble.

A change ΔS_{stat} of the statistical entropy function given by Eq. 4.8.1 is the same as the change ΔS of the macroscopic second-law entropy, because the derivation of Eq. 4.8.1 is based on the macroscopic relation $\mathrm{d}S_{\text{stat}} = đq/T = (\mathrm{d}U - đw)/T$ with $\mathrm{d}U$ and $đw$ given by statistical theory. If the integration constant C is set equal to zero, S_{stat} becomes the third-law entropy S to be described in Chap. 6.

Equation 4.8.1 shows that a reversible process in which entropy increases is accompanied by an increase in the number of accessible microstates of equal, or nearly equal, internal energies. This interpretation of entropy increase has been described as the spreading and sharing of energy (Harvey S. Leff, Am. J. Phys., 64, 1261–1271, 1996) and as the dispersal of energy (Frank L. Lambert, J. Chem. Educ., 79, 1241–1246, 2002). It has even been proposed that entropy should be thought of as a “spreading function” with its symbol S suggesting *spreading* (Frank L. Lambert and Harvey S. Leff, J. Chem. Educ., 86, 94–98, 2009). The symbol S for entropy seems originally to have been an arbitrary choice by Clausius.

4.9: Chapter 4 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.
4.1 Explain why an electric refrigerator, which transfers energy by means of heat from the cold food storage compartment to the warmer air in the room, is not an impossible "Clausius device."

4.2 A system consisting of a fixed amount of an ideal gas is maintained in thermal equilibrium with a heat reservoir at temperature T. The system is subjected to the following isothermal cycle:

1. The gas, initially in an equilibrium state with volume V_0, is allowed to expand into a vacuum and reach a new equilibrium state of volume V'.

2. The gas is reversibly compressed from V' to V_0.
For this cycle, find expressions or values for w, $\oint \mathrm{d}q/T$, and $\oint \mathrm{d}S$.

4.3 In an irreversible isothermal process of a closed system:
(a) Is it possible for ΔS to be negative?
(b) Is it possible for ΔS to be less than q/T ?

4.4 Suppose you have two blocks of copper, each of heat capacity $C_V = 200.0 \mathrm{JK}^{-1}$. Initially one block has a uniform temperature of $300.00\ \mathrm{K}$ and the other $310.00\ \mathrm{K}$. Calculate the entropy change that occurs when you place the two blocks in thermal contact with one another and surround them with perfect thermal insulation. Is the sign of ΔS consistent with the second law? (Assume the process occurs at constant volume.)

4.5 Refer to the apparatus shown in Figs. 3.23 on page 101 and 3.26 on page 103 and described in Probs. 3.3 and 3.8. For both systems, evaluate ΔS for the process that results from opening the stopcock. Also evaluate $\int \mathrm{d}q/T_{\text{ext}}$ for both processes (for the apparatus in Fig. 3.26, assume the vessels have adiabatic walls). Are your results consistent with the mathematical statement of the second law?
Figure 4.13

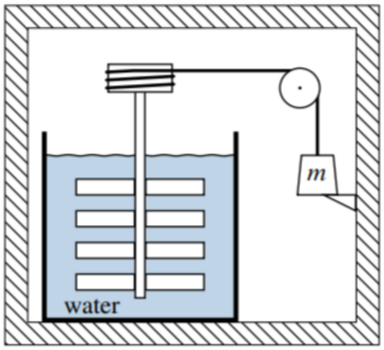


Figure 4.13

4.6 Figure 4.13 shows the walls of a rigid thermally-insulated box (cross hatching). The system is the contents of this box. In the box is a paddle wheel immersed in a container of water, connected by a cord and pulley to a weight of mass m. The weight rests on a stop located a distance h above the bottom of the box. Assume the heat capacity of the system, C_V, is independent of temperature. Initially the system is in an equilibrium state at temperature T_1.

When the stop is removed, the weight irreversibly sinks to the bottom of the box, causing the paddle wheel to rotate in the water. Eventually the system reaches a final equilibrium state with thermal equilibrium. Describe a reversible process with the same entropy change as this irreversible process, and derive a formula for ΔS in terms of m, h, C_V, and T_1.

CHAPTER OVERVIEW

5: Thermodynamic Potentials

This chapter begins with a discussion of mathematical properties of the total differential of a dependent variable. Three extensive state functions with dimensions of energy are introduced: enthalpy, Helmholtz energy, and Gibbs energy. These functions, together with internal energy, are called **thermodynamic potentials**. (The term *thermodynamic potential* should not be confused with the *chemical potential*, μ, to be introduced in Sec. 5.2.) Some formal mathematical manipulations of the four thermodynamic potentials are described that lead to expressions for heat capacities, surface work, and criteria for spontaneity in closed systems.

5.1: Total Differential of a Dependent Variable

Recall from Sec. 2.4.1 that the state of the system at each instant is defined by a certain minimum number of state functions, the independent variables. State functions not treated as independent variables are dependent variables. Infinitesimal changes in any of the independent variables will, in general, cause an infinitesimal change in each dependent variable.

A dependent variable is a function of the independent variables. The **total differential** of a dependent variable is an expression for the infinitesimal change of the variable in terms of the infinitesimal changes of the independent variables. As explained in Sec. F.2 of Appendix F, the expression can be written as a sum of terms, one for each independent variable. Each term is the product of a partial derivative with respect to one of the independent variables and the infinitesimal change of that independent variable. For example, if the system has two independent variables, and we take these to be T and V, the expression for the total differential of the pressure is

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V \tag{5.1.1}$$

Thus, in the case of a fixed amount of an ideal gas with pressure given by $p = nRT/V$, the total differential of the pressure can be written

$$\mathrm{d}p = \frac{nR}{V}\,\mathrm{d}T - \frac{nRT}{V^2}\,\mathrm{d}V \tag{5.1.2}$$

5.2: Total Differential of the Internal Energy

For a closed system undergoing processes in which the only kind of work is expansion work, the first law becomes $\mathrm{d}U = đq + đw = đq - p_\mathrm{b}\,\mathrm{d}V$. Since it will often be useful to make a distinction between expansion work and other kinds of work, this e-book will sometimes write the first law in the form

$$\mathrm{d}U = đq - p_\mathrm{b}\,\mathrm{d}V + đw' \tag{5.2.1}$$

(closed system)

where $đw'$ is **nonexpansion work**—that is, any thermodynamic work that is not expansion work.

Consider a closed system of one chemical component (e.g., a pure substance) in a single homogeneous phase. The only kind of work is expansion work, with V as the work variable. This kind of system has *two* independent variables (Sec. 2.4.3). During a *reversible* process in this system, the heat is $đq = T\,\mathrm{d}S$, the work is $đw = -p\,\mathrm{d}V$, and an infinitesimal internal energy change is given by

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{5.2.2}$$

(closed system, C=1, P=1, $đw'$=0)

In the conditions of validity shown next to this equation, C=1 means there is one component (C is the number of components) and P=1 means there is one phase (P is the number of phases).

The appearance of the intensive variables T and p in Eq. 5.2.2 implies, of course, that the temperature and pressure are uniform throughout the system during the process. If they were not uniform, the phase would not be homogeneous and there would be more than two independent variables. The temperature and pressure are strictly uniform only if the process is reversible; it is not necessary to include "reversible" as one of the conditions of validity.

A real process approaches a reversible process in the limit of infinite slowness. For all practical purposes, therefore, we may apply Eq. 5.2.2 to a process obeying the conditions of validity and taking place so slowly that the temperature and pressure remain essentially uniform—that is, for a process in which the system stays very close to thermal and mechanical equilibrium.

Because the system under consideration has two independent variables, Eq. 5.2.2 is an expression for the total differential of U with S and V as the independent variables. In general, an expression for the differential $\mathrm{d}X$ of a state function X is a total differential if

1. Note that the work coordinate of any kind of dissipative work—work without a reversible limit—cannot appear in the expression for a total differential, because it is not a state function (Sec. 3.10).

   As explained in Appendix F, we may identify the coefficient of each term in an expression for the total differential of a state function as a partial derivative of the function. We identify the coefficients on the right side of Eq. 5.2.2 as follows:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S \tag{5.2.3}$$

   The quantity given by the third partial derivative, $(\partial U/\partial n)_{S,V}$, is represented by the symbol μ (mu). This quantity is an intensive state function called the **chemical potential**.

   With these substitutions, Eq. 5.2.4 becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \tag{5.2.5}$$

   (pure substance, P=1, $đw'$=0)

   and this is a valid expression for the total differential of U under the given conditions.

   If a system contains a mixture of s different substances in a single phase, and the system is open so that the amount of each substance can vary independently, there are $2+s$ independent variables and the total differential of U can be written

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{s}\mu_i\,\mathrm{d}n_i \tag{5.2.6}$$

   (open system, P=1, $đw'$=0)

The coefficient μ_i is the chemical potential of substance i. We identify it as the partial derivative $(\partial U/\partial n_i)_{S,V,n_{j\neq i}}$.

> The term $-p\,\mathrm{d}V$ on the right side of Eq. 5.2.6 is the reversible work. However, the term $T\,\mathrm{d}S$ does not equal the reversible heat as it would if the system were closed. This is because the entropy change $\mathrm{d}S$ is partly due to the entropy of the matter transferred across the boundary. It follows that the remaining term, $\sum_i \mu_i\,\mathrm{d}n_i$ (sometimes called the "chemical work"), should not be interpreted as the energy brought into the system by the transfer of matter.

Suppose that in addition to expansion work, other kinds of reversible work are possible. Each work coordinate adds an additional independent variable. Thus, for a closed system of one component in one phase, with reversible nonexpansion work given by $đw' = Y\,\mathrm{d}X$, the total differential of U becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y\,\mathrm{d}X \tag{5.2.7}$$

(closed system, $C{=}1$, $P{=}1$)

5.3: Enthalpy, Helmholtz Energy, and Gibbs Energy

For the moment we shall confine our attention to closed systems with one component in one phase. The total differential of the internal energy in such a system is given by Eq. 5.2.2: $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$. The independent variables in this equation, S and V, are called the *natural variables* of U.

In the laboratory, entropy and volume may not be the most convenient variables to measure and control. Entropy is especially inconvenient, as its value cannot be measured directly. The way to change the independent variables is to make Legendre transforms, as explained in Sec. F.4 in Appendix F.

A Legendre transform of a dependent variable is made by subtracting one or more products of *conjugate variables*. In the total differential $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$, T and S are conjugates (that is, they comprise a *conjugate pair*), and $-p$ and V are conjugates. Thus the products that can be subtracted from U are either TS or $-pV$, or both. Three Legendre transforms of the internal energy are possible, defined as follows:

$$\textbf{Enthalpy} \qquad H \overset{\text{def}}{=} U + pV \tag{5.3.1}$$

$$\textbf{Helmholtz energy} \qquad A \overset{\text{def}}{=} U - TS \tag{5.3.2}$$

$$\textbf{Gibbs energy} \qquad G \overset{\text{def}}{=} U - TS + pV = H - TS \tag{5.3.3}$$

These definitions are used whether or not the system has only two independent variables.

The enthalpy, Helmholtz energy, and Gibbs energy are important functions used extensively in thermodynamics. They are state functions (because the quantities used to define them are state functions) and are extensive (because U, S, and V are extensive). If temperature or pressure are not uniform in the system, we can apply the definitions to constituent phases, or to subsystems small enough to be essentially uniform, and sum over the phases or subsystems.

> Alternative names for the Helmholtz energy are Helmholtz function, Helmholtz free energy, and work function. Alternative names for the Gibbs energy are Gibbs function and Gibbs free energy. Both the Helmholtz energy and Gibbs energy have been called simply free energy, and the symbol F has been used for both. The nomenclature in this e-book follows the recommendations of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007).

Expressions for infinitesimal changes of H, A, and G are obtained by applying the rules of differentiation to their defining equations:

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p \tag{5.3.4}$$

$$\mathrm{d}A = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T \tag{5.3.5}$$

$$\mathrm{d}G = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T + p\,\mathrm{d}V + V\,\mathrm{d}p \tag{5.3.6}$$

These expressions for $\mathrm{d}H$, $\mathrm{d}A$, and $\mathrm{d}G$ are general expressions for any system or phase with uniform T and p. They are *not* total differentials of H, A, and G, as the variables in the differentials in each expression are not independent.

A useful property of the enthalpy in a closed system can be found by replacing $\mathrm{d}U$ in Eq. 5.3.4 by the first law expression $đq - p\,\mathrm{d}V + đw'$, to obtain $\mathrm{d}H = đq + V\,\mathrm{d}p + đw'$. Thus, in a process at constant pressure ($\mathrm{d}p = 0$) with expansion work only ($đw' = 0$), we have

$$\mathrm{d}H = đq \tag{5.3.7}$$

(closed system, constant p, $đw' = 0$)

The enthalpy change under these conditions is equal to the heat. The integrated form of this relation is $\int \mathrm{d}H = \int đq$, or

$$\Delta H = q \tag{5.3.8}$$

(closed system, constant p, $w' = 0$)

Equation 5.3.7 is analogous to the following relation involving the internal energy, obtained from the first law:

$$dU = đq \tag{5.3.9}$$

(closed system, constant V, $đw'$=0)

That is, in a process at constant volume with expansion work only, the internal energy change is equal to the heat.

5.4: Closed Systems

In order to find expressions for the total differentials of H, A, and G in a closed system with one component in one phase, we must replace $\mathrm{d}U$ in Eqs. 5.3.4–5.3.6 with

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{5.4.1}$$

to obtain

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p \tag{5.4.2}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V \tag{5.4.3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p \tag{5.4.4}$$

Equations 5.4.1–5.4.4 are sometimes called the **Gibbs equations**. They are expressions for the total differentials of the thermodynamic potentials U, H, A, and G in closed systems of one component in one phase with expansion work only. Each equation shows how the dependent variable on the left side varies as a function of changes in two independent variables (the natural variables of the dependent variable) on the right side.

By identifying the coefficients on the right side of Eqs. 5.4.1–5.4.4, we obtain the following relations (which again are valid for a closed system of one component in one phase with expansion work only):

from Eq. 5.4.1:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{5.4.5}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{5.4.6}$$

from Eq. 5.4.2:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{5.4.7}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{5.4.8}$$

from Eq. 5.4.3:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.4.9}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.4.10}$$

from Eq. 5.4.4:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.4.11}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.4.12}$$

This e-book now uses for the first time an extremely useful mathematical tool called the **reciprocity relation** of a total differential (Sec. F.2). Suppose the independent variables are x and y and the total differential of a dependent state function f is given by

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y \tag{5.4.13}$$

where a and b are functions of x and y. Then the reciprocity relation is

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \tag{5.4.14}$$

The reciprocity relations obtained from the Gibbs equations (Eqs. 5.4.1–5.4.4) are called **Maxwell relations** (again valid for a closed system with $C=1$, $P=1$, and $đw'=0$):

from Eq. 5.4.1:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{5.4.15}$$

from Eq. 5.4.2:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{5.4.16}$$

from Eq. 5.4.3:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.4.17}$$

from Eq. 5.4.4:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{5.4.18}$$

5.5: Open Systems

An open system of one substance in one phase, with expansion work only, has three independent variables. The total differential of U is given by Eq. 5.2.5:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \tag{5.5.1}$$

In this open system the natural variables of U are S, V, and n. Substituting this expression for $\mathrm{d}U$ into the expressions for $\mathrm{d}H$, $\mathrm{d}A$, and $\mathrm{d}G$ given by Eqs. 5.3.4–5.3.6, we obtain the following total differentials:

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}n \tag{5.5.2}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}n \tag{5.5.3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}n \tag{5.5.4}$$

Note that these are the same as the four Gibbs equations (Eqs. 5.4.1–5.4.4) with the addition of a term $\mu\,\mathrm{d}n$ to allow for a change in the amount of substance.

Identification of the coefficient of the last term on the right side of each of these equations shows that the chemical potential can be equated to four different partial derivatives:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,p} = \left(\frac{\partial A}{\partial n}\right)_{T,V} = \left(\frac{\partial G}{\partial n}\right)_{T,p} \tag{5.5.5}$$

All four of these partial derivatives must have the same value for a given state of the system; the value, of course, depends on what that state is.

The last partial derivative on the right side of Eq. 5.5.5, $(\partial G/\partial n)_{T,p}$, is especially interesting because it is the rate at which the Gibbs energy increases with the amount of substance added to a system whose intensive properties remain constant. Thus, μ is revealed to be equal to G_{m}, the molar Gibbs energy of the substance.

Suppose the system contains several substances or species in a single phase (a mixture) whose amounts can be varied independently. We again assume the only work is expansion work. Then, making use of Eq. 5.2.6, we find the total differentials of the thermodynamic potentials are given by

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.6}$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.7}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.8}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.9}$$

The independent variables on the right side of each of these equations are the natural variables of the corresponding thermodynamic potential. Section F.4 shows that all of the information contained in an algebraic expression for a state function is preserved in a Legendre transform of the function. What this means for the thermodynamic potentials is that an expression for any one of them, as a function of its natural variables, can be converted to an expression for each of the other thermodynamic potentials as a function of its natural variables.

Willard Gibbs, after whom the Gibbs energy is named, called Eqs. 5.5.6–5.5.9 the *fundamental equations* of thermodynamics, because from any single one of them not only the other thermodynamic potentials but also all thermal, mechanical, and chemical properties of the system can be deduced (J. Willard Gibbs, in Henry Andrews Bumstead and Ralph Gibbs Van Name, editors, *The Scientific Papers of J. Willard Gibbs*, Vol. I, Ox Bow Press, Woodbridge, Connecticut, 1993, p. 86). Problem 5.4 illustrates this useful application of the total differential of a thermodynamic potential.

In Eqs. 5.5.6–5.5.9, the coefficient μ_i is the chemical potential of species i. The equations show that μ_i can be equated to four different partial derivatives, similar to the equalities shown in Eq. 5.5.5 for a pure substance:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{5.5.10}$$

The partial derivative $(\partial G/\partial n_i)_{T,P,n_{j\neq i}}$ is called the *partial molar Gibbs energy* of species i, another name for the chemical potential as will be discussed in Sec. 9.2.6.

5.6: Expressions for Heat Capacity

As explained in Sec. 3.1.5, the heat capacity of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change: $\text{heat capacity} \overset{\text{def}}{=} đq/\,\mathrm{d}T$. The heat capacities of isochoric (constant volume) and isobaric (constant pressure) processes are of particular interest.

The **heat capacity at constant volume**, C_V, is the ratio $đq/\,\mathrm{d}T$ for a process in a closed constant-volume system with no nonexpansion work—that is, no work at all. The first law shows that under these conditions the internal energy change equals the heat: $\mathrm{d}U = đq$ (Eq. 5.3.9). We can replace $đq$ by $\mathrm{d}U$ and write C_V as a partial derivative:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{5.6.1}$$

(closed system)

> If the closed system has more than two independent variables, additional conditions are needed to define C_V unambiguously. For instance, if the system is a gas mixture in which reaction can occur, we might specify that the system remains in reaction equilibrium as T changes at constant V.
>
> Equation 5.6.1 does not require the condition $đw'{=}0$, because all quantities appearing in the equation are *state* functions whose relations to one another are fixed by the nature of the system and not by the path. Thus, if heat transfer into the system at constant V causes U to increase at a certain rate with respect to T, and this rate is defined as C_V, the performance of electrical work on the system at constant V will cause the same rate of increase of U with respect to T and can equally well be used to evaluate C_V.

Note that C_V is a state function whose value depends on the state of the system—that is, on T, V, and any additional independent variables. C_V is an *extensive* property: the combination of two identical phases has twice the value of C_V that one of the phases has by itself.

For a phase containing a pure substance, the **molar heat capacity at constant volume** is defined by $C_{V,\mathrm{m}} \overset{\text{def}}{=} C_V/n$. $C_{V,\mathrm{m}}$ is an *intensive* property.

If the system is an ideal gas, its internal energy depends only on T, regardless of whether V is constant, and Eq. 5.6.1 can be simplified to

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \tag{5.6.2}$$

(closed system, ideal gas)

Thus the internal energy change of an ideal gas is given by $\mathrm{d}U = C_V\,\mathrm{d}T$, as mentioned earlier in Sec. 3.5.3.

The **heat capacity at constant pressure**, C_p, is the ratio $đq/\,\mathrm{d}T$ for a process in a closed system with a constant, uniform pressure and with expansion work only. Under these conditions, the heat $đq$ is equal to the enthalpy change $\mathrm{d}H$ (Eq. 5.3.7), and we obtain a relation analogous to Eq. 5.6.1:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{5.6.3}$$

(closed system)

C_p is an extensive state function. For a phase containing a pure substance, the **molar heat capacity at constant pressure** is $C_{p,\mathrm{m}} = C_p/n$, an intensive property.

Since the enthalpy of a fixed amount of an ideal gas depends only on T (Prob. 5.1), we can write a relation analogous to Eq. 5.6.2:

$$C_p = \frac{\mathrm{d}H}{\mathrm{d}T} \tag{5.6.4}$$

(closed system, ideal gas)

5.7: Surface Work

Sometimes we need more than the usual two independent variables to describe an equilibrium state of a closed system of one substance in one phase. This is the case when, in addition to expansion work, another kind of work is possible. The total differential of U is then given by $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y\,\mathrm{d}X$ (Eq. 5.2.7), where $Y\,\mathrm{d}X$ represents the nonexpansion work $đw'$.

A good example of this situation is surface work in a system in which surface area is relevant to the description of the state.

A liquid–gas interface behaves somewhat like a stretched membrane. The upper and lower surfaces of the liquid film in the device depicted in Fig. 5.1 exert a force F on the sliding rod, tending to pull it in the direction that reduces the surface area. We can measure the force by determining the opposing force F_{ext} needed to prevent the rod from moving. This force is found to be proportional to the length of the rod and independent of the rod position x. The force also depends on the temperature and pressure.

The **surface tension** or interfacial tension, γ, is the force exerted by an interfacial surface per unit length. The film shown in Fig. 5.1 has two surfaces, so we have $\gamma = F/2l$ where l is the rod length.

To increase the surface area of the film by a practically-reversible process, we slowly pull the rod to the right in the $+x$ direction. The *system* is the liquid. The x component of the force exerted by the system on the surroundings at the moving boundary, F_x^{sys}, is equal to $-F$ (F is positive and F_x^{sys} is negative). The displacement of the rod results in surface work given by Eq. 3.1.2: $đw' = -F_x^{\text{sys}}\,\mathrm{d}x = 2\gamma l\,\mathrm{d}x$. The increase in surface area, $\mathrm{d}A_{\text{s}}$, is $2l\,\mathrm{d}x$, so the surface work is $đw' = \gamma\,\mathrm{d}A_{\text{s}}$ where γ is the work coefficient and A_{s} is the work coordinate. Equation 5.2.7 becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \gamma\,\mathrm{d}A_{\text{s}} \tag{5.7.1}$$

Substitution into Eq. 5.3.6 gives

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \gamma\,\mathrm{d}A_{\text{s}} \tag{5.7.2}$$

which is the total differential of G with T, p, and A_{s} as the independent variables. Identifying the coefficient of the last term on the right side as a partial derivative, we find the following expression for the surface tension:

$$\gamma = \left(\frac{\partial G}{\partial A_{\text{s}}}\right)_{T,p} \tag{5.7.3}$$

That is, the surface tension is not only a force per unit length, but also a Gibbs energy per unit area.

From Eq. 5.7.2, we obtain the reciprocity relation

$$\left(\frac{\partial \gamma}{\partial T}\right)_{p,A_{\text{s}}} = -\left(\frac{\partial S}{\partial A_{\text{s}}}\right)_{T,p} \tag{5.7.4}$$

It is valid to replace the partial derivative on the left side by $(\partial\gamma/\partial T)_p$ because γ is independent of A_{s}. Thus, the variation of surface tension with temperature tells us how the entropy of the liquid varies with surface area.

5.8: Criteria for Spontaneity

In this section we combine the first and second laws in order to derive some general relations for changes during a reversible or irreversible process of a closed system. The temperature and pressure will be assumed to be practically uniform during the process, even if the process is irreversible. For example, the volume might be changing at a finite rate but very slowly, or there might be a spontaneous homogeneous reaction in a mixture of uniform temperature and pressure.

The second law states that $\mathrm{d}S$ is equal to $\text{đ}q/T$ if the process is reversible, and is greater than $\text{đ}q/T$ if the process is irreversible:

$$\mathrm{d}S \geq \text{đ}q/T \tag{5.8.1}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

or

$$\text{đ}q \leq T\,\mathrm{d}S \tag{5.8.2}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

The *inequalities* in these relations refer to an irreversible process and the *equalities* to a reversible process, as indicated by the notation $\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}$.

When we substitute $\text{đ}q$ from Eq. 5.8.2 into the first law in the form $\mathrm{d}U = \text{đ}q - p\,\mathrm{d}V + \text{đ}w'$, where $\text{đ}w'$ is nonexpansion work, we obtain the relation

$$\mathrm{d}U \leq T\,\mathrm{d}S - p\,\mathrm{d}V + \text{đ}w' \tag{5.8.3}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

We substitute this relation for $\mathrm{d}U$ into the differentials of enthalpy, Helmholtz energy, and Gibbs energy given by Eqs. 5.3.4–5.3.6 to obtain three more relations:

$$\mathrm{d}H \leq T\,\mathrm{d}S + V\,\mathrm{d}p + \text{đ}w' \tag{5.8.4}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

$$\mathrm{d}A \leq -S\,\mathrm{d}T - p\,\mathrm{d}V + \text{đ}w' \tag{5.8.5}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

$$\mathrm{d}G \leq -S\,\mathrm{d}T + V\,\mathrm{d}p + \text{đ}w' \tag{5.8.6}$$

$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

The last two of these relations provide valuable criteria for spontaneity under common laboratory conditions. Equation 5.8.5 shows that during a spontaneous irreversible change at constant temperature and volume, $\mathrm{d}A$ is less than $\text{đ}w'$. If the only work is expansion work (i.e., $\text{đ}w'$ is zero), the Helmholtz energy decreases during a spontaneous process at constant T and V and has its minimum value when the system reaches an equilibrium state.

Equation 5.8.6 is especially useful. From it, we can conclude the following:

- Ben-Amotz and Honig (*J. Chem. Phys.*, **118**, 5932–5936, 2003; *J. Chem. Educ.*, **83**, 132–137, 2006) developed a “rectification” procedure that simplifies the mathematical manipulation of inequalities. Following this procedure, we can write

  $$\mathrm{d}S = \text{đ}q/T + \text{đ}\theta \tag{5.8.7}$$

  where $\text{đ}\theta$ is an *excess entropy function* that is positive for an irreversible change and zero for a reversible change ($\text{đ}\theta \geq 0$). Solving for $\text{đ}q$ gives the expression $\text{đ}q = T\,\mathrm{d}S - T\,\text{đ}\theta$ that, when substituted in the first law expression $\mathrm{d}U = \text{đ}q - p\,\mathrm{d}V + \text{đ}w'$, produces

  $$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \text{đ}w' - T\,\text{đ}\theta \tag{5.8.8}$$

  The equality of this equation is equivalent to the combined equality and inequality of Eq. 5.8.3. Then by substitution of this expression for $\mathrm{d}U$ into Eqs. 5.3.4–5.3.6, we obtain equalities equivalent to Eqs. 5.8.4–5.8.6, for example

  $$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \text{đ}w' - T\,\text{đ}\theta \tag{5.8.9}$$

  Equation 5.8.9 tells us that during a process at constant T and p, with expansion work only ($\text{đ}w'=0$), $\mathrm{d}G$ has the same sign as $-T\,\text{đ}\theta$: negative for an irreversible change and zero for a reversible change.

5.9: Chapter 5 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

5.1

Show that the enthalpy of a fixed amount of an ideal gas depends only on the temperature.

5.2

From concepts in this chapter, show that the heat capacities C_V and C_p of a fixed amount of an ideal gas are functions only of T.

5.3

During the reversible expansion of a fixed amount of an ideal gas, each increment of heat is given by the expression $đq = C_V\,\mathrm{d}T + (nRT/V)\,\mathrm{d}V$ (Eq. 4.3.4).

(a) A necessary and sufficient condition for this expression to be an exact differential is that the reciprocity relation must be satisfied for the independent variables T and V (see Appendix F). Apply this test to show that the expression is *not* an exact differential, and that heat therefore is not a state function.

(b) By the same method, show that the entropy increment during the reversible expansion, given by the expression $\mathrm{d}S = đq/T$, is an exact differential, so that entropy is a state function.

5.4

This problem illustrates how an expression for one of the thermodynamic potentials as a function of its natural variables contains the information needed to obtain expressions for the other thermodynamic potentials and many other state functions.

From statistical mechanical theory, a simple model for a hypothetical "hard-sphere" liquid (spherical molecules of finite size without attractive intermolecular forces) gives the following expression for the Helmholtz energy with its natural variables T, V, and n as the independent variables:

$$A = -nRT\ln\left[cT^{3/2}\left(\frac{V}{n} - b\right)\right] - nRT + na \tag{5.9.1}$$

Here a, b, and c are constants. Derive expressions for the following state functions of this hypothetical liquid as functions of T, V, and n.

(a) The entropy, S

(b) The pressure, p

(c) The chemical potential, μ

(d) The internal energy, U

(e) The enthalpy, H

(f) The Gibbs energy, G

(g) The heat capacity at constant volume, C_V

(h) The heat capacity at constant pressure, C_p (hint: use the expression for p to solve for V as a function of T, p, and n; then use $H = U + pV$)

5.6

Use the data in Table 5.1 to evaluate $(\partial S/\partial A_\mathrm{s})_{T,p}$ at $25\,^\circ\mathrm{C}$, which is the rate at which the entropy changes with the area of the air–water interface at this temperature.

5.7

When an ordinary rubber band is hung from a clamp and stretched with constant downward force F by a weight attached to the bottom end, gentle heating is observed to cause the rubber band to contract in length. To keep the length l of the rubber band constant during heating, F must be increased. The stretching work is given by $đw' = F\,\mathrm{d}l$. From this information, find the sign of the partial derivative $(\partial T/\partial l)_{S,p}$; then predict whether stretching of the rubber band will cause a heating or a cooling effect.

(Hint: make a Legendre transform of U whose total differential has the independent variables needed for the partial derivative, and write a reciprocity relation.)

You can check your prediction experimentally by touching a rubber band to the side of your face before and after you rapidly stretch it.

CHAPTER OVERVIEW

6: The Third Law and Cryogenics

The third law of thermodynamics concerns the entropy of perfectly-ordered crystals at zero kelvins.

When a chemical reaction or phase transition is studied at low temperatures, and all substances are pure crystals presumed to be perfectly ordered, the entropy change is found to approach zero as the temperature approaches zero kelvins:

$$\lim_{T\to 0} \Delta S = 0 \tag{6.0.1}$$

$$\text{(pure, perfectly-ordered crystals)}$$

Equation 6.0.1 is the mathematical statement of the *Nernst heat theorem* or **third law of thermodynamics**. It is true in general only if each reactant and product is a pure crystal with identical unit cells arranged in perfect spatial order.

> Nernst preferred to avoid the use of the entropy function and to use in its place the partial derivative $-(\partial A/\partial T)_V$ (Eq. 5.4.9). The original 1906 version of his heat theorem was in the form $\lim_{T\to 0}(\partial \Delta A/\partial T)_V = 0$ (William H. Cropper, *J. Chem. Educ.*, **64**, 3–8, 1987).

6.1: The Zero of Entropy

There is no theoretical relation between the entropies of different chemical elements. We can arbitrarily choose the entropy of every pure crystalline element to be zero at zero kelvins. Then the experimental observation expressed by Eq. 6.0.1 requires that the entropy of every pure crystalline *compound* also be zero at zero kelvins, in order that the entropy change for the formation of a compound from its elements will be zero at this temperature.

A classic statement of the third law principle appears in the 1923 book *Thermodynamics and the Free Energy of Chemical Substances* by G. N. Lewis and M. Randall (McGraw-Hill, New York, p. 448):

> “If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature: *every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances*.”

According to this principle, every substance (element or compound) in a pure, perfectly-ordered crystal at 0 K, at any pressure, has a molar entropy of zero:

$$S_{\text{m}}(0\text{ K}) = 0 \tag{6.1.1}$$

$$\text{(pure, perfectly-ordered crystal)}$$

This convention establishes a scale of absolute entropies at temperatures above zero kelvins called **third-law entropies**, as explained in Sec. 6.2.

> The entropy becomes independent of pressure as T approaches zero kelvins. This behavior can be deduced from the relation $(\partial S/\partial p)_T = -\alpha V$ (Table 7.1) combined with the experimental observation that the cubic expansion coefficient α approaches zero as T approaches zero kelvins.

6.2: Molar Entropies

With the convention that the entropy of a pure, perfectly-ordered crystalline solid at zero kelvins is zero, we can establish the third-law value of the molar entropy of a pure substance at any temperature and pressure. Absolute values of S_{m} are what are usually tabulated for calculational use.

6.2.1 Third-law molar entropies

Suppose we wish to evaluate the entropy of an amount n of a pure substance at a certain temperature T' and a certain pressure. The same substance, in a perfectly-ordered crystal at zero kelvins and the same pressure, has an entropy of zero. The entropy at the temperature and pressure of interest, then, is the entropy change $\Delta S = \int_0^{T'} đq/T$ of a reversible heating process at constant pressure that converts the perfectly-ordered crystal at zero kelvins to the state of interest.

Consider a reversible isobaric heating process of a pure substance while it exists in a single phase. The definition of heat capacity as $đq/\,\mathrm{d}T$ (Eq. 3.1.9) allows us to substitute $C_p\,\mathrm{d}T$ for $đq$, where C_p is the heat capacity of the phase at constant pressure.

If the substance in the state of interest is a liquid or gas, or a crystal of a different form than the perfectly-ordered crystal present at zero kelvins, the heating process will include one or more equilibrium phase transitions under conditions where two phases are in equilibrium at the same temperature and pressure (Sec. 2.2.2). For example, a reversible heating process at a pressure above the triple point that transforms the crystal at $0\,\mathrm{K}$ to a gas may involve transitions from one crystal form to another, and also melting and vaporization transitions.

Each such reversible phase transition requires positive heat q_{trs}. Because the pressure is constant, the heat is equal to the enthalpy change (Eq. 5.3.8). The ratio q_{trs}/n is called the molar heat or molar enthalpy of the transition, $\Delta_{\mathrm{trs}}H$ (see Sec. 8.3.1). Because the phase transition is reversible, the entropy change during the transition is given by $\Delta_{\mathrm{trs}}S = q_{\mathrm{trs}}/nT_{\mathrm{trs}}$ where T_{trs} is the transition temperature.

With these considerations, we can write the following expression for the entropy change of the entire heating process:

$$\Delta S = \int_0^{T'} \frac{C_p}{T}\,\mathrm{d}T + \sum \frac{n\Delta_{\mathrm{trs}}H}{T_{\mathrm{trs}}} \tag{6.2.1}$$

The resulting operational equation for the calculation of the *molar* entropy of the substance at the temperature and pressure of interest is

$$S_{\mathrm{m}}(T') = \frac{\Delta S}{n} = \int_0^{T'} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T + \sum \frac{\Delta_{\mathrm{trs}}H}{T_{\mathrm{trs}}} \tag{6.2.2}$$

(pure substance, constant p)

where $C_{p,\mathrm{m}} = C_p/n$ is the molar heat capacity at constant pressure. The summation is over each equilibrium phase transition occurring during the heating process.

Since $C_{p,\mathrm{m}}$ is positive at all temperatures above zero kelvins, and $\Delta_{\mathrm{trs}}H$ is positive for all transitions occurring during a reversible heating process, the molar entropy of a substance is *positive* at all temperatures above zero kelvins.

The heat capacity and transition enthalpy data required to evaluate $S_{\mathrm{m}}(T')$ using Eq. 6.2.2 come from calorimetry. The calorimeter can be cooled to about $10\,\mathrm{K}$ with liquid hydrogen, but it is difficult to make measurements below this temperature. Statistical mechanical theory may be used to approximate the part of the integral in Eq. 6.2.2 between zero kelvins and the lowest temperature at which a value of $C_{p,\mathrm{m}}$ can be measured. The appropriate formula for nonmagnetic nonmetals comes from the Debye theory for the lattice vibration of a monatomic crystal. This theory predicts that at low temperatures (from $0\,\mathrm{K}$ to about $30\,\mathrm{K}$), the molar heat capacity at constant volume is proportional to T^3: $C_{V,\mathrm{m}} = aT^3$, where a is a constant. For a solid, the molar heat capacities at constant volume and at constant pressure are practically equal. Thus for the integral on the right side of Eq. 6.2.2 we can, to a good approximation, write

$$\int_0^{T'} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T = a\int_0^{T''} T^2\,\mathrm{d}T + \int_{T''}^{T'} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T \tag{6.2.3}$$

where T'' is the lowest temperature at which $C_{p,\mathrm{m}}$ is measured. The first term on the right side of Eq. 6.2.3 is

$$a\int_0^{T''} T^2\,\mathrm{d}T = (aT^3/3)\big|_0^{T''} = a(T'')^3/3 \tag{6.2.4}$$

But $a(T'')^3$ is the value of $C_{p,\mathrm{m}}$ at T'', so Eq. 6.2.2 becomes

$$S_\mathrm{m}(T') = \frac{C_{p,\mathrm{m}}(T'')}{3} + \int_{T''}^{T'} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T + \sum \frac{\Delta_\mathrm{trs}H}{T_\mathrm{trs}} \tag{6.2.5}$$

(pure substance,
constant p)

> In the case of a metal, statistical mechanical theory predicts an electronic contribution to the molar heat capacity, proportional to T at low temperature, that should be added to the Debye T^3 term: $C_{p,\mathrm{m}} = aT^3 + bT$. The error in using Eq. 6.2.5, which ignores the electronic term, is usually negligible if the heat capacity measurements are made down to about $10\ \mathrm{K}$.

We may evaluate the integral on the right side of Eq. 6.2.5 by numerical integration. We need the area under the curve of $C_{p,\mathrm{m}}/T$ plotted as a function of T between some low temperature, T'', and the temperature T' at which the molar entropy is to be evaluated. Since the integral may be written in the form

$$\int_{T''}^{T'} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T = \int_{T=T''}^{T=T'} C_{p,\mathrm{m}}\,\mathrm{d}\ln(T/\mathrm{K}) \tag{6.2.6}$$

we may also evaluate the integral from the area under a curve of $C_{p,\mathrm{m}}$ plotted as a function of $\ln(T/K)$.

Ideally, the molar entropy values obtained by the calorimetric (third-law) method for a gas should agree closely with the values calculated from spectroscopic data. Table 6.1 shows that for some substances this agreement is not present. The table lists values of S°_m for ideal gases at $298.15\ \mathrm{K}$evaluated by both the calorimetric and spectroscopic methods. The quantity $S_{\mathrm{m},0}$ in the last column is the difference between the two S°_m values, and is called the molar *residual entropy*.

In the case of HCl, the experimental value of the residual entropy is comparable to its uncertainty, indicating good agreement between the calorimetric and spectroscopic methods. This agreement is typical of most substances, particularly those like HCl whose molecules are polar and asymmetric with a large energetic advantage of forming perfectly-ordered crystals.

The other substances listed in Table 6.1 have residual entropies that are greater than zero within the uncertainty of the data. What is the meaning of this discrepancy between the calorimetric and spectroscopic results? We can assume that the true values of S°_m at $298.15\ \mathrm{K}$are the *spectroscopic* values, because their calculation assumes the solid has only one microstate at $0\ \mathrm{K}$, with an entropy of zero, and takes into account all of the possible accessible microstates of the ideal gas. The *calorimetric* values, on the other hand, are based on Eq. 6.2.2 which assumes the solid becomes a perfectly-ordered crystal as the temperature approaches $0\ \mathrm{K}$.

> The calorimetric values in Table 6.1 were calculated as follows. Measurements of heat capacities and heats of transition were used in Eq. 6.2.2 to find the third-law value of S_m for the vapor at the boiling point of the substance at $p = 1\ \mathrm{atm}$. This calculated value for the gas was corrected to that for the ideal gas at $p = 1\ \mathrm{bar}$ and adjusted to $T = 298.15\ \mathrm{K}$ with spectroscopic data.

The conventional explanation of a nonzero residual entropy is the presence of random rotational orientations of molecules in the solid at the lowest temperature at which the heat capacity can be measured, so that the crystals are not perfectly ordered. The random structure is established as the crystals form from the liquid, and becomes frozen into the crystals as the temperature is lowered below the freezing point. This tends to happen with almost-symmetric molecules with small dipole moments which in the crystal can have random rotational orientations of practically equal energy. In the case of solid $\mathrm{H_2O}$ it is the arrangement of intermolecular hydrogen bonds that is random. Crystal imperfections such as dislocations can also contribute to the residual entropy. If such crystal imperfection is present at the lowest experimental temperature, the calorimetric value of S°_m for the gas at $298.15\ \mathrm{K}$ is the molar entropy increase for the change at $1\ \mathrm{bar}$ from the imperfectly-ordered solid at $0\ \mathrm{K}$ to the ideal gas at $298.15\ \mathrm{K}$, and the residual entropy $S_{\mathrm{m},0}$ is the molar entropy of this imperfectly-ordered solid.

6.3: Cryogenics

The field of cryogenics involves the production of very low temperatures, and the study of the behavior of matter at these temperatures. These low temperatures are needed to evaluate third-law entropies using calorimetric measurements. There are some additional interesting thermodynamic applications.

6.3.1 Joule–Thomson expansion

A gas can be cooled by expanding it adiabatically with a piston (Sec. 3.5.3), and a liquid can be cooled by pumping on its vapor to cause evaporation (vaporization). An evaporation procedure with a refrigerant fluid is what produces the cooling in an ordinary kitchen refrigerator.

For further cooling of a fluid, a common procedure is to use a continuous **throttling process** in which the fluid is forced to flow through a porous plug, valve, or other constriction that causes an abrupt drop in pressure. A slow continuous adiabatic throttling of a gas is called the **Joule–Thomson experiment**, or Joule–Kelvin experiment, after the two scientists who collaborated between 1852 and 1862 to design and analyze this procedure. (William Thomson later became Lord Kelvin.)

Figure 6.3 illustrates the principle of the technique. The solid curve shows the temperature dependence of the entropy of a paramagnetic solid in the absence of an applied magnetic field, and the dashed curve is for the solid in a constant, finite magnetic field. The temperature range shown is from $0\,\mathrm{K}$ to approximately $1\,\mathrm{K}$. At $0\,\mathrm{K}$, the magnetic dipoles are perfectly ordered. The increase of S shown by the solid curve between $0\,\mathrm{K}$ and $1\,\mathrm{K}$ is due almost entirely to increasing disorder in the orientations of the magnetic dipoles as heat enters the system.

Path A represents the process that occurs when the paramagnetic solid, surrounded by gaseous helium in thermal contact with liquid helium that has been cooled to about $1\,\mathrm{K}$, is slowly moved into a strong magnetic field. The process is *isothermal magnetization*, which partially orients the magnetic dipoles and reduces the entropy. During this process there is heat transfer to the liquid helium, which partially boils away. In path B, the thermal contact between the solid and the liquid helium has been broken by pumping away the gas surrounding the solid, and the sample is slowly moved away from the magnetic field. This step is a reversible adiabatic demagnetization. Because the process is reversible and adiabatic, the entropy change is zero, which brings the state of the solid to a lower temperature as shown.

The sign of $(\partial T/\partial B)_{S,p}$ is of interest because it tells us the sign of the temperature change during a reversible adiabatic demagnetization (path B of Fig. 6.3). To change the independent variables in Eq. 6.3.4 to S, p, and B, we define the Legendre transform

$$H' \overset{\text{def}}{=} U + pV - Bm_{\text{mag}} \tag{6.3.5}$$

(H' is sometimes called the *magnetic enthalpy*.) From Eqs. 6.3.4 and 6.3.5 we obtain the total differential

$$\mathrm{d}H' = T\,\mathrm{d}S + V\,\mathrm{d}p - m_{\text{mag}}\,\mathrm{d}B \tag{6.3.6}$$

From it we find the reciprocity relation

$$\left(\frac{\partial T}{\partial B}\right)_{S,p} = -\left(\frac{\partial m_{\text{mag}}}{\partial S}\right)_{p,B} \tag{6.3.7}$$

According to Curie's law of magnetization, the magnetic dipole moment m_{mag} of a paramagnetic phase at constant magnetic flux density B is proportional to $1/T$. This law applies when B is small, but even if B is not small m_{mag} decreases with increasing T. To increase the temperature of a phase at constant B, we allow heat to enter the system, and S then increases. Thus, $(\partial m_{\text{mag}}/\partial S)_{p,B}$ is negative and, according to Eq. 6.3.7, $(\partial T/\partial B)_{S,p}$ must be positive. Adiabatic demagnetization is a constant-entropy process in which B decreases, and therefore the temperature also *decreases*.

We can find the sign of the entropy change during the isothermal magnetization process shown as path A in Fig. 6.3. In order to use T, p, and B as the independent variables, we define the Legendre transform $G' \overset{\text{def}}{=} H' - TS$. Its total differential is

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}p - m_{\text{mag}}\,\mathrm{d}B \tag{6.3.8}$$

From this total differential, we obtain the reciprocity relation

$$\left(\frac{\partial S}{\partial B}\right)_{T,p} = \left(\frac{\partial m_{\text{mag}}}{\partial T}\right)_{p,B} \tag{6.3.9}$$

Since m_{mag} at constant B decreases with increasing T, as explained above, we see that the entropy change during isothermal magnetization is *negative*.

By repeatedly carrying out a procedure of isothermal magnetization and adiabatic demagnetization, starting each stage at the temperature produced by the previous stage, it has been possible to attain a temperature as low as $0.0015\,\text{K}$. The temperature can be reduced still further, down to 16 microkelvins, by using adiabatic nuclear demagnetization. However, as is evident from the figure, if in accordance with the third law both of the entropy curves come together at the absolute zero of the kelvin scale, then it is not possible to attain a temperature of zero kelvins in a finite number of stages of adiabatic demagnetization. This conclusion is called the *principle of the unattainability of absolute zero*.

6.4: Chapter 6 Problem

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

6.1

Calculate the molar entropy of carbon disulfide at $25.00\,^\circ\mathrm{C}$ and $1\ \mathrm{bar}$ from the heat capacity data for the solid in Table 6.2 and the following data for $p = 1\ \mathrm{bar}$. At the melting point, $161.11\ \mathrm{K}$, the molar enthalpy of fusion is $\Delta_{\mathrm{fus}}H = 4.39 \times 10^{3}\ \mathrm{J\ mol^{-1}}$. The molar heat capacity of the liquid in the range 161–300 K is described by $C_{p,\mathrm{m}} = a + bT$, where the constants have the values $a = 74.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $b = 0.0034\ \mathrm{J\ K^{-2}\ mol^{-1}}$.

CHAPTER OVERVIEW

7: Pure Substances in Single Phases

This chapter applies concepts introduced in earlier chapters to the simplest kind of system, one consisting of a pure substance or a single component in a single phase. The system has three independent variables if it is open, and two if it is closed. Relations among various properties of a single phase are derived, including temperature, pressure, and volume. The important concepts of standard states and chemical potential are introduced.

7.1: Volume Properties

Two volume properties of a closed system are defined as follows:

$$\textbf{cubic expansion coefficient} \quad \alpha \overset{\text{def}}{=} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{7.1.1}$$

$$\textbf{isothermal compressibility} \quad \kappa_T \overset{\text{def}}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{7.1.2}$$

> The cubic expansion coefficient is also called the coefficient of thermal expansion and the expansivity coefficient. Other symbols for the isothermal compressibility are β and γ_T.

These definitions show that α is the fractional volume increase per unit temperature increase at constant pressure, and κ_T is the fractional volume decrease per unit pressure increase at constant temperature. Both quantities are *intensive* properties. Most substances have positive values of α, and all substances have positive values of κ_T, because a pressure increase at constant temperature requires a volume decrease.

> The cubic expansion coefficient is not always positive. α is negative for liquid water below its temperature of maximum density, $3.98\,^{\circ}\mathrm{C}$. The crystalline ceramics zirconium tungstate ($\mathrm{ZrW_2O_8}$) and hafnium tungstate ($\mathrm{HfW_2O_8}$) have the remarkable behavior of contracting uniformly and continuously in all three dimensions when they are heated from $0.3\,\mathrm{K}$ to about $1050\,\mathrm{K}$; α is negative throughout this very wide temperature range (T. A. Mary et al, *Science*, **272**, 90–92, 1996). The intermetallic compound YbGaGe has been found to have a value of α that is practically zero in the range 100–$300\,\mathrm{K}$ (James R. Salvador et al, *Nature*, **425**, 702–705, 2003).

If an amount n of a substance is in a single phase, we can divide the numerator and denominator of the right sides of Eqs. 7.1.1 and 7.1.2 by n to obtain the alternative expressions

$$\alpha = \frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p \tag{7.1.3}$$

(pure substance, P=1)

$$\kappa_T = -\frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_T \tag{7.1.4}$$

(pure substance, P=1)

where V_{m} is the molar volume. P in the conditions of validity is the number of phases. Note that only intensive properties appear in Eqs. 7.1.3 and 7.1.4; the amount of the substance is irrelevant. Figures 7.1 and 7.2 show the temperature variation of α and κ_T for several substances.

If we choose T and p as the independent variables of the closed system, the total differential of V is given by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p \tag{7.1.5}$$

With the substitutions $(\partial V/\partial T)_p = \alpha V$ (from Eq. 7.1.1) and $(\partial V/\partial p)_T = -\kappa_T V$ (from Eq. 7.1.2), the expression for the total differential of V becomes

$$\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p \tag{7.1.6}$$

(closed system,
C=1, P=1)

To find how p varies with T in a closed system kept at constant volume, we set $\mathrm{d}V$ equal to zero in Eq. 7.1.6: $0 = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p$, or $\mathrm{d}p/\,\mathrm{d}T = \alpha/\kappa_T$. Since $\mathrm{d}p/\,\mathrm{d}T$ under the condition of constant volume is the partial derivative $(\partial p/\partial T)_V$, we have the general relation

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} \tag{7.1.7}$$

(closed system,
C=1, P=1)

7.2: Internal Pressure

The partial derivative $(\partial U / \partial V)_T$ applied to a fluid phase in a closed system is called the **internal pressure**. (Note that U and pV have dimensions of energy; therefore, U/V has dimensions of pressure.)

To relate the internal pressure to other properties, we divide Eq. 5.2.2 by $\mathrm{d}V$: $\mathrm{d}U/\mathrm{d}V = T(\mathrm{d}S/\mathrm{d}V) - p$. Then we impose a condition of constant T: $(\partial U/\partial V)_T = T(\partial S/\partial V)_T - p$. When we make a substitution for $(\partial S/\partial V)_T$ from the Maxwell relation of Eq. 5.4.17, we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{7.2.1}$$

(closed system,
fluid phase, C=1)

This equation is sometimes called the “thermodynamic equation of state” of the fluid.

For an ideal-gas phase, we can write $p = nRT/V$ and then

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \tag{7.2.2}$$

Making this substitution in Eq. 7.2.1 gives us

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{7.2.3}$$

(closed system of an ideal gas)

showing that the internal pressure of an ideal gas is zero.

> In Sec. 3.5.1, an ideal gas was defined as a gas (1) that obeys the ideal gas equation, and (2) for which U in a closed system depends only on T. Equation 7.2.3, derived from the first part of this definition, expresses the second part. It thus appears that the second part of the definition is redundant, and that we could define an ideal gas simply as a gas obeying the ideal gas equation. This argument is valid only if we assume the ideal-gas temperature is the same as the thermodynamic temperature (Secs. 2.3.5 and 4.3.4) since this assumption is required to derive Eq. 7.2.3. Without this assumption, we can’t define an ideal gas solely by $pV = nRT$, where T is the ideal gas temperature.

Here is a simplified interpretation of the significance of the internal pressure. When the volume of a fluid increases, the average distance between molecules increases and the potential energy due to intermolecular forces changes. If attractive forces dominate, as they usually do unless the fluid is highly compressed, expansion causes the potential energy to *increase*. The internal energy is the sum of the potential energy and thermal energy. The internal pressure, $(\partial U/\partial V)_T$, is the rate at which the internal energy changes with volume at constant temperature. At constant temperature, the thermal energy is constant so that the internal pressure is the rate at which just the potential energy changes with volume. Thus, the internal pressure is a measure of the strength of the intermolecular forces and is positive if attractive forces dominate. (These attractive intermolecular forces are the cohesive forces that can allow a negative pressure to exist in a liquid; see Sec. 2.3.4.) In an ideal gas, intermolecular forces are absent and therefore the internal pressure of an ideal gas is zero.

With the substitution $(\partial p/\partial T)_V = \alpha/\kappa_T$ (Eq. 7.1.7), Eq. 7.2.1 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p \tag{7.2.4}$$

(closed system,
fluid phase, C=1)

The internal pressure of a liquid at $p = 1$ bar is typically much larger than 1 bar (see Prob. 7.6). Equation 7.2.4 shows that, in this situation, the internal pressure is approximately equal to $\alpha T/\kappa_T$.

7.3: Thermal Properties

For convenience in derivations to follow, expressions from Chap. 5 are repeated here that apply to processes in a closed system in the absence of nonexpansion work (i.e., $đw' = 0$). For a process at constant volume we have [3]

$$\mathrm{d}U = \mathrm{d}q \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{7.3.1}$$

and for a process at constant pressure we have [4]

$$\mathrm{d}H = \mathrm{d}q \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{7.3.2}$$

A closed system of one component in a single phase has only two independent variables. In such a system, the partial derivatives above are complete and unambiguous definitions of C_V and C_p because they are expressed with two independent variables- T and V for C_V, and T and p for C_p. As mentioned on page 146, additional conditions would have to be specified to define C_V for a more complicated system; the same is true for C_p.

For a closed system of an ideal gas we have 5

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \quad C_p = \frac{\mathrm{d}H}{\mathrm{d}T} \tag{7.3.3}$$

7.3.1 The relation between $C_{V,\mathrm{m}}$ and $C_{p,\mathrm{m}}$

The value of $C_{p,\mathrm{m}}$ for a substance is greater than $C_{V,\mathrm{m}}$. The derivation is simple in the case of a fixed amount of an ideal gas. Using substitutions from Eq. 7.3.3, we write

$$C_p - C_V = \frac{\mathrm{d}H}{\mathrm{d}T} - \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{\mathrm{d}(H-U)}{\mathrm{d}T} = \frac{\mathrm{d}(pV)}{\mathrm{d}T} = nR \tag{7.3.4}$$

Division by n to obtain molar quantities and rearrangement then gives

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R \tag{7.3.5}$$

For any phase in general, we proceed as follows. First we write

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left[\frac{\partial(U+pV)}{\partial T}\right]_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{7.3.6}$$

Then we write the total differential of U with T and V as independent variables and identify one of the coefficients as C_V :

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = C_V\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \tag{7.3.7}$$

When we divide both sides of the preceding equation by $\mathrm{d}T$ and impose a condition of constant p, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{7.3.8}$$

Substitution of this expression for $(\partial U/\partial T)_p$ in the equation for C_p yields

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{7.3.9}$$

Finally we set the partial derivative $(\partial U/\partial V)_T$ (the internal pressure) equal to $(\alpha T/\kappa_T) - p$ (Eq. 7.2.4) and $(\partial V/\partial T)_p$ equal to αV to obtain

$$C_p = C_V + \frac{\alpha^2 TV}{\kappa_T} \tag{7.3.10}$$

and divide by n to obtain molar quantities:

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + \frac{\alpha^2 T V_{\mathrm{m}}}{\kappa_T} \tag{7.3.11}$$

Since the quantity $\alpha^2 T V_{\mathrm{m}} / \kappa_T$ must be positive, $C_{p,\mathrm{m}}$ is greater than $C_{V,\mathrm{m}}$.

7.3.2 The measurement of heat capacities

The most accurate method of evaluating the heat capacity of a phase is by measuring the temperature change resulting from heating with electrical work. The procedure in general is called calorimetry, and the apparatus containing the phase of interest and the electric heater is a calorimeter. The principles of three commonly-used types of calorimeters with electrical heating are described below.

Adiabatic calorimeters

An adiabatic calorimeter is designed to have negligible heat flow to or from its surroundings. The calorimeter contains the phase of interest, kept at either constant volume or constant pressure, and also an electric heater and a temperature-measuring device such as a platinum resistance thermometer, thermistor, or quartz crystal oscillator. The contents may be stirred to ensure temperature uniformity.

To minimize conduction and convection, the calorimeter usually is surrounded by a jacket separated by an air gap or an evacuated space. The outer surface of the calorimeter and inner surface of the jacket may be polished to minimize radiation emission from these surfaces. These measures, however, are not sufficient to ensure a completely adiabatic boundary, because energy can be transferred by heat along the mounting hardware and through the electrical leads. Therefore, the temperature of the jacket, or of an outer metal shield, is adjusted throughout the course of the experiment so as to be as close as possible to the varying temperature of the calorimeter. This goal is most easily achieved when the temperature change is slow.

To make a heat capacity measurement, a constant electric current is passed through the heater circuit for a known period of time. The system is the calorimeter and its contents. The electrical work w_{el} performed on the system by the heater circuit is calculated from the integrated form of Eq. $3.8.5$ on page 91: $w_{\mathrm{el}} = I^2 R_{\mathrm{el}} \Delta t$, where I is the electric current, R_{el} is the electric resistance, and Δt is the time interval. We assume the boundary is adiabatic and write the first law in the form

$$\mathrm{d}U = -p\,\mathrm{d}V + \mathrm{d}w_{\mathrm{el}} + \mathrm{d}w_{\mathrm{cont}} \tag{7.3.12}$$

where $-p\,\mathrm{d}V$ is expansion work and w_{cont} is any continuous mechanical work from stirring (the subscript "cont" stands for continuous). If electrical work is done on the system by a thermometer using an external electrical circuit, such as a platinum resistance thermometer, this work is included in w_{cont}.

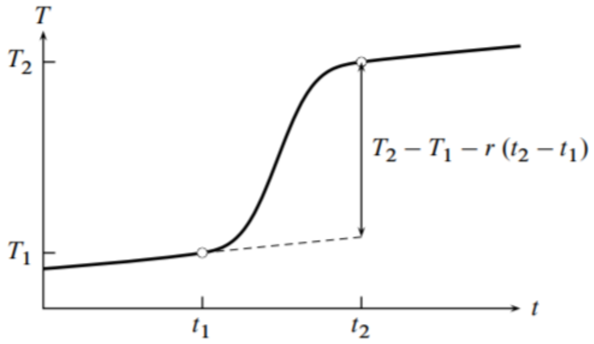


Figure 7.3: Typical heating curve of an adiabatic calorimet

Consider first an adiabatic calorimeter in which the heating process is carried out at constant volume. There is no expansion work, and Eq. $7.3.12$ becomes

$$\mathrm{d}U = \mathrm{d}w_{\mathrm{el}} + \mathrm{d}w_{\mathrm{cont}} \tag{7.3.13}$$

(constant V)

An example of a measured heating curve (temperature T as a function of time t) is shown in Fig. 7.3. We select two points on the heating curve, indicated in the figure by open circles. Time t_1 is at or shortly before the instant the heater circuit is closed and electrical heating begins, and time t_2 is after the heater circuit has been opened and the slope of the curve has become essentially constant.

In the time periods before t_1 and after t_2, the temperature may exhibit a slow rate of increase due to the continuous work w_{cont} from stirring and temperature measurement. If this work is performed at a constant rate throughout the course of the experiment, the slope is constant and the same in both time periods as shown in the figure.

The relation between the slope and the rate of work is given by a quantity called the energy equivalent, ϵ. The energy equivalent is the heat capacity of the calorimeter under the conditions of an experiment. The heat capacity of a constant-volume calorimeter is given by $\epsilon = (\partial U/\partial T)_V$ (Eq. 5.6.1). Thus, at times before t_1 or after t_2, when $đ\, w_{\text{el}}$ is zero and $\mathrm{d}U$ equals w_{cont}, the slope r of the heating curve is given by

$$r = \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\mathrm{d}T}{\mathrm{d}U}\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{1}{\epsilon}\frac{\mathrm{d}w_{\text{cont}}}{\mathrm{d}t} \tag{7.3.14}$$

The rate of the continuous work is therefore $\mathrm{d}w_{\text{cont}}/\mathrm{d}t = \epsilon r$. This rate is constant throughout the experiment. In the time interval from t_1 to t_2, the total quantity of continuous work is $w_{\text{cont}} = \epsilon r(t_2 - t_1)$, where r is the slope of the heating curve measured outside this time interval.

To find the energy equivalent, we integrate Eq. $7.3.13$ between the two points on the curve:

$$\Delta U = w_{\text{el}} + w_{\text{cont}} = w_{\text{el}} + \epsilon r(t_2 - t_1) \tag{7.3.15}$$

(constant V)

Then the average heat capacity between temperatures T_1 and T_2 is

$$\epsilon = \frac{\Delta U}{T_2 - T_1} = \frac{w_{\text{el}} + \epsilon r(t_2 - t_1)}{T_2 - T_1} \tag{7.3.16}$$

Solving for ϵ, we obtain

$$\epsilon = \frac{w_{\text{el}}}{T_2 - T_1 - r(t_2 - t_1)} \tag{7.3.17}$$

The value of the denominator on the right side is indicated by the vertical line in Fig. 7.3. It is the temperature change that would have been observed if the same quantity of electrical work had been performed without the continuous work.

Next, consider the heating process in a calorimeter at constant pressure. In this case the enthalpy change is given by $\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V$ which, with substitution from Eq. 7.3.12, becomes

$$\mathrm{d}H = \mathrm{d}w_{\text{el}} + \mathrm{d}w_{\text{cont}} \tag{7.3.18}$$

(constant p)

We follow the same procedure as for the constant-volume calorimeter, using Eq. $7.3.18$ in place of Eq. $7.3.13$ and equating the energy equivalent ϵ to $(\partial H/\partial T)_p$, the heat capacity of the calorimeter at constant pressure (Eq. 5.6.3). We obtain the relation

$$\Delta H = w_{\text{el}} + w_{\text{cont}} = w_{\text{el}} + \epsilon r(t_2 - t_1) \tag{7.3.19}$$

(constant p)

in place of Eq. $7.3.15$ and end up again with the expression of Eq. $7.3.17$ for ϵ.

The value of ϵ calculated from Eq. $7.3.17$ is an average value for the temperature interval from T_1 to T_2, and we can identify this value with the heat capacity at the temperature of the midpoint of the interval. By taking the difference of values of ϵ measured with and without the phase of interest present in the calorimeter, we obtain C_V or C_p for the phase alone.

It may seem paradoxical that we can use an adiabatic process, one without heat, to evaluate a quantity defined by heat (heat capacity $= \mathrm{d}q/\mathrm{d}T$). The explanation is that energy transferred into the adiabatic calorimeter as electrical work, and dissipated completely to thermal energy, substitutes for the heat that would be needed for the same change of state without electrical work.

Isothermal-jacket calorimeters

A second common type of calorimeter is similar in construction to an adiabatic calorimeter, except that the surrounding jacket is maintained at constant temperature. It is sometimes called an isoperibol calorimeter. A correction is made for heat transfer resulting from the difference in temperature across the gap separating the jacket from the outer surface of the calorimeter. It is important in making this correction that the outer surface have a uniform temperature without "hot spots."

Assume the outer surface of the calorimeter has a uniform temperature T that varies with time, the jacket temperature has a constant value T_{ext} , and convection has been eliminated by evacuating the gap. Then heat transfer is by conduction and radiation, and its rate

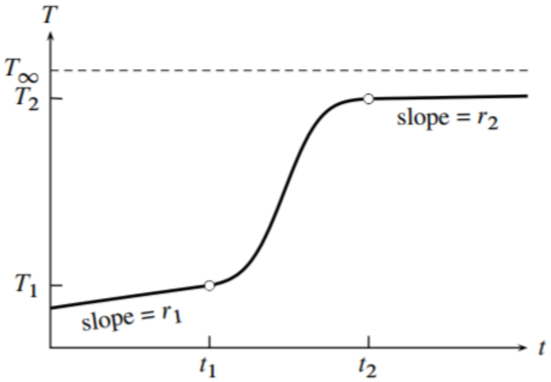


Figure 7.4 Typical heating curve of an isothermal-jacket calorimeter

is given by Newton's law of cooling

$$\frac{\text{d}q}{\text{d}t} = -k\left(T - T_{\text{ext}}\right) \tag{7.3.20}$$

where k is a constant (the thermal conductance). Heat flows from a warmer to a cooler body, so $\text{đ}\, q/\text{d}t$ is positive if T is less than T_{ext} and negative if T is greater than T_{ext} .

The possible kinds of work are the same as for the adiabatic calorimeter: expansion work $-p\,\text{d}V$, intermittent work w_{el} done by the heater circuit, and continuous work w_{cont} . By combining the first law and Eq. 7.3.20, we obtain the following relation for the rate at which the internal energy changes:

$$\frac{\text{d}U}{\text{d}t} = \frac{\text{d}q}{\text{d}t} + \frac{\text{d}w}{\text{d}t} = -k\left(T - T_{\text{ext}}\right) - p\frac{\text{d}V}{\text{d}t} + \frac{\text{d}w_{\text{el}}}{\text{d}t} + \frac{\text{d}w_{\text{cont}}}{\text{d}t} \tag{7.3.21}$$

For heating at constant volume $(\text{d}V/\text{d}t = 0)$, this relation becomes

$$\frac{\text{d}U}{\text{d}t} = -k\left(T - T_{\text{ext}}\right) + \frac{\text{d}w_{\text{el}}}{\text{d}t} + \frac{\text{d}w_{\text{cont}}}{\text{d}t} \tag{7.3.22}$$

(constant V)

An example of a heating curve is shown in Fig. 7.4. In contrast to the curve of Fig. 7.3, the slopes are different before and after the heating interval due to changed rate of heat flow. Times t_1 and t_2 are before and after the heater circuit is closed. In any time interval before time t_1 or after time t_2, the system behaves as if it is approaching a steady state of constant temperature T_∞ (called the convergence temperature), which it would eventually reach if the experiment were continued without closing the heater circuit. T_∞ is greater than T_{ext} because of the energy transferred to the system by stirring and electrical temperature measurement. By setting $\text{d}U/\text{d}t$ and $\text{d}w_{\text{el}}/\text{d}t$ equal to zero and T equal to T_∞ in Eq. 7.3.22, we obtain $\text{đ}\, w_{\text{cont}}\,/\text{d}t = k\left(T_\infty - T_{\text{ext}}\right)$. We assume d $w_{\text{cont}}\,/\text{d}t$ is constant. Substituting this expression into Eq. $7.3.22$ gives us a general expression for the rate at which U changes in terms of the unknown quantities k and T_∞ :

$$\frac{\text{d}U}{\text{d}t} = -k\left(T - T_\infty\right) + \frac{\text{d}w_{\text{el}}}{\text{d}t} \tag{7.3.23}$$

(constant V)

This relation is valid throughout the experiment, not only while the heater circuit is closed. If we multiply by $\mathrm{d}t$ and integrate from t_1 to t_2, we obtain the internal energy change in the time interval from t_1 to t_2 :

$$\Delta U = -k \int_{t_1}^{t_2} (T - T_\infty)\,\mathrm{d}t + w_{\text{el}} \tag{7.3.24}$$

(constant V)

All the intermittent work w_{el} is performed in this time interval.

The derivation of Eq. $7.3.24$ is a general one. The equation can be applied also to a isothermal-jacket calorimeter in which a reaction is occurring. Section $11.5.2$ will mention the use of this equation for an internal energy correction of a reaction calorimeter with an isothermal jacket.

The average value of the energy equivalent in the temperature range T_1 to T_2 is

$$\epsilon = \frac{\Delta U}{T_2 - T_1} = \frac{-\epsilon(k/\epsilon)\int_{t_1}^{t_2} (T - T_\infty)\,\mathrm{d}t + w_{\text{el}}}{T_2 - T_1} \tag{7.3.25}$$

Solving for ϵ, we obtain

$$\epsilon = \frac{w_{\text{el}}}{(T_2 - T_1) + (k/\epsilon)\int_{t_1}^{t_2} (T - T_\infty)\,\mathrm{d}t} \tag{7.3.26}$$

The value of w_{el} is known from $w_{\text{el}} = I^2 R_{\text{el}} \Delta t$, where Δt is the time interval during which the heater circuit is closed. The integral can be evaluated numerically once T_∞ is known.
For heating at constant pressure, $\mathrm{d}H$ is equal to $\mathrm{d}U + p\,\mathrm{d}V$, and we can write

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\mathrm{d}U}{\mathrm{d}t} + p\frac{\mathrm{d}V}{\mathrm{d}t} = -k(T - T_{\text{ext}}) + \frac{\mathrm{d}w_{\text{el}}}{\mathrm{d}t} + \frac{\mathrm{d}w_{\text{cont}}}{\mathrm{d}t} \tag{7.3.27}$$

(constant p)

which is analogous to Eq. 7.3.22. By the procedure described above for the case of constant V, we obtain

$$\Delta H = -k \int_{t_1}^{t_2} (T - T_\infty)\,\mathrm{d}t + w_{\text{el}} \tag{7.3.28}$$

(constant p)

At constant p, the energy equivalent is equal to $C_p = \Delta H/(T_2 - T_1)$, and the final expression for ϵ is the same as that given by Eq. 7.3.26.

To obtain values of k/ϵ and T_∞ for use in Eq. 7.3.26, we need the slopes of the heating curve in time intervals (rating periods) just before t_1 and just after t_2. Consider the case of constant volume. In these intervals, $\mathrm{d}w_{\text{el}}/\mathrm{d}t$ is zero and $\mathrm{d}U/\mathrm{d}t$ equals $-k(T - T_\infty)$ (from Eq. 7.3.23). The heat capacity at constant volume is $C_V = \mathrm{d}U/\mathrm{d}T$. The slope r in general is then given by

$$r = \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\mathrm{d}T}{\mathrm{d}U}\frac{\mathrm{d}U}{\mathrm{d}t} = -(k/\epsilon)(T - T_\infty) \tag{7.3.29}$$

Applying this relation to the points at times t_1 and t_2, we have the following simultaneous equations in the unknowns k/ϵ and T_∞ :

$$r_1 = -(k/\epsilon)(T_1 - T_\infty) \qquad r_2 = -(k/\epsilon)(T_2 - T_\infty) \tag{7.3.30}$$

The solutions are

$$(k/\epsilon) = \frac{r_1 - r_2}{T_2 - T_1} \qquad T_\infty = \frac{r_1 T_2 - r_2 T_1}{r_1 - r_2} \tag{7.3.31}$$

Finally, k is given by

$$k = (k/\epsilon)\epsilon = \left(\frac{r_1 - r_2}{T_2 - T_1}\right)\epsilon \tag{7.3.32}$$

When the pressure is constant, this procedure yields the same relations for k/ϵ, T_∞, and k.

Continuous-flow calorimeters

A flow calorimeter is a third type of calorimeter used to measure the heat capacity of a fluid phase. The gas or liquid flows through a tube at a known constant rate past an electrical heater of known constant power input. After a steady state has been achieved in the tube, the temperature increase $\backslash\mathrm{Del}T$ at the heater is measured.

If $\backslash\mathrm{dw}\backslash\mathrm{el}/\backslash\mathrm{dt}$ is the rate at which electrical work is performed (the electric power) and $\backslash\mathrm{dif}m/\backslash\mathrm{dt}$ is the mass flow rate, then in time interval $\backslash\mathrm{Del}t$ a quantity $w = (\backslash\mathrm{dw}\backslash\mathrm{el}/\backslash\mathrm{dt})\backslash\mathrm{Del}t$ of work is performed on an amount $n = (\backslash\mathrm{dif}m/\backslash\mathrm{dt})\backslash\mathrm{Del}t/M$ of the fluid (where M is the molar mass). If heat flow is negligible, the molar heat capacity of the substance is given by

$$\backslash\mathrm{Cpm} = \frac{w}{n\backslash\mathrm{Del}T} = \frac{M(\backslash\mathrm{dw}\backslash\mathrm{el}/\backslash\mathrm{dt})}{\backslash\mathrm{Del}T(\backslash\mathrm{dif}m/\backslash\mathrm{dt})} \tag{7.3.33}$$

To correct for the effects of heat flow, $\backslash\mathrm{Del}T$ is usually measured over a range of flow rates and the results extrapolated to infinite flow rate.

7.3.3 Typical values

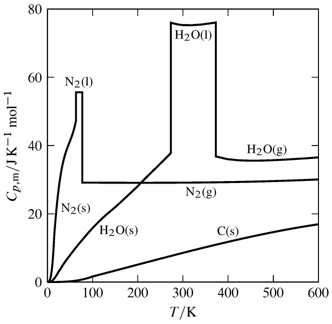


Figure 7.5 Temperature dependence of molar heat capacity at constant pressure ($p = 1\backslash\mathrm{br}$) of H_2O, N_2, and C(graphite).

Figure 7.5 shows the temperature dependence of $\backslash\mathrm{Cpm}$ for several substances. The discontinuities seen at certain temperatures occur at equilibrium phase transitions. At these temperatures the heat capacity is in effect infinite, since the phase transition of a pure substance involves finite heat with zero temperature change.

7.4: Heating at Constant Volume or Pressure

Consider the process of changing the temperature of a phase at constant volume.

> Keeping the volume exactly constant while increasing the temperature is not as simple as it may sound. Most solids expand when heated, unless we arrange to increase the external pressure at the same time. If we use solid walls to contain a fluid phase, the container volume will change with temperature. For practical purposes, these volume changes are usually negligible.

The rate of change of internal energy with T at constant V is the heat capacity at constant volume: $C_V = (\partial U/\partial T)_V$ (Eq. 7.3.1). Accordingly, an infinitesimal change of U is given by

$$\mathrm{d}U = C_V\,\mathrm{d}T \tag{7.4.1}$$

(closed system,
C=1, P=1, constant V)

and the finite change of U between temperatures T_1 and T_2 is

$$\Delta U = \int_{T_1}^{T_2} C_V\,\mathrm{d}T \tag{7.4.2}$$

(closed system,
C=1, P=1, constant V)

Three comments, relevant to these and other equations in this chapter, are in order:

1.
2. If, at a fixed volume and over the temperature range T_1 to T_2, the value of C_V is essentially constant (i.e., independent of T), Eq. 7.4.2 becomes

$$\Delta U = C_V(T_2 - T_1) \tag{7.4.5}$$

(closed system, C=1,
P=1, constant V and C_V)

An infinitesimal entropy change during a reversible process in a closed system is given according to the second law by $\mathrm{d}S = đq/T$. At constant volume, $đq$ is equal to $\mathrm{d}U$ which in turn equals $C_V\,\mathrm{d}T$. Therefore, the entropy change is

$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T \tag{7.4.6}$$

(closed system,
C=1, P=1, constant V)

Integration yields the finite change

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T}\,\mathrm{d}T \tag{7.4.7}$$

(closed system,
C=1, P=1, constant V)

If C_V is treated as constant, Eq. 7.4.7 becomes

$$\Delta S = C_V \ln\frac{T_2}{T_1} \tag{7.4.8}$$

(closed system, C=1,
P=1, constant V and C_V)

(More general versions of the two preceding equations have already been given in Sec. 4.6.1.)

We may derive relations for a temperature change at constant *pressure* by the same methods. From $C_p = (\partial H/\partial T)_p$ (Eq. 7.3.2), we obtain

$$\Delta H = \int_{T_1}^{T_2} C_p\,\mathrm{d}T \tag{7.4.9}$$

(closed system,
C=1, P=1, constant p)

If C_p is treated as constant, Eq. 7.4.9 becomes

$$\Delta H = C_p(T_2 - T_1) \tag{7.4.10}$$

(closed system, $C{=}1$, $P{=}1$, constant p and C_p)

From $\mathrm{d}S = đq/T$ and Eq. 7.3.2 we obtain for the entropy change at constant pressure

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T \tag{7.4.11}$$

(closed system, $C{=}1$, $P{=}1$, constant p)

Integration gives

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\,\mathrm{d}T \tag{7.4.12}$$

(closed system, $C{=}1$, $P{=}1$, constant p)

or, with C_p treated as constant,

$$\Delta S = C_p \ln\frac{T_2}{T_1} \tag{7.4.13}$$

(closed system, $C{=}1$, $P{=}1$, constant p and C_p)

C_p is positive, so heating a phase at constant pressure causes H and S to increase.

The Gibbs energy changes according to $(\partial G/\partial T)_p = -S$ (Eq. 5.4.11), so heating at constant pressure causes G to decrease.

7.5: Partial Derivatives with Respect to T T , p p , and V V

7.5.1 Tables of partial derivatives

The tables in this section collect useful expressions for partial derivatives of the eight state functions T, p, V, U, H, A, G, and S in a closed, single-phase system. Each derivative is taken with respect to one of the three easily-controlled variables T, p, or V while another of these variables is held constant. We have already seen some of these expressions, and the derivations of the others are indicated below.

We can use these partial derivatives (1) for writing an expression for the total differential of any of the eight quantities, and (2) for expressing the finite change in one of these quantities as an integral under conditions of constant T, p, or V. For instance, given the expressions

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\alpha V \tag{7.5.1}$$

we may write the total differential of S, taking T and p as the independent variables, as

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T - \alpha V\,\mathrm{d}p \tag{7.5.2}$$

Furthermore, the first expression is equivalent to the differential form

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T \tag{7.5.3}$$

provided p is constant; we can integrate this equation to obtain the finite change ΔS under isobaric conditions as shown in Eq. 7.4.12.

Both general expressions and expressions valid for an ideal gas are given in Tables 7.1, 7.2, and 7.3.

> We may derive the general expressions as follows. We are considering differentiation with respect only to T, p, and V. Expressions for $(\partial V/\partial T)_p$, $(\partial V/\partial p)_T$, and $(\partial p/\partial T)_V$ come from Eqs. 7.1.1, 7.1.2, and 7.1.7 and are shown as functions of α and κ_T. The reciprocal of each of these three expressions provides the expression for another partial derivative from the general relation
>
> $$(\partial y/\partial x)_z = \frac{1}{(\partial x/\partial y)_z} \tag{7.5.4}$$
>
> This procedure gives us expressions for the six partial derivatives of T, p, and V.
>
> The remaining expressions are for partial derivatives of U, H, A, G, and S. We obtain the expression for $(\partial U/\partial T)_V$ from Eq. 7.3.1, for $(\partial U/\partial V)_T$ from Eq. 7.2.4, for $(\partial H/\partial T)_p$ from Eq. 7.3.2, for $(\partial A/\partial T)_V$ from Eq. 5.4.9, for $(\partial A/\partial V)_T$ from Eq. 5.4.10, for $(\partial G/\partial p)_T$ from Eq. 5.4.12, for $(\partial G/\partial T)_p$ from Eq. 5.4.11, for $(\partial S/\partial T)_V$ from Eq. 7.4.6, for $(\partial S/\partial T)_p$ from Eq. 7.4.11, and for $(\partial S/\partial p)_T$ from Eq. 5.4.18.
>
> We can transform each of these partial derivatives, and others derived in later steps, to two other partial derivatives with the same variable held constant and the variable of differentiation changed. The transformation involves multiplying by an appropriate partial derivative of T, p, or V. For instance, from the partial derivative $(\partial U/\partial V)_T = (\alpha T/\kappa_T) - p$, we obtain
>
> $$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\alpha T}{\kappa_T} - p\right)(-\kappa_T V) = (-\alpha T + \kappa_T p)\,V \tag{7.5.5}$$
>
> The remaining partial derivatives can be found by differentiating $U = H - pV$, $H = U + pV$, $A = U - TS$, and $G = H - TS$ and making appropriate substitutions. Whenever a partial derivative appears in a derived expression, it is replaced with an expression derived in an earlier step. The expressions derived by these steps constitute the full set shown in Tables 7.1, 7.2, and 7.3.
>
> Bridgman devised a simple method to obtain expressions for these and many other partial derivatives from a relatively small set of formulas (*Phys. Rev.*, **3**, 273–281, 1914; *The Thermodynamics of Electrical Phenomena in*

Metals and a Condensed Collection of Thermodynamic Formulas, Dover, New York, 1961, p. 199–241).

7.5.2 The Joule–Thomson coefficient

The Joule–Thomson coefficient of a gas was defined in Eq. 6.3.3 by $\mu_{\text{JT}} = (\partial T/\partial p)_H$. It can be evaluated with measurements of T and p during adiabatic throttling processes as described in Sec. 6.3.1.

To relate μ_{JT} to other properties of the gas, we write the total differential of the enthalpy of a closed, single-phase system in the form

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \tag{7.5.6}$$

and divide both sides by $\mathrm{d}p$:

$$\frac{\mathrm{d}H}{\mathrm{d}p} = \left(\frac{\partial H}{\partial T}\right)_p \frac{\mathrm{d}T}{\mathrm{d}p} + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.7}$$

Next we impose a condition of constant H; the ratio $\mathrm{d}T/\,\mathrm{d}p$ becomes a partial derivative:

$$0 = \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.8}$$

Rearrangement gives

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \tag{7.5.9}$$

The left side of this equation is the Joule–Thomson coefficient. An expression for the partial derivative $(\partial H/\partial p)_T$ is given in Table 7.1, and the partial derivative $(\partial H/\partial T)_p$ is the heat capacity at constant pressure (Eq. 5.6.3). These substitutions give us the desired relation

$$\mu_{\text{JT}} = \frac{(\alpha T - 1)V}{C_p} = \frac{(\alpha T - 1)V_{\text{m}}}{C_{p,\text{m}}} \tag{7.5.10}$$

7.6: Isothermal Pressure Changes

In various applications, we will need expressions for the effect of changing the pressure at constant temperature on the internal energy, enthalpy, entropy, and Gibbs energy of a phase. We obtain the expressions by integrating expressions found in Table 7.1. For example, ΔU is given by $\int (\partial U/\partial p)_T \, \mathrm{d}p$. The results are listed in the second column of Table 7.4.

7.6.1 Ideal gases

Simplifications result when the phase is an ideal gas. In this case, we can make the substitutions $V = nRT/p$, $\alpha = 1/T$, and $\kappa_T = 1/p$, resulting in the expressions in the third column of Table 7.4.

The expressions in the third column of Table 7.4 may be summarized by the statement that, when an ideal gas expands isothermally, the internal energy and enthalpy stay constant, the entropy increases, and the Helmholtz energy and Gibbs energy decrease.

7.6.2 Condensed phases

Solids, and liquids under conditions of temperature and pressure not close to the critical point, are much less compressible than gases. Typically the isothermal compressibility, κ_T, of a liquid or solid at room temperature and atmospheric pressure is no greater than $1 \times 10^{-4}\ \mathrm{bar}^{-1}$ (see Fig. 7.2), whereas an ideal gas under these conditions has $\kappa_T = 1/p = 1\ \mathrm{bar}^{-1}$. Consequently, it is frequently valid to treat V for a liquid or solid as essentially constant during a pressure change at constant temperature. Because κ_T is small, the product $\kappa_T p$ for a liquid or solid is usually much smaller than the product αT. Furthermore, κ_T for liquids and solids does not change rapidly with p as it does for gases, and neither does α.

With the approximations that V, α, and κ_T are constant during an isothermal pressure change, and that $\kappa_T p$ is negligible compared with αT, we obtain the expressions in the last column of Table 7.4.

7.7: Standard States of Pure Substances

It is often useful to refer to a reference pressure, the **standard pressure**, denoted p°. The standard pressure has an arbitrary but constant value in any given application. Until 1982, chemists used a standard pressure of 1 atm $(1.01325 \times 10^5\text{ Pa})$. The IUPAC now recommends the value $p^\circ = 1\text{ bar}$ (exactly 10^5 Pa). This e-book uses the latter value unless stated otherwise. (Note that there is no defined standard *temperature*.)

A superscript degree symbol (○) denotes a standard quantity or standard-state conditions. An alternative symbol for this purpose, used extensively outside the U.S., is a superscript Plimsoll mark (⊖). (The Plimsoll mark is named after the British merchant Samuel Plimsoll, at whose instigation Parliament passed an act in 1875 requiring the symbol to be placed on the hulls of cargo ships to indicate the maximum depth for safe loading.)

A **standard state** of a pure substance is a particular reference state appropriate for the kind of phase and is described by intensive variables. This e-book follows the recommendations of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 61–62) for various standard states.

- Section 9.7 will introduce additional standard states for constituents of mixtures.

7.8: Chemical Potential and Fugacity

The **chemical potential**, μ, of a pure substance has as one of its definitions (Sec. 5.5)

$$\mu \overset{\text{def}}{=} G_{\text{m}} = \frac{G}{n} \qquad (7.8.1)\ \text{(pure substance)}$$

That is, μ is equal to the molar Gibbs energy of the substance at a given temperature and pressure. (Section 9.2.6 will introduce a more general definition of chemical potential that applies also to a constituent of a mixture.) The chemical potential is an intensive state function.

The total differential of the Gibbs energy of a fixed amount of a pure substance in a single phase, with T and p as independent variables, is $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$ (Eq. 5.4.4). Dividing both sides of this equation by n gives the total differential of the chemical potential with these same independent variables:

$$\mathrm{d}\mu = -S_{\text{m}}\,\mathrm{d}T + V_{\text{m}}\,\mathrm{d}p \qquad (7.8.2)\ \text{(pure substance, } P{=}1\text{)}$$

(Since all quantities in this equation are intensive, it is not necessary to specify a closed system; the amount of the substance in the system is irrelevant.)

We identify the coefficients of the terms on the right side of Eq. 7.8.2 as the partial derivatives

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_{\text{m}} \qquad (7.8.3)\ \text{(pure substance, } P{=}1\text{)}$$

and

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_{\text{m}} \qquad (7.8.4)\ \text{(pure substance, } P{=}1\text{)}$$

Since V_{m} is positive, Eq. 7.8.4 shows that the chemical potential increases with increasing pressure in an isothermal process.

The **standard chemical potential**, μ°, of a pure substance in a given phase and at a given temperature is the chemical potential of the substance when it is in the standard state of the phase at this temperature and the standard pressure p°.

There is no way we can evaluate the absolute value of μ at a given temperature and pressure, or of μ° at the same temperature—at least not to any useful degree of precision. The values of μ and μ° include the molar internal energy whose absolute value can only be calculated from the Einstein relation; see Sec. 2.6.2. We can however measure or calculate the *difference* $\mu - \mu^{\circ}$. The general procedure is to integrate $\mathrm{d}\mu = V_{\text{m}}\,\mathrm{d}p$ (Eq. 7.8.2 with $\mathrm{d}T$ set equal to zero) from the standard state at pressure p° to the experimental state at pressure p':

$$\mu(p') - \mu^{\circ} = \int_{p^{\circ}}^{p'} V_{\text{m}}\,\mathrm{d}p \qquad (7.8.5)\ \text{(constant } T\text{)}$$

7.8.1 Gases

For the standard chemical potential of a gas, this e-book will usually use the notation $\mu^{\circ}(\text{g})$ to emphasize the choice of a *gas* standard state.

An *ideal gas* is in its standard state at a given temperature when its pressure is the standard pressure. We find the relation of the chemical potential of an ideal gas to its pressure and its standard chemical potential at the same temperature by setting V_{m} equal to RT/p in Eq. 7.8.5: $\mu(p') - \mu^{\circ} = \int_{p^{\circ}}^{p'} (RT/p)\,\mathrm{d}p = RT\ln(p'/p^{\circ})$. The general relation for μ as a function of p, then, is

$$\mu = \mu^{\circ}(\text{g}) + RT\ln\frac{p}{p^{\circ}} \qquad (7.8.6)\ \text{(pure ideal gas, constant } T\text{)}$$

This function is shown as the dashed curve in Fig. 7.6.

If a gas is *not* an ideal gas, its standard state is a hypothetical state. The **fugacity**, f, of a real gas (a gas that is not necessarily an ideal gas) is defined by an equation with the same form as Eq. 7.8.6:

$$\mu = \mu^\circ(\mathrm{g}) + RT\ln\frac{f}{p^\circ} \tag{7.8.7}$$
(pure gas)

or

$$f \overset{\text{def}}{=} p^\circ \exp\left[\frac{\mu - \mu^\circ(\mathrm{g})}{RT}\right] \tag{7.8.8}$$
(pure gas)

Note that fugacity has the dimensions of pressure. Fugacity is a kind of effective pressure. Specifically, it is the pressure that the hypothetical ideal gas (the gas with intermolecular forces “turned off”) would need to have in order for its chemical potential at the given temperature to be the same as the chemical potential of the real gas (see point C in Fig. 7.6). If the gas is an ideal gas, its fugacity is equal to its pressure.

To evaluate the fugacity of a real gas at a given T and p, we must relate the chemical potential to the pressure–volume behavior. Let μ' be the chemical potential and f' be the fugacity at the pressure p' of interest; let μ'' be the chemical potential and f'' be the fugacity of the same gas at some low pressure p'' (all at the same temperature). Then we use Eq. 7.8.5 to write $\mu' - \mu^\circ(\mathrm{g}) = RT\ln(f'/p^\circ)$ and $\mu'' - \mu^\circ(\mathrm{g}) = RT\ln(f''/p^\circ)$, from which we obtain

$$\mu' - \mu'' = RT\ln\frac{f'}{f''} \tag{7.8.9}$$

By integrating $\mathrm{d}\mu = V_\mathrm{m}\,\mathrm{d}p$ from pressure p'' to pressure p', we obtain

$$\mu' - \mu'' = \int_{\mu''}^{\mu'} \mathrm{d}\mu = \int_{p''}^{p'} V_\mathrm{m}\,\mathrm{d}p \tag{7.8.10}$$

Equating the two expressions for $\mu' - \mu''$ and dividing by RT gives

$$\ln\frac{f'}{f''} = \int_{p''}^{p'} \frac{V_\mathrm{m}}{RT}\,\mathrm{d}p \tag{7.8.11}$$

In principle, we could use the integral on the right side of Eq. 7.8.11 to evaluate f' by choosing the lower integration limit p'' to be such a low pressure that the gas behaves as an ideal gas and replacing f'' by p''. However, because the integrand V_m/RT becomes very large at low pressure, the integral is difficult to evaluate. We avoid this difficulty by subtracting from the preceding equation the identity

$$\ln\frac{p'}{p''} = \int_{p''}^{p'} \frac{\mathrm{d}p}{p} \tag{7.8.12}$$

which is simply the result of integrating the function $1/p$ from p'' to p'. The result is

$$\ln\frac{f'p''}{f''p'} = \int_{p''}^{p'} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p}\right)\mathrm{d}p \tag{7.8.13}$$

Now we take the limit of both sides of Eq. 7.8.13 as p'' approaches zero. In this limit, the gas at pressure p'' approaches ideal-gas behavior, f'' approaches p'', and the ratio $f'p''/f''p'$ approaches f'/p':

$$\ln\frac{f'}{p'} = \int_{0}^{p'} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p}\right)\mathrm{d}p \tag{7.8.14}$$

The integrand $(V_\mathrm{m}/RT - 1/p)$ of this integral approaches zero at low pressure, making it feasible to evaluate the integral from experimental data.

The **fugacity coefficient** ϕ of a gas is defined by

$$\phi \overset{\text{def}}{=} \frac{f}{p} \quad \text{or} \quad f = \phi p \tag{7.8.15}$$
(pure gas)

The fugacity coefficient at pressure p' is then given by Eq. 7.8.14:

$$\ln \phi(p') = \int_0^{p'} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p} \right) \mathrm{d}p \tag{7.8.16}$$
(pure gas, constant T)

The isothermal behavior of real gases at low to moderate pressures (up to at least 1 bar) is usually adequately described by a two-term equation of state of the form given in Eq. 2.2.8:

$$V_\mathrm{m} \approx \frac{RT}{p} + B \tag{7.8.17}$$

Here B is the second virial coefficient, a function of T. With this equation of state, Eq. 7.8.16 becomes

$$\ln \phi \approx \frac{Bp}{RT} \tag{7.8.18}$$

For a real gas at temperature T and pressure p, Eq. 7.8.16 or 7.8.18 allows us to evaluate the fugacity coefficient from an experimental equation of state or a second virial coefficient. We can then find the fugacity from $f = \phi p$.

> As we will see in Sec. 9.7, the dimensionless ratio $\phi = f/p$ is an example of an *activity coefficient* and the dimensionless ratio f/p° is an example of an *activity*.

7.8.2 Liquids and solids

The dependence of the chemical potential on pressure at constant temperature is given by Eq. 7.8.5. With an approximation of zero compressibility, this becomes

$$\mu \approx \mu^\circ + V_\mathrm{m}(p - p^\circ) \tag{7.8.19}$$
(pure liquid or solid,
constant T)

7.9: Standard Molar Quantities of a Gas

A **standard molar quantity** of a substance is the molar quantity in the standard state at the temperature of interest. We have seen (Sec. 7.7) that the standard state of a pure *liquid* or *solid* is a real state, so any standard molar quantity of a pure liquid or solid is simply the molar quantity evaluated at the standard pressure and the temperature of interest.

The standard state of a *gas*, however, is a hypothetical state in which the gas behaves ideally at the standard pressure without influence of intermolecular forces. The properties of the gas in this standard state are those of an ideal gas. We would like to be able to relate molar properties of the real gas at a given temperature and pressure to the molar properties in the standard state at the same temperature.

We begin by using Eq. 7.8.7 to write an expression for the chemical potential of the real gas at pressure p':

$$\mu(p') = \mu^\circ(\mathrm{g}) + RT\ln\frac{f(p')}{p^\circ} = \mu^\circ(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + RT\ln\frac{f(p')}{p'} \tag{7.9.1}$$

We then substitute from Eq. 7.8.14 to obtain a relation between the chemical potential, the standard chemical potential, and measurable properties, all at the same temperature:

$$\mu(p') = \mu^\circ(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + \int_0^{p'}\left(V_\mathrm{m} - \frac{RT}{p}\right)\mathrm{d}p \qquad \text{(7.9.2)} \quad \text{(pure gas)}$$

Note that this expression for μ is not what we would obtain by simply integrating $\mathrm{d}\mu = V_\mathrm{m}\,\mathrm{d}p$ from p° to p', because the real gas is not necessarily in its standard state of ideal-gas behavior at a pressure of 1 bar.

Recall that the chemical potential μ of a pure substance is also its molar Gibbs energy $G_\mathrm{m} = G/n$. The standard chemical potential $\mu^\circ(\mathrm{g})$ of the gas is the standard molar Gibbs energy, $G^\circ_\mathrm{m}(\mathrm{g})$. Therefore Eq. 7.9.2 can be rewritten in the form

$$G_\mathrm{m}(p') = G^\circ_\mathrm{m}(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + \int_0^{p'}\left(V_\mathrm{m} - \frac{RT}{p}\right)\mathrm{d}p \tag{7.9.3}$$

The middle column of Table 7.5 contains an expression for $G_\mathrm{m}(p') - G^\circ_\mathrm{m}(\mathrm{g})$ taken from this equation. This expression contains all the information needed to find a relation between any other molar property and its standard molar value in terms of measurable properties. The way this can be done is as follows.

The relation between the chemical potential of a pure substance and its molar entropy is given by Eq. 7.8.3:

$$S_\mathrm{m} = -\left(\frac{\partial\mu}{\partial T}\right)_p \tag{7.9.4}$$

The standard molar entropy of the gas is found from Eq. 7.9.4 by changing μ to $\mu^\circ(\mathrm{g})$:

$$S^\circ_\mathrm{m}(\mathrm{g}) = -\left(\frac{\partial\mu^\circ(\mathrm{g})}{\partial T}\right)_p \tag{7.9.5}$$

By substituting the expression for μ given by Eq. 7.9.2 into Eq. 7.9.4 and comparing the result with Eq. 7.9.5, we obtain

$$S_\mathrm{m}(p') = S^\circ_\mathrm{m}(\mathrm{g}) - R\ln\frac{p'}{p^\circ} - \int_0^{p'}\left[\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p - \frac{R}{p}\right]\mathrm{d}p \tag{7.9.6}$$

The expression for $S_\mathrm{m} - S^\circ_\mathrm{m}(\mathrm{g})$ in the middle column of Table 7.5 comes from this equation. The equation, together with a value of S_m for a real gas obtained by the calorimetric method described in Sec. 6.2.1, can be used to evaluate $S^\circ_\mathrm{m}(\mathrm{g})$.

Now we can use the expressions for G_m and S_m to find expressions for molar quantities such as H_m and $C_{p,\mathrm{m}}$ relative to the respective standard molar quantities. The general procedure for a molar quantity X_m is to write an expression for X_m as a function of G_m and S_m and an analogous expression for $X^\circ_\mathrm{m}(\mathrm{g})$ as a function of $G^\circ_\mathrm{m}(\mathrm{g})$ and $S^\circ_\mathrm{m}(\mathrm{g})$. Substitutions for G_m and S_m from Eqs. 7.9.3 and 7.9.6 are then made in the expression for X_m, and the difference $X_\mathrm{m} - X^\circ_\mathrm{m}(\mathrm{g})$ taken.

For example, the expression for $U_\mathrm{m} - U^\circ_\mathrm{m}(\mathrm{g})$ in the middle column Table 7.5 was derived as follows. The equation defining the Gibbs energy, $G = U - TS + pV$, was divided by the amount n and rearranged to

$$U_\mathrm{m} = G_\mathrm{m} + TS_\mathrm{m} - pV_\mathrm{m} \tag{7.9.7}$$

The standard-state version of this relation is

$$U^\circ_\mathrm{m}(\mathrm{g}) = G^\circ_\mathrm{m}(\mathrm{g}) + TS^\circ_\mathrm{m}(\mathrm{g}) - p^\circ V^\circ_\mathrm{m}(\mathrm{g}) \tag{7.9.8}$$

where from the ideal gas law $p^\circ V^\circ_\mathrm{m}(\mathrm{g})$ can be replaced by RT. Substitutions from Eqs. 7.9.3 and 7.9.6 were made in Eq. 7.9.7 and the expression for $U^\circ_\mathrm{m}(\mathrm{g})$ in Eq. 7.9.8 was subtracted, resulting in the expression in the table.

For a real gas at low to moderate pressures, we can approximate V_m by $(RT/p) + B$ where B is the second virial coefficient (Eq. 7.8.17). Equation 7.9.2 then becomes

$$\mu \approx \mu^\circ(\mathrm{g}) + RT \ln \frac{p}{p^\circ} + Bp \tag{7.9.9}$$

The expressions in the last column of Table 7.5 use this equation of state. We can see what the expressions look like if the gas is ideal simply by setting B equal to zero. They show that when the pressure of an ideal gas increases at constant temperature, G_m and A_m increase, S_m decreases, and U_m, H_m, and $C_{p,\mathrm{m}}$ are unaffected.

7.10: Chapter 7 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

7.1 Derive the following relations from the definitions of α, κ_T, and ρ :

$$\alpha=-\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \quad \kappa_T=\frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{7.10.1}$$

7.2 Use equations in this chapter to derive the following expressions for an ideal gas:

$$\alpha=1 / T \quad \kappa_T=1 / p \tag{7.10.2}$$

7.3 For a gas with the simple equation of state

$$V_{\mathrm{m}}=\frac{R T}{p}+B \tag{7.10.3}$$

(Eq. 2.2.8), where B is the second virial coefficient (a function of T), find expressions for α, κ_T, and $\left(\partial U_{\mathrm{m}} / \partial V\right)_T$ in terms of $\mathrm{d} B / \mathrm{d} T$ and other state functions.

7.4 Show that when the virial equation $p V_{\mathrm{m}}=R T\left(1+B_p p+C_p p^2+\cdots\right)$ (Eq. 2.2.3) adequately represents the equation of state of a real gas, the Joule-Thomson coefficient is given by

$$\mu_{\mathrm{JT}}=\frac{R T^2\left[\mathrm{~d} B_p / \mathrm{d} T+\left(\mathrm{d} C_p / \mathrm{d} T\right) p+\cdots\right]}{C_{p, \mathrm{~m}}} \tag{7.10.4}$$

Note that the limiting value at low pressure, $R T^2\left(\mathrm{~d} B_p / \mathrm{d} T\right) / C_{p, \mathrm{~m}}$, is not necessarily equal to zero even though the equation of state approaches that of an ideal gas in this limit.

7.5 The quantity $(\partial T / \partial V)_U$ is called the Joule coefficient. James Joule attempted to evaluate this quantity by measuring the temperature change accompanying the expansion of air into a vacuum - the "Joule experiment." Write an expression for the total differential of U with T and V as independent variables, and by a procedure similar to that used in Sec. 7.5.2 show that the Joule coefficient is equal to

$$\frac{p-\alpha T / \kappa_T}{C_V} \tag{7.10.5}$$

7.6 $p-V-T$ data for several organic liquids were measured by Gibson and Loeffler. [11] The following formulas describe the results for aniline.

Molar volume as a function of temperature at $p=1$ bar $(298-358 \mathrm{~K})$:

$$V_{\mathrm{m}}=a+b T+c T^2+d T^3 \tag{7.10.6}$$

where the parameters have the values

$$\begin{array}{ll}
a=69.287 \mathrm{~cm}^3 \mathrm{~mol}^{-1} & c=-1.0443 \times 10^{-4} \mathrm{~cm}^3 \mathrm{~K}^{-2} \mathrm{~mol}^{-1} \\
b=0.08852 \mathrm{~cm}^3 \mathrm{~K}^{-1} \mathrm{~mol}^{-1} & d=1.940 \times 10^{-7} \mathrm{~cm}^3 \mathrm{~K}^{-3} \mathrm{~mol}^{-1}
\end{array} \tag{7.10.7}$$

Molar volume as a function of pressure at $T=298.15 \mathrm{~K}$ (1-1000 bar):

$$V_{\mathrm{m}}=e-f \ln (g+p / \text { bar }) \tag{7.10.8}$$

where the parameter values are

$$e=156.812 \mathrm{~cm}^3 \mathrm{~mol}^{-1} \quad f=8.5834 \mathrm{~cm}^3 \mathrm{~mol}^{-1} \quad g=2006.6 \tag{7.10.9}$$

(a) Use these formulas to evaluate α, κ_T, $(\partial p / \partial T)_V$, and $(\partial U / \partial V)_T$ (the internal pressure) for aniline at $T=298.15 \mathrm{~K}$ and $p=1.000$ bar.

(b) Estimate the pressure increase if the temperature of a fixed amount of aniline is increased by $0.10 \mathrm{~K}$ at constant volume.

7.7 (a) From the total differential of H with T and p as independent variables, derive the relation $\left(\partial C_{p, \mathrm{~m}} / \partial p\right)_T=-T\left(\partial^2 V_{\mathrm{m}} / \partial T^2\right)_p$
(b) Evaluate $\left(\partial C_{p, \mathrm{~m}} / \partial p\right)_T$ for liquid aniline at $300.0 \mathrm{~K}$ and 1 bar using data in Prob. 7.6.

7.8 (a) From the total differential of V with T and p as independent variables, derive the relation $(\partial \alpha / \partial p)_T=-\left(\partial \kappa_T / \partial T\right)_p$.
(b) Use this relation to estimate the value of α for benzene at $25^{\circ} \mathrm{C}$ and 500 bar, given that the value of α is $1.2 \times 10^{-3} \mathrm{~K}^{-1}$ at $25^{\circ} \mathrm{C}$ and 1 bar. (Use information from Fig. 7.2 on page 168.)

7.9 Certain equations of state supposed to be applicable to nonpolar liquids and gases are of the form $p=T f\left(V_{\mathrm{m}}\right)-a / V_{\mathrm{m}}^2$, where $f\left(V_{\mathrm{m}}\right)$ is a function of the molar volume only and a is a constant.
(a) Show that the van der Waals equation of state $\left(p+a / V_{\mathrm{m}}^2\right)\left(V_{\mathrm{m}}-b\right)=R T$ (where a and b are constants) is of this form.
(b) Show that any fluid with an equation of state of this form has an internal pressure equal to a / V_{m}^2.

7.10 Suppose that the molar heat capacity at constant pressure of a substance has a temperature dependence given by $C_{p, \mathrm{~m}}=a+b T+c T^2$, where a, b, and c are constants. Consider the heating of an amount n of the substance from T_1 to T_2 at constant pressure. Find expressions for ΔH and ΔS for this process in terms of a, b, c, n, T_1, and T_2.

7.11 At $p=1$ atm, the molar heat capacity at constant pressure of aluminum is given by

$$C_{p, \mathrm{~m}}=a+b T \tag{7.10.10}$$

where the constants have the values

$$a=20.67 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \quad b=0.01238 \mathrm{JK}^{-2} \mathrm{~mol}^{-1} \tag{7.10.11}$$

Calculate the quantity of electrical work needed to heat $2.000 \mathrm{~mol}$ of aluminum from $300.00 \mathrm{~K}$ to $400.00 \mathrm{~K}$ at $1 \mathrm{~atm}$ in an adiabatic enclosure.

7.12 The temperature dependence of the standard molar heat capacity of gaseous carbon dioxide in the temperature range $298 \mathrm{~K}-2000 \mathrm{~K}$ is given by

$$C_{p, \mathrm{~m}}^{\circ}=a+b T+\frac{c}{T^2} \tag{7.10.12}$$

where the constants have the values

$$a=44.2 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} \quad b=8.8 \times 10^{-3} \mathrm{~J} \mathrm{~K}^{-2} \mathrm{~mol}^{-1} \quad c=-8.6 \times 10^5 \mathrm{~J} \mathrm{~K} \mathrm{~mol}^{-1} \tag{7.10.13}$$

Calculate the enthalpy and entropy changes when one mole of CO_2 is heated at 1 bar from $300.00 \mathrm{~K}$ to $800.00 \mathrm{~K}$. You can assume that at this pressure $C_{p, \mathrm{~m}}$ is practically equal to $C_{p, \mathrm{~m}}^{\circ}$.

7.13 This problem concerns gaseous carbon dioxide. At $400 \mathrm{~K}$, the relation between p and V_{m} at pressures up to at least 100 bar is given to good accuracy by a virial equation of state truncated at the second virial coefficient, B. In the temperature range $300 \mathrm{~K}-800 \mathrm{~K}$ the dependence of B on temperature is given by

$$B=a^{\prime}+b^{\prime} T+c^{\prime} T^2+d^{\prime} T^3 \tag{7.10.14}$$

where the constants have the values

$$\begin{aligned}
a^{\prime} &=-521 \mathrm{~cm}^3 \mathrm{~mol}^{-1} \\
b^{\prime} &=2.08 \mathrm{~cm}^3 \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
c^{\prime} &=-2.89 \times 10^{-3} \mathrm{~cm}^3 \mathrm{~K}^{-2} \mathrm{~mol}^{-1} \\
d^{\prime} &=1.397 \times 10^{-6} \mathrm{~cm}^3 \mathrm{~K}^{-3} \mathrm{~mol}^{-1}
\end{aligned}$$

(a) From information in Prob. 7.12, calculate the standard molar heat capacity at constant pressure, $C_{p, \mathrm{~m}}^{\circ}$, at $T=400.0 \mathrm{~K}$.

(b) Estimate the value of $C_{p, \mathrm{~m}}$ under the conditions $T=400.0 \mathrm{~K}$ and $p=100.0$ bar.

7.14 A chemist, needing to determine the specific heat capacity of a certain liquid but not having an electrically heated calorimeter at her disposal, used the following simple procedure known as drop calorimetry. She placed $500.0 \mathrm{~g}$ of the liquid in a thermally insulated container equipped with a lid and a thermometer. After recording the initial temperature of the liquid, $24.80^{\circ} \mathrm{C}$, she removed a 60.17-g block of aluminum metal from a boiling water bath at $100.00^{\circ} \mathrm{C}$ and quickly immersed it in the liquid in the container. After the contents of the container had become thermally equilibrated, she recorded a final temperature of $27.92^{\circ} \mathrm{C}$. She calculated the specific heat capacity C_p / m of the liquid from these data, making use of the molar mass of aluminum $\left(M=26.9815 \mathrm{~g} \mathrm{~mol}^{-1}\right)$ and the formula for the molar heat capacity of aluminum given in Prob. 7.11.

(a) From these data, find the specific heat capacity of the liquid under the assumption that its value does not vary with temperature. Hint: Treat the temperature equilibration process as adiabatic and isobaric $(\Delta H=0)$, and equate ΔH to the sum of the enthalpy changes in the two phases.

(b) Show that the value obtained in part (a) is actually an average value of C_p / m over the temperature range between the initial and final temperatures of the liquid given by

$$\frac{\int_{T_1}^{T_2}\left(C_p / m\right) \mathrm{d} T}{T_2-T_1} \tag{7.10.15}$$

7.15 Suppose a gas has the virial equation of state $p V_{\mathrm{m}}=R T\left(1+B_p p+C_p p^2\right)$, where B_p and C_p depend only on T, and higher powers of p can be ignored.
(a) Derive an expression for the fugacity coefficient, ϕ, of this gas as a function of p.
(b) For $\mathrm{CO}_2(\mathrm{~g})$ at $0.00^{\circ} \mathrm{C}$, the virial coefficients have the values $B_p=-6.67 \times 10^{-3}$ bar $^{-1}$ and $C_p=-3.4 \times 10^{-5} \mathrm{bar}^{-2}$. Evaluate the fugacity f at $0.00^{\circ} \mathrm{C}$ and $p=20.0$ bar.

7.16 Table 7.6 on the next page lists values of the molar volume of gaseous $\mathrm{H}_2 \mathrm{O}$ at $400.00^{\circ} \mathrm{C}$ and 12 pressures.
(a) Evaluate the fugacity coefficient and fugacity of $\mathrm{H}_2 \mathrm{O}(\mathrm{g})$ at $400.00^{\circ} \mathrm{C}$ and 200 bar.
(b) Show that the second virial coefficient B in the virial equation of state, $p V_{\mathrm{m}}=R T\left(1+B / V_{\mathrm{m}}+C / V_{\mathrm{m}}^2+\cdots\right)$, is given by

$$B=R T \lim _{p \rightarrow 0}\left(\frac{V_{\mathrm{m}}}{R T}-\frac{1}{p}\right) \tag{7.10.16}$$

where the limit is taken at constant T. Then evaluate B for $\mathrm{H}_2 \mathrm{O}(\mathrm{g})$ at $400.00^{\circ} \mathrm{C}$.

Table 7.6 Molar volume of $\mathrm{H}_2 \mathrm{O}(\mathrm{g})$ at $400.00^{\circ} \mathrm{C}^a$

$p / 10^{5} \mathrm{~Pa}$	$V_{\mathrm{m}} / 10^{-3} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$	$p / 10^{5} \mathrm{~Pa}$	$V_{\mathrm{m}} / 10^{-3} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$
1	55.896	100	0.47575
10	5.5231	120	0.37976
20	2.7237	140	0.31020
40	1.3224	160	0.25699
60	0.85374	180	0.21447
80	0.61817	200	0.17918

^{a} based on data in Ref. [75]

CHAPTER OVERVIEW

8: Phase Transitions and Equilibria of Pure Substances

A system of two or more phases of a single substance, in the absence of internal constraints, is in an equilibrium state when each phase has the same temperature, the same pressure, and the same chemical potential. This chapter describes the derivation and consequences of this simple principle, the general appearance of phase diagrams of single-substance systems, and quantitative aspects of the equilibrium phase transitions of these systems.

8.1: Phase Equilibria

8.1.1 Equilibrium conditions

If the state of an isolated system is an equilibrium state, this state does not change over time (Sec. 2.4.4). We expect an isolated system that is *not* in an equilibrium state to undergo a spontaneous, irreversible process and eventually to reach an equilibrium state. Just how rapidly this process occurs is a matter of kinetics, not thermodynamics. During this irreversible adiabatic process, the entropy increases until it reaches a maximum in the equilibrium state.

A general procedure will now be introduced for finding conditions for equilibrium with given constraints. The procedure is applied to phase equilibria of single-substance, multiphase systems in the next section, to transfer equilibria in multicomponent, multiphase systems in Sec. 9.2.7, and to reaction equilibria in Sec. 11.7.3.

The procedure has five steps:

1. In this section we consider a system of a single substance in two or more uniform phases with distinctly different intensive properties. For instance, one phase might be a liquid and another a gas. We assume the phases are not separated by internal partitions, so that there is no constraint preventing the transfer of matter and energy among the phases. (A tall column of gas in a gravitational field is a different kind of system in which intensive properties of an equilibrium state vary continuously with elevation; this case will be discussed in Sec. 8.1.4.)

   Phase α' will be the reference phase. Since internal energy is extensive, we can write $U = U^{\alpha'} + \sum_{\alpha\neq\alpha'} U^{\alpha}$ and $\mathrm{d}U = \mathrm{d}U^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}U^{\alpha}$. We assume any changes are slow enough to allow each phase to be practically uniform at all times. Treating each phase as an open subsystem with expansion work only, we use the relation $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n$ (Eq. 5.2.5) to replace each $\mathrm{d}U^{\alpha}$ term:

   $$\mathrm{d}U = (T^{\alpha'}\,\mathrm{d}S^{\alpha'} - p^{\alpha'}\,\mathrm{d}V^{\alpha'} + \mu^{\alpha'}\,\mathrm{d}n^{\alpha'}) + \sum_{\alpha\neq\alpha'} (T^{\alpha}\,\mathrm{d}S^{\alpha} - p^{\alpha}\,\mathrm{d}V^{\alpha} + \mu^{\alpha}\,\mathrm{d}n^{\alpha}) \tag{8.1.1}$$

   This is an expression for the total differential of U when there are no constraints.

   In an isolated system, an equilibrium state cannot change spontaneously to a different state. Once the isolated system has reached an equilibrium state, an imagined finite change of any of the independent variables consistent with the constraints (a so-called *virtual displacement*) corresponds to an impossible process with an entropy decrease. Thus, the equilibrium state has the *maximum* entropy that is possible for the isolated system. In order for S to be a maximum, $\mathrm{d}S$ must be zero for an infinitesimal change of any of the independent variables of the isolated system.

   This requirement is satisfied in the case of the multiphase system only if the coefficient of each term in the sums on the right side of Eq. 8.1.6 is zero. Therefore, in an equilibrium state the temperature of each phase is equal to the temperature $T^{\alpha'}$ of the reference phase, the pressure of each phase is equal to $p^{\alpha'}$, and the chemical potential in each phase is equal to $\mu^{\alpha'}$. That is, at equilibrium the temperature, pressure, and chemical potential are uniform throughout the system. These are, respectively, the conditions described in Sec. 2.4.4 of *thermal equilibrium*, *mechanical equilibrium*, and *transfer equilibrium*. These conditions must hold in order for a multiphase system of a pure substance without internal partitions to be in an equilibrium state, regardless of the process by which the system attains that state.

   ### 8.1.3 Simple derivation of equilibrium conditions

   Here is a simpler, less formal derivation of the three equilibrium conditions in a multiphase system of a single substance.

   It is intuitively obvious that, unless there are special constraints (such as internal partitions), an equilibrium state must have thermal and mechanical equilibrium. A temperature difference between two phases would cause a spontaneous transfer of heat from the warmer to the cooler phase; a pressure difference would cause spontaneous flow of matter.

   When some of the substance is transferred from one phase to another under conditions of constant T and p, the intensive properties of each phase remains the same including the chemical potential. The chemical potential of a pure phase is the Gibbs energy per amount of substance in the phase. We know that in a closed system of constant T and p with expansion work only, the total Gibbs energy decreases during a spontaneous process and is constant during a reversible process (Eq. 5.8.6). The Gibbs energy will decrease only if there is a transfer of substance from a phase of higher chemical potential to a phase of lower chemical potential, and this will be a spontaneous change. No spontaneous transfer is possible if both phases have the same chemical potential, so this is a condition for an equilibrium state.

8.1.4 Tall column of gas in a gravitational field

The earth's gravitational field is an example of an external force field that acts on a system placed in it. Usually we ignore its effects on the state of the system. If, however, the system's vertical extent is considerable we must take the presence of the field into account to explain, for example, why gas pressure varies with elevation in an equilibrium state.

A tall column of gas whose intensive properties are a function of elevation may be treated as an infinite number of uniform phases, each of infinitesimal vertical height. We can approximate this system with a vertical stack of many slab-shaped gas phases, each thin enough to be practically uniform in its intensive properties, as depicted in Fig. 8.1. The system can be isolated from the surroundings by confining the gas in a rigid adiabatic container. In order to be able to associate each of the thin slab-shaped phases with a definite constant elevation, we specify that the volume of each phase is constant so that in the rigid container the vertical thickness of a phase cannot change.

We can use the phase of lowest elevation as the reference phase α', as indicated in the figure. We repeat the derivation of Sec. 8.1.2 with one change: for each phase α the volume change $\mathrm{d}V^\alpha$ is set equal to zero. Then the second sum on the right side of Eq. 8.1.6, with terms proportional to $\mathrm{d}V^\alpha$, drops out and we are left with

$$\mathrm{d}S = \sum_{\alpha\neq\alpha'} \frac{T^{\alpha'} - T^\alpha}{T^{\alpha'}} \mathrm{d}S^\alpha + \sum_{\alpha\neq\alpha'} \frac{\mu^{\alpha'} - \mu^\alpha}{T^{\alpha'}} \mathrm{d}n^\alpha \tag{8.1.7}$$

In the equilibrium state of the isolated system, $\mathrm{d}S$ is equal to zero for an infinitesimal change of any of the independent variables. In this state, therefore, the coefficient of each term in the sums on the right side of Eq. 8.1.7 must be zero. We conclude that in an equilibrium state of a tall column of a pure gas, *the temperature and chemical potential are uniform throughout*. The equation, however, gives us no information about pressure.

We will use this result to derive an expression for the dependence of the fugacity f on elevation in an equilibrium state. We pick an arbitrary position such as the earth's surface for a reference elevation at which h is zero, and define the standard chemical potential $\mu^\circ(\mathrm{g})$ as the chemical potential of the gas under standard state conditions at this reference elevation. At h=0, the chemical potential and fugacity are related by Eq. 7.8.7 which we write in the following form, indicating the elevation in parentheses:

$$\mu(0) = \mu^\circ(\mathrm{g}) + RT \ln \frac{f(0)}{p^\circ} \tag{8.1.8}$$

Imagine a small sample of gas of mass m that is initially at elevation h=0. The vertical extent of this sample should be small enough for the variation of the gravitational force field within the sample to be negligible. The gravitational work needed to raise the gas to an arbitrary elevation h is $w' = mgh$ (Sec. 3.6). We assume this process is carried out reversibly at constant volume and without heat, so that there is no change in T, p, V, S, or f. The internal energy U of the gas must increase by $mgh = nMgh$, where M is the molar mass. Then, because the Gibbs energy G depends on U according to $G = U - TS + pV$, G must also increase by $nMgh$.

The chemical potential μ is the molar Gibbs energy G/n. During the elevation process, f remains the same and μ increases by Mgh:

$$\mu(h) = \mu(0) + Mgh \tag{8.1.9}$$

$(f(h)$=$f(0))$

From Eqs. 8.1.8 and 8.1.9, we can deduce the following general relation between chemical potential, fugacity, and elevation:

$$\mu(h) = \mu^\circ(\mathrm{g}) + RT \ln \frac{f(h)}{p^\circ} + Mgh \tag{8.1.10}$$

(pure gas in gravitational field)

Compare this relation with the equation that defines the fugacity when the effect of a gravitational field is negligible: $\mu = \mu^\circ(\mathrm{g}) + RT \ln(f/p^\circ)$ (Eq. 7.8.7). The additional term Mgh is needed when the vertical extent of the gas is considerable.

> Some thermodynamicists call the expression on the right side of Eq. 8.1.10 the "total chemical potential" or "gravitochemical potential" and reserve the term "chemical potential" for the function $\mu^{\circ}(\mathrm{g})+RT\ln(f/p^{\circ})$. With these definitions, in an equilibrium state the "total chemical potential" is the same at all elevations and the "chemical potential" decreases with increasing elevation.
>
> This e-book instead defines the chemical potential μ of a pure substance at any elevation as the molar Gibbs energy at that elevation, as recommended in a 2001 IUPAC technical report (Robert A. Alberty, *Pure Appl. Chem.*, **73**, 1349–1380, 2001). When the chemical potential is defined in this way, it has the same value at all elevations in an equilibrium state.

We know that in the equilibrium state of the gas column, the chemical potential $\mu(h)$ has the same value at each elevation h. Equation 8.1.10 shows that in order for this to be possible, the fugacity must decrease with increasing elevation. By equating expressions from Eq. 8.1.10 for $\mu(h)$ at an arbitrary elevation h, and for $\mu(0)$ at the reference elevation, we obtain

$$\mu^{\circ}(\mathrm{g})+RT\ln\frac{f(h)}{p^{\circ}}+Mgh=\mu^{\circ}(\mathrm{g})+RT\ln\frac{f(0)}{p^{\circ}} \tag{8.1.11}$$

Solving for $f(h)$ gives

$$f(h)=f(0)e^{-Mgh/RT} \tag{8.1.12}$$

(pure gas at equilibrium
in gravitational field)

If we treat the gas as ideal, so that the fugacity equals the pressure, this equation becomes

$$p(h)=p(0)e^{-Mgh/RT} \tag{8.1.13}$$

(pure ideal gas at equilibrium
in gravitational field)

Equation 8.1.13 is the *barometric formula* for a pure ideal gas. It shows that in the equilibrium state of a tall column of an ideal gas, the pressure decreases exponentially with increasing elevation.

This derivation of the barometric formula has introduced a method that will be used in Sec. 9.8.1 for dealing with *mixtures* in a gravitational field. There is, however, a shorter derivation based on Newton's second law and not involving the chemical potential. Consider one of the thin slab-shaped phases of Fig. 8.1. Let the density of the phase be ρ, the area of each horizontal face be A_{s}, and the thickness of the slab be δh. The mass of the phase is then $m=\rho A_{\mathrm{s}}\delta h$. The pressure difference between the top and bottom of the phase is δp. Three vertical forces act on the phase: an upward force pA_{s} at its lower face, a downward force $-(p+\delta p)A_{\mathrm{s}}$ at its upper face, and a downward gravitational force $-mg=-\rho A_{\mathrm{s}}g\delta h$. If the phase is at rest, the net vertical force is zero: $pA_{\mathrm{s}}-(p+\delta p)A_{\mathrm{s}}-\rho A_{\mathrm{s}}g\delta h=0$, or $\delta p=-\rho g\delta h$. In the limit as the number of phases becomes infinite and δh and δp become infinitesimal, this becomes

$$\mathrm{d}p=-\rho g\,\mathrm{d}h \tag{8.1.14}$$

(fluid at equilibrium
in gravitational field)

Equation 8.1.14 is a general relation between changes in elevation and hydrostatic pressure in *any* fluid. To apply it to an ideal gas, we replace the density by $\rho=nM/V=M/V_{\mathrm{m}}=Mp/RT$ and rearrange to $\mathrm{d}p/p=-(gM/RT)\,\mathrm{d}h$. Treating g and T as constants, we integrate from h=0 to an arbitrary elevation h and obtain the same result as Eq. 8.1.13.

8.1.5 The pressure in a liquid droplet

The equilibrium shape of a small liquid droplet surrounded by vapor of the same substance, when the effects of gravity and other external forces are negligible, is spherical. This is the result of the surface tension of the liquid–gas interface which acts to minimize the ratio of surface to volume. The interface acts somewhat like the stretched membrane of an inflated balloon, resulting in a greater pressure inside the droplet than the pressure of the vapor in equilibrium with it.

We can derive the pressure difference by considering a closed system containing a spherical liquid droplet and surrounding vapor. We treat both phases as open subsystems. An infinitesimal change $\mathrm{d}U$ of the internal energy is the sum of contributions from the liquid and gas phases and from the surface work $\gamma\,\mathrm{d}A_{\mathrm{s}}$, where γ is the surface tension of the liquid–gas interface and A_{s} is the surface area of the droplet (Sec. 5.7):

$$dU = dU^{\mathrm{l}} + dU^{\mathrm{g}} + \gamma\, dA_{\mathrm{s}} = T^{\mathrm{l}}\, dS^{\mathrm{l}} - p^{\mathrm{l}}\, dV^{\mathrm{l}} + \mu^{\mathrm{l}}\, dn^{\mathrm{l}} + T^{\mathrm{g}}\, dS^{\mathrm{g}} - p^{\mathrm{g}}\, dV^{\mathrm{g}} + \mu^{\mathrm{g}}\, dn^{\mathrm{g}} + \gamma\, dA_{\mathrm{s}} \tag{8.1.15}$$

Note that Eq. 8.1.15 is not an expression for the total differential of U, because V^{l} and A_{s} are not independent variables. A derivation by a procedure similar to the one used in Sec. 8.1.2 shows that at equilibrium the liquid and gas have equal temperatures and equal chemical potentials, and the pressure in the droplet is greater than the gas pressure by an amount that depends on r:

$$p^{\mathrm{l}} = p^{\mathrm{g}} + \frac{2\gamma}{r} \tag{8.1.16}$$

Equation 8.1.16 is the *Laplace equation*. The pressure difference is significant if r is small, and decreases as r increases. The limit $r \to \infty$ represents the flat surface of bulk liquid with p^{l} equal to p^{g}.

The derivation of Eq. 8.1.16 is left as an exercise (Prob. 8.1). The Laplace equation is valid also for a liquid droplet in which the liquid and the surrounding gas may both be mixtures (Prob. 9.3).

The Laplace equation can also be applied to the pressure in a gas *bubble* surrounded by liquid. In this case the liquid and gas phases switch roles, and the equation becomes $p^{\mathrm{g}} = p^{\mathrm{l}} + 2\gamma/r$.

8.1.6 The number of independent variables

From this point on in this e-book, unless stated otherwise, the discussions of multiphase systems will implicitly assume the existence of thermal, mechanical, and transfer equilibrium. Equations will not explicitly show these equilibria as a condition of validity.

In the rest of this chapter, we shall assume the state of each phase can be described by the usual variables: temperature, pressure, and amount. That is, variables such as elevation in a gravitational field, interface surface area, and extent of stretching of a solid, are not relevant.

How many of the usual variables of an open multiphase one-substance equilibrium system are independent? To find out, we go through the following argument. In the absence of any kind of equilibrium, we could treat phase α as having the three independent variables T^{α}, p^{α}, and n^{α}, and likewise for every other phase. A system of P phases without thermal, mechanical, or transfer equilibrium would then have $3P$ independent variables.

> We must decide how to count the number of phases. It is usually of no thermodynamic significance whether a phase, with particular values of its intensive properties, is contiguous. For instance, splitting a crystal into several pieces is not usually considered to change the number of phases or the state of the system, provided the increased surface area makes no significant contribution to properties such as internal energy. Thus, the number of phases P refers to the number of different *kinds* of phases.

Each independent relation resulting from equilibrium imposes a restriction on the system and reduces the number of independent variables by one. A two-phase system with thermal equilibrium has the single relation $T^{\beta} = T^{\alpha}$. For a three-phase system, there are two such relations that are independent, for instance $T^{\beta} = T^{\alpha}$ and $T^{\gamma} = T^{\alpha}$. (The additional relation $T^{\gamma} = T^{\beta}$ is not independent since we may deduce it from the other two.) In general, thermal equilibrium gives $P-1$ independent relations among temperatures.

By the same reasoning, mechanical equilibrium involves $P-1$ independent relations among pressures, and transfer equilibrium involves $P-1$ independent relations among chemical potentials.

The total number of independent relations for equilibrium is $3(P-1)$, which we subtract from $3P$ (the number of independent variables in the absence of equilibrium) to obtain the number of independent variables in the equilibrium system: $3P - 3(P-1) = 3$. Thus, *an open single-substance system with any number of phases has at equilibrium three independent variables*. For example, in equilibrium states of a two-phase system we may vary T, n^{α}, and n^{β} independently, in which case p is a dependent variable; for a given value of T, the value of p is the one that allows both phases to have the same chemical potential.

8.1.7 The Gibbs phase rule for a pure substance

The complete description of the state of a system must include the value of an *extensive* variable of each phase (e.g., the volume, mass, or amount) in order to specify how much of the phase is present. For an equilibrium system of P phases with a total of 3 independent variables, we may choose the remaining $3-P$ variables to be *intensive*. The number of these intensive independent variables is called the **number of degrees of freedom** or **variance**, F, of the system:

$$F=3-P \tag{8.1.17}$$

$$\text{(pure substance)}$$

> The application of the phase rule to multicomponent systems will be taken up in Sec. 13.1. Equation 8.1.17 is a special case, for $C=1$, of the more general Gibbs phase rule $F=C-P+2$.

We may interpret the variance F in either of two ways:

- A system with two degrees of freedom is called *bivariant*, one with one degree of freedom is *univariant*, and one with no degrees of freedom is *invariant*. For a system of a pure substance, these three cases correspond to one, two, and three phases respectively. For instance, a system of liquid and gaseous H_2O (and no other substances) is univariant ($F=3-P=3-2=1$); we are able to independently vary only one intensive property, such as T, while the liquid and gas remain in equilibrium.

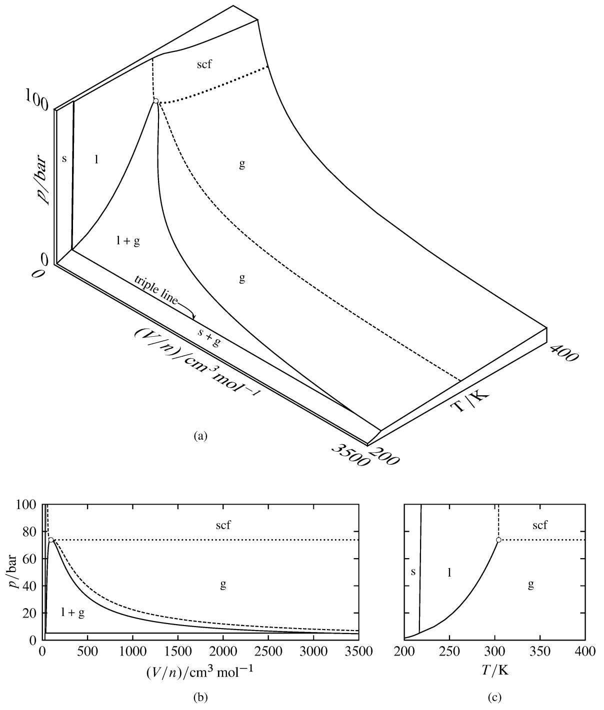
8.2: Phase Diagrams of Pure Substances

A **phase diagram** is a two-dimensional map showing which phase or phases are able to exist in an equilibrium state under given conditions. This chapter describes pressure–volume and pressure–temperature phase diagrams for a single substance, and Chap. 13 will describe numerous types of phase diagrams for multicomponent systems.

8.2.1 Features of phase diagrams

Two-dimensional phase diagrams for a single-substance system can be generated as projections of a three-dimensional surface in a coordinate system with Cartesian axes p, V/n, and T. A point on the three-dimensional surface corresponds to a physically-realizable combination of values, for an equilibrium state of the system containing a total amount n of the substance, of the variables p, V/n, and T.

The concepts needed to interpret single-substance phase diagrams will be illustrated with carbon dioxide.



(a)

(b)

(c)

Figure 8.2 Relations among p, V/n, and T for carbon dioxide (based on data in NIST Chemistry WebBook and in S. Angus, B. Armstrong, and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State, Vol. 3, Carbon Dioxide*, Pergamon Press, Oxford, 1976). Areas are labeled with the stable phase or phases (scf stands for supercritical fluid). The open circle indicates the critical point.

(a) Three-dimensional p–(V/n)–T surface. The dashed curve is the critical isotherm at $T = 304.21\,\mathrm{K}$, and the dotted curve is a portion of the critical isobar at $p = 73.8\,\mathrm{bar}$.

(b) Pressure–volume phase diagram (projection of the surface onto the p–(V/n) plane).

(c) Pressure–temperature phase diagram (projection of the surface onto the p–T plane).

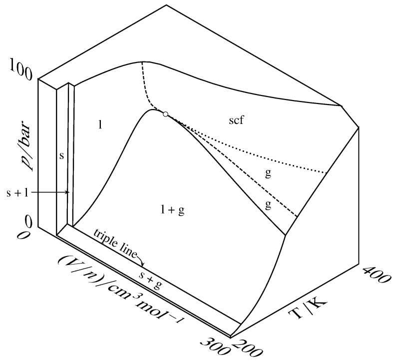


Figure 8.3 Three-dimensional p–(V/n)–T surface for CO_2, magnified along the V/n axis compared to Fig. 8.2. The open circle is the critical point, the dashed curve is the critical isotherm, and the dotted curve is a portion of the critical isobar.

Three-dimensional surfaces for carbon dioxide are shown at two different scales in Fig. 8.2 and in Fig. 8.3. In these figures, some areas of the surface are labeled with a single physical state: solid, liquid, gas, or supercritical fluid. A point in one of these areas corresponds to an equilibrium state of the system containing a single phase of the labeled physical state. The shape of the surface in this one-phase area gives the equation of state of the phase (i.e., the dependence of one of the variables on the other two). A point in an area labeled with two physical states corresponds to two coexisting phases. The **triple line** is the locus of points for all possible equilibrium systems of three coexisting phases, which in this case are solid, liquid, and gas. A point on the triple line can also correspond to just one or two phases.

The two-dimensional projections shown in Figs. 8.2(b) and 8.2(c) are pressure–volume and pressure–temperature phase diagrams. Because all phases of a multiphase equilibrium system have the same temperature and pressure (assuming there are no constraints such as internal adiabatic partitions), the projection of each two-phase area onto the pressure–temperature diagram is a curve, called a **coexistence curve** or **phase boundary**, and the projection of the triple line is a point, called a **triple point**.

How may we use a phase diagram? The two axes represent values of two independent variables, such as p and V/n or p and T. For given values of these variables, we place a point on the diagram at the intersection of the corresponding coordinates; this is the **system point**. Then depending on whether the system point falls in an area or on a coexistence curve, the diagram tells us the number and kinds of phases that can be present in the equilibrium system.

If the system point falls within an area labeled with the physical state of a *single* phase, only that one kind of phase can be present in the equilibrium system. A system containing a pure substance in a single phase is bivariant ($F = 3 - 1 = 2$), so we may vary two intensive properties independently. That is, the system point may move independently along two coordinates (p and V/n, or p and T) and still remain in the one-phase area of the phase diagram. When V and n refer to a single phase, the variable V/n is the molar volume V_m in the phase.

If the system point falls in an area of the pressure–volume phase diagram labeled with symbols for *two* phases, these two phases coexist in equilibrium. The phases have the same pressure and different molar volumes. To find the molar volumes of the individual phases, we draw a horizontal line of constant pressure, called a **tie line**, through the system point and extending from one edge of the area to the other. The horizontal position of each end of the tie line, where it terminates at the boundary with a one-phase area, gives the molar volume in that phase in the two-phase system. For an example of a tie line, see Fig. 8.9.

The triple line on the pressure–volume diagram represents the range of values of V/n in which three phases (solid, liquid, and gas) can coexist at equilibrium.

> Helium is the only substance lacking a solid–liquid–gas triple line. When a system containing the coexisting liquid and gas of ^{4}He is cooled to $2.17\,\text{K}$, a triple point is reached in which the third phase is a liquid called He-II, which has the unique property of superfluidity. It is only at high pressures ($10\,\text{bar}$ or greater) that solid helium can exist.

A three-phase one-component system is invariant ($F=3-3=0$); there is only one temperature (the triple-point temperature T_{tp}) and one pressure (the triple-point pressure p_{tp}) at which the three phases can coexist. The values of T_{tp} and p_{tp} are unique to each substance, and are shown by the position of the triple point on the pressure–temperature phase diagram. The molar volumes in the three coexisting phases are given by the values of V/n at the three points on the pressure–volume diagram where the triple line touches a one-phase area. These points are at the two ends and an intermediate position of the triple line. If the system point is at either end of the triple line, only the one phase of corresponding molar volume at temperature T_{tp} and pressure p_{tp} can be present. When the system point is on the triple line anywhere between the two ends, either two or three phases can be present. If the system point is at the position on the triple line corresponding to the phase of intermediate molar volume, there might be only that one phase present.

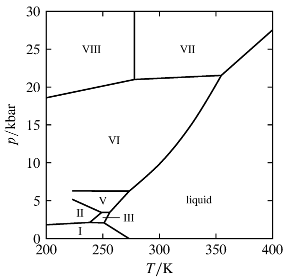


Figure 8.4 High-pressure pressure–temperature phase diagram of H_2O (based on data in D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, New York, 1969, Table 3.5, and Carl W. F. T. Pistorius et al, *J. Chem. Phys.*, **38**, 600–602, 1963). The roman numerals designate seven forms of ice.

At high pressures, a substance may have additional triple points for two solid phases and the liquid, or for three solid phases. This is illustrated by the pressure–temperature phase diagram of H_2O in Fig. 8.4, which extends to pressures up to $30\,\text{kbar}$. (On this scale, the liquid–gas coexistence curve lies too close to the horizontal axis to be visible.) The diagram shows seven different solid phases of H_2O differing in crystal structure and designated ice I, ice II, and so on. Ice I is the ordinary form of ice, stable below $2\,\text{bar}$. On the diagram are four triple points for two solids and the liquid and three triple points for three solids. Each triple point is invariant. Note how H_2O can exist as solid ice VI or ice VII above its standard melting point of $273\,\text{K}$ if the pressure is high enough ("hot ice").

8.2.2 Two-phase equilibrium

A system containing two phases of a pure substance in equilibrium is univariant. Both phases have the same values of T and of p, but these values are not independent because of the requirement that the phases have equal chemical potentials. We may vary only one intensive variable of a pure substance (such as T or p) independently while two phases coexist in equilibrium.

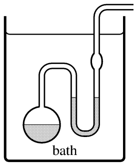


Figure 8.5 An isoteniscope. The liquid to be investigated is placed in the vessel and U-tube, as indicated by shading, and maintained at a fixed temperature in the bath. The pressure in the side tube is reduced until the liquid boils gently and its vapor sweeps out the air. The pressure is

adjusted until the liquid level is the same in both limbs of the U-tube; the vapor pressure of the liquid is then equal to the pressure in the side tube, which can be measured with a manometer.

At a given temperature, the pressure at which solid and gas or liquid and gas are in equilibrium is called the **vapor pressure** or **saturation vapor pressure** of the solid or liquid. The vapor pressure of a solid is sometimes called the **sublimation pressure**. We may measure the vapor pressure of a liquid at a fixed temperature with a simple device called an isoteniscope (Fig. 8.5).

> In a system of more than one substance, *vapor pressure* can refer to the partial pressure of a substance in a gas mixture equilibrated with a solid or liquid of that substance. The effect of total pressure on vapor pressure will be discussed in Sec. 12.8.1. This e-book refers to the *saturation* vapor pressure of a liquid when it is necessary to indicate that it is the pure liquid and pure gas phases that are in equilibrium at the same pressure.

At a given pressure, the **melting point** or **freezing point** is the temperature at which solid and liquid are in equilibrium, the **boiling point** or **saturation temperature** is the temperature at which liquid and gas are in equilibrium, and the **sublimation temperature** or **sublimation point** is the temperature at which solid and gas are in equilibrium.

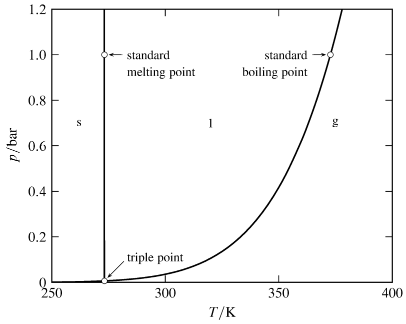


Figure 8.6 Pressure–temperature phase diagram of H_2O. (Based on data in *NIST Chemistry WebBook*.)

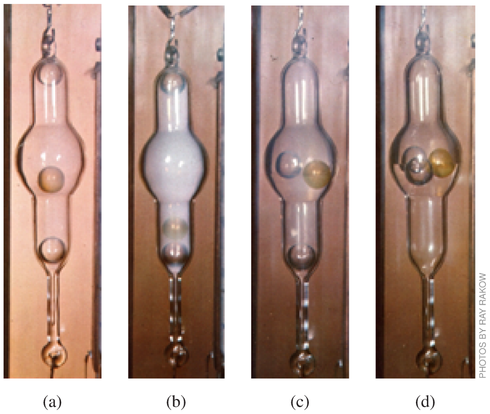
The relation between temperature and pressure in a system with two phases in equilibrium is shown by the coexistence curve separating the two one-phase areas on the pressure–temperature diagram (see Fig. 8.6). Consider the liquid–gas curve. If we think of T as the independent variable, the curve is a **vapor-pressure curve** showing how the vapor pressure of the liquid varies with temperature. If, however, p is the independent variable, then the curve is a **boiling-point curve** showing the dependence of the boiling point on pressure.

The *normal* melting point or boiling point refers to a pressure of one atmosphere, and the *standard* melting point or boiling point refers to the standard pressure. Thus, the normal boiling point of water ($99.97\,^{\circ}\mathrm{C}$) is the boiling point at $1\ \mathrm{atm}$; this temperature is also known as the *steam point*. The standard boiling point of water ($99.61\,^{\circ}\mathrm{C}$) is the boiling point at the slightly lower pressure of $1\ \mathrm{bar}$.

Coexistence curves will be discussed further in Sec. 8.4.

8.2.3 The critical point

Every substance has a certain temperature, the **critical temperature**, above which only one fluid phase can exist at any volume and pressure (Sec. 2.2.3). The **critical point** is the point on a phase diagram corresponding to liquid–gas coexistence at the critical temperature, and the **critical pressure** is the pressure at this point.



(a) (b) (c) (d)

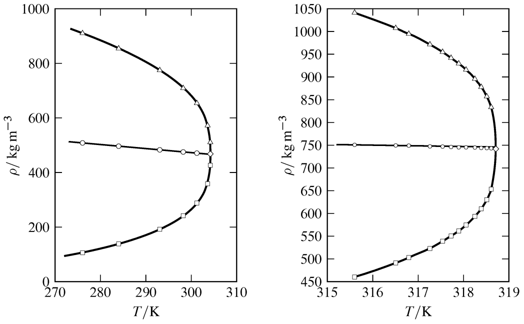
Figure 8.7 Glass bulb filled with CO_2 at a value of V/n close to the critical value, viewed at four different temperatures. The three balls have densities less than, approximately equal to, and greater than the critical density. (Photos by permission of the photographer; they appeared in Jan V. Sengers and Anneke Levelt Sengers, *Chem. Eng. News*, June 10, 104–118, 1968.)
(a) Supercritical fluid at a temperature above the critical temperature.
(b) Intense opalescence just above the critical temperature.
(c) Meniscus formation slightly below the critical temperature; liquid and gas of nearly the same density.
(d) Temperature well below the critical temperature; liquid and gas of greatly different densities.

To observe the critical point of a substance experimentally, we can evacuate a glass vessel, introduce an amount of the substance such that V/n is approximately equal to the molar volume at the critical point, seal the vessel, and raise the temperature above the critical temperature. The vessel now contains a single fluid phase. When the substance is slowly cooled to a temperature slightly above the critical temperature, it exhibits a cloudy appearance, a phenomenon called *critical opalescence* (Fig. 8.7). The opalescence is the scattering of light caused by large local density fluctuations. At the critical temperature, a meniscus forms between liquid and gas phases of practically the same density. With further cooling, the density of the liquid increases and the density of the gas decreases.

At temperatures above the critical temperature and pressures above the critical pressure, the one existing fluid phase is called a **supercritical fluid**. Thus, a supercritical fluid of a pure substance is a fluid that does not undergo a phase transition to a different fluid phase when we change the pressure at constant temperature or change the temperature at constant pressure.

If, however, we increase p at constant T, the supercritical fluid will change to a solid. In the phase diagram of H_2O, the coexistence curve for ice VII and liquid shown in Fig. 8.4 extends to a higher temperature than the critical temperature of $647\,\mathrm{K}$. Thus, supercritical water can be converted to ice VII by isothermal compression.

A fluid in the supercritical region can have a density comparable to that of the liquid, and can be more compressible than the liquid. Under supercritical conditions, a substance is often an excellent solvent for solids and liquids. By varying the pressure or temperature, the solvating power can be changed; by reducing the pressure isothermally, the substance can be easily removed as a gas from dissolved solutes. These properties make supercritical fluids useful for chromatography and solvent extraction.



(a) (b)

Figure 8.8 Densities of coexisting gas and liquid phases close to the critical point as functions of temperature for (a) CO_2 (based on data in A. Michels, B. Blaisse, and C. Michels, *Proc. R. Soc. London, Ser. A*, **160**, 358–375, 1937); (b) SF_6 (data of M. W. Pestak et al, *Phys. Rev. B*, **36**, 599–614, 1987, Table VII). Experimental gas densities are shown by open squares and experimental liquid densities by open triangles. The mean density at each experimental temperature is shown by an open circle. The open diamond is at the critical temperature and critical density.

The critical temperature of a substance can be measured quite accurately by observing the appearance or disappearance of a liquid–gas meniscus, and the critical pressure can be measured at this temperature with a high-pressure manometer. To evaluate the density at the critical point, it is best to extrapolate the mean density of the coexisting liquid and gas phases, $(\rho^{\mathrm{l}}+\rho^{\mathrm{g}})/2$, to the critical temperature as illustrated in Fig. 8.8. The observation that the mean density closely approximates a linear function of temperature, as shown in the figure, is known as the **law of rectilinear diameters**, or the law of Cailletet and Matthias. This law is an approximation, as can be seen by the small deviation of the mean density of SF_6 from a linear relation very close to the critical point in Fig. 8.8(b). This failure of the law of rectilinear diameters is predicted by recent theoretical treatments (Jingtao Wang and Mikhail A. Anisimov, *Phys. Rev. E*, **75**, 051107, 2007; Hassan Behnejad, Jan V. Sengers, and Mikhail A. Anisimov, in A. R. H. Goodwin, J. V. Sengers, and C. J. Peters, editors, *Applied Thermodynamics of Fluids*, pages 321–367, Royal Society of Chemistry, Cambridge, 2010).

8.2.4 The lever rule

Consider a single-substance system whose system point is in a two-phase area of a pressure–volume phase diagram. How can we determine the amounts in the two phases?

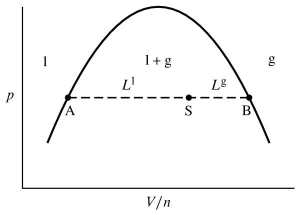


Figure 8.9 Tie line (dashed) at constant T and p in the liquid–gas area of a pressure–volume phase diagram. Points A and B are at the ends of the tie line, and point S is a system point on the tie line. L^{l} and L^{g} are the lengths AS and SB, respectively.

As an example, let the system contain a fixed amount n of a pure substance divided into liquid and gas phases, at a temperature and pressure at which these phases can coexist in equilibrium. When heat is transferred into the system at this T and p, some of the liquid vaporizes by a liquid–gas phase transition and V increases; withdrawal of heat at this T and p causes gas to condense and V to decrease. The molar volumes and other intensive properties of the individual liquid and gas phases remain constant during these changes at constant T and p. On the pressure–volume phase diagram of Fig. 8.9, the volume changes correspond to movement of the system point to the right or left along the tie line AB.

When enough heat is transferred into the system to vaporize all of the liquid at the given T and p, the system point moves to point B at the right end of the tie line. V/n at this point must be the same as the molar volume of the gas, $V_{\mathrm{m}}^{\mathrm{g}}$. We can see this because the system point could have moved from within the one-phase gas area to this position on the boundary without undergoing a phase transition.

When, on the other hand, enough heat is transferred out of the system to condense all of the gas, the system point moves to point A at the left end of the tie line. V/n at this point is the molar volume of the liquid, $V_{\mathrm{m}}^{\mathrm{l}}$.

When the system point is at position S on the tie line, both liquid and gas are present. Their amounts must be such that the total volume is the sum of the volumes of the individual phases, and the total amount is the sum of the amounts in the two phases:

$$V = V^{\mathrm{l}} + V^{\mathrm{g}} = n^{\mathrm{l}}V_{\mathrm{m}}^{\mathrm{l}} + n^{\mathrm{g}}V_{\mathrm{m}}^{\mathrm{g}} \tag{8.2.1}$$

$$n = n^{\mathrm{l}} + n^{\mathrm{g}} \tag{8.2.2}$$

The value of V/n at the system point is then given by the equation

$$\frac{V}{n} = \frac{n^{\mathrm{l}}V_{\mathrm{m}}^{\mathrm{l}} + n^{\mathrm{g}}V_{\mathrm{m}}^{\mathrm{g}}}{n^{\mathrm{l}} + n^{\mathrm{g}}} \tag{8.2.3}$$

which can be rearranged to

$$n^{\mathrm{l}}\left(V_{\mathrm{m}}^{\mathrm{l}} - \frac{V}{n}\right) = n^{\mathrm{g}}\left(\frac{V}{n} - V_{\mathrm{m}}^{\mathrm{g}}\right) \tag{8.2.4}$$

The quantities $V_{\mathrm{m}}^{\mathrm{l}} - V/n$ and $V/n - V_{\mathrm{m}}^{\mathrm{g}}$ are the lengths L^{l} and L^{g}, respectively, defined in the figure and measured in units of V/n. This gives us the **lever rule** for liquid–gas equilibrium:

$$n^{\mathrm{l}}L^{\mathrm{l}} = n^{\mathrm{g}}L^{\mathrm{g}} \quad \text{or} \quad \frac{n^{\mathrm{g}}}{n^{\mathrm{l}}} = \frac{L^{\mathrm{l}}}{L^{\mathrm{g}}} \tag{8.2.5}$$

(coexisting liquid and gas phases of a pure substance)

(The relation is called the lever rule by analogy to a stationary mechanical lever, each end of which has the same value of the product of applied force and distance from the fulcrum.)

In Fig. 8.9 the system point S is positioned on the tie line two thirds of the way from the left end, making length L^{l} twice as long as L^{g}. The lever rule then gives the ratio of amounts: $n^{\mathrm{g}}/n^{\mathrm{l}} = L^{\mathrm{l}}/L^{\mathrm{g}} = 2$. One-third of the total amount is liquid and two-thirds is gas.

We cannot apply the lever rule to a point on the triple line, because we need more than the value of V/n to determine the relative amounts present in three phases.

> We can derive a more general form of the lever rule that will be needed in Chap. 13 for phase diagrams of multicomponent systems. This general form can be applied to any two-phase area of a two-dimensional phase diagram in which a tie-line construction is valid, with the position of the system point along the tie line given by the variable
>
> $$F \overset{\text{def}}{=} \frac{a}{b} \tag{8.2.6}$$
>
> where a and b are extensive state functions. (In the pressure–volume phase diagram of Fig. 8.9, these functions are $a = V$ and $b = n$ and the system point position is given by $F = V/n$.) We repeat the steps of the derivation above, labeling the two phases by superscripts α and β instead of l and g. The relation corresponding to Eq. 8.2.4 is
>
> $$b^{\alpha}(F^{\alpha} - F) = b^{\beta}(F - F^{\beta}) \tag{8.2.7}$$

If L^α and L^β are lengths measured along the tie line from the system point to the ends of the tie line at single phases α and β, respectively, Eq. 8.2.7 is equivalent to the general lever rule

$$b^\alpha L^\alpha = b^\beta L^\beta \qquad \text{or} \qquad \frac{b^\beta}{b^\alpha} = \frac{L^\alpha}{L^\beta} \tag{8.2.8}$$

8.2.5 Volume properties

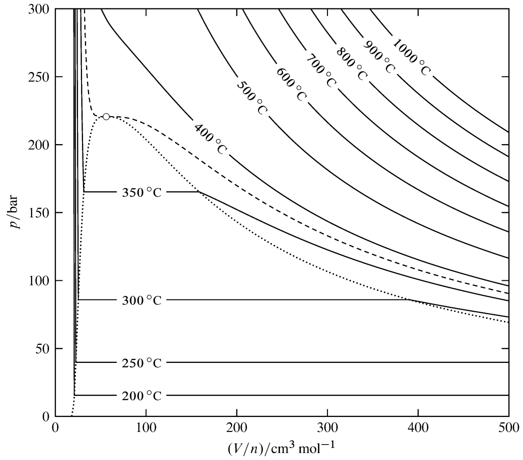


Figure 8.10 Isotherms for the fluid phases of H_2O (based on data in *NIST Chemistry WebBook*). The open circle indicates the critical point, the dashed curve is the critical isotherm at $373.95\,^\circ\text{C}$, and the dotted curve encloses the two-phase area of the pressure–volume phase diagram. The triple line lies too close to the bottom of the diagram to be visible on this scale.

Figure 8.10 is a pressure–volume phase diagram for H_2O. On the diagram are drawn *isotherms* (curves of constant T). These isotherms define the shape of the three-dimensional p–(V/n)–T surface. The area containing the horizontal isotherm segments is the two-phase area for coexisting liquid and gas phases. The boundary of this area is defined by the dotted curve drawn through the ends of the horizontal segments. The one-phase liquid area lies to the left of this curve, the one-phase gas area lies to the right, and the critical point lies at the top.

The diagram contains the information needed to evaluate the molar volume at any temperature and pressure in the one-phase region and the derivatives of the molar volume with respect to temperature and pressure. At a system point in the one-phase region, the slope of the isotherm passing through the point is the partial derivative $(\partial p/\partial V_\text{m})_T$. Since the isothermal compressibility is given by $\kappa_T = -(1/V_\text{m})(\partial V_\text{m}/\partial p)_T$, we have

$$\kappa_T = -\frac{1}{V_\text{m} \times \text{slope of isotherm}} \tag{8.2.9}$$

We see from Fig. 8.10 that the slopes of the isotherms are large and negative in the liquid region, smaller and negative in the gas and supercritical fluid regions, and approach zero at the critical point. Accordingly, the isothermal compressibility of the gas and the supercritical fluid is much greater than that of the liquid, approaching infinity at the critical point. The critical opalescence seen in Fig. 8.7 is caused by local density fluctuations, which are large when κ_T is large.

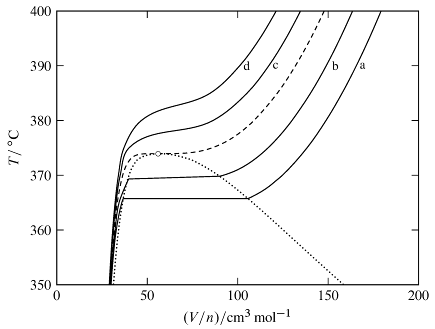


Figure 8.11 Isobars for the fluid phases of H_2O (based on data in *NIST Chemistry WebBook*). The open circle indicates the critical point, the dashed curve is the critical isobar at $220.64\ \mathrm{bar}$, and the dotted curve encloses the two-phase area of the temperature–volume phase diagram. Solid curves: a, $p = 200\ \mathrm{bar}$; b, $p = 210\ \mathrm{bar}$; c, $p = 230\ \mathrm{bar}$; d, $p = 240\ \mathrm{bar}$.

Figure 8.11 shows isobars for H_2O instead of isotherms. At a system point in the one-phase region, the slope of the isobar passing through the point is the partial derivative $(\partial T/\partial V_{\mathrm{m}})_p$. The cubic expansion coefficient α is equal to $(1/V_{\mathrm{m}})(\partial V_{\mathrm{m}}/\partial T)_p$, so we have

$$\alpha = \frac{1}{V_{\mathrm{m}} \times \text{slope of isobar}} \tag{8.2.10}$$

The figure shows that the slopes of the isobars are large and positive in the liquid region, smaller and negative in the gas and supercritical fluid regions, and approach zero at the critical point. Thus the gas and the supercritical fluid have much larger cubic expansion coefficients than the liquid. The value of α approaches infinity at the critical point, meaning that in the critical region the density distribution is greatly affected by temperature gradients. This may account for the low position of the middle ball in Fig. 8.7(b).

8.3: Phase Transitions

Recall (Sec. 2.2.2) that an equilibrium phase transition of a pure substance is a process in which some or all of the substance is transferred from one coexisting phase to another at constant temperature and pressure.

8.3.1 Molar transition quantities

The quantity $\Delta_{\text{vap}}H$ is the molar enthalpy change for the reversible process in which liquid changes to gas *at a temperature and pressure at which the two phases coexist at equilibrium*. This quantity is called the **molar enthalpy of vaporization**. (Because $\Delta_{\text{vap}}H$ is an enthalpy *change* per amount of vaporization, it would be more accurate to call it the "molar enthalpy change of vaporization.") Since the pressure is constant during the process, $\Delta_{\text{vap}}H$ is equal to the heat per amount of vaporization (Eq. 5.3.8). Hence, $\Delta_{\text{vap}}H$ is also called the **molar heat of vaporization**.

> The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 58) recommends that Δ_{p} be interpreted as an operator symbol: $\Delta_{\text{p}} \overset{\text{def}}{=} \partial/\partial\xi_{\text{p}}$, where "p" is the abbreviation for a process at constant T and p (in this case "vap") and ξ_{p} is its advancement. Thus $\Delta_{\text{vap}}H$ is the same as $(\partial H/\partial\xi_{\text{vap}})_{T,p}$ where ξ_{vap} is the amount of liquid changed to gas.

Here is a list of symbols for the molar enthalpy changes of various equilibrium phase transitions:

$$\begin{array}{ll} \Delta_{\text{vap}}H & \text{molar enthalpy of vaporization (liquid}\rightarrow\text{gas)} \\ \Delta_{\text{sub}}H & \text{molar enthalpy of sublimation (solid}\rightarrow\text{gas)} \\ \Delta_{\text{fus}}H & \text{molar enthalpy of fusion (solid}\rightarrow\text{liquid)} \\ \Delta_{\text{trs}}H & \text{molar enthalpy of a transition between any two phases in general} \end{array} \tag{8.3.1}$$

Molar enthalpies of vaporization, sublimation, and fusion are *positive*. The reverse processes of condensation (gas$\rightarrow$liquid), condensation or deposition (gas$\rightarrow$solid), and freezing (liquid$\rightarrow$solid) have *negative* enthalpy changes.

The subscripts in the list above are also used for other molar transition quantities. Thus, there is the molar entropy of vaporization $\Delta_{\text{vap}}S$, the molar internal energy of sublimation $\Delta_{\text{sub}}U$, and so on.

A molar transition quantity of a pure substance is the change of an extensive property divided by the amount transferred between the phases. For example, when an amount n in a liquid phase is allowed to vaporize to gas at constant T and p, the enthalpy change is $\Delta H = nH_{\text{m}}^{\text{g}} - nH_{\text{m}}^{\text{l}}$ and the molar enthalpy of vaporization is

$$\Delta_{\text{vap}}H = \frac{\Delta H}{n} = H_{\text{m}}^{\text{g}} - H_{\text{m}}^{\text{l}} \tag{8.3.1}$$

(pure substance)

In other words, $\Delta_{\text{vap}}H$ is the enthalpy change per amount vaporized and is also the difference between the molar enthalpies of the two phases.

A molar property of a phase, being intensive, usually depends on two independent intensive variables such as T and p. Despite the fact that $\Delta_{\text{vap}}H$ is the difference of the two molar properties H_{m}^{g} and H_{m}^{l}, its value depends on only *one* intensive variable, because the two phases are in transfer equilibrium and the system is univariant. Thus, we may treat $\Delta_{\text{vap}}H$ as a function of T only. The same is true of any other molar transition quantity.

The molar Gibbs energy of an equilibrium phase transition, $\Delta_{\text{trs}}G$, is a special case. For the phase transition $\alpha \rightarrow \beta$, we may write an equation analogous to Eq. 8.3.1 and equate the molar Gibbs energy in each phase to a chemical potential (see Eq. 7.8.1):

$$\Delta_{\text{trs}}G = G_{\text{m}}^{\beta} - G_{\text{m}}^{\alpha} = \mu^{\beta} - \mu^{\alpha} \tag{8.3.2}$$

(pure substance)

But the transition is between two phases at equilibrium, requiring both phases to have the same chemical potential: $\mu^{\beta} - \mu^{\alpha} = 0$. Therefore, the molar Gibbs energy of *any* equilibrium phase transition is zero:

$$\Delta_{\text{trs}}G = 0 \tag{8.3.3}$$

(pure substance)

Since the Gibbs energy is defined by $G = H - TS$, in phase α we have $G_{\text{m}}^{\alpha} = G^{\alpha}/n^{\alpha} = H_{\text{m}}^{\alpha} - TS_{\text{m}}^{\alpha}$. Similarly, in phase β we have $G_{\text{m}}^{\beta} = H_{\text{m}}^{\beta} - TS_{\text{m}}^{\beta}$. When we substitute these expressions in $\Delta_{\text{trs}}G = G_{\text{m}}^{\beta} - G_{\text{m}}^{\alpha}$ (Eq. 8.3.2) and set T equal to the transition temperature T_{trs}, we obtain

$$\Delta_{\mathrm{trs}} G=(H_{\mathrm{m}}^{\beta}-H_{\mathrm{m}}^{\alpha})-T_{\mathrm{trs}}(S_{\mathrm{m}}^{\beta}-S_{\mathrm{m}}^{\alpha}) \ =\Delta_{\mathrm{trs}} H-T_{\mathrm{trs}} \Delta_{\mathrm{trs}} S \tag{8.3.4}$$

Then, by setting $\Delta_{\mathrm{trs}} G$ equal to zero, we find the molar entropy and molar enthalpy of the equilibrium phase transition are related by

$$\Delta_{\mathrm{trs}} S=\frac{\Delta_{\mathrm{trs}} H}{T_{\mathrm{trs}}} \tag{8.3.5}$$

(pure substance)

where $\Delta_{\mathrm{trs}} S$ and $\Delta_{\mathrm{trs}} H$ are evaluated at the transition temperature T_{trs}.

> We may obtain Eq. 8.3.5 directly from the second law. With the phases in equilibrium, the transition process is reversible. The second law gives $\Delta S=q / T_{\mathrm{trs}}=\Delta H / T_{\mathrm{trs}}$. Dividing by the amount transferred between the phases gives Eq. 8.3.5.

8.3.2 Calorimetric measurement of transition enthalpies

The most precise measurement of the molar enthalpy of an equilibrium phase transition uses electrical work. A known quantity of electrical work is performed on a system containing coexisting phases, in a constant-pressure adiabatic calorimeter, and the resulting amount of substance transferred between the phases is measured. The first law shows that the electrical work $I^2 R_{\mathrm{el}} \Delta t$ equals the heat that would be needed to cause the same change of state. This heat, at constant p, is the enthalpy change of the process.

The method is similar to that used to measure the heat capacity of a phase at constant pressure (Sec. 7.3.2), except that now the temperature remains constant and there is no need to make a correction for the heat capacity of the calorimeter.

8.3.3 Standard molar transition quantities

The *standard* molar enthalpy of vaporization, $\Delta_{\mathrm{vap}} H^{\circ}$, is the enthalpy change when pure liquid in its standard state at a specified temperature changes to gas in its standard state at the same temperature, divided by the amount changed.

Note that the initial state of this process is a real one (the pure liquid at pressure p°), but the final state (the gas behaving ideally at pressure p°) is hypothetical. The liquid and gas are not necessarily in equilibrium with one another at pressure p° and the temperature of interest, and we cannot evaluate $\Delta_{\mathrm{vap}} H^{\circ}$ from a calorimetric measurement with electrical work without further corrections. The same difficulty applies to the evaluation of $\Delta_{\mathrm{sub}} H^{\circ}$. In contrast, $\Delta_{\mathrm{vap}} H$ and $\Delta_{\mathrm{sub}} H$ (without the $^{\circ}$ symbol), as well as $\Delta_{\mathrm{fus}} H^{\circ}$, all refer to reversible transitions between two *real* phases coexisting in equilibrium.

Let X represent one of the thermodynamic potentials or the entropy of a phase. The standard molar transition quantities $\Delta_{\mathrm{vap}} X^{\circ}=X_{\mathrm{m}}^{\circ}(\mathrm{g})-X_{\mathrm{m}}(\mathrm{l})$ and $\Delta_{\mathrm{sub}} X^{\circ}=X_{\mathrm{m}}^{\circ}(\mathrm{g})-X_{\mathrm{m}}(\mathrm{s})$ are functions only of T. To evaluate $\Delta_{\mathrm{vap}} X^{\circ}$ or $\Delta_{\mathrm{sub}} X^{\circ}$ at a given temperature, we must calculate the change of X_{m} for a path that connects the standard state of the liquid or solid with that of the gas. The simplest choice of path is one of constant temperature T with the following steps:

1. The sum of ΔX_{m} for these three steps is the desired quantity $\Delta_{\mathrm{vap}} X^{\circ}$ or $\Delta_{\mathrm{sub}} X^{\circ}$.

8.4: Coexistence Curves

A coexistence curve on a pressure–temperature phase diagram shows the conditions under which two phases can coexist in equilibrium, as explained in Sec. 8.2.2.

8.4.1 Chemical potential surfaces

From the relation $(\partial\mu/\partial T)_p = -S_{\mathrm{m}}$, we see that at constant p the slope of μ versus T is negative since molar entropy is always positive. Furthermore, the magnitude of the slope increases on going from solid to liquid and from liquid to gas, because the molar entropies of sublimation and vaporization are positive. This difference in slope is illustrated by the curves for $\mathrm{H_2O}$ in Fig. 8.13(a). The triple-point pressure of $\mathrm{H_2O}$ is $0.0062\ \mathrm{bar}$. At a pressure of $0.03\ \mathrm{bar}$, greater than the triple-point pressure, the curves for solid and liquid intersect at a melting point (point A) and the curves for liquid and gas intersect at a boiling point (point B).

From $(\partial\mu/\partial p)_T = V_{\mathrm{m}}$, we see that a pressure reduction at constant temperature lowers the chemical potential of a phase. The result of a pressure reduction from $0.03\ \mathrm{bar}$ to $0.003\ \mathrm{bar}$ (below the triple-point pressure of $\mathrm{H_2O}$) is a downward shift of each of the curves of Fig. 8.13(a) by a distance proportional to the molar volume of the phase. The shifts of the solid and liquid curves are too small to see ($\Delta\mu$ is only $-0.002\ \mathrm{kJ\ mol^{-1}}$). Because the gas has a large molar volume, the gas curve shifts substantially to a position where it intersects with the solid curve at a sublimation point (point C). At $0.003\ \mathrm{bar}$, or any other pressure below the triple-point pressure, only a solid–gas equilibrium is possible for $\mathrm{H_2O}$. The liquid phase is not stable at any pressure below the triple-point pressure, as shown by the pressure–temperature phase diagram of $\mathrm{H_2O}$ in Fig. 8.13(b).

8.4.2 The Clapeyron equation

If we start with two coexisting phases, α and β, of a pure substance and change the temperature of both phases equally without changing the pressure, the phases will no longer be in equilibrium, because their chemical potentials change unequally. In order for the phases to remain in equilibrium during the temperature change $\mathrm{d}T$ of both phases, there must be a certain simultaneous change $\mathrm{d}p$ in the pressure of both phases. The changes $\mathrm{d}T$ and $\mathrm{d}p$ must be such that the chemical potentials of both phases change equally so as to remain equal to one another: $\mathrm{d}\mu^\alpha = \mathrm{d}\mu^\beta$.

The infinitesimal change of μ in a phase is given by $\mathrm{d}\mu = -S_{\mathrm{m}}\,\mathrm{d}T + V_{\mathrm{m}}\,\mathrm{d}p$ (Eq. 7.8.2). Thus, the two phases remain in equilibrium if $\mathrm{d}T$ and $\mathrm{d}p$ satisfy the relation

$$-S_{\mathrm{m}}^{\alpha}\,\mathrm{d}T + V_{\mathrm{m}}^{\alpha}\,\mathrm{d}p = -S_{\mathrm{m}}^{\beta}\,\mathrm{d}T + V_{\mathrm{m}}^{\beta}\,\mathrm{d}p \tag{8.4.2}$$

which we rearrange to

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_{\mathrm{m}}^{\beta} - S_{\mathrm{m}}^{\alpha}}{V_{\mathrm{m}}^{\beta} - V_{\mathrm{m}}^{\alpha}} \tag{8.4.3}$$

or

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V} \qquad \text{(8.4.4)} \quad \text{(pure substance)}$$

Equation 8.4.4 is one form of the **Clapeyron equation**, which contains no approximations. We find an alternative form by substituting $\Delta_{\mathrm{trs}}S = \Delta_{\mathrm{trs}}H/T_{\mathrm{trs}}$ (Eq. 8.3.5):

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}H}{T\Delta_{\mathrm{trs}}V} \qquad \text{(8.4.5)} \quad \text{(pure substance)}$$

Equations 8.4.4 and 8.4.5 give the slope of the coexistence curve, $\mathrm{d}p/\mathrm{d}T$, as a function of quantities that can be measured. For the sublimation and vaporization processes, both $\Delta_{\mathrm{trs}}H$ and $\Delta_{\mathrm{trs}}V$ are positive. Therefore, according to Eq. 8.4.5, the solid–gas and liquid–gas coexistence curves have positive slopes. For the fusion process, however, $\Delta_{\mathrm{fus}}H$ is positive, but $\Delta_{\mathrm{fus}}V$ may be positive or negative depending on the substance, so that the slope of the solid–liquid coexistence curve may be either positive or negative. The absolute value of $\Delta_{\mathrm{fus}}V$ is small, causing the solid–liquid coexistence curve to be relatively steep; see Fig. 8.13(b) for an example.

> Most substances *expand* on melting, making the slope of the solid–liquid coexistence curve positive. This is true of carbon dioxide, although in Fig. 8.2(c) the curve is so steep that it is difficult to see the slope is positive. Exceptions

at ordinary pressures, substances that *contract* on melting, are H_2O, rubidium nitrate, and the elements antimony, bismuth, and gallium.

The phase diagram for H_2O in Fig. 8.4 clearly shows that the coexistence curve for ice I and liquid has a negative slope due to ordinary ice being less dense than liquid water. The high-pressure forms of ice are more dense than the liquid, causing the slopes of the other solid–liquid coexistence curves to be positive. The ice VII–ice VIII coexistence curve is vertical, because these two forms of ice have identical crystal structures, except for the orientations of the H_2O molecule; therefore, within experimental uncertainty, the two forms have equal molar volumes.

We may rearrange Eq. 8.4.5 to give the variation of p with T along the coexistence curve:

$$\mathrm{d}p = \frac{\Delta_{\mathrm{trs}} H}{\Delta_{\mathrm{trs}} V} \cdot \frac{\mathrm{d}T}{T} \tag{8.4.6}$$

Consider the transition from solid to liquid (fusion). Because of the fact that the cubic expansion coefficient and isothermal compressibility of a condensed phase are relatively small, $\Delta_{\mathrm{fus}} V$ is approximately constant for small changes of T and p. If $\Delta_{\mathrm{fus}} H$ is also practically constant, integration of Eq. 8.4.6 yields the relation

$$p_2 - p_1 \approx \frac{\Delta_{\mathrm{fus}} H}{\Delta_{\mathrm{fus}} V} \ln \frac{T_2}{T_1} \tag{8.4.7}$$

or

$$T_2 \approx T_1 \exp\left[\frac{\Delta_{\mathrm{fus}} V (p_2 - p_1)}{\Delta_{\mathrm{fus}} H}\right] \tag{8.4.8}$$

(pure substance)

from which we may estimate the dependence of the melting point on pressure.

8.4.3 The Clausius–Clapeyron equation

When the gas phase of a substance coexists in equilibrium with the liquid or solid phase, and provided T and p are not close to the critical point, the molar volume of the gas is much greater than that of the condensed phase. Thus, we may write for the processes of vaporization and sublimation

$$\Delta_{\mathrm{vap}} V = V_{\mathrm{m}}^{\mathrm{g}} - V_{\mathrm{m}}^{\mathrm{l}} \approx V_{\mathrm{m}}^{\mathrm{g}} \qquad \Delta_{\mathrm{sub}} V = V_{\mathrm{m}}^{\mathrm{g}} - V_{\mathrm{m}}^{\mathrm{s}} \approx V_{\mathrm{m}}^{\mathrm{g}} \tag{8.4.9}$$

The further approximation that the gas behaves as an ideal gas, $V_{\mathrm{m}}^{\mathrm{g}} \approx RT/p$, then changes Eq. 8.4.5 to

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{p \Delta_{\mathrm{trs}} H}{RT^2} \tag{8.4.10}$$

(pure substance,
vaporization or sublimation)

Equation 8.4.10 is the **Clausius–Clapeyron equation**. It gives an approximate expression for the slope of a liquid–gas or solid–gas coexistence curve. The expression is not valid for coexisting solid and liquid phases, or for coexisting liquid and gas phases close to the critical point.

At the temperature and pressure of the triple point, it is possible to carry out all three equilibrium phase transitions of fusion, vaporization, and sublimation. When fusion is followed by vaporization, the net change is sublimation. Therefore, the molar transition enthalpies at the triple point are related by

$$\Delta_{\mathrm{fus}} H + \Delta_{\mathrm{vap}} H = \Delta_{\mathrm{sub}} H \tag{8.4.11}$$

Since all three of these transition enthalpies are positive, it follows that $\Delta_{\mathrm{sub}} H$ is greater than $\Delta_{\mathrm{vap}} H$ at the triple point. Therefore, according to Eq. 8.4.10, the slope of the solid–gas coexistence curve at the triple point is slightly greater than the slope of the liquid–gas coexistence curve.

We divide both sides of Eq. 8.4.10 by p° and rearrange to the form

$$\frac{\mathrm{d}(p/p^{\circ})}{p/p^{\circ}} \approx \frac{\Delta_{\mathrm{trs}} H}{R} \cdot \frac{\mathrm{d}T}{T^2} \tag{8.4.12}$$

Then, using the mathematical identities $\mathrm{d}(p/p^\circ)/(p/p^\circ) = \mathrm{d}\ln(p/p^\circ)$ and $\mathrm{d}T/T^2 = -\mathrm{d}(1/T)$, we can write Eq. 8.4.12 in three alternative forms:

$$\frac{\mathrm{d}\ln(p/p^\circ)}{\mathrm{d}T} \approx \frac{\Delta_{\mathrm{trs}}H}{RT^2} \tag{8.4.13}$$

(pure substance,
vaporization or sublimation)

$$\mathrm{d}\ln(p/p^\circ) \approx -\frac{\Delta_{\mathrm{trs}}H}{R}\,\mathrm{d}(1/T) \tag{8.4.14}$$

(pure substance,
vaporization or sublimation)

$$\frac{\mathrm{d}\ln(p/p^\circ)}{\mathrm{d}(1/T)} \approx -\frac{\Delta_{\mathrm{trs}}H}{R} \tag{8.4.15}$$

(pure substance,
vaporization or sublimation)

Equation 8.4.15 shows that the curve of a plot of $\ln(p/p^\circ)$ versus $1/T$ (where p is the vapor pressure of a pure liquid or solid) has a slope at each temperature equal, usually to a high degree of accuracy, to $-\Delta_{\mathrm{vap}}H/R$ or $-\Delta_{\mathrm{sub}}H/R$ at that temperature. This kind of plot provides an alternative to calorimetry for evaluating molar enthalpies of vaporization and sublimation.

> If we use the recommended standard pressure of 1 bar, the ratio p/p° appearing in these equations becomes p/bar. That is, p/p° is simply the numerical value of p when p is expressed in bars. For the purpose of using Eq. 8.4.15 to evaluate $\Delta_{\mathrm{trs}}H$, we can replace p° by any convenient value. Thus, the curves of plots of $\ln(p/\mathrm{bar})$ versus $1/T$, $\ln(p/\mathrm{Pa})$ versus $1/T$, and $\ln(p/\mathrm{Torr})$ versus $1/T$ using the same temperature and pressure data all have the same slope (but different intercepts) and yield the same value of $\Delta_{\mathrm{trs}}H$.

If we assume $\Delta_{\mathrm{vap}}H$ or $\Delta_{\mathrm{sub}}H$ is essentially constant in a temperature range, we may integrate Eq. 8.4.14 from an initial to a final state along the coexistence curve to obtain

$$\ln\frac{p_2}{p_1} \approx -\frac{\Delta_{\mathrm{trs}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.4.16}$$

(pure substance,
vaporization or sublimation)

Equation 8.4.16 allows us to estimate any one of the quantities p_1, p_2, T_1, T_2, or $\Delta_{\mathrm{trs}}H$, given values of the other four.

8.5: Chapter 8 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

8.1

Consider the system described in Sec. 8.1.5 containing a spherical liquid droplet of radius r surrounded by pure vapor. Starting with Eq. 8.1.15, find an expression for the total differential of U. Then impose conditions of isolation and show that the equilibrium conditions are $T^{\mathrm{g}} = T^{\mathrm{l}}$, $\mu^{\mathrm{g}} = \mu^{\mathrm{l}}$, and $p^{\mathrm{l}} = p^{\mathrm{g}} + 2\gamma/r$, where γ is the surface tension.

8.2

This problem concerns diethyl ether at $T = 298.15\,\mathrm{K}$. At this temperature, the standard molar entropy of the gas calculated from spectroscopic data is $S^{\circ}_{\mathrm{m}}(\mathrm{g}) = 342.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The saturation vapor pressure of the liquid at this temperature is $0.6691\,\mathrm{bar}$, and the molar enthalpy of vaporization is $\Delta_{\mathrm{vap}}H = 27.10\,\mathrm{kJ\,mol^{-1}}$. The second virial coefficient of the gas at this temperature has the value $B = -1.227 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$, and its variation with temperature is given by $\mathrm{d}B/\,\mathrm{d}T = 1.50 \times 10^{-5}\,\mathrm{m^3\,K^{-1}\,mol^{-1}}$.

(a) Use these data to calculate the standard molar entropy of liquid diethyl ether at $298.15\,\mathrm{K}$. A small pressure change has a negligible effect on the molar entropy of a liquid, so that it is a good approximation to equate $S^{\circ}_{\mathrm{m}}(\mathrm{l})$ to $S_{\mathrm{m}}(\mathrm{l})$ at the saturation vapor pressure.

(b) Calculate the standard molar entropy of vaporization and the standard molar enthalpy of vaporization of diethyl ether at $298.15\,\mathrm{K}$. It is a good approximation to equate $H^{\circ}_{\mathrm{m}}(\mathrm{l})$ to $H_{\mathrm{m}}(\mathrm{l})$ at the saturation vapor pressure.

8.3

Explain why the chemical potential surfaces shown in Fig. 8.12 are concave downward; that is, why $(\partial\mu/\partial T)_p$ becomes more negative with increasing T and $(\partial\mu/\partial p)_T$ becomes less positive with increasing p.

8.4

Potassium has a standard boiling point of $773\,^{\circ}\mathrm{C}$ and a molar enthalpy of vaporization $\Delta_{\mathrm{vap}}H = 84.9\,\mathrm{kJ\,mol^{-1}}$. Estimate the saturation vapor pressure of liquid potassium at $400.\,^{\circ}\mathrm{C}$.

8.5

Naphthalene has a melting point of $78.2\,^{\circ}\mathrm{C}$ at $1\,\mathrm{bar}$ and $81.7\,^{\circ}\mathrm{C}$ at $100\,\mathrm{bar}$. The molar volume change on melting is $\Delta_{\mathrm{fus}}V = 0.019\,\mathrm{cm^3\,mol^{-1}}$. Calculate the molar enthalpy of fusion to two significant figures.

8.6

The dependence of the vapor pressure of a liquid on temperature, over a limited temperature range, is often represented by the *Antoine equation*, $\log_{10}(p/\mathrm{Torr}) = A - B/(t + C)$, where t is the Celsius temperature and A, B, and C are constants determined by experiment. A variation of this equation, using a natural logarithm and the thermodynamic temperature, is

$$\ln(p/\mathrm{bar}) = a - \frac{b}{T + c} \tag{8.5.1}$$

The vapor pressure of liquid benzene at temperatures close to $298\,\mathrm{K}$ is adequately represented by the preceding equation with the following values of the constants:

$$a = 9.25092 \qquad b = 2771.233\,\mathrm{K} \qquad c = -53.262\,\mathrm{K} \tag{8.5.2}$$

(a) Find the standard boiling point of benzene.

(b) Use the Clausius–Clapeyron equation to evaluate the molar enthalpy of vaporization of benzene at $298.15\,\mathrm{K}$.

8.7

At a pressure of one atmosphere, water and steam are in equilibrium at $99.97\,^{\circ}\mathrm{C}$ (the normal boiling point of water). At this pressure and temperature, the water density is $0.958\,\mathrm{g\,cm^{-3}}$, the steam density is $5.98 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$, and the molar enthalpy of vaporization is $40.66\,\mathrm{kJ\,mol^{-1}}$.

(a) Use the Clapeyron equation to calculate the slope $\mathrm{d}p/\,\mathrm{d}T$ of the liquid–gas coexistence curve at this point.

(b) Repeat the calculation using the Clausius–Clapeyron equation.

(c) Use your results to estimate the standard boiling point of water. (Note: The experimental value is $99.61\,^{\circ}\mathrm{C}$.)

8.8

At the standard pressure of 1 bar, liquid and gaseous H_2O coexist in equilibrium at $372.76\,\mathrm{K}$, the standard boiling point of water.

(a) Do you expect the standard molar enthalpy of vaporization to have the same value as the molar enthalpy of vaporization at this temperature? Explain.

(b) The molar enthalpy of vaporization at $372.76\,\mathrm{K}$ has the value $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\ mol^{-1}}$. Estimate the value of $\Delta_{\mathrm{vap}}H^{\circ}$ at this temperature with the help of Table 7.5 and the following data for the second virial coefficient of gaseous H_2O at $372.76\,\mathrm{K}$:

$$B = -4.60 \times 10^{-4}\,\mathrm{m^3\ mol^{-1}} \qquad \mathrm{d}B/\mathrm{d}T = 3.4 \times 10^{-6}\,\mathrm{m^3\ K^{-1}\ mol^{-1}} \tag{8.5.3}$$

(c) Would you expect the values of $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{fus}}H^{\circ}$ to be equal at the standard freezing point of water? Explain.

8.9

The standard boiling point of H_2O is $99.61\,^{\circ}\mathrm{C}$. The molar enthalpy of vaporization at this temperature is $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\ mol^{-1}}$. The molar heat capacity of the liquid at temperatures close to this value is given by

$$C_{p,\mathrm{m}} = a + b(t - c)$$

where t is the Celsius temperature and the constants have the values

$$a = 75.94\,\mathrm{J\ K^{-1}\ mol^{-1}} \qquad b = 0.022\,\mathrm{J\ K^{-2}\ mol^{-1}} \qquad c = 99.61\,^{\circ}\mathrm{C} \tag{8.5.4}$$

Suppose $100.00\,\mathrm{mol}$ of liquid H_2O is placed in a container maintained at a constant pressure of 1 bar, and is carefully heated to a temperature $5.00\,^{\circ}\mathrm{C}$ above the standard boiling point, resulting in an unstable phase of superheated water. If the container is enclosed with an adiabatic boundary and the system subsequently changes spontaneously to an equilibrium state, what amount of water will vaporize? (Hint: The temperature will drop to the standard boiling point, and the enthalpy change will be zero.)

CHAPTER OVERVIEW

9: Mixtures

A homogeneous mixture is a phase containing more than one substance. This chapter discusses composition variables and partial molar quantities of mixtures in which no chemical reaction is occurring. The ideal mixture is defined. Chemical potentials, activity coefficients, and activities of individual substances in both ideal and nonideal mixtures are discussed.

Except for the use of fugacities to determine activity coefficients in condensed phases, a discussion of phase equilibria involving mixtures will be postponed to Chap. 13.

9.1: Composition Variables

A **composition variable** is an intensive property that indicates the relative amount of a particular species or substance in a phase.

9.1.1 Species and substances

We sometimes need to make a distinction between a species and a substance. A **species** is any entity of definite elemental composition and charge and can be described by a chemical formula, such as H_2O, H_3O^+, NaCl, or Na^+. A **substance** is a species that can be prepared in a pure state (e.g., N_2 and NaCl). Since we cannot prepare a macroscopic amount of a single kind of ion by itself, a charged species such as H_3O^+ or Na^+ is not a substance. Chap. 10 will discuss the special features of mixtures containing charged species.

9.1.2 Mixtures in general

The **mole fraction** of species i is defined by

$$x_i \overset{\text{def}}{=} \frac{n_i}{\sum_j n_j} \qquad \text{or} \qquad y_i \overset{\text{def}}{=} \frac{n_i}{\sum_j n_j} \tag{9.1.1}$$

$(P{=}1)$

where n_i is the amount of species i and the sum is taken over all species in the mixture. The symbol x_i is used for a mixture in general, and y_i is used when the mixture is a gas.

The **mass fraction**, or weight fraction, of species i is defined by

$$w_i \overset{\text{def}}{=} \frac{m(i)}{m} = \frac{n_i M_i}{\sum_j n_j M_j} \tag{9.1.2}$$

$(P{=}1)$

where $m(i)$ is the mass of species i and m is the total mass.

The **concentration**, or molarity, of species i in a mixture is defined by

$$c_i \overset{\text{def}}{=} \frac{n_i}{V} \tag{9.1.3}$$

$(P{=}1)$

The symbol M is often used to stand for units of mol L^{-1}, or mol dm^{-3}. Thus, a concentration of 0.5 M is 0.5 moles per liter, or 0.5 molar.

> Concentration is sometimes called “amount concentration” or “molar concentration” to avoid confusion with number concentration (the number of *particles* per unit volume). An alternative notation for c_A is [A].

A **binary mixture** is a mixture of *two* substances.

9.1.3 Solutions

A **solution**, strictly speaking, is a mixture in which one substance, the **solvent**, is treated in a special way. Each of the other species comprising the mixture is then a **solute**. The solvent is denoted by A and the solute species by B, C, and so on. (Some chemists denote the solvent by subscript 1 and use 2, 3, and so on for solutes.) Although in principle a solution can be a gas mixture, in this section we will consider only liquid and solid solutions.

We can prepare a solution of varying composition by gradually mixing one or more solutes with the solvent so as to continuously increase the solute mole fractions. During this mixing process, the physical state (liquid or solid) of the solution remains the same as that of the pure solvent. When the sum of the solute mole fractions is small compared to x_A (i.e., x_A is close to unity), the solution is called *dilute*. As the solute mole fractions increase, we say the solution becomes more *concentrated*.

Mole fraction, mass fraction, and concentration can be used as composition variables for both solvent and solute, just as they are for mixtures in general. A fourth composition variable, molality, is often used for a solute. The **molality** of solute species B is defined by

$$m_B \overset{\text{def}}{=} \frac{n_B}{m(A)} \tag{9.1.4}$$

(solution)

where $m(\mathrm{A}) = n_\mathrm{A} M_\mathrm{A}$ is the mass of solvent. The symbol m is sometimes used to stand for units of mol kg^{-1}, although this should be discouraged because m is also the symbol for meter. For example, a solute molality of 0.6 m is 0.6 moles of solute per kilogram of solvent, or 0.6 molal.

9.1.4 Binary solutions

We may write simplified equations for a binary solution of two substances, solvent A and solute B. Equations 9.1.1–9.1.4 become

$$x_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A} + n_\mathrm{B}} \tag{9.1.5}$$
(binary solution)

$$w_\mathrm{B} = \frac{n_\mathrm{B} M_\mathrm{B}}{n_\mathrm{A} M_\mathrm{A} + n_\mathrm{B} M_\mathrm{B}} \tag{9.1.6}$$
(binary solution)

$$c_\mathrm{B} = \frac{n_\mathrm{B}}{V} = \frac{n_\mathrm{B} \rho}{n_\mathrm{A} M_\mathrm{A} + n_\mathrm{B} M_\mathrm{B}} \tag{9.1.7}$$
(binary solution)

$$m_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A} M_\mathrm{A}} \tag{9.1.8}$$
(binary solution)

The right sides of Eqs. 9.1.5–9.1.8 express the solute composition variables in terms of the amounts and molar masses of the solvent and solute and the density ρ of the solution.

To be able to relate the values of these composition variables to one another, we solve each equation for n_B and divide by n_A to obtain an expression for the mole ratio $n_\mathrm{B}/n_\mathrm{A}$:

$$\text{from Eq. 9.1.5} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{x_\mathrm{B}}{1 - x_\mathrm{B}} \tag{9.1.9}$$
(binary solution)

$$\text{from Eq. 9.1.6} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{M_\mathrm{A} w_\mathrm{B}}{M_\mathrm{B}(1 - w_\mathrm{B})} \tag{9.1.10}$$
(binary solution)

$$\text{from Eq. 9.1.7} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{M_\mathrm{A} c_\mathrm{B}}{\rho - M_\mathrm{B} c_\mathrm{B}} \tag{9.1.11}$$
(binary solution)

$$\text{from Eq. 9.1.8} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = M_\mathrm{A} m_\mathrm{B} \tag{9.1.12}$$
(binary solution)

These expressions for $n_\mathrm{B}/n_\mathrm{A}$ allow us to find one composition variable as a function of another. For example, to find molality as a function of concentration, we equate the expressions for $n_\mathrm{B}/n_\mathrm{A}$ on the right sides of Eqs. 9.1.11 and 9.1.12 and solve for m_B to obtain

$$m_\mathrm{B} = \frac{c_\mathrm{B}}{\rho - M_\mathrm{B} c_\mathrm{B}} \tag{9.1.13}$$

A binary solution becomes more dilute as any of the solute composition variables becomes smaller. In the limit of infinite dilution, the expressions for $n_\mathrm{B}/n_\mathrm{A}$ become:

$$\begin{aligned} \frac{n_\mathrm{B}}{n_\mathrm{A}} &= x_\mathrm{B} \\ &= \frac{M_\mathrm{A}}{M_\mathrm{B}} w_\mathrm{B} \\ &= \frac{M_\mathrm{A}}{\rho^*_\mathrm{A}} c_\mathrm{B} = V^*_\mathrm{m,A} c_\mathrm{B} \\ &= M_\mathrm{A} m_\mathrm{B} \end{aligned} \tag{9.1.14}$$
(binary solution at infinite dilution)

where a superscript asterisk (*) denotes a pure phase. We see that, in the limit of infinite dilution, the composition variables x_B, w_B, c_B, and m_B are proportional to one another. These expressions are also valid for solute B in a *multi*solute solution in which *each* solute is very dilute; that is, in the limit $x_\mathrm{A} \to 1$.

> The rule of thumb that the molarity and molality values of a dilute aqueous solution are approximately equal is explained by the relation $M_\mathrm{A} c_\mathrm{B}/\rho^*_\mathrm{A} = M_\mathrm{A} m_\mathrm{B}$ (from Eq. 9.1.14), or $c_\mathrm{B}/\rho^*_\mathrm{A} = m_\mathrm{B}$, and the fact that the density ρ^*_A

of water is approximately $1\ \mathrm{kg\ L^{-1}}$. Hence, if the solvent is water and the solution is dilute, the numerical value of c_{B} expressed in mol $\mathrm{L^{-1}}$ is approximately equal to the numerical value of m_{B} expressed in mol $\mathrm{kg^{-1}}$.

9.1.5 The composition of a mixture

We can describe the composition of a phase with the amounts of each species, or with any of the composition variables defined earlier: mole fraction, mass fraction, concentration, or molality. If we use mole fractions or mass fractions to describe the composition, we need the values for all but one of the species, since the sum of all fractions is unity.

Other composition variables are sometimes used, such as volume fraction, mole ratio, and mole percent. To describe the composition of a gas mixture, partial pressures can be used (Sec. 9.3.1).

When the composition of a mixture is said to be *fixed* or *constant* during changes of temperature, pressure, or volume, this means there is no change in the relative *amounts* or *masses* of the various species. A mixture of fixed composition has fixed values of mole fractions, mass fractions, and molalities, but not necessarily of concentrations and partial pressures. Concentrations will change if the volume changes, and partial pressures in a gas mixture will change if the pressure changes.

9.2: Partial Molar Quantities

The symbol X_i, where X is an extensive property of a homogeneous mixture and the subscript i identifies a constituent species of the mixture, denotes the **partial molar quantity** of species i defined by

$$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad (9.2.1) \text{ (mixture)}$$

This is the rate at which property X changes with the amount of species i added to the mixture as the temperature, the pressure, and the amounts of all other species are kept constant. A partial molar quantity is an *intensive* state function. Its value depends on the temperature, pressure, and composition of the mixture.

Keep in mind that as a practical matter, a macroscopic amount of a charged species (i.e., an ion) cannot be added by itself to a phase because of the huge electric charge that would result. Thus if species i is charged, X_i as defined by Eq. 9.2.1 is a theoretical concept whose value cannot be determined experimentally.

> An older notation for a partial molar quantity uses an overbar: $\overline{X}_i$. The notation X_i' was suggested in the first edition of the IUPAC Green Book (Ian Mills et al, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell, Oxford, 1988, p. 44), but is not mentioned in later editions.

Example 9.2.1

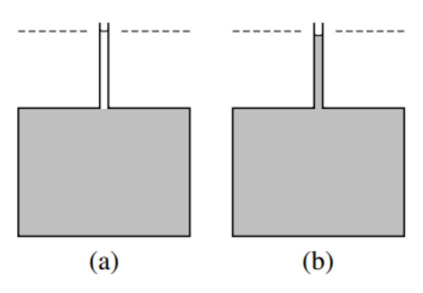


Figure 9.2.1: Addition of pure methanol (substance B) to a water-methanol mixture at constant T and p.

(a) $40.75\ \text{cm}^3$ (one mole) of methanol is placed in a narrow tube above a much greater volume of a mixture (shaded) of composition $x_B = 0.307$. The dashed line indicates the level of the upper meniscus.

(b) After the two liquid phases have mixed by diffusion, the volume of the mixture has increased by only $38.8\ \text{cm}^3$.

9.2.1 Partial molar volume

In order to gain insight into the significance of a partial molar quantity as defined by Eq. 9.2.1, let us first apply the concept to the *volume* of an open single-phase system. Volume has the advantage for our example of being an extensive property that is easily visualized. Let the system be a binary mixture of water (substance A) and methanol (substance B), two liquids that mix in all proportions. The partial molar volume of the methanol, then, is the rate at which the system volume changes with the amount of methanol added to the mixture at constant temperature and pressure: $V_B = (\partial V/\partial n_B)_{T,p,n_A}$.

At $25\ ^\circ\text{C}$ and $1\ \text{bar}$, the molar volume of pure water is $V^*_{\text{m,A}} = 18.07\ \text{cm}^3\ \text{mol}^{-1}$ and that of pure methanol is $V^*_{\text{m,B}} = 40.75\ \text{cm}^3\ \text{mol}^{-1}$. If we mix $100.0\ \text{cm}^3$ of water at $25\ ^\circ\text{C}$ with $100.0\ \text{cm}^3$ of methanol at $25\ ^\circ\text{C}$, we find the volume of the resulting mixture at $25\ ^\circ\text{C}$ is not the sum of the separate volumes, $200.0\ \text{cm}^3$, but rather the slightly smaller value $193.1\ \text{cm}^3$. The difference is due to new intermolecular interactions in the mixture compared to the pure liquids.

Let us calculate the mole fraction composition of this mixture:

$$n_A = \frac{V^*_A}{V^*_{\text{m,A}}} = \frac{100.0\ \text{cm}^3}{18.07\ \text{cm}^3\ \text{mol}^{-1}} = 5.53\ \text{mol} \qquad (9.2.2)$$

$$n_{\mathrm{B}}=\frac{V_{\mathrm{B}}^{*}}{V_{\mathrm{m,B}}^{*}}=\frac{100.0\ \mathrm{cm}^{3}}{40.75\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}}=2.45\ \mathrm{mol} \tag{9.2.3}$$

$$x_{\mathrm{B}}=\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}+n_{\mathrm{B}}}=\frac{2.45\ \mathrm{mol}}{5.53\ \mathrm{mol}+2.45\ \mathrm{mol}}=0.307 \tag{9.2.4}$$

Now suppose we prepare a large volume of a mixture of this composition $(x_{\mathrm{B}}=0.307)$ and add an additional $40.75\ \mathrm{cm}^{3}$ (one mole) of pure methanol, as shown in Fig. 9.1(a). If the initial volume of the mixture at $25^{\circ}\mathrm{C}$ was $10,000.0\ \mathrm{cm}^{3}$, we find the volume of the new mixture at the same temperature is $10,038.8\ \mathrm{cm}^{3}$, an increase of $38.8\ \mathrm{cm}^{3}$ - see Fig. 9.1(b). The amount of methanol added is not infinitesimal, but it is small enough compared to the amount of initial mixture to cause very little change in the mixture composition: x_{B}

increases by only 0.5%. Treating the mixture as an open system, we see that the addition of one mole of methanol to the system at constant T, p, and n_{A} causes the system volume to increase by $38.8\ \mathrm{cm}^{3}$. To a good approximation, then, the partial molar volume of methanol in the mixture, $V_{\mathrm{B}}=(\partial V/\partial n_{\mathrm{B}})_{T,p,n_{\mathrm{A}}}$, is given by $\Delta V/\Delta n_{\mathrm{B}}=38.8\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$.

The volume of the mixture to which we add the methanol does not matter as long as it is large. We would have observed practically the same volume increase, $38.8\ \mathrm{cm}^{3}$, if we had mixed one mole of pure methanol with $100,000.0\ \mathrm{cm}^{3}$ of the mixture instead of only $10,000.0\ \mathrm{cm}^{3}$.

Thus, we may interpret the partial molar volume of B as the volume change per amount of B added at constant T and p when B is mixed with such a large volume of mixture that the composition is not appreciably affected. We may also interpret the partial molar volume as the volume change per amount when an infinitesimal amount is mixed with a finite volume of mixture.

The partial molar volume of B is an intensive property that is a function of the composition of the mixture, as well as of T and p. The limiting value of V_{B} as x_{B} approaches 1 (pure B) is $V_{\mathrm{m,B}}^{*}$, the molar volume of pure B. We can see this by writing $V=n_{\mathrm{B}}V_{\mathrm{m,B}}^{*}$ for pure B, giving us $V_{\mathrm{B}}(x_{\mathrm{B}}=1)=\left(\partial n_{\mathrm{B}}V_{\mathrm{m,B}}^{*}/\partial n_{\mathrm{B}}\right)_{T,p,n_{\mathrm{A}}}=V_{\mathrm{m,B}}^{*}$.

If the mixture is a binary mixture of A and B, and x_{B} is small, we may treat the mixture as a dilute solution of solvent A and solute B. As x_{B} approaches 0 in this solution, V_{B} approaches a certain limiting value that is the volume increase per amount of B mixed with a large amount of pure A. In the resulting mixture, each solute molecule is surrounded only by solvent molecules. We denote this limiting value of V_{B} by V_{B}^{∞}, the partial molar volume of solute B at infinite dilution.
It is possible for a partial molar volume to be negative. Magnesium sulfate, in aqueous solutions of molality less than $0.07\ \mathrm{mol\ kg}^{-1}$, has a negative partial molar volume. Physically, this means that when a small amount of crystalline MgSO_4 dissolves at constant temperature in water, the liquid phase contracts. This unusual behavior is due to strong attractive water-ion interactions.

9.2.2 The total differential of the volume in an open system

Consider an open single-phase system consisting of a mixture of nonreacting substances. How many independent variables does this system have?

We can prepare the mixture with various amounts of each substance, and we are able to adjust the temperature and pressure to whatever values we wish (within certain limits that prevent the formation of a second phase). Each choice of temperature, pressure, and amounts results in a definite value of every other property, such as volume, density, and mole fraction composition. Thus, an open single-phase system of C substances has $2+C$ independent variables. [3]

Footnote

3. C in this kind of system is actually the number of components. The number of components is usually the same as the number of substances, but is less if certain constraints exist, such as reaction equilibrium or a fixed mixture composition. The general meaning of C will be discussed in Sec. 13.

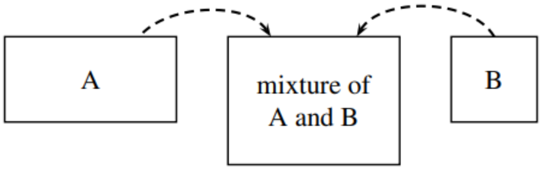


Figure 9.2.2: Mixing of water (A) and methanol (B) in a 2:1 ratio of volumes to form a mixture of increasing volume and constant composition. The system is the mixture.

For a binary mixture $(C=2)$, the number of independent variables is four. We may choose these variables to be T, p, n_{A}, and n_{B}, and write the total differential of V in the general form

$$\begin{aligned} \mathrm{d}V = & \left(\frac{\partial V}{\partial T}\right)_{p,n_{\mathrm{A}},n_{\mathrm{B}}} \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_{T,n_{\mathrm{A}},n_{\mathrm{B}}} \mathrm{d}p \\ & + \left(\frac{\partial V}{\partial n_{\mathrm{A}}}\right)_{T,p,n_{\mathrm{B}}} \mathrm{d}n_{\mathrm{A}} + \left(\frac{\partial V}{\partial n_{\mathrm{B}}}\right)_{T,p,n_{\mathrm{A}}} \mathrm{d}n_{\mathrm{B}} \end{aligned}$$

(binary mixture)

We know the first two partial derivatives on the right side are given by [4]

Footnote

4. See Eqs. 7.1.1 and 7.1.2, which are for closed syste

$$\left(\frac{\partial V}{\partial T}\right)_{p,n_{\mathrm{A}},n_{\mathrm{B}}} = \alpha V \quad \left(\frac{\partial V}{\partial p}\right)_{T,n_{\mathrm{A}},n_{\mathrm{B}}} = -\kappa_T V \tag{9.2.1}$$

We identify the last two partial derivatives on the right side of Eq. 9.2.5 as the partial molar volumes V_{A} and V_{B}. Thus, we may write the total differential of V for this open system in the compact form

$$\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p + V_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + V_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} \tag{9.2.2}$$

(binary mixture)

If we compare this equation with the total differential of V for a one-component closed system, $\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p$ (Eq. 7.1.6), we see that an additional term is required for each constituent of the mixture to allow the system to be open and the composition to vary.

When T and p are held constant, Eq. 9.2.7 becomes

$$\mathrm{d}V = V_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + V_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} \tag{9.2.3}$$

(binary mixture, constant T and p)

We obtain an important relation between the mixture volume and the partial molar volumes by imagining the following process. Suppose we continuously pour pure water and pure methanol at constant but not necessarily equal volume rates into a stirred, thermostatted container to form a mixture of increasing volume and constant composition, as shown schematically in Fig. 9.2. If this mixture remains at constant T and p as it is formed, none of its intensive properties change during the process, and the partial molar volumes V_{A} and V_{B} remain constant. Under these conditions, we can integrate Eq. 9.2.8 to obtain the additivity rule for volume: [5]

$$V = V_{\mathrm{A}}n_{\mathrm{A}} + V_{\mathrm{B}}n_{\mathrm{B}} \tag{9.2.4}$$

(binary mixture)

This equation allows us to calculate the mixture volume from the amounts of the constituents and the appropriate partial molar volumes for the particular temperature, pressure, and composition.

For example, given that the partial molar volumes in a water-methanol mixture of composition $x_{\mathrm{B}}=0.307$ are $V_{\mathrm{A}}=17.74\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ and $V_{\mathrm{B}}=38.76\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$, we calculate the volume of the water-methanol mixture described at the beginning of Sec. 9.2.1 as follows:

$$\begin{aligned} V &= \left(17.74\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\right)(5.53\ \mathrm{mol})+\left(38.76\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\right)(2.45\ \mathrm{mol}) \\ &= 193.1\ \mathrm{cm}^3 \end{aligned}$$

We can differentiate Eq. 9.2.9 to obtain a general expression for $\mathrm{d}V$ under conditions of constant T and p :

$$\mathrm{d}V=V_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}}+V_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}}+n_{\mathrm{A}}\mathrm{d}V_{\mathrm{A}}+n_{\mathrm{B}}\mathrm{d}V_{\mathrm{B}} \tag{9.2.5}$$

But this expression for $\mathrm{d}V$ is consistent with Eq. 9.2.8 only if the sum of the last two terms on the right is zero:

$$n_{\mathrm{A}}\mathrm{d}V_{\mathrm{A}}+n_{\mathrm{B}}\mathrm{d}V_{\mathrm{B}}=0 \tag{9.2.6}$$

(binary mixture, constant T and p)
Equation 9.2.12 is the Gibbs-Duhem equation for a binary mixture, applied to partial molar volumes. (Section 9.2.4 will give a general version of this equation.) Dividing both sides of the equation by $n_{\mathrm{A}}+n_{\mathrm{B}}$ gives the equivalent form

$$x_{\mathrm{A}}\mathrm{d}V_{\mathrm{A}}+x_{\mathrm{B}}\mathrm{d}V_{\mathrm{B}}=0 \tag{9.2.7}$$

(binary mixture, constant T and p)
Equation 9.2.12 shows that changes in the values of V_{A} and V_{B} are related when the composition changes at constant T and p. If we rearrange the equation to the form

$$\mathrm{d}V_{\mathrm{A}}=-\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}}\mathrm{d}V_{\mathrm{B}} \tag{9.2.8}$$

(binary mixture, constant T and p)
we see that a composition change that increases V_{B} (so that $\mathrm{d}V_{\mathrm{B}}$ is positive) must make V_{A} decrease.

9.2.3 Evaluation of partial molar volumes in binary mixtures

The partial molar volumes V_{A} and V_{B} in a binary mixture can be evaluated by the method of intercepts. To use this method, we plot experimental values of the quantity V/n (where n is $n_{\mathrm{A}}+n_{\mathrm{B}}$) versus the mole fraction x_{B}. V/n is called the mean molar volume.

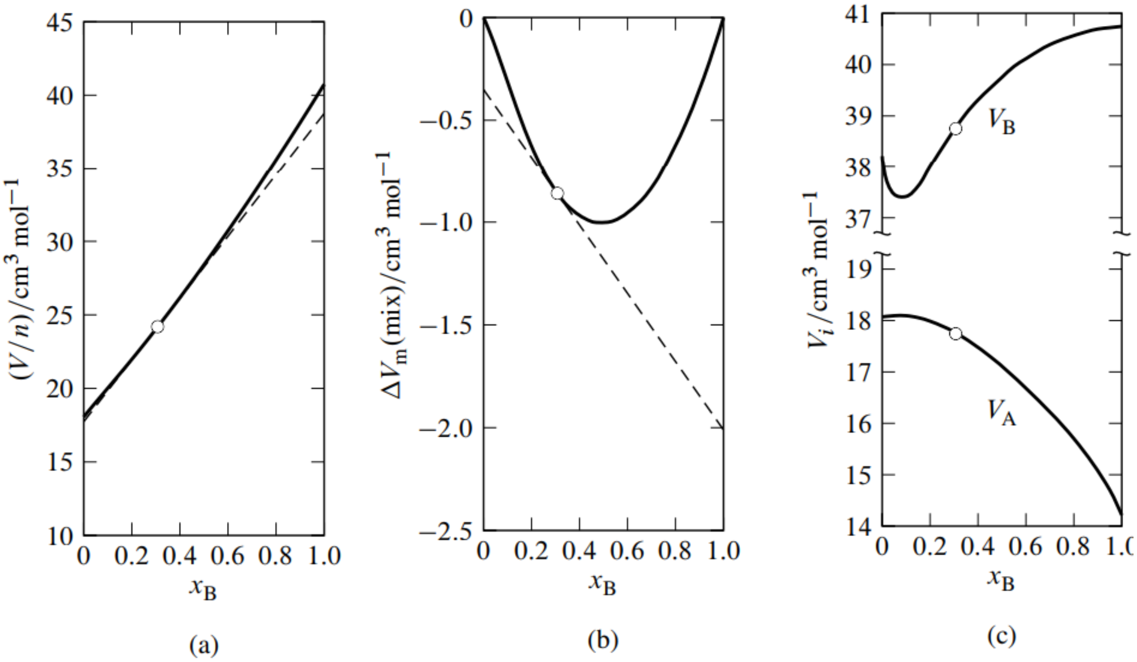


Figure 9.2.3: Figure 9.3 Mixtures of water (A) and methanol (B) at 25°C and 1 bar. [a]

a. Mean molar volume as a function of x_B. The dashed line is the tangent to the curve at $x_B = 0.307$.
b. Molar volume of mixing as a function of x_B. The dashed line is the tangent to the curve at $x_B = 0.307$.
c. Partial molar volumes as functions of x_B. The points at $x_B = 0.307$ (open circles) are obtained from the intercepts of the dashed line in either (a) or (b).

[a] Based on data in Ref. [12].

See Fig. 9.3(a) for an example. In this figure, the tangent to the curve drawn at the point on the curve at the composition of interest (the composition used as an illustration in Sec. 9.2.1) intercepts the vertical line where x_B equals 0 at $V/n = V_A = 17.7\ \mathrm{cm^3\ mol^{-1}}$, and intercepts the vertical line where x_B equals 1 at $V/n = V_B = 38.8\ \mathrm{cm^3\ mol^{-1}}$.

To derive this property of a tangent line for the plot of V/n versus x_B, we use Eq. 9.2.9 to write

$$\begin{aligned}(V/n) &= \frac{V_A n_A + V_B n_B}{n} = V_A x_A + V_B x_B \\ &= V_A(1-x_B) + V_B x_B = (V_B - V_A)x_B + V_A\end{aligned} \tag{9.2.15}$$

Footnote

[5] The equation is an example of the result of applying Euler's theorem on homogeneous functions to V treated as a function of n_A and n_B.

When we differentiate this expression for V/n with respect to x_B, keeping in mind that V_A and V_B are functions of x_B, we obtain

$$\begin{aligned}\frac{\mathrm{d}(V/n)}{\mathrm{d}x_B} &= \frac{\mathrm{d}[(V_B - V_A)x_B + V_A]}{\mathrm{d}x_B} \\ &= V_B - V_A + \left(\frac{\mathrm{d}V_B}{\mathrm{d}x_B} - \frac{\mathrm{d}V_A}{\mathrm{d}x_B}\right)x_B + \frac{\mathrm{d}V_A}{\mathrm{d}x_B} \\ &= V_B - V_A + \left(\frac{\mathrm{d}V_A}{\mathrm{d}x_B}\right)(1-x_B) + \left(\frac{\mathrm{d}V_B}{\mathrm{d}x_B}\right)x_B \\ &= V_B - V_A + \left(\frac{\mathrm{d}V_A}{\mathrm{d}x_B}\right)x_A + \left(\frac{\mathrm{d}V_B}{\mathrm{d}x_B}\right)x_B\end{aligned} \tag{9.2.16}$$

The differentials $\mathrm{d}V_{\mathrm{A}}$ and $\mathrm{d}V_{\mathrm{B}}$ are related to one another by the Gibbs–Duhem equation (Eq. 9.2.13): $x_{\mathrm{A}}\,\mathrm{d}V_{\mathrm{A}}+x_{\mathrm{B}}\,\mathrm{d}V_{\mathrm{B}}=0$. We divide both sides of this equation by $\mathrm{d}x_{\mathrm{B}}$ to obtain

$$\left(\frac{\mathrm{d}V_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{A}}+\left(\frac{\mathrm{d}V_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{B}}=0 \tag{9.2.17}$$

and substitute in Eq. 9.2.16 to obtain

$$\frac{\mathrm{d}(V/n)}{\mathrm{d}x_{\mathrm{B}}}=V_{\mathrm{B}}-V_{\mathrm{A}} \tag{9.2.18}$$

Let the partial molar volumes of the constituents of a binary mixture of arbitrary composition x'_{B} be V'_{A} and V'_{B}. Equation 9.2.15 shows that the value of V/n at the point on the curve of V/n versus x_{B} where the composition is x'_{B} is $(V'_{\mathrm{B}}-V'_{\mathrm{A}})x'_{\mathrm{B}}+V'_{\mathrm{A}}$. Equation 9.2.18 shows that the tangent to the curve at this point has a slope of $V'_{\mathrm{B}}-V'_{\mathrm{A}}$. The equation of the line that passes through this point and has this slope, and thus is the tangent to the curve at this point, is $y=(V'_{\mathrm{B}}-V'_{\mathrm{A}})x_{\mathrm{B}}+V'_{\mathrm{A}}$, where y is the vertical ordinate on the plot of (V/n) versus x_{B}. The line has intercepts $y{=}V'_{\mathrm{A}}$ at $x_{\mathrm{B}}{=}0$ and $y{=}V'_{\mathrm{B}}$ at $x_{\mathrm{B}}{=}1$.

A variant of the method of intercepts is to plot the molar integral volume of mixing given by

$$\Delta V_{\mathrm{m}}(\mathrm{mix})=\frac{\Delta V(\mathrm{mix})}{n}=\frac{V-n_{\mathrm{A}}V^{*}_{\mathrm{m,A}}-n_{\mathrm{B}}V^{*}_{\mathrm{m,B}}}{n} \tag{9.2.19}$$

versus x_{B}, as illustrated in Fig. 9.3(b). $\Delta V(\mathrm{mix})$ is the integral volume of mixing—the volume change at constant T and p when solvent and solute are mixed to form a mixture of volume V and total amount n (see Sec. 11.1.1). The tangent to the curve at the composition of interest has intercepts $V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}$ at $x_{\mathrm{B}}{=}0$ and $V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}$ at $x_{\mathrm{B}}{=}1$.

To see this, we write

$$\begin{aligned}\Delta V_{\mathrm{m}}(\mathrm{mix})&=(V/n)-x_{\mathrm{A}}V^{*}_{\mathrm{m,A}}-x_{\mathrm{B}}V^{*}_{\mathrm{m,B}}\\&=(V/n)-(1-x_{\mathrm{B}})V^{*}_{\mathrm{m,A}}-x_{\mathrm{B}}V^{*}_{\mathrm{m,B}}\end{aligned} \tag{9.2.20}$$

We make the substitution $(V/n)=(V_{\mathrm{B}}-V_{\mathrm{A}})x_{\mathrm{B}}+V_{\mathrm{A}}$ from Eq. 9.2.15 and rearrange:

$$\Delta V_{\mathrm{m}}(\mathrm{mix})=\left[\left(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}\right)-\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right)\right]x_{\mathrm{B}}+\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right) \tag{9.2.21}$$

Differentiation with respect to x_{B} yields

$$\begin{aligned}\frac{\mathrm{d}\Delta V_{\mathrm{m}}(\mathrm{mix})}{\mathrm{d}x_{\mathrm{B}}}&=\left(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}\right)-\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right)+\left(\frac{\mathrm{d}V_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}}-\frac{\mathrm{d}V_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{B}}+\frac{\mathrm{d}V_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{B}}}\\&=\left(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}\right)-\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right)+\left(\frac{\mathrm{d}V_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{B}}}\right)(1-x_{\mathrm{B}})+\left(\frac{\mathrm{d}V_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{B}}\\&=\left(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}\right)-\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right)+\left(\frac{\mathrm{d}V_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{A}}+\left(\frac{\mathrm{d}V_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}}\right)x_{\mathrm{B}}\end{aligned} \tag{9.2.22}$$

With a substitution from Eq. 9.2.17, this becomes

$$\frac{\mathrm{d}\Delta V_{\mathrm{m}}(\mathrm{mix})}{\mathrm{d}x_{\mathrm{B}}}=\left(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}\right)-\left(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}\right) \tag{9.2.23}$$

Equations 9.2.21 and 9.2.23 are analogous to Eqs. 9.2.15 and 9.2.18, with V/n replaced by $\Delta V_{\mathrm{m}}(\mathrm{mix})$, V_{A} by $(V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}})$, and V_{B} by $(V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}})$. Using the same reasoning as for a plot of V/n versus x_{B}, we find the intercepts of the tangent to a point on the curve of $\Delta V_{\mathrm{m}}(\mathrm{mix})$ versus x_{B} are at $V_{\mathrm{A}}-V^{*}_{\mathrm{m,A}}$ and $V_{\mathrm{B}}-V^{*}_{\mathrm{m,B}}$.

Figure 9.3 shows smoothed experimental data for water–methanol mixtures plotted in both kinds of graphs, and the resulting partial molar volumes as functions of composition. Note in Fig. 9.3(c) how the V_{A} curve mirrors the V_{B} curve as x_{B} varies, as predicted by the Gibbs–Duhem equation. The minimum in V_{B} at $x_{\mathrm{B}}{\approx}0.09$ is mirrored by a maximum in V_{A} in agreement with Eq. 9.2.14; the maximum is much attenuated because $n_{\mathrm{B}}/n_{\mathrm{A}}$ is much less than unity.

> Macroscopic measurements are unable to provide unambiguous information about molecular structure. Nevertheless, it is interesting to speculate on the implications of the minimum observed for the partial molar volume of methanol. One interpretation is that in a mostly aqueous environment, there is association of methanol molecules, perhaps involving the formation of dimers.

9.2.4 General relations

The discussion above of partial molar volumes used the notation $V^*_{\mathrm{m,A}}$ and $V^*_{\mathrm{m,B}}$ for the molar volumes of pure A and B. The partial molar volume of a pure substance is the same as the molar volume, so we can simplify the notation by using V^*_{A} and V^*_{B} instead. Hereafter, this e-book will denote molar quantities of pure substances by such symbols as V^*_{A}, H^*_{B}, and S^*_i.

The relations derived above for the volume of a binary mixture may be generalized for any extensive property X of a mixture of any number of constituents. The partial molar quantity of species i, defined by

$$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.24}$$

is an intensive property that depends on T, p, and the composition of the mixture. The additivity rule for property X is

$$X = \sum_i n_i X_i \qquad \text{(9.2.25) (mixture)}$$

and the Gibbs–Duhem equation applied to X can be written in the equivalent forms

$$\sum_i n_i \,\mathrm{d}X_i = 0 \qquad \text{(9.2.26) (constant } T \text{ and } p)$$

and

$$\sum_i x_i \,\mathrm{d}X_i = 0 \qquad \text{(9.2.27) (constant } T \text{ and } p)$$

These relations can be applied to a mixture in which each species i is a nonelectrolyte substance, an electrolyte substance that is dissociated into ions, or an individual ionic species. In Eq. 9.2.27, the mole fraction x_i must be based on the different species considered to be present in the mixture. For example, an aqueous solution of NaCl could be treated as a mixture of components A=H_2O and B=NaCl, with x_{B} equal to $n_{\mathrm{B}}/(n_{\mathrm{A}}+n_{\mathrm{B}})$; or the constituents could be taken as H_2O, Na^+, and Cl^-, in which case the mole fraction of Na^+ would be $x_+ = n_+/(n_{\mathrm{A}}+n_+ +n_-)$.

A general method to evaluate the partial molar quantities X_{A} and X_{B} in a binary mixture is based on the variant of the method of intercepts described in Sec. 9.2.3. The molar mixing quantity $\Delta X(\mathrm{mix})/n$ is plotted versus x_{B}, where $\Delta X(\mathrm{mix})$ is $(X - n_{\mathrm{A}}X^*_{\mathrm{A}} - n_{\mathrm{B}}X^*_{\mathrm{B}})$. On this plot, the tangent to the curve at the composition of interest has intercepts equal to $X_{\mathrm{A}} - X^*_{\mathrm{A}}$ at x_{B}=0 and $X_{\mathrm{B}} - X^*_{\mathrm{B}}$ at x_{B}=1.

We can obtain experimental values of such partial molar quantities of an uncharged species as V_i, $C_{p,i}$, and S_i. It is not possible, however, to evaluate the partial molar quantities U_i, H_i, A_i, and G_i because these quantities involve the internal energy brought into the system by the species, and we cannot evaluate the absolute value of internal energy (Sec. 2.6.2). For example, while we can evaluate the difference $H_i - H^*_i$ from calorimetric measurements of enthalpies of mixing, we cannot evaluate the partial molar enthalpy H_i itself. We can, however, include such quantities as H_i in useful theoretical relations.

> A partial molar quantity of a *charged* species is something else we cannot evaluate. It is possible, however, to obtain values relative to a reference ion. Consider an aqueous solution of a fully-dissociated electrolyte solute with the formula $M_{\nu_+}X_{\nu_-}$, where ν_+ and ν_- are the numbers of cations and anions per solute formula unit. The partial molar volume V_{B} of the solute, which can be determined experimentally, is related to the (unmeasurable) partial molar volumes V_+ and V_- of the constituent ions by
>
> $$V_{\mathrm{B}} = \nu_+ V_+ + \nu_- V_- \tag{9.2.28}$$
>
> For aqueous solutions, the usual reference ion is H^+, and the partial molar volume of this ion at infinite dilution is arbitrarily set equal to zero: $V^\infty_{\mathrm{H}^+} = 0$.

For example, given the value (at $298.15\,\mathrm{K}$ and $1\,\mathrm{bar}$) of the partial molar volume at infinite dilution of aqueous hydrogen chloride

$$V^{\infty}_{\mathrm{HCl}} = 17.82\,\mathrm{cm^3\,mol^{-1}} \tag{9.2.29}$$

we can find the so-called "conventional" partial molar volume of $\mathrm{Cl^-}$ ion:

$$V^{\infty}_{\mathrm{Cl^-}} = V^{\infty}_{\mathrm{HCl}} - V^{\infty}_{\mathrm{H^+}} = 17.82\,\mathrm{cm^3\,mol^{-1}} \tag{9.2.30}$$

Going one step further, the measured value $V^{\infty}_{\mathrm{NaCl}} = 16.61\,\mathrm{cm^3\,mol^{-1}}$ gives, for $\mathrm{Na^+}$ ion, the conventional value

$$V^{\infty}_{\mathrm{Na^+}} = V^{\infty}_{\mathrm{NaCl}} - V^{\infty}_{\mathrm{Cl^-}} = (16.61 - 17.82)\,\mathrm{cm^3\,mol^{-1}} = -1.21\,\mathrm{cm^3\,mol^{-1}} \tag{9.2.31}$$

9.2.5 Partial specific quantities

A **partial specific quantity** of a substance is the partial molar quantity divided by the molar mass, and has dimensions of volume divided by mass. For example, the partial specific volume v_{B} of solute B in a binary solution is given by

$$v_{\mathrm{B}} = \frac{V_{\mathrm{B}}}{M_{\mathrm{B}}} = \left[\frac{\partial V}{\partial m(\mathrm{B})}\right]_{T,p,m(\mathrm{A})} \tag{9.2.32}$$

where $m(\mathrm{A})$ and $m(\mathrm{B})$ are the masses of solvent and solute.

Although this e-book makes little use of specific quantities and partial specific quantities, in some applications they have an advantage over molar quantities and partial molar quantities because they can be evaluated without knowledge of the molar mass. For instance, the value of a solute's partial specific volume is used to determine its molar mass by the method of sedimentation equilibrium (Sec. 9.8.2).

The general relations in Sec. 9.2.4 involving partial molar quantities may be turned into relations involving partial specific quantities by replacing amounts by masses, mole fractions by mass fractions, and partial molar quantities by partial specific quantities. Using volume as an example, we can write an additivity relation $V = \sum_i m(i) v_i$, and Gibbs–Duhem relations $\sum_i m(i)\,\mathrm{d}v_i = 0$ and $\sum_i w_i\,\mathrm{d}v_i = 0$. For a binary mixture of A and B, we can plot the specific volume v versus the mass fraction w_{B}; then the tangent to the curve at a given composition has intercepts equal to v_{A} at w_{B}=0 and v_{B} at w_{B}=1. A variant of this plot is $\left(v - w_{\mathrm{A}} v^*_{\mathrm{A}} - w_{\mathrm{B}} v^*_{\mathrm{B}}\right)$ versus w_{B}; the intercepts are then equal to $v_{\mathrm{A}} - v^*_{\mathrm{A}}$ and $v_{\mathrm{B}} - v^*_{\mathrm{B}}$.

9.2.6 The chemical potential of a species in a mixture

Just as the molar Gibbs energy of a pure substance is called the *chemical potential* and given the special symbol μ, the partial molar Gibbs energy G_i of species i in a mixture is called the **chemical potential** of species i, defined by

$$\mu_i \overset{\mathrm{def}}{=} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.33}$$
(mixture)

If there are work coordinates for nonexpansion work, the partial derivative is taken at constant values of these coordinates.

The chemical potential of a species in a phase plays a crucial role in equilibrium problems, because it is a measure of the escaping tendency of the species from the phase. Although we cannot determine the absolute value of μ_i for a given state of the system, we are usually able to evaluate the difference between the value in this state and the value in a defined reference state.

In an open single-phase system containing a mixture of s different nonreacting species, we may in principle independently vary T, p, and the amount of each species. This is a total of $2+s$ independent variables. The total differential of the Gibbs energy of this system is given by Eq. 5.5.9, often called the Gibbs fundamental equation:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{i=1}^{s} \mu_i\,\mathrm{d}n_i \tag{9.2.34}$$
(mixture)

Consider the special case of a mixture containing *charged* species, for example an aqueous solution of the electrolyte KCl. We could consider the constituents to be either the substances $\mathrm{H_2O}$ and KCl, or else $\mathrm{H_2O}$ and the species $\mathrm{K^+}$ and $\mathrm{Cl^-}$. Any mixture we can prepare in the laboratory must remain electrically neutral, or virtually so. Thus, while we are able to independently vary the amounts of $\mathrm{H_2O}$ and KCl, we cannot in practice independently vary the amounts of $\mathrm{K^+}$ and $\mathrm{Cl^-}$ in the mixture. The chemical potential of the $\mathrm{K^+}$ ion is defined as the rate at which the Gibbs energy changes with the amount of $\mathrm{K^+}$ added at constant T and p

while the amount of Cl^- is kept constant. This is a hypothetical process in which the net charge of the mixture increases. The chemical potential of a ion is therefore a valid but purely theoretical concept. Let A stand for H_2O, B for KCl, $+$ for K^+, and $-$ for Cl^-. Then it is theoretically valid to write the total differential of G for the KCl solution either as

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} \tag{9.2.35}$$

or as

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_+\,\mathrm{d}n_+ + \mu_-\,\mathrm{d}n_- \tag{9.2.36}$$

9.2.7 Equilibrium conditions in a multiphase, multicomponent system

This section extends the derivation described in Sec. 8.1.2, which was for equilibrium conditions in a multiphase system containing a single substance, to a more general kind of system: one with two or more homogeneous phases containing mixtures of nonreacting species. The derivation assumes there are no internal partitions that could prevent transfer of species and energy between the phases, and that effects of gravity and other external force fields are negligible.

The system consists of a reference phase, α', and other phases labeled by $\alpha \neq \alpha'$. Species are labeled by subscript i. Following the procedure of Sec. 8.1.1, we write for the total differential of the internal energy

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}U^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}U^\alpha \\ &= T^{\alpha'}\,\mathrm{d}S^{\alpha'} - p^{\alpha'}\,\mathrm{d}V^{\alpha'} + \sum_i \mu_i^{\alpha'}\,\mathrm{d}n_i^{\alpha'} \\ &\quad + \sum_{\alpha\neq\alpha'}\left(T^\alpha\,\mathrm{d}S^\alpha - p^\alpha\,\mathrm{d}V^\alpha + \sum_i \mu_i^\alpha\,\mathrm{d}n_i^\alpha\right)\end{aligned} \tag{9.2.37}$$

The conditions of isolation are

$$\mathrm{d}U = 0 \qquad \text{(constant internal energy)} \tag{9.2.38}$$

$$\mathrm{d}V^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}V^\alpha = 0 \qquad \text{(no expansion work)} \tag{9.2.39}$$

$$\begin{gathered}\text{For each species } i\text{:} \\ \mathrm{d}n_i^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}n_i^\alpha = 0 \qquad \text{(closed system)}\end{gathered} \tag{9.2.40}$$

We use these relations to substitute for $\mathrm{d}U$, $\mathrm{d}V^{\alpha'}$, and $\mathrm{d}n_i^{\alpha'}$ in Eq. 9.2.37. After making the further substitution $\mathrm{d}S^{\alpha'} = \mathrm{d}S - \sum_{\alpha\neq\alpha'} \mathrm{d}S^\alpha$ and solving for $\mathrm{d}S$, we obtain

$$\mathrm{d}S = \sum_{\alpha\neq\alpha'} \frac{T^{\alpha'} - T^\alpha}{T^{\alpha'}}\,\mathrm{d}S^\alpha - \sum_{\alpha\neq\alpha'} \frac{p^{\alpha'} - p^\alpha}{T^{\alpha'}}\,\mathrm{d}V^\alpha + \sum_i \sum_{\alpha\neq\alpha'} \frac{\mu_i^{\alpha'} - \mu_i^\alpha}{T^{\alpha'}}\,\mathrm{d}n_i^\alpha \tag{9.2.41}$$

This equation is like Eq. 8.1.6 with provision for more than one species.

In the equilibrium state of the isolated system, S has the maximum possible value, $\mathrm{d}S$ is equal to zero for an infinitesimal change of any of the independent variables, and the coefficient of each term on the right side of Eq. 9.2.41 is zero. We find that in this state each phase has the same temperature and the same pressure, and for each species the chemical potential is the same in each phase.

Suppose the system contains a species i' that is effectively excluded from a particular phase, α''. For instance, sucrose molecules dissolved in an aqueous phase are not accommodated in the crystal structure of an ice phase, and a nonpolar substance may be essentially insoluble in an aqueous phase. We can treat this kind of situation by setting $\mathrm{d}n_{i'}^{\alpha''}$ equal to zero. Consequently there is no equilibrium condition involving the chemical potential of this species in phase α''.

To summarize these conclusions: In an equilibrium state of a multiphase, multicomponent system without internal partitions, the temperature and pressure are uniform throughout the system, and each species has a uniform chemical potential except in phases where it is excluded.

> This statement regarding the uniform chemical potential of a species applies to both a substance and an ion, as the following argument explains. The derivation in this section begins with Eq. 9.2.37, an expression for the total

differential of U. Because it is a total differential, the expression requires the amount n_i of each species i in each phase to be an independent variable. Suppose one of the phases is the aqueous solution of KCl used as an example at the end of the preceding section. In principle (but not in practice), the amounts of the species H_2O, K^+, and Cl^- can be varied independently, so that it is valid to include these three species in the sums over i in Eq. 9.2.37. The derivation then leads to the conclusion that K^+ has the same chemical potential in phases that are in transfer equilibrium with respect to K^+, and likewise for Cl^-. This kind of situation arises when we consider a Donnan membrane equilibrium (Sec. 12.7.3) in which transfer equilibrium of ions exists between solutions of electrolytes separated by a semipermeable membrane.

9.2.8 Relations involving partial molar quantities

Here we derive several useful relations involving partial molar quantities in a single-phase system that is a mixture. The independent variables are T, p, and the amount n_i of each constituent species i.

From Eqs. 9.2.26 and 9.2.27, the Gibbs–Duhem equation applied to the chemical potentials can be written in the equivalent forms

$$\sum_i n_i \, \mathrm{d}\mu_i = 0 \qquad (9.2.42)$$

(constant T and p)

and

$$\sum_i x_i \, \mathrm{d}\mu_i = 0 \qquad (9.2.43)$$

(constant T and p)

These equations show that the chemical potentials of different species cannot be varied independently at constant T and p.

A more general version of the Gibbs–Duhem equation, without the restriction of constant T and p, is

$$S \, \mathrm{d}T - V \, \mathrm{d}p + \sum_i n_i \, \mathrm{d}\mu_i = 0 \qquad (9.2.44)$$

This version is derived by comparing the expression for $\mathrm{d}G$ given by Eq. 9.2.34 with the differential $\mathrm{d}G = \sum_i \mu_i \, \mathrm{d}n_i + \sum_i n_i \, \mathrm{d}\mu_i$ obtained from the additivity rule $G = \sum_i \mu_i n_i$.

The Gibbs energy is defined by $G = H - TS$. Taking the partial derivatives of both sides of this equation with respect to n_i at constant T, p, and $n_{j \neq i}$ gives us

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad (9.2.45)$$

We recognize each partial derivative as a partial molar quantity and rewrite the equation as

$$\mu_i = H_i - TS_i \qquad (9.2.46)$$

This is analogous to the relation $\mu = G/n = H_\mathrm{m} - TS_\mathrm{m}$ for a pure substance.

From the total differential of the Gibbs energy, $\mathrm{d}G = -S \, \mathrm{d}T + V \, \mathrm{d}p + \sum_i \mu_i \, \mathrm{d}n_i$ (Eq. 9.2.34), we obtain the following reciprocity relations:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{n_i\}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{n_i\}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad (9.2.47)$$

The symbol $\{n_i\}$ stands for the set of amounts of all species, and subscript $\{n_i\}$ on a partial derivative means the amount of *each* species is constant—that is, the derivative is taken at constant composition of a closed system. Again we recognize partial derivatives as partial molar quantities and rewrite these relations as follows:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{n_i\}} = -S_i \qquad (9.2.48)$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{n_i\}} = V_i \qquad (9.2.49)$$

These equations are the equivalent for a mixture of the relations $(\partial\mu/\partial T)_p = -S_\mathrm{m}$ and $(\partial\mu/\partial p)_T = V_\mathrm{m}$ for a pure phase (Eqs. 7.8.3 and 7.8.4).

Taking the partial derivatives of both sides of $U = H - pV$ with respect to n_i at constant T, p, and $n_{j\neq i}$ gives

$$U_i = H_i - pV_i \tag{9.2.50}$$

Finally, we can obtain a formula for $C_{p,i}$, the partial molar heat capacity at constant pressure of species i, by writing the total differential of H in the form

$$\begin{aligned} \mathrm{d}H &= \left(\frac{\partial H}{\partial T}\right)_{p,\{n_i\}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\{n_i\}} \mathrm{d}p + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}} \mathrm{d}n_i \\ &= C_p\,\mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\{n_i\}} \mathrm{d}p + \sum_i H_i\,\mathrm{d}n_i \end{aligned} \tag{9.2.51}$$

from which we have the reciprocity relation $(\partial C_p/\partial n_i)_{T,p,n_{j\neq i}} = (\partial H_i/\partial T)_{p,\{n_i\}}$, or

$$C_{p,i} = \left(\frac{\partial H_i}{\partial T}\right)_{p,\{n_i\}} \tag{9.2.52}$$

9.3: Gas Mixtures

The gas mixtures described in this chapter are assumed to be mixtures of nonreacting gaseous substances.

9.3.1 Partial pressure

The **partial pressure** p_i of substance i in a gas mixture is defined as the product of its mole fraction in the gas phase and the pressure of the phase:

$$p_i \overset{\text{def}}{=} y_i p \tag{9.3.1}$$

(gas mixture)

The sum of the partial pressures of all substances in a gas mixture is $\sum_i p_i = \sum_i y_i p = p \sum_i y_i$. Since the sum of the mole fractions of all substances in a mixture is 1, this sum becomes

$$\sum_i p_i = p \tag{9.3.2}$$

(gas mixture)

Thus, the sum of the partial pressures equals the pressure of the gas phase. This statement is known as **Dalton's Law**. It is valid for any gas mixture, regardless of whether or not the gas obeys the ideal gas equation.

9.3.2 The ideal gas mixture

As discussed in Sec. 3.5.1, an ideal gas (whether pure or a mixture) is a gas with negligible intermolecular interactions. It obeys the ideal gas equation $p = nRT/V$ (where n in a mixture is the sum $\sum_i n_i$) and its internal energy in a closed system is a function only of temperature. The partial pressure of substance i in an ideal gas mixture is $p_i = y_i p = y_i nRT/V$; but $y_i n$ equals n_i, giving

$$p_i = \frac{n_i RT}{V} \tag{9.3.3}$$

(ideal gas mixture)

Equation 9.3.3 is the ideal gas equation with the partial pressure of a constituent substance replacing the total pressure, and the amount of the substance replacing the total amount. The equation shows that the partial pressure of a substance in an ideal gas mixture is the pressure the substance by itself, with all others removed from the system, would have at the same T and V as the mixture. Note that this statement is only true for an *ideal* gas mixture. The partial pressure of a substance in a real gas mixture is in general different from the pressure of the pure substance at the same T and V, because the intermolecular interactions are different.

9.3.3 Partial molar quantities in an ideal gas mixture

We need to relate the chemical potential of a constituent of a gas mixture to its partial pressure. We cannot measure the absolute value of a chemical potential, but we can evaluate its value relative to the chemical potential in a particular reference state called the standard state.

The *standard state of substance* i *in a gas mixture* is the same as the standard state of the pure gas described in Sec. 7.7: It is the hypothetical state in which pure gaseous i has the same temperature as the mixture, is at the standard pressure p°, and behaves as an ideal gas. The standard chemical potential $\mu_i^\circ(\text{g})$ of gaseous i is the chemical potential of i in this gas standard state, and is a function of temperature.

By combining Eqs. 9.3.12 and 9.3.16, we obtain

$$\mu_i(p') = \mu_i^\circ(\text{g}) + RT \ln \frac{p_i'}{p^\circ} + \int_0^{p'} \left(V_i - \frac{RT}{p} \right) \mathrm{d}p \tag{9.3.19}$$

(gas mixture,
constant T)

which is the analogue for a gas mixture of Eq. 7.9.2 for a pure gas. Section 7.9 describes the procedure needed to obtain formulas for various molar quantities of a pure gas from Eq. 7.9.2. By following a similar procedure with Eq. 9.3.19, we obtain the formulas for differences between partial molar and standard molar quantities of a constituent of a gas mixture shown in the second column of Table 9.1. These formulas are obtained with the help of Eqs. 9.2.46, 9.2.48, 9.2.50, and 9.2.52.

Equation of state

The equation of state of a real gas mixture can be written as the virial equation

$$pV/n = RT\left[1+\frac{B}{(V/n)}+\frac{C}{(V/n)^2}+\cdots\right] \tag{9.3.20}$$

This equation is the same as Eq. 2.2.2 for a pure gas, except that the molar volume V_m is replaced by the mean molar volume V/n, and the virial coefficients $B, C, \ldots$ depend on composition as well as temperature.

At low to moderate pressures, the simple equation of state

$$V/n = \frac{RT}{p}+B \tag{9.3.21}$$

describes a gas mixture to a sufficiently high degree of accuracy (see Eq. 2.2.8). This is equivalent to a compression factor given by

$$Z \overset{\text{def}}{=} \frac{pV}{nRT} = 1+\frac{Bp}{RT} \tag{9.3.22}$$

From statistical mechanical theory, the dependence of the second virial coefficient B of a binary gas mixture on the mole fraction composition is given by

$$B = y_A^2 B_{AA} + 2y_A y_B B_{AB} + y_B^2 B_{BB} \tag{9.3.23}$$

(binary gas mixture)

where B_{AA} and B_{BB} are the second virial coefficients of pure A and B, and B_{AB} is a mixed second virial coefficient. B_{AA}, B_{BB}, and B_{AB} are functions of T only. For a gas mixture with any number of constituents, the composition dependence of B is given by

$$B = \sum_i \sum_j y_i y_j B_{ij} \tag{9.3.24}$$

(gas mixture, $B_{ij}{=}B_{ji}$)

Here B_{ij} is the second virial of i if i and j are the same, or a mixed second virial coefficient if i and j are different.

If a gas mixture obeys the equation of state of Eq. 9.3.21, the partial molar volume of constituent i is given by

$$V_i = \frac{RT}{p}+B_i' \tag{9.3.25}$$

where the quantity B_i', in order to be consistent with $V_i = (\partial V/\partial n_i)_{T,p,n_{j\neq i}}$, is found to be given by

$$B_i' = 2\sum_j y_j B_{ij} - B \tag{9.3.26}$$

For the constituents of a binary mixture of A and B, Eq. 9.3.26 becomes

$$B_A' = B_{AA} + (-B_{AA} + 2B_{AB} - B_{BB})y_B^2 \tag{9.3.27}$$

(binary gas mixture)

$$B_B' = B_{BB} + (-B_{AA} + 2B_{AB} - B_{BB})y_A^2 \tag{9.3.28}$$

(binary gas mixture)

When we substitute the expression of Eq. 9.3.25 for V_i in Eq. 9.3.18, we obtain a relation between the fugacity coefficient of constituent i and the function B_i':

$$\ln \phi_i = \frac{B_i' p}{RT} \tag{9.3.29}$$

The third column of Table 9.1 gives formulas for various partial molar quantities of constituent i in terms of B_i' and its temperature derivative. The formulas are the same as the approximate formulas in the third column of Table 7.5 for molar quantities of a *pure* gas, with B_i' replacing the second virial coefficient B.

9.4: Liquid and Solid Mixtures of Nonelectrolytes

Homogeneous liquid and solid mixtures are condensed phases of variable composition. Most of the discussion of condensed-phase mixtures in this section focuses on liquids. The same principles, however, apply to homogeneous solid mixtures, often called solid solutions. These solid mixtures include most metal alloys, many gemstones, and doped semiconductors.

The relations derived in this section apply to mixtures of nonelectrolytes—substances that do not dissociate into charged species. Solutions of electrolytes behave quite differently in many ways, and will be discussed in the next chapter.

9.4.1 Raoult's law

In 1888, the French physical chemist François Raoult published his finding that when a dilute liquid solution of a volatile solvent and a nonelectrolyte solute is equilibrated with a gas phase, the partial pressure p_{A} of the solvent in the gas phase is proportional to the mole fraction x_{A} of the solvent in the solution:

$$p_{\mathrm{A}}=x_{\mathrm{A}} p_{\mathrm{A}}^{*} \tag{9.4.1}$$

Here p_{A}^{*} is the saturation vapor pressure of the pure solvent (the pressure at which the pure liquid and pure gas phases are in equilibrium).

Consider the *solvent*, A, of a solution that is dilute enough to be in the ideal-dilute range. In this range, the solvent fugacity obeys Raoult's law, and the partial molar quantities of the solvent are the same as those in an ideal mixture. Formulas for these quantities were given in Eqs. 9.4.8–9.4.13 and are collected in the first column of Table 9.2. The formulas show that the chemical potential and partial molar entropy of the solvent, at constant T and p, vary with the solution composition and, in the limit of infinite dilution ($x_{\mathrm{A}} \rightarrow 1$), approach the values for the pure solvent. The partial molar enthalpy, volume, internal energy, and heat capacity, on the other hand, are independent of composition in the ideal-dilute region and are equal to the corresponding molar quantities for the pure solvent.

Next consider a *solute*, B, of a binary ideal-dilute solution. The solute obeys Henry's law, and its chemical potential is given by $\mu_{\mathrm{B}}=\mu_{x, \mathrm{B}}^{\mathrm{ref}}+R T \ln x_{\mathrm{B}}$ (Eq. 9.4.24) where $\mu_{x, \mathrm{B}}^{\mathrm{ref}}$ is a function of T and p, but not of composition. μ_{B} varies with the composition and goes to $-\infty$ as the solution becomes infinitely dilute ($x_{\mathrm{A}} \rightarrow 1$ and $x_{\mathrm{B}} \rightarrow 0$).

For the partial molar entropy of the solute, we use $S_{\mathrm{B}}=-\left(\partial \mu_{\mathrm{B}} / \partial T\right)_{p,\left\{n_{i}\right\}}$ (Eq. 9.2.48) and obtain

$$S_{\mathrm{B}}=-\left(\frac{\partial \mu_{x, \mathrm{B}}^{\mathrm{ref}}}{\partial T}\right)_{p}-R \ln x_{\mathrm{B}} \tag{9.4.36}$$

The term $-\left(\partial \mu_{x, \mathrm{B}}^{\mathrm{ref}} / \partial T\right)_{p}$ represents the partial molar entropy $S_{x, \mathrm{B}}^{\mathrm{ref}}$ of B in the fictitious reference state of unit solute mole fraction. Thus, we can write Eq. 9.4.36 in the form

$$S_{\mathrm{B}}=S_{x, \mathrm{B}}^{\mathrm{ref}}-R \ln x_{\mathrm{B}} \tag{9.4.37}$$

(ideal-dilute solution of a nonelectrolyte)

This equation shows that the partial molar entropy varies with composition and goes to $+\infty$ in the limit of infinite dilution. From the expressions of Eqs. 9.4.27 and 9.4.28, we can derive similar expressions for S_{B} in terms of the solute reference states on a concentration or molality basis.

The relation $H_{\mathrm{B}}=\mu_{\mathrm{B}}+T S_{\mathrm{B}}$ (from Eq. 9.2.46), combined with Eqs. 9.4.24 and 9.4.37, yields

$$H_{\mathrm{B}}=\mu_{x, \mathrm{B}}^{\mathrm{ref}}+T S_{x, \mathrm{B}}^{\mathrm{ref}}=H_{x, \mathrm{B}}^{\mathrm{ref}} \tag{9.4.38}$$

showing that at constant T and p, the partial molar enthalpy of the solute is constant throughout the ideal-dilute solution range. Therefore, we can write

$$H_{\mathrm{B}}=H_{\mathrm{B}}^{\infty} \tag{9.4.39}$$

(ideal-dilute solution of a nonelectrolyte)

where H_{B}^{∞} is the partial molar enthalpy at infinite dilution. By similar reasoning, using Eqs. 9.2.49–9.2.52, we find that the partial molar volume, internal energy, and heat capacity of the solute are constant in the ideal-dilute range and equal to the values at infinite dilution. The expressions are listed in the second column of Table 9.2.

When the pressure is equal to the standard pressure p°, the quantities H_B^∞, V_B^∞, U_B^∞, and $C_{p,B}^\infty$ are the same as the standard values H_B°, V_B°, U_B°, and $C_{p,B}^\circ$.

9.5: Activity Coefficients in Mixtures of Nonelectrolytes

An *activity coefficient* of a species is a kind of adjustment factor that relates the actual behavior to ideal behavior at the same temperature and pressure. The ideal behavior is based on a *reference state* for the species.

We begin by describing reference states for nonelectrolytes. The thermodynamic behavior of an electrolyte solution is more complicated than that of a mixture of nonelectrolytes, and will be discussed in the next chapter.

9.5.1 Reference states and standard states

A *reference state* of a constituent of a mixture has the same temperature and pressure as the mixture. When species i is in its reference state, its chemical potential μ_i^{ref} depends only on the temperature and pressure of the mixture.

If the pressure is the standard pressure p°, the reference state of species i becomes its *standard state*. In the standard state, the chemical potential is the *standard chemical potential* μ_i°, which is a function only of temperature.

Reference states are useful for derivations involving processes taking place at constant T and p when the pressure is not necessarily the standard pressure.

Table 9.3 describes the reference states of nonelectrolytes used in this e-book, and lists symbols for chemical potentials of substances in these states. The symbols for solutes include x, c, or m in the subscript to indicate the basis of the reference state.

9.5.2 Ideal mixtures

Since the activity coefficient of a species relates its actual behavior to its ideal behavior at the same T and p, let us begin by examining behavior in ideal mixtures.

Consider first an ideal gas mixture at pressure p. The chemical potential of substance i in this ideal gas mixture is given by Eq. 9.3.5 (the superscript “id” stands for ideal):

$$\mu_i^{\text{id}}(\text{g}) = \mu_i^\circ(\text{g}) + RT\ln\frac{p_i}{p^\circ} \tag{9.5.1}$$

The reference state of gaseous substance i is pure i acting as an ideal gas at pressure p. Its chemical potential is given by

$$\mu_i^{\text{ref}}(\text{g}) = \mu_i^\circ(\text{g}) + RT\ln\frac{p}{p^\circ} \tag{9.5.2}$$

Subtracting Eq. 9.5.2 from Eq. 9.5.1, we obtain

$$\mu_i^{\text{id}}(\text{g}) - \mu_i^{\text{ref}}(\text{g}) = RT\ln\frac{p_i}{p} \tag{9.5.3}$$

Consider the following expressions for chemical potentials in ideal mixtures and ideal-dilute solutions of nonelectrolytes. The first equation is a rearrangement of Eq. 9.5.3, and the others are from earlier sections of this chapter (in order of occurrence, Eqs. 9.4.8, 9.4.35, 9.4.24, 9.4.27, and 9.4.28).

$$\text{Constituent of an ideal gas mixture}\quad \mu_i^{\text{id}}(\text{g}) = \mu_i^{\text{ref}}(\text{g}) + RT\ln\frac{p_i}{p} \tag{9.5.4}$$

$$\text{Constituent of an ideal liquid or solid mixture}\quad \mu_i^{\text{id}} = \mu_i^* + RT\ln x_i \tag{9.5.5}$$

$$\text{Solvent of an ideal-dilute solution}\quad \mu_{\text{A}}^{\text{id}} = \mu_{\text{A}}^* + RT\ln x_{\text{A}} \tag{9.5.6}$$

$$\text{Solute, ideal-dilute solution, mole fraction basis}\quad \mu_{\text{B}}^{\text{id}} = \mu_{x,\text{B}}^{\text{ref}} + RT\ln x_{\text{B}} \tag{9.5.7}$$

$$\text{Solute, ideal-dilute solution, concentration basis}\quad \mu_{\text{B}}^{\text{id}} = \mu_{c,\text{B}}^{\text{ref}} + RT\ln\frac{c_{\text{B}}}{c^\circ} \tag{9.5.8}$$

$$\text{Solute, ideal-dilute solution, molality basis}\quad \mu_{\text{B}}^{\text{id}} = \mu_{m,\text{B}}^{\text{ref}} + RT\ln\frac{m_{\text{B}}}{m^\circ} \tag{9.5.9}$$

Note that the equations for the condensed phases have the general form

$$\mu_i^{\text{id}} = \mu_i^{\text{ref}} + RT\ln\left(\frac{\text{composition variable}}{\text{standard composition}}\right) \tag{9.5.10}$$

where μ_i^{ref} is the chemical potential of component i in an appropriate reference state. (The standard composition on a mole fraction basis is $x^\circ = 1$.)

9.5.3 Real mixtures

If a mixture is *not* ideal, we can write an expression for the chemical potential of each component that includes an **activity coefficient**. The expression is like one of those for the ideal case (Eqs. 9.5.4–9.5.9) with the activity coefficient multiplying the quantity within the logarithm.

Consider constituent i of a gas mixture. If we eliminate $\mu_i^\circ(\text{g})$ from Eqs. 9.3.12 and 9.5.2, we obtain

$$\begin{aligned}\mu_i &= \mu_i^{\text{ref}}(\text{g}) + RT\ln\frac{f_i}{p}\\ &= \mu_i^{\text{ref}}(\text{g}) + RT\ln\frac{\phi_i p_i}{p}\end{aligned} \tag{9.5.11}$$

where f_i is the fugacity of constituent i and ϕ_i is its fugacity coefficient. Here the activity coefficient is the fugacity coefficient ϕ_i.

For components of a condensed-phase mixture, we write expressions for the chemical potential having a form similar to that in Eq. 9.5.10, with the composition variable now multiplied by an activity coefficient:

$$\mu_i = \mu_i^{\text{ref}} + RT\ln\left[(\text{activity coefficient of } i) \times \left(\frac{\text{composition variable}}{\text{standard composition}}\right)\right] \tag{9.5.12}$$

The activity coefficient of a species is a dimensionless quantity whose value depends on the temperature, the pressure, the mixture composition, and the choice of the reference state for the species. Under conditions in which the mixture behaves ideally, the activity coefficient is unity and the chemical potential is given by one of the expressions of Eqs. 9.5.4–9.5.9; otherwise, the activity coefficient has the value that gives the actual chemical potential.

This e-book will use various symbols for activity coefficients, as indicated in the following list of expressions for the chemical potentials of nonelectrolytes:

$$\text{Constituent of a gas mixture} \quad \mu_i = \mu_i^{\text{ref}}(\text{g}) + RT\ln\left(\phi_i\frac{p_i}{p}\right) \tag{9.5.13}$$

$$\text{Constituent of a liquid or solid mixture} \quad \mu_i = \mu_i^* + RT\ln(\gamma_i x_i) \tag{9.5.14}$$

$$\text{Solvent of a solution} \quad \mu_{\text{A}} = \mu_{\text{A}}^* + RT\ln(\gamma_{\text{A}} x_{\text{A}}) \tag{9.5.15}$$

$$\text{Solute of a solution, mole fraction basis} \quad \mu_{\text{B}} = \mu_{x,\text{B}}^{\text{ref}} + RT\ln(\gamma_{x,\text{B}} x_{\text{B}}) \tag{9.5.16}$$

$$\text{Solute of a solution, concentration basis} \quad \mu_{\text{B}} = \mu_{c,\text{B}}^{\text{ref}} + RT\ln\left(\gamma_{c,\text{B}}\frac{c_{\text{B}}}{c^\circ}\right) \tag{9.5.17}$$

$$\text{Solute of a solution, molality basis} \quad \mu_{\text{B}} = \mu_{m,\text{B}}^{\text{ref}} + RT\ln\left(\gamma_{m,\text{B}}\frac{m_{\text{B}}}{m^\circ}\right) \tag{9.5.18}$$

Equation 9.5.14 refers to a component of a liquid or solid mixture of substances that mix in all proportions. Equation 9.5.15 refers to the solvent of a solution. The reference states of these components are the pure liquid or solid at the temperature and pressure of the mixture. For the activity coefficients of these components, this e-book uses the symbols γ_i and γ_{A}.

> The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 59) recommends the symbol f_i for the activity coefficient of component i when the reference state is the pure liquid or solid. This e-book instead uses symbols such as γ_i and γ_{A}, in order to avoid confusion with the symbol usually used for fugacity, f_i.

In Eqs. 9.5.16–9.5.18, the symbols $\gamma_{x,\text{B}}$, $\gamma_{c,\text{B}}$, and $\gamma_{m,\text{B}}$ for activity coefficients of a nonelectrolyte solute include x, c, or m in the subscript to indicate the choice of the solute reference state. Although three different expressions for μ_{B} are shown, for a given solution composition they must all represent the same *value* of μ_{B}, equal to the rate at which the Gibbs energy increases with the amount of substance B added to the solution at constant T and p. The value of a solute activity coefficient, on the other hand, depends on the choice of the solute reference state.

You may find it helpful to interpret products appearing on the right sides of Eqs. 9.5.13–9.5.18 as follows.

- In other words, the value of one of these products is the value of a partial pressure or composition variable that would give the same chemical potential in an ideal mixture as the actual chemical potential in the real mixture. These effective composition variables are an alternative way to express the escaping tendency of a substance from a phase; they are related exponentially to the chemical potential, which is also a measure of escaping tendency.

  A change in pressure or composition that causes a mixture to approach the behavior of an ideal mixture or ideal-dilute solution must cause the activity coefficient of each mixture constituent to approach unity:

9.5.4 Nonideal dilute solutions

How would we expect the activity coefficient of a nonelectrolyte solute to behave in a dilute solution as the solute mole fraction increases beyond the range of ideal-dilute solution behavior?

> The following argument is based on molecular properties at constant T and p.
>
> We focus our attention on a single solute molecule. This molecule has interactions with nearby solute molecules. Each interaction depends on the intermolecular distance and causes a change in the internal energy compared to the interaction of the solute molecule with solvent at the same distance.
>
> In Sec. 11.1.5, it will be shown that roughly speaking the internal energy change is negative if the average of the attractive forces between two solute molecules and two solvent molecules is greater than the attractive force between a solute molecule and a solvent molecule at the same distance, and is positive for the opposite situation.
>
> The number of solute molecules in a volume element at a given distance from the solute molecule we are focusing on is proportional to the local solute concentration. If the solution is dilute and the interactions weak, we expect the local solute concentration to be proportional to the macroscopic solute mole fraction. Thus, the partial molar quantities U_{B} and V_{B} of the solute should be approximately linear functions of x_{B} in a dilute solution at constant T and p.
>
> From Eqs. 9.2.46 and 9.2.50, the solute chemical potential is given by $\mu_{\mathrm{B}}=U_{\mathrm{B}}+pV_{\mathrm{B}}-TS_{\mathrm{B}}$. In the dilute solution, we assume U_{B} and V_{B} are linear functions of x_{B} as explained above. We also assume the dependence of S_{B} on x_{B} is approximately the same as in an ideal mixture; this is a prediction from statistical mechanics for a mixture in which all molecules have similar sizes and shapes. Thus we expect the deviation of the chemical potential from ideal-dilute behavior, $\mu_{\mathrm{B}}=\mu_{x,\mathrm{B}}^{\mathrm{ref}}+RT\ln x_{\mathrm{B}}$, can be described by adding a term proportional to x_{B}: $\mu_{\mathrm{B}}=\mu_{x,\mathrm{B}}^{\mathrm{ref}}+RT\ln x_{\mathrm{B}}+k_x x_{\mathrm{B}}$, where k_x is a positive or negative constant related to solute-solute interactions.
>
> If we equate this expression for μ_{B} with the one that defines the activity coefficient, $\mu_{\mathrm{B}}=\mu_{x,\mathrm{B}}^{\mathrm{ref}}+RT\ln(\gamma_{x,\mathrm{B}}x_{\mathrm{B}})$ (Eq. 9.5.16), and solve for the activity coefficient, we obtain the relation $\gamma_{x,\mathrm{B}}=\exp(k_x x_{\mathrm{B}}/RT)$. (This is essentially the result of the McMillan–Mayer solution theory from statistical mechanics.) An expansion of the exponential in powers of x_{B} converts this to
>
> $$\gamma_{x,\mathrm{B}}=1+(k_x/RT)x_{\mathrm{B}}+\cdots \tag{9.5.25}$$
>
> Thus we predict that at constant T and p, $\gamma_{x,\mathrm{B}}$ is a linear function of x_{B} at low x_{B}. An ideal-dilute solution, then, is one in which x_{B} is much smaller than RT/k_x so that $\gamma_{x,\mathrm{B}}$ is approximately 1. An ideal mixture requires the interaction constant k_x to be zero.
>
> By similar reasoning, we reach analogous conclusions for solute activity coefficients on a concentration or molality basis. For instance, at low m_{B} the chemical potential of B should be approximately $\mu_{m,\mathrm{B}}^{\mathrm{ref}}+RT\ln(m_{\mathrm{B}}/m^{\circ})+k_m m_{\mathrm{B}}$, where k_m is a constant at a given T and p; then the activity coefficient at low m_{B} is given by
>
> $$\gamma_{m,\mathrm{B}}=\exp(k_m m_{\mathrm{B}}/RT)=1+(k_m/RT)m_{\mathrm{B}}+\cdots \tag{9.5.26}$$

The prediction from the theoretical argument above, that a solute activity coefficient in a dilute solution is a linear function of the composition variable, is borne out experimentally as illustrated in Fig. 9.10. This prediction applies only to a nonelectrolyte solute; for an electrolyte, the slope of activity coefficient versus molality approaches $-\infty$ at low molality.

9.6: Evaluation of Activity Coefficients

This section describes several methods by which activity coefficients of nonelectrolyte substances may be evaluated. Section 9.6.3 describes an osmotic coefficient method that is also suitable for electrolyte solutes, as will be explained in Sec. 10.6.

9.6.1 Activity coefficients from gas fugacities

Suppose we equilibrate a liquid mixture with a gas phase. If component i of the liquid mixture is a volatile nonelectrolyte, and we are able to evaluate its fugacity f_i in the gas phase, we have a convenient way to evaluate the activity coefficient γ_i in the liquid. The relation between γ_i and f_i will now be derived.

When component i is in transfer equilibrium between two phases, its chemical potential is the same in both phases. Equating expressions for μ_i in the liquid mixture and the equilibrated gas phase (from Eqs. 9.5.14 and 9.5.11, respectively), and then solving for γ_i, we have

$$\mu_i^* + RT\ln(\gamma_i x_i) = \mu_i^{\text{ref}}(\text{g}) + RT\ln(f_i/p) \tag{9.6.1}$$

$$\gamma_i = \exp\left[\frac{\mu_i^{\text{ref}}(\text{g}) - \mu_i^*}{RT}\right] \times \frac{f_i}{x_i p} \tag{9.6.2}$$

On the right side of Eq. 9.6.2, only f_i and x_i depend on the liquid composition. We can therefore write

$$\gamma_i = C_i \frac{f_i}{x_i} \tag{9.6.3}$$

where C_i is a factor whose value depends on T and p, but not on the liquid composition. Solving Eq. 9.6.3 for C_i gives $C_i = \gamma_i x_i / f_i$.

Now consider Eq. 9.5.20. It says that as x_i approaches 1 at constant T and p, γ_i also approaches 1. We can use this limit to evaluate C_i:

$$C_i = \lim_{x_i \to 1} \frac{\gamma_i x_i}{f_i} = \frac{1}{f_i^*} \tag{9.6.4}$$

Here f_i^* is the fugacity of i in a gas phase equilibrated with pure liquid i at the temperature and pressure of the mixture. Then substitution of this value of C_i (which is independent of x_i) in Eq. 9.6.3 gives us an expression for γ_i at any liquid composition:

$$\gamma_i = \frac{f_i}{x_i f_i^*} \tag{9.6.5}$$

We can follow the same procedure for a solvent or solute of a liquid solution. We replace the left side of Eq. 9.6.1 with an expression from among Eqs. 9.5.15–9.5.18, then derive an expression analogous to Eq. 9.6.3 for the activity coefficient with a composition-independent factor, and finally apply the limiting conditions that cause the activity coefficient to approach unity (Eqs. 9.5.21–9.5.24) and allow us to evaluate the factor. When we take the limits that cause the solute activity coefficients to approach unity, the ratios $f_{\text{B}}/x_{\text{B}}$, $f_{\text{B}}/c_{\text{B}}$, and $f_{\text{B}}/m_{\text{B}}$ become Henry's law constants (Eqs. 9.4.19–9.4.21). The resulting expressions for activity coefficients as functions of fugacity are listed in Table 9.4.

Examples

Figure 9.11(a) shows the function $(\phi_m - 1)/m_{\text{B}}$ for aqueous sucrose solutions over a wide range of molality. The dependence of the solute activity coefficient on molality, generated from Eq. 9.6.20, is shown in Fig. 9.11(b). Figure 9.11(c) is a plot of the effective sucrose molality $\gamma_{m,\text{B}} m_{\text{B}}$ as a function of composition. Note how the activity coefficient becomes greater than unity beyond the ideal-dilute region, and how in consequence the effective molality $\gamma_{m,\text{B}} m_{\text{B}}$ becomes considerably greater than the actual molality m_{B}.

9.6.4 Fugacity measurements

Section 9.6.1 described the evaluation of the activity coefficient of a constituent of a liquid mixture from its fugacity in a gas phase equilibrated with the mixture. Section 9.6.3 mentioned the use of solvent fugacities in gas phases equilibrated with pure solvent and with a solution, in order to evaluate the osmotic coefficient of the solution.

Various experimental methods are available for measuring a partial pressure in a gas phase equilibrated with a liquid mixture. A correction for gas nonideality, such as that given by Eq. 9.3.16, can be used to convert the partial pressure to fugacity.

If the solute of a solution is nonvolatile, we may pump out the air above the solution and use a manometer to measure the pressure, which is the partial pressure of the solvent. Dynamic methods involve passing a stream of inert gas through a liquid mixture and analyzing the gas mixture to evaluate the partial pressures of volatile components. For instance, we could pass dry air successively through an aqueous solution and a desiccant and measure the weight gained by the desiccant.

The **isopiestic vapor pressure technique** is one of the most useful methods for determining the fugacity of H_2O in a gas phase equilibrated with an aqueous solution. This is a comparative method using a binary solution of the solute of interest, B, and a nonvolatile reference solute of known properties. Some commonly used reference solutes for which data are available are sucrose, NaCl, and $CaCl_2$.

In this method, solute B can be either a nonelectrolyte or electrolyte. Dishes, each containing water and an accurately weighed sample of one of the solutes, are placed in wells drilled in a block made of metal for good thermal equilibration. The assembly is placed in a gas-tight chamber, the air is evacuated, and the apparatus is gently rocked in a thermostat for a period of up to several days, or even weeks. During this period, H_2O is transferred among the dishes through the vapor space until the chemical potential of the water becomes the same in each solution. The solutions are then said to be *isopiestic*. Finally, the dishes are removed from the apparatus and weighed to establish the molality of each solution. The H_2O fugacity is known as a function of the molality of the reference solute, and is the same as the H_2O fugacity in equilibrium with the solution of solute B at its measured molality.

The isopiestic vapor pressure method can also be used for nonaqueous solutions.

9.7: Activity of an Uncharged Species

The **activity** a_i of uncharged species i (i.e., a substance) is defined by the relation

$$a_i \overset{\text{def}}{=} \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right) \tag{9.7.1}$$
(uncharged species)

or

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{9.7.2}$$
(uncharged species)

where μ_i° is the standard chemical potential of the species. The activity of a species in a given phase is a dimensionless quantity whose value depends on the choice of the standard state and on the intensive properties of the phase: temperature, pressure, and composition.

> Some chemists define the activity by $\mu_i = \mu_i^{\text{ref}} + RT \ln a_i$. The activity defined this way is not the same as the activity used in this e-book unless the phase is at the standard pressure.

The quantity a_i is sometimes called the *relative activity* of i, because it depends on the chemical potential relative to a standard chemical potential. An important application of the activity concept is the definition of equilibrium constants (Sec. 11.8.1).

For convenience in later applications, we specify that the value of a_i is the same in phases that have the same temperature, pressure, and composition but are at different elevations in a gravitational field, or are at different electric potentials. Section 9.8 10.1 will describe a modification of the defining equation $\mu_i = \mu_i^\circ + RT \ln a_i$ for a system with phases of different elevations, and Sec. 10.1 will describe the modification needed for a charged species.

9.7.1 Standard states

The standard states of different kinds of mixture components have the same definitions as those for reference states (Table 9.3), with the additional stipulation in each case that the pressure is equal to the standard pressure p°.

When component i is in its standard state, its chemical potential is the standard chemical potential μ_i°. It is important to note from Eq. 9.7.2 that when μ_i equals μ_i°, the logarithm of a_i is zero and the activity in the standard state is therefore unity.

The following equations in the form of Eq. 9.7.2 show the notation used in this e-book for the standard chemical potentials and activities of various kinds of uncharged mixture components:

$$\text{Substance } i \text{ in a gas mixture} \qquad \mu_i = \mu_i^\circ(\text{g}) + RT \ln a_i(\text{g}) \tag{9.7.3}$$

$$\text{Substance } i \text{ in a liquid or solid mixture} \qquad \mu_i = \mu_i^\circ + RT \ln a_i \tag{9.7.4}$$

$$\text{Solvent A of a solution} \qquad \mu_\text{A} = \mu_\text{A}^\circ + RT \ln a_\text{A} \tag{9.7.5}$$

$$\text{Solute B, mole fraction basis} \qquad \mu_\text{B} = \mu_{x,\text{B}}^\circ + RT \ln a_{x,\text{B}} \tag{9.7.6}$$

$$\text{Solute B, concentration basis} \qquad \mu_\text{B} = \mu_{c,\text{B}}^\circ + RT \ln a_{c,\text{B}} \tag{9.7.7}$$

$$\text{Solute B, molality basis} \qquad \mu_\text{B} = \mu_{m,\text{B}}^\circ + RT \ln a_{m,\text{B}} \tag{9.7.8}$$

9.7.2 Activities and composition

We need to be able to relate the activity of component i to the mixture composition. We can do this by finding the relation between the chemical potential of component i in its reference state and in its standard state, both at the same temperature. These two chemical potentials, μ_i^{ref} and μ_i°, are equal only if the mixture is at the standard pressure p°.

It will be useful to define the following dimensionless quantity:

$$\Gamma_i \overset{\text{def}}{=} \exp\left(\frac{\mu_i^{\text{ref}} - \mu_i^\circ}{RT}\right) \tag{9.7.9}$$

The symbol Γ_i for this quantity was introduced by Pitzer and Brewer (*Thermodynamics*, 2nd edition, McGraw-Hill, New York, 1961, p. 249). They called it *the activity in a reference state*. To see why, compare the definition of activity given by

$\mu_i = \mu_i^\circ + RT \ln a_i$ with a rearrangement of Eq. 9.7.9: $\mu_i^{\text{ref}} = \mu_i^\circ + RT \ln \mathit{\Gamma}_i$.

At a given temperature, the difference $\mu_i^{\text{ref}} - \mu_i^\circ$ depends only on the pressure p of the mixture, and is zero when p is equal to p°. Thus $\mathit{\Gamma}_i$ is a function of p with a value of 1 when p is equal to p°. This e-book will call $\mathit{\Gamma}_i$ the **pressure factor** of species i.

To understand how activity is related to composition, let us take as an example the activity $a_{m,\text{B}}$ of solute B based on molality. From Eqs. 9.5.18 and 9.7.8, we have

$$\begin{aligned}\mu_{\text{B}} &= \mu_{m,\text{B}}^{\text{ref}} + RT \ln\left(\gamma_{m,\text{B}} \frac{m_{\text{B}}}{m^\circ}\right) \\ &= \mu_{m,\text{B}}^\circ + RT \ln a_{m,\text{B}}\end{aligned} \tag{9.7.10}$$

The activity is then given by

$$\begin{aligned}\ln a_{m,\text{B}} &= \frac{\mu_{m,\text{B}}^{\text{ref}} - \mu_{m,\text{B}}^\circ}{RT} + \ln\left(\gamma_{m,\text{B}} \frac{m_{\text{B}}}{m^\circ}\right) \\ &= \ln \mathit{\Gamma}_{m,\text{B}} + \ln\left(\gamma_{m,\text{B}} \frac{m_{\text{B}}}{m^\circ}\right)\end{aligned} \tag{9.7.11}$$

$$a_{m,\text{B}} = \mathit{\Gamma}_{m,\text{B}} \gamma_{m,\text{B}} \frac{m_{\text{B}}}{m^\circ} \tag{9.7.12}$$

The activity of a constituent of a condensed-phase mixture is in general equal to the product of the pressure factor, the activity coefficient, and the composition variable divided by the standard composition.

We are now able to write explicit formulas for $\mathit{\Gamma}_i$ for each kind of mixture component. They are collected in Table 9.6.

Considering a constituent of a condensed-phase mixture, by how much is the pressure factor likely to differ from unity? If we use the values $p^\circ = 1\,\text{bar}$ and $T = 300\,\text{K}$, and assume the molar volume of pure i is $V_i^* = 100\,\text{cm}^3\,\text{mol}^{-1}$ at all pressures, we find that $\mathit{\Gamma}_i$ is 0.996 in the limit of zero pressure, unity at 1 bar, 1.004 at 2 bar, 1.04 at 10 bar, and 1.49 at 100 bar. For a solution with $V_{\text{B}}^\infty = 100\,\text{cm}^3\,\text{mol}^{-1}$, we obtain the same values as these for $\mathit{\Gamma}_{x,\text{B}}$, $\mathit{\Gamma}_{m,\text{B}}$, and $\mathit{\Gamma}_{c,\text{B}}$. These values demonstrate that it is only at high pressures that the pressure factor differs appreciably from unity. For this reason, it is common to see expressions for activity in which this factor is omitted: $a_i = \gamma_i x_i$, $a_{m,\text{B}} = \gamma_{m,\text{B}} m_{\text{B}}/m^\circ$, and so on.

> In principle, we can specify any convenient value for the standard pressure p°. For a chemist making measurements at high pressures, it would be convenient to specify a value of p° within the range of the experimental pressures, for example $p^\circ = 1\,\text{kbar}$, in order that the value of each pressure factor be close to unity.

9.8: Mixtures in Gravitational and Centrifugal Fields

A tall column of a gas mixture in a gravitational field, and a liquid solution in the cell of a spinning centrifuge rotor, are systems with equilibrium states that are nonuniform in pressure and composition. This section derives the ways in which pressure and composition vary spatially within these kinds of systems at equilibrium.

9.8.1 Gas mixture in a gravitational field

Consider a tall column of a gas mixture in an earth-fixed lab frame. Our treatment will parallel that for a tall column of a pure gas in Sec. 8.1.4. We imagine the gas to be divided into many thin slab-shaped phases at different elevations in a rigid container, as in Fig. 8.1. We want to find the equilibrium conditions reached spontaneously when the system is isolated from its surroundings.

The derivation is the same as that in Sec. 9.2.7, with the additional constraint that for each phase α, $\mathrm{d}V^{\alpha}$ is zero in order that each phase stays at a constant elevation. The result is the relation

$$\mathrm{d}S=\sum_{\alpha\neq\alpha'}\frac{T^{\alpha'}-T^{\alpha}}{T^{\alpha'}}\,\mathrm{d}S^{\alpha}+\sum_{i}\sum_{\alpha\neq\alpha'}\frac{\mu_i^{\alpha'}-\mu_i^{\alpha}}{T^{\alpha'}}\,\mathrm{d}n_i^{\alpha} \tag{9.8.1}$$

In an equilibrium state, S is at a maximum and $\mathrm{d}S$ is zero for an infinitesimal change of any of the independent variables. This requires the coefficient of each term in the sums on the right side of Eq. 9.8.1 to be zero. The equation therefore tells that at equilibrium *the temperature and the chemical potential of each constituent are uniform throughout the gas mixture*. The equation says nothing about the pressure.

Just as the chemical potential of a pure substance at a given elevation is defined in this e-book as the molar Gibbs energy at that elevation (Sec. 8.1.4), the chemical potential of substance i in a mixture at elevation h is the partial molar Gibbs energy at that elevation.

We define the standard potential $\mu_i^{\circ}(\mathrm{g})$ of component i of the gas mixture as the chemical potential of i under standard state conditions at the reference elevation h=0. At this elevation, the chemical potential and fugacity are related by

$$\mu_i(0)=\mu_i^{\circ}(\mathrm{g})+RT\ln\frac{f_i(0)}{p^{\circ}} \tag{9.8.2}$$

If we reversibly raise a small sample of mass m of the gas mixture by an infinitesimal distance $\mathrm{d}h$, without heat and at constant T and V, the fugacity f_i remains constant. The gravitational work during the elevation process is $đw'=mg\,\mathrm{d}h$. This work contributes to the internal energy change: $\mathrm{d}U=T\,\mathrm{d}S-p\,\mathrm{d}V+\sum_i\mu_i\,\mathrm{d}n_i+mg\,\mathrm{d}h$. The total differential of the Gibbs energy of the sample is

$$\begin{aligned}\mathrm{d}G&=\mathrm{d}(U-TS+pV)\\&=-S\,\mathrm{d}T+V\,\mathrm{d}p+\sum_i\mu_i\,\mathrm{d}n_i+mg\,\mathrm{d}h\end{aligned} \tag{9.8.3}$$

From this total differential, we write the reciprocity relation

$$\left(\frac{\partial\mu_i}{\partial h}\right)_{T,p,\{n_i\}}=\left(\frac{\partial mg}{\partial n_i}\right)_{T,p,n_{j\neq i},h} \tag{9.8.4}$$

With the substitution $m=\sum_i n_iM_i$ in the partial derivative on the right side, the partial derivative becomes M_ig. At constant T, p, and composition, therefore, we have $\mathrm{d}\mu_i=M_ig\,\mathrm{d}h$. Integrating over a finite elevation change from $h=0$ to $h=h'$, we obtain

$$\mu_i(h')-\mu_i(0)=\int_0^{h'}M_ig\,\mathrm{d}h=M_igh' \tag{9.8.5}$$

$(f_i(h')$=$f_i(0)$)

The general relation between μ_i, f_i, and h that agrees with Eqs. 9.8.2 and 9.8.5 is

$$\mu_i(h)=\mu_i^{\circ}(\mathrm{g})+RT\ln\frac{f_i(h)}{p^{\circ}}+M_igh \tag{9.8.6}$$

In the equilibrium state of the tall column of gas, $\mu_i(h)$ is equal to $\mu_i(0)$. Equation 9.8.6 shows that this is only possible if f_i decreases as h increases. Equating the expressions given by this equation for $\mu_i(h)$ and $\mu_i(0)$, we have

$$\mu_i^\circ(\mathrm{g}) + RT\ln\frac{f_i(h)}{p^\circ} + M_i gh = \mu_i^\circ(\mathrm{g}) + RT\ln\frac{f_i(0)}{p^\circ} \tag{9.8.7}$$

Solving for $f_i(h)$ gives

$$f_i(h) = f_i(0)e^{-M_i gh/RT} \tag{9.8.8}$$

$$\text{(gas mixture at equilibrium)}$$

If the gas is an ideal gas mixture, f_i is the same as the partial pressure p_i:

$$p_i(h) = p_i(0)e^{-M_i gh/RT} \tag{9.8.9}$$

$$\text{(ideal gas mixture at equilibrium)}$$

Equation 9.8.9 shows that each constituent of an ideal gas mixture individually obeys the barometric formula given by Eq. 8.1.13.

The pressure at elevation h is found from $p(h) = \sum_i p_i(h)$. If the constituents have different molar masses, the mole fraction composition changes with elevation. For example, in a binary ideal gas mixture the mole fraction of the constituent with the greater molar mass decreases with increasing elevation, and the mole fraction of the other constituent increases.

9.8.2 Liquid solution in a centrifuge cell

This section derives equilibrium conditions of a dilute binary solution confined to a cell embedded in a spinning centrifuge rotor.

The *system* is the solution. The rotor's angle of rotation with respect to a lab frame is not relevant to the state of the system, so we use a local reference frame fixed in the rotor as shown in Fig. 9.12(a). The values of heat, work, and energy changes measured in this rotating frame are different from those in a lab frame (Sec. G.9 in Appendix G). Nevertheless, the laws of thermodynamics and the relations derived from them are obeyed in the local frame when we measure the heat, work, and state functions in this frame (Sec. G.6).

Note that an equilibrium state can only exist relative to the rotating local frame; an observer fixed in this frame would see no change in the state of the isolated solution over time. While the rotor rotates, however, there is no equilibrium state relative to the lab frame, because the system's position in the frame constantly changes.

We assume the centrifuge rotor rotates about the vertical z axis at a constant angular velocity ω. As shown in Fig. 9.12(a), the elevation of a point within the local frame is given by z and the radial distance from the axis of rotation is given by r.

In the rotating local frame, a body of mass m has exerted on it a centrifugal force $F^{\text{centr}} = m\omega^2 r$ directed horizontally in the outward $+r$ radial direction (Sec. G.9). The gravitational force in this frame, directed in the downward $-z$ direction, is the same as the gravitational force in a lab frame. Because the height of a typical centrifuge cell is usually no greater than about one centimeter, in an equilibrium state the variation of pressure and composition between the top and bottom of the cell at any given distance from the axis of rotation is completely negligible—all the measurable variation is along the radial direction.

> There is also a Coriolis force that vanishes as the body's velocity in the rotating local frame approaches zero. The centrifugal and Coriolis forces are *apparent* or *fictitious* forces, in the sense that they are caused by the acceleration of the rotating frame rather than by interactions between particles. When we treat these forces as if they are real forces, we can use Newton's second law of motion to relate the net force on a body and the body's acceleration in the rotating frame (see Sec. G.6).

To find conditions for equilibrium, we imagine the solution to be divided into many thin curved volume elements at different distances from the axis of rotation as depicted in Fig. 9.12(b). We treat each volume element as a uniform phase held at constant volume so that it is at a constant distance from the axis of rotation. The derivation is the same as the one used in the preceding section to obtain Eq. 9.8.1, and leads to the same conclusion: in an equilibrium state *the temperature and the chemical potential of each substance (solvent and solute) are uniform throughout the solution*.

We find the dependence of pressure on r as follows. Consider one of the thin slab-shaped volume elements of Fig. 9.12(b). The volume element is located at radial position r and its faces are perpendicular to the direction of increasing r. The thickness of the volume element is δr, the surface area of each face is A_s, and the mass of the solution in the volume element is $m = \rho A_\mathrm{s}\delta r$. Expressed as components in the direction of increasing r of the forces exerted on the volume element, the force at the inner face is pA_s, the force at the outer face is $-(p+\delta p)A_\mathrm{s}$, and the centrifugal force is $m\omega^2 r = \rho A_\mathrm{s}\omega^2 r\delta r$. From Newton's second law, the sum of these components is zero at equilibrium:

$$pA_s - (p+\delta p)A_s + \rho A_s \omega^2 r \delta r = 0 \tag{9.8.10}$$

or $\delta p = \rho \omega^2 r \delta r$. In the limit as δr and δp are made infinitesimal, this becomes

$$\mathrm{d}p = \rho \omega^2 r \,\mathrm{d}r \tag{9.8.11}$$

We will assume the density ρ is uniform throughout the solution. (In the centrifugal field, this assumption is strictly true only if the solution is incompressible and its density is independent of composition.) Then integration of Eq. 9.8.11 yields

$$p'' - p' = \int_{p'}^{p''} \mathrm{d}p = \rho \omega^2 \int_{r'}^{r''} r \,\mathrm{d}r = \frac{\rho \omega^2}{2}\left[(r'')^2 - (r')^2\right] \tag{9.8.12}$$

where the superscripts $'$ and $''$ denote positions at two different values of r in the cell. The pressure is seen to increase with increasing distance from the axis of rotation.

Next we investigate the dependence of the solute concentration c_B on r in the equilibrium state of the binary solution. Consider a small sample of the solution of mass m. Assume the extent of this sample in the radial direction is small enough for the variation of the centrifugal force field to be negligible. The reversible work in the local frame needed to move this small sample an infinitesimal distance $\mathrm{d}r$ at constant z, T, and p, using an external force $-F^\mathrm{centr}$ that opposes the centrifugal force, is

$$đw' = F^\mathrm{sur}\,\mathrm{d}r = (-F^\mathrm{centr})\,\mathrm{d}r = -m\omega^2 r \,\mathrm{d}r \tag{9.8.13}$$

This work is a contribution to the change $\mathrm{d}U$ of the internal energy. The Gibbs energy of the small sample in the local frame is a function of the independent variables T, p, n_A, n_B, and r, and its total differential is

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}(U - TS + pV)\\ &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} - m\omega^2 r\,\mathrm{d}r\end{aligned} \tag{9.8.14}$$

We use Eq. 9.8.14 to write the reciprocity relation

$$\left(\frac{\partial \mu_\mathrm{B}}{\partial r}\right)_{T,p,n_\mathrm{A},n_\mathrm{B}} = -\omega^2 r \left(\frac{\partial m}{\partial n_\mathrm{B}}\right)_{T,p,n_\mathrm{A},r} \tag{9.8.15}$$

Then, using $m = n_\mathrm{A} M_\mathrm{A} + n_\mathrm{B} M_\mathrm{B}$, we obtain

$$\left(\frac{\partial \mu_\mathrm{B}}{\partial r}\right)_{T,p,n_\mathrm{A},n_\mathrm{B}} = -M_\mathrm{B}\omega^2 r \tag{9.8.16}$$

Thus at constant T, p, and composition, which are the conditions that allow the activity $a_{c,\mathrm{B}}$ to remain constant, μ_B for the sample varies with r according to $\mathrm{d}\mu_\mathrm{B} = -M_\mathrm{B}\omega^2 r\,\mathrm{d}r$. We integrate from radial position r' to position r'' to obtain

$$\begin{aligned}\mu_\mathrm{B}(r'') - \mu_\mathrm{B}(r') &= -M_\mathrm{B}\omega^2 \int_{r'}^{r''} r\,\mathrm{d}r\\ &= -\tfrac{1}{2}M_\mathrm{B}\omega^2\left[(r'')^2 - (r')^2\right]\end{aligned} \tag{9.8.17}$$

$$(a_{c,\mathrm{B}}(r'')=a_{c,\mathrm{B}}(r')\,)$$

Let us take r' as a reference position, such as the end of the centrifuge cell farthest from the axis of rotation. We define the standard chemical potential $\mu^\circ_{c,\mathrm{B}}$ as the solute chemical potential under standard state conditions on a concentration basis at this position. The solute chemical potential and activity at this position are related by

$$\mu_\mathrm{B}(r') = \mu^\circ_{c,\mathrm{B}} + RT\ln a_{c,\mathrm{B}}(r') \tag{9.8.18}$$

From Eqs. 9.8.17 and 9.8.18, we obtain the following general relation between μ_B and $a_{c,\mathrm{B}}$ at an arbitrary radial position r'':

$$\mu_\mathrm{B}(r'') = \mu^\circ_{c,\mathrm{B}} + RT\ln a_{c,\mathrm{B}}(r'') - \tfrac{1}{2}M_\mathrm{B}\omega^2\left[(r'')^2 - (r')^2\right] \tag{9.8.19}$$

We found earlier that when the solution is in an equilibrium state, μ_B is independent of r—that is, $\mu_\mathrm{B}(r'')$ is equal to $\mu_\mathrm{B}(r')$ for any value of r''. When we equate expressions given by Eq. 9.8.19 for $\mu_\mathrm{B}(r'')$ and $\mu_\mathrm{B}(r')$ and rearrange, we obtain the following relation between the activities at the two radial positions:

$$\ln \frac{a_{c,\mathrm{B}}(r'')}{a_{c,\mathrm{B}}(r')} = \frac{M_{\mathrm{B}}\omega^2}{2RT}\left[(r'')^2 - (r')^2\right] \tag{9.8.20}$$

(solution in centrifuge cell at equilibrium)

The solute activity is related to the concentration c_{B} by $a_{c,\mathrm{B}} = \Gamma_{c,\mathrm{B}}\gamma_{c,\mathrm{B}}c_{\mathrm{B}}/c^{\circ}$. We assume the solution is sufficiently dilute for the activity coefficient $\gamma_{c,\mathrm{B}}$ to be approximated by 1. The pressure factor is given by $\Gamma_{c,\mathrm{B}} \approx \exp\left[V_{\mathrm{B}}^{\infty}(p-p^{\circ})/RT\right]$ (Table 9.6). These relations give us another expression for the logarithm of the ratio of activities:

$$\ln \frac{a_{c,\mathrm{B}}(r'')}{a_{c,\mathrm{B}}(r')} = \frac{V_{\mathrm{B}}^{\infty}(p''-p')}{RT} + \ln \frac{c_{\mathrm{B}}(r'')}{c_{\mathrm{B}}(r')} \tag{9.8.21}$$

We substitute for $p''-p'$ from Eq. 9.8.12. It is also useful to make the substitution $V_{\mathrm{B}}^{\infty} = M_{\mathrm{B}}v_{\mathrm{B}}^{\infty}$, where v_{B}^{∞} is the partial specific volume of the solute at infinite dilution.

When we equate the two expressions for $\ln[a_{c,\mathrm{B}}(r'')/a_{c,\mathrm{B}}(r')]$, we obtain finally

$$\ln \frac{c_{\mathrm{B}}(r'')}{c_{\mathrm{B}}(r')} = \frac{M_{\mathrm{B}}\left(1-v_{\mathrm{B}}^{\infty}\rho\right)\omega^2}{2RT}\left[(r'')^2 - (r')^2\right] \tag{9.8.22}$$

(solution in centrifuge cell at equilibrium)

This equation shows that if the solution density ρ is less than the effective solute density $1/v_{\mathrm{B}}^{\infty}$, so that $v_{\mathrm{B}}^{\infty}\rho$ is less than 1, the solute concentration increases with increasing distance from the axis of rotation in the equilibrium state. If, however, ρ is greater than $1/v_{\mathrm{B}}^{\infty}$, the concentration decreases with increasing r. The factor $\left(1-v_{\mathrm{B}}^{\infty}\rho\right)$ is like a buoyancy factor for the effect of the centrifugal field on the solute.

Equation 9.8.22 is needed for *sedimentation equilibrium*, a method of determining the molar mass of a macromolecule. A dilute solution of the macromolecule is placed in the cell of an analytical ultracentrifuge, and the angular velocity is selected to produce a measurable solute concentration gradient at equilibrium. The solute concentration is measured optically as a function of r. The equation predicts that a plot of $\ln(c_{\mathrm{B}}/c^{\circ})$ versus r^2 will be linear, with a slope equal to $M_{\mathrm{B}}\left(1-v_{\mathrm{B}}^{\infty}\rho\right)\omega^2/2RT$. The partial specific volume v_{B}^{∞} is found from measurements of solution density as a function of solute mass fraction (Sec. 9.2.5). By this means, the molar mass M_{B} of the macromolecule is evaluated.

9.9: Chapter 9 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

9.1 For a binary solution, find expressions for the mole fractions x_{B} and x_{A} as functions of the solute molality m_{B}.

9.2 Consider a binary mixture of two liquids, A and B. The molar volume of mixing, $\Delta V(\mathrm{mix})/n$, is given by Eq. 9.2.19.

(a) Find a formula for calculating the value of $\Delta V(\mathrm{mix})/n$ of a binary mixture from values of $x_{\mathrm{A}}, x_{\mathrm{B}}, M_{\mathrm{A}}, M_{\mathrm{B}}, \rho, \rho_{\mathrm{A}}^{*}$, and ρ_{B}^{*}.

Table 9.7 Molar volumes of mixing of binary mixtures of 1-hexanol (A) and 1 -octene (B) at $25^{\circ}\mathrm{C}$.[a]

x_{B}	$[\Delta V(\mathrm{mix})/n]/\mathrm{cm}^{3}\ \mathrm{mol}^{-1}$	x_{B}	$[\Delta V(\mathrm{mix})/n]/\mathrm{cm}^{3}\ \mathrm{mol}^{-1}$
0	0	0.555	0.005
0.049	-0.027	0.597	0.011
0.097	-0.050	0.702	0.029
0.146	-0.063	0.716	0.035
0.199	-0.077	0.751	0.048
0.235	-0.073	0.803	0.056
0.284	-0.074	0.846	0.058
0.343	-0.065	0.897	0.057
0.388	-0.053	0.944	0.049
0.448	-0.032	1	0
0.491	-0.016		

[a] Ref. [170].

(b) The molar volumes of mixing for liquid binary mixtures of 1-hexanol (A) and 1-octene (B) at $25^{\circ}\mathrm{C}$ have been calculated from their measured densities. The data are in Table 9.7. The molar volumes of the pure constituents are $V_{\mathrm{A}}^{*}=125.31\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$ and $V_{\mathrm{B}}^{*}=157.85\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$. Use the method of intercepts to estimate the partial molar volumes of both constituents in an equimolar mixture $(x_{\mathrm{A}}=x_{\mathrm{B}}=0.5)$, and the partial molar volume V_{B}^{∞} of B at infinite dilution.

9.3 Extend the derivation of Prob. 8.1, concerning a liquid droplet of radius r suspended in a gas, to the case in which the liquid and gas are both mixtures. Show that the equilibrium conditions are $T^{\mathrm{g}}=T^{1}, \mu_{i}^{\mathrm{g}}=\mu_{i}^{1}$ (for each species i that can equilibrate between the two phases), and $p^{1}=p^{g}+2\gamma/r$, where γ is the surface tension. (As in Prob. 8.1, the last relation is the Laplace equation.)

9.4 Consider a gaseous mixture of 4.0000×10^{-2} mol of N_2 (A) and 4.0000×10^{-2} mol of CO_2 (B) in a volume of $1.0000\times10^{-3}\ \mathrm{m}^{3}$ at a temperature of $298.15\ \mathrm{K}$. The second virial coefficients at this temperature have the values [14]

$$\begin{aligned}
B_{\mathrm{AA}} &= -4.8\times10^{-6}\ \mathrm{m}^{3}\ \mathrm{mol}^{-1} \\
B_{\mathrm{BB}} &= -124.5\times10^{-6}\ \mathrm{m}^{3}\ \mathrm{mol}^{-1} \\
B_{\mathrm{AB}} &= -47.5\times10^{-6}\ \mathrm{m}^{3}\ \mathrm{mol}^{-1}
\end{aligned}$$

Compare the pressure of the real gas mixture with that predicted by the ideal gas equation. See Eqs. 9.3.20 and 9.3.23.

[14] Refs. [3], [49], and [50].

9.5 At $25^{\circ}\mathrm{C}$ and 1 bar, the Henry's law constants of nitrogen and oxygen dissolved in water are $k_{\mathrm{H,N_2}}=8.64\times10^{4}$ bar and $k_{\mathrm{H,O_2}}=4.41\times10^{4}$ bar. [15] The vapor pressure of water at this temperature and pressure is $p_{\mathrm{H_2O}}=0.032$ bar. Assume that dry air contains only N_2 and O_2 at mole fractions $y_{\mathrm{N_2}}=0.788$ and $y_{\mathrm{O_2}}=0.212$. Consider liquid-gas systems formed by equilibrating liquid water and air at $25^{\circ}\mathrm{C}$ and $1.000\mathrm{bar}$, and assume that the gas phase behaves as an ideal gas mixture.

Hint: The sum of the partial pressures of N_2 and O_2 must be $(1.000-0.032)\mathrm{bar}=0.968$ bar. If the volume of one of the phases is much larger than that of the other, then almost all of the N_2 and O_2 will be in the predominant phase and the ratio of their amounts in this phase must be practically the same as in dry air.

Determine the mole fractions of N_2 and O_2 in both phases in the following limiting cases:

(a) A large volume of air is equilibrated with just enough water to leave a small drop of liquid.

(b) A large volume of water is equilibrated with just enough air to leave a small bubble of gas.

9.6 Derive the expression for $\gamma_{m,\mathrm{B}}$ given in Table 9.4, starting with Eq. 9.5.18.

9.7 Consider a nonideal binary gas mixture with the simple equation of state $V=nRT/p+nB$ (Eq. $9.3.21$).

(a) The rule of Lewis and Randall states that the value of the mixed second virial coefficient B_{AB} is the average of B_{AA} and B_{BB}. Show that when this rule holds, the fugacity coefficient of A in a binary gas mixture of any composition is given by $\ln\phi_{\mathrm{A}}=B_{\mathrm{AA}}p/RT$. By comparing this expression with Eq. $7.8.18$ for a pure gas, express the fugacity of A in the mixture as a function of the fugacity of pure A at the same temperature and pressure as the mixture.

(b) The rule of Lewis and Randall is not accurately obeyed when constituents A and B are chemically dissimilar. For example, at $298.15\ \mathrm{K}$, the second virial coefficients of $\mathrm{H_2O}$ (A) and N_2 (B) are $B_{\mathrm{AA}}=-1158\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$ and $B_{\mathrm{BB}}=-5\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$, respectively, whereas the mixed second virial coefficient is $B_{\mathrm{AB}}=-40\ \mathrm{cm}^{3}\ \mathrm{mol}^{-1}$.

When liquid water is equilibrated with nitrogen at $298.15\ \mathrm{K}$ and 1 bar, the partial pressure of $\mathrm{H_2O}$ in the gas phase is $p_{\mathrm{A}}=0.03185$ bar. Use the given values of $B_{\mathrm{AA}}, B_{\mathrm{BB}}$, and B_{AB} to calculate the fugacity of the gaseous $\mathrm{H_2O}$ in this binary mixture. Compare this fugacity with the fugacity calculated with the value of B_{AB} predicted by the rule of Lewis and Randall.

Table 9.8 Activity coefficient of benzene (A) in mixtures of benzene and 1 -octanol at $20^{\circ}\mathrm{C}$. The reference state
is the pure liquid.

x_{A}	γ_{A}	x_{A}	γ_{A}
0	2.0^{a}	0.7631	1.183
0.1334	1.915	0.8474	1.101
0.2381	1.809	0.9174	1.046
0.4131	1.594	0.9782	1.005
0.5805	1.370		

$a_{\text{extrapolated}}$

[15] Ref. [184].

9.8 Benzene and 1-octanol are two liquids that mix in all proportions. Benzene has a measurable vapor pressure, whereas 1-octanol is practically nonvolatile. The data in Table 9.8 on the preceding page were obtained by Platford [16] using the isopiestic vapor pressure method.

(a) Use numerical integration to evaluate the integral on the right side of Eq. $9.6.10$ at each of the values of x_{A} listed in the table, and thus find γ_{B} at these compositions.

(b) Draw two curves on the same graph showing the effective mole fractions $\gamma_{\mathrm{A}}x_{\mathrm{A}}$ and $\gamma_{\mathrm{B}}x_{\mathrm{B}}$ as functions of x_{A}. Are the deviations from ideal-mixture behavior positive or negative?

Table 9.9 Liquid and gas compositions in the two-phase system of methanol (A) and benzene (B) at $45^{\circ}\mathrm{C}$[a]

x_{A}	y_{A}	p / kPa	x_{A}	y_{A}	p / kPa
0	0	29.894	0.4201	0.5590	60.015
0.0207	0.2794	40.962	0.5420	0.5783	60.416
0.0314	0.3391	44.231	0.6164	0.5908	60.416
0.0431	0.3794	46.832	0.7259	0.6216	59.868
0.0613	0.4306	50.488	0.8171	0.6681	58.321
0.0854	0.4642	53.224	0.9033	0.7525	54.692
0.1811	0.5171	57.454	0.9497	0.8368	51.009
0.3217	0.5450	59.402	1	1	44.608

[a] Ref. [169].

9.9 Table 9.9 lists measured values of gas-phase composition and total pressure for the binary two-phase methanol-benzene system at constant temperature and varied liquid-phase composition. x_{A} is the mole fraction of methanol in the liquid mixture, and y_{A} is the mole fraction of methanol in the equilibrated gas phase.

(a) For each of the 16 different liquid-phase compositions, tabulate the partial pressures of A and B in the equilibrated gas phase.

(b) Plot p_{A} and p_{B} versus x_{A} on the same graph. Notice that the behavior of the mixture is far from that of an ideal mixture. Are the deviations from Raoult's law positive or negative?

(c) Tabulate and plot the activity coefficient γ_{B} of the benzene as a function of x_{A} using a pure-liquid reference state. Assume that the fugacity f_{B} is equal to p_{B}, and ignore the effects of variable pressure.

(d) Estimate the Henry's law constant $k_{\mathrm{H,A}}$ of methanol in the benzene environment at $45^{\circ}\mathrm{C}$ by the graphical method suggested in Fig. 9.7(b). Again assume that f_{A} and p_{A} are equal, and ignore the effects of variable pressure.

9.10 Consider a dilute binary nonelectrolyte solution in which the dependence of the chemical potential of solute B on composition is given by

$$\mu_{\mathrm{B}}=\mu_{m, \mathrm{B}}^{\mathrm{ref}}+R T \ln \frac{m_{\mathrm{B}}}{m^{\circ}}+k_m m_{\mathrm{B}} \tag{9.9.1}$$

where $\mu_{m, \mathrm{B}}^{\mathrm{ref}}$ and k_m are constants at a given T and p. (The derivation of this equation is sketched in Sec. 9.5.4.) Use the Gibbs-Duhem equation in the form $\mathrm{d} \mu_{\mathrm{A}}=-\left(n_{\mathrm{B}} / n_{\mathrm{A}}\right) \mathrm{d} \mu_{\mathrm{B}}$ to obtain an expression for $\mu_{\mathrm{A}}-\mu_{\mathrm{A}}^*$ as a function of m_{B} in this solution.
[16] Ref. [145].

9.11 By means of the isopiestic vapor pressure technique, the osmotic coefficients of aqueous solutions of urea at $25^{\circ}\mathrm{C}$ have been measured at molalities up to the saturation limit of about $20 \mathrm{~mol} \mathrm{~kg}^{-1}$.[17] The experimental values are closely approximated by the function

$$\phi_m=1.00-\frac{0.050 m_{\mathrm{B}} / m^{\circ}}{1.00+0.179 m_{\mathrm{B}} / m^{\circ}} \tag{9.9.2}$$

where m° is $1 \mathrm{~mol} \mathrm{~kg}^{-1}$. Calculate values of the solvent and solute activity coefficients γ_{A} and $\gamma_{m, \mathrm{B}}$ at various molalities in the range $0-20 \mathrm{~mol} \mathrm{~kg}^{-1}$, and plot them versus $m_{\mathrm{B}} / m^{\circ}$. Use enough points to be able to see the shapes of the curves. What are the limiting slopes of these curves as m_{B} approaches zero?

9.12 Use Eq. 9.2.49 to derive an expression for the rate at which the logarithm of the activity coefficient of component i of a liquid mixture changes with pressure at constant temperature and composition: $\left(\partial \ln \gamma_i / \partial p\right)_{T,\left\{n_i\right\}}=$?

9.13 Assume that at sea level the atmosphere has a pressure of 1.00 bar and a composition given by $y_{\mathrm{N}_2}=0.788$ and $y_{\mathrm{O}_2}=0.212$. Find the partial pressures and mole fractions of N_2 and O_2, and the total pressure, at an altitude of $10.0 \mathrm{~km}$, making the (drastic) approximation that the atmosphere is an ideal gas mixture in an equilibrium state at $0^{\circ}\mathrm{C}$. For g use the value of the standard acceleration of free fall listed in Appendix B.

9.14 Consider a tall column of a dilute binary liquid solution at equilibrium in a gravitational field.

(a) Derive an expression for $\ln \left[c_{\mathrm{B}}(h) / c_{\mathrm{B}}(0)\right]$, where $c_{\mathrm{B}}(h)$ and $c_{\mathrm{B}}(0)$ are the solute concentrations at elevations h and 0 . Your expression should be a function of $h, M_{\mathrm{B}}, T, \rho$, and the partial specific volume of the solute at infinite dilution, v_{B}^{∞}. For the dependence of pressure on elevation, you may use the hydrostatic formula $\mathrm{d} p=-\rho g \mathrm{~d} h$ (Eq. 8.1.14 on page 200) and assume the solution density ρ is the same at all elevations. Hint: use the derivation leading to Eq. 9.8.22 as a guide.

(b) Suppose you have a tall vessel containing a dilute solution of a macromolecule solute of molar mass $M_{\mathrm{B}}=10.0 \mathrm{~kg} \mathrm{~mol}^{-1}$ and partial specific volume $v_{\mathrm{B}}^{\infty}=0.78 \mathrm{~cm}^3 \mathrm{~g}^{-1}$. The solution density is $\rho=1.00 \mathrm{~g} \mathrm{~cm}^{-3}$ and the temperature is $T=300 \mathrm{~K}$. Find the height h from the bottom of the vessel at which, in the equilibrium state, the concentration c_{B} has decreased to 99 percent of the concentration at the bottom.

9.15 FhuA is a protein found in the outer membrane of the Escherichia coli bacterium. From the known amino acid sequence, its molar mass is calculated to be $78.804 \mathrm{~kg} \mathrm{~mol}^{-1}$. In aqueous solution, molecules of the detergent dodecyl maltoside bind to a FhuA molecule to form an aggregate that behaves as a single solute species. Figure 9.13 on the next page shows data collected in a sedimentation equilibrium experiment with a dilute solution of the aggregate.[18] In the graph, A is the absorbance measured at a wavelength of $280 \mathrm{~nm}$ (a property that is a linear function of the aggregate concentration) and r is the radial distance from the axis of rotation of the centrifuge rotor. The experimental points fall very close to the straight line shown in the graph. The sedimentation conditions were $\omega=838 \mathrm{~s}^{-1}$ and $T=293 \mathrm{~K}$. The authors used the values $v_{\mathrm{B}}^{\infty}=0.776 \mathrm{~cm}^3 \mathrm{~g}^{-1}$ and $\rho=1.004 \mathrm{~g} \mathrm{~cm}^{-3}$.

(a) The values of r at which the absorbance was measured range from $6.95 \mathrm{~cm}$ to $7.20 \mathrm{~cm}$. Find the difference of pressure in the solution between these two positions.

(b) Find the molar mass of the aggregate solute species, and use it to estimate the mass binding ratio (the mass of bound detergent divided by the mass of protein).
[17] Ref. [160]. [18] Ref. [18].

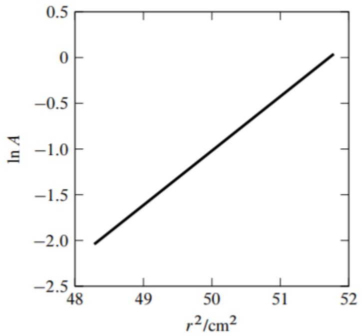


Figure 9.13: Sedimentation equilibrium of a dilute solution of the FhuA-dodecyl maltoside aggr

CHAPTER OVERVIEW

10: Electrolyte Solutions

The thermodynamic properties of electrolyte solutions differ in significant ways from the properties of mixtures of nonelectrolytes.

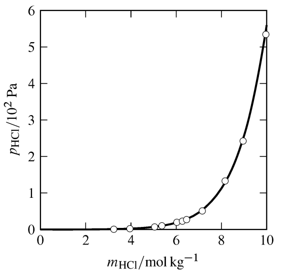


Figure 10.1 Partial pressure of HCl in a gas phase equilibrated with aqueous HCl at $25\,^\circ\mathrm{C}$ and $1\,\mathrm{bar}$. Open circles: experimental data from Stuart J. Bates and H. Darwin Kirschman, *J. Am. Chem. Soc.*, **41**, 1991–2001, 1919.

Here is an example. Pure HCl (hydrogen chloride) is a gas that is very soluble in water. A plot of the partial pressure of gaseous HCl in equilibrium with aqueous HCl, as a function of the solution molality (Fig. 10.1), shows that the limiting slope at infinite dilution is not finite, but zero. What is the reason for this non-Henry's law behavior? It must be because HCl is an electrolyte—it dissociates (ionizes) in the aqueous environment.

It is customary to use a *molality* basis for the reference and standard states of electrolyte solutes. This is the only basis used in this chapter, even when not explicitly indicated for ions. The symbol μ_+°, for instance, denotes the chemical potential of a cation in a standard state based on molality.

In dealing with an electrolyte solute, we can refer to the solute (a substance) as a whole and to the individual charged ions that result from dissociation. We can apply the same general definitions of chemical potential, activity coefficient, and activity to these different species, but only the activity coefficient and activity of the solute as a whole can be evaluated experimentally.

Contributors

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10.1: Single-ion Quantities

Consider a solution of an electrolyte solute that dissociates completely into a cation species and an anion species. Subscripts $+$ and $-$ will be used to denote the cation and anion, respectively. The solute molality $m_{\rm B}$ is defined as the amount of solute formula unit divided by the mass of solvent.

We first need to investigate the relation between the chemical potential of an ion species and the electric potential of the solution phase.

The electric potential ϕ in the interior of a phase is called the *inner electric potential*, or *Galvani potential*. It is defined as the work needed to reversibly move an infinitesimal test charge into the phase from a position infinitely far from other charges, divided by the value of the test charge. The electrical potential energy of a charge in the phase is the product of ϕ and the charge.

Consider a hypothetical process in which an infinitesimal amount $\mathrm{d}n_+$ of the cation is transferred into a solution phase at constant T and p. The quantity of charge transferred is $\delta Q = z_+ F\,\mathrm{d}n_+$, where z_+ is the charge number ($+1$, $+2$, etc.) of the cation, and F is the Faraday constant. (The Faraday constant is the charge per amount of protons.) If the phase is at zero electric potential, the process causes no change in its electrical potential energy. However, if the phase has a finite electric potential ϕ, the transfer process changes its electrical potential energy by $\phi\delta Q = z_+ F\phi\,\mathrm{d}n_+$. Consequently, the internal energy change depends on ϕ according to

$$\mathrm{d}U(\phi) = \mathrm{d}U(0) + z_+ F\phi\,\mathrm{d}n_+ \tag{10.1.1}$$

where the electric potential is indicated in parentheses. The change in the Gibbs energy of the phase is given by $\mathrm{d}G = \mathrm{d}(U - TS + pV)$, where T, S, p, and V are unaffected by the value of ϕ. The dependence of $\mathrm{d}G$ on ϕ is therefore

$$\mathrm{d}G(\phi) = \mathrm{d}G(0) + z_+ F\phi\,\mathrm{d}n_+ \tag{10.1.2}$$

The Gibbs fundamental equation for an open system, $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i$ (Eq. 9.2.34), assumes the electric potential is zero. From this equation and Eq. 10.1.2, the Gibbs energy change during the transfer process at constant T and p is found to depend on ϕ according to

$$\mathrm{d}G(\phi) = [\mu_+(0) + z_+ F\phi]\,\mathrm{d}n_+ \tag{10.1.3}$$

The chemical potential of the cation in a phase of electric potential ϕ, defined by the partial molar Gibbs energy $[\partial G(\phi)/\partial n_+]_{T,p}$, is therefore given by

$$\mu_+(\phi) = \mu_+(0) + z_+ F\phi \tag{10.1.4}$$

The corresponding relation for an anion is

$$\mu_-(\phi) = \mu_-(0) + z_- F\phi \tag{10.1.5}$$

where z_- is the charge number of the anion (-1, -2, etc.). For a charged species in general, we have

$$\mu_i(\phi) = \mu_i(0) + z_i F\phi \tag{10.1.6}$$

We define the *standard state of an ion* on a molality basis in the same way as for a nonelectrolyte solute, with the additional stipulation that the ion is in a phase of zero electric potential. Thus, the standard state is a hypothetical state in which the ion is at molality m° with behavior extrapolated from infinite dilution on a molality basis, in a phase of pressure $p = p^\circ$ and electric potential ϕ=0.

The *standard chemical potential* μ_+° or μ_-° of a cation or anion is the chemical potential of the ion in its standard state. Single-ion activities a_+ and a_- in a phase of zero electric potential are defined by relations having the form of Eq. 9.7.8:

$$\mu_+(0) = \mu_+^\circ + RT\ln a_+ \qquad \mu_-(0) = \mu_-^\circ + RT\ln a_- \tag{10.1.7}$$

As explained in Sec. 9.7, a_+ and a_- should depend on the temperature, pressure, and composition of the phase, and not on the value of ϕ.

From Eqs. 10.1.4, 10.1.5, and 10.1.7, the relations between the chemical potential of a cation or anion, its activity, and the electric potential of its phase, are found to be

$$\mu_+ = \mu_+^\circ + RT\ln a_+ + z_+ F\phi \qquad \mu_- = \mu_-^\circ + RT\ln a_- + z_i F\phi \tag{10.1.8}$$

These relations are definitions of single-ion activities in a phase of electric potential ϕ.

For a charged species in general, we can write

$$\mu_i = \mu_i^\circ + RT\ln a_i + z_i F\phi \tag{10.1.9}$$

Note that we can also apply this equation to an uncharged species, because the charge number z_i is then zero and Eq. 10.1.9 becomes the same as Eq. 9.7.2.

> Some thermodynamicists call the quantity $(\mu_i^\circ + RT\ln a_i)$, which depends only on T, p, and composition, the *chemical potential* of ion i, and the quantity $(\mu_i^\circ + RT\ln a_i + z_i F\phi)$ the *electrochemical potential* with symbol $\tilde{\mu}_i$.

Of course there is no experimental way to evaluate either μ_+ or μ_- relative to a reference state or standard state, because it is impossible to add cations or anions by themselves to a solution. We can nevertheless write some theoretical relations involving μ_+ and μ_-.

For a given temperature and pressure, we can write the dependence of the chemical potentials of the ions on their molalities in the same form as that given by Eq. 9.5.18 for a nonelectrolyte solute:

$$\mu_+ = \mu_+^{\text{ref}} + RT\ln\left(\gamma_+ \frac{m_+}{m^\circ}\right) \qquad \mu_- = \mu_-^{\text{ref}} + RT\ln\left(\gamma_- \frac{m_-}{m^\circ}\right) \tag{10.1.10}$$

Here μ_+^{ref} and μ_-^{ref} are the chemical potentials of the cation and anion in solute reference states. Each reference state is defined as a hypothetical solution with the same temperature, pressure, and electric potential as the solution under consideration; in this solution, the molality of the ion has the standard value m°, and the ion behaves according to Henry's law based on molality. γ_+ and γ_- are single-ion activity coefficients on a molality basis.

The single-ion activity coefficients approach unity in the limit of infinite dilution:

$$\gamma_+ \to 1 \quad \text{and} \quad \gamma_- \to 1 \quad \text{as} \quad m_{\text{B}} \to 0 \tag{10.1.11}$$

$$(\text{constant } T,\, p,\, \text{and } \phi)$$

In other words, we assume that in an extremely dilute electrolyte solution each individual ion behaves like a nonelectrolyte solute species in an ideal-dilute solution. At a finite solute molality, the values of γ_+ and γ_- are the ones that allow Eq. 10.1.10 to give the correct values of the quantities $(\mu_+ - \mu_+^{\text{ref}})$ and $(\mu_- - \mu_-^{\text{ref}})$. We have no way to actually measure these quantities experimentally, so we cannot evaluate either γ_+ or γ_-.

We can define single-ion pressure factors Γ_+ and Γ_- as follows:

$$\Gamma_+ \overset{\text{def}}{=} \exp\left(\frac{\mu_+^{\text{ref}} - \mu_+^\circ}{RT}\right) \approx \exp\left[\frac{V_+^\infty (p - p^\circ)}{RT}\right] \tag{10.1.12}$$

$$\Gamma_- \overset{\text{def}}{=} \exp\left(\frac{\mu_-^{\text{ref}} - \mu_-^\circ}{RT}\right) \approx \exp\left[\frac{V_-^\infty (p - p^\circ)}{RT}\right] \tag{10.1.13}$$

The approximations in these equations are like those in Table 9.6 for nonelectrolyte solutes; they are based on the assumption that the partial molar volumes V_+ and V_- are independent of pressure.

From Eqs. 10.1.7, 10.1.10, 10.1.12, and 10.1.13, the single-ion activities are related to the solution composition by

$$a_+ = \Gamma_+ \gamma_+ \frac{m_+}{m^\circ} \qquad a_- = \Gamma_- \gamma_- \frac{m_-}{m^\circ} \tag{10.1.14}$$

Then, from Eq. 10.1.9, we have the following relations between the chemical potentials and molalities of the ions:

$$\mu_+ = \mu_+^\circ + RT\ln(\Gamma_+ \gamma_+ m_+/m^\circ) + z_+ F\phi \tag{10.1.15}$$

$$\mu_- = \mu_-^\circ + RT\ln(\Gamma_- \gamma_- m_-/m^\circ) + z_- F\phi \tag{10.1.16}$$

Like the values of γ_+ and γ_-, values of the single-ion quantities a_+, a_-, Γ_+, and Γ_- cannot be determined by experiment.

10.2: Solution of a Symmetrical Electrolyte

Let us consider properties of an electrolyte solute as a whole. The simplest case is that of a binary solution in which the solute is a symmetrical strong electrolyte—a substance whose formula unit has one cation and one anion that dissociate completely. This condition will be indicated by $\nu = 2$, where ν is the number of ions per formula unit. In an aqueous solution, the solute with ν equal to 2 might be a 1:1 salt such as NaCl, a 2:2 salt such as $\mathrm{MgSO_4}$, or a strong monoprotic acid such as HCl.

In this binary solution, the chemical potential of the solute as a whole is defined in the usual way as the partial molar Gibbs energy

$$\mu_{\mathrm{B}} \overset{\text{def}}{=} \left(\frac{\partial G}{\partial n_{\mathrm{B}}}\right)_{T,p,n_{\mathrm{A}}} \tag{10.2.1}$$

and is a function of T, p, and the solute molality m_{B}. Although μ_{B} under given conditions must in principle have a definite value, we are not able to actually evaluate it because we have no way to measure precisely the energy brought into the system by the solute. This energy contributes to the internal energy and thus to G. We can, however, evaluate the differences $\mu_{\mathrm{B}} - \mu_{m,\mathrm{B}}^{\mathrm{ref}}$ and $\mu_{\mathrm{B}} - \mu_{m,\mathrm{B}}^{\circ}$.

We can write the additivity rule (Eq. 9.2.25) for G as either

$$G = n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mu_{\mathrm{B}} \tag{10.2.2}$$

or

$$G = n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{+}\mu_{+} + n_{-}\mu_{-} \tag{10.2.3}$$

A comparison of these equations for a symmetrical electrolyte ($n_{\mathrm{B}} = n_{+} = n_{-}$) gives us the relation

$$\mu_{\mathrm{B}} = \mu_{+} + \mu_{-} \qquad (10.2.4)\ (\nu{=}2)$$

We see that the solute chemical potential in this case is the *sum* of the single-ion chemical potentials.

The solution is a phase of electric potential ϕ. From Eqs. 10.1.4 and 10.1.5, the sum $\mu_{+} + \mu_{-}$ appearing in Eq. 10.2.4 is

$$\mu_{+}(\phi) + \mu_{-}(\phi) = \mu_{+}(0) + \mu_{-}(0) + (z_{+} + z_{-})F\phi \tag{10.2.5}$$

For the symmetrical electrolyte, the sum $(z_{+} + z_{-})$ is zero, so that μ_{B} is equal to $\mu_{+}(0) + \mu_{-}(0)$. We substitute the expressions of Eq. 10.1.10, use the relation $\mu_{m,\mathrm{B}}^{\mathrm{ref}} = \mu_{+}^{\mathrm{ref}} + \mu_{-}^{\mathrm{ref}}$ with reference states at ϕ=0, set the ion molalities m_{+} and m_{-} equal to m_{B}, and obtain

$$\mu_{\mathrm{B}} = \mu_{m,\mathrm{B}}^{\mathrm{ref}} + RT\ln\left[\gamma_{+}\gamma_{-}\left(\frac{m_{\mathrm{B}}}{m^{\circ}}\right)^{2}\right] \qquad (10.2.6)\ (\nu{=}2)$$

The important feature of this relation is the appearance of the *second* power of m_{B}/m°, instead of the first power as in the case of a nonelectrolyte. Also note that μ_{B} does not depend on ϕ, unlike μ_{+} and μ_{-}.

Although we cannot evaluate γ_{+} or γ_{-} individually, we can evaluate the product $\gamma_{+}\gamma_{-}$. This product is the square of the **mean ionic activity coefficient** $\gamma_{\pm}$, defined for a symmetrical electrolyte by

$$\gamma_{\pm} \overset{\text{def}}{=} \sqrt{\gamma_{+}\gamma_{-}} \qquad (10.2.7)\ (\nu{=}2)$$

With this definition, Eq. 10.2.6 becomes

$$\mu_{\mathrm{B}} = \mu_{m,\mathrm{B}}^{\mathrm{ref}} + RT\ln\left[(\gamma_{\pm})^{2}\left(\frac{m_{\mathrm{B}}}{m^{\circ}}\right)^{2}\right] \qquad (10.2.8)\ (\nu{=}2)$$

Since it is possible to determine the value of $\mu_{\mathrm{B}} - \mu_{m,\mathrm{B}}^{\mathrm{ref}}$ for a solution of known molality, $\gamma_{\pm}$ is a measurable quantity.

> If the electrolyte (e.g., HCl) is sufficiently volatile, its mean ionic activity coefficient in a solution can be evaluated from partial pressure measurements of an equilibrated gas phase. Section 10.6 will describe a general method by

which $\gamma_{\pm}$ can be found from osmotic coefficients. Section 14.5 describes how, in favorable cases, it is possible to evaluate $\gamma_{\pm}$ from the equilibrium cell potential of a galvanic cell.

The activity $a_{m,\mathrm{B}}$ of a solute substance on a molality basis is defined by Eq. 9.7.8:

$$\mu_{\mathrm{B}} = \mu^{\circ}_{m,\mathrm{B}} + RT \ln a_{m,\mathrm{B}} \tag{10.2.9}$$

Here $\mu^{\circ}_{m,\mathrm{B}}$ is the chemical potential of the solute in its standard state, which is the solute reference state at the standard pressure. By equating the expressions for μ_{B} given by Eqs. 10.2.8 and 10.2.9 and solving for the activity, we obtain

$$a_{m,\mathrm{B}} = \mathit{\Gamma}_{m,\mathrm{B}} (\gamma_{\pm})^2 \left(\frac{m_{\mathrm{B}}}{m^{\circ}}\right)^2 \qquad \begin{array}{r}(10.2.10)\\ (\nu{=}2)\end{array}$$

where $\mathit{\Gamma}_{m,\mathrm{B}}$ is the pressure factor defined by

$$\mathit{\Gamma}_{m,\mathrm{B}} \overset{\text{def}}{=} \exp\left(\frac{\mu^{\text{ref}}_{m,\mathrm{B}} - \mu^{\circ}_{m,\mathrm{B}}}{RT}\right) \tag{10.2.11}$$

We can use the appropriate expression in Table 9.6 to evaluate $\mathit{\Gamma}_{m,\mathrm{B}}$ at an arbitrary pressure p':

$$\mathit{\Gamma}_{m,\mathrm{B}}(p') = \exp\left(\int_{p^{\circ}}^{p'} \frac{V^{\infty}_{\mathrm{B}}}{RT}\,\mathrm{d}p\right) \approx \exp\left[\frac{V^{\infty}_{\mathrm{B}}(p' - p^{\circ})}{RT}\right] \tag{10.2.12}$$

The value of $\mathit{\Gamma}_{m,\mathrm{B}}$ is 1 at the standard pressure, and close to 1 at any reasonably low pressure. For this reason it is common to see Eq. 10.2.10 written as $a_{m,\mathrm{B}} = \gamma^2_{\pm}(m_{\mathrm{B}}/m^{\circ})^2$, with $\mathit{\Gamma}_{m,\mathrm{B}}$ omitted.

Equation 10.2.10 predicts that the activity of HCl in aqueous solutions is proportional, in the limit of infinite dilution, to the *square* of the HCl molality. In contrast, the activity of a *non*electrolyte solute is proportional to the *first* power of the molality in this limit. This predicted behavior of aqueous HCl is consistent with the data plotted in Fig. 10.1, and is confirmed by the data for dilute HCl solutions shown in Fig. 10.2(a). The dashed line in Fig. 10.2(a) is the extrapolation of the ideal-dilute behavior given by $a_{m,\mathrm{B}} = (m_{\mathrm{B}}/m^{\circ})^2$. The extension of this line to $m_{\mathrm{B}} = m^{\circ}$ establishes the hypothetical solute reference state based on molality, indicated by a filled circle in Fig. 10.2(b). (Since the data are for solutions at the standard pressure of $1\ \mathrm{bar}$, the solute reference state shown in the figure is also the solute standard state.)

The solid curve of Fig. 10.2(c) shows how the mean ionic activity coefficient of HCl varies with molality in approximately the same range of molalities as the data shown in Fig. 10.2(b). In the limit of infinite dilution, $\gamma_{\pm}$ approaches unity. The slope of the curve approaches $-\infty$ in this limit, quite unlike the behavior described in Sec. 9.5.4 for the activity coefficient of a nonelectrolyte solute.

For a symmetrical strong electrolyte, $\gamma_{\pm}$ is the geometric average of the single-ion activity coefficients γ_{+} and γ_{-}. We have no way of evaluating γ_{+} or γ_{-} individually, even if we know the value of $\gamma_{\pm}$. For instance, we cannot assume that γ_{+} and γ_{-} are equal.

10.3: Electrolytes in General

The formula unit of a *non*symmetrical electrolyte solute has more than two ions. General formulas for the solute as a whole are more complicated than those for the symmetrical case treated in the preceding section, but are derived by the same reasoning.

Again we assume the solute dissociates completely into its constituent ions. We define the following symbols:

$\nu_+ =$ the number of cations per solute formula unit

$\nu_- =$ the number of anions per solute formula unit

$\nu =$ the sum $\nu_+ + \nu_-$

For example, if the solute formula is $\mathrm{Al_2(SO_4)_3}$, the values are $\nu_+=2$, $\nu_-=3$, and $\nu=5$.

10.3.1 Solution of a single electrolyte

In a solution of a single electrolyte solute that is not necessarily symmetrical, the ion molalities are related to the overall solute molality by

$$m_+ = \nu_+ m_\mathrm{B} \qquad m_- = \nu_- m_\mathrm{B} \tag{10.3.1}$$

From the additivity rule for the Gibbs energy, we have

$$\begin{aligned} G &= n_\mathrm{A}\mu_\mathrm{A} + n_\mathrm{B}\mu_\mathrm{B} \\ &= n_\mathrm{A}\mu_\mathrm{A} + \nu_+ n_\mathrm{B}\mu_+ + \nu_- n_\mathrm{B}\mu_- \end{aligned} \tag{10.3.2}$$

giving the relation

$$\mu_\mathrm{B} = \nu_+\mu_+ + \nu_-\mu_- \tag{10.3.3}$$

in place of Eq. 10.2.4. The cations and anions are in the same phase of electric potential ϕ. We use Eqs. 10.1.4 and 10.1.5 to obtain

$$\nu_+\mu_+(\phi) + \nu_-\mu_-(\phi) = \nu_+\mu_+(0) + \nu_-\mu_-(0) + (\nu_+ z_+ + \nu_- z_-)F\phi \tag{10.3.4}$$

Electrical neutrality requires that $(\nu_+ z_+ + \nu_- z_-)$ be zero, giving

$$\mu_\mathrm{B} = \nu_+\mu_+(0) + \nu_-\mu_-(0) \tag{10.3.5}$$

By combining Eq. 10.3.5 with Eqs. 10.1.10, 10.3.1, and 10.3.3, we obtain

$$\mu_\mathrm{B} = \mu_\mathrm{B}^\mathrm{ref} + RT\ln\left[(\nu_+^{\nu_+}\nu_-^{\nu_-})(\gamma_+^{\nu_+})(\gamma_-^{\nu_-})\left(\frac{m_\mathrm{B}}{m^\circ}\right)^{\nu}\right] \tag{10.3.6}$$

where $\mu_\mathrm{B}^\mathrm{ref} = \nu_+\mu_+^\mathrm{ref} + \nu_-\mu_-^\mathrm{ref}$ is the chemical potential of the solute in the hypothetical reference state at $\phi=0$ in which B is at the standard molality and behaves as at infinite dilution. Equation 10.3.6 is the generalization of Eq. 10.2.6. It shows that although μ_+ and μ_- depend on ϕ, μ_B does not.

The mean ionic activity coefficient $\gamma_\pm$ is defined in general by

$$\gamma_\pm^\nu = (\gamma_+^{\nu_+})(\gamma_-^{\nu_-}) \tag{10.3.7}$$

or

$$\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/\nu} \tag{10.3.8}$$

Thus $\gamma_\pm$ is a geometric average of γ_+ and γ_- weighted by the numbers of the cations and anions in the solute formula unit. With a substitution from Eq. 10.3.7, Eq. 10.3.6 becomes

$$\mu_\mathrm{B} = \mu_\mathrm{B}^\mathrm{ref} + RT\ln\left[(\nu_+^{\nu_+}\nu_-^{\nu_-})\gamma_\pm^\nu\left(\frac{m_\mathrm{B}}{m^\circ}\right)^{\nu}\right] \tag{10.3.9}$$

Since $\mu_\mathrm{B} - \mu_\mathrm{B}^\mathrm{ref}$ is a measurable quantity, so also is $\gamma_\pm$.

The solute activity, defined by $\mu_\mathrm{B} = \mu_{m,\mathrm{B}}^\circ + RT\ln a_{m,\mathrm{B}}$, is

$$a_{m,\mathrm{B}} = (\nu_+^{\nu_+}\nu_-^{\nu_-})\varGamma_{m,\mathrm{B}}\gamma_\pm^\nu\left(\frac{m_\mathrm{B}}{m^\circ}\right)^{\nu} \tag{10.3.10}$$

where $\mathit{\Gamma}_{m,\mathrm{B}}$ is the pressure factor that we can evaluate with Eq. 10.2.12. Equation 10.3.10 is the generalization of Eq. 10.2.10. From Eqs. 10.1.12, 10.1.13, and 10.2.11 and the relations $\mu_{\mathrm{B}}^{\mathrm{ref}}=\nu_{+}\mu_{+}^{\mathrm{ref}}+\nu_{-}\mu_{-}^{\mathrm{ref}}$ and $\mu_{\mathrm{B}}^{\circ}=\nu_{+}\mu_{+}^{\circ}+\nu_{-}\mu_{-}^{\circ}$, we obtain the relation

$$\mathit{\Gamma}_{m,\mathrm{B}}=\mathit{\Gamma}_{+}^{\nu_{+}}\mathit{\Gamma}_{-}^{\nu_{-}} \tag{10.3.11}$$

10.3.2 Multisolute solution

Equation 10.3.3 relates the chemical potential of electrolyte B in a binary solution to the single-ion chemical potentials of its constituent ions:

$$\mu_{\mathrm{B}}=\nu_{+}\mu_{+}+\nu_{-}\mu_{-} \tag{10.3.12}$$

This relation is valid for each individual solute substance in a multisolute solution, even when two or more of the electrolyte solutes have an ion species in common.

As an illustration of this principle, consider a solution prepared by dissolving amounts n_{B} of $\mathrm{BaI_2}$ and n_{C} of CsI in an amount n_{A} of $\mathrm{H_2O}$. Assume the dissolved salts are completely dissociated into ions, with the $\mathrm{I^-}$ ion common to both. The additivity rule for the Gibbs energy of this solution can be written in the form

$$G=n_{\mathrm{A}}\mu_{\mathrm{A}}+n_{\mathrm{B}}\mu_{\mathrm{B}}+n_{\mathrm{C}}\mu_{\mathrm{C}} \tag{10.3.13}$$

and also, using single-ion quantities, in the form

$$G=n_{\mathrm{A}}\mu_{\mathrm{A}}+n_{\mathrm{B}}\mu(\mathrm{Ba}^{2+})+2n_{\mathrm{B}}\mu(\mathrm{I}^{-})+n_{\mathrm{C}}\mu(\mathrm{Cs}^{+})+n_{\mathrm{C}}\mu(\mathrm{I}^{-}) \tag{10.3.14}$$

Comparing Eqs. 10.3.13 and 10.3.14, we find the following relations must exist between the chemical potentials of the solute substances and the ion species:

$$\mu_{\mathrm{B}}=\mu(\mathrm{Ba}^{2+})+2\mu(\mathrm{I}^{-}) \qquad \mu_{\mathrm{C}}=\mu(\mathrm{Cs}^{+})+\mu(\mathrm{I}^{-}) \tag{10.3.15}$$

These relations agree with Eq. 10.3.12. Note that $\mu(\mathrm{I}^{-})$, the chemical potential of the ion common to both salts, appears in both relations.

The solute activity $a_{m,\mathrm{B}}$ is defined by the relation $\mu_{\mathrm{B}}=\mu_{\mathrm{B}}^{\circ}+RT\ln a_{m,\mathrm{B}}$ (Eq. 10.2.9). Using this relation together with Eqs. 10.1.7 and 10.1.14, we find that the solute activity is related to ion molalities by

$$a_{m,\mathrm{B}}=\mathit{\Gamma}_{m,\mathrm{B}}\gamma_{\pm}^{\nu}\left(\frac{m_{+}}{m^{\circ}}\right)^{\nu_{+}}\left(\frac{m_{-}}{m^{\circ}}\right)^{\nu_{-}} \tag{10.3.16}$$

where the pressure factor $\mathit{\Gamma}_{m,\mathrm{B}}$ is defined in Eq. 10.2.11. The ion molalities in this expression refer to the constituent ions of solute B, which in a multisolute solution are not necessarily present in the same stoichiometric ratio as in the solute substance.

For instance, suppose we apply Eq. 10.3.16 to the solution of $\mathrm{BaI_2}$ and CsI used above as an illustration of a multisolute solution, letting $a_{m,\mathrm{B}}$ be the activity of solute substance $\mathrm{BaI_2}$. The quantities m_{+} and m_{-} in the equation are then the molalities of the $\mathrm{Ba^{2+}}$ and $\mathrm{I^-}$ ions, and $\gamma_{\pm}$ is the mean ionic activity coefficient of the dissolved $\mathrm{BaI_2}$. Note that in this solution the $\mathrm{Ba^{2+}}$ and $\mathrm{I^-}$ ions are not present in the 1:2 ratio found in $\mathrm{BaI_2}$, because $\mathrm{I^-}$ is a constituent of both solutes.

10.3.3 Incomplete dissociation

In the preceding sections of this chapter, the electrolyte solute or solutes have been assumed to be completely dissociated into their constituent ions at all molalities. Some solutions, however, contain *ion pairs*—closely associated ions of opposite charge. Furthermore, in solutions of some electrolytes (often called “weak” electrolytes), an equilibrium is established between ions and electrically-neutral molecules. In these kinds of solutions, the relations between solute molality and ion molalities given by Eq. 10.3.1 are no longer valid. When dissociation is not complete, the expression for μ_{B} given by Eq. 10.3.9 can still be used. However, the quantity $\gamma_{\pm}$ appearing in the expression no longer has the physical significance of being the geometric average of the activity coefficients of the actual dissociated ions, and is called the **stoichiometric activity coefficient** of the electrolyte.

10.4: The Debye-Hückel Theory

The theory of Peter Debye and Erich Hückel (1923) provides theoretical expressions for single-ion activity coefficients and mean ionic activity coefficients in electrolyte solutions. The expressions in one form or another are very useful for extrapolation of quantities that include mean ionic activity coefficients to low solute molality or infinite dilution.

The only interactions the theory considers are the electrostatic interactions between ions. These interactions are much stronger than those between uncharged molecules, and they die off more slowly with distance. If the positions of ions in an electrolyte solution were completely random, the net effect of electrostatic ion–ion interactions would be zero, because each cation–cation or anion–anion repulsion would be balanced by a cation–anion attraction. The positions are not random, however: each cation has a surplus of anions in its immediate environment, and each anion has a surplus of neighboring cations. Each ion therefore has a net attractive interaction with the surrounding ion atmosphere. The result for a cation species at low electrolyte molality is a decrease of μ_+ compared to the cation at same molality in the absence of ion–ion interactions, meaning that the single-ion activity coefficient γ_+ becomes less than 1 as the electrolyte molality is increased beyond the ideal-dilute range. Similarly, γ_- also becomes less than 1.

According to the Debye–Hückel theory, the single-ion activity coefficient γ_i of ion i in a solution of one or more electrolytes is given by

$$\ln \gamma_i = -\frac{A_{\text{DH}} z_i^2 \sqrt{I_m}}{1 + B_{\text{DH}} a \sqrt{I_m}} \tag{10.4.1}$$

where

- The definitions of the quantities A_{DH} and B_{DH} appearing in Eq. 10.4.1 are

$$A_{\text{DH}} \overset{\text{def}}{=} \left(N_{\text{A}}^2 e^3/8\pi\right) \left(2\rho_{\text{A}}^*\right)^{1/2} (\epsilon_{\text{r}} \epsilon_0 RT)^{-3/2} \tag{10.4.3}$$

$$B_{\text{DH}} \overset{\text{def}}{=} N_{\text{A}} e \left(2\rho_{\text{A}}^*\right)^{1/2} (\epsilon_{\text{r}} \epsilon_0 RT)^{-1/2} \tag{10.4.4}$$

  where N_{A} is the Avogadro constant, e is the elementary charge (the charge of a proton), ρ_{A}^* and ϵ_{r} are the density and relative permittivity (dielectric constant) of the solvent, and ϵ_0 is the electric constant (or permittivity of vacuum).

> Lewis and Randall (*J. Am. Chem. Soc.*, 1112–1154, 1921) introduced the term *ionic strength*, defined by Eq. 10.4.2, two years before the Debye–Hückel theory was published. They found empirically that in dilute solutions, the mean ionic activity coefficient of a given strong electrolyte is the same in all solutions having the same ionic strength.

From Eqs. 10.3.8 and 10.4.1 and the electroneutrality condition $\nu_+ z_+ = \nu_- z_-$, we obtain the following expression for the logarithm of the mean ionic activity coefficient of an electrolyte solute:

$$\ln \gamma_\pm = -\frac{A_{\text{DH}} \left| z_+ z_- \right| \sqrt{I_m}}{1 + B_{\text{DH}} a \sqrt{I_m}} \tag{10.4.7}$$

In this equation, z_+ and z_- are the charge numbers of the cation and anion of the solute. Since the right side of Eq. 10.4.7 is negative at finite solute molalities, and zero at infinite dilution, the theory predicts that $\gamma_\pm$ is less than 1 at finite solute molalities and approaches 1 at infinite dilution.

Figure 10.4 shows $\ln \gamma_\pm$ as a function of $\sqrt{I_m}$ for aqueous HCl and $CaCl_2$. The experimental curves have the limiting slopes predicted by the Debye–Hückel limiting law (Eq. 10.4.8), but at a low ionic strength the curves begin to deviate significantly from the linear relations predicted by that law. The full Debye–Hückel equation (Eq. 10.4.7) fits the experimental curves over a wider range of ionic strength.

10.5: Derivation of the Debye-Hückel Theory

Debye and Hückel derived Eq. 10.4.1 using a combination of electrostatic theory, statistical mechanical theory, and thermodynamics. This section gives a brief outline of their derivation.

The derivation starts by focusing on an individual ion of species i as it moves through the solution; call it the central ion. Around this central ion, the time-average spatial distribution of any ion species j is not random, on account of the interaction of these ions of species j with the central ion. (Species i and j may be the same or different.) The distribution, whatever it is, must be spherically symmetric about the central ion; that is, a function only of the distance r from the center of the ion. The local concentration, c'_j, of the ions of species j at a given value of r depends on the ion charge $z_j e$ and the electric potential ϕ at that position. The time-average electric potential in turn depends on the distribution of all ions and is symmetric about the central ion, so expressions must be found for c'_j and ϕ as functions of r that are mutually consistent.

Debye and Hückel assumed that c'_j is given by the Boltzmann distribution

$$c'_j = c_j e^{-z_j e\phi/kT} \tag{10.5.1}$$

where $z_j e\phi$ is the electrostatic energy of an ion of species j, and k is the Boltzmann constant ($k = R/N_{\mathrm{A}}$). As r becomes large, ϕ approaches zero and c'_j approaches the macroscopic concentration c_j. As T increases, c'_j at a fixed value of r approaches c_j because of the randomizing effect of thermal energy. Debye and Hückel expanded the exponential function in powers of $1/T$ and retained only the first two terms: $c'_j \approx c_j(1 - z_j e\phi/kT)$. The distribution of each ion species is assumed to follow this relation. The electric potential function consistent with this distribution and with the electroneutrality of the solution as a whole is

$$\phi = (z_i e/4\pi\epsilon_{\mathrm{r}}\epsilon_0 r)e^{\kappa(a-r)}/(1+\kappa a) \tag{10.5.2}$$

Here κ is defined by $\kappa^2 = 2N_{\mathrm{A}}^2 e^2 I_c/\epsilon_r\epsilon_0 RT$, where I_c is the *ionic strength on a concentration basis* defined by $I_c = (1/2)\sum_i c_i z_i^2$.

The electric potential ϕ at a point is assumed to be a sum of two contributions: the electric potential the central ion would cause at infinite dilution, $z_i e/4\pi\epsilon_r\epsilon_0 r$, and the electric potential due to all other ions, ϕ'. Thus, ϕ' is equal to $\phi - z_i e/4\pi\epsilon_r\epsilon_0 r$, or

$$\phi' = (z_i e/4\pi\epsilon_{\mathrm{r}}\epsilon_0 r)[e^{\kappa(a-r)}/(1+\kappa a) - 1] \tag{10.5.3}$$

This expression for ϕ' is valid for distances from the center of the central ion down to a, the distance of closest approach of other ions. At smaller values of r, ϕ' is constant and equal to the value at $r = a$, which is $\phi'(a) = -(z_i e/4\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)$. The interaction energy between the central ion and the surrounding ions (the ion atmosphere) is the product of the central ion charge and $\phi'(a)$.

The last step of the derivation is the calculation of the work of a hypothetical reversible process in which the surrounding ions stay in their final distribution, and the charge of the central ion gradually increases from zero to its actual value $z_i e$. Let $\alpha z_i e$ be the charge at each stage of the process, where α is a fractional advancement that changes from 0 to 1. Then the work w' due to the interaction of the central ion with its ion atmosphere is $\phi'(a)$ integrated over the charge:

$$\begin{aligned} w' &= -\int_{\alpha=0}^{\alpha=1} [(\alpha z_i e/4\pi\epsilon_{\mathrm{r}}\epsilon_0)\kappa/(1+\kappa a)]\,\mathrm{d}(\alpha z_i \epsilon) \\ &= -(z_i^2 e^2/8\pi\epsilon_{\mathrm{r}}\epsilon_0)\kappa/(1+\kappa a) \end{aligned} \tag{10.5.4}$$

Since the infinitesimal Gibbs energy change in a reversible process is given by $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \text{đ}w'$ (Eq. 5.8.6), this reversible nonexpansion work at constant T and p is equal to the Gibbs energy change. The Gibbs energy change per amount of species i is $w' N_{\mathrm{A}} = -(z_i^2 e^2 N_{\mathrm{A}}/8\pi\epsilon_{\mathrm{r}}\epsilon_0)\kappa/(1+\kappa a)$. This quantity is $\Delta G/n_i$ for the process in which a solution of fixed composition changes from a hypothetical state lacking ion–ion interactions to the real state with ion–ion interactions present. $\Delta G/n_i$ may be equated to the difference of the chemical potentials of i in the final and initial states. If the chemical potential without ion–ion interactions is taken to be that for ideal-dilute behavior on a molality basis, $\mu_i = \mu_{m,i}^{\mathrm{ref}} + RT\ln(m_i/m^\circ)$, then $-(z_i^2 e^2 N_{\mathrm{A}}/8\pi\epsilon_{\mathrm{r}}\epsilon_0)\kappa/(1+\kappa a)$ is equal to $\mu_i - [\mu_{m,i}^{\mathrm{ref}} + RT\ln(m_i/m^\circ)] = RT\ln\gamma_{m,i}$. In a dilute solution, c_i can with little error be set equal to $\rho_{\mathrm{A}}^* m_i$, and I_c to $\rho_{\mathrm{A}}^* I_m$. Equation 10.4.1 follows.

10.6: Mean Ionic Activity Coefficients from Osmotic Coefficients

Recall that $\gamma_{\pm}$ is the mean ionic activity coefficient of a strong electrolyte, or the stoichiometric activity coefficient of an electrolyte that does not dissociate completely.

The general procedure described in this section for evaluating $\gamma_{\pm}$ requires knowledge of the osmotic coefficient ϕ_m as a function of molality. ϕ_m is commonly evaluated by the isopiestic method (Sec. 9.6.4) or from measurements of freezing-point depression (Sec. 12.2).

The osmotic coefficient of a binary solution of an electrolyte is defined by

$$\phi_m \overset{\text{def}}{=} \frac{\mu_{\mathrm{A}}^{*}-\mu_{\mathrm{A}}}{RTM_{\mathrm{A}}\nu m_{\mathrm{B}}} \tag{10.6.1}$$

(binary electrolyte solution)

That is, for an electrolyte the sum $\sum_{i\neq\mathrm{A}} m_i$ appearing in the definition of ϕ_m for a nonelectrolyte solution (Eq. 9.6.11) is replaced by νm_{B}, the sum of the ion molalities assuming complete dissociation. It will now be shown that ϕ_m defined this way can be used to evaluate $\gamma_{\pm}$.

The derivation is like that described in Sec. 9.6.3 for a binary solution of a nonelectrolyte. Solving Eq. 10.6.1 for μ_{A} and taking the differential of μ_{A} at constant T and p, we obtain

$$\mathrm{d}\mu_{\mathrm{A}} = -RTM_{\mathrm{A}}\nu(\phi_m\,\mathrm{d}m_{\mathrm{B}} + m_{\mathrm{B}}\,\mathrm{d}\phi_m) \tag{10.6.2}$$

From Eq. 10.3.9, we obtain

$$\mathrm{d}\mu_{\mathrm{B}} = RT\nu\left(\mathrm{d}\ln\gamma_{\pm} + \frac{\mathrm{d}m_{\mathrm{B}}}{m_{\mathrm{B}}}\right) \tag{10.6.3}$$

Substitution of these expressions in the Gibbs–Duhem equation $n_{\mathrm{A}}\,\mathrm{d}\mu_{\mathrm{A}} + n_{\mathrm{B}}\,\mathrm{d}\mu_{\mathrm{B}} = 0$, together with the substitution $n_{\mathrm{A}}M_{\mathrm{A}} = n_{\mathrm{B}}/m_{\mathrm{B}}$, yields

$$\mathrm{d}\ln\gamma_{\pm} = \mathrm{d}\phi_m + \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.4}$$

Then integration from $m_{\mathrm{B}} = 0$ to any desired molality m_{B}' gives the result

$$\ln\gamma_{\pm}(m_{\mathrm{B}}') = \phi_m(m_{\mathrm{B}}') - 1 + \int_0^{m_{\mathrm{B}}'} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.5}$$

The right side of this equation is the same expression as derived for $\ln\gamma_{m,\mathrm{B}}$ for a nonelectrolyte (Eq. 9.6.20).

The integrand of the integral on the right side of Eq. 10.6.5 approaches $-\infty$ as m_{B} approaches zero, making it difficult to evaluate the integral by numerical integration starting at $m_{\mathrm{B}} = 0$. (This difficulty does not exist when the solute is a nonelectrolyte.) Instead, we can split the integral into two parts

$$\int_0^{m_{\mathrm{B}}'} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} = \int_0^{m_{\mathrm{B}}''} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} + \int_{m_{\mathrm{B}}''}^{m_{\mathrm{B}}'} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.6}$$

where the integration limit m_{B}'' is a low molality at which the value of ϕ_m is available and at which $\gamma_{\pm}$ can either be measured or estimated from the Debye–Hückel equation.

We next rewrite Eq. 10.6.5 with m_{B}' replaced with m_{B}'':

$$\ln\gamma_{\pm}(m_{\mathrm{B}}'') = \phi_m(m_{\mathrm{B}}'') - 1 + \int_0^{m_{\mathrm{B}}''} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.7}$$

By eliminating the integral with an upper limit of m_{B}'' from Eqs. 10.6.6 and 10.6.7, we obtain

$$\int_0^{m_{\mathrm{B}}'} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} = \ln\gamma_{\pm}(m_{\mathrm{B}}'') - \phi_m(m_{\mathrm{B}}'') + 1 + \int_{m_{\mathrm{B}}''}^{m_{\mathrm{B}}'} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.8}$$

Equation 10.6.5 becomes

$$\ln\gamma_{\pm}(m'_{\mathrm{B}}) = \phi_m(m'_{\mathrm{B}}) - \phi_m(m''_{\mathrm{B}}) + \ln\gamma_{\pm}(m''_{\mathrm{B}}) + \int_{m''_{\mathrm{B}}}^{m'_{\mathrm{B}}} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \tag{10.6.9}$$

The integral on the right side of this equation can easily be evaluated by numerical integration.

10.7: Chapter 10 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

10.1

The mean ionic activity coefficient of NaCl in a 0.100 molal aqueous solution at $298.15\,\mathrm{K}$ has been evaluated with measurements of equilibrium cell potentials, with the result $\ln\gamma_{\pm}=-0.2505$ (R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd edition, Butterworths, London, 1959, Table 9.3). Use this value in Eq. 10.6.9, together with the values of osmotic coefficients in Table 10.1, to evaluate $\gamma_{\pm}$ at each of the molalities shown in the table; then plot $\gamma_{\pm}$ as a function of m_{B}.

CHAPTER OVERVIEW

11: Reactions and Other Chemical Processes

This chapter discusses the thermodynamics of mixing processes and processes described by reaction equations (chemical equations). It introduces the important concepts of molar mixing and reaction quantities, advancement, and the thermodynamic equilibrium constant. The focus is on chemical processes that take place in closed systems at constant pressure, with no work other than expansion work. Under these conditions, the enthalpy change is equal to the heat (Eq. 5.3.7). The processes either take place at constant temperature, or have initial and final states of the same temperature.

Most of the processes to be described involve mixtures and have intermediate states that are nonequilibrium states. At constant temperature and pressure, these processes proceed spontaneously with decreasing Gibbs energy (Sec. 5.8). (Processes in which G decreases are sometimes called *exergonic*.) When the rates of change are slow enough for thermal and mechanical equilibrium to be maintained, the spontaneity is due to lack of transfer equilibrium or reaction equilibrium. An equilibrium phase transition of a pure substance, however, is a special case: it is a reversible process of constant Gibbs energy (Sec. 8.3).

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11.1: Mixing Processes

11.2: The Advancement and Molar Reaction Quantities

Many of the processes of interest to chemists can be described by balanced reaction equations, or chemical equations, for the conversion of reactants into products. Thus, for the vaporization of water we write

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H_2O(g)} \tag{11.2.1}$$

For the dissolution of sodium chloride in water, we write

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} \tag{11.2.2}$$

For the Haber synthesis of ammonia, the reaction equation can be written

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightarrow 2\,\mathrm{NH_3(g)}$$

The essential feature of a reaction equation is that equal amounts of each element and equal net charges appear on both sides; the equation is said to be *balanced*. Thus, matter and charge are conserved during the process, and the process can take place in a closed system. The species to the left of a single arrow are called *reactants*, the species to the right are called *products*, and the arrow indicates the *forward* direction of the process.

A reaction equation is sometimes written with right and left arrows

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)} \tag{11.2.3}$$

to indicate that the process is at reaction equilibrium. It can also be written as a *stoichiometric equation* with an equal sign:

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} = 2\,\mathrm{NH_3(g)} \tag{11.2.4}$$

A reaction equation shows stoichiometric relations among the reactants and products. It is important to keep in mind that it specifies neither the initial and final states of a chemical process, nor the change in the amount of a reactant or product during the process. For example, the reaction equation $\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3}$ does not imply that the system initially contains only $\mathrm{N_2}$ and $\mathrm{H_2}$, or that only $\mathrm{NH_3}$ is present in the final state; and it does not mean that the process consists of the conversion of exactly one mole of $\mathrm{N_2}$ and three moles of $\mathrm{H_2}$ to two moles of $\mathrm{NH_3}$ (although this is a possibility). Instead, the reaction equation tells us that a change in the amount of $\mathrm{N_2}$ is accompanied by three times this change in the amount of $\mathrm{H_2}$ and by twice this change, with the opposite sign, in the amount of $\mathrm{NH_3}$.

11.2.1 An example: ammonia synthesis

It is convenient to indicate the progress of a chemical process with a variable called the *advancement*. The reaction equation $\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3}$ for the synthesis of ammonia synthesis will serve to illustrate this concept. Let the system be a gaseous mixture of $\mathrm{N_2}$, $\mathrm{H_2}$, and $\mathrm{NH_3}$.

If the system is *open* and the intensive properties remain uniform throughout the gas mixture, there are five independent variables. We can choose them to be T, p, and the amounts of the three substances. We can write the total differential of the enthalpy, for instance, as

$$\begin{gathered} \mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{p,\{n_i\}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\{n_i\}} \mathrm{d}p \\ + H_{\mathrm{N_2}}\,\mathrm{d}n_{\mathrm{N_2}} + H_{\mathrm{H_2}}\,\mathrm{d}n_{\mathrm{H_2}} + H_{\mathrm{NH_3}}\,\mathrm{d}n_{\mathrm{NH_3}} \end{gathered} \tag{11.2.1}$$

The notation $\{n_i\}$ stands for the set of amounts of all substances in the mixture, and the quantities $H_{\mathrm{N_2}}$, $H_{\mathrm{H_2}}$, and $H_{\mathrm{NH_3}}$ are partial molar enthalpies. For example, $H_{\mathrm{N_2}}$ is defined by

$$H_{\mathrm{N_2}} = \left(\frac{\partial H}{\partial n_{\mathrm{N_2}}}\right)_{T,p,n_{\mathrm{H_2}},n_{\mathrm{NH_3}}} \tag{11.2.2}$$

If the system is *closed*, the amounts of the three substances can still change because of the reaction $\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3}$, and the number of independent variables is reduced from five to three. We can choose them to be T, p, and a variable called advancement.

The **advancement** (or extent of reaction), ξ, is the amount by which the reaction defined by the reaction equation has advanced in the forward direction from specified initial conditions. The quantity ξ has dimensions of amount of substance, the usual unit being the mole.

Let the initial amounts be $n_{\mathrm{N_2},0}$, $n_{\mathrm{H_2},0}$, and $n_{\mathrm{NH_3},0}$. Then at any stage of the reaction process in the closed system, the amounts are given by

$$n_{\mathrm{N_2}} = n_{\mathrm{N_2},0} - \xi \qquad n_{\mathrm{H_2}} = n_{\mathrm{H_2},0} - 3\xi \qquad n_{\mathrm{NH_3}} = n_{\mathrm{NH_3},0} + 2\xi \tag{11.2.3}$$

These relations come from the stoichiometry of the reaction as expressed by the stoichiometric coefficients in the reaction equation. The second relation, for example, expresses the fact that when one mole of reaction has occurred ($\xi = 1\,\mathrm{mol}$), the amount of $\mathrm{H_2}$ in the closed system has decreased by three moles.

Taking the differentials of Eqs. 11.2.3, we find that infinitesimal changes in the amounts are related to the change of ξ as follows:

$$\mathrm{d}n_{\mathrm{N_2}} = -\,\mathrm{d}\xi \qquad \mathrm{d}n_{\mathrm{H_2}} = -3\,\mathrm{d}\xi \qquad \mathrm{d}n_{\mathrm{NH_3}} = 2\,\mathrm{d}\xi \tag{11.2.4}$$

These relations show that in a closed system, the changes in the various amounts are not independent. Substitution in Eq. 11.2.1 of the expressions for $\mathrm{d}n_{\mathrm{N_2}}$, $\mathrm{d}n_{\mathrm{H_2}}$, and $\mathrm{d}n_{\mathrm{NH_3}}$ gives

$$\begin{aligned} \mathrm{d}H = & \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}p \\ & + \left(-H_{\mathrm{N_2}} - 3H_{\mathrm{H_2}} + 2H_{\mathrm{NH_3}}\right) \mathrm{d}\xi \end{aligned} \tag{11.2.5}$$

(closed system)

(The subscript $\{n_i\}$ on the partial derivatives has been replaced by ξ to indicate the same thing: that the derivative is taken with the amount of each species held constant.)

Equation 11.2.5 gives an expression for the total differential of the enthalpy with T, p, and ξ as the independent variables. The coefficient of $\mathrm{d}\xi$ in this equation is called the **molar reaction enthalpy**, or molar enthalpy of reaction, $\Delta_{\mathrm{r}}H$:

$$\Delta_{\mathrm{r}}H = -H_{\mathrm{N_2}} - 3H_{\mathrm{H_2}} + 2H_{\mathrm{NH_3}} \tag{11.2.6}$$

We identify this coefficient as the partial derivative

$$\Delta_{\mathrm{r}}H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \tag{11.2.7}$$

That is, the molar reaction enthalpy is the rate at which the enthalpy changes with the advancement as the reaction proceeds in the forward direction at constant T and p.

> The partial molar enthalpy of a species is the enthalpy change per amount of the species added to an *open* system. To see why the particular combination of partial molar enthalpies on the right side of Eq. 11.2.6 is the rate at which enthalpy changes with advancement in the *closed* system, we can imagine the following process at constant T and p: An infinitesimal amount $\mathrm{d}n$ of $\mathrm{N_2}$ is removed from an open system, three times this amount of $\mathrm{H_2}$ is removed from the same system, and twice this amount of $\mathrm{NH_3}$ is added to the system. The total enthalpy change in the open system is $\mathrm{d}H = \left(-H_{\mathrm{N_2}} - 3H_{\mathrm{H_2}} + 2H_{\mathrm{NH_3}}\right)\mathrm{d}n$. The net change in the state of the system is equivalent to an advancement $\mathrm{d}\xi = \mathrm{d}n$ in a closed system, so $\mathrm{d}H/\mathrm{d}\xi$ in the closed system is equal to $\left(-H_{\mathrm{N_2}} - 3H_{\mathrm{H_2}} + 2H_{\mathrm{NH_3}}\right)$ in agreement with Eqs. 11.2.6 and 11.2.7.

Note that because the advancement is defined by how we write the reaction equation, the value of $\Delta_{\mathrm{r}}H$ also depends on the reaction equation. For instance, if we change the reaction equation for ammonia synthesis from $\mathrm{N_2}$ + 3 $\mathrm{H_2}$ $\rightarrow$ 2 $\mathrm{NH_3}$ to

$$\tfrac{1}{2}\mathrm{N_2} + \tfrac{3}{2}\mathrm{H_2} \rightarrow \mathrm{NH_3} \tag{11.2.5}$$

then the value of $\Delta_{\mathrm{r}}H$ is halved.

11.2.2 Molar reaction quantities in general

Now let us generalize the relations of the preceding section for any chemical process in a closed system. Suppose the stoichiometric equation has the form

$$a\mathrm{A} + b\mathrm{B} = d\mathrm{D} + e\mathrm{E} \tag{11.2.8}$$

where A and B are reactant species, D and E are product species, and a, b, d, and e are the corresponding stoichiometric coefficients. We can rearrange this equation to

$$0 = -a\mathrm{A} - b\mathrm{B} + d\mathrm{D} + e\mathrm{E} \tag{11.2.9}$$

In general, the stoichiometric relation for any chemical process is

$$0=\sum_i \nu_i \mathrm{A}_i \tag{11.2.10}$$

where ν_i is the **stoichiometric number** of species A_i, a dimensionless quantity taken as negative for a reactant and positive for a product. In the ammonia synthesis example of the previous section, the stoichiometric relation is $0=-\mathrm{N}_2-3\mathrm{H}_2+2\mathrm{NH}_3$ and the stoichiometric numbers are $\nu_{\mathrm{N}_2}=-1$, $\nu_{\mathrm{H}_2}=-3$, and $\nu_{\mathrm{NH}_3}=+2$. In other words, each stoichiometric number is the same as the stoichiometric coefficient in the reaction equation, except that the sign is negative for a reactant.

The amount of reactant or product species i present in the closed system at any instant depends on the advancement at that instant, and is given by

$$n_i=n_{i,0}+\nu_i\xi \tag{11.2.11}$$
(closed system)

The infinitesimal change in the amount due to an infinitesimal change in the advancement is

$$\mathrm{d}n_i=\nu_i\,\mathrm{d}\xi \tag{11.2.12}$$
(closed system)

In an open system, the total differential of extensive property X is

$$\mathrm{d}X=\left(\frac{\partial X}{\partial T}\right)_{p,\{n_i\}}\mathrm{d}T+\left(\frac{\partial X}{\partial p}\right)_{T,\{n_i\}}\mathrm{d}p+\sum_i X_i\,\mathrm{d}n_i \tag{11.2.13}$$

where X_i is a partial molar quantity. We restrict the system to a closed one with T, p, and ξ as the independent variables. Then, with the substitution $\mathrm{d}n_i=\nu_i\,\mathrm{d}\xi$ from Eq. 11.2.12, the total differential of X becomes

$$\mathrm{d}X=\left(\frac{\partial X}{\partial T}\right)_{p,\xi}\mathrm{d}T+\left(\frac{\partial X}{\partial p}\right)_{T,\xi}\mathrm{d}p+\Delta_{\mathrm{r}}X\,\mathrm{d}\xi \tag{11.2.14}$$
(closed system)

where the coefficient $\Delta_{\mathrm{r}}X$ is the **molar reaction quantity** defined by

$$\Delta_{\mathrm{r}}X\overset{\mathrm{def}}{=}\sum_i\nu_iX_i \tag{11.2.15}$$

Equation 11.2.14 allows us to identify the molar reaction quantity as a partial derivative:

$$\Delta_{\mathrm{r}}X=\left(\frac{\partial X}{\partial\xi}\right)_{T,p} \tag{11.2.16}$$
(closed system)

It is important to observe the distinction between the notations ΔX, the finite change of X during a process, and $\Delta_{\mathrm{r}}X$, a differential quantity that is a property of the system in a given state. The fact that both notations use the symbol Δ can be confusing. Equation 11.2.16 shows that we can think of Δ_{r} as an *operator*.

In dealing with the change of an extensive property X as ξ changes, we must distinguish between molar integral and molar differential reaction quantities.

- $\Delta X/\Delta\xi$ is a molar *integral* reaction quantity, the ratio of two finite differences between the final and initial states of a process. These states are assumed to have the same temperature and the same pressure. This e-book will use a notation such as $\Delta H_{\mathrm{m}}(\mathrm{rxn})$ for a molar integral reaction enthalpy:

$$\Delta H_{\mathrm{m}}(\mathrm{rxn})=\frac{\Delta H(\mathrm{rxn})}{\Delta\xi}=\frac{H(\xi_2)-H(\xi_1)}{\xi_2-\xi_1} \tag{11.2.17}$$
$(T_2{=}T_1, p_2{=}p_1)$

- $\Delta_{\mathrm{r}}X$ is a molar *differential* reaction quantity. Equation 11.2.16 shows that $\Delta_{\mathrm{r}}X$ is the rate at which the extensive property X changes with the advancement in a closed system at constant T and p. The value of $\Delta_{\mathrm{r}}X$ is in general a function of the independent variables T, p, and ξ.

The notation for a molar differential reaction quantity such as $\Delta_r H$ includes a subscript following the Δ symbol to indicate the kind of chemical process. The subscript "r" denotes a reaction or process in general. The meanings of "vap," "sub," "fus," and "trs" were described in Sec. 8.3.1. Subscripts for specific kinds of reactions and processes are listed in Sec. D.2 of Appendix D and are illustrated in sections to follow.

For certain kinds of processes, it may happen that a partial molar quantity X_i remains constant for each species i as the process advances at constant T and p. If X_i remains constant for each i, then according to Eq. 11.2.15 the value of $\Delta_r X$ must also remain constant as the process advances. Since $\Delta_r X$ is the rate at which X changes with ξ, in such a situation X is a linear function of ξ. This means that the molar integral reaction quantity $\Delta X_m(\text{rxn})$ defined by $\Delta X/\Delta\xi$ is equal, for any finite change of ξ, to $\Delta_r X$.

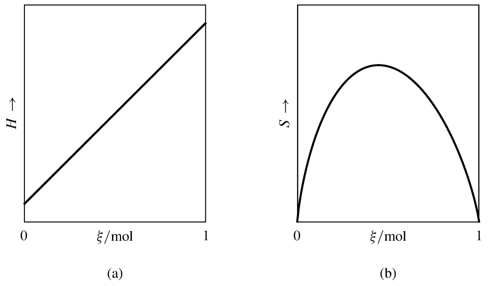

Figure 11.6 Enthalpy and entropy as functions of advancement at constant T and p. The curves are for a reaction A→2B with positive $\Delta_r H$ taking place in an ideal gas mixture with initial amounts $n_{A,0} = 1\ \text{mol}$ and $n_{B,0} = 0$.

An example is the partial molar enthalpy H_i of a constituent of an ideal gas mixture, an ideal condensed-phase mixture, or an ideal-dilute solution. In these ideal mixtures, H_i is independent of composition at constant T and p (Secs. 9.3.3, 9.4.3, and 9.4.7). When a reaction takes place at constant T and p in one of these mixtures, the molar differential reaction enthalpy $\Delta_r H$ is constant during the process, H is a linear function of ξ, and $\Delta_r H$ and $\Delta H_m(\text{rxn})$ are equal. Figure 11.6(a) illustrates this linear dependence for a reaction in an ideal gas mixture.

In contrast, Fig. 11.6(b) shows the nonlinearity of the entropy as a function of ξ during the same reaction. The nonlinearity is a consequence of the dependence of the partial molar entropy S_i on the mixture composition (Eq. 11.1.24). In the figure, the slope of the curve at each value of ξ equals $\Delta_r S$ at that point; its value changes as the reaction advances and the composition of the reaction mixture changes. Consequently, the molar integral reaction entropy $\Delta S_m(\text{rxn}) = \Delta S(\text{rxn})/\Delta\xi$ approaches the value of $\Delta_r S$ only in the limit as $\Delta\xi$ approaches zero.

11.2.3 Standard molar reaction quantities

If a chemical process takes place at constant temperature while each reactant and product remains in its standard state of unit activity, the molar reaction quantity $\Delta_r X$ is called the **standard molar reaction quantity** and is denoted by $\Delta_r X^\circ$. For instance, $\Delta_{\text{vap}} H^\circ$ is a standard molar enthalpy of vaporization (already discussed in Sec. 8.3.3), and $\Delta_r G^\circ$ is the standard molar Gibbs energy of a reaction.

From Eq. 11.2.15, the relation between a standard molar reaction quantity and the standard molar quantities of the reactants and products at the same temperature is

$$\Delta_r X^\circ \overset{\text{def}}{=} \sum_i \nu_i X_i^\circ \qquad (11.2.18)$$

Two comments are in order.

1. Whereas a molar reaction quantity is usually a function of T, p, and ξ, a *standard* molar reaction quantity is a function only of T. This is evident because standard-state conditions imply that each reactant and product is in a separate phase of constant defined composition and constant pressure p°.
2. Since the value of a standard molar reaction quantity is independent of ξ, the standard molar integral and differential quantities are identical (Sec. 11.2.2):

$$\Delta X_{\mathrm{m}}^{\circ}(\mathrm{rxn})=\Delta_{\mathrm{r}} X^{\circ} \tag{11.2.19}$$

These general concepts will now be applied to some specific chemical processes.

11.3: Molar Reaction Enthalpy

Recall that $\Delta H_{\mathrm{m}}(\mathrm{rxn})$ is a molar integral reaction enthalpy equal to $\Delta H(\mathrm{rxn})/\Delta\xi$, and that $\Delta_{\mathrm{r}}H$ is a molar differential reaction enthalpy defined by $\sum_i \nu_i H_i$ and equal to $(\partial H/\partial\xi)_{T,p}$.

11.3.1 Molar reaction enthalpy and heat

During a process in a closed system at constant pressure with expansion work only, the enthalpy change equals the energy transferred across the boundary in the form of heat: $\mathrm{d}H = \mathrm{đ}q$ (Eq. 5.3.7). Thus for the molar reaction enthalpy $\Delta_{\mathrm{r}}H = (\partial H/\partial\xi)_{T,p}$, which refers to a process not just at constant pressure but also at constant temperature, we can write

$$\Delta_{\mathrm{r}}H = \frac{\mathrm{đ}q}{\mathrm{d}\xi} \tag{11.3.1}$$

$$(\text{constant } T \text{ and } p,\ \mathrm{đ}w'{=}0)$$

Note that when there is nonexpansion work (w'), such as electrical work, the enthalpy change is not equal to the heat. For example, if we compare a reaction taking place in a galvanic cell with the same reaction in a reaction vessel, the heats at constant T and p for a given change of ξ are different, and may even have opposite signs. The value of $\Delta_{\mathrm{r}}H$ is the same in both systems, but the ratio of heat to advancement, $\mathrm{đ}q/\,\mathrm{d}\xi$, is different.

An **exothermic** reaction is one for which $\Delta_{\mathrm{r}}H$ is negative, and an **endothermic** reaction is one for which $\Delta_{\mathrm{r}}H$ is positive. Thus in a reaction at constant temperature and pressure with expansion work only, heat is transferred out of the system during an exothermic process and into the system during an endothermic process. If the process takes place at constant pressure in a system with thermally-insulated walls, the temperature increases during an exothermic process and decreases during an endothermic process.

These comments apply not just to chemical reactions, but to the other chemical processes at constant temperature and pressure discussed in this chapter.

11.3.2 Standard molar enthalpies of reaction and formation

A **standard molar reaction enthalpy**, $\Delta_{\mathrm{r}}H^{\circ}$, is the same as the molar integral reaction enthalpy $\Delta H_{\mathrm{m}}(\mathrm{rxn})$ for the reaction taking place under standard state conditions (each reactant and product at unit activity) at constant temperature.

At constant temperature, partial molar enthalpies depend only mildly on pressure. It is therefore usually safe to assume that unless the experimental pressure is much greater than p°, the reaction is exothermic if $\Delta_{\mathrm{r}}H^{\circ}$ is negative and endothermic if $\Delta_{\mathrm{r}}H^{\circ}$ is positive.

The **formation reaction** of a substance is the reaction in which the substance, at a given temperature and in a given physical state, is formed from the constituent elements in their reference states at the same temperature. The *reference state of an element* is usually chosen to be the standard state of the element in the allotropic form and physical state that is stable at the given temperature and the standard pressure. For instance, at $298.15\ \mathrm{K}$ and $1\ \mathrm{bar}$ the stable allotrope of carbon is crystalline graphite rather than diamond.

Phosphorus is an exception to the rule regarding reference states of elements. Although red phosphorus is the stable allotrope at $298.15\ \mathrm{K}$, it is not well characterized. Instead, the reference state is white phosphorus (crystalline P_4) at 1 bar.

At $298.15\ \mathrm{K}$, the reference states of the elements are the following:

- The **standard molar enthalpy of formation** (or standard molar heat of formation), $\Delta_{\mathrm{f}}H^{\circ}$, of a substance is the enthalpy change per amount of substance produced in the formation reaction of the substance in its standard state. Thus, the standard molar enthalpy of formation of gaseous methyl bromide at $298.15\ \mathrm{K}$ is the molar reaction enthalpy of the reaction

  $$\mathrm{C}(\mathrm{s, graphite}, p^{\circ}) + \tfrac{3}{2}\mathrm{H}_2(\text{ideal gas}, p^{\circ}) + \tfrac{1}{2}\mathrm{Br}_2(\mathrm{l}, p^{\circ}) \rightarrow \mathrm{CH_3Br}(\text{ideal gas}, p^{\circ}) \tag{11.3.1}$$

  The value of $\Delta_{\mathrm{f}}H^{\circ}$ for a given substance depends only on T. By definition, $\Delta_{\mathrm{f}}H^{\circ}$ for the reference state of an element is zero.

  A principle called **Hess's law** can be used to calculate the standard molar enthalpy of formation of a substance at a given temperature from standard molar reaction enthalpies at the same temperature, and to calculate a standard molar reaction enthalpy from tabulated values of standard molar enthalpies of formation. The principle is an application of the fact that enthalpy is a state function. Therefore, ΔH for a given change of the state of the system is independent of the path and is equal to the sum of ΔH values for any sequence of changes whose net result is the given change. (We may apply the same principle to a change of *any* state function.)

This value is one of the many standard molar enthalpies of formation to be found in compilations of thermodynamic properties of individual substances, such as the table in Appendix H. We may use the tabulated values to evaluate the standard molar reaction enthalpy $\Delta_r H^\circ$ of a reaction using a formula based on Hess's law. Imagine the reaction to take place in two steps: First each reactant in its standard state changes to the constituent elements in their reference states (the reverse of a formation reaction), and then these elements form the products in their standard states. The resulting formula is

$$\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i) \tag{11.3.3}$$
(Hess's law)

where $\Delta_f H^\circ(i)$ is the standard molar enthalpy of formation of substance i. Recall that the stoichiometric number ν_i of each reactant is negative and that of each product is positive, so according to Hess's law the standard molar reaction enthalpy is the sum of the standard molar enthalpies of formation of the products minus the sum of the standard molar enthalpies of formation of the reactants. Each term is multiplied by the appropriate stoichiometric coefficient from the reaction equation.

A standard molar enthalpy of formation can be defined for a *solute in solution* to use in Eq. 11.3.3. For instance, the formation reaction of aqueous sucrose is

$$12\ \mathrm{C(s, graphite)} + 11\ \mathrm{H_2(g)} + \tfrac{11}{2}\mathrm{O_2(g)} \rightarrow \mathrm{C_{12}H_{22}O_{11}(aq)} \tag{11.3.2}$$

and $\Delta_f H^\circ$ for $C_{12}H_{22}O_{11}(aq)$ is the enthalpy change per amount of sucrose formed when the reactants and product are in their standard states. Note that this formation reaction does *not* include the formation of the solvent H_2O from H_2 and O_2. Instead, the solute once formed combines with the amount of pure liquid water needed to form the solution. If the aqueous solute is formed in its standard state, the amount of water needed is very large so as to have the solute exhibit infinite-dilution behavior.

There is no ordinary reaction that would produce an individual *ion in solution* from its element or elements without producing other species as well. We can, however, prepare a consistent set of standard molar enthalpies of formation of ions by assigning a value to a single reference ion. ({This procedure is similar to that described in Sec. 9.2.4 for partial molar volumes of ions.) We can use these values for ions in Eq. 11.3.3 just like values of $\Delta_f H^\circ$ for substances and nonionic solutes. Aqueous hydrogen ion is the usual reference ion, to which is assigned the arbitrary value

$$\Delta_f H^\circ(\mathrm{H^+, aq}) = 0 \qquad \text{(at all temperatures)} \tag{11.3.4}$$

To see how we can use this reference value, consider the reaction for the formation of aqueous HCl (hydrochloric acid):

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

The standard molar reaction enthalpy at $298.15\,\mathrm{K}$ for this reaction is known, from reaction calorimetry, to have the value $\Delta_r H^\circ = -167.08\,\mathrm{kJ\,mol^{-1}}$. The standard states of the gaseous H_2 and Cl_2 are, of course, the pure gases acting ideally at pressure p°, and the standard state of each of the aqueous ions is the ion at the standard molality and standard pressure, acting as if its activity coefficient on a molality basis were 1. From Eq. 11.3.3, we equate the value of $\Delta_r H^\circ$ to the sum

$$-\tfrac{1}{2}\Delta_f H^\circ(\mathrm{H_2, g}) - \tfrac{1}{2}\Delta_f H^\circ(\mathrm{Cl_2, g}) + \Delta_f H^\circ(\mathrm{H^+, aq}) + \Delta_f H^\circ(\mathrm{Cl^-, aq}) \tag{11.3.3}$$

But the first three terms of this sum are zero. Therefore, the value of $\Delta_f H^\circ(\mathrm{Cl^-, aq})$ is $-167.08\,\mathrm{kJ\,mol^{-1}}$.

Next we can combine this value of $\Delta_f H^\circ(\mathrm{Cl^-, aq})$ with the measured standard molar enthalpy of formation of aqueous sodium chloride

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} \tag{11.3.4}$$

to evaluate the standard molar enthalpy of formation of aqueous sodium ion. By continuing this procedure with other reactions, we can build up a consistent set of $\Delta_f H^\circ$ values of various ions in aqueous solution.

11.3.3 Molar reaction heat capacity

The molar reaction enthalpy $\Delta_r H$ is in general a function of T, p, and ξ. Using the relations $\Delta_r H = \sum_i \nu_i H_i$ (from Eq. 11.2.15) and $C_{p,i} = (\partial H_i/\partial T)_{p,\xi}$ (Eq. 9.2.52), we can write

$$\left(\frac{\partial \Delta_{\rm r} H}{\partial T}\right)_{p,\xi} = \left(\frac{\partial \sum_i \nu_i H_i}{\partial T}\right)_{p,\xi} = \sum_i \nu_i C_{p,i} = \Delta_{\rm r} C_p \tag{11.3.5}$$

where $\Delta_{\rm r} C_p$ is the molar reaction heat capacity at constant pressure, equal to the rate at which the heat capacity C_p changes with ξ at constant T and p.

Under standard state conditions, Eq. 11.3.5 becomes

$$\mathrm{d}\Delta_{\rm r} H^\circ / \mathrm{d}T = \Delta_{\rm r} C_p^\circ \tag{11.3.6}$$

11.3.4 Effect of temperature on reaction enthalpy

Consider a reaction occurring with a certain finite change of the advancement in a closed system at temperature T' and at constant pressure. The reaction is characterized by a change of the advancement from ξ_1 to ξ_2, and the integral reaction enthalpy at this temperature is denoted $\Delta H(\mathrm{rxn}, T')$. We wish to find an expression for the reaction enthalpy $\Delta H(\mathrm{rxn}, T'')$ for the same values of ξ_1 and ξ_2 at the same pressure but at a different temperature, T''.

The heat capacity of the system at constant pressure is related to the enthalpy by Eq. 5.6.3: $C_p = (\partial H/\partial T)_{p,\xi}$. We integrate $\mathrm{d}H = C_p\,\mathrm{d}T$ from T' to T'' at constant p and ξ, for both the final and initial values of the advancement:

$$H(\xi_2, T'') = H(\xi_2, T') + \int_{T'}^{T''} C_p(\xi_2)\,\mathrm{d}T \tag{11.3.7}$$

$$H(\xi_1, T'') = H(\xi_1, T') + \int_{T'}^{T''} C_p(\xi_1)\,\mathrm{d}T \tag{11.3.8}$$

Subtracting Eq. 11.3.8 from Eq. 11.3.7, we obtain

$$\Delta H(\mathrm{rxn}, T'') = \Delta H(\mathrm{rxn}, T') + \int_{T'}^{T''} \Delta C_p\,\mathrm{d}T \tag{11.3.9}$$

where ΔC_p is the difference between the heat capacities of the system at the final and initial values of ξ, a function of T: $\Delta C_p = C_p(\xi_2) - C_p(\xi_1)$. Equation 11.3.9 is the **Kirchhoff equation**.

When ΔC_p is essentially constant in the temperature range from T' to T'', the Kirchhoff equation becomes

$$\Delta H(\mathrm{rxn}, T'') = \Delta H(\mathrm{rxn}, T') + \Delta C_p (T'' - T') \tag{11.3.10}$$

Figure 11.7 illustrates the principle of the Kirchhoff equation as expressed by Eq. 11.3.10. ΔC_p equals the difference in the slopes of the two dashed lines in the figure, and the product of ΔC_p and the temperature difference $T'' - T'$ equals the change in the value of $\Delta H(\mathrm{rxn})$. The figure illustrates an exothermic reaction with negative ΔC_p, resulting in a more negative value of $\Delta H(\mathrm{rxn})$ at the higher temperature.

We can also find the effect of temperature on the molar differential reaction enthalpy $\Delta_{\rm r} H$. From Eq. 11.3.5, we have $(\partial \Delta_{\rm r} H/\partial T)_{p,\xi} = \Delta_{\rm r} C_p$. Integration from temperature T' to temperature T'' yields the relation

$$\Delta_{\rm r} H(T'', \xi) = \Delta_{\rm r} H(T', \xi) + \int_{T'}^{T''} \Delta_{\rm r} C_p(T, \xi)\,\mathrm{d}T \tag{11.3.11}$$

This relation is analogous to Eq. 11.3.9, using molar differential reaction quantities in place of integral reaction quantities.

11.4: Enthalpies of Solution and Dilution

The processes of solution (dissolution) and dilution are related. The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, Sec. 2.11.1) recommends the abbreviations sol and dil for these processes.

For an electrolyte solute, a plot of $\Delta H_{\mathrm{m}}(\mathrm{sol}, m_{\mathrm{B}})$ versus m_{B} has a limiting slope of $+\infty$ at $m_{\mathrm{B}}{=}0$, whereas the limiting slope of $\Delta H_{\mathrm{m}}(\mathrm{sol}, m_{\mathrm{B}})$ versus $\sqrt{m_{\mathrm{B}}}$ is finite and can be predicted from the Debye–Hückel limiting law. Accordingly, a satisfactory procedure is to plot $\Delta H_{\mathrm{m}}(\mathrm{sol}, m_{\mathrm{B}})$ versus $\sqrt{m_{\mathrm{B}}}$, perform a linear extrapolation of the experimental points to $\sqrt{m_{\mathrm{B}}}{=}0$, and then shift the origin to the extrapolated intercept. The result is a plot of $\mathit{\Phi}_L$ versus $\sqrt{m_{\mathrm{B}}}$. An example for aqueous NaCl solutions is shown in Fig. 11.10(a).

We can also evaluate $\mathit{\Phi}_L$ from experimental enthalpies of dilution. From Eqs. 11.4.10 and 11.4.22, we obtain the relation

$$\mathit{\Phi}_L(m''_{\mathrm{B}}) - \mathit{\Phi}_L(m'_{\mathrm{B}}) = \Delta H_{\mathrm{m}}(\mathrm{dil},\, m'_{\mathrm{B}} \rightarrow m''_{\mathrm{B}}) \tag{11.4.25}$$

We can measure the enthalpy changes for diluting a solution of initial molality m'_{B} to various molalities m''_{B}, plot the values of $\Delta H_{\mathrm{m}}(\mathrm{dil},\, m'_{\mathrm{B}} \rightarrow m''_{\mathrm{B}})$ versus $\sqrt{m_{\mathrm{B}}}$, extrapolate the curve to $\sqrt{m_{\mathrm{B}}}{=}0$, and shift the origin to the extrapolated intercept, resulting in a plot of $\mathit{\Phi}_L$ versus $\sqrt{m_{\mathrm{B}}}$.

In order to be able to use Eq. 11.4.23, we need to relate the derivative $\mathrm{d}\mathit{\Phi}_L/\,\mathrm{d}m_{\mathrm{B}}$ to the slope of the curve of $\mathit{\Phi}_L$ versus $\sqrt{m_{\mathrm{B}}}$. We write

$$\mathrm{d}\sqrt{m_{\mathrm{B}}} = \frac{1}{2\sqrt{m_{\mathrm{B}}}}\,\mathrm{d}m_{\mathrm{B}} \qquad \mathrm{d}m_{\mathrm{B}} = 2\sqrt{m_{\mathrm{B}}}\,\mathrm{d}\sqrt{m_{\mathrm{B}}} \tag{11.4.26}$$

Substituting this expression for $\mathrm{d}m_{\mathrm{B}}$ into Eq. 11.4.23, we obtain the following operational equation for evaluating L_{B} from the plot of $\mathit{\Phi}_L$ versus $\sqrt{m_{\mathrm{B}}}$:

$$L_{\mathrm{B}} = \mathit{\Phi}_L + \frac{\sqrt{m_{\mathrm{B}}}}{2}\,\frac{\mathrm{d}\mathit{\Phi}_L}{\mathrm{d}\sqrt{m_{\mathrm{B}}}} \tag{11.4.27}$$

(constant T and p)

The value of $\mathit{\Phi}_L$ goes to zero at infinite dilution. When the solute is an electrolyte, the dependence of $\mathit{\Phi}_L$ on m_{B} in solutions dilute enough for the Debye–Hückel limiting law to apply is given by

$$\mathit{\Phi}_L = C_{\mathit{\Phi}_L}\sqrt{m_{\mathrm{B}}} \tag{11.4.28}$$

(very dilute solution)

For aqueous solutions of a 1:1 electrolyte at $25\,^{\circ}\mathrm{C}$, the coefficient $C_{\mathit{\Phi}_L}$ has the value

$$C_{\mathit{\Phi}_L} = 1.988 \times 10^{3}\ \mathrm{J\ kg^{1/2}\ mol^{-3/2}} \tag{11.4.29}$$

(The fact that $C_{\mathit{\Phi}_L}$ is positive means, according to Eq. 11.4.25, that dilution of a very dilute electrolyte solution is an exothermic process.) $C_{\mathit{\Phi}_L}$ is equal to the limiting slope of $\mathit{\Phi}_L$ versus $\sqrt{m_{\mathrm{B}}}$, of $\Delta H_{\mathrm{m}}(\mathrm{sol}, m_{\mathrm{B}})$ versus $\sqrt{m_{\mathrm{B}}}$, and of $\Delta H_{\mathrm{m}}(\mathrm{dil},\, m'_{\mathrm{B}} \rightarrow m''_{\mathrm{B}})$ versus $\sqrt{m'_{\mathrm{B}}}$. The value given by Eq. 11.4.29 can be used for extrapolation of measurements at $25\,^{\circ}\mathrm{C}$ and low molality to infinite dilution.

> Equation 11.4.28 can be derived as follows. For simplicity, we assume the pressure is the standard pressure p°. At this pressure H_{B}^{∞} is the same as H_{B}°, and Eq. 11.4.17 becomes $L_{\mathrm{B}} = H_{\mathrm{B}} - H_{\mathrm{B}}^{\circ}$. From Eqs. 12.1.3 and 12.1.6 in the next chapter, we can write the relations
>
> $$H_{\mathrm{B}} = -T^2\left[\frac{\partial(\mu_{\mathrm{B}}/T)}{\partial T}\right]_{p,\{n_i\}} \qquad H_{\mathrm{B}}^{\circ} = -T^2\,\frac{\mathrm{d}(\mu_{m,\mathrm{B}}^{\circ}/T)}{\mathrm{d}T} \tag{11.4.30}$$
>
> Subtracting the second of these relations from the first, we obtain
>
> $$H_{\mathrm{B}} - H_{\mathrm{B}}^{\circ} = -T^2\left[\frac{\partial(\mu_{\mathrm{B}} - \mu_{m,\mathrm{B}}^{\circ})/T}{\partial T}\right]_{p,\{n_i\}} \tag{11.4.31}$$

The solute activity on a molality basis, $a_{m,\mathrm{B}}$, is defined by $\mu_\mathrm{B} - \mu^\circ_{m,\mathrm{B}} = RT\ln a_{m,\mathrm{B}}$. The activity of an electrolyte solute at the standard pressure, from Eq. 10.3.10, is given by $a_{m,\mathrm{B}} = (\nu_+^{\nu_+}\nu_-^{\nu_-})\gamma_\pm^\nu (m_\mathrm{B}/m^\circ)^\nu$. Accordingly, the relative partial molar enthalpy of the solute is related to the mean ionic activity coefficient by

$$L_\mathrm{B} = -RT^2\nu\left(\frac{\partial\ln\gamma_\pm}{\partial T}\right)_{p,\{n_i\}} \tag{11.4.32}$$

We assume the solution is sufficiently dilute for the mean ionic activity coefficient to be adequately described by the Debye–Hückel limiting law, Eq. 10.4.8: $\ln\gamma_\pm = -A_\mathrm{DH}\,|z_+z_-|\,\sqrt{I_m}$, where A_DH is a temperature-dependent quantity defined in Sec. 10.4. Then Eq. 11.4.32 becomes

$$L_\mathrm{B} = RT^2\nu\,|z_+z_-|\,\sqrt{I_m}\left(\frac{\partial A_\mathrm{DH}}{\partial T}\right)_{p,\{n_i\}} \tag{11.4.33}$$
(very dilute solution)

Substitution of the expression given by Eq. 10.4.9 for I_m in a solution of a single completely-dissociated electrolyte converts Eq. 11.4.33 to

$$L_\mathrm{B} = \left[\frac{RT^2}{\sqrt{2}}\left(\frac{\partial\rho^*_\mathrm{A}A_\mathrm{DH}}{\partial T}\right)_{p,\{n_i\}}(\nu\,|z_+z_-|)^{3/2}\right]\sqrt{m_\mathrm{B}} = C_{L_\mathrm{B}}\sqrt{m_\mathrm{B}} \tag{11.4.34}$$
(very dilute solution)

The coefficient C_{L_B} (the quantity in brackets) depends on T, the kind of solvent, and the ion charges and number of ions per solute formula unit, but not on the solute molality.

Let C_{Φ_L} represent the limiting slope of Φ_L versus $\sqrt{m_\mathrm{B}}$. In a very dilute solution we have $\Phi_L = C_{\Phi_L}\sqrt{m_\mathrm{B}}$, and Eq. 11.4.27 becomes

$$L_\mathrm{B} = \Phi_L + \frac{\sqrt{m_\mathrm{B}}}{2}\frac{\mathrm{d}\Phi_L}{\mathrm{d}\sqrt{m_\mathrm{B}}} = C_{\Phi_L}\sqrt{m_\mathrm{B}} + \frac{\sqrt{m_\mathrm{B}}}{2}C_{\Phi_L} \tag{11.4.35}$$

By equating this expression for L_B with the one given by Eq. 11.4.34 and solving for C_{Φ_L}, we obtain $C_{\Phi_L} = (2/3)C_{L_\mathrm{B}}$ and $\Phi_L = (2/3)C_{L_\mathrm{B}}\sqrt{m_\mathrm{B}}$.

11.5: Reaction Calorimetry

Reaction calorimetry is used to evaluate the molar integral reaction enthalpy $\Delta H_{\text{m}}(\text{rxn})$ of a reaction or other chemical process at constant temperature and pressure. The measurement actually made, however, is a temperature change.

Sections 11.5.1 and 11.5.2 will describe two common types of calorimeters designed for reactions taking place at either constant pressure or constant volume. The constant-pressure type is usually called a *reaction calorimeter*, and the constant-volume type is known as a *bomb calorimeter* or *combustion calorimeter*.

In either type of calorimeter, the chemical process takes place in a reaction vessel surrounded by an outer jacket. The jacket may be of either the adiabatic type or the isothermal-jacket type described in Sec. 7.3.2 in connection with heat capacity measurements. A temperature-measuring device is immersed either in the vessel or in a phase in thermal contact with it. The measured temperature change is caused by the chemical process, instead of by electrical work as in the determination of heat capacity. One important way in which these calorimeters differ from ones used for heat capacity measurements is that work is kept deliberately small, in order to minimize changes of internal energy and enthalpy during the experimental process.

11.5.1 The constant-pressure reaction calorimeter

The contents of a constant-pressure calorimeter are usually open to the atmosphere, so this type of calorimeter is unsuitable for processes involving gases. It is, however, a convenient apparatus in which to study a liquid-phase chemical reaction, the dissolution of a solid or liquid solute in a liquid solvent, or the dilution of a solution with solvent.

The process is initiated in the calorimeter by allowing the reactants to come into contact. The temperature in the reaction vessel is measured over a period of time starting before the process initiation and ending after the advancement has reached a final value with no further change.

The heating or cooling curve (temperature as a function of time) is observed over a period of time that includes the period during which the advancement ξ changes. For an exothermic reaction occurring in an adiabatic calorimeter, the heating curve may resemble that shown in Fig. 7.3, and the heating curve in an isothermal-jacket calorimeter may resemble that shown in Fig. 7.4. Two points are designated on the heating or cooling curve: one at temperature T_1, before the reaction is initiated, and the other at T_2, after ξ has reached its final value. These points are indicated by open circles in Figs. 7.3 and 7.4.

The relations derived here parallel those of Sec. 11.5.1 for a constant-pressure calorimeter. The three paths depicted in Fig. 11.13 are similar to those in Fig. 11.11, except that instead of being at constant pressure they are at constant volume. We shall assume the combustion reaction is exothermic, with T_2 being greater than T_1.

The internal energy change of the experimental process that actually occurs in the calorimeter between times t_1 and t_2 is denoted $\Delta U(\text{expt})$ in the figure. Conceptually, the overall change of state during this process would be duplicated by a path in which the temperature of the system with the reactants present increases from T_1 to T_2, followed by the isothermal bomb process at temperature T_2. (When one investigates a combustion reaction, the path in which temperature changes without reaction is best taken with reactants rather than products present because the reactants are more easily characterized.) In the figure these paths are labeled with the internal energy changes $\Delta U(\text{R})$ and $\Delta U(\text{IBP}, T_2)$, and we can write

$$\Delta U(\text{expt}) = \Delta U(\text{R}) + \Delta U(\text{IBP}, T_2) \tag{11.5.4}$$

To evaluate $\Delta U(\text{R})$, we can use the energy equivalent ϵ_{R} of the calorimeter with reactants present in the bomb vessel. ϵ_{R} is the average heat capacity of the system between T_1 and T_2—that is, the ratio $q/(T_2 - T_1)$, where q is the heat that would be needed to change the temperature from T_1 to T_2. From the first law, with expansion work assumed negligible, the internal energy change equals this heat, giving us the relation

$$\Delta U(\text{R}) = \epsilon_{\text{R}}(T_2 - T_1) \tag{11.5.5}$$

The initial and final states of the path are assumed to be equilibrium states, and there may be some transfer of reactants or H_2O from one phase to another within the bomb vessel during the heating process.

The value of ϵ_{R} is obtained in a separate calibration experiment. The calibration is usually carried out with the combustion of a reference substance, such as benzoic acid, whose internal energy of combustion under controlled conditions is precisely known from standardization based on electrical work. If the bomb vessel is immersed in the same mass of water in both experiments and other conditions are similar, the difference in the values of ϵ_{R} in the two experiments is equal to the known difference in the heat capacities of the initial contents (reactants, water, etc.) of the bomb vessel in the two experiments.

The internal energy change we wish to find is $\Delta U(\mathrm{IBP}, T_2)$, that of the isothermal bomb process in which reactants change to products at temperature T_2, accompanied perhaps by some further transfer of substances between phases. From Eqs. 11.5.4 and 11.5.5, we obtain

$$\Delta U(\mathrm{IBP}, T_2) = -\epsilon(T_2 - T_1) + \Delta U(\mathrm{expt}) \tag{11.5.6}$$

The value of $\Delta U(\mathrm{expt})$ is small. To evaluate it, we must look in detail at the possible sources of energy transfer between the system and the surroundings during the experimental process. These sources are

1. The ignition work occurs during only a short time interval at the beginning of the process, and its value is known. The effects of heat transfer, stirring work, and temperature measurement continue throughout the course of the experiment. With these considerations, Eq. 11.5.6 becomes

   $$\Delta U(\mathrm{IBP}, T_2) = -\epsilon(T_2 - T_1) + w_{\mathrm{ign}} + \Delta U'(\mathrm{expt}) \tag{11.5.7}$$

   where $\Delta U'(\mathrm{expt})$ is the internal energy change due to heat, stirring, and temperature measurement. $\Delta U'(\mathrm{expt})$ can be evaluated from the energy equivalent and the observed rates of temperature change at times t_1 and t_2; the relevant relations for an isothermal jacket are Eq. 7.3.24 (with w_{el} set equal to zero) and Eq. 7.3.32.

   ### Correction to the reference temperature

   ### Reduction to standard states

   We want to obtain the value of $\Delta_{\mathrm{c}} U^{\circ}(T_{\mathrm{ref}})$, the molar internal energy change for the main combustion reaction at the reference temperature under standard-state conditions. Once we have this value, it is an easy matter to find the molar *enthalpy* change under standard-state conditions, our ultimate goal.

   Consider a hypothetical process with the following three isothermal steps carried out at the reference temperature T_{ref}:

   1. The net change is a decrease in the amount of each reactant in its standard state and an increase in the amount of each product in its standard state. The internal energy change of step 2 is $\Delta U(\mathrm{IBP}, T_{\mathrm{ref}})$, whose value is found from Eq. 11.5.8. The internal energy changes of steps 1 and 3 are called **Washburn corrections** (Edward W. Washburn, *J. Res. Natl. Bur. Stand. (U.S.)*, **10**, 525–558, 1933).

      Thus, we calculate the standard internal energy change of the main combustion reaction at temperature T_{ref} from

      $$\Delta U^{\circ}(\mathrm{cmb}, T_{\mathrm{ref}}) = \Delta U(\mathrm{IBP}, T_{\mathrm{ref}}) + (\text{Washburn corrections}) - \sum_i \Delta\xi_i \Delta_{\mathrm{r}} U^{\circ}(i) \tag{11.5.9}$$

      where the sum over i is for side reactions and auxiliary reactions if present. Finally, we calculate the standard *molar* internal energy of combustion from

      $$\Delta_{\mathrm{c}} U^{\circ}(T_{\mathrm{ref}}) = \frac{\Delta U^{\circ}(\mathrm{cmb}, T_{\mathrm{ref}})}{\Delta\xi_{\mathrm{c}}} \tag{11.5.10}$$

      where $\Delta\xi_{\mathrm{c}}$ is the advancement of the main combustion reaction in the bomb vessel.

      ### Standard molar enthalpy change

      ### Washburn corrections

      The Washburn corrections needed in Eq. 11.5.9 are internal energy changes for certain hypothetical physical processes occurring at the reference temperature T_{ref} involving the substances present in the bomb vessel. In these processes, substances change from their standard states to the initial state of the isothermal bomb process, or change from the final state of the isothermal bomb process to their standard states.

      For example, consider the complete combustion of a solid or liquid compound of carbon, hydrogen, and oxygen in which the combustion products are CO_2 and H_2O and there are no side reactions or auxiliary reactions. In the initial state of the isothermal bomb process, the bomb vessel contains the pure reactant, liquid water with O_2 dissolved in it, and a gaseous mixture of O_2 and H_2O, all at a high pressure p_1. In the final state, the bomb vessel contains liquid water with O_2 and CO_2

dissolved in it and a gaseous mixture of O_2, H_2O, and CO_2, all at pressure p_2. In addition, the bomb vessel contains internal parts of constant mass such as the sample holder and ignition wires.

In making Washburn corrections, we must use a single standard state for each substance in order for Eq. 11.5.9 to correctly give the standard internal energy of combustion. In the present example we choose the following standard states: pure solid or liquid for the reactant compound, pure liquid for the H_2O, and pure ideal gases for the O_2 and CO_2, each at pressure $p^\circ = 1\,\mathrm{bar}$.

We can calculate the amount of each substance in each phase, in both the initial state and final state of the isothermal bomb process, from the following information: the internal volume of the bomb vessel; the mass of solid or liquid reactant initially placed in the vessel; the initial amount of H_2O; the initial O_2 pressure; the water vapor pressure; the solubilities (estimated from Henry's law constants) of O_2 and CO_2 in the water; and the stoichiometry of the combustion reaction. Problem 11.7 guides you through these calculations.

11.5.3 Other calorimeters

Experimenters have used great ingenuity in designing calorimeters to measure reaction enthalpies and to improve their precision. In addition to the constant-pressure reaction calorimeter and bomb calorimeter described above, three additional types will be briefly mentioned.

A *phase-change calorimeter* has two coexisting phases of a pure substance in thermal contact with the reaction vessel and an adiabatic outer jacket. The two coexisting phases constitute a univariant subsystem that at constant pressure is at the fixed temperature of the equilibrium phase transition. The thermal energy released or absorbed by the reaction, instead of changing the temperature, is transferred isothermally to or from the coexisting phases and can be measured by the volume change of the phase transition. A reaction enthalpy, of course, can only be measured by this method at the temperature of the equilibrium phase transition. The well-known Bunsen ice calorimeter uses the ice–water transition at $0\,^\circ\mathrm{C}$. The solid–liquid transition of diphenyl ether has a relatively large volume change and is useful for measurements at $26.9\,^\circ\mathrm{C}$. Phase-transition calorimeters are especially useful for slow reactions.

A *heat-flow calorimeter* is a variation of an isothermal-jacket calorimeter. It uses a thermopile (Fig. 2.7) to continuously measure the temperature difference between the reaction vessel and an outer jacket acting as a constant-temperature heat sink. The heat transfer takes place mostly through the thermocouple wires, and to a high degree of accuracy is proportional to the temperature difference integrated over time. This is the best method for an extremely slow reaction, and it can also be used for rapid reactions.

A *flame calorimeter* is a flow system in which oxygen, fluorine, or another gaseous oxidant reacts with a gaseous fuel. The heat transfer between the flow tube and a heat sink can be measured with a thermopile, as in a heat-flow calorimeter.

11.6: Adiabatic Flame Temperature

With a few simple approximations, we can estimate the temperature of a flame formed in a flowing gas mixture of oxygen or air and a fuel. We treat a moving segment of the gas mixture as a closed system in which the temperature increases as combustion takes place. We assume that the reaction occurs at a constant pressure equal to the standard pressure, and that the process is adiabatic and the gas is an ideal-gas mixture.

The principle of the calculation is similar to that used for a constant-pressure calorimeter as explained by the paths shown in Fig. 11.11. When the combustion reaction in the segment of gas reaches reaction equilibrium, the advancement has changed by $\Delta\xi$ and the temperature has increased from T_1 to T_2. Because the reaction is assumed to be adiabatic at constant pressure, $\Delta H(\mathrm{expt})$ is zero. Therefore, the sum of $\Delta H(\mathrm{rxn}, T_1)$ and $\Delta H(\mathrm{P})$ is zero, and we can write

$$\Delta\xi\Delta_{\mathrm{c}}H^{\circ}(T_1) + \int_{T_1}^{T_2} C_p(\mathrm{P})\,\mathrm{d}T = 0 \tag{11.6.1}$$

where $\Delta_{\mathrm{c}}H^{\circ}(T_1)$ is the standard molar enthalpy of combustion at the initial temperature, and $C_p(\mathrm{P})$ is the heat capacity at constant pressure of the product mixture.

The value of T_2 that satisfies Eq. 11.6.1 is the *estimated* flame temperature. Problem 11.9 presents an application of this calculation. Several factors cause the actual temperature in a flame to be lower: the process is never completely adiabatic, and in the high temperature of the flame there may be product dissociation and other reactions in addition to the main combustion reaction.

11.7: Gibbs Energy and Reaction Equilibrium

This section begins by examining the way in which the Gibbs energy changes as a chemical process advances in a closed system at constant T and p with expansion work only. A universal criterion for reaction equilibrium is derived involving the molar reaction Gibbs energy.

The molar reaction Gibbs energy

Applying the general definition of a molar differential reaction quantity (Eq. 11.2.15) to the Gibbs energy of a closed system with T, p, and ξ as the independent variables, we obtain the definition of the **molar reaction Gibbs energy** or molar Gibbs energy of reaction, $\Delta_{\mathrm{r}}G$:

$$\Delta_{\mathrm{r}}G \overset{\mathrm{def}}{=} \sum_i \nu_i \mu_i \tag{11.7.1}$$

Equation 11.2.16 shows that this quantity is also given by the partial derivative

$$\Delta_{\mathrm{r}}G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} \tag{11.7.2}$$
(closed system)

The total differential of G is then

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \Delta_{\mathrm{r}}G\,\mathrm{d}\xi \tag{11.7.3}$$
(closed system)

Spontaneity and reaction equilibrium

In Sec. 5.8, we found that the spontaneous direction of a process taking place in a closed system at constant T and p, with expansion work only, is the direction of decreasing G. In the case of a chemical process occurring at constant T and p, $\Delta_{\mathrm{r}}G$ is the rate at which G changes with ξ. Thus if $\Delta_{\mathrm{r}}G$ is positive, ξ spontaneously decreases; if $\Delta_{\mathrm{r}}G$ is negative, ξ spontaneously increases. During a spontaneous process $\mathrm{d}\xi$ and $\Delta_{\mathrm{r}}G$ have opposite signs.

> Sometimes reaction spontaneity at constant T and p is ascribed to the “driving force” of a quantity called the **affinity of reaction**, defined as the negative of $\Delta_{\mathrm{r}}G$. ξ increases spontaneously if the affinity is positive and decreases spontaneously if the affinity is negative; the system is at equilibrium when the affinity is zero.
>
> Note how the equality of Equation 11.7.3 agrees with the inequality $\mathrm{d}G < -S\,\mathrm{d}T + V\,\mathrm{d}p$, a criterion of spontaneity in a closed system with expansion work only (Eq. 5.8.6). When $\mathrm{d}\xi$ and $\Delta_{\mathrm{r}}G$ have opposite signs, $\Delta_{\mathrm{r}}G\,\mathrm{d}\xi$ is negative and $\mathrm{d}G = (-S\,\mathrm{d}T + V\,\mathrm{d}p + \Delta_{\mathrm{r}}G\,\mathrm{d}\xi)$ is less than $(-S\,\mathrm{d}T + V\,\mathrm{d}p)$.

If the system is closed and contains at least one phase that is a mixture, a state of reaction equilibrium can be approached spontaneously at constant T and p in either direction of the reaction; that is, by both positive and negative changes of ξ. In this equilibrium state, therefore, G has its minimum value for the given T and p. Since G is a smooth function of ξ, its rate of change with respect to ξ is zero in the equilibrium state. The condition for *reaction equilibrium*, then, is that $\Delta_{\mathrm{r}}G$ must be zero:

$$\Delta_{\mathrm{r}}G = \sum_i \nu_i \mu_i = 0 \tag{11.7.4}$$
(reaction equilibrium)

It is important to realize that this condition is independent of whether or not reaction equilibrium is approached at constant temperature and pressure. It is a universal criterion of reaction equilibrium. The value of $\Delta_{\mathrm{r}}G$ is equal to $\sum_i \nu_i \mu_i$ and depends on the state of the system. If the state is such that $\Delta_{\mathrm{r}}G$ is positive, the direction of spontaneous change is one that, under the existing constraints, allows $\Delta_{\mathrm{r}}G$ to decrease. If $\Delta_{\mathrm{r}}G$ is negative, the spontaneous change increases the value of $\Delta_{\mathrm{r}}G$. When the system reaches reaction equilibrium, whatever the path of the spontaneous process, the value of $\Delta_{\mathrm{r}}G$ becomes zero.

General derivation

We can obtain the condition of reaction equilibrium given by Eq. 11.7.4 in a more general and rigorous way by an extension of the derivation of Sec. 9.2.7, which was for equilibrium conditions in a multiphase, multicomponent system.

Consider a system with a reference phase, α', and optionally other phases labeled by $\alpha \neq \alpha'$. Each phase contains one or more species labeled by subscript i, and some or all of the species are the reactants and products of a reaction.

The total differential of the internal energy is given by Eq. 9.2.37:

$$\begin{aligned} \mathrm{d}U &= T^{\alpha'}\,\mathrm{d}S^{\alpha'} - p^{\alpha'}\,\mathrm{d}V^{\alpha'} + \sum_i \mu_i^{\alpha'}\,\mathrm{d}n_i^{\alpha'} \\ &\quad + \sum_{\alpha\neq\alpha'}\left(T^{\alpha}\,\mathrm{d}S^{\alpha} - p^{\alpha}\,\mathrm{d}V^{\alpha} + \sum_i \mu_i^{\alpha}\,\mathrm{d}n_i^{\alpha}\right) \end{aligned} \tag{11.7.5}$$

The conditions of isolation are

$$\mathrm{d}U = 0 \qquad \text{(constant internal energy)} \tag{11.7.6}$$

$$\mathrm{d}V^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}V^{\alpha} = 0 \qquad \text{(no expansion work)} \tag{11.7.7}$$

$$\begin{aligned} &\text{For each species } i\text{:} \\ &\mathrm{d}n_i^{\alpha'} + \sum_{\alpha\neq\alpha'} \mathrm{d}n_i^{\alpha} = \nu_i\,\mathrm{d}\xi \qquad \text{(closed system)} \end{aligned} \tag{11.7.8}$$

In Eq. 11.7.8, $\mathrm{d}n_{i'}^{\alpha''}$ should be set equal to zero for a species i' that is excluded from phase α'', and $\nu_{i''}$ should be set equal to zero for a species i'' that is not a reactant or product of the reaction.

We use these conditions of isolation to substitute for $\mathrm{d}U$, $\mathrm{d}V^{\alpha'}$, and $\mathrm{d}n_i^{\alpha'}$ in Eq. 11.7.5, and make the further substitution $\mathrm{d}S^{\alpha'} = \mathrm{d}S - \sum_{\alpha\neq\alpha'} \mathrm{d}S^{\alpha}$. Solving for $\mathrm{d}S$, we obtain

$$\begin{aligned} \mathrm{d}S &= \sum_{\alpha\neq\alpha'} \frac{(T^{\alpha'} - T^{\alpha})}{T^{\alpha'}}\,\mathrm{d}S^{\alpha} - \sum_{\alpha\neq\alpha'} \frac{(p^{\alpha'} - p^{\alpha})}{T^{\alpha'}}\,\mathrm{d}V^{\alpha} \\ &\quad + \sum_i \sum_{\alpha\neq\alpha'} \frac{(\mu_i^{\alpha'} - \mu_i^{\alpha})}{T^{\alpha'}}\,\mathrm{d}n_i^{\alpha} - \frac{\sum_i \nu_i \mu_i^{\alpha'}}{T^{\alpha'}}\,\mathrm{d}\xi \end{aligned} \tag{11.7.9}$$

The equilibrium condition is that the coefficient multiplying each differential on the right side of Eq. 11.7.9 must be zero. We conclude that at equilibrium the temperature of each phase is equal to that of phase α'; the pressure of each phase is equal to that of phase α'; the chemical potential of each species, in each phase containing that species, is equal to the chemical potential of the species in phase α'; and the quantity $\sum_i \nu_i \mu_i^{\alpha'}$ (which is equal to $\Delta_r G$) is zero.

In short, *in an equilibrium state each phase has the same temperature and the same pressure, each species has the same chemical potential in the phases in which it is present, and the molar reaction Gibbs energy of each phase is zero*.

Pure phases

Consider a chemical process in which each reactant and product is in a separate pure phase. For example, the decomposition of calcium carbonate,

$$\mathrm{CaCO_3(s)} \longrightarrow \mathrm{CaO(s)} + \mathrm{CO_2(g)} \tag{11.7.4}$$

involves three pure phases if no other gas is allowed to mix with the $\mathrm{CO_2}$.

The situation is different when the number of molecules changes during the reaction. Consider the reaction A $\rightarrow$ 2 B in an ideal gas mixture. As this reaction proceeds to the right at constant T, the volume increases if the pressure is held constant and the pressure increases if the volume is held constant. Figure 11.17 shows how G depends on both p and V for this reaction. Movement along the horizontal dashed line in the figure corresponds to reaction at constant T and p. The minimum of G along this line is at the volume indicated by the open circle. At this volume, G has an even lower minimum at the pressure indicated by the filled circle, where the vertical dashed line is tangent to one of the contours of constant G. The condition needed for reaction equilibrium, however, is that $\Delta_r G$ must be zero. This condition is satisfied along the vertical dashed line only at the position of the open circle.

This example demonstrates that for a reaction occurring at constant temperature and *volume* in which the pressure changes, the point of reaction equilibrium is not the point of minimum G. Instead, the point of reaction equilibrium in this case is at the minimum of the Helmholtz energy A (Sec. 11.7.5).

11.8: The Thermodynamic Equilibrium Constant

11.8.1 Activities and the definition of K

Equation 10.1.9 gives the general relation between the chemical potential μ_i and the activity a_i of species i in a phase of electric potential ϕ:

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F\phi \tag{11.8.1}$$

The electric potential affects μ_i only if the charge number z_i is nonzero, i.e., only if species i is an ion.

Consider a reaction in which any reactants and products that are ions are in a single phase of electric potential ϕ', or in several phases of equal electric potential ϕ'. Under these conditions, substitution of the expression above for μ_i in $\Delta_\text{r}G = \sum_i \nu_i \mu_i$ gives

$$\Delta_\text{r}G = \sum_i \nu_i \mu_i^\circ + RT\sum_i \nu_i \ln a_i + F\phi' \sum_i \nu_i z_i \tag{11.8.2}$$
$$\text{(all ions at } \phi{=}\phi')$$

The first term on the right side of Eq. 11.8.2 is the **standard molar reaction Gibbs energy**, or standard molar Gibbs energy of reaction:

$$\Delta_\text{r}G^\circ \overset{\text{def}}{=} \sum_i \nu_i \mu_i^\circ \tag{11.8.3}$$

Since the standard chemical potential μ_i° of each species i is a function only of T, the value of $\Delta_\text{r}G^\circ$ for a given reaction as defined by the reaction equation depends only on T and on the choice of a standard state for each reactant and product.

The last term on the right side of Eq. 11.8.2 is the sum $\sum_i \nu_i z_i$. Because charge is conserved during the advancement of a reaction in a closed system, this sum is zero.

With these substitutions, Eq. 11.8.2 becomes

$$\Delta_\text{r}G = \Delta_\text{r}G^\circ + RT\sum_i \nu_i \ln a_i \tag{11.8.4}$$
$$\text{(all ions at same } \phi)$$

This relation enables us to say that for a reaction at a given temperature in which any charged reactants or products are all in the same phase, or in phases of equal electric potential, the value of $\Delta_\text{r}G$ and $\sum_i \nu_i \mu_i$ depends only on the activities of the reactants and products and is independent of what the electric potentials of any of the phases might happen to be.

Unless a reaction involving ions is carried out in a galvanic cell, the ions are usually present in a single phase, and this will not be shown as a condition of validity in the rest of this chapter. The special case of a reaction in a galvanic cell will be discussed in Sec. 14.3.

We may use properties of logarithms to write the sum on the right side of Eq. 11.8.4 as follows:

$$\sum_i \nu_i \ln a_i = \sum_i \ln\left(a_i^{\nu_i}\right) = \ln \prod_i a_i^{\nu_i} \tag{11.8.5}$$

> The symbol $\prod$ stands for a continued product. If, for instance, there are three species, $\prod_i a_i^{\nu_i}$ is the product $(a_1^{\nu_1})(a_2^{\nu_2})(a_3^{\nu_3})$.

The product $\prod_i a_i^{\nu_i}$ is called the **reaction quotient** or activity quotient, Q_rxn:

$$Q_\text{rxn} \overset{\text{def}}{=} \prod_i a_i^{\nu_i} \tag{11.8.6}$$

Q_rxn consists of a factor for each reactant and product. Each factor is the activity raised to the power of the stoichiometric number ν_i. Since the value of ν_i is positive for a product and negative for a reactant, Q_rxn is a quotient in which the activities of the products appear in the numerator and those of the reactants appear in the denominator, with each activity raised to a power equal to the corresponding stoichiometric coefficient in the reaction equation. Such a quotient, with quantities raised to these powers, is called a **proper quotient**. The reaction quotient is a proper quotient of activities.

For instance, for the ammonia synthesis reaction N_2(g) + 3 H_2(g) $\rightarrow$ 2 NH_3(g) the reaction quotient is given by

$$Q_{\mathrm{rxn}} = \frac{a^2_{\mathrm{NH_3}}}{a_{\mathrm{N_2}}a^3_{\mathrm{H_2}}} \tag{11.8.7}$$

Q_{rxn} is a dimensionless quantity. It is a function of T, p, and the mixture composition, so its value changes as the reaction advances.

The expression for the molar reaction Gibbs energy given by Eq. 11.8.4 can now be written

$$\Delta_{\mathrm{r}}G = \Delta_{\mathrm{r}}G^\circ + RT\ln Q_{\mathrm{rxn}} \tag{11.8.8}$$

The value of Q_{rxn} under equilibrium conditions is the **thermodynamic equilibrium constant**, K. The general definition of K is

$$K \overset{\mathrm{def}}{=} \prod_i (a_i)^{\nu_i}_{\mathrm{eq}} \tag{11.8.9}$$

where the subscript eq indicates an equilibrium state. Note that K, like Q_{rxn}, is dimensionless.

> The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 58) gives $K^\ominus$ as an alternative symbol for the thermodynamic equilibrium constant, the appended superscript denoting "standard." An IUPAC Commission on Thermodynamics (M. B. Ewing et al, *Pure Appl. Chem.*, **66**, 533–552, 1994) has furthermore recommended the name "standard equilibrium constant," apparently because its value depends on the choice of standard states. Using this alternative symbol and name could cause confusion, since the quantity defined by Eq. 11.8.9 does not refer to reactants and products in their standard states but rather to reactants and products in an *equilibrium* state.

Substituting the equilibrium conditions $\Delta_{\mathrm{r}}G = 0$ and $Q_{\mathrm{rxn}} = K$ in Eq. 11.8.8 gives an important relation between the standard molar reaction Gibbs energy and the thermodynamic equilibrium constant:

$$\Delta_{\mathrm{r}}G^\circ = -RT\ln K \tag{11.8.10}$$

We can solve this equation for K to obtain the equivalent relation

$$K = \exp\left(-\frac{\Delta_{\mathrm{r}}G^\circ}{RT}\right) \tag{11.8.11}$$

We have seen that the value of $\Delta_{\mathrm{r}}G^\circ$ depends only on T and the choice of the standard states of the reactants and products. This being so, Eq. 11.8.11 shows that the value of K for a given reaction depends only on T and the choice of standard states. No other condition, neither pressure nor composition, can affect the value of K. We also see from Eq. 11.8.11 that K is less than 1 if $\Delta_{\mathrm{r}}G^\circ$ is positive and greater than 1 if $\Delta_{\mathrm{r}}G^\circ$ is negative. At a fixed temperature, reaction equilibrium is attained only if and only if the value of Q_{rxn} becomes equal to the value of K at that temperature.

The thermodynamic equilibrium constant K is the proper quotient of the activities of species in reaction equilibrium. At typical temperatures and pressures, an activity cannot be many orders of magnitude greater than 1. For instance, a partial pressure cannot be greater than the total pressure, so at a pressure of $10\,\mathrm{bar}$ the activity of a gaseous constituent cannot be greater than about 10. The molarity of a solute is rarely much greater than $10\,\mathrm{mol\,dm^{-3}}$, corresponding to an activity (on a concentration basis) of about 10. Activities can, however, be extremely small.

These considerations lead us to the conclusion that in an equilibrium state of a reaction with a very *large* value of K, the activity of at least one of the *reactants* must be very small. That is, if K is very large then the reaction goes practically to completion and at equilibrium a limiting reactant is essentially entirely exhausted. The opposite case, a reaction with a very *small* value of K, must have at equilibrium one or more *products* with very small activities. These two cases are the two extremes of the trends shown in Fig. 11.16.

Equation 11.8.10 correctly relates $\Delta_{\mathrm{r}}G^\circ$ and K only if they are both calculated with the same standard states. For instance, if we base the standard state of a particular solute species on molality in calculating $\Delta_{\mathrm{r}}G^\circ$, the activity of that species appearing in the expression for K (Eq. 11.8.9) must also be based on molality.

11.8.2 Reaction in a gas phase

If a reaction takes place in a gaseous mixture, the standard state of each reactant and product is the pure gas behaving ideally at the standard pressure p° (Sec. 9.3.3). In this case, each activity is given by $a_i(\mathrm{g}) = f_i/p^\circ = \phi_i p_i/p^\circ$ where ϕ_i is a fugacity coefficient

(Table 9.5). When we substitute this expression into Eq. 11.8.9, we find we can express the thermodynamic equilibrium constant as the product of three factors:

$$K=\left[\prod_i(\phi_i)_{\text{eq}}^{\nu_i}\right]\left[\prod_i(p_i)_{\text{eq}}^{\nu_i}\right]\left[(p^\circ)^{-\sum_i \nu_i}\right] \tag{11.8.12}$$
$$\text{(gas mixture)}$$

On the right side of this equation, the first factor is the proper quotient of fugacity coefficients in the mixture at reaction equilibrium, the second factor is the proper quotient of partial pressures in this mixture, and the third factor is the power of p° needed to make K dimensionless.

The proper quotient of equilibrium partial pressures is an **equilibrium constant on a pressure basis**, K_p:

$$K_p=\prod_i(p_i)_{\text{eq}}^{\nu_i} \tag{11.8.13}$$
$$\text{(gas mixture)}$$

Note that K_p is dimensionless only if $\sum_i\nu_i$ is equal to zero.

The value of K_p can vary at constant temperature, so K_p is not a thermodynamic equilibrium constant. For instance, consider what happens when we take an ideal gas mixture at reaction equilibrium and compress it isothermally. As the gas pressure increases, the fugacity coefficient of each constituent changes from its low pressure value of 1 and the gas mixture becomes nonideal. In order for the mixture to remain in reaction equilibrium, and the product of factors on the right side of Eq. 11.8.12 to remain constant, there must be a change in the value of K_p. In other words, the reaction equilibrium *shifts* as we increase p at constant T, an effect that will be considered in more detail in Sec. 11.9.

As an example of the difference between K and K_p, consider again the ammonia synthesis $\mathrm{N_2(g)+3\,H_2(g)\rightarrow 2\,NH_3(g)}$ in which the sum $\sum_i\nu_i$ equals -2. For this reaction, the expression for the thermodynamic equilibrium constant is

$$K=\left(\frac{\phi_{\mathrm{NH_3}}^2}{\phi_{\mathrm{N_2}}\phi_{\mathrm{H_2}}^3}\right)_{\text{eq}}K_p(p^\circ)^2 \tag{11.8.14}$$

where K_p is given by

$$K_p=\left(\frac{p_{\mathrm{NH_3}}^2}{p_{\mathrm{N_2}}p_{\mathrm{H_2}}^3}\right)_{\text{eq}} \tag{11.8.15}$$

11.8.3 Reaction in solution

If any of the reactants or products are solutes in a solution, the value of K depends on the choice of the solute standard state.

For a given reaction at a given temperature, we can derive relations between values of K that are based on different solute standard states. In the limit of infinite dilution, each solute activity coefficient is unity, and at the standard pressure each pressure factor is unity. Under these conditions of infinite dilution and standard pressure, the activities of solute B on a mole fraction, concentration, and molality basis are therefore

$$a_{x,\mathrm{B}}=x_{\mathrm{B}}\qquad a_{c,\mathrm{B}}=c_{\mathrm{B}}/c^\circ\qquad a_{m,\mathrm{B}}=m_{\mathrm{B}}/m^\circ \tag{11.8.16}$$

In the limit of infinite dilution, the solute composition variables approach values given by the relations in Eq. 9.1.14: $x_{\mathrm{B}}=V_{\mathrm{A}}^*c_{\mathrm{B}}=M_{\mathrm{A}}m_{\mathrm{B}}$. Combining these with $a_{x,\mathrm{B}}=x_{\mathrm{B}}$ from Eq. 11.8.16, we write

$$a_{x,\mathrm{B}}=V_{\mathrm{A}}^*c_{\mathrm{B}}=M_{\mathrm{A}}m_{\mathrm{B}} \tag{11.8.17}$$

Then, using the relations for $a_{c,\mathrm{B}}$ and $a_{m,\mathrm{B}}$ in Eq. 11.8.16, we find that the activities of solute B at infinite dilution and pressure p° are related by

$$a_{x,\mathrm{B}}=V_{\mathrm{A}}^*c^\circ a_{c,\mathrm{B}}=M_{\mathrm{A}}m^\circ a_{m,\mathrm{B}} \tag{11.8.18}$$

The expression $K=\prod_i(a_i)_{\text{eq}}^{\nu_i}$ has a factor $(a_{\mathrm{B}})_{\text{eq}}^{\nu_{\mathrm{B}}}$ for each solute B that is a reactant or product. From Eq. 11.8.18, we see that for solutes at infinite dilution at pressure p°, the relations between the values of K based on different solute standard states are

$$K(x\text{ basis})=\prod_{\mathrm{B}}(V_{\mathrm{A}}^*c^\circ)^{\nu_{\mathrm{B}}}K(c\text{ basis})=\prod_{\mathrm{B}}(M_{\mathrm{A}}m^\circ)^{\nu_{\mathrm{B}}}K(m\text{ basis}) \tag{11.8.19}$$

For a given reaction at a given temperature, and with a given choice of solute standard state, the value of K is not affected by pressure or dilution. The relations of Eq. 11.8.19 are therefore valid under all conditions.

11.8.4 Evaluation of K

The relation $K=\exp(-\Delta_r G^\circ/RT)$ (Eq. 11.8.11) gives us a way to evaluate the thermodynamic equilibrium constant K of a reaction at a given temperature from the value of the standard molar reaction Gibbs energy $\Delta_r G^\circ$ at that temperature. If we know the value of $\Delta_r G^\circ$, we can calculate the value of K.

One method is to calculate $\Delta_r G^\circ$ from values of the **standard molar Gibbs energy of formation** $\Delta_f G^\circ$ of each reactant and product. These values are the standard molar reaction Gibbs energies for the formation reactions of the substances. To relate $\Delta_f G^\circ$ to measurable quantities, we make the substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) in $\Delta_r G = \sum_i \nu_i \mu_i$ to give $\Delta_r G = \sum_i \nu_i H_i - T\sum_i \nu_i S_i$, or

$$\Delta_r G = \Delta_r H - T\Delta_r S \tag{11.8.20}$$

When we apply this equation to a reaction with each reactant and product in its standard state, it becomes

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \tag{11.8.21}$$

where the standard molar reaction entropy is given by

$$\Delta_r S^\circ = \sum_i \nu_i S_i^\circ \tag{11.8.22}$$

If the reaction is the *formation* reaction of a substance, we have

$$\Delta_f G^\circ = \Delta_f H^\circ - T\sum_i \nu_i S_i^\circ \tag{11.8.23}$$

where the sum over i is for the reactants and product of the formation reaction. We can evaluate the standard molar Gibbs energy of formation of a substance, then, from its standard molar enthalpy of formation and the standard molar entropies of the reactants and product.

Extensive tables are available of values of $\Delta_f G^\circ$ for substances and ions. An abbreviated version at the single temperature $298.15\ \mathrm{K}$is given in Appendix H. For a reaction of interest, the tabulated values enable us to evaluate $\Delta_r G^\circ$, and then K, from the expression (analogous to Hess's law)

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \tag{11.8.24}$$

The sum over i is for the reactants and products of the reaction of interest.

Recall that the standard molar enthalpies of formation needed in Eq. 11.8.23 can be evaluated by calorimetric methods (Sec. 11.3.2). The absolute molar entropy values S_i° come from heat capacity data or statistical mechanical theory by methods discussed in Sec. 6.2. Thus, it is entirely feasible to use nothing but calorimetry to evaluate an equilibrium constant, a goal sought by thermodynamicists during the first half of the 20th century. (Another method, for a reaction that can be carried out reversibly in a galvanic cell, is described in Sec. 14.3.3.)

For *ions in aqueous solution*, the values of S_m° and $\Delta_f G^\circ$ found in Appendix H are based on the reference values $S_m^\circ = 0$ and $\Delta_f G^\circ = 0$ for H^+(aq) at all temperatures, similar to the convention for $\Delta_f H^\circ$ values discussed in Sec. 11.3.2. For a reaction with aqueous ions as reactants or products, these values correctly give $\Delta_r S^\circ$ using Eq. 11.8.22, or $\Delta_r G^\circ$ using Eq. 11.8.24.

> Note that the values of S_m° in Appendix H for some ions, unlike the values for substances, are *negative*; this simply means that the standard molar entropies of these ions are less than that of H^+(aq).
>
> The relation of Eq. 11.8.23 does not apply to an ion, because we cannot write a formation reaction for a single ion. Instead, the relation between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and S_m° is more complicated.
>
> Consider first a hypothetical reaction in which hydrogen ions and one or more elements form $\mathrm{H_2}$ and a cation M^{z_+} with charge number z_+:
>
> $$z_+\mathrm{H}^+(\mathrm{aq}) + \text{elements} \rightarrow (z_+/2)\mathrm{H_2(g)} + \mathrm{M}^{z_+}(\mathrm{aq}) \tag{11.8.1}$$

For this reaction, using the convention that $\Delta_f H^\circ$, S°_m, and $\Delta_f G^\circ$ are zero for the aqueous H^+ ion and the fact that $\Delta_f H^\circ$ and $\Delta_f G^\circ$ are zero for the elements, we can write the following expressions for standard molar reaction quantities:

$$\Delta_r H^\circ = \Delta_f H^\circ(M^{z_+}) \tag{11.8.25}$$

$$\Delta_r S^\circ = (z_+/2)S^\circ_m(H_2) + S^\circ_m(M^{z_+}) - \sum_{\text{elements}} S^\circ_i \tag{11.8.26}$$

$$\Delta_r G^\circ = \Delta_f G^\circ(M^{z_+}) \tag{11.8.27}$$

Then, from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find

$$\Delta_f G^\circ(M^{z_+}) = \Delta_f H^\circ(M^{z_+}) \quad -T\left[S^\circ_m(M^{z_+}) - \sum_{\text{elements}} S^\circ_i + (z_+/2)S^\circ_m(H_2)\right] \tag{11.8.28}$$

For example, the standard molar Gibbs energy of the aqueous mercury(I) ion is found from

$$\Delta_f G^\circ({Hg_2}^{2+}) = \Delta_f H^\circ({Hg_2}^{2+}) - TS^\circ_m({Hg_2}^{2+}) + 2TS^\circ_m(Hg) - \frac{2}{2}TS^\circ_m(H_2) \tag{11.8.29}$$

For an anion X^{z_-} with negative charge number z_-, using the hypothetical reaction

$$|z_-/2|H_2(g) + \text{elements} \rightarrow |z_-|H^+(aq) + X^{z_-}(aq) \tag{11.8.2}$$

we find by the same method

$$\Delta_f G^\circ(X^{z_-}) = \Delta_f H^\circ(X^{z_-}) - T\left[S^\circ_m(X^{z_-}) - \sum_{\text{elements}} S^\circ_i - |z_-/2|S^\circ_m(H_2)\right] \tag{11.8.30}$$

For example, the calculation for the nitrate ion is

$$\Delta_f G^\circ({NO_3}^-) = \Delta_f H^\circ({NO_3}^-) - TS^\circ_m({NO_3}^-) + \frac{1}{2}TS^\circ_m(N_2) + \frac{3}{2}TS^\circ_m(O_2) + \frac{1}{2}TS^\circ_m(H_2) \tag{11.8.31}$$

11.9: Effects of Temperature and Pressure on Equilibrium Position

The advancement ξ of a chemical reaction in a closed system describes the changes in the amounts of the reactants and products from specified initial values of these amounts. We have seen that if the system is maintained at constant temperature and pressure, ξ changes spontaneously in the direction that decreases the Gibbs energy. The change continues until the system reaches a state of reaction equilibrium at the minimum of G. The value of the advancement in this equilibrium state will be denoted ξ_{eq}, as shown in Fig. 11.15. The value of ξ_{eq} depends in general on the values of T and p. Thus when we change the temperature or pressure of a closed system that is at equilibrium, ξ_{eq} usually changes also and the reaction spontaneously *shifts* to a new equilibrium position.

To investigate this effect, we write the total differential of G with T, p, and ξ as independent variables

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \Delta_{\text{r}}G\,\mathrm{d}\xi \tag{11.9.1}$$

and obtain the reciprocity relations

$$\left(\frac{\partial \Delta_{\text{r}}G}{\partial T}\right)_{p,\xi} = -\left(\frac{\partial S}{\partial \xi}\right)_{T,p} \qquad \left(\frac{\partial \Delta_{\text{r}}G}{\partial p}\right)_{T,\xi} = \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \tag{11.9.2}$$

We recognize the partial derivative on the right side of each of these relations as a molar differential reaction quantity:

$$\left(\frac{\partial \Delta_{\text{r}}G}{\partial T}\right)_{p,\xi} = -\Delta_{\text{r}}S \qquad \left(\frac{\partial \Delta_{\text{r}}G}{\partial p}\right)_{T,\xi} = \Delta_{\text{r}}V \tag{11.9.3}$$

We use these expressions for two of the coefficients in an expression for the total differential of $\Delta_{\text{r}}G$:

$$\mathrm{d}\Delta_{\text{r}}G = -\Delta_{\text{r}}S\,\mathrm{d}T + \Delta_{\text{r}}V\,\mathrm{d}p + \left(\frac{\partial \Delta_{\text{r}}G}{\partial \xi}\right)_{T,p}\mathrm{d}\xi \tag{11.9.4}$$

(closed system)

Since $\Delta_{\text{r}}G$ is the partial derivative of G with respect to ξ at constant T and p, the coefficient $(\partial\Delta_{\text{r}}G/\partial\xi)_{T,p}$ is the partial *second* derivative of G with respect to ξ:

$$\left(\frac{\partial \Delta_{\text{r}}G}{\partial \xi}\right)_{T,p} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} \tag{11.9.5}$$

We know that at a fixed T and p, a plot of G versus ξ has a slope at each point equal to $\Delta_{\text{r}}G$ and a minimum at the position of reaction equilibrium where ξ is ξ_{eq}. At the minimum of the plotted curve, the slope $\Delta_{\text{r}}G$ is zero and the second derivative is positive (see Fig. 11.15). By setting $\Delta_{\text{r}}G$ equal to zero in the general relation $\Delta_{\text{r}}G = \Delta_{\text{r}}H - T\Delta_{\text{r}}S$, we obtain the equation $\Delta_{\text{r}}S = \Delta_{\text{r}}H/T$ which is valid only at reaction equilibrium where ξ equals ξ_{eq}. Making this substitution in Eq. 11.9.4, and setting $\mathrm{d}\Delta_{\text{r}}G$ equal to zero and $\mathrm{d}\xi$ equal to $\mathrm{d}\xi_{\text{eq}}$, we obtain

$$0 = -\frac{\Delta_{\text{r}}H}{T}\,\mathrm{d}T + \Delta_{\text{r}}V\,\mathrm{d}p + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\mathrm{d}\xi_{\text{eq}} \tag{11.9.6}$$

(closed system)

which shows how infinitesimal changes in T, p, and ξ_{eq} are related.

Now we are ready to see how ξ_{eq} is affected by changes in T or p. Solving Eq. 11.9.6 for $\mathrm{d}\xi_{\text{eq}}$ gives

$$\mathrm{d}\xi_{\text{eq}} = \frac{\dfrac{\Delta_{\text{r}}H}{T}\,\mathrm{d}T - \Delta_{\text{r}}V\,\mathrm{d}p}{\left(\dfrac{\partial^2 G}{\partial \xi^2}\right)_{T,p}} \tag{11.9.7}$$

(closed system)

The right side of Eq. 11.9.7 is the expression for the total differential of ξ in a closed system at reaction equilibrium, with T and p as the independent variables. Thus, at constant pressure the equilibrium shifts with temperature according to

$$\left(\frac{\partial \xi_{\text{eq}}}{\partial T}\right)_p = \frac{\Delta_{\text{r}}H}{T\left(\dfrac{\partial^2 G}{\partial \xi^2}\right)_{T,p}} \tag{11.9.8}$$

(closed system)

and at constant temperature the equilibrium shifts with pressure according to

$$\left(\frac{\partial \xi_{\text{eq}}}{\partial p}\right)_T = -\frac{\Delta_{\text{r}} V}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}} \tag{11.9.9}$$
(closed system)

Because the partial second derivative $(\partial^2 G/\partial \xi^2)_{T,p}$ is positive, Eqs. 11.9.8 and 11.9.9 show that $(\partial \xi_{\text{eq}}/\partial T)_p$ and $\Delta_{\text{r}} H$ have the same sign, whereas $(\partial \xi_{\text{eq}}/\partial p)_T$ and $\Delta_{\text{r}} V$ have opposite signs.

These statements express the application to temperature and pressure changes of what is known as *Le Chatelier's principle*: When a change is made to a closed system at equilibrium, the equilibrium shifts in the direction that tends to oppose the change. Here are two examples.

1. It is easy to misuse or to be misled by Le Chatelier's principle. Consider the solution process $\text{B}^*(\text{s}) \rightarrow \text{B(sln)}$ for which $(\partial \xi_{\text{eq}}/\partial T)_p$, the rate of change of solubility with T, has the same sign as the molar differential enthalpy of solution $\Delta_{\text{sol}} H$ at saturation. The sign of $\Delta_{\text{sol}} H$ at saturation may be different from the sign of the molar *integral* enthalpy of solution, $\Delta H_{\text{m}}(\text{sol})$. This is the situation for the dissolution of sodium acetate shown in Fig. 11.9. The equilibrium position (saturation) with one kilogram of water is at $\xi_{\text{sol}} \approx 15\,\text{mol}$, indicated in the figure by an open circle. At this position, $\Delta_{\text{sol}} H$ is positive and $\Delta H_{\text{m}}(\text{sol})$ is negative. So, despite the fact that the dissolution of 15 moles of sodium acetate in one kilogram of water to form a saturated solution is an exothermic process, the solubility of sodium acetate actually *increases* with increasing temperature, contrary to what one might predict from Le Chatelier's principle (L. K. Brice, *J. Chem. Educ.*, **60**, 387–389, 1983).

   Another kind of change for which Le Chatelier's principle gives an incorrect prediction is the addition of an inert gas to a gas mixture of constant volume. Adding the inert gas at constant V increases the pressure, but has little effect on the equilibrium position of a gas-phase reaction regardless of the value of $\Delta_{\text{r}} V$. This is because the inert gas affects the activities of the reactants and products only slightly, and not at all if the gas mixture is ideal, so there is little or no effect on the value of Q_{rxn}. (Note that the dependence of ξ_{eq} on p expressed by Eq. 11.9.9 does not apply to an open system.)

11.10: Chapter 11 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

11.1

Use values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ in Appendix H to evaluate the standard molar reaction enthalpy and the thermodynamic equilibrium constant at $298.15\ \mathrm{K}$ for the oxidation of nitrogen to form aqueous nitric acid:

$$\tfrac{1}{2}\mathrm{N_2(g)}+\tfrac{5}{4}\mathrm{O_2(g)}+\tfrac{1}{2}\mathrm{H_2O(l)} \rightarrow \mathrm{H^+(aq)}+\mathrm{NO_3^-(aq)} \tag{11.10.1}$$

11.2

In 1982, the International Union of Pure and Applied Chemistry recommended that the value of the standard pressure p° be changed from $1\ \mathrm{atm}$ to $1\ \mathrm{bar}$. This change affects the values of some standard molar quantities of a substance calculated from experimental data.

(a) Find the changes in H°_m, S°_m, and G°_m for a gaseous substance when the standard pressure is changed isothermally from $1.01325\ \mathrm{bar}\,(1\ \mathrm{atm})$ to exactly $1\ \mathrm{bar}$. (Such a small pressure change has an entirely negligible effect on these quantities for a substance in a condensed phase.)

(b) What are the values of the corrections that need to be made to the standard molar enthalpy of formation, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of $\mathrm{N_2O_4(g)}$ at $298.15\ \mathrm{K}$ when the standard pressure is changed from $1.01325\ \mathrm{bar}$to $1\ \mathrm{bar}$?

11.3

From data for mercury listed in Appendix H, calculate the saturation vapor pressure of liquid mercury at both $298.15\ \mathrm{K}$ and $273.15\ \mathrm{K}$ You may need to make some reasonable approximations.

11.4

Given the following experimental values at $T = 298.15\ \mathrm{K}$, $p = 1\ \mathrm{bar}$:

$\mathrm{H^+(aq)}+\mathrm{OH^-(aq)} \rightarrow \mathrm{H_2O(l)}$	$\Delta_r H^\circ = -55.82\ \mathrm{kJ\ mol^{-1}}$
$\mathrm{Na(s)}+\mathrm{H_2O(l)} \rightarrow \mathrm{Na^+(aq)}+\mathrm{OH^-(aq)}+\tfrac{1}{2}\mathrm{H_2(g)}$	$\Delta_r H^\circ = -184.52\ \mathrm{kJ\ mol^{-1}}$
$\mathrm{NaOH(s)} \rightarrow \mathrm{NaOH(aq)}$	$\Delta_\mathrm{sol} H^\infty = -44.75\ \mathrm{kJ\ mol^{-1}}$
$\mathrm{NaOH\ in\ 5\ H_2O} \rightarrow \mathrm{NaOH\ in}\ \infty\ \mathrm{H_2O}$	$\Delta H_\mathrm{m}(\mathrm{dil}) = -4.93\ \mathrm{kJ\ mol^{-1}}$
$\mathrm{NaOH(s)}$	$\Delta_f H^\circ = -425.61\ \mathrm{kJ\ mol^{-1}}$

Using only these values, calculate:

(a) $\Delta_f H^\circ$ for Na$^+$(aq), NaOH(aq), and OH$^-$(aq);

(b) $\Delta_f H$ for NaOH in 5 H_2O;

(c) $\Delta H_\mathrm{m}(\mathrm{sol})$ for the dissolution of $1\ \mathrm{mol}$ NaOH(s) in $5\ \mathrm{mol}$ H_2O.

States 1 and 2 referred to in this problem are the initial and final states of the isothermal bomb process. The temperature is the reference temperature of $298.15\ \mathrm{K}$

(a) Parts (a)–(c) consist of simple calculations of some quantities needed in later parts of the problem. Begin by using the masses of C_6H_{14} and H_2O placed in the bomb vessel, and their molar masses, to calculate the amounts (moles) of C_6H_{14} and H_2O present initially in the bomb vessel. Then use the stoichiometry of the combustion reaction to find the amount of O_2 consumed and the amounts of H_2O and CO_2 present in state 2. (There is not enough information at this stage to allow you to find the amount of O_2 present, just the change.) Also find the final mass of H_2O. Assume that oxygen is present in excess and the combustion reaction goes to completion.

(b) From the molar masses and the densities of liquid C_6H_{14} and H_2O, calculate their molar volumes.

(c) From the amounts present initially in the bomb vessel and the internal volume, find the volumes of liquid C_6H_{14}, liquid H_2O, and gas in state 1 and the volumes of liquid H_2O and gas in state 2. For this calculation, you can neglect the small change in the volume of liquid H_2O due to its vaporization.

(d) When the bomb vessel is charged with oxygen and before the inlet valve is closed, the pressure at $298.15\ \mathrm{K}$ measured on an external gauge is found to be $p_1 = 30.00\ \mathrm{bar}$. To a good approximation, the gas phase of state 1 has the equation of state of pure O

$_2$ (since the vapor pressure of water is only $0.1\,\%$ of $30.00\,\mathrm{bar}$). Assume that this equation of state is given by $V_\mathrm{m} = RT/p + B_\mathrm{BB}$ (Eq. 2.2.8), where B_BB is the second virial coefficient of O_2 listed in Table 11.3. Solve for the amount of O_2 in the gas phase of state 1. The gas phase of state 2 is a mixture of O_2 and CO_2, again with a negligible partial pressure of H_2O. Assume that only small fractions of the total amounts of O_2 and CO_2 dissolve in the liquid water, and find the amount of O_2 in the gas phase of state 2 and the mole fractions of O_2 and CO_2 in this phase.

(e) You now have the information needed to find the pressure in state 2, which cannot be measured directly. For the mixture of O_2 and CO_2 in the gas phase of state 2, use Eq. 9.3.23 to calculate the second virial coefficient. Then solve the equation of state of Eq. 9.3.21 for the pressure. Also calculate the partial pressures of the O_2 and CO_2 in the gas mixture.

(f) Although the amounts of H_2O in the gas phases of states 1 and 2 are small, you need to know their values in order to take the energy of vaporization into account. In this part, you calculate the fugacities of the H_2O in the initial and final gas phases, in part (g) you use gas equations of state to evaluate the fugacity coefficients of the H_2O (as well as of the O_2 and CO_2), and then in part (h) you find the amounts of H_2O in the initial and final gas phases.

The pressure at which the pure liquid and gas phases of H_2O are in equilibrium at $298.15\,\mathrm{K}$ (the saturation vapor pressure of water) is $0.03169\,\mathrm{bar}$. Use Eq. 7.8.18 to estimate the fugacity of $H_2O(g)$ in equilibrium with pure liquid water at this temperature and pressure. The effect of pressure on fugacity in a one-component liquid–gas system is discussed in Sec. 12.8.1; use Eq. 12.8.3 to find the fugacity of H_2O in gas phases equilibrated with liquid water at the pressures of states 1 and 2 of the isothermal bomb process. (The mole fraction of O_2 dissolved in the liquid water is so small that you can ignore its effect on the chemical potential of the water.)

(g) Calculate the fugacity coefficients of H_2O and O_2 in the gas phase of state 1 and of H_2O, O_2, and CO_2 in the gas phase of state 2.

For state 1, in which the gas phase is practically-pure O_2, you can use Eq. 7.8.18 to calculate ϕ_{O_2}. The other calculations require Eq. 9.3.29, with the value of B'_i found from the formulas of Eq. 9.3.26 or Eqs. 9.3.27 and 9.3.28 (y_A is so small that you can set it equal to zero in these formulas).

Use the fugacity coefficient and partial pressure of O_2 to evaluate its fugacity in states 1 and 2; likewise, find the fugacity of CO_2 in state 2. [You calculated the fugacity of the H_2O in part (f).]

(h) From the values of the fugacity and fugacity coefficient of a constituent of a gas mixture, you can calculate the partial pressure with Eq. 9.3.17, then the mole fraction with $y_i = p_i/p$, and finally the amount with $n_i = y_i n$. Use this method to find the amounts of H_2O in the gas phases of states 1 and 2, and also calculate the amounts of H_2O in the liquid phases of both states.

(i) Next, consider the O_2 dissolved in the water of state 1 and the O_2 and CO_2 dissolved in the water of state 2. Treat the solutions of these gases as ideal dilute with the molality of solute i given by $m_i = f_i/k_{m,i}$ (Eq. 9.4.21). The values of the Henry's law constants of these gases listed in Table 11.3 are for the standard pressure of $1\,\mathrm{bar}$. Use Eq. 12.8.35 to find the appropriate values of $k_{m,i}$ at the pressures of states 1 and 2, and use these values to calculate the amounts of the dissolved gases in both states.

(j) At this point in the calculations, you know the values of all properties needed to describe the initial and final states of the isothermal bomb process. You are now able to evaluate the various Washburn corrections. These corrections are the internal energy changes, at the reference temperature of $298.15\,\mathrm{K}$, of processes that connect the standard states of substances with either state 1 or state 2 of the isothermal bomb process.

First, consider the gaseous H_2O. The Washburn corrections should be based on a pure-liquid standard state for the H_2O. Section 7.9 shows that the molar internal energy of a pure gas under ideal-gas conditions (low pressure) is the same as the molar internal energy of the gas in its standard state at the same temperature. Thus, the molar internal energy change when a substance in its pure-liquid standard state changes isothermally to an ideal gas is equal to the standard molar internal energy of vaporization, $\Delta_\mathrm{vap}U^\circ$. Using the value of $\Delta_\mathrm{vap}U^\circ$ for H_2O given in Table 11.3, calculate ΔU for the vaporization of liquid H_2O at pressure p° to ideal gas in the amount present in the gas phase of state 1. Also calculate ΔU for the condensation of ideal gaseous H_2O in the amount present in the gas phase of state 2 to liquid at pressure p°.

(k) Next, consider the dissolved O_2 and CO_2, for which gas standard states are used. Assume that the solutions are sufficiently dilute to have infinite-dilution behavior; then the partial molar internal energy of either solute in the solution at the standard pressure $p^\circ = 1\,\mathrm{bar}$ is equal to the standard partial molar internal energy based on a solute standard state (Sec. 9.7.1). Values of $\Delta_\mathrm{sol}U^\circ$ are listed in Table 11.3. Find ΔU for the dissolution of O_2 from its gas standard state to ideal-dilute solution at pressure p°

in the amount present in the aqueous phase of state 1. Find ΔU for the desolution (transfer from solution to gas phase) of O_2 and of CO_2 from ideal-dilute solution at pressure p°, in the amounts present in the aqueous phase of state 2, to their gas standard states.

(l) Calculate the internal energy changes when the liquid phases of state 1 (n-hexane and aqueous solution) are compressed from p° to p_1 and the aqueous solution of state 2 is decompressed from p_2 to p°. Use an approximate expression from Table 7.4, and treat the cubic expansion coefficient of the aqueous solutions as being the same as that of pure water.

(m) The final Washburn corrections are internal energy changes of the gas phases of states 1 and 2. H_2O has such low mole fractions in these phases that you can ignore H_2O in these calculations; that is, treat the gas phase of state 1 as pure O_2 and the gas phase of state 2 as a binary mixture of O_2 and CO_2.

One of the internal energy changes is for the compression of gaseous O_2, starting at a pressure low enough for ideal-gas behavior ($U_m = U_m^\circ$) and ending at pressure p_1 to form the gas phase present in state 1. Use the approximate expression for $U_m - U_m^\circ(g)$ in Table 7.5 to calculate $\Delta U = U(p_1) - nU_m^\circ(g)$; a value of dB/dT for pure O_2 is listed in Table 11.3.

The other internal energy change is for a process in which the gas phase of state 2 at pressure p_2 is expanded until the pressure is low enough for the gas to behave ideally, and the mixture is then separated into ideal-gas phases of pure O_2 and CO_2. The molar internal energies of the separated low-pressure O_2 and CO_2 gases are the same as the standard molar internal energies of these gases. The internal energy of unmixing ideal gases is zero (Eq. 11.1.11). The dependence of the internal energy of the gas mixture is given, to a good approximation, by $U = \sum_i U_i^\circ(g) - npT\,dB/dT$, where B is the second virial coefficient of the gas mixture; this expression is the analogy for a gas mixture of the approximate expression for $U_m - U_m^\circ(g)$ in Table 7.5. Calculate the value of dB/dT for the mixture of O_2 and CO_2 in state 2 (you need Eq. 9.3.23 and the values of dB_{ij}/dT in Table 11.3) and evaluate $\Delta U = \sum_i n_i U_i^\circ(g) - U(p_2)$ for the gas expansion.

(n) Add the internal energy changes you calculated in parts (j)–(m) to find the total internal energy change of the Washburn corrections. Note that most of the corrections occur in pairs of opposite sign and almost completely cancel one another. Which contributions are the greatest in magnitude?

(o) The internal energy change of the isothermal bomb process in the bomb vessel, corrected to the reference temperature of $298.15\,K$, is found to be $\Delta U(\text{IBP}, T_{\text{ref}}) = -32.504\,\text{kJ}$. Assume there are no side reactions or auxiliary reactions. From Eqs. 11.5.9 and 11.5.10, calculate the standard molar internal energy of combustion of n-hexane at $298.15\,K$

(p) From Eq. 11.5.13, calculate the standard molar enthalpy of combustion of n-hexane at $298.15\,K$

11.8

By combining the results of Prob. 11.7(p) with the values of standard molar enthalpies of formation from Appendix H, calculate the standard molar enthalpy of formation of liquid n-hexane at $298.15\,K$

11.9

Consider the combustion of methane:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \tag{11.10.2}$$

Suppose the reaction occurs in a flowing gas mixture of methane and air. Assume that the pressure is constant at $1\,\text{bar}$, the reactant mixture is at a temperature of $298.15\,K$ and has stoichiometric proportions of methane and oxygen, and the reaction goes to completion with no dissociation. For the quantity of gaseous product mixture containing $1\,\text{mol}\,CO_2$, $2\,\text{mol}\,H_2O$, and the nitrogen and other substances remaining from the air, you may use the approximate formula $C_p(P) = a + bT$, where the coefficients have the values $a = 297.0\,J\,K^{-1}$ and $b = 8.520 \times 10^{-2}\,J\,K^{-2}$. Solve Eq. 11.6.1 for T_2 to estimate the flame temperature to the nearest kelvin.

11.10

The standard molar Gibbs energy of formation of crystalline mercury(II) oxide at $600.00\,K$ has the value $\Delta_f G^\circ = -26.386\,\text{kJ}\,\text{mol}^{-1}$. Estimate the partial pressure of O_2 in equilibrium with HgO at this temperature: $2\,HgO(s) \rightleftharpoons 2\,Hg(l) + O_2(g)$.

11.11

The combustion of hydrogen is a reaction that is known to “go to completion.”

(a) Use data in Appendix H to evaluate the thermodynamic equilibrium constant at $298.15\,K$ for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \tag{11.10.3}$$

(b) Assume that the reaction is at equilibrium at $298.15\ \text{K}$ in a system in which the partial pressure of O_2 is $1.0\ \text{bar}$. Assume ideal-gas behavior and find the equilibrium partial pressure of H_2 and the number of H_2 *molecules* in $1.0\ \text{m}^3$ of the gas phase.

(c) In the preceding part, you calculated a very small value (a fraction) for the number of H_2 molecules in $1.0\ \text{m}^3$. Statistically, this fraction can be interpreted as the fraction of a given length of time during which one molecule is present in the system. Take the age of the universe as 1.0×10^{10} years and find the total length of time in seconds, during the age of the universe, that a H_2 molecule is present in the equilibrium system. (This hypothetical value is a dramatic demonstration of the statement that the limiting reactant is essentially entirely exhausted during a reaction with a large value of K.)

11.12

Let G represent carbon in the form of *graphite* and D represent the *diamond* crystal form. At $298.15\ \text{K}$, the thermodynamic equilibrium constant for $\text{G} \rightleftharpoons \text{D}$, based on a standard pressure $p^\circ = 1\ \text{bar}$, has the value $K = 0.31$. The molar volumes of the two crystal forms at this temperature are $V_\text{m}(\text{G}) = 5.3 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$ and $V_\text{m}(\text{D}) = 3.4 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$.

(a) Write an expression for the reaction quotient Q_rxn as a function of pressure. Use the approximate expression of the pressure factor given in Table 9.6.

(b) Use the value of K to estimate the pressure at which the D and G crystal forms are in equilibrium with one another at $298.15\ \text{K}$ (This is the lowest pressure at which graphite could in principle be converted to diamond at this temperature.)

11.13

Consider the dissociation reaction $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\,\text{NO}_2(\text{g})$ taking place at a constant temperature of $298.15\ \text{K}$ and a constant pressure of $0.0500\ \text{bar}$. Initially (at $\xi = 0$) the system contains $1.000\ \text{mol}$ of N_2O_4 and no NO_2. Other needed data are found in Appendix H. Assume ideal-gas behavior.

(a) For values of the advancement ξ ranging from 0 to $1\ \text{mol}$, at an interval of $0.1\ \text{mol}$ or less, calculate $[G(\xi) - G(0)]$ to the nearest $0.01\ \text{kJ}$. A computer spreadsheet would be a convenient way to make the calculations.

(b) Plot your values of $G(\xi) - G(0)$ as a function of ξ, and draw a smooth curve through the points.

(c) On your curve, indicate the estimated position of ξ_eq. Calculate the activities of N_2O_4 and NO_2 for this value of ξ, use them to estimate the thermodynamic equilibrium constant K, and compare your result with the value of K calculated from Eq. 11.8.11.

CHAPTER OVERVIEW

12: Equilibrium Conditions in Multicomponent Systems

This chapter applies equilibrium theory to a variety of chemical systems of more than one component. Two different approaches will be used as appropriate: one based on the relation *[Math Processing Error]* for transfer equilibrium, the other based on *[Math Processing Error]* or *[Math Processing Error]* for reaction equilibrium.

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12.1: Effects of Temperature

For some of the derivations in this chapter, we will need an expression for the rate at which the ratio μ_i/T varies with temperature in a phase of fixed composition maintained at constant pressure. This expression leads, among other things, to an important relation between the temperature dependence of an equilibrium constant and the standard molar reaction enthalpy.

12.1.1 Variation of μ_i/T with temperature

In a phase containing species i, either pure or in a mixture, the partial derivative of μ_i/T with respect to T at constant p and a fixed amount of each species is given by

$$\left[\frac{\partial\left(\mu_i/T\right)}{\partial T}\right]_{p,\{n_i\}} = \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{n_i\}} - \frac{\mu_i}{T^2}$$

This equality comes from a purely mathematical operation; no thermodynamics is involved.

> The relation is obtained from the formula $\mathrm{d}(uv)/\mathrm{d}x = u(\mathrm{d}v/\mathrm{d}x) + v(\mathrm{d}u/\mathrm{d}x)$ (Appendix E), where u is $1/T$, v is μ_i, and x is T.

The partial derivative $(\partial\mu_i/\partial T)_{p,\{n_i\}}$ is equal to $-S_i$ (Eq. 9.2.48), so that Eq. 12.1.1 becomes

$$\left[\frac{\partial\left(\mu_i/T\right)}{\partial T}\right]_{p,\{n_i\}} = -\frac{S_i}{T} - \frac{\mu_i}{T^2} = -\frac{TS_i + \mu_i}{T^2}$$

The further substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) gives finally

$$\left[\frac{\partial\left(\mu_i/T\right)}{\partial T}\right]_{p,\{n_i\}} = -\frac{H_i}{T^2}$$

> For a pure substance in a closed system, Eq. 12.1.3 when multiplied by the amount n becomes
>
> $$\left[\frac{\partial(G/T)}{\partial T}\right]_{p} = -\frac{H}{T^2}$$
>
> This is the *Gibbs–Helmholtz equation*.

12.1.2 Variation of μ_i°/T with temperature

If we make the substitution $\mu_i = \mu_i^{\circ} + RT\ln a_i$ in Eq. 12.1.3 and rearrange, we obtain

$$\frac{\mathrm{d}(\mu_i^{\circ}/T)}{\mathrm{d}T} = -\frac{H_i}{T^2} - R\left(\frac{\partial \ln a_i}{\partial T}\right)_{p,\{n_i\}}$$

Because μ_i°/T is a function only of T, its derivative with respect to T is itself a function only of T. We can therefore use any convenient combination of pressure and composition in the expression on the right side of Eq. 12.1.5 in order to evaluate $\mathrm{d}(\mu_i^{\circ}/T)/\mathrm{d}T$ at a given temperature.

If species i is a constituent of a gas mixture, we take a constant pressure of the gas that is low enough for the gas to behave ideally.

d molar enthalpy H_i° (Eq. 9.3.7). In the expression for activity, $a_i(\mathrm{g}) = \Gamma_i(\mathrm{g})\phi_i p_i/p$ (Table

9.5), the pressure factor $\Gamma_i(\mathrm{g})$ is constant when p is constant, the fugacity coefficient ϕ_i for the ideal gas is unity, and $p_i/p = y_i$ is constant at constant $\{n_i\}$, so that the partial derivative $[\partial \ln a_i(\mathrm{g})/\partial T]_{p,\{n_i\}}$ is zero.

For component i of a condensed-phase mixture, we take a constant pressure equal to the standard pressure p°, and a mixture composition in the limit given by Eqs. 9.5.20–9.5.24 in which the activity coefficient is unity. H_i is then the standard molar enthalpy H_i°, and the activity is given by an expression in Table 9.5 with the pressure factor and activity coefficient set equal to 1: $a_i = x_i$, $a_\mathrm{A} = x_\mathrm{A}$, $a_{x,\mathrm{B}} = x_\mathrm{B}$, $a_{c,\mathrm{B}} = c_\mathrm{B}/c^\circ$, or $a_{m,\mathrm{B}} = m_\mathrm{B}/m^\circ$. With the exception of $a_{c,\mathrm{B}}$, these activities are constant as T changes at constant p and $\{n_i\}$.

> If solute B is an electrolyte, $a_{m,\mathrm{B}}$ is given instead by Eq. 10.3.10; like $a_{m,\mathrm{B}}$ for a nonelectrolyte, it is constant as T changes at constant p and $\{n_i\}$.

Thus for a gas-phase species, or a species with a standard state based on mole fraction or molality, $[\partial \ln a_i(\mathrm{g})/\partial T]_{p,\{n_i\}}$ is zero and Eq. 12.1.5 becomes

$$\frac{\mathrm{d}(\mu_i^\circ/T)}{\mathrm{d}T} = -\frac{H_i^\circ}{T^2}$$

Equation 12.1.6, as the conditions of validity indicate, does not apply to a solute standard state based on concentration, except as an approximation. The reason is the volume change that accompanies an isobaric temperature change. We can treat this case by considering the following behavior of $\ln(c_\mathrm{B}/c^\circ)$:

$$\begin{aligned}\left[\frac{\partial \ln(c_\mathrm{B}/c^\circ)}{\partial T}\right]_{p,\{n_i\}} &= \frac{1}{c_\mathrm{B}}\left(\frac{\partial c_\mathrm{B}}{\partial T}\right)_{p,\{n_i\}} = \frac{1}{n_\mathrm{B}/V}\left[\frac{\partial (n_\mathrm{B}/V)}{\partial T}\right]_{p,\{n_i\}} \\ &= V\left[\frac{\partial (1/V)}{\partial T}\right]_{p,\{n_i\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\{n_i\}} \\ &= -\alpha\end{aligned}$$

Here α is the cubic expansion coefficient of the solution (Eq. 7.1.1). If the activity coefficient is to be unity, the solution must be an ideal-dilute solution, and α is then α_A^*, the cubic expansion coefficient of the pure solvent. Eq. 12.1.5 for a nonelectrolyte becomes

$$\frac{\mathrm{d}(\mu_{c,\mathrm{B}}^\circ/T)}{\mathrm{d}T} = -\frac{H_\mathrm{B}^\circ}{T^2} + R\alpha_\mathrm{A}^*$$

12.1.3 Variation of $\ln K$ with temperature

The thermodynamic equilibrium constant K, for a given reaction equation and a given choice of reactant and product standard states, is a function of T and *only* of T. By equating two expressions for the standard molar reaction Gibbs energy, $\Delta_\mathrm{r}G^\circ = \sum_i \nu_i \mu_i^\circ$ and $\Delta_\mathrm{r}G^\circ = -RT\ln K$ (Eqs. 11.8.3 and 11.8.10), we obtain

$$\ln K = -\frac{1}{RT}\sum_i \nu_i \mu_i^\circ$$

The rate at which $\ln K$ varies with T is then given by

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = -\frac{1}{R}\sum_i \nu_i \frac{\mathrm{d}(\mu_i^\circ/T)}{\mathrm{d}T}$$

Combining Eq. 12.1.10 with Eqs. 12.1.6 or 12.1.8, and recognizing that $\sum_i \nu_i H_i^\circ$ is the standard molar reaction enthalpy $\Delta_r H^\circ$, we obtain the final expression for the temperature dependence of $\ln K$:

$$\frac{d\ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} - \alpha_A^* \sum_{\substack{\text{solutes,}\\ \text{conc. basis}}} \nu_i$$

The sum on the right side includes only solute species whose standard states are based on concentration. The expression is simpler if all solute standard states are based on mole fraction or molality:

$$\frac{d\ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

We can rearrange Eq. 12.1.12 to

$$\Delta_r H^\circ = RT^2 \frac{d\ln K}{dT}$$

We can convert this expression for $\Delta_r H^\circ$ to an equivalent form by using the mathematical identity $d(1/T) = -(1/T^2)dT$:

$$\Delta_r H^\circ = -R\frac{d\ln K}{d(1/T)}$$

Equations 12.1.13 and 12.1.14 are two forms of the **van't Hoff equation**. They allow us to evaluate the standard molar reaction enthalpy of a reaction by a noncalorimetric method from the temperature dependence of $\ln K$. For example, we can plot $\ln K$ versus $1/T$; then according to Eq. 12.1.14, the slope of the curve at any value of $1/T$ is equal to $-\Delta_r H^\circ/R$ at the corresponding temperature T.

> A simple way to derive the equation for this last procedure is to substitute $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ in $\Delta_r G^\circ = -RT\ln K$ and rearrange to
>
> $$\ln K = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta_r S^\circ}{R}$$
>
> Suppose we plot $\ln K$ versus $1/T$. In a small temperature interval in which $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are practically constant, the curve will appear linear. According to Eq. 12.1.15, the curve in this interval has a slope of $-\Delta_r H^\circ/R$, and the tangent to a point on the curve has its intercept at $1/T = 0$ equal to $\Delta_r S^\circ/R$.

When we apply Eq. 12.1.14 to the *vaporization process* $A(l) \rightarrow A(g)$ of pure A, it resembles the Clausius–Clapeyron equation for the same process (Eq. 8.4.15). These equations are not exactly equivalent, however, as the comparison in Table 12.1 shows.

12.2: Solvent Chemical Potentials from Phase Equilibria

Section 9.6.3 explained how we can evaluate the activity coefficient *[Math Processing Error]* of a nonelectrolyte solute of a binary solution if we know the variation of the osmotic coefficient of the solution from infinite dilution to the molality of interest. A similar procedure for the mean ionic activity coefficient of an electrolyte solute was described in Sec. 10.6.

The physical measurements needed to find the osmotic coefficient *[Math Processing Error]* of a binary solution must be directed to the calculation of the quantity *[Math Processing Error]*, the difference between the chemical potentials of the pure solvent and the solvent in the solution at the temperature and pressure of interest. This difference is positive, because the presence of the solute reduces the solvent's chemical potential.

To calculate *[Math Processing Error]* from *[Math Processing Error]*, we use Eq. 9.6.16 for a nonelectrolyte solute, or Eq. 10.6.1 for an electrolyte solute. Both equations are represented by *[Math Processing Error]* where *[Math Processing Error]* for a nonelectrolyte is *[Math Processing Error]* and for an electrolyte is the number of ions per formula unit.

The sequence of steps, then, is (1) the determination of *[Math Processing Error]* over a range of molality at constant *[Math Processing Error]* and *[Math Processing Error]*, (2) the conversion of these values to *[Math Processing Error]* using Eq. 12.2.1, and (3) the evaluation of the solute activity coefficient by a suitable integration from infinite dilution to the molality of interest.

> A measurement of *[Math Processing Error]* also gives us the *solvent* activity coefficient, based on the pure-solvent reference state, through the relation *[Math Processing Error]* (Eq. 9.5.15).

Sections 12.2.1 and 12.2.2 will describe freezing-point and osmotic-pressure measurements, two much-used methods for evaluating *[Math Processing Error]* in a binary solution at a given *[Math Processing Error]* and *[Math Processing Error]*. The isopiestic vapor-pressure method was described in Sec. 9.6.4. The freezing-point and isopiestic vapor-pressure methods are often used for electrolyte solutions, and osmotic pressure is especially useful for solutions of macromolecules.

12.2.1 Freezing-point measurements

This section explains how we can evaluate *[Math Processing Error]* for a solution of a given composition at a given *[Math Processing Error]* and *[Math Processing Error]* from the freezing point of the solution combined with additional data obtained from calorimetric measurements.

Consider a binary solution of solvent A and solute B. We assume that when this solution is cooled at constant pressure and composition, the solid that first appears is pure A. For example, for a dilute aqueous solution the solid would be ice. The temperature at which solid A first appears is *[Math Processing Error]*, the freezing point of the solution. This temperature is lower than the freezing point *[Math Processing Error]* of the pure solvent, a consequence of the lowering of *[Math Processing Error]* by the presence of the solute. Both *[Math Processing Error]* and *[Math Processing Error]* can be measured experimentally.

Let *[Math Processing Error]* be a temperature of interest that is equal to or greater than *[Math Processing Error]*. We wish to determine the value of *[Math Processing Error]*, where *[Math Processing Error]* refers to pure liquid solvent and *[Math Processing Error]* refers to the solution.

A second method for evaluating *[Math Processing Error]* uses the solution property called *osmotic pressure*. A simple apparatus to measure the osmotic pressure of a binary solution is shown schematically in Fig. 12.2. The system consists of two liquid phases separated by a semipermeable membrane. Phase *[Math Processing Error]* is pure solvent and phase *[Math Processing Error]* is a solution with the same solvent at the same temperature. The semipermeable membrane is permeable to the solvent and impermeable to the solute.

The presence of the membrane makes this system different from the multiphase, multicomponent system of Sec. 9.2.7, used there to derive conditions for transfer equilibrium. By a modification of that procedure, we can derive the conditions of equilibrium for the present system. We take phase *[Math Processing Error]* as the reference phase because it includes both solvent and solute. In order to prevent expansion work in the isolated system, both pistons shown in the figure must be fixed in stationary positions. This keeps the volume of each phase constant: *[Math Processing Error]*. Equation 9.2.41, expressing the total differential of the entropy in an isolated multiphase, multicomponent system, becomes *[Math Processing Error]* In an equilibrium state, the coefficients *[Math Processing Error]* and *[Math Processing Error]* must be zero. Therefore, in an equilibrium state the temperature is the same in both phases and the solvent has the same chemical potential in both phases. The presence of the membrane, however, allows the pressures of the two phases to be unequal in the equilibrium state.

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Suppose we start with both phases shown in Fig. 12.2 at the same temperature and pressure. Under these conditions, the value of *[Math Processing Error]* is less in the solution than in the pure liquid, and a spontaneous flow of solvent will occur through the membrane from the pure solvent to the solution. This phenomenon is called *osmosis* (Greek for *push*). If we move the right-hand piston down slightly in order to increase the pressure *[Math Processing Error]* of the solution in phase *[Math Processing Error]*, *[Math Processing Error]* increases in this phase. The **osmotic pressure** of the solution, *[Math Processing Error]*, is defined as the additional pressure the solution must have, compared to the pressure *[Math Processing Error]* of the pure solvent at the same temperature, to establish an equilibrium state with no flow of solvent in either direction through the membrane: *[Math Processing Error]*.

> In practice, the membrane may not be completely impermeable to a solute. All that is required for the establishment of an equilibrium state with different pressures on either side of the membrane is that solvent transfer equilibrium be established on a short time scale compared to the period of observation, and that the amount of solute transferred during this period be negligible.

The osmotic pressure *[Math Processing Error]* is an intensive property of a solution whose value depends on the solution's temperature, pressure, and composition. Strictly speaking, *[Math Processing Error]* in an equilibrium state of the system shown in Fig. 12.2 refers to the osmotic pressure of the solution at pressure *[Math Processing Error]*, the pressure of the pure solvent. In other words, the osmotic pressure of a solution at temperature *[Math Processing Error]* and pressure *[Math Processing Error]* is the additional pressure that would have to be exerted on the solution to establish transfer equilibrium with pure solvent that has temperature *[Math Processing Error]* and pressure *[Math Processing Error]*. A solution has the property called osmotic pressure regardless of whether this additional pressure is actually present, just as a solution has a freezing point even when its actual temperature is different from the freezing point.

Because in an equilibrium state the solvent chemical potential must be the same on both sides of the semipermeable membrane, there is a relation between chemical potentials and osmotic pressure given by *[Math Processing Error]* We can use this relation to derive an expression for *[Math Processing Error]* as a function of *[Math Processing Error]*. The dependence of *[Math Processing Error]* on pressure is given according to Eq. 9.2.49 by *[Math Processing Error]* where *[Math Processing Error]* is the partial molar volume of the solvent in the solution. Rewriting this equation in the form *[Math Processing Error]* and integrating at constant temperature and composition from *[Math Processing Error]* to *[Math Processing Error]*, we obtain *[Math Processing Error]* Substitution from Eq. 12.2.7 changes this to *[Math Processing Error]* which is the desired expression for *[Math Processing Error]* at a single temperature and pressure. To evaluate the integral, we need an experimental value of the osmotic pressure *[Math Processing Error]* of the solution. If we assume *[Math Processing Error]* is constant in the pressure range from *[Math Processing Error]* to *[Math Processing Error]*, Eq. 12.2.10 becomes simply *[Math Processing Error]*

12.3: Binary Mixture in Equilibrium with a Pure Phase

This section considers a binary liquid mixture of components A and B in equilibrium with either pure solid A or pure gaseous A. The aim is to find general relations among changes of temperature, pressure, and mixture composition in the two-phase equilibrium system that can be applied to specific situations in later sections.

In this section, *[Math Processing Error]* is the chemical potential of component A in the mixture and *[Math Processing Error]* is for the pure solid or gaseous phase. We begin by writing the total differential of *[Math Processing Error]* with *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* as the independent variables. These quantities refer to the binary liquid mixture, and we have not yet imposed a condition of equilibrium with another phase. The general expression for the total differential is *[Math Processing Error]* With substitutions from Eqs. 9.2.49 and 12.1.3, this becomes *[Math Processing Error]*

Next we write the total differential of *[Math Processing Error]* for pure solid or gaseous A. The independent variables are *[Math Processing Error]* and *[Math Processing Error]*; the expression is like Eq. 12.3.2 with the last term missing: *[Math Processing Error]*

When the two phases are in transfer equilibrium, *[Math Processing Error]* and *[Math Processing Error]* are equal. If changes occur in *[Math Processing Error]*, *[Math Processing Error]*, or *[Math Processing Error]* while the phases remain in equilibrium, the condition *[Math Processing Error]* must be satisfied. Equating the expressions on the right sides of Eqs. 12.3.2 and 12.3.3 and combining terms, we obtain the equation *[Math Processing Error]* which we can rewrite as *[Math Processing Error]* Here *[Math Processing Error]* is the molar differential enthalpy of solution of solid or gaseous A in the liquid mixture, and *[Math Processing Error]* is the molar differential volume of solution. Equation 12.3.5 is a relation between changes in the variables *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]*, only two of which are independent in the equilibrium system.

Suppose we set *[Math Processing Error]* equal to zero in Eq. 12.3.5 and solve for *[Math Processing Error]*. This gives us the rate at which *[Math Processing Error]* changes with *[Math Processing Error]* at constant *[Math Processing Error]*: *[Math Processing Error]* We can also set *[Math Processing Error]* equal to zero in Eq. 12.3.5 and find the rate at which *[Math Processing Error]* changes with *[Math Processing Error]* at constant *[Math Processing Error]*: *[Math Processing Error]*

Equations 12.3.6 and 12.3.7 will be needed in Secs. 12.4 and 12.5.

12.4: Colligative Properties of a Dilute Solution

The **colligative properties** of a solution are usually considered to be:

1. Note that all four properties are defined by an equilibrium between the liquid solution and a solid, liquid, or gas phase of the pure solvent. The properties called colligative (Latin: *tied together*) have in common a dependence on the concentration of solute particles that affects the solvent chemical potential.

   Figure 12.3 illustrates the freezing-point depression and boiling-point elevation of an aqueous solution. At a fixed pressure, pure liquid water is in equilibrium with ice at the freezing point and with steam at the boiling point. These are the temperatures at which H_2O has the same chemical potential in both phases at this pressure. At these temperatures, the chemical potential curves for the phases intersect, as indicated by open circles in the figure. The presence of dissolved solute in the solution causes a lowering of the H_2O chemical potential compared to pure water at the same temperature. Consequently, the curve for the chemical potential of H_2O in the solution intersects the curve for ice at a lower temperature, and the curve for steam at a higher temperature, as indicated by open triangles. The freezing point is depressed by ΔT_{f}, and the boiling point (if the solute is nonvolatile) is elevated by ΔT_{b}.

   Although these expressions provide no information about the activity coefficient of a solute, they are useful for estimating the solute molar mass. For example, from a measurement of any of the colligative properties of a dilute solution and the appropriate theoretical relation, we can obtain an approximate value of the solute molality m_{B}. (It is only approximate because, for a measurement of reasonable precision, the solution cannot be extremely dilute.) If we prepare the solution with a known amount n_{A} of solvent and a known mass of solute, we can calculate the amount of solute from $n_{\mathrm{B}} = n_{\mathrm{A}} M_{\mathrm{A}} m_{\mathrm{B}}$; then the solute molar mass is the solute mass divided by n_{B}.

12.4.1 Freezing-point depression

As in Sec. 12.2.1, we assume the solid that forms when a dilute solution is cooled to its freezing point is pure component A.

Equation 12.3.6 gives the general dependence of temperature on the composition of a binary liquid mixture of A and B that is in equilibrium with pure solid A. We treat the mixture as a solution. The solvent is component A, the solute is B, and the temperature is the freezing point T_{f}:

$$\left(\frac{\partial T_{\mathrm{f}}}{\partial x_{\mathrm{A}}}\right)_p = \frac{T_{\mathrm{f}}^2}{\Delta_{\mathrm{sol,A}} H}\left[\frac{\partial(\mu_{\mathrm{A}}/T)}{\partial x_{\mathrm{A}}}\right]_{T,p} \tag{12.4.1}$$

Consider the expression on the right side of this equation in the limit of infinite dilution. In this limit, T_{f} becomes T_{f}^*, the freezing point of the pure solvent, and $\Delta_{\mathrm{sol,A}} H$ becomes $\Delta_{\mathrm{fus,A}} H$, the molar enthalpy of fusion of the pure solvent.

To deal with the partial derivative on the right side of Eq. 12.4.1 in the limit of infinite dilution, we use the fact that the solvent activity coefficient γ_{A} approaches 1 in this limit. Then the solvent chemical potential is given by the Raoult's law relation

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^* + RT \ln x_{\mathrm{A}} \tag{12.4.2}$$

(solution at infinite dilution)

where μ_{A}^* is the chemical potential of A in a pure-liquid reference state at the same T and p as the mixture. (At the freezing point of the mixture, the reference state is an unstable supercooled liquid.)

If the solute is an electrolyte, Eq. 12.4.2 can be derived by the same procedure as described in Sec. 9.4.6 for an ideal-dilute binary solution of a nonelectrolyte. We must calculate x_{A} from the amounts of all species present at infinite dilution. In the limit of infinite dilution, any electrolyte solute is completely dissociated to its constituent ions: ion pairs and weak electrolytes are completely dissociated in this limit. Thus, for a binary solution of electrolyte B with ν ions per formula unit, we should calculate x_{A} from

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + \nu n_{\mathrm{B}}} \tag{12.4.3}$$

where n_{B} is the amount of solute formula unit. (If the solute is a nonelectrolyte, we simply set ν equal to 1 in this equation.)

From Eq. 12.4.2, we can write

$$\left[\frac{\partial(\mu_{\rm A}/T)}{\partial x_{\rm A}}\right]_{T,p} \to R \quad \text{as} \quad x_{\rm A} \to 1 \tag{12.4.4}$$

In the limit of infinite dilution, then, Eq. 12.4.1 becomes

$$\lim_{x_{\rm A}\to 1}\left(\frac{\partial T_{\rm f}}{\partial x_{\rm A}}\right)_p = \frac{R(T_{\rm f}^*)^2}{\Delta_{\rm fus,A}H} \tag{12.4.5}$$

It is customary to relate freezing-point depression to the solute concentration $c_{\rm B}$ or molality $m_{\rm B}$. From Eq. 12.4.3, we obtain

$$1-x_{\rm A} = \frac{\nu n_{\rm B}}{n_{\rm A}+\nu n_{\rm B}} \tag{12.4.6}$$

In the limit of infinite dilution, when $\nu n_{\rm B}$ is much smaller than $n_{\rm A}$, $1-x_{\rm A}$ approaches the value $\nu n_{\rm B}/n_{\rm A}$. Then, using expressions in Eq. 9.1.14, we obtain the relations

$$\begin{aligned} {\rm d}x_{\rm A} &= -{\rm d}(1-x_{\rm A}) = -\nu\,{\rm d}(n_{\rm B}/n_{\rm A}) \\ &= -\nu V_{\rm A}^*\,{\rm d}c_{\rm B} \\ &= -\nu M_{\rm A}\,{\rm d}m_{\rm B} \end{aligned} \tag{12.4.7}$$

(binary solution at infinite dilution)

which transform Eq. 12.4.5 into the following (ignoring a small dependence of $V_{\rm A}^*$ on T):

$$\lim_{c_{\rm B}\to 0}\left(\frac{\partial T_{\rm f}}{\partial c_{\rm B}}\right)_p = -\frac{\nu V_{\rm A}^* R(T_{\rm f}^*)^2}{\Delta_{\rm fus,A}H} \tag{12.4.8}$$

$$\lim_{m_{\rm B}\to 0}\left(\frac{\partial T_{\rm f}}{\partial m_{\rm B}}\right)_p = -\frac{\nu M_{\rm A} R(T_{\rm f}^*)^2}{\Delta_{\rm fus,A}H} \tag{12.4.1}$$

We can apply these equations to a nonelectrolyte solute by setting ν equal to 1.

As $c_{\rm B}$ or $m_{\rm B}$ approaches zero, $T_{\rm f}$ approaches $T_{\rm f}^*$. The freezing-point depression (a negative quantity) is $\Delta T_{\rm f} = T_{\rm f} - T_{\rm f}^*$. In the range of molalities of a dilute solution in which $(\partial T_{\rm f}/\partial m_{\rm B})_p$ is given by the expression on the right side of Eq. 12.4.8, we can write

$$\Delta T_{\rm f} = -\frac{\nu M_{\rm A} R(T_{\rm f}^*)^2}{\Delta_{\rm fus,A}H} m_{\rm B} \tag{12.4.9}$$

The **molal freezing-point depression constant** or cryoscopic constant, $K_{\rm f}$, is defined for a binary solution by

$$K_{\rm f} \overset{\rm def}{=} -\lim_{m_{\rm B}\to 0}\frac{\Delta T_{\rm f}}{\nu m_{\rm B}} \tag{12.4.10}$$

and, from Eq. 12.4.9, has a value given by

$$K_{\rm f} = \frac{M_{\rm A} R(T_{\rm f}^*)^2}{\Delta_{\rm fus,A}H} \tag{12.4.11}$$

The value of $K_{\rm f}$ calculated from this formula depends only on the kind of solvent and the pressure. For $\rm H_2O$ at 1 bar, the calculated value is $K_{\rm b} = 1.860\,{\rm K\,kg\,mol^{-1}}$ (Prob. 12.4).

In the dilute binary solution, we have the relation

$$\Delta T_{\rm f} = -\nu K_{\rm f} m_{\rm B} \tag{12.4.12}$$

(dilute binary solution)

This relation is useful for estimating the molality of a dilute nonelectrolyte solution (ν=1) from a measurement of the freezing point. The relation is of little utility for an electrolyte solute, because at any electrolyte molality that is high enough to give a measurable depression of the freezing point, the mean ionic activity coefficient deviates greatly from unity and the relation is not accurate.

12.4.2 Boiling-point elevation

We can apply Eq. 12.3.6 to the boiling point $T_{\rm b}$ of a dilute binary solution. The pure phase of A in equilibrium with the solution is now a gas instead of a solid. (We must assume the solute is nonvolatile or has negligible partial pressure in the gas phase.) Following the procedure of Sec. 12.4.1, we obtain

$$\lim_{m_{\rm B}\to 0}\left(\frac{\partial T_{\rm b}}{\partial m_{\rm B}}\right)_p = \frac{\nu M_{\rm A} R (T_{\rm b}^*)^2}{\Delta_{\rm vap,A} H} \tag{12.4.13}$$

where $\Delta_{\rm vap,A}H$ is the molar enthalpy of vaporization of pure solvent at its boiling point $T_{\rm b}^*$.

The **molal boiling-point elevation constant** or ebullioscopic constant, $K_{\rm b}$, is defined for a binary solution by

$$K_{\rm b} \overset{\rm def}{=} \lim_{m_{\rm B}\to 0} \frac{\Delta T_{\rm b}}{\nu m_{\rm B}} \tag{12.4.14}$$

where $\Delta T_{\rm b} = T_{\rm b} - T_{\rm b}^*$ is the boiling-point elevation. Accordingly, $K_{\rm b}$ has a value given by

$$K_{\rm b} = \frac{M_{\rm A} R (T_{\rm b}^*)^2}{\Delta_{\rm vap,A} H} \tag{12.4.15}$$

For the boiling point of a dilute solution, the analogy of Eq. 12.4.12 is

$$\Delta T_{\rm b} = \nu K_{\rm b} m_{\rm B} \tag{12.4.16}$$

(dilute binary solution)

Since $K_{\rm f}$ has a larger value than $K_{\rm b}$ (because $\Delta_{\rm fus,A}H$ is smaller than $\Delta_{\rm vap,A}H$), the measurement of freezing-point depression is more useful than that of boiling-point elevation for estimating the molality of a dilute solution.

12.4.3 Vapor-pressure lowering

In a binary two-phase system in which a solution of volatile solvent A and nonvolatile solute B is in equilibrium with gaseous A, the vapor pressure of the solution is equal to the system pressure p.

Equation 12.3.7 gives the general dependence of p on $x_{\rm A}$ for a binary liquid mixture in equilibrium with pure gaseous A. In this equation, $\Delta_{\rm sol,A}V$ is the molar differential volume change for the dissolution of the gas in the solution. In the limit of infinite dilution, $-\Delta_{\rm sol,A}V$ becomes $\Delta_{\rm vap,A}V$, the molar volume change for the vaporization of pure solvent. We also apply the limiting expressions of Eqs. 12.4.4 and 12.4.7. The result is

$$\lim_{c_{\rm B}\to 0}\left(\frac{\partial p}{\partial c_{\rm B}}\right)_T = -\frac{\nu V_{\rm A}^* RT}{\Delta_{\rm vap,A} V} \qquad \lim_{m_{\rm B}\to 0}\left(\frac{\partial p}{\partial m_{\rm B}}\right)_T = -\frac{\nu M_{\rm A} RT}{\Delta_{\rm vap,A} V} \tag{12.4.17}$$

If we neglect the molar volume of the liquid solvent compared to that of the gas, and assume the gas is ideal, then we can replace $\Delta_{\rm vap,A}V$ in the expressions above by $V_{\rm A}^*({\rm g}) = RT/p_{\rm A}^*$ and obtain

$$\lim_{c_{\rm B}\to 0}\left(\frac{\partial p}{\partial c_{\rm B}}\right)_T \approx -\nu V_{\rm A}^* p_{\rm A}^* \qquad \lim_{m_{\rm B}\to 0}\left(\frac{\partial p}{\partial m_{\rm B}}\right)_T \approx -\nu M_{\rm A} p_{\rm A}^* \tag{12.4.18}$$

where $p_{\rm A}^*$ is the vapor pressure of the pure solvent at the temperature of the solution.

Thus, approximate expressions for vapor-pressure lowering in the limit of infinite dilution are

$$\Delta p \approx -\nu V_{\rm A}^* p_{\rm A}^* c_{\rm B} \qquad \text{and} \qquad \Delta p \approx -\nu M_{\rm A} p_{\rm A}^* m_{\rm B} \tag{12.4.19}$$

We see that the lowering in this limit depends on the kind of solvent and the solution composition, but not on the kind of solute.

12.4.4 Osmotic pressure

The osmotic pressure $\varPi$ is an intensive property of a solution and was defined in Sec. 12.2.2. In a dilute solution of low $\varPi$, the approximation used to derive Eq. 12.2.11 (that the partial molar volume $V_{\rm A}$ of the solvent is constant in the pressure range from p to $p + \varPi$) becomes valid, and we can write

$$\varPi = \frac{\mu_{\rm A}^* - \mu_{\rm A}}{V_{\rm A}} \tag{12.4.20}$$

In the limit of infinite dilution, $\mu_{\text{A}}^{*}-\mu_{\text{A}}$ approaches $-RT\ln x_{\text{A}}$ (Eq. 12.4.2) and V_{A} becomes the molar volume V_{A}^{*} of the pure solvent. In this limit, Eq. 12.4.20 becomes

$$\mathit{\Pi}=-\frac{RT\ln x_{\text{A}}}{V_{\text{A}}^{*}} \tag{12.4.21}$$

from which we obtain the equation

$$\lim_{x_{\text{A}}\to 1}\left(\frac{\partial\mathit{\Pi}}{\partial x_{\text{A}}}\right)_{T,p}=-\frac{RT}{V_{\text{A}}^{*}} \tag{12.4.22}$$

The relations in Eq. 12.4.7 transform Eq. 12.4.22 into

$$\lim_{c_{\text{B}}\to 0}\left(\frac{\partial\mathit{\Pi}}{\partial c_{\text{B}}}\right)_{T,p}=\nu RT \tag{12.4.23}$$

$$\lim_{m_{\text{B}}\to 0}\left(\frac{\partial\mathit{\Pi}}{\partial m_{\text{B}}}\right)_{T,p}=\frac{\nu RTM_{\text{A}}}{V_{\text{A}}^{*}}=\nu\rho_{\text{A}}^{*}RT \tag{12.4.24}$$

Equations 12.4.23 and 12.4.24 show that the osmotic pressure becomes independent of the kind of solute as the solution approaches infinite dilution. The integrated forms of these equations are

$$\mathit{\Pi}=\nu c_{\text{B}}RT \tag{12.4.25}$$

(dilute binary solution)

$$\mathit{\Pi}=\frac{RTM_{\text{A}}}{V_{\text{A}}^{*}}\nu m_{\text{B}}=\rho_{\text{A}}^{*}RT\nu m_{\text{B}} \tag{12.4.26}$$

(dilute binary solution)

Equation 12.4.25 is **van’t Hoff’s equation** for osmotic pressure. If there is more than one solute species, νc_{B} can be replaced by $\sum_{i\neq\text{A}}c_i$ and νm_{B} by $\sum_{i\neq\text{A}}m_i$ in these expressions.

In Sec. 9.6.3, it was stated that $\mathit{\Pi}/m_{\text{B}}$ is equal to the product of ϕ_m and the limiting value of $\mathit{\Pi}/m_{\text{B}}$ at infinite dilution, where $\phi_m=(\mu_{\text{A}}^{*}-\mu_{\text{A}})/RTM_{\text{A}}\sum_{i\neq\text{A}}m_i$ is the osmotic coefficient. This relation follows directly from Eqs. 12.2.11 and 12.4.26.

12.5: Solid-Liquid Equilibria

A *freezing-point curve* (freezing point as a function of liquid composition) and a *solubility curve* (composition of a solution in equilibrium with a pure solid as a function of temperature) are different ways of describing the same physical situation. Thus, strange as it may sound, the composition x_{A} of an aqueous solution at the freezing point is the mole fraction solubility of ice in the solution.

12.5.1 Freezing points of ideal binary liquid mixtures

Section 12.2.1 described the use of freezing-point measurements to determine the solvent chemical potential in a solution of arbitrary composition relative to the chemical potential of the pure solvent. The way in which freezing point varies with solution composition in the limit of infinite dilution was derived in Sec. 12.4.1. Now let us consider the freezing behavior over the entire composition range of an *ideal* liquid mixture.

Let T_{f}' be the freezing point of a liquid mixture of composition x_{A}' and $x_{\mathrm{B}}' = 1 - x_{\mathrm{A}}'$, and let T_{f}'' be the melting point of the solid compound of composition $x_{\mathrm{A}}'' = a/(a+b)$ and $x_{\mathrm{B}}'' = b/(a+b)$. Figure 12.7 shows an example of a molten metal mixture that solidifies to an alloy of fixed composition. The freezing-point curve of this system is closely approximated by Eq. 12.5.23.

12.5.5 Solubility of a solid electrolyte

Consider an equilibrium between a crystalline salt (or other kind of ionic solid) and a solution containing the solvated ions:

$$\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}(\mathrm{s}) \rightleftharpoons \nu_+\mathrm{M}^{z_+}(\mathrm{aq}) + \nu_-\mathrm{X}^{z_-}(\mathrm{aq}) \qquad (12.5.1)$$

Here ν_+ and ν_- are the numbers of cations and anions in the formula unit of the salt, and z_+ and z_- are the charge numbers of these ions. The solution in equilibrium with the solid salt is a saturated solution. The thermodynamic equilibrium constant for this kind of equilibrium is called a **solubility product**, K_{s}.

We can readily derive a relation between K_{s} and the molalities of the ions in the saturated solution by treating the dissolved salt as a single solute substance, B. We write the equilibrium in the form $\mathrm{B}^*(\mathrm{s}) \rightleftharpoons \mathrm{B}(\mathrm{sln})$, and write the expression for the solubility product as a proper quotient of activities:

$$K_{\mathrm{s}} = \frac{a_{m,\mathrm{B}}}{a_{\mathrm{B}}^*} \qquad (12.5.24)$$

From Eq. 10.3.16, we have $a_{m,\mathrm{B}} = \mathit{\Gamma}_{m,\mathrm{B}}\gamma_{\pm}^{\nu}(m_+/m^\circ)^{\nu_+}(m_-/m^\circ)^{\nu_-}$. This expression is valid whether or not the ions M^{z_+} and X^{z_-} are present in solution in the same ratio as in the solid salt. When we replace $a_{m,\mathrm{B}}$ with this expression, and replace a_{B}^* with $\mathit{\Gamma}_{\mathrm{B}}^*$ (Table 9.5), we obtain

$$K_{\mathrm{s}} = \left(\frac{\mathit{\Gamma}_{m,\mathrm{B}}}{\mathit{\Gamma}_{\mathrm{B}}^*}\right)\gamma_{\pm}^{\nu}\left(\frac{m_+}{m^\circ}\right)^{\nu_+}\left(\frac{m_-}{m^\circ}\right)^{\nu_-} \qquad (12.5.25)$$

where $\nu = \nu_+ + \nu_-$ is the total number of ions per formula unit. $\gamma_{\pm}$ is the mean ionic activity coefficient of the dissolved salt in the saturated solution, and the molalities m_+ and m_- refer to the ions M^{z_+} and X^{z_-} in this solution.

The first factor on the right side of Eq. 12.5.25, the proper quotient of pressure factors for the reaction $\mathrm{B}^*(\mathrm{s}) \rightarrow \mathrm{B}(\mathrm{sln})$, will be denoted $\mathit{\Gamma}_{\mathrm{r}}$ (the subscript “r” stands for reaction). The value of $\mathit{\Gamma}_{\mathrm{r}}$ is exactly 1 if the system is at the standard pressure, and is otherwise approximately 1 unless the pressure is very high.

If the aqueous solution is produced by allowing the salt to dissolve in pure water, or in a solution of a second solute containing no ions in common with the salt, then the ion molalities in the saturated solution are $m_+ = \nu_+ m_{\mathrm{B}}$ and $m_- = \nu_- m_{\mathrm{B}}$ where m_{B} is the solubility of the salt expressed as a molality. Under these conditions, Eq. 12.5.25 becomes

$$K_{\mathrm{s}} = \mathit{\Gamma}_{\mathrm{r}}\gamma_{\pm}^{\nu}\left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)\left(\frac{m_{\mathrm{B}}}{m^\circ}\right)^{\nu} \qquad (12.5.26)$$

(no common ion)

We could also have obtained this equation by using the expression of Eq. 10.3.10 for $a_{m,\mathrm{B}}$.

If the ionic strength of the saturated salt solution is sufficiently low (i.e., the solubility is sufficiently low), it may be practical to evaluate the solubility product with Eq. 12.5.26 and an estimate of $\gamma_{\pm}$ from the Debye–Hückel limiting law (see Prob. 12.19). The most accurate method of measuring a solubility product, however, is through the standard cell potential of an appropriate galvanic cell (Sec. 14.3.3).

Since K_{s} is a thermodynamic equilibrium constant that depends only on T, and $\mathit{\Gamma}_{\text{r}}$ depends only on T and p, Eq. 12.5.26 shows that any change in the solution composition at constant T and p that decreases $\gamma_{\pm}$ must increase the solubility. For example, the solubility of a sparingly-soluble salt increases when a second salt, lacking a common ion, is dissolved in the solution; this is a *salting-in effect*.

Equation 12.5.25 is a general equation that applies even if the solution saturated with one salt contains a second salt with a common ion. For instance, consider the sparingly-soluble salt $\text{M}_{\nu_+}\text{X}_{\nu_-}$ in transfer equilibrium with a solution containing the more soluble salt $\text{M}_{\nu'_+}\text{Y}_{\nu'_-}$ at molality m_{C}. The common ion in this example is the cation M^{z_+}. The expression for the solubility product is now

$$K_{\text{s}} = \mathit{\Gamma}_{\text{r}}\gamma_{\pm}^{\nu}(\nu_+ m_{\text{B}} + \nu'_+ m_{\text{C}})^{\nu_+}(\nu_- m_{\text{B}})^{\nu_-}/(m^{\circ})^{\nu} \tag{12.5.27}$$

(common cation)

where m_{B} again is the solubility of the sparingly-soluble salt, and m_{C} is the molality of the second salt. K_{s} and $\mathit{\Gamma}_{\text{r}}$ are constant if T and p do not change, so any increase in m_{C} at constant T and p must cause a decrease in the solubility m_{B}. This is called the *common ion effect*.

From the measured solubility of a salt in pure solvent, or in an electrolyte solution with a common cation, and a known value of K_{s}, we can evaluate the mean ionic activity coefficient $\gamma_{\pm}$ through Eq. 12.5.26 or 12.5.27. This procedure has the disadvantage of being limited to the value of m_{B} existing in the saturated solution.

We find the temperature dependence of K_{s} by applying Eq. 12.1.12:

$$\frac{\text{d}\ln K_{\text{s}}}{\text{d}T} = \frac{\Delta_{\text{sol,B}}H^{\circ}}{RT^2} \tag{12.5.28}$$

At the standard pressure, $\Delta_{\text{sol,B}}H^{\circ}$ is the same as the molar enthalpy of solution at infinite dilution, $\Delta_{\text{sol,B}}H^{\infty}$.

12.6: Liquid-Liquid Equilibria

12.6.1 Miscibility in binary liquid systems

When two different pure liquids are unable to mix in all proportions, they are said to be *partially miscible*. When these liquids are placed in contact with one another and allowed to come to thermal, mechanical, and transfer equilibrium, the result is two coexisting liquid mixtures of different compositions.

Liquids are never actually completely *immiscible*. To take an extreme case, liquid mercury, when equilibrated with water, has some $\mathrm{H_2O}$ dissolved in it, and some mercury dissolves in the water, although the amounts may be too small to measure.

The Gibbs phase rule for a multicomponent system to be described in Sec. 13.1 shows that a two-component, two-phase system at equilibrium has only two independent intensive variables. Thus at a given temperature and pressure, the mole fraction compositions of both phases are fixed; the compositions depend only on the identity of the substances and the temperature and pressure.

Figure 13.5 shows a phase diagram for a typical binary liquid mixture that spontaneously separates into two phases when the temperature is lowered. The thermodynamic conditions for phase separation of this kind were discussed in Sec. 11.1.6. The phase separation is usually the result of positive deviations from Raoult’s law. Typically, when phase separation occurs, one of the substances is polar and the other nonpolar.

12.6.2 Solubility of one liquid in another

Suppose substances A and B are both liquids when pure. In discussing the solubility of liquid B in liquid A, we can treat B as either a solute or as a constituent of a liquid mixture. The difference lies in the choice of the standard state or reference state of B.

We can define the solubility of B in A as the maximum amount of B that can dissolve without phase separation in a given amount of A at the given temperature and pressure. Treating B as a solute, we can express its solubility as the mole fraction of B in the phase at the point of phase separation. The addition of any more B to the system will result in two coexisting liquid phases of fixed composition, one of which will have mole fraction x_{B} equal to its solubility.

Experimentally, the solubility of B in A can be determined from the *cloud point*, the point during titration of A with B at which persistent turbidity is observed.

Consider a system with two coexisting liquid phases α and β containing components A and B. Let α be the A-rich phase and β be the B-rich phase. For example, A could be water and B could be benzene, a hydrophobic substance. Phase α would then be an aqueous phase polluted with a low concentration of dissolved benzene, and phase β would be wet benzene. x_{B}^{α} would be the solubility of the benzene in water, expressed as a mole fraction.

Below, relations are derived for this kind of system using both choices of standard state or reference state.

Solute standard state

Assume that the two components have low mutual solubilities, so that B has a low mole fraction in phase α and a mole fraction close to 1 in phase β. It is then appropriate to treat B as a solute in phase α and as a constituent of a liquid mixture in phase β. The value of x_{B}^{α} is the solubility of liquid B in liquid A.

The equilibrium when two liquid phases are present is $\mathrm{B}(\beta) \rightleftharpoons \mathrm{B}(\alpha)$, and the expression for the thermodynamic equilibrium constant, with the solute standard state based on mole fraction, is

$$K=\frac{a_{x,\mathrm{B}}^{\alpha}}{a_{\mathrm{B}}^{\beta}}=\frac{\Gamma_{x,\mathrm{B}}^{\alpha}\gamma_{x,\mathrm{B}}^{\alpha}x_{\mathrm{B}}^{\alpha}}{\Gamma_{\mathrm{B}}^{\beta}\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}} \tag{12.6.1}$$

The solubility of B is then given by

$$x_{\mathrm{B}}^{\alpha}=\frac{\Gamma_{\mathrm{B}}^{\beta}\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}}{\Gamma_{x,\mathrm{B}}^{\alpha}\gamma_{x,\mathrm{B}}^{\alpha}}K \tag{12.6.2}$$

The values of the pressure factors and activity coefficients are all close to 1, so that the solubility of B in A is given by $x_{\mathrm{B}}^{\alpha}\approx K$. The temperature dependence of the solubility is given by

$$\frac{\mathrm{d}\ln x_{\mathrm{B}}^{\alpha}}{\mathrm{d}T} \approx \frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sol,B}}H^{\circ}}{RT^{2}} \tag{12.6.3}$$

where $\Delta_{\mathrm{sol,B}}H^{\circ}$ is the molar enthalpy change for the transfer at pressure p° of pure liquid solute to the solution at infinite dilution.

$\mathrm{H_2O}$ and *n*-butylbenzene are two liquids with very small mutual solubilities. Figure 12.8 shows that the solubility of *n*-butylbenzene in water exhibits a minimum at about $12\,^{\circ}\mathrm{C}$. Equation 12.6.3 allows us to deduce from this behavior that $\Delta_{\mathrm{sol,B}}H^{\circ}$ is negative below this temperature, and positive above.

Pure-liquid reference state

The condition for transfer equilibrium of component B is $\mu_{\mathrm{B}}^{\alpha} = \mu_{\mathrm{B}}^{\beta}$. If we use a pure-liquid reference state for B in both phases, this condition becomes

$$\mu_{\mathrm{B}}^{*} + RT\ln(\gamma_{\mathrm{B}}^{\alpha}x_{\mathrm{B}}^{\alpha}) = \mu_{\mathrm{B}}^{*} + RT\ln(\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}) \tag{12.6.4}$$

This results in the following relation between the compositions and activity coefficients:

$$\gamma_{\mathrm{B}}^{\alpha}x_{\mathrm{B}}^{\alpha} = \gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta} \tag{12.6.5}$$

As before, we assume the two components have low mutual solubilities, so that the B-rich phase is almost pure liquid B. Then x_{B}^{β} is only slightly less than 1, $\gamma_{\mathrm{B}}^{\beta}$ is close to 1, and Eq. 12.6.5 becomes $x_{\mathrm{B}}^{\alpha} \approx 1/\gamma_{\mathrm{B}}^{\alpha}$. Since x_{B}^{α} is much less than 1, $\gamma_{\mathrm{B}}^{\alpha}$ must be much greater than 1.

In environmental chemistry it is common to use a pure-liquid reference state for a nonpolar liquid solute that has very low solubility in water, so that the aqueous solution is essentially at infinite dilution. Let the nonpolar solute be component B, and let the aqueous phase that is equilibrated with liquid B be phase α. The activity coefficient $\gamma_{\mathrm{B}}^{\alpha}$ is then a *limiting activity coefficient* or *activity coefficient at infinite dilution*. As explained above, the aqueous solubility of B in this case is given by $x_{\mathrm{B}}^{\alpha} \approx 1/\gamma_{\mathrm{B}}^{\alpha}$, and $\gamma_{\mathrm{B}}^{\alpha}$ is much greater than 1.

We can also relate the solubility of B to its Henry's law constant $k_{\mathrm{H,B}}^{\alpha}$. Suppose the two liquid phases are equilibrated not only with one another but also with a gas phase. Since B is equilibrated between phase α and the gas, we have $\gamma_{x,\mathrm{B}}^{\alpha} = f_{\mathrm{B}}/k_{\mathrm{H,B}}^{\alpha}x_{\mathrm{B}}^{\alpha}$ (Table 9.4). From the equilibration of B between phase β and the gas, we also have $\gamma_{\mathrm{B}}^{\beta} = f_{\mathrm{B}}/x_{\mathrm{B}}^{\beta}f_{\mathrm{B}}^{*}$. By eliminating the fugacity f_{B} from these relations, we obtain the general relation

$$x_{\mathrm{B}}^{\alpha} = \frac{\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}f_{\mathrm{B}}^{*}}{\gamma_{x,\mathrm{B}}^{\alpha}k_{\mathrm{H,B}}^{\alpha}} \tag{12.6.6}$$

If we assume as before that the activity coefficients and x_{B}^{β} are close to 1, and that the gas phase behaves ideally, the solubility of B is given by $x_{\mathrm{B}}^{\alpha} \approx p_{\mathrm{B}}^{*}/k_{\mathrm{H,B}}^{\alpha}$, where p_{B}^{*} is the vapor pressure of the pure solute.

12.6.3 Solute distribution between two partially-miscible solvents

Consider a two-component system of two equilibrated liquid phases, α and β. If we add a small quantity of a third component, C, it will distribute itself between the two phases. It is appropriate to treat C as a solute in *both* phases. The thermodynamic equilibrium constant for the equilibrium $\mathrm{C}(\beta) \rightleftharpoons \mathrm{C}(\alpha)$, with solute standard states based on mole fraction, is

$$K = \frac{a_{x,\mathrm{C}}^{\alpha}}{a_{x,\mathrm{C}}^{\beta}} = \frac{\Gamma_{x,\mathrm{C}}^{\alpha}\gamma_{x,\mathrm{C}}^{\alpha}x_{\mathrm{C}}^{\alpha}}{\Gamma_{x,\mathrm{C}}^{\beta}\gamma_{x,\mathrm{C}}^{\beta}x_{\mathrm{C}}^{\beta}} \tag{12.6.7}$$

We define K' as the ratio of the mole fractions of C in the two phases at equilibrium:

$$K' \overset{\mathrm{def}}{=} \frac{x_{\mathrm{C}}^{\alpha}}{x_{\mathrm{C}}^{\beta}} = \frac{\Gamma_{x,\mathrm{C}}^{\beta}\gamma_{x,\mathrm{C}}^{\beta}}{\Gamma_{x,\mathrm{C}}^{\alpha}\gamma_{x,\mathrm{C}}^{\alpha}}K \tag{12.6.8}$$

At a fixed T and p, the pressure factors and equilibrium constant are constants. If x_{C} is low enough in both phases for $\gamma_{x,\mathrm{C}}^{\alpha}$ and $\gamma_{x,\mathrm{C}}^{\beta}$ to be close to unity, K' becomes a constant for the given T and p. The constancy of K' over a range of dilute composition is the **Nernst distribution law**.

Since solute molality and concentration are proportional to mole fraction in dilute solutions, the ratios $m_{\mathrm{C}}^{\alpha}/m_{\mathrm{C}}^{\beta}$ and $c_{\mathrm{C}}^{\alpha}/c_{\mathrm{C}}^{\beta}$ also approach constant values at a given T and p. The ratio of concentrations is called the **partition coefficient** or **distribution coefficient**.

In the limit of infinite dilution of C, the two phases have the compositions that exist when only components A and B are present. As C is added and x_{C}^{α} and x_{C}^{β} increase beyond the region of dilute solution behavior, the ratios $x_{\mathrm{B}}^{\alpha}/x_{\mathrm{A}}^{\alpha}$ and $x_{\mathrm{B}}^{\beta}/x_{\mathrm{A}}^{\beta}$ may change. Continued addition of C may increase the mutual solubilities of A and B, resulting, when enough C has been added, in a single liquid phase containing all three components. It is easier to understand this behavior with the help of a ternary phase diagram such as Fig. 13.17.

12.7: Membrane Equilibria

A semipermeable membrane used to separate two liquid phases can, in principle, be permeable to certain species and impermeable to others. A membrane, however, may not be perfect in this respect over a long time period. We will assume that during the period of observation, those species to which the membrane is supposed to be permeable quickly achieve transfer equilibrium, and only negligible amounts of the other species are transferred across the membrane.

Section 12.2.2 sketched a derivation of the conditions needed for equilibrium in a two-phase system in which a membrane permeable only to solvent separates a solution from pure solvent. We can generalize the results for any system with two liquid phases separated by a semipermeable membrane: in an equilibrium state, both phases must have the same temperature, and any species to which the membrane is permeable must have the same chemical potential in both phases. The two phases, however, need not and usually do not have the same pressure.

12.7.1 Osmotic membrane equilibrium

An equilibrium state in a system with two solutions of the same solvent and different solute compositions, separated by a membrane permeable only to the solvent, is called an **osmotic membrane equilibrium**. We have already seen this kind of equilibrium in an apparatus that measures osmotic pressure (Fig. 12.2).

Consider a system with transfer equilibrium of the solvent across a membrane separating phases α and β. The phases have equal solvent chemical potentials but different pressures:

$$\mu_{\mathrm{A}}^{\beta}(p^{\beta})=\mu_{\mathrm{A}}^{\alpha}(p^{\alpha}) \tag{12.7.1}$$

The dependence of μ_{A} on pressure in a phase of fixed temperature and composition is given by $(\partial\mu_{\mathrm{A}}/\partial p)_{T,\{n_i\}}=V_{\mathrm{A}}$ (from Eq. 9.2.49), where V_{A} is the partial molar volume of A in the phase. If we apply this relation to the solution of phase β, treat the partial molar volume V_{A} as independent of pressure, and integrate at constant temperature and composition from the pressure of phase α to that of phase β, we obtain

$$\mu_{\mathrm{A}}^{\beta}(p^{\beta})=\mu_{\mathrm{A}}^{\beta}(p^{\alpha})+V_{\mathrm{A}}^{\beta}(p^{\beta}-p^{\alpha}) \tag{12.7.2}$$

By equating the two expressions for $\mu_{\mathrm{A}}^{\beta}(p^{\beta})$ and rearranging, we obtain the following expression for the pressure difference needed to achieve transfer equilibrium:

$$p^{\beta}-p^{\alpha}=\frac{\mu_{\mathrm{A}}^{\alpha}(p^{\alpha})-\mu_{\mathrm{A}}^{\beta}(p^{\alpha})}{V_{\mathrm{A}}^{\beta}} \tag{12.7.3}$$

The pressure difference can be related to the osmotic pressures of the two phases. From Eq. 12.2.11, the solvent chemical potential in a solution phase can be written $\mu_{\mathrm{A}}(p)=\mu_{\mathrm{A}}^{*}(p)-V_{\mathrm{A}}\mathit{\Pi}(p)$. Using this to substitute for $\mu_{\mathrm{A}}^{\alpha}(p^{\alpha})$ and $\mu_{\mathrm{A}}^{\beta}(p^{\alpha})$ in Eq. 12.7.3, we obtain

$$p^{\beta}-p^{\alpha}=\mathit{\Pi}^{\beta}(p^{\alpha})-\left(\frac{V_{\mathrm{A}}^{\alpha}}{V_{\mathrm{A}}^{\beta}}\right)\mathit{\Pi}^{\alpha}(p^{\alpha}) \tag{12.7.4}$$

12.7.2 Equilibrium dialysis

Equilibrium dialysis is a useful technique for studying the binding of a small uncharged solute species (a ligand) to a macromolecule. The macromolecule solution is placed on one side of a membrane through which it cannot pass, with a solution without the macromolecule on the other side, and the ligand is allowed to come to transfer equilibrium across the membrane. If the same solute standard state is used for the ligand in both solutions, at equilibrium the unbound ligand must have the same activity in both solutions. Measurements of the total ligand molality in the macromolecule solution and the ligand molality in the other solution, combined with estimated values of the unbound ligand activity coefficients, allow the amount of ligand bound per macromolecule to be calculated.

12.7.3 Donnan membrane equilibrium

If one of the solutions in a two-phase membrane equilibrium contains certain *charged* solute species that are unable to pass through the membrane, whereas other ions can pass through, the situation is more complicated than the osmotic membrane equilibrium described in Sec. 12.7.1. Usually if the membrane is impermeable to one kind of ion, an ion species to which it is permeable achieves transfer equilibrium across the membrane only when the phases have different pressures and different electric potentials. The equilibrium state in this case is a **Donnan membrane equilibrium**, and the resulting electric potential difference across the membrane is called the **Donnan potential**. This phenomenon is related to the membrane potentials that are important in the functioning of nerve and muscle cells (although the cells of a living organism are not, of course, in equilibrium states).

A Donnan potential can be measured electrically, with some uncertainty due to unknown liquid junction potentials, by connecting silver-silver chloride electrodes (described in Sec. 14.1) to both phases through salt bridges.

General expressions

Consider solution phases α and β separated by a semipermeable membrane. Both phases contain a dissolved salt, designated solute B, that has ν_+ cations and ν_- anions in each formula unit. The membrane is permeable to these ions. Phase β also contains a protein or other polyelectrolyte with a net positive or negative charge, together with counterions of the opposite charge that are the same species as the cation or anion of the salt. The presence of the counterions in phase β prevents the cation and anion of the salt from being present in stoichiometric amounts in this phase. The membrane is impermeable to the polyelectrolyte, perhaps because the membrane pores are too small to allow the polyelectrolyte to pass through.

The condition for transfer equilibrium of solute B is $\mu^\alpha_{\mathrm{B}} = \mu^\beta_{\mathrm{B}}$, or

$$(\mu^\circ_{m,\mathrm{B}})^\alpha + RT\ln a^\alpha_{m,\mathrm{B}} = (\mu^\circ_{m,\mathrm{B}})^\beta + RT\ln a^\beta_{m,\mathrm{B}} \tag{12.7.5}$$

Solute B has the same standard state in the two phases, so that $(\mu^\circ_{m,\mathrm{B}})^\alpha$ and $(\mu^\circ_{m,\mathrm{B}})^\beta$ are equal. The activities $a^\alpha_{m,\mathrm{B}}$ and $a^\beta_{m,\mathrm{B}}$ are therefore equal at equilibrium. Using the expression for solute activity from Eq. 10.3.16, which is valid for a multisolute solution, we find that at transfer equilibrium the following relation must exist between the molalities of the salt ions in the two phases:

$$\Gamma^\alpha_{m,\mathrm{B}}(\gamma^\alpha_\pm)^\nu(m^\alpha_+)^{\nu_+}(m^\alpha_-)^{\nu_-} = \Gamma^\beta_{m,\mathrm{B}}\left(\gamma^\beta_\pm\right)^\nu\left(m^\beta_+\right)^{\nu_+}\left(m^\beta_-\right)^{\nu_-} \tag{12.7.6}$$

To find an expression for the Donnan potential, we can equate the single-ion chemical potentials of the salt cation: $\mu^\alpha_+(\phi^\alpha) = \mu^\beta_+(\phi^\beta)$. When we use the expression of Eq. 10.1.15 for $\mu_+(\phi)$, we obtain

$$\phi^\alpha - \phi^\beta = \frac{RT}{z_+F}\ln\frac{\Gamma^\beta_+\gamma^\beta_+m^\beta_+}{\Gamma^\alpha_+\gamma^\alpha_+m^\alpha_+} \tag{12.7.7}$$

(Donnan potential)

The condition needed for an osmotic membrane equilibrium related to the solvent can be written

$$\mu^\beta_{\mathrm{A}}(p^\beta) - \mu^\alpha_{\mathrm{A}}(p^\alpha) = 0 \tag{12.7.8}$$

The chemical potential of the solvent is $\mu_{\mathrm{A}} = \mu^\circ_{\mathrm{A}} + RT\ln a_{\mathrm{A}} = \mu^\circ_{\mathrm{A}} + RT\ln(\Gamma_{\mathrm{A}}\gamma_{\mathrm{A}}x_{\mathrm{A}})$. From Table 9.6, we have to a good approximation the expression $RT\ln\Gamma_{\mathrm{A}} = V^*_{\mathrm{A}}(p - p^\circ)$. With these substitutions, Eq. 12.7.8 becomes

$$RT\ln\frac{\gamma^\beta_{\mathrm{A}}x^\beta_{\mathrm{A}}}{\gamma^\alpha_{\mathrm{A}}x^\alpha_{\mathrm{A}}} + V^*_{\mathrm{A}}\left(p^\beta - p^\alpha\right) = 0 \tag{12.7.9}$$

We can use this equation to estimate the pressure difference needed to maintain an equilibrium state. For dilute solutions, with $\gamma^\alpha_{\mathrm{A}}$ and $\gamma^\beta_{\mathrm{A}}$ set equal to 1, the equation becomes

$$p^\beta - p^\alpha \approx \frac{RT}{V^*_{\mathrm{A}}}\ln\frac{x^\alpha_{\mathrm{A}}}{x^\beta_{\mathrm{A}}} \tag{12.7.10}$$

In the limit of infinite dilution, $\ln x_{\mathrm{A}}$ can be replaced by $-M_{\mathrm{A}}\sum_{i\neq\mathrm{A}} m_i$ (Eq. 9.6.12), giving the relation

$$p^\beta - p^\alpha \approx \frac{M_{\mathrm{A}}RT}{V^*_{\mathrm{A}}}\sum_{i\neq\mathrm{A}}\left(m^\beta_i - m^\alpha_i\right) = \rho^*_{\mathrm{A}}RT\sum_{i\neq\mathrm{A}}\left(m^\beta_i - m^\alpha_i\right) \tag{12.7.11}$$

Example

As a specific example of a Donnan membrane equilibrium, consider a system in which an aqueous solution of a polyelectrolyte with a net negative charge, together with a counterion M^+ and a salt MX of the counterion, is equilibrated with an aqueous solution of the salt across a semipermeable membrane. The membrane is permeable to the H_2O solvent and to the ions M^+ and X^-, but is impermeable to the polyelectrolyte. The species in phase α are H_2O, M^+, and X^-; those in phase β are H_2O, M^+, X^-, and the polyelectrolyte. In an equilibrium state, the two phases have the same temperature but different compositions, electric potentials, and pressures.

Because the polyelectrolyte in this example has a negative charge, the system has more M^+ ions than X^- ions. Figure 12.9(a) is a schematic representation of an initial state of this kind of system. Phase β is shown as a solution confined to a closed dialysis bag immersed in phase α. The number of cations and anions shown in each phase indicate the relative amounts of these ions.

For simplicity, let us assume the two phases have equal masses of water, so that the molality of an ion is proportional to its amount by the same ratio in both phases. It is clear that in the initial state shown in the figure, the chemical potentials of both M^+ and X^- are greater in phase β (greater amounts) than in phase α, and this is a nonequilibrium state. A certain quantity of salt MX will therefore pass spontaneously through the membrane from phase β to phase α until equilibrium is attained.

The equilibrium ion molalities must agree with Eq. 12.7.6. We make the approximation that the pressure factors and mean ionic activity coefficients are unity. Then for the present example, with $\nu_+ = \nu_- = 1$, the equation becomes

$$m_+^\alpha m_-^\alpha \approx m_+^\beta m_-^\beta \tag{12.7.12}$$

There is furthermore an electroneutrality condition for each phase:

$$m_+^\alpha = m_-^\alpha \qquad m_+^\beta = m_-^\beta + |z_\mathrm{P}| m_\mathrm{P} \tag{12.7.13}$$

Here z_P is the negative charge of the polyelectrolyte, and m_P is its molality. Substitution of these expressions into Eq. 12.7.12 gives the relation

$$(m_-^\alpha)^2 \approx \left(m_-^\beta + |z_\mathrm{P}| m_\mathrm{P}\right) m_-^\beta \tag{12.7.14}$$

This shows that in the equilibrium state, m_-^α is greater than m_-^β. Then Eq. 12.7.12 shows that m_+^α is less than m_+^β. These equilibrium molalities are depicted in Fig. 12.9(b).

The chemical potential of a cation, its activity, and the electric potential of the phase are related by Eq. 10.1.9: $\mu_+ = \mu_+^\circ + RT \ln a_+ + z_+ F\phi$. In order for M^+ to have the same chemical potential in both phases, despite its lower activity in phase α, the electric potential of phase α must be greater than that of phase β. Thus the Donnan potential $\phi^\alpha - \phi^\beta$ in the present example is positive. Its value can be estimated from Eq. 12.7.7 with the values of the single-ion pressure factors and activity coefficients approximated by 1 and with z_+ for this example set equal to 1:

$$\phi^\alpha - \phi^\beta \approx \frac{RT}{F} \ln \frac{m_+^\beta}{m_+^\alpha} \tag{12.7.15}$$

> The existence of a Donnan potential in the equilibrium state is the result of a very small departure of the phases on both sides of the membrane from exact electroneutrality. In the example, phase α has a minute net positive charge and phase β has a net negative charge of equal magnitude. The amount of M^+ ion transferred across the membrane to achieve equilibrium is slightly greater than the amount of X^- ion transferred; the difference between these two amounts is far too small to be measured chemically. At equilibrium, the excess charge on each side of the membrane is distributed over the boundary surface of the solution phase on that side, and is not part of the bulk phase composition.

The pressure difference $p^\beta - p^\alpha$ at equilibrium can be estimated with Eq. 12.7.11, and for the present example is found to be positive. Without this pressure difference, the solution in phase α would move spontaneously through the membrane into phase β until phase α completely disappears. With phase α open to the atmosphere, as in Fig. 12.9, the volume of phase β must be constrained in order to allow its pressure to differ from atmospheric pressure. If the volume of phase β remains practically constant, the transfer of a minute quantity of solvent across the membrane is sufficient to cause the pressure difference.

It should be clear that the existence of a Donnan membrane equilibrium introduces complications that would make it difficult to use a measured pressure difference to estimate the molar mass of the polyelectrolyte by the method of Sec. 12.4, or to study the binding of a charged ligand by equilibrium dialysis.

12.8: Liquid-Gas Equilibria

This section describes multicomponent systems in which a liquid phase is equilibrated with a gas phase.

12.8.1 Effect of liquid pressure on gas fugacity

If we vary the pressure of a liquid mixture at constant temperature and composition, there is a small effect on the fugacity of each volatile component in an equilibrated gas phase. One way to vary the pressure at essentially constant liquid composition is to change the partial pressure of a component of the gas phase that has negligible solubility in the liquid.

At transfer equilibrium, component i has the same chemical potential in both phases: $\mu_i(\mathrm{l}) = \mu_i(\mathrm{g})$. Combining the relations $[\partial\mu_i(\mathrm{l})/\partial p]_{T,\{n_i\}} = V_i(\mathrm{l})$ and $\mu_i(\mathrm{g}) = \mu_i^\circ(\mathrm{g}) + RT\ln(f_i/p^\circ)$ (Eqs. 9.2.49 and 9.3.12), we obtain

$$\frac{\mathrm{d}\ln(f_i/p^\circ)}{\mathrm{d}p} = \frac{V_i(\mathrm{l})}{RT} \tag{12.8.1}$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

Equation 12.8.1 shows that an increase in pressure, at constant temperature and liquid composition, causes an increase in the fugacity of each component in the gas phase.

Integration of Eq. 12.8.1 between pressures p_1 and p_2 yields

$$f_i(p_2) = f_i(p_1)\exp\left[\int_{p_1}^{p_2} \frac{V_i(\mathrm{l})}{RT}\,\mathrm{d}p\right] \tag{12.8.2}$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

The exponential on the right side is called the **Poynting factor**.

The integral in the Poynting factor is simplified if we make the approximation that $V_i(\mathrm{l})$ is independent of pressure. Then we obtain the approximate relation

$$f_i(p_2) \approx f_i(p_1)\exp\left[\frac{V_i(\mathrm{l})(p_2 - p_1)}{RT}\right] \tag{12.8.3}$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

> The effect of pressure on fugacity is usually small, and can often be neglected. For typical values of the partial molar volume $V_i(\mathrm{l})$, the exponential factor is close to unity unless $|p_2 - p_1|$ is very large. For instance, for $V_i(\mathrm{l}) = 100\ \mathrm{cm^3\ mol^{-1}}$ and $T = 300\ \mathrm{K}$, we obtain a value for the ratio $f_i(p_2)/f_i(p_1)$ of 1.004 if $p_2 - p_1$ is 1 bar, 1.04 if $p_2 - p_1$ is 10 bar, and 1.5 if $p_2 - p_1$ is 100 bar. Thus, unless the pressure change is large, we can to a good approximation neglect the effect of total pressure on fugacity. This statement applies only to the fugacity of a substance in a gas phase that is equilibrated with a liquid phase of constant composition containing the same substance. If the liquid phase is absent, the fugacity of i in a gas phase of constant composition is of course approximately proportional to the total gas pressure.

We can apply Eqs. 12.8.2 and 12.8.3 to *pure* liquid A, in which case $V_i(\mathrm{l})$ is the molar volume $V_\mathrm{A}^*(\mathrm{l})$. Suppose we have pure liquid A in equilibrium with pure gaseous A at a certain temperature. This is a one-component, two-phase equilibrium system with one degree of freedom (Sec. 8.1.7), so that at the given temperature the value of the pressure is fixed. This pressure is the saturation vapor pressure of pure liquid A at this temperature. We can make the pressure p greater than the saturation vapor pressure by adding a second substance to the gas phase that is essentially insoluble in the liquid, without changing the temperature or volume. The fugacity f_A is greater at this higher pressure than it was at the saturation vapor pressure. The vapor pressure p_A, which is approximately equal to f_A, has now become greater than the saturation vapor pressure. It is, however, safe to say that the difference is negligible unless the difference between p and p_A is much greater than 1 bar.

As an application of these relations, consider the effect of the size of a liquid droplet on the equilibrium vapor pressure. The calculation of Prob. 12.8(b) shows that the fugacity of H_2O in a gas phase equilibrated with liquid water in a small droplet is slightly greater than when the liquid is in a bulk phase. The smaller the radius of the droplet, the greater is the fugacity and the vapor pressure.

12.8.2 Effect of liquid composition on gas fugacities

Consider system 1 in Fig. 9.5. A binary liquid mixture of two volatile components, A and B, is equilibrated with a gas mixture containing A, B, and a third gaseous component C of negligible solubility used to control the total pressure. In order for A and B to be in transfer equilibrium, their chemical potentials must be the same in both phases:

$$\mu_{\mathrm{A}}(\mathrm{l})=\mu_{\mathrm{A}}^{\circ}(\mathrm{g})+RT\ln\frac{f_{\mathrm{A}}}{p^{\circ}}\qquad \mu_{\mathrm{B}}(\mathrm{l})=\mu_{\mathrm{B}}^{\circ}(\mathrm{g})+RT\ln\frac{f_{\mathrm{B}}}{p^{\circ}} \tag{12.8.4}$$

Suppose we make an infinitesimal change in the liquid composition at constant T and p. This causes infinitesimal changes in the chemical potentials and fugacities:

$$\mathrm{d}\mu_{\mathrm{A}}(\mathrm{l})=RT\frac{\mathrm{d}f_{\mathrm{A}}}{f_{\mathrm{A}}}\qquad \mathrm{d}\mu_{\mathrm{B}}(\mathrm{l})=RT\frac{\mathrm{d}f_{\mathrm{B}}}{f_{\mathrm{B}}} \tag{12.8.5}$$

By inserting these expressions in the Gibbs–Duhem equation $x_{\mathrm{A}}\,\mathrm{d}\mu_{\mathrm{A}}=-x_{\mathrm{B}}\,\mathrm{d}\mu_{\mathrm{B}}$ (Eq. 9.2.43), we obtain

$$\frac{x_{\mathrm{A}}}{f_{\mathrm{A}}}\,\mathrm{d}f_{\mathrm{A}}=-\frac{x_{\mathrm{B}}}{f_{\mathrm{B}}}\,\mathrm{d}f_{\mathrm{B}} \tag{12.8.6}$$

(binary liquid mixture equilibrated with gas, constant T and p)

This equation is a relation between changes in gas-phase fugacities caused by a change in the liquid-phase composition. It shows that a composition change at constant T and p that increases the fugacity of A in the equilibrated gas phase must decrease the fugacity of B.

Now let us treat the liquid mixture as a binary solution with component B as the solute. In the ideal-dilute region, at constant T and p, the solute obeys Henry's law for fugacity:

$$f_{\mathrm{B}}=k_{\mathrm{H,B}}x_{\mathrm{B}} \tag{12.8.7}$$

For composition changes in the ideal-dilute region, we can write

$$\frac{\mathrm{d}f_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}}=k_{\mathrm{H,B}}=\frac{f_{\mathrm{B}}}{x_{\mathrm{B}}} \tag{12.8.8}$$

With the substitution $\mathrm{d}x_{\mathrm{B}}=-\mathrm{d}x_{\mathrm{A}}$ and rearrangement, Eq. 12.8.8 becomes

$$-\frac{x_{\mathrm{B}}}{f_{\mathrm{B}}}\,\mathrm{d}f_{\mathrm{B}}=\mathrm{d}x_{\mathrm{A}} \tag{12.8.9}$$

Combined with Eq. 12.8.6, this is $(x_{\mathrm{A}}/f_{\mathrm{A}})\,\mathrm{d}f_{\mathrm{A}}=\mathrm{d}x_{\mathrm{A}}$, which we can rearrange and integrate as follows within the ideal-dilute region:

$$\int_{f_{\mathrm{A}}^{*}}^{f_{\mathrm{A}}'}\frac{\mathrm{d}f_{\mathrm{A}}}{f_{\mathrm{A}}}=\int_{1}^{x_{\mathrm{A}}'}\frac{\mathrm{d}x_{\mathrm{A}}}{x_{\mathrm{A}}}\qquad \ln\frac{f_{\mathrm{A}}'}{f_{\mathrm{A}}^{*}}=\ln x_{\mathrm{A}}' \tag{12.8.10}$$

The result is

$$f_{\mathrm{A}}=x_{\mathrm{A}}f_{\mathrm{A}}^{*} \tag{12.8.11}$$

(ideal-dilute binary solution)

Here f_{A}^{*} is the fugacity of A in a gas phase equilibrated with pure liquid A at the same T and p as the mixture. Equation 12.8.11 is Raoult's law for fugacity applied to component A.

If component B obeys Henry's law at all compositions, then the Henry's law constant $k_{\mathrm{H,B}}$ is equal to f_{B}^{*} and B obeys Raoult's law, $f_{\mathrm{B}}=x_{\mathrm{B}}f_{\mathrm{B}}^{*}$, over the entire range of x_{B}.

We can draw two conclusions:

1. Figure 12.11 illustrates the case of a binary mixture in which component B has only positive deviations from Raoult's law, whereas component A has both positive and negative deviations (f_{A} is slightly less than $x_{\mathrm{A}}f_{\mathrm{A}}^{*}$ for x_{B} less than 0.3). This

unusual behavior is possible because both fugacity curves have two inflection points instead of the usual one. Other types of unusual nonideal behavior are possible (M. L. McGlashan, *J. Chem. Educ.*, **40**, 516–518, 1963).

12.8.3 The Duhem–Margules equation

To a good approximation, by assuming an ideal gas mixture and neglecting the effect of total pressure on fugacity, we can apply Eq. 12.8.20 to a liquid–gas system in which the total pressure is *not* constant, but instead is the sum of p_{A} and p_{B}. Under these conditions, we obtain the following expression for the rate at which the total pressure changes with the liquid composition at constant T:

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}x_{\mathrm{A}}} &= \frac{\mathrm{d}(p_{\mathrm{A}}+p_{\mathrm{B}})}{\mathrm{d}x_{\mathrm{A}}} = \frac{\mathrm{d}p_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{A}}} - \frac{x_{\mathrm{A}}p_{\mathrm{B}}}{x_{\mathrm{B}}p_{\mathrm{A}}}\frac{\mathrm{d}p_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{A}}} = \frac{\mathrm{d}p_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{A}}}\left(1-\frac{x_{\mathrm{A}}/x_{\mathrm{B}}}{p_{\mathrm{A}}/p_{\mathrm{B}}}\right) \\ &= \frac{\mathrm{d}p_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{A}}}\left(1-\frac{x_{\mathrm{A}}/x_{\mathrm{B}}}{y_{\mathrm{A}}/y_{\mathrm{B}}}\right)\end{aligned} \tag{12.8.21}$$

Here y_{A} and y_{B} are the mole fractions of A and B in the gas phase given by $y_{\mathrm{A}} = p_{\mathrm{A}}/p$ and $y_{\mathrm{B}} = p_{\mathrm{B}}/p$.

We can use Eq. 12.8.21 to make several predictions for a binary liquid–gas system at constant T.

- In some binary liquid–gas systems, the total pressure at constant temperature exhibits a maximum or minimum at a particular liquid composition. At this composition, $\mathrm{d}p/\mathrm{d}x_{\mathrm{A}}$ is zero but $\mathrm{d}p_{\mathrm{A}}/\mathrm{d}x_{\mathrm{A}}$ is positive. From Eq. 12.8.21, we see that at this composition $x_{\mathrm{A}}/x_{\mathrm{B}}$ must equal $y_{\mathrm{A}}/y_{\mathrm{B}}$, meaning that the liquid and gas phases have identical mole fraction compositions. The liquid with this composition is called an *azeotrope*. The behavior of systems with azeotropes will be discussed in Sec. 13.2.5.

12.8.4 Gas solubility

The activity of B in the gas phase is given by $a_{\mathrm{B}}(\mathrm{g}) = f_{\mathrm{B}}/p^{\circ}$. If the solute is a nonelectrolyte and we choose a standard state based on mole fraction, the activity in the solution is $a_{\mathrm{B}}(\mathrm{sln}) = \Gamma_{x,\mathrm{B}}\gamma_{x,\mathrm{B}}x_{\mathrm{B}}$. The equilibrium constant is then given by

$$K = \frac{\Gamma_{x,\mathrm{B}}\gamma_{x,\mathrm{B}}x_{\mathrm{B}}}{f_{\mathrm{B}}/p^{\circ}} \tag{12.8.22}$$

and the solubility, expressed as the equilibrium mole fraction of solute in the solution, is given by

$$x_{\mathrm{B}} = \frac{Kf_{\mathrm{B}}/p^{\circ}}{\Gamma_{x,\mathrm{B}}\gamma_{x,\mathrm{B}}} \tag{12.8.23}$$

(nonelectrolyte solute in equilibrium with gas)

At a fixed T and p, the values of K and $\Gamma_{x,\mathrm{B}}$ are constant. Therefore any change in the solution composition that increases the value of the activity coefficient $\gamma_{x,\mathrm{B}}$ will decrease the solubility for the same gas fugacity. This solubility decrease is often what happens when a salt is dissolved in an aqueous solution, and is known as the *salting-out effect* (Prob. 12.11).

Unless the pressure is much greater than p°, we can with negligible error set the pressure factor $\Gamma_{x,\mathrm{B}}$ equal to 1. When the gas solubility is low and the solution contains no other solutes, the activity coefficient $\gamma_{x,\mathrm{B}}$ is close to 1. If furthermore we assume ideal gas behavior, then Eq. 12.8.23 becomes

$$x_{\mathrm{B}} = K\frac{p_{\mathrm{B}}}{p^{\circ}} \tag{12.8.24}$$

(nonelectrolyte solute in equilibrium with ideal gas, $\Gamma_{x,\mathrm{B}}=1$, $\gamma_{x,\mathrm{B}}=1$)

The solubility is predicted to be proportional to the partial pressure. The solubility of a gas that dissociates into ions in solution has a quite different dependence on partial pressure. An example is the solubility of gaseous HCl in water to form an electrolyte solution, shown in Fig. 10.1.

If the actual conditions are close to those assumed for Eq. 12.8.24, we can use Eq. 12.1.13 to derive an expression for the temperature dependence of the solubility for a fixed partial pressure of the gas:

$$\left(\frac{\partial \ln x_{\mathrm{B}}}{\partial T}\right)_{p_{\mathrm{B}}} = \frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sol,B}}H^{\circ}}{RT^2} \tag{12.8.25}$$

At the standard pressure, $\Delta_{\text{sol,B}}H^{\circ}$ is the same as the molar enthalpy of solution at infinite dilution.

Since the dissolution of a gas in a liquid is invariably an exothermic process, $\Delta_{\text{sol,B}}H^{\circ}$ is negative, and Eq. 12.8.25 predicts the solubility decreases with increasing temperature.

Note the similarity of Eq. 12.8.25 and the expressions derived previously for the temperature dependence of the solubilities of solids (Eq. 12.5.8) and liquids (Eq. 12.6.3). When we substitute the mathematical identity $\mathrm{d}T = -T^2\,\mathrm{d}(1/T)$, Eq. 12.8.25 becomes

$$\left[\frac{\partial \ln x_{\text{B}}}{\partial(1/T)}\right]_{p_{\text{B}}} = -\frac{\Delta_{\text{sol,B}}H^{\circ}}{R} \tag{12.8.26}$$

We can use this form to evaluate $\Delta_{\text{sol,B}}H^{\circ}$ from a plot of $\ln x_{\text{B}}$ versus $1/T$.

The **ideal solubility** of a gas is the solubility calculated on the assumption that the dissolved gas obeys Raoult's law for partial pressure: $p_{\text{B}} = x_{\text{B}}p^{*}_{\text{B}}$. The ideal solubility, expressed as a mole fraction, is then given as a function of partial pressure by

$$x_{\text{B}} = \frac{p_{\text{B}}}{p^{*}_{\text{B}}} \tag{12.8.27}$$

(ideal solubility of a gas)

Here p^{*}_{B} is the vapor pressure of pure liquid solute at the same temperature and total pressure as the solution. If the pressure is too low for pure B to exist as a liquid at this temperature, we can with little error replace p^{*}_{B} with the saturation vapor pressure of liquid B at the same temperature, because the effect of total pressure on the vapor pressure of a liquid is usually negligible (Sec. 12.8.1). If the temperature is above the critical temperature of pure B, we can estimate a hypothetical vapor pressure by extrapolating the liquid–vapor coexistence curve beyond the critical point.

We can use Eq. 12.8.27 to make several predictions regarding the ideal solubility of a gas at a fixed value of p_{B}.

1. Of course, these predictions apply only to solutions that behave approximately as ideal liquid mixtures, but even for many nonideal mixtures the predictions are found to have good agreement with experiment.

> As an example of the general validity of prediction 1, Hildebrand and Scott (*The Solubility of Nonelectrolytes*, 3rd edition, Dover, New York, 1964, Chap. XV) list the following solubilities of gaseous Cl_2 in several dissimilar solvents at $0\,^{\circ}\text{C}$ and a partial pressure of $1.01\,\text{bar}$: $x_{\text{B}} = 0.270$ in heptane, $x_{\text{B}} = 0.288$ in SiCl_4, and $x_{\text{B}} = 0.298$ in CCl_4. These values are similar to one another and close to the ideal value $p_{\text{B}}/p^{*}_{\text{B}} = 0.273$.

12.8.5 Effect of temperature and pressure on Henry's law constants

At the standard pressure $p^{\circ} = 1\,\text{bar}$, the value of $\Gamma_{x,\text{B}}$ is unity, and Eqs. 12.1.13 and 12.1.14 then give the following expressions for the dependence of the dimensionless quantity $k_{\text{H,B}}/p^{\circ}$ on temperature:

$$\frac{\mathrm{d}\ln(k_{\text{H,B}}/p^{\circ})}{\mathrm{d}T} = -\frac{\mathrm{d}\ln K}{\mathrm{d}T} = -\frac{\Delta_{\text{sol,B}}H^{\circ}}{RT^2} \tag{12.8.31}$$

$(p{=}p^{\circ})$

$$\frac{\mathrm{d}\ln(k_{\text{H,B}}/p^{\circ})}{\mathrm{d}(1/T)} = -\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\Delta_{\text{sol,B}}H^{\circ}}{R} \tag{12.8.32}$$

$(p{=}p^{\circ})$

These expressions can be used with little error at any pressure that is not much greater than p°, say up to at least $2\,\text{bar}$, because under these conditions $\Gamma_{x,\text{B}}$ does not differ appreciably from unity.

To find the dependence of $k_{\text{H,B}}$ on pressure, we substitute $\Gamma_{x,\text{B}}$ in Eq. 12.8.30 with the expression for $\Gamma_{x,\text{B}}$ at pressure p' found in Table 9.6:

$$k_{\text{H,B}}(p') = \frac{\Gamma_{x,\text{B}}(p')p^{\circ}}{K} = \frac{p^{\circ}}{K}\exp\left(\int_{p^{\circ}}^{p'} \frac{V^{\infty}_{\text{B}}}{RT}\,\mathrm{d}p\right) \tag{12.8.33}$$

We can use Eq. 12.8.33 to compare the values of $k_{\text{H,B}}$ at the same temperature and two different pressures, p_1 and p_2:

$$k_{\mathrm{H,B}}(p_2) = k_{\mathrm{H,B}}(p_1)\exp\left(\int_{p_1}^{p_2} \frac{V_{\mathrm{B}}^{\infty}}{RT}\,\mathrm{d}p\right) \tag{12.8.34}$$

An approximate version of this relation, found by treating V_{B}^{∞} as independent of pressure, is

$$k_{\mathrm{H,B}}(p_2) \approx k_{\mathrm{H,B}}(p_1)\exp\left[\frac{V_{\mathrm{B}}^{\infty}(p_2 - p_1)}{RT}\right] \tag{12.8.35}$$

Unless $|p_2 - p_1|$ is much greater than 1 bar, the effect of pressure on $k_{\mathrm{H,B}}$ is small; see Prob. 12.12 for an example.

12.9: Reaction Equilibria

The definition of the thermodynamic equilibrium constant of a reaction or other chemical process is given by Eq. 11.8.9:

$$K=\prod_i (a_i)_{\text{eq}}^{\nu_i} \tag{12.9.1}$$

The activity a_i of each reactant or product species is based on an appropriate standard state. We can replace each activity on the right side of Eq. 12.9.1 by an expression in Table 12.2.

For example, consider the following heterogeneous equilibrium that is important in the formation of limestone caverns:

$$\mathrm{CaCO_3(cr,\,calcite)+CO_2(g)+H_2O(sln)} \rightleftharpoons \mathrm{Ca^{2+}(aq)+2\,HCO_3^-(aq)} \tag{12.9.1}$$

If we treat H_2O as a solvent and Ca^{2+} and $HCO_3{}^-$ as the solute species, then we write the thermodynamic equilibrium constant as follows:

$$K=\frac{a_+a_-^2}{a_{\mathrm{CaCO_3}}a_{\mathrm{CO_2}}a_{\mathrm{H_2O}}}=\varGamma_{\mathrm{r}}\frac{\gamma_+\gamma_-^2 m_+m_-^2/(m^\circ)^3}{(f_{\mathrm{CO_2}}/p^\circ)\,\gamma_{\mathrm{H_2O}}x_{\mathrm{H_2O}}} \tag{12.9.2}$$

The subscripts $+$ and $-$ refer to the Ca^{2+} and $HCO_3{}^-$ ions, and all quantities are for the system at reaction equilibrium. $\varGamma_{\mathrm{r}}$ is the proper quotient of pressure factors, given for this reaction by

$$\varGamma_{\mathrm{r}}=\frac{\varGamma_+\varGamma_-^2}{\varGamma_{\mathrm{CaCO_3}}\varGamma_{\mathrm{H_2O}}} \tag{12.9.3}$$

Unless the pressure is very high, we can with little error set the value of $\varGamma_{\mathrm{r}}$ equal to unity.

The product $\varGamma_+\varGamma_-^2$ in the numerator of Eq. 12.9.3 is the pressure factor $\varGamma_{m,\mathrm{B}}$ for the solute $Ca(HCO_3)_2$ (see Eq. 10.3.11).

Equation 12.9.2 is an example of a “mixed” equilibrium constant—one using more than one kind of standard state. From the definition of the mean ionic activity coefficient (Eq. 10.3.7), we can replace the product $\gamma_+\gamma_-^2$ by $\gamma_\pm^3$, where $\gamma_\pm$ is the mean ionic activity coefficient of aqueous $Ca(HCO_3)_2$:

$$K=\varGamma_{\mathrm{r}}\frac{\gamma_\pm^3 m_+m_-^2/(m^\circ)^3}{(f_{\mathrm{CO_2}}/p^\circ)\,\gamma_{\mathrm{H_2O}}x_{\mathrm{H_2O}}} \tag{12.9.4}$$

Instead of treating the aqueous Ca^{2+} and $HCO_3{}^-$ ions as solute species, we can regard the dissolved $Ca(HCO_3)_2$ electrolyte as the solute and write

$$K=\frac{a_{m,\mathrm{B}}}{a_{\mathrm{CaCO_3}}a_{\mathrm{CO_2}}a_{\mathrm{H_2O}}} \tag{12.9.5}$$

We then obtain Eq. 12.9.4 by replacing $a_{m,\mathrm{B}}$ with the expression in Table 12.2 for an electrolyte solute.

The value of K depends only on T, and the value of $\varGamma_{\mathrm{r}}$ depends only on T and p. Suppose we dissolve some NaCl in the aqueous phase while maintaining the system at constant T and p. The increase in the ionic strength will alter $\gamma_\pm$ and necessarily cause a compensating change in the solute molarity in order for the system to remain in reaction equilibrium.

An example of a different kind of reaction equilibrium is the dissociation (ionization) of a weak monoprotic acid such as acetic acid

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)+A^-(aq)} \tag{12.9.2}$$

for which the thermodynamic equilibrium constant (the *acid dissociation constant*) is

$$K_{\mathrm{a}}=\varGamma_{\mathrm{r}}\frac{\gamma_+\gamma_-m_+m_-}{\gamma_{m,\mathrm{HA}}m_{\mathrm{HA}}m^\circ}=\varGamma_{\mathrm{r}}\frac{\gamma_\pm^2 m_+m_-}{\gamma_{m,\mathrm{HA}}m_{\mathrm{HA}}m^\circ} \tag{12.9.6}$$

Suppose the solution is prepared from water and the acid, and H^+ from the dissociation of H_2O is negligible compared to H^+ from the acid dissociation. We may then write $m_+=m_-=\alpha m_{\mathrm{B}}$, where α is the degree of dissociation and m_{B} is the overall molality of the acid. The molality of the undissociated acid is $m_{\mathrm{HA}}=(1-\alpha)m_{\mathrm{B}}$, and the dissociation constant can be written

$$K_{\mathrm{a}} = \mathit{\Gamma}_{\mathrm{r}} \frac{\gamma_{\pm}^{2} \alpha^{2} m_{\mathrm{B}} / m^{\circ}}{\gamma_{m,\mathrm{HA}} (1-\alpha)} \tag{12.9.7}$$

From this equation, we see that a change in the ionic strength that decreases $\gamma_{\pm}$ when T, p, and m_{B} are held constant must increase the degree of dissociation (Prob. 12.17).

12.10: Evaluation of Standard Molar Quantities

Some of the most useful experimentally-derived data for thermodynamic calculations are values of standard molar reaction enthalpies, standard molar reaction Gibbs energies, and standard molar reaction entropies. The values of these quantities for a given reaction are related, as we know (Eq. 11.8.21), by

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \tag{12.10.1}$$

and $\Delta_r S^\circ$ can be calculated from the standard molar entropies of the reactants and products using Eq. 11.8.22:

$$\Delta_r S^\circ = \sum_i \nu_i S_i^\circ \tag{12.10.2}$$

The standard molar quantities appearing in Eqs. 12.10.1 and 12.10.2 can be evaluated through a variety of experimental techniques. Reaction calorimetry can be used to evaluate $\Delta_r H^\circ$ for a reaction (Sec. 11.5). Calorimetric measurements of heat capacity and phase-transition enthalpies can be used to obtain the value of S_i° for a solid or liquid (Sec. 6.2.1). For a gas, spectroscopic measurements can be used to evaluate S_i° (Sec. 6.2.2). Evaluation of a thermodynamic equilibrium constant and its temperature derivative, for any of the kinds of equilibria discussed in this chapter (vapor pressure, solubility, chemical reaction, etc.), can provide values of $\Delta_r G^\circ$ and $\Delta_r H^\circ$ through the relations $\Delta_r G^\circ = -RT\ln K$ and $\Delta_r H^\circ = -R\,\mathrm{d}\ln K/\,\mathrm{d}(1/T)$.

In addition to these methods, measurements of cell potentials are useful for a reaction that can be carried out reversibly in a galvanic cell. Section 14.3.3 will describe how the standard cell potential and its temperature derivative allow $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ to be evaluated for such a reaction.

An efficient way of tabulating the results of experimental measurements is in the form of standard molar enthalpies and Gibbs energies of *formation*. These values can be used to generate the values of standard molar reaction quantities for reactions not investigated directly. The relations between standard molar reaction and formation quantities (Sec. 11.3.2) are

$$\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i) \qquad \Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \tag{12.10.3}$$

and for ions the conventions used are

$$\Delta_f H^\circ(\mathrm{H^+, aq}) = 0 \qquad \Delta_f G^\circ(\mathrm{H^+, aq}) = 0 \qquad S_m^\circ(\mathrm{H^+, aq}) = 0 \tag{12.10.4}$$

Appendix H gives an abbreviated set of values of $\Delta_f H^\circ$, S_m°, and $\Delta_f G^\circ$ at $298.15\,\mathrm{K}$

For examples of the evaluation of standard molar reaction quantities and standard molar formation quantities from measurements made by various experimental techniques, see Probs. 12.18–12.20, 14.3, and 14.4.

12.11: Chapter 12 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

12.1

Consider the heterogeneous equilibrium $\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$. Table 12.3 lists pressures measured over a range of temperatures for this system.

12.14

The method described in Prob. 12.13 has been used to obtain high-precision values of the Henry's law constant, $k_{\mathrm{H,B}}$, for gaseous methane dissolved in water (Timothy R. Rettich, Y. Paul Handa, Rubin Battino, and Emmerich Wilhelm, *J. Phys. Chem.*, **85**, 3230–3237, 1981). Table 12.6 lists values of $\ln(k_{\mathrm{H,B}}/p^\circ)$ at eleven temperatures in the range $275\,\mathrm{K}$–$328\,\mathrm{K}$ and at pressures close to $1\,\mathrm{bar}$. Use these data to evaluate $\Delta_{\mathrm{sol,B}}H^\circ$ and $\Delta_{\mathrm{sol,B}}C_p^\circ$ at $T = 298.15\,\mathrm{K}$. This can be done by a graphical method. Better precision will be obtained by making a least-squares fit of the data to the three-term polynomial

$$\ln(k_{\mathrm{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$$

and using the values of the coefficients a, b, and c for the evaluations.

12.15

Liquid water and liquid benzene have very small mutual solubilities. Equilibria in the binary water–benzene system were investigated by Tucker, Lane, and Christian (*J. Solution Chem.*, **10**, 1–20, 1981) as follows. A known amount of distilled water was admitted to an evacuated, thermostatted vessel. Part of the water vaporized to form a vapor phase. Small, precisely measured volumes of liquid benzene were then added incrementally from the sample loop of a liquid-chromatography valve. The benzene distributed itself between the liquid and gaseous phases in the vessel. After each addition, the pressure was read with a precision pressure gauge. From the known amounts of water and benzene and the total pressure, the liquid composition and the partial pressure of the benzene were calculated. The fugacity of the benzene in the vapor phase was calculated from its partial pressure and the second virial coefficient.

At a fixed temperature, for mole fractions x_{B} of benzene in the liquid phase up to about 3×10^{-4} (less than the solubility of benzene in water), the fugacity of the benzene in the equilibrated gas phase was found to have the following dependence on x_{B}:

$$\frac{f_{\mathrm{B}}}{x_{\mathrm{B}}} = k_{\mathrm{H,B}} - A x_{\mathrm{B}} \tag{12.11.1}$$

Here $k_{\mathrm{H,B}}$ is the Henry's law constant and A is a constant related to deviations from Henry's law. At $30\,^\circ\mathrm{C}$, the measured values were $k_{\mathrm{H,B}} = 385.5\,\mathrm{bar}$ and $A = 2.24 \times 10^4\,\mathrm{bar}$.

(a) Treat benzene (B) as the solute and find its activity coefficient on a mole fraction basis, $\gamma_{x,\mathrm{B}}$, at $30\,^\circ\mathrm{C}$ in the solution of composition $x_{\mathrm{B}} = 3.00 \times 10^{-4}$.

(b) The fugacity of benzene vapor in equilibrium with pure liquid benzene at $30\,^\circ\mathrm{C}$ is $f_{\mathrm{B}}^* = 0.1576\,\mathrm{bar}$. Estimate the mole fraction solubility of liquid benzene in water at this temperature.

(c) The calculation of $\gamma_{x,\mathrm{B}}$ in part (a) treated the benzene as a single solute species with deviations from infinite-dilution behavior. Tucker et al suggested a dimerization model to explain the observed negative deviations from Henry's law. (Classical thermodynamics, of course, cannot prove such a molecular interpretation of observed macroscopic behavior.) The model assumes that there are two solute species, a monomer (M) and a dimer (D), in reaction equilibrium: $2\,\mathrm{M} \rightleftharpoons \mathrm{D}$. Let n_{B} be the total amount of $\mathrm{C_6H_6}$ present in solution, and define the mole fractions

$$x_{\mathrm{B}} \overset{\mathrm{def}}{=} \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \approx \frac{n_{\mathrm{B}}}{n_{\mathrm{A}}} \tag{12.11.2}$$

$$x_{\mathrm{M}} \overset{\mathrm{def}}{=} \frac{n_{\mathrm{M}}}{n_{\mathrm{A}} + n_{\mathrm{M}} + n_{\mathrm{D}}} \approx \frac{n_{\mathrm{M}}}{n_{\mathrm{A}}} \qquad x_{\mathrm{D}} \overset{\mathrm{def}}{=} \frac{n_{\mathrm{D}}}{n_{\mathrm{A}} + n_{\mathrm{M}} + n_{\mathrm{D}}} \approx \frac{n_{\mathrm{D}}}{n_{\mathrm{A}}} \tag{12.11.3}$$

where the approximations are for dilute solution. In the model, the individual monomer and dimer particles behave as solutes in an ideal-dilute solution, with activity coefficients of unity. The monomer is in transfer equilibrium with the gas phase: $x_{\mathrm{M}} = f_{\mathrm{B}}/k_{\mathrm{H,B}}$. The equilibrium constant expression (using a mole fraction basis for the solute standard states and setting pressure factors equal to 1) is $K = x_{\mathrm{D}}/x_{\mathrm{M}}^2$. From the relation $n_{\mathrm{B}} = n_{\mathrm{M}} + 2n_{\mathrm{D}}$, and because the solution is very dilute, the expression becomes

$$K = \frac{x_B - x_M}{2x_M^2} \tag{12.11.4}$$

Make individual calculations of K from the values of f_B measured at $x_B = 1.00 \times 10^{-4}$, $x_B = 2.00 \times 10^{-4}$, and $x_B = 3.00 \times 10^{-4}$. Extrapolate the calculated values of K to x_B=0 in order to eliminate nonideal effects such as higher aggregates. Finally, find the fraction of the benzene molecules present in the dimer form at $x_B = 3.00 \times 10^{-4}$ if this model is correct.

12.16

Use data in Appendix H to evaluate the thermodynamic equilibrium constant at $298.15\ \mathrm{K}$for the limestone reaction

$$\mathrm{CaCO_3(cr, calcite) + CO_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq)} \tag{12.11.5}$$

12.17

For the dissociation equilibrium of formic acid, $\mathrm{HCO_2H(aq) \rightleftharpoons H^+(aq) + HCO_2^-(aq)}$, the acid dissociation constant at $298.15\ \mathrm{K}$has the value $K_a = 1.77 \times 10^{-4}$.

(a) Use Eq. 12.9.7 to find the degree of dissociation and the hydrogen ion molality in a 0.01000 molal formic acid solution. You can safely set Γ_r and $\gamma_{m,\mathrm{HA}}$ equal to 1, and use the Debye–Hückel limiting law (Eq. 10.4.8) to calculate $\gamma_\pm$. You can do this calculation by iteration: Start with an initial estimate of the ionic strength (in this case 0), calculate $\gamma_\pm$ and α, and repeat these steps until the value of α no longer changes.

(b) Estimate the degree of dissociation of formic acid in a solution that is 0.01000 molal in both formic acid and sodium nitrate, again using the Debye–Hückel limiting law for $\gamma_\pm$. Compare with the value in part (a).

12.18

Use the following experimental information to evaluate the standard molar enthalpy of formation and the standard molar entropy of the aqueous chloride ion at $298.15\ \mathrm{K}$, based on the conventions $\Delta_f H^\circ(\mathrm{H^+, aq}) = 0$ and $S_m^\circ(\mathrm{H^+, aq}) = 0$ (Secs. 11.3.2 and 11.8.4). (Your calculated values will be close to, but not exactly the same as, those listed in Appendix H, which are based on the same data combined with data of other workers.)

- **12.19**

  The solubility of crystalline AgCl in ultrapure water has been determined from the electrical conductivity of the saturated solution (J. A. Gledhill and G. McP. Malan, *Trans. Faraday Soc.*, **48**, 258–262, 1952). The average of five measurements at $298.15\ \mathrm{K}$is $s_B = 1.337 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$. The density of water at this temperature is $\rho_A^* = 0.9970\ \mathrm{kg\ dm^{-3}}$.

  (a) From these data and the Debye–Hückel limiting law, calculate the solubility product K_s of AgCl at $298.15\ \mathrm{K}$

  12.20

  The following reaction was carried out in an adiabatic solution calorimeter by Wagman and Kilday (*J. Res. Natl. Bur. Stand. (U.S.)*, **77A**, 569–579, 1973):

$$\mathrm{AgNO_3(s) + KCl(aq,}\ m_B = 0.101\ \mathrm{mol\ kg^{-1}) \rightarrow AgCl(s) + KNO_3(aq)} \tag{12.11.6}$$

  The reaction can be assumed to go to completion, and the amount of KCl was in slight excess, so the amount of AgCl formed was equal to the initial amount of $\mathrm{AgNO_3}$. After correction for the enthalpies of diluting the solutes in the initial and final solutions to infinite dilution, the standard molar reaction enthalpy at $298.15\ \mathrm{K}$was found to be $\Delta_r H^\circ = -43.042\ \mathrm{kJ\ mol^{-1}}$. The same workers used solution calorimetry to obtain the molar enthalpy of solution at infinite dilution of crystalline $\mathrm{AgNO_3}$ at $298.15\ \mathrm{K}$: $\Delta_{\mathrm{sol,B}} H^\infty = 22.727\ \mathrm{kJ\ mol^{-1}}$.

  (a) Show that the difference of these two values is the standard molar reaction enthalpy for the precipitation reaction

$$\mathrm{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)} \tag{12.11.7}$$

  and evaluate this quantity.

  (b) Evaluate the standard molar enthalpy of formation of aqueous $\mathrm{Ag^+}$ ion at $298.15\ \mathrm{K}$, using the results of part (a) and the values $\Delta_f H^\circ(\mathrm{Cl^-, aq}) = -167.08\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\circ(\mathrm{AgCl, s}) = -127.01\ \mathrm{kJ\ mol^{-1}}$ from Appendix H. (These values come from calculations similar to those in Probs. 12.18 and 14.4.) The calculated value will be close to, but not exactly the same as, the value listed in Appendix H, which is based on the same data combined with data of other workers.

CHAPTER OVERVIEW

13: The Phase Rule and Phase Diagrams

We encountered the Gibbs phase rule and phase diagrams in Chapter 8 in connection with single-substance systems. The present chapter derives the full version of the Gibbs phase rule for multicomponent systems. It then discusses phase diagrams for some representative types of multicomponent systems, and shows how they are related to the phase rule and to equilibrium concepts developed in Chapters 11 and 12.

13.1: The Gibbs Phase Rule for Multicomponent Systems

In Sec. 8.1.7, the Gibbs phase rule for a pure substance was written $F = 3 - P$. We now consider a system of more than one substance and more than one phase in an equilibrium state. The phase rule assumes the system is at thermal and mechanical equilibrium. We shall assume furthermore that in addition to the temperature and pressure, the only other state functions needed to describe the state are the amounts of the species in each phase; this means for instance that surface effects are ignored.

The derivations to follow will show that the phase rule may be written either in the form

$$F = 2 + C - P \tag{13.1.1}$$

or

$$F = 2 + s - r - P \tag{13.1.2}$$

where the symbols have the following meanings:

$F =$ the number of degrees of freedom (or variance)
$=$ the maximum number of intensive variables that can be varied independently while the system remains in an equilibrium state;

$C =$ the number of components
$=$ the minimum number of substances (or fixed-composition mixtures of substances)
that could be used to prepare each phase individually;

$P =$ the number of different phases;

$s =$ the number of different species;

$r =$ the number of independent relations among intensive variables of individual phases other than relations
needed for thermal, mechanical, and transfer equilibrium.

If we subdivide a phase, that does not change the number of phases P. That is, we treat noncontiguous regions of the system that have identical intensive properties as parts of the same phase.

13.1.1 Degrees of freedom

Consider a system in an equilibrium state. In this state, the system has one or more phases; each phase contains one or more species; and intensive properties such as T, p, and the mole fraction of a species in a phase have definite values. Starting with the system in this state, we can make changes that place the system in a new equilibrium state having the same kinds of phases and the same species, but different values of some of the intensive properties. The number of different independent intensive variables that we may change in this way is the **number of degrees of freedom** or **variance**, F, of the system.

Clearly, the system remains in equilibrium if we change the *amount* of a phase without changing its temperature, pressure, or composition. This, however, is the change of an extensive variable and is not counted as a degree of freedom.

The phase rule, in the form to be derived, applies to a system that continues to have complete thermal, mechanical, and transfer equilibrium as intensive variables change. This means different phases are not separated by adiabatic or rigid partitions, or by semipermeable or impermeable membranes. Furthermore, every conceivable reaction among the species is either at reaction equilibrium or else is frozen at a fixed advancement during the time period we observe the system.

The number of degrees of freedom is the maximum number of intensive properties of the equilibrium system we may independently vary, or fix at arbitrary values, without causing a change in the number and kinds of phases and species. We cannot, of course, change one of these properties to just any value whatever. We are able to vary the value only within a certain finite (sometimes quite narrow) range before a phase disappears or a new one appears.

The number of degrees of freedom is also the number of independent intensive variables needed to specify the equilibrium state in all necessary completeness, aside from the amount of each phase. In other words, when we specify values of F different independent intensive variables, then the values of all other intensive variables of the equilibrium state have definite values determined by the physical nature of the system.

Just as for a one-component system, we can use the terms *bivariant*, *univariant*, and *invariant* depending on the value of F (Sec. 8.1.7).

13.1.2 Species approach to the phase rule

This section derives an expression for the number of degrees of freedom, F, based on *species*. Section 13.1.3 derives an expression based on *components*. Both approaches yield equivalent versions of the phase rule.

Recall that a *species* is an entity, uncharged or charged, distinguished from other species by its chemical formula (Sec. 9.1.1). Thus, CO_2 and $CO_3{}^{2-}$ are different species, but CO_2(aq) and CO_2(g) is the same species in different phases.

Consider an equilibrium system of P phases, each of which contains the same set of species. Let the number of different species be s. If we could make changes while the system remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we could independently vary the temperature and pressure of the system as a whole and the amount of each species in each phase; there would then be $2+Ps$ independent variables.

The equilibrium system is, however, in transfer equilibrium, which requires each species to have the same chemical potential in each phase: $\mu_i^\beta=\mu_i^\alpha$, $\mu_i^\gamma=\mu_i^\alpha$, and so on. There are $P-1$ independent relations like this for each species, and a total of $s(P-1)$ independent relations for all species. Each such independent relation introduces a constraint and reduces the number of independent variables by one. Accordingly, taking transfer equilibrium into account, the number of independent variables is $2+Ps-s(P-1)=2+s$.

We obtain the same result if a species present in one phase is totally excluded from another. For example, solvent molecules of a solution are not found in a pure perfectly-ordered crystal of the solute, undissociated molecules of a volatile strong acid such as HCl can exist in a gas phase but not in aqueous solution, and ions of an electrolyte solute are usually not found in a gas phase. For each such species absent from a phase, there is one fewer amount variable and also one fewer relation for transfer equilibrium; on balance, the number of independent variables is still $2+s$.

Next, we consider the possibility that further independent relations exist among intensive variables in addition to the relations needed for thermal, mechanical, and transfer equilibrium. (Relations such as $\sum_i p_i=p$ for a gas phase or $\sum_i x_i=1$ for a phase in general have already been accounted for in the derivation by the specification of p and the amount of each species.) If there are r of these additional relations, the total number of independent variables is reduced to $2+s-r$. These relations may come from

1. In the case of a reaction equilibrium, the relation is $\Delta_{\mathrm{r}}G=\sum_i\nu_i\mu_i=0$, or the equivalent relation $K=\prod_i(a_i)^{\nu_i}$ for the thermodynamic equilibrium constant. Thus, r is the sum of the number of independent reaction equilibria, the number of phases containing ions, and the number of independent initial conditions. Several examples will be given in Sec. 13.1.4.

   There is an infinite variety of possible choices of the independent variables (both extensive and intensive) for the equilibrium system, but the total *number* of independent variables is fixed at $2+s-r$. Keeping intensive properties fixed, we can always vary how much of each phase is present (e.g., its volume, mass, or amount) without destroying the equilibrium. Thus, at least P of the independent variables, one for each phase, must be extensive. It follows that the maximum number of independent *intensive* variables is the difference $(2+s-r)-P$.

   Since the maximum number of independent intensive variables is the number of degrees of freedom, our expression for F based on species is

$$F=2+s-r-P \tag{13.1.3}$$

13.1.3 Components approach to the phase rule

The derivation of the phase rule in this section uses the concept of **components**. The number of components, C, is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed-composition mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system.

It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of $CaCO_3$ and CaO and a gas phase of CO_2. Assume the reaction $CaCO_3$(s) $\rightarrow$ CaO(s) + CO_2(g) is at equilibrium. We could prepare the $CaCO_3$ phase from CaO and CO_2 by the reverse of this reaction, but we can only prepare the CaO and CO_2 phases from the individual substances. We could not use $CaCO_3$ to prepare either the CaO phase or the CO_2 phase, because CO_2 or CaO would be left over. Thus this system has three substances but only two components, namely CaO and CO_2.

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of P phases in which each substance present is a component (i.e., there are no reactions) and each of the C components is present in each phase. If we make changes to the system while it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation $\sum_i x_i = 1$). This is a total of $2+P(C-1)$ independent intensive variables.

When there also exist transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish $P-1$ independent relations for each component ($\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, etc.) and a total of $C(P-1)$ relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

$$F = [2+P(C-1)] - C(P-1) = 2+C-P \tag{13.1.4}$$

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of F, which is still equal to $2+C-P$. If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation $\sum_i \nu_i \mu_i = 0$ for the reaction; again the changes cancel.

> We may need to *remove* a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electroneutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured.

We conclude that, regardless of the kind of system, the expression for F based on components is given by $F=2+C-P$. By comparing this expression and $F=2+s-r-P$, we see that the number of components is related to the number of species by

$$C = s-r \tag{13.1.5}$$

13.1.4 Examples

The five examples below illustrate various aspects of using the phase rule.

Example 1: liquid water

For a single phase of pure water, P equals 1. If we treat the water as the single species H_2O, s is 1 and r is 0. The phase rule then predicts two degrees of freedom:

$$\begin{aligned} F &= 2+s-r-P \\ &= 2+1-0-1 = 2 \end{aligned} \tag{13.1.6}$$

Since F is the number of intensive variables that can be varied independently, we could for instance vary T and p independently, or T and ρ, or any other pair of independent intensive variables.

Next let us take into account the proton transfer equilibrium

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{13.1.1}$$

and consider the system to contain the three species H_2O, H_3O^+, and OH^-. Then for the species approach to the phase rule, we have $s=3$. We can write two independent relations:

1. Thus, we have two relations involving intensive variables only. Now s is 3, r is 2, P is 1, and the number of degrees of freedom is given by

   $$F = 2+s-r-P = 2 \tag{13.1.7}$$

   which is the same value of F as before.

If we consider water to contain additional cation species (e.g., $H_5O_2^+$), each such species would add 1 to s and 1 to r, but F would remain equal to 2. Thus, no matter how complicated are the equilibria that actually exist in liquid water, the number of degrees of freedom remains 2.

Example 2: carbon, oxygen, and carbon oxides

Consider a system containing solid carbon (graphite) and a gaseous mixture of O_2, CO, and CO_2. There are four species and two phases. If reaction equilibrium is absent, as might be the case at low temperature in the absence of a catalyst, we have $r = 0$ and $C = s - r = 4$. The four components are the four substances. The phase rule tells us the system has four degrees of freedom. We could, for instance, arbitrarily vary T, p, y_{O_2}, and y_{CO}.

Now suppose we raise the temperature or introduce an appropriate catalyst to allow the following reaction equilibria to exist:

1. These equilibria introduce two new independent relations among chemical potentials and among activities. We could also consider the equilibrium $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$, but it does not contribute an additional independent relation because it depends on the other two equilibria: the reaction equation is obtained by subtracting the reaction equation for equilibrium 1 from twice the reaction equation for equilibrium 2. By the species approach, we have $s = 4$, $r = 2$, and $P = 2$; the number of degrees of freedom from these values is

$$F = 2 + s - r - P = 2 \tag{13.1.8}$$

If we wish to calculate F by the components approach, we must decide on the minimum number of substances we could use to prepare each phase separately. (This does not refer to how we actually prepare the two-phase system, but to a hypothetical preparation of each phase with any of the compositions that can actually exist in the equilibrium system.) Assume equilibria 1 and 2 are present. We prepare the solid phase with carbon, and we can prepare any possible equilibrium composition of the gas phase from carbon and O_2 by using the reactions of both equilibria. Thus, there are two components (C and O_2) giving the same result of two degrees of freedom.

   1. Now to introduce an additional complexity: Suppose we prepare the system by placing a certain amount of O_2 and twice this amount of carbon in an evacuated container, and wait for the reactions to come to equilibrium. This method of preparation imposes an initial condition on the system, and we must decide whether the number of degrees of freedom is affected. Equating the total amount of carbon atoms to the total amount of oxygen atoms in the equilibrated system gives the relation

$$n_C + n_{CO} + n_{CO_2} = 2n_{O_2} + n_{CO} + 2n_{CO_2} \qquad \text{or} \qquad n_C = 2n_{O_2} + n_{CO_2} \tag{13.1.9}$$

Either equation is a relation among extensive variables of the two phases. From them, we are unable to obtain any relation among *intensive* variables of the phases. Therefore, this particular initial condition does not change the value of r, and F remains equal to 2.

Example 3: a solid salt and saturated aqueous solution

Applying the components approach to this system is straightforward. The solid phase is prepared from $PbCl_2$ and the aqueous phase could be prepared by dissolving solid $PbCl_2$ in H_2O. Thus, there are two components and two phases:

$$F = 2 + C - P = 2 \tag{13.1.10}$$

For the species approach, we note that there are four species ($PbCl_2$, Pb^{2+}, Cl^-, and H_2O) and two independent relations among intensive variables:

1. We have $s = 4$, $r = 2$, and $P = 2$, giving the same result as the components approach:

$$F = 2 + s - r - P = 2 \tag{13.1.11}$$

Example 4: liquid water and water-saturated air

If there is no special relation among the total amounts of N_2 and O_2, there are three components and the phase rule gives

$$F = 2 + C - P = 3 \tag{13.1.12}$$

Since there are three degrees of freedom, we could, for instance, specify arbitrary values of T, p, and $y_{\mathrm{N_2}}$ (arbitrary, that is, within the limits that would allow the two phases to coexist); then the values of other intensive variables such as the mole fractions $y_{\mathrm{H_2O}}$ and $x_{\mathrm{N_2}}$ would have definite values.

Now suppose we impose an initial condition by preparing the system with water and dry air of a *fixed* composition. The mole ratio of $\mathrm{N_2}$ and $\mathrm{O_2}$ in the aqueous solution is not necessarily the same as in the equilibrated gas phase; consequently, the air does not behave like a single substance. The number of components is still three: $\mathrm{H_2O}$, $\mathrm{N_2}$, and $\mathrm{O_2}$ are all required to prepare each phase individually, just as when there was no initial condition, giving $F = 3$ as before.

The fact that the compositions of both phases depend on the relative amounts of the phases is illustrated in Prob. 9.5.

We can reach the same conclusion with the species approach. The initial condition can be expressed by an equation such as

$$\frac{(n^{\mathrm{l}}_{\mathrm{N_2}} + n^{\mathrm{g}}_{\mathrm{N_2}})}{(n^{\mathrm{l}}_{\mathrm{O_2}} + n^{\mathrm{g}}_{\mathrm{O_2}})} = a \tag{13.1.13}$$

where a is a constant equal to the mole ratio of $\mathrm{N_2}$ and $\mathrm{O_2}$ in the dry air. This equation cannot be changed to a relation between intensive variables such as $x_{\mathrm{N_2}}$ and $x_{\mathrm{O_2}}$, so that r is zero and there are still three degrees of freedom.

Finally, let us assume that we prepare the system with dry air of fixed composition, as before, but consider the solubilities of $\mathrm{N_2}$ and $\mathrm{O_2}$ in water to be negligible. Then $n^{\mathrm{l}}_{\mathrm{N_2}}$ and $n^{\mathrm{l}}_{\mathrm{O_2}}$ are zero and Eq. 13.1.13 becomes $n^{\mathrm{g}}_{\mathrm{N_2}}/n^{\mathrm{g}}_{\mathrm{O_2}} = a$, or $y_{\mathrm{N_2}} = a y_{\mathrm{O_2}}$, which is a relation between intensive variables. In this case, r is 1 and the phase rule becomes

$$F = 2 + s - r - P = 2 \tag{13.1.14}$$

The reduction in the value of F from 3 to 2 is a consequence of our inability to detect any dissolved $\mathrm{N_2}$ or $\mathrm{O_2}$. According to the components approach, we may prepare the liquid phase with $\mathrm{H_2O}$ and the gas phase with $\mathrm{H_2O}$ and air of fixed composition that behaves as a single substance; thus, there are only two components.

Example 5: equilibrium between two solid phases and a gas phase

Consider the following reaction equilibrium:

$$3\,\mathrm{CuO(s)} + 2\,\mathrm{NH_3(g)} \rightleftharpoons 3\,\mathrm{Cu(s)} + 3\,\mathrm{H_2O(g)} + \mathrm{N_2(g)} \tag{13.1.2}$$

According to the species approach, there are five species, one relation (for reaction equilibrium), and three phases. The phase rule gives

$$F = 2 + s - r - P = 3 \tag{13.1.15}$$

It is more difficult to apply the components approach to this example. As components, we might choose CuO and Cu (from which we could prepare the solid phases) and also $\mathrm{NH_3}$ and $\mathrm{H_2O}$. Then to obtain the $\mathrm{N_2}$ needed to prepare the gas phase, we could use CuO and $\mathrm{NH_3}$ as reactants in the reaction $3\,\mathrm{CuO} + 2\,\mathrm{NH_3} \rightarrow 3\,\mathrm{Cu} + 3\,\mathrm{H_2O} + \mathrm{N_2}$ and remove the products Cu and $\mathrm{H_2O}$. In the components approach, we are allowed to remove substances from the system provided they are counted as components.

13.2: Phase Diagrams- Binary Systems

As explained in Sec. 8.2, a phase diagram is a kind of two-dimensional map that shows which phase or phases are stable under a given set of conditions. This section discusses some common kinds of binary systems, and Sec. 13.3 will describe some interesting ternary systems.

13.2.1 Generalities

A binary system has two components; C equals 2, and the number of degrees of freedom is $F = 4 - P$. There must be at least one phase, so the maximum possible value of F is 3. Since F cannot be negative, the equilibrium system can have no more than four phases.

We can independently vary the temperature, pressure, and composition of the system as a whole. Instead of using these variables as the coordinates of a three-dimensional phase diagram, we usually draw a two-dimensional phase diagram that is either a temperature–composition diagram at a fixed pressure or a pressure–composition diagram at a fixed temperature. The position of the system point on one of these diagrams then corresponds to a definite temperature, pressure, and overall composition. The composition variable usually varies along the horizontal axis and can be the mole fraction, mass fraction, or mass percent of one of the components, as will presently be illustrated by various examples.

The way in which we interpret a two-dimensional phase diagram to obtain the compositions of individual phases depends on the number of phases present in the system.

- If the system point falls within a *one-phase* area of the phase diagram, the composition variable is the composition of that single phase. There are three degrees of freedom. On the phase diagram, the value of either T or p has been fixed, so there are two other independent intensive variables. For example, on a temperature–composition phase diagram, the pressure is fixed and the temperature and composition can be changed independently within the boundaries of the one-phase area of the diagram.
- If the system point is in a *two-phase* area of the phase diagram, we draw a horizontal *tie line* of constant temperature (on a temperature–composition phase diagram) or constant pressure (on a pressure–composition phase diagram). The lever rule applies. The position of the point at each end of the tie line, at the boundary of the two-phase area, gives the value of the composition variable of one of the phases and also the physical state of this phase: either the state of an adjacent one-phase area, or the state of a phase of fixed composition when the boundary is a vertical line. Thus, a boundary that separates a two-phase area for phases α and β from a one-phase area for phase α is a curve that describes the composition of phase α as a function of T or p when it is in equilibrium with phase β. The curve is called a *solidus*, *liquidus*, or *vaporus* depending on whether phase α is a solid, liquid, or gas.
- A binary system with *three* phases has only one degree of freedom and cannot be represented by an area on a two-dimensional phase diagram. Instead, there is a horizontal boundary line between areas, with a special point along the line at the junction of several areas. The compositions of the three phases are given by the positions of this point and the points at the two ends of the line. The position of the system point on this line does not uniquely specify the relative amounts in the three phases.

The examples that follow show some of the simpler kinds of phase diagrams known for binary systems.

13.2.2 Solid–liquid systems

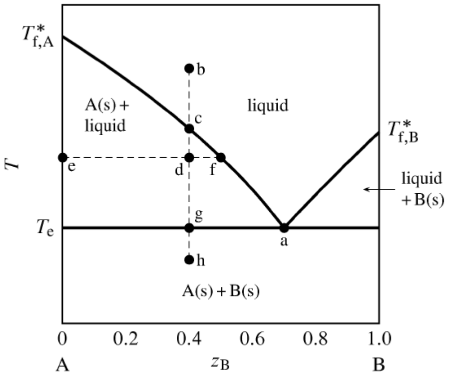


Figure 13.1 Temperature–composition phase diagram for a binary system exhibiting a eutectic point.

Figure 13.1 is a temperature–composition phase diagram at a fixed pressure. The composition variable z_B is the mole fraction of component B in the system as a whole. The phases shown are a binary liquid mixture of A and B, pure solid A, and pure solid B.

The one-phase liquid area is bounded by two curves, which we can think of either as freezing-point curves for the liquid or as solubility curves for the solids. These curves comprise the liquidus. As the mole fraction of either component in the liquid phase decreases from unity, the freezing point decreases. The curves meet at point a, which is a **eutectic point**. At this point, both solid A and solid B can coexist in equilibrium with a binary liquid mixture. The composition at this point is the *eutectic composition*, and the temperature here (denoted T_e) is the *eutectic temperature*. ("Eutectic" comes from the Greek for *easy melting*.) T_e is the lowest temperature for the given pressure at which the liquid phase is stable.

Suppose we combine $0.60\,\text{mol}$ A and $0.40\,\text{mol}$ B ($z_\text{B} = 0.40$) and adjust the temperature so as to put the system point at b. This point is in the one-phase liquid area, so the equilibrium system at this temperature has a single liquid phase. If we now place the system in thermal contact with a cold reservoir, heat is transferred out of the system and the system point moves down along the *isopleth* (path of constant overall composition) b–h. The cooling rate depends on the temperature gradient at the system boundary and the system's heat capacity.

At point c on the isopleth, the system point reaches the boundary of the one-phase area and is about to enter the two-phase area labeled A(s) + liquid. At this point in the cooling process, the liquid is saturated with respect to solid A, and solid A is about to freeze out from the liquid. There is an abrupt decrease (break) in the cooling rate at this point, because the freezing process involves an extra enthalpy decrease.

At the still lower temperature at point d, the system point is within the two-phase solid–liquid area. The tie line through this point is line e–f. The compositions of the two phases are given by the values of z_B at the ends of the tie line: $x^\text{s}_\text{B} = 0$ for the solid and $x^\text{l}_\text{B} = 0.50$ for the liquid. From the general lever rule (Eq. 8.2.8), the ratio of the amounts in these phases is

$$\frac{n^\text{l}}{n^\text{s}} = \frac{z_\text{B} - x^\text{s}_\text{B}}{x^\text{l}_\text{B} - z_\text{B}} = \frac{0.40 - 0}{0.50 - 0.40} = 4.0 \tag{13.2.1}$$

Since the total amount is $n^\text{s} + n^\text{l} = 1.00\,\text{mol}$, the amounts of the two phases must be $n^\text{s} = 0.20\,\text{mol}$ and $n^\text{l} = 0.80\,\text{mol}$.

When the system point reaches the eutectic temperature at point g, cooling halts until all of the liquid freezes. Solid B freezes out as well as solid A. During this *eutectic halt*, there are at first three phases: liquid with the eutectic composition, solid A, and solid B. As heat continues to be withdrawn from the system, the amount of liquid decreases and the amounts of the solids increase until finally only $0.60\,\text{mol}$ of solid A and $0.40\,\text{mol}$ of solid B are present. The temperature then begins to decrease again and the system point enters the two-phase area for solid A and solid B; tie lines in this area extend from $z_\text{B}=0$ to $z_\text{B}=1$.

Temperature–composition phase diagrams such as this are often mapped out experimentally by observing the cooling curve (temperature as a function of time) along isopleths of various compositions. This procedure is *thermal analysis*. A break in the slope of a cooling curve at a particular temperature indicates the system point has moved from a one-phase liquid area to a two-phase area of liquid and solid. A temperature halt indicates the temperature is either the freezing point of the liquid to form a solid of the same composition, or else a eutectic temperature.

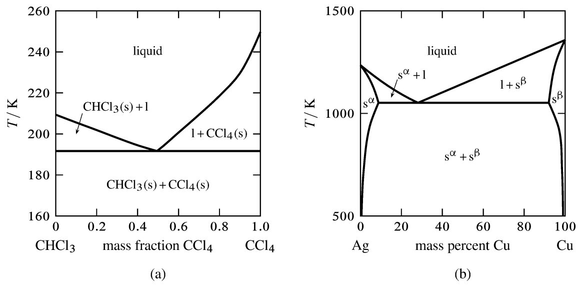


Figure 13.2 Temperature–composition phase diagrams with single eutectics.
(a) Two pure solids and a liquid mixture (E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. IV, McGraw-Hill, New York, 1928, p. 98).
(b) Two solid solutions and a liquid mixture.

Figure 13.2 shows two temperature–composition phase diagrams with single eutectic points. The left-hand diagram is for the binary system of chloroform and carbon tetrachloride, two liquids that form nearly ideal mixtures. The solid phases are pure crystals, as in Fig. 13.1. The right-hand diagram is for the silver–copper system and involves solid phases that are solid solutions (substitutional alloys of variable composition). The area labeled s^{α} is a solid solution that is mostly silver, and s^{β} is a solid solution that is mostly copper. Tie lines in the two-phase areas do not end at a vertical line for a pure solid component as they do in the system shown in the left-hand diagram. The three phases that can coexist at the eutectic temperature of $1{,}052\ \mathrm{K}$ are the melt of the eutectic composition and the two solid solutions.

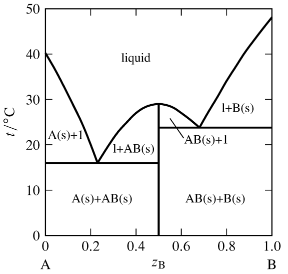


Figure 13.3 Temperature–composition phase diagram for the binary system of α-naphthylamine (A) and phenol (B) at $1\ \mathrm{bar}$ (J. C. Philip, *J. Chem. Soc.*, **83**, 814–834, 1903).

Section 12.5.4 discussed the possibility of the appearance of a *solid compound* when a binary liquid mixture is cooled. An example of this behavior is shown in Fig. 13.3, in which the solid compound contains equal amounts of the two components α-naphthylamine and phenol. The possible solid phases are pure A, pure B, and the solid compound AB. Only one or two of these solids can be present simultaneously in an equilibrium state. The vertical line in the figure at $z_{\mathrm{B}} = 0.5$ represents the solid compound. The temperature at the upper end of this line is the melting point of the solid compound, $29\ {}^{\circ}\mathrm{C}$. The solid melts *congruently* to give a liquid of the same composition. A melting process with this behavior is called a *dystectic reaction*. The cooling curve for liquid of this composition would display a halt at the melting point.

The phase diagram in Fig. 13.3 has two eutectic points. It resembles two simple phase diagrams like Fig. 13.1 placed side by side. There is one important difference: the slope of the freezing-point curve (liquidus curve) is nonzero at the composition of a pure component, but is zero at the composition of a solid compound that is completely dissociated in the liquid (as derived theoretically in Sec. 12.5.4). Thus, the curve in Fig. 13.3 has a relative maximum at the composition of the solid compound ($z_B = 0.5$) and is rounded there, instead of having a cusp—like a Romanesque arch rather than a Gothic arch.

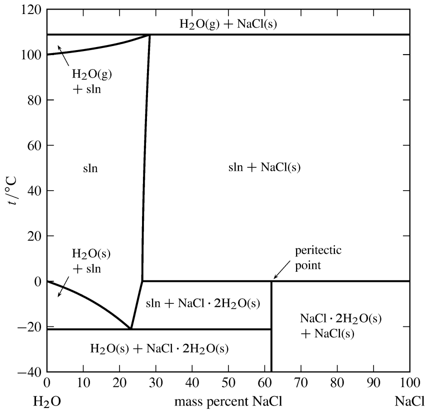


Figure 13.4 Temperature–composition phase diagram for the binary system of H_2O and NaCl at 1 bar. (Data from Roger Cohen-Adad and John W. Lorimer, *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*, Solubility Data Series, Vol. 47, Pergamon Press, Oxford, 1991; and E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. III, McGraw-Hill, New York, 1928.)

An example of a solid compound that does not melt congruently is shown in Fig. 13.4. The solid hydrate $NaCl \cdot 2\,H_2O$ is 61.9% NaCl by mass. It decomposes at $0\,^\circ C$ to form an aqueous solution of composition 26.3% NaCl by mass and a solid phase of anhydrous NaCl. These three phases can coexist at equilibrium at $0\,^\circ C$. A phase transition like this, in which a solid compound changes into a liquid and a different solid, is called *incongruent* or *peritectic* melting, and the point on the phase diagram at this temperature at the composition of the liquid is a *peritectic point*.

Figure 13.4 shows there are two other temperatures at which three phases can be present simultaneously: $-21\,^\circ C$, where the phases are ice, the solution at its eutectic point, and the solid hydrate; and $109\,^\circ C$, where the phases are gaseous H_2O, a solution of composition 28.3% NaCl by mass, and solid NaCl. Note that both segments of the right-hand boundary of the one-phase solution area have positive slopes, meaning that the solubilities of the solid hydrate and the anhydrous salt both increase with increasing temperature.

13.2.3 Partially-miscible liquids

When two liquids that are partially miscible are combined in certain proportions, phase separation occurs (Sec. 11.1.6). Two liquid phases in equilibrium with one another are called *conjugate phases*. Obviously the two phases must have different compositions or they would be identical; the difference is called a *miscibility gap*. A binary system with two phases has two degrees of freedom, so that at a given temperature and pressure each conjugate phase has a fixed composition.

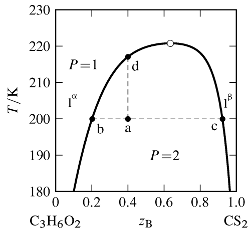


Figure 13.5 Temperature–composition phase diagram for the binary system of methyl acetate (A) and carbon disulfide (B) at $1\,\mathrm{bar}$ (data from P. Ferloni and G. Spinolo, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*, 70, 1974). All phases are liquids. The open circle indicates the critical point.

The typical dependence of a miscibility gap on temperature is shown in Fig. 13.5. The miscibility gap (the difference in compositions at the left and right boundaries of the two-phase area) decreases as the temperature increases until at the *upper consolute temperature*, also called the *upper critical solution temperature*, the gap vanishes. The point at the maximum of the boundary curve of the two-phase area, where the temperature is the upper consolute temperature, is the *consolute point* or *critical point*. At this point, the two liquid phases become identical, just as the liquid and gas phases become identical at the critical point of a pure substance. Critical opalescence (Sec. 8.2.3) is observed in the vicinity of this point, caused by large local composition fluctuations. At temperatures at and above the critical point, the system is a single binary liquid mixture.

Suppose we combine $6.0\,\mathrm{mol}$ of component A (methyl acetate) and $4.0\,\mathrm{mol}$ of component B (carbon disulfide) in a cylindrical vessel and adjust the temperature to $200\,\mathrm{K}$. The overall mole fraction of B is $z_\mathrm{B} = 0.40$. The system point is at point a in the two-phase region. From the positions of points b and c at the ends of the tie line through point a, we find the two liquid layers have compositions $x^\alpha_\mathrm{B} = 0.20$ and $x^\beta_\mathrm{B} = 0.92$. Since carbon disulfide is the more dense of the two pure liquids, the bottom layer is phase β, the layer that is richer in carbon disulfide. According to the lever rule, the ratio of the amounts in the two phases is given by

$$\frac{n^\beta}{n^\alpha} = \frac{z_\mathrm{B} - x^\alpha_\mathrm{B}}{x^\beta_\mathrm{B} - z_\mathrm{B}} = \frac{0.40 - 0.20}{0.92 - 0.40} = 0.38 \tag{13.2.2}$$

Combining this value with $n^\alpha + n^\beta = 10.0\,\mathrm{mol}$ gives us $n^\alpha = 7.2\,\mathrm{mol}$ and $n^\beta = 2.8\,\mathrm{mol}$.

If we gradually add more carbon disulfide to the vessel while gently stirring and keeping the temperature constant, the system point moves to the right along the tie line. Since the ends of this tie line have fixed positions, neither phase changes its composition, but the amount of phase β increases at the expense of phase α. The liquid–liquid interface moves up in the vessel toward the top of the liquid column until, at overall composition $z_\mathrm{B} = 0.92$ (point c), there is only one liquid phase.

Now suppose the system point is back at point a and we raise the temperature while keeping the overall composition constant at $z_\mathrm{B} = 0.40$. The system point moves up the isopleth a–d. The phase diagram shows that the ratio $(z_\mathrm{B} - x^\alpha_\mathrm{B})/(x^\beta_\mathrm{B} - z_\mathrm{B})$ decreases during this change. As a result, the amount of phase α increases, the amount of phase β decreases, and the liquid–liquid interface moves down toward the bottom of the vessel until at $217\,\mathrm{K}$ (point d) there again is only one liquid phase.

13.2.4 Liquid–gas systems with ideal liquid mixtures

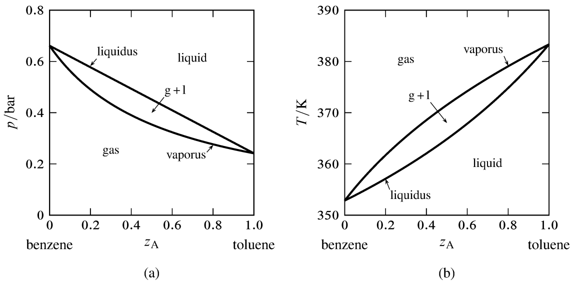


Figure 13.6 Phase diagrams for the binary system of toluene (A) and benzene (B). The curves are calculated from Eqs. 13.2.6 and 13.2.7 and the saturation vapor pressures of the pure liquids.
(a) Pressure–composition diagram at $T = 340\,\mathrm{K}$.
(b) Temperature–composition diagram at $p = 1\,\mathrm{bar}$.

Toluene and benzene form liquid mixtures that are practically ideal and closely obey Raoult's law for partial pressure. For the binary system of these components, we can use the vapor pressures of the pure liquids to generate the liquidus and vaporus curves of the pressure–composition and temperature–composition phase diagram. The results are shown in Fig. 13.6. The composition variable z_A is the overall mole fraction of component A (toluene).

The equations needed to generate the curves can be derived as follows. Consider a binary liquid mixture of components A and B and mole fraction composition x_A that obeys Raoult's law for partial pressure (Eq. 9.4.2):

$$p_A = x_A p_A^* \qquad p_B = (1 - x_A) p_B^* \tag{13.2.3}$$

Strictly speaking, Raoult's law applies to a liquid–gas system maintained at a constant pressure by means of a third gaseous component, and p_A^* and p_B^* are the vapor pressures of the pure liquid components at this pressure and the temperature of the system. However, when a liquid phase is equilibrated with a gas phase, the partial pressure of a constituent of the liquid is practically independent of the total pressure (Sec. 12.8.1), so that it is a good approximation to apply the equations to a *binary* liquid–gas system and treat p_A^* and p_B^* as functions only of T.

When the binary system contains a liquid phase and a gas phase in equilibrium, the pressure is the sum of p_A and p_B, which from Eq. 13.2.3 is given by

$$\begin{aligned} p &= x_A p_A^* + (1 - x_A) p_B^* \\ &= p_B^* + (p_A^* - p_B^*) x_A \end{aligned} \qquad \begin{array}{r} (13.2.4) \\ (C{=}2,\ \text{ideal liquid mixture}) \end{array}$$

where x_A is the mole fraction of A in the liquid phase. Equation 13.2.4 shows that in the two-phase system, p has a value between p_A^* and p_B^*, and that if T is constant, p is a linear function of x_A. The mole fraction composition of the gas in the two-phase system is given by

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} \tag{13.2.5}$$

A binary two-phase system has two degrees of freedom. At a given T and p, each phase must have a fixed composition. We can calculate the liquid composition by rearranging Eq. 13.2.4:

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*} \qquad \begin{array}{r} (13.2.6) \\ (C{=}2,\ \text{ideal liquid mixture}) \end{array}$$

The gas composition is then given by

$$\begin{aligned} y_{\mathrm{A}} &= \frac{p_{\mathrm{A}}}{p} = \frac{x_{\mathrm{A}} p_{\mathrm{A}}^{*}}{p} \\ &= \left(\frac{p - p_{\mathrm{B}}^{*}}{p_{\mathrm{A}}^{*} - p_{\mathrm{B}}^{*}} \right) \frac{p_{\mathrm{A}}^{*}}{p} \end{aligned} \qquad \begin{matrix} (13.2.7) \\ (C{=}2,\ \text{ideal liquid mixture}) \end{matrix}$$

If we know p_{A}^{*} and p_{B}^{*} as functions of T, we can use Eqs. 13.2.6 and 13.2.7 to calculate the compositions for any combination of T and p at which the liquid and gas phases can coexist, and thus construct a pressure–composition or temperature–composition phase diagram.

In Fig. 13.6(a), the liquidus curve shows the relation between p and x_{A} for equilibrated liquid and gas phases at constant T, and the vaporus curve shows the relation between p and y_{A} under these conditions. We see that p is a linear function of x_{A} but not of y_{A}.

In a similar fashion, the liquidus curve in Fig. 13.6(b) shows the relation between T and x_{A}, and the vaporus curve shows the relation between T and y_{A}, for equilibrated liquid and gas phases at constant p. Neither curve is linear.

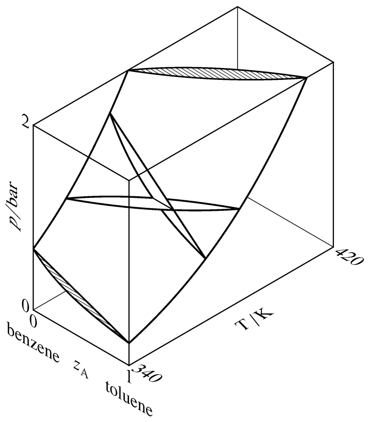
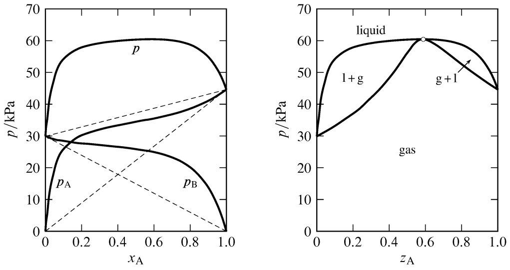


Figure 13.7 Liquidus and vaporus surfaces for the binary system of toluene (A) and benzene. Cross-sections through the two-phase region are drawn at constant temperatures of $340\,\mathrm{K}$ and $370\,\mathrm{K}$ and at constant pressures of $1\,\mathrm{bar}$ and $2\,\mathrm{bar}$. Two of the cross-sections intersect at a tie line at $T = 370\,\mathrm{K}$ and $p = 1\,\mathrm{bar}$, and the other cross-sections are hatched in the direction of the tie lines.

A liquidus curve is also called a *bubble-point* curve or a *boiling-point* curve. Other names for a vaporus curve are *dew-point* curve and *condensation* curve. These curves are actually cross-sections of liquidus and vaporus *surfaces* in a three-dimensional T–p–z_{A} phase diagram, as shown in Fig. 13.7. In this figure, the liquidus surface is in view at the front and the vaporus surface is hidden behind it.

13.2.5 Liquid–gas systems with nonideal liquid mixtures

Most binary liquid mixtures do not behave ideally. The most common situation is *positive* deviations from Raoult's law. (In the molecular model of Sec. 11.1.5, positive deviations correspond to a less negative value of k_{AB} than the average of k_{AA} and k_{BB}.) Some mixtures, however, have specific A–B interactions, such as solvation or molecular association, that prevent random mixing of the molecules of A and B, and the result is then *negative* deviations from Raoult's law. If the deviations from Raoult's law, either positive or negative, are large enough, the constant-temperature liquidus curve exhibits a maximum or minimum and *azeotropic* behavior results.



(a)

(b)

Figure 13.8 Binary system of methanol (A) and benzene at $45\,^{\circ}\mathrm{C}$ (Hossein Toghiani, Rebecca K. Toghiani, and Dabir S. Viswanath, *J. Chem. Eng. Data*, **39**, 63–67, 1994).

(a) Partial pressures and total pressure in the gas phase equilibrated with liquid mixtures. The dashed lines indicate Raoult's law behavior.

(b) Pressure–composition phase diagram at $45\,^{\circ}\mathrm{C}$. Open circle: azeotropic point at $z_A = 0.59$ and $p = 60.5\,\mathrm{kPa}$.

Figure 13.8 shows the azeotropic behavior of the binary methanol-benzene system at constant temperature. In Fig. 13.8(a), the experimental partial pressures in a gas phase equilibrated with the nonideal liquid mixture are plotted as a function of the liquid composition. The partial pressures of both components exhibit positive deviations from Raoult's law, consistent with the statement in Sec. 12.8.2 that if one constituent of a binary liquid mixture exhibits positive deviations from Raoult's law, with only one inflection point in the curve of fugacity versus mole fraction, the other constituent also has positive deviations from Raoult's law. The total pressure (equal to the sum of the partial pressures) has a maximum value greater than the vapor pressure of either pure component. The curve of p versus x_A becomes the liquidus curve of the pressure–composition phase diagram shown in Fig. 13.8(b). Points on the vaporus curve are calculated from $p = p_A/y_A$.

> In practice, the data needed to generate the liquidus and vaporus curves of a nonideal binary system are usually obtained by allowing liquid mixtures of various compositions to boil in an equilibrium still at a fixed temperature or pressure. When the liquid and gas phases have become equilibrated, samples of each are withdrawn for analysis. The partial pressures shown in Fig. 13.8(a) were calculated from the experimental gas-phase compositions with the relations $p_A = y_A p$ and $p_B = p - p_A$.

If the constant-temperature liquidus curve has a maximum pressure at a liquid composition not corresponding to one of the pure components, which is the case for the methanol–benzene system, then the liquid and gas phases are mixtures of identical compositions at this pressure. This behavior was deduced at the end of Sec. 12.8.3. On the pressure–composition phase diagram, the liquidus and vaporus curves both have maxima at this pressure, and the two curves coincide at an *azeotropic point*. A binary system with negative deviations from Raoult's law can have an isothermal liquidus curve with a *minimum* pressure at a particular mixture composition, in which case the liquidus and vaporus curves coincide at an azeotropic point at this minimum. The general phenomenon in which equilibrated liquid and gas mixtures have identical compositions is called *azeotropy*, and the liquid with this composition is an azeotropic mixture or **azeotrope** (Greek: *boils unchanged*). An azeotropic mixture vaporizes as if it were a pure substance, undergoing an equilibrium phase transition to a gas of the same composition.

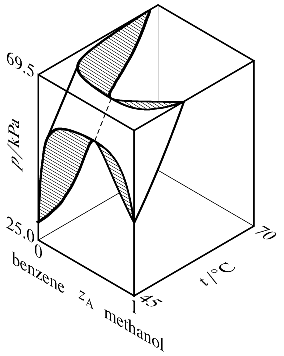
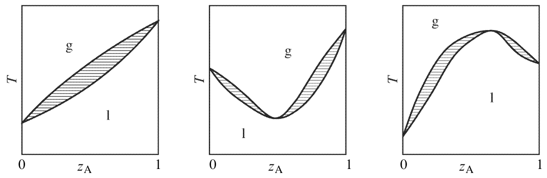


Figure 13.9 Liquidus and vaporus surfaces for the binary system of methanol (A) and benzene (Hossein Toghiani, Rebecca K. Toghiani, and Dabir S. Viswanath, *J. Chem. Eng. Data*, **39**, 63–67, 1994). Cross-sections are hatched in the direction of the tie lines. The dashed curve is the azeotrope vapor-pressure curve.

If the liquidus and vaporus curves exhibit a *maximum* on a pressure–composition phase diagram, then they exhibit a *minimum* on a temperature–composition phase diagram. This relation is explained for the methanol–benzene system by the three-dimensional liquidus and vaporus surfaces drawn in Fig. 13.9. In this diagram, the vaporus surface is hidden behind the liquidus surface. The hatched cross-section at the front of the figure is the same as the pressure–composition diagram of Fig. 13.8(b), and the hatched cross-section at the top of the figure is a temperature–composition phase diagram in which the system exhibits a *minimum-boiling azeotrope*.

A binary system containing an azeotropic mixture in equilibrium with its vapor has two species, two phases, and one relation among intensive variables: $x_A = y_A$. The number of degrees of freedom is then $F = 2 + s - r - P = 2 + 2 - 1 - 2 = 1$; the system is univariant. At a given temperature, the azeotrope can exist at only one pressure and have only one composition. As T changes, so do p and z_A along an *azeotrope vapor-pressure curve* as illustrated by the dashed curve in Fig. 13.9.



(a) (b) (c)

Figure 13.10 Temperature–composition phase diagrams of binary systems exhibiting (a) no azeotropy, (b) a minimum-boiling azeotrope, and (c) a maximum-boiling azeotrope. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

Figure 13.10 summarizes the general appearance of some relatively simple temperature–composition phase diagrams of binary systems. If the system does not form an azeotrope (*zeotropic* behavior), the equilibrated gas phase is richer in one component than the liquid phase at all liquid compositions, and the liquid mixture can be separated into its two components by fractional distillation. The gas in equilibrium with an azeotropic mixture, however, is not enriched in either component. Fractional distillation of a system with an azeotrope leads to separation into one pure component and the azeotropic mixture.

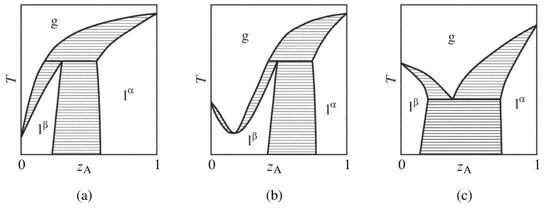


Figure 13.11 Temperature–composition phase diagrams of binary systems with partially-miscible liquids exhibiting (a) the ability to be separated into pure components by fractional distillation, (b) a minimum-boiling azeotrope, and (c) boiling at a lower temperature than the boiling point of either pure component. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

More complicated behavior is shown in the phase diagrams of Fig. 13.11. These are binary systems with partially-miscible liquids in which the boiling point is reached before an upper consolute temperature can be observed.

13.2.6 Solid–gas systems

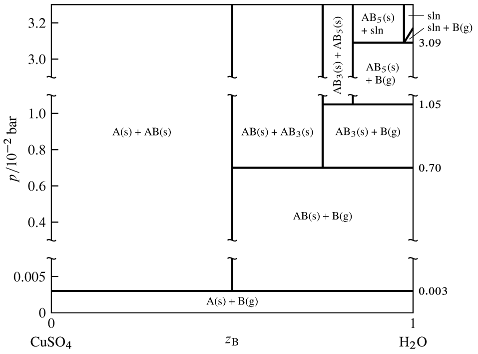


Figure 13.12 Pressure–composition phase diagram for the binary system of $CuSO_4$ (A) and H_2O (B) at $25\,^{\circ}C$ (Thomas S. Logan, *J. Chem. Educ.*, **35**, 148–149, 1958; E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. VII, McGraw-Hill, New York, 1930, p. 263).

As an example of a two-component system with equilibrated solid and gas phases, consider the components $CuSO_4$ and H_2O, denoted A and B respectively. In the pressure–composition phase diagram shown in Fig. 13.12, the composition variable z_B is as usual the mole fraction of component B in the system as a whole.

The anhydrous salt and its hydrates (solid compounds) form the series of solids $CuSO_4$, $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 3\,H_2O$, and $CuSO_4 \cdot 5\,H_2O$. In the phase diagram these formulas are abbreviated A, AB, AB$_3$, and AB$_5$. The following dissociation equilibria (dehydration equilibria) are possible:

$$\begin{aligned}
CuSO_4 \cdot H_2O(s) &\rightleftharpoons CuSO_4(s) + H_2O(g)\\
\tfrac{1}{2}CuSO_4 \cdot 3\,H_2O(s) &\rightleftharpoons \tfrac{1}{2}CuSO_4 \cdot H_2O(s) + H_2O(g)\\
\tfrac{1}{2}CuSO_4 \cdot 5\,H_2O(s) &\rightleftharpoons \tfrac{1}{2}CuSO_4 \cdot 3\,H_2O(s) + H_2O(g)
\end{aligned}$$

The equilibria are written above with coefficients that make the coefficient of $H_2O(g)$ unity. When one of these equilibria is established in the system, there are two components and three phases; the phase rule then tells us the system is univariant and the pressure has only one possible value at a given temperature. This pressure is called the *dissociation pressure* of the higher hydrate.

The dissociation pressures of the three hydrates are indicated by horizontal lines in Fig. 13.12. For instance, the dissociation pressure of $\mathrm{CuSO_4 \cdot 5\,H_2O}$ is 1.05×10^{-2} bar. At the pressure of each horizontal line, the equilibrium system can have one, two, or three phases, with compositions given by the intersections of the line with vertical lines. A fourth three-phase equilibrium is shown at $p = 3.09 \times 10^{-2}$ bar; this is the equilibrium between solid $\mathrm{CuSO_4 \cdot 5\,H_2O}$, the saturated aqueous solution of this hydrate, and water vapor.

Consider the thermodynamic equilibrium constant of one of the dissociation reactions. At the low pressures shown in the phase diagram, the activities of the solids are practically unity and the fugacity of the water vapor is practically the same as the pressure, so the equilibrium constant is almost exactly equal to p_d/p°, where p_d is the dissociation pressure of the higher hydrate in the reaction. Thus, a hydrate cannot exist in equilibrium with water vapor at a pressure below the dissociation pressure of the hydrate because dissociation would be spontaneous under these conditions. Conversely, the salt formed by the dissociation of a hydrate cannot exist in equilibrium with water vapor at a pressure above the dissociation pressure because hydration would be spontaneous.

> If the system contains dry air as an additional gaseous component and one of the dissociation equilibria is established, the partial pressure $p_{\mathrm{H_2O}}$ of H_2O is equal (approximately) to the dissociation pressure p_d of the higher hydrate. The prior statements regarding dissociation and hydration now depend on the value of $p_{\mathrm{H_2O}}$. If a hydrate is placed in air in which $p_{\mathrm{H_2O}}$ is less than p_d, dehydration is spontaneous; this phenomenon is called **efflorescence** (Latin: *blossoming*). If $p_{\mathrm{H_2O}}$ is greater than the vapor pressure of the saturated solution of the highest hydrate that can form in the system, the anhydrous salt and any of its hydrates will spontaneously absorb water and form the saturated solution; this is **deliquescence** (Latin: *becoming fluid*).

If the two-component equilibrium system contains only two phases, it is bivariant corresponding to one of the areas in Fig. 13.12. Here both the temperature and the pressure can be varied. In the case of areas labeled with two *solid* phases, the pressure has to be applied to the solids by a fluid (other than H_2O) that is not considered part of the system.

13.2.7 Systems at high pressure

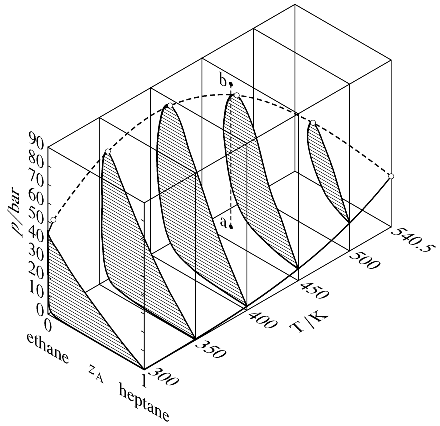


Figure 13.13 Pressure–temperature–composition behavior in the binary heptane–ethane system (W. B. Kay, *Ind. Eng. Chem.*, **30**, 459–465, 1938). The open circles are critical points; the dashed curve is the critical curve. The dashed line a–b illustrates retrograde condensation at 450 K.

Binary phase diagrams begin to look different when the pressure is greater than the critical pressure of either of the pure components. Various types of behavior have been observed in this region. One common type, that found in the binary system of heptane and ethane, is shown in Fig. 13.13. This figure shows sections of a three-dimensional phase diagram at five temperatures. Each section is a pressure–composition phase diagram at constant T. The two-phase areas are hatched in the direction of the tie lines. At the left end of each tie line (at low z_{A}) is a vaporus curve, and at the right end is a liquidus curve. The vapor pressure curve of pure ethane ($z_{\mathrm{A}}=0$) ends at the critical point of ethane at $305.4\ \mathrm{K}$; between this point and the critical point of heptane at $540.5\ \mathrm{K}$, there is a continuous *critical curve*, which is the locus of critical points at which gas and liquid mixtures become identical in composition and density.

Consider what happens when the system point is at point a in Fig. 13.13 and the pressure is then increased by isothermal compression along line a–b. The system point moves from the area for a gas phase into the two-phase gas–liquid area and then out into the gas-phase area again. This curious phenomenon, condensation followed by vaporization, is called *retrograde condensation*.

Under some conditions, an isobaric increase of T can result in vaporization followed by condensation; this is *retrograde vaporization*.

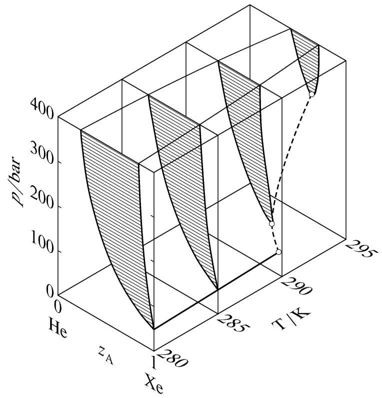


Figure 13.14 Pressure–temperature–composition behavior in the binary xenon–helium system (J. de Swann Arons and G. A. M. Diepen, *J. Chem. Phys.*, **44**, 2322–2330, 1966). The open circles are critical points; the dashed curve is the critical curve.

A different type of high-pressure behavior, that found in the xenon–helium system, is shown in Fig. 13.14. Here, the critical curve begins at the critical point of the less volatile component (xenon) and continues to *higher* temperatures and pressures than the critical temperature and pressure of either pure component. The two-phase region at pressures above this critical curve is sometimes said to represent *gas–gas equilibrium*, or *gas–gas immiscibility*, because we would not usually consider a liquid to exist beyond the critical points of the pure components. Of course, the coexisting phases in this two-phase region are not gases in the ordinary sense of being tenuous fluids, but are instead high-pressure fluids of liquid-like densities. If we want to call both phases gases, then we have to say that pure gaseous substances at high pressure do not necessarily mix spontaneously in all proportions as they do at ordinary pressures.

If the pressure of a system is increased isothermally, eventually solid phases will appear; these are not shown in Figs. 13.13 and Fig. 13.14.

13.3: Phase Diagrams- Ternary Systems

13.4: Chapter 13 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

13.1 Consider a single-phase system that is a gaseous mixture of N_2, H_2, and NH_3. For each of the following cases, find the number of degrees of freedom and give an example of the independent intensive variables that could be used to specify the equilibrium state, apart from the total amount of gas.

(a) There is no reaction.

(b) The reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is at equilibrium.

(c) The reaction is at equilibrium and the system is prepared from NH_3 only.

13.2 How many components has a mixture of water and deuterium oxide in which the equilibrium $H_2O + D_2O \rightleftharpoons 2\ \mathrm{HDO}$ exists?

13.3 Consider a system containing only $NH_4Cl(s)$, $NH_3(g)$, and $HCl(g)$. Assume that the equilibrium $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ exists.

(a) Suppose you prepare the system by placing solid NH_4Cl in an evacuated flask and heating to $400\ \mathrm{K}$. Use the phase rule to decide whether you can vary the pressure while both phases remain in equilibrium at $400\ \mathrm{K}$.

(b) According to the phase rule, if the system is not prepared as described in part (a) could you vary the pressure while both phases remain in equilibrium at $400\ \mathrm{K}$? Explain.

(c) Rationalize your conclusions for these two cases on the basis of the thermodynamic equilibrium constant. Assume that the gas phase is an ideal gas mixture and use the approximate expression $K = p_{NH_3} p_{HCl} / (p^\circ)^2$.

13.4 Consider the lime-kiln process $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Find the number of intensive variables that can be varied independently in the equilibrium system under the following conditions:

(a) The system is prepared by placing calcium carbonate, calcium oxide, and carbon dioxide in a container.

(b) The system is prepared from calcium carbonate only.

(c) The temperature is fixed at $1000\ \mathrm{K}$.

13.5 What are the values of C and F in systems consisting of solid $AgCl$ in equilibrium with an aqueous phase containing H_2O, $Ag^+(aq)$, $Cl^-(aq)$, $Na^+(aq)$, and $NO_3^-(aq)$ prepared in the following ways? Give examples of intensive variables that could be varied independently.

(a) The system is prepared by equilibrating excess solid $AgCl$ with an aqueous solution of $NaNO_3$.

(b) The system is prepared by mixing aqueous solutions of $AgNO_3$ and $NaCl$ in arbitrary proportions; some solid $AgCl$ forms by precipitation.

13.6 How many degrees of freedom has a system consisting of solid $NaCl$ in equilibrium with an aqueous phase containing H_2O, $Na^+(aq)$, $Cl^-(aq)$, $H^+(aq)$, and $OH^-(aq)$? Would it be possible to independently vary T, p, and m_{OH^-} ? If so, explain how you could do this.

13.7 Consult the phase diagram shown in Fig. 13.4 on page 430. Suppose the system contains $36.0\ \mathrm{g}$ (2.00 mol) H_2O and $58.4\ \mathrm{g}$ (1.00 mol) $NaCl$ at $25^\circ\mathrm{C}$ and 1 bar.

(a) Describe the phases present in the equilibrium system and their masses.

(b) Describe the changes that occur at constant pressure if the system is placed in thermal contact with a heat reservoir at $-30^\circ\mathrm{C}$.

(c) Describe the changes that occur if the temperature is raised from $25^\circ\mathrm{C}$ to $120^\circ\mathrm{C}$ at constant pressure.

(d) Describe the system after $200\ \mathrm{g} H_2O$ is added at $25^\circ\mathrm{C}$.

Table 13.1 Aqueous solubilities of sodium sulfate decahydrate and anhydrous sodium sulfate ^{a}

```
\begin{tabular}{lccc}
\hline \(\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}\) & & \multicolumn{2}{c}{\(\mathrm{Na}_{2} \mathrm{SO}_{4}\)} \\
\cline { 1 - 2 } \cline { 5 }\(t /{ }^{\circ} \mathrm{C}\) & \(x_{\mathrm{B}}\) & \(t /{ }^{\circ} \mathrm{C}\) & \(x_{\mathrm{B}}\) \\
\hline 10 & \(0.011\) & 40 & \(0.058\) \\
15 & \(0.016\) & 50 & \(0.056\) \\
20 & \(0.024\) & & \\
25 & \(0.034\) & & \\
30 & \(0.048\) & & \\
\hline\({ }^{a}\) Ref. [59], p. 179-180. & & \\
& & &
\end{tabular}
```

13.8 Use the following information to draw a temperature-composition phase diagram for the binary system of $H_2O(A)$ and $Na_2SO_4(B)$ at $p = 1$ bar, confining t to the range -20 to $50^\circ\mathrm{C}$ and z_B to the range $0 - 0.2$. The solid decahydrate, $Na_2SO_4 \cdot 10H_2O$, is stable below $32.4^\circ\mathrm{C}$. The anhydrous salt, Na_2SO_4, is stable above this temperature. There is a peritectic point for these two solids and the solution at $x_B = 0.059$ and $t = 32.4^\circ\mathrm{C}$. There is a eutectic point for ice, $Na_2SO_4 \cdot 10H_2O$, and the solution at $x_B = 0.006$ and $t = -1.3^\circ\mathrm{C}$. Table 13.1 gives the temperature dependence of the solubilities of the ionic solids.

Table 13.2 Data for Problem 13.9. Temperatures of saturated solutions of aqueous iron(III) chloride at $p = 1$ bar (\left(\mathrm{A}=\mathrm{FeCl}_{3}, \mathrm{~B}=\mathrm{H}_{2} \mathrm{O}\right)^{a}\)

x_{A}	$t/{}^{\circ}\mathrm{C}$	x_{A}	$t/{}^{\circ}\mathrm{C}$	x_{A}	$t/{}^{\circ}\mathrm{C}$
0.000	0.0	0.119	35.0	0.286	56.0
0.020	-10.0	0.143	37.0	0.289	55.0
0.032	-20.5	0.157	36.0	0.293	60.0
0.037	-27.5	0.173	33.0	0.301	69.0
0.045	-40.0	0.183	30.0	0.318	72.5
0.052	-55.0	0.195	27.4	0.333	73.5
0.053	-41.0	0.213	32.0	0.343	72.5
0.056	-27.0	0.222	32.5	0.358	70.0
0.076	0.0	0.232	30.0	0.369	66.0
0.083	10.0	0.238	35.0	0.369	80.0
0.093	20.0	0.259	50.0	0.373	100.0
0.106	30.0	0.277	55.0		

[a] Data from Ref. [59], page 193.

13.9 Iron(III) chloride forms various solid hydrates, all of which melt congruently. Table 13.2 on the preceding page lists the temperatures t of aqueous solutions of various compositions that are saturated with respect to a solid phase.

(a) Use these data to construct a $t-z_{\mathrm{B}}$ phase diagram for the binary system of FeCl_3 (A) and $\mathrm{H}_2\mathrm{O}$ (B). Identify the formula and melting point of each hydrate. Hint: derive a formula for the mole ratio $n_{\mathrm{B}}/n_{\mathrm{A}}$ as a function of x_{A} in a binary mixture.

(b) For the following conditions, determine the phase or phases present at equilibrium and the composition of each.

1. $t=-70.0^{\circ}\mathrm{C}$ and $z_{\mathrm{A}}=0.100$
2. $t=50.0^{\circ}\mathrm{C}$ and $z_{\mathrm{A}}=0.275$

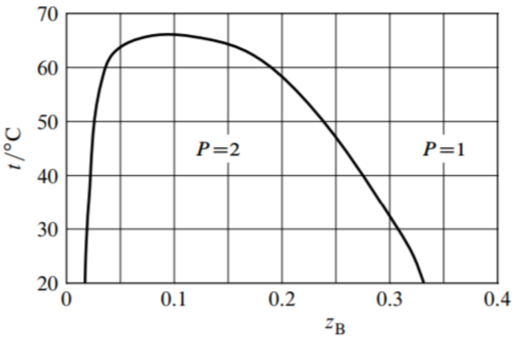


Figure 13.19 Temperature-composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar. [a] Only liquid phases are present.

\(\overline

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\) Ref. [59], p. 95.

13.10 Figure 13.19 is a temperature-composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar. These liquids are partially miscible below $67^{\circ}\mathrm{C}$. Phenol is more dense than water, so the layer with the higher mole fraction of phenol is the bottom layer. Suppose you place 4.0 mol of $\mathrm{H}_2\mathrm{O}$ and 1.0 mol of phenol in a beaker at $30^{\circ}\mathrm{C}$ and gently stir to allow the layers to equilibrate.

(a) What are the compositions of the equilibrated top and bottom layers?

(b) Find the amount of each component in the bottom layer.

(c) As you gradually stir more phenol into the beaker, maintaining the temperature at $30^{\circ}\mathrm{C}$, what changes occur in the volumes and compositions of the two layers? Assuming that one layer eventually disappears, what additional amount of phenol is needed to cause this to happen?

13.11 The standard boiling point of propane is $-41.8^{\circ}\mathrm{C}$ and that of n-butane is $-0.2^{\circ}\mathrm{C}$. Table 13.3 on the next page lists vapor pressure data for the pure liquids. Assume that the liquid mixtures obey Raoult's law.

(a) Calculate the compositions, x_{A}, of the liquid mixtures with boiling points of $-10.0^{\circ}\mathrm{C}$, $-20.0^{\circ}\mathrm{C}$, and $-30.0^{\circ}\mathrm{C}$ at a pressure of $1\,\mathrm{bar}$.

(b) Calculate the compositions, y_{A}, of the equilibrium vapor at these three temperatures.

Table 13.3 Saturation vapor pressures of propane (A) and n-butane (B)

```
\begin{tabular}{ccc}
\hline\(t /{ }^{\circ} \mathrm{C}\) & \(p_{\mathrm{A}}^{*} /\) bar & \(p_{\mathrm{B}}^{*} / \mathrm{bar}\) \\
\hline\(-10.0\) & \(3.360\) & \(0.678\) \\
\(-20.0\) & \(2.380\) & \(0.441\) \\
\(-30.0\) & \(1.633\) & \(0.275\) \\
\hline
\end{tabular}
```

(c) Plot the temperature-composition phase diagram at $p=1$ bar using these data, and label the areas appropriately.

(d) Suppose a system containing 10.0 mol propane and 10.0 mol$n$-butane is brought to a pressure of 1 bar and a temperature of $-25^{\circ}\mathrm{C}$. From your phase diagram, estimate the compositions and amounts of both phases.

Table 13.4 Liquid and gas compositions in the two-phase system of 2-propanol (A) and benzene at $45^{\circ}\mathrm{C}^{a}$

```
\begin{tabular}{llcccc}
\hline\(x_{\mathrm{A}}\) & \(y_{\mathrm{A}}\) & \(p / \mathrm{kPa}\) & \(x_{\mathrm{A}}\) & \(y_{\mathrm{A}}\) & \(p / \mathrm{kPa}\) \\
\hline 0 & 0 & \(29.89\) & \(0.5504\) & \(0.3692\) & \(35.32\) \\
\(0.0472\) & \(0.1467\) & \(33.66\) & \(0.6198\) & \(0.3951\) & \(34.58\) \\
\(0.0980\) & \(0.2066\) & \(35.21\) & \(0.7096\) & \(0.4378\) & \(33.02\) \\
\(0.2047\) & \(0.2663\) & \(36.27\) & \(0.8073\) & \(0.5107\) & \(30.28\) \\
\(0.2960\) & \(0.2953\) & \(36.45\) & \(0.9120\) & \(0.6658\) & \(25.24\) \\
\(0.3862\) & \(0.3211\) & \(36.29\) & \(0.9655\) & \(0.8252\) & \(21.30\) \\
\(0.4753\) & \(0.3463\) & \(35.93\) & \(1.0000\) & \(1.0000\) & \(18.14\) \\
\hline
\end{tabular}
```

[a] Ref. [24].

13.12 Use the data in Table 13.4 to draw a pressure-composition phase diagram for the 2-propanolbenzene system at $45^{\circ}\mathrm{C}$. Label the axes and each area.

Table 13.5 Liquid and gas compositions in the twophase system of acetone (A) and chloroform at $35.2^{\circ}\mathrm{C}$

```
\begin{tabular}{lllccc}
\hline\(x_{\mathrm{A}}\) & \(y_{\mathrm{A}}\) & \(p / \mathrm{kPa}\) & \(x_{\mathrm{A}}\) & \(y_{\mathrm{A}}\) & \(p / \mathrm{kPa}\) \\
\hline 0 & 0 & \(39.08\) & \(0.634\) & \(0.727\) & \(36.29\) \\
\(0.083\) & \(0.046\) & \(37.34\) & \(0.703\) & \(0.806\) & \(38.09\) \\
\(0.200\) & \(0.143\) & \(34.92\) & \(0.815\) & \(0.896\) & \(40.97\) \\
\(0.337\) & \(0.317\) & \(33.22\) & \(0.877\) & \(0.936\) & \(42.62\) \\
\(0.413\) & \(0.437\) & \(33.12\) & \(0.941\) & \(0.972\) & \(44.32\) \\
\(0.486\) & \(0.534\) & \(33.70\) & \(1.000\) & \(1.000\) & \(45.93\) \\
\(0.577\) & \(0.662\) & \(35.09\) & & & \\
\hline
\end{tabular}
```

[a] Ref. [179], p. 286.

CHAPTER OVERVIEW

14: Galvanic Cells

An *electrochemical cell* is a system in which passage of an electric current through an electrical circuit is linked to an internal cell reaction. A **galvanic cell**, or voltaic cell, is an electrochemical cell that, when isolated, has an electric potential difference between its terminals; the cell is said to be a *seat of electromotive force*.

The cell reaction in a galvanic cell differs in a fundamental way from the same reaction (i.e., one with the same reaction equation) taking place in a reaction vessel that is not part of an electrical circuit. In the reaction vessel, the reactants and products are in the same phase or in phases in contact with one another, and the reaction advances in the spontaneous direction until reaction equilibrium is reached. This reaction is the *direct reaction*.

The galvanic cell, in contrast, is arranged with the reactants physically separated from one another so that the cell reaction can advance only when an electric current passes through the cell. If there is no current, the cell reaction is constrained from taking place. When the electrical circuit is open and the cell is isolated from its surroundings, a state of thermal, mechanical, and transfer equilibrium is rapidly reached. In this state of *cell equilibrium* or *electrochemical equilibrium*, however, reaction equilibrium is not necessarily present—that is, if the reactants and products were moved to a reaction vessel at the same activities, there might be spontaneous advancement of the reaction.

As will be shown, measurements of the cell potential of a galvanic cell are capable of yielding precise values of molar reaction quantities of the cell reaction and thermodynamic equilibrium constants, and of mean ionic activity coefficients in electrolyte solutions.

Contributors

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14.1: Cell Diagrams and Cell Reactions

14.1.1 Elements of a galvanic cell

We will treat a galvanic cell as a *system*. The cell has two metal wires called *terminals* that pass through the system boundary. Within the cell are phases that can conduct an electric current and are collectively called *electrical conductors*. Each terminal is attached to an *electron conductor* that is usually a metal, but might also be graphite or a semiconductor. Each electron conductor is in contact with an *ionic conductor*, usually an electrolyte solution, through which ions but not electrons can move. Both of the electron conductors can be in contact with the same ionic conductor; or they can be in contact with separate ionic conductors, in which case the ionic conductors contact one another at a *liquid junction*. The general arrangement of the physical elements of a galvanic cell is therefore

$$\text{terminal} - \text{electron conductor} - \text{ionic conductor(s)} - \text{electron conductor} - \text{terminal} \tag{14.1.1}$$

Both terminals must be the same metal (usually copper) in order for it to be possible to measure the electric potential difference between them.

The combination of an electron conductor and the ionic conductor in contact with it is called an **electrode**, or half-cell. (The term “electrode” is sometimes used to refer to just the electron conductor.) To describe a galvanic cell, it is conventional to distinguish the *left* and *right* electrodes. In this way, we establish a left–right association with the reactants and products of the reactions at the electrodes.

14.1.2 Cell diagrams

The cell of Fig. 14.1 has a single electrolyte phase with essentially the same composition at both electrodes, and is an example of a *cell without liquid junction* or *cell without transference*. As an example of a *cell with transference*, consider the cell diagram

$$\mathrm{Zn} \mid \mathrm{Zn}_2^+(\mathrm{aq}) \,\vdots\, \mathrm{Cu}_2^+(\mathrm{aq}) \mid \mathrm{Cu} \tag{14.1.2}$$

This is the zinc–copper cell depicted in Fig. 14.2, sometimes called a Daniell cell. The two electrolyte phases are separated by a liquid junction represented in the cell diagram by the dashed vertical bar. If the liquid junction potential can be assumed to be negligible, the liquid junction is instead represented by a pair of dashed vertical bars:

$$\mathrm{Zn} \mid \mathrm{Zn}_2^+(\mathrm{aq}) \,\vdots\vdots\, \mathrm{Cu}_2^+(\mathrm{aq}) \mid \mathrm{Cu}$$

14.1.4 Advancement and charge

The **electron number** or charge number, z, of the cell reaction is defined as the amount of electrons entering at the right terminal per unit advancement of the cell reaction. z is a positive dimensionless quantity equal to $|\nu_{\mathrm{e}}|$, where ν_{e} is the stoichiometric number of the electrons in either of the electrode reactions whose sum is the cell reaction.

Because both electrode reactions are written with the same value of $|\nu_{\mathrm{e}}|$, the advancements of these reactions and of the cell reaction are all described by the same advancement variable ξ. For an infinitesimal change $\mathrm{d}\xi$, an amount of electrons equal to $z\,\mathrm{d}\xi$ enters the system at the right terminal, an equal amount of electrons leaves at the left terminal, and there is no buildup of charge in any of the internal phases.

The **Faraday constant** F is a physical constant defined as the charge per amount of protons, and is equal to the product of the elementary charge (the charge of a proton) and the Avogadro constant: $F = eN_{\mathrm{A}}$. Its value to five significant figures is $F = 96,485\ \mathrm{C\ mol^{-1}}$. The charge per amount of electrons is $-F$. Thus, the charge entering the right terminal during advancement $\mathrm{d}\xi$ is

$$\text{đ}Q_{\text{sys}} = -zF\,\mathrm{d}\xi \tag{14.1.1}$$

14.2: Electric Potentials in the Cell

14.3: Molar Reaction Quantities of the Cell Reaction

This e-book will denote the molar reaction Gibbs energy of a cell reaction by $\Delta_r G_{\text{cell}}$. This notation distinguishes it from the molar reaction Gibbs energy $\Delta_r G$ of the direct reaction, which may have a different value because in the cell the chemical potential of an ionic species is affected by the electric potential of its phase. $\Delta_r G_{\text{cell}}$ is defined by

$$\Delta_r G_{\text{cell}} \overset{\text{def}}{=} \sum_i \nu_i \mu_i \tag{14.3.1}$$

where the sum is over the reactants and products of the cell reaction. $\Delta_r G_{\text{cell}}$ is also equal to the partial derivative $(\partial G_{\text{cell}}/\partial\xi)_{T,p}$, where ξ is the advancement of the cell reaction.

14.3.1 Relation between $\boldsymbol{\Delta_r G_{\text{cell}}}$ and $\boldsymbol{E_{\text{cell, eq}}}$

When a galvanic cell is in a zero-current equilibrium state, both electrode reactions are at reaction equilibrium. In the electrode reaction at the left electrode, electrons are a product with stoichiometric number equal to z. At the right electrode, electrons are a reactant with stoichiometric number equal to $-z$. We can write the conditions for electrode reaction equilibria as follows:

$$\text{At the left electrode} \quad \sum_i \nu_i \mu_i + z\mu_e(\text{LE}) = 0 \tag{14.3.2}$$

$$\text{At the right electrode} \quad \sum_j \nu_j \mu_j - z\mu_e(\text{RE}) = 0 \tag{14.3.3}$$

In these equations, the sum over i is for the chemical species (excluding electrons) of the electrode reaction at the left electrode, and the sum over j is for the chemical species of the electrode reaction at the right electrode. $\mu_e(\text{LE})$ is the chemical potential of electrons in the electron conductor of the left electrode, and $\mu_e(\text{RE})$ is the chemical potential of electrons in the electron conductor of the right electrode.

Adding Eqs. 14.3.2 and 14.3.3, we obtain

$$\sum_i \nu_i \mu_i + \sum_j \nu_j \mu_j + z[\mu_e(\text{LE}) - \mu_e(\text{RE})] = 0 \tag{14.3.4}$$

The first two terms on the left side of Eq. 14.3.4 are sums over all the reactants and products of the cell reaction. From Eq. 14.3.1, we recognize the sum of these terms as the molar reaction Gibbs energy of the cell reaction:

$$\sum_i \nu_i \mu_i + \sum_j \nu_j \mu_j = \Delta_r G_{\text{cell}} \tag{14.3.5}$$

Substituting from Eq. 14.3.5 into Eq. 14.3.4 and solving for $\Delta_r G_{\text{cell}}$, we obtain

$$\Delta_r G_{\text{cell}} = -z[\mu_e(\text{LE}) - \mu_e(\text{RE})] \tag{14.3.6}$$

In a zero-current equilibrium state, there is electron transfer equilibrium between the left electron conductor and the left terminal, and between the right electron conductor and the right terminal: $\mu_e(\text{LE}) = \mu_e(\text{LT})$ and $\mu_e(\text{RE}) = \mu_e(\text{RT})$, where $\mu_e(\text{LT})$ and $\mu_e(\text{RT})$ are the chemical potentials of electrons in the left terminal and right terminal, respectively. Thus we can rewrite Eq. 14.3.6 as

$$\Delta_r G_{\text{cell}} = -z[\mu_e(\text{LT}) - \mu_e(\text{RT})] \tag{14.3.7}$$

Making substitutions from Eq. 14.2.2 for $\mu_e(\text{LT})$ and $\mu_e(\text{RT})$, and recognizing that $\mu_e(0)$ is the same in both terminals because they have the same composition, we obtain

$$\begin{aligned} \Delta_r G_{\text{cell}} &= -zF(\phi_R - \phi_L) \\ &= -zFE_{\text{cell, eq}} \end{aligned} \tag{14.3.8}$$

We can see from Eq. 14.3.1 that the value of $\Delta_r G_{\text{cell}}$ has nothing to do with the composition of the terminals. The relations of Eq. 14.3.8 were derived for a cell with both terminals made of the same metal. We can make the following deductions for such a cell:

1. Equation 14.3.8 can be derived by a different route. According to Eq. 5.8.6, reversible electrical work at constant T and p is equal to the Gibbs energy change: $đw_{\text{el, rev}} = dG_{\text{cell}}$. Making the substitution $đw_{\text{el, rev}} = E_{\text{cell, eq}}\, đQ_{\text{sys}}$ (from Eq. 3.8.8), with

$đQ_{\text{sys}}$ set equal to $-zF\,\mathrm{d}\xi$ (Eq. 14.1.1), followed by division by $\mathrm{d}\xi$, gives $-zFE_{\text{cell, eq}} = (\partial G_{\text{cell}}/\partial\xi)_{T,p}$, or $\Delta_{\text{r}}G_{\text{cell}} = -zFE_{\text{cell, eq}}$.

> Strictly speaking, this derivation applies only to a cell without a liquid junction. In a cell with a liquid junction, the electric current is carried across the junction by different ions depending on the direction of the current, and the cell is therefore not reversible.

14.3.2 Relation between $\Delta_{\text{r}}G_{\text{cell}}$ and $\Delta_{\text{r}}G$

Now imagine a reaction vessel that has the same temperature and pressure as the galvanic cell, and contains the same reactants and products at the same activities as in the cell. This reaction vessel, unlike the cell, is not part of an electrical circuit. In it, the reactants and products are in direct contact with one another, so there is no constraint preventing a spontaneous direct reaction. For example, the reaction vessel corresponding to the zinc–copper cell of Fig. 14.2 would have zinc and copper strips in contact with a solution of both $ZnSO_4$ and $CuSO_4$. Another example is the slow direct reaction in a cell without liquid junction described in Sec. 14.2.1.

Let the reaction equation of the direct reaction be written with the same stoichiometric numbers ν_i as in the reaction equation for the cell reaction. The direct reaction in the reaction vessel is described by this equation or its reverse, depending on which direction is spontaneous for the given activities.

The question now arises whether the molar reaction Gibbs energy $\Delta_{\text{r}}G_{\text{cell}}$ of the cell reaction is equal to the molar reaction Gibbs energy $\Delta_{\text{r}}G$ of the direct reaction. Both $\Delta_{\text{r}}G_{\text{cell}}$ and $\Delta_{\text{r}}G$ are defined by the sum $\sum_i \nu_i\mu_i$. Both reactions have the same values of ν_i, but the values of μ_i for charged species are in general different in the two systems because the electric potentials are different.

Consider first a cell without a liquid junction. This kind of cell has a single electrolyte solution, and all of the reactant and product ions of the cell reaction are in this solution phase. The same solution phase is present in the reaction vessel during the direct reaction. When all ions are in the same phase, the value of $\sum_i \nu_i\mu_i$ is independent of the electric potentials of any of the phases (see the comment following Eq. 11.8.4), so that the molar reaction Gibbs energies are the same for the cell reaction and the direct reaction:

$$\Delta_{\text{r}}G_{\text{cell}} = \Delta_{\text{r}}G \tag{14.3.9}$$

(no liquid junction)

Next, consider a cell with two electrolyte solutions separated by a liquid junction. For the molar reaction Gibbs energy of the cell reaction, we write

$$\Delta_{\text{r}}G_{\text{cell}} = \sum_i \nu_i\mu_i(\phi_i) + \sum_j \nu_j\mu_j(\phi_j) \tag{14.3.10}$$

The sums here include all of the reactants and products appearing in the cell reaction, those with index i being at the left electrode and those with index j at the right electrode. Let the solution at the left electrode be phase α and the solution at the right electrode be phase β. Then making the substitution $\mu_i(\phi) = \mu_i(0) + z_iF\phi$ (Eq. 10.1.6) gives us

$$\Delta_{\text{r}}G_{\text{cell}} = \sum_i \nu_i\mu_i(0) + \sum_j \nu_j\mu_j(0) + \sum_i \nu_i z_i F\phi^\alpha + \sum_j \nu_j z_j F\phi^\beta \tag{14.3.11}$$

The sum of the first two terms on the right side of Eq. 14.3.11 is the molar reaction Gibbs energy of a reaction in which the reactants and products are in phases of zero electric potential. According to the comment following Eq. 11.8.4, the molar reaction Gibbs energy would be the same if the ions were in a single phase of any electric potential. Consequently the sum $\sum_i \nu_i\mu_i(0) + \sum_j \nu_j\mu_j(0)$ is equal to $\Delta_{\text{r}}G$ for the direct reaction.

The conservation of charge during advancement of the electrode reactions at the left electrode and the right electrode is expressed by $\sum_i \nu_i z_i - z = 0$ and $\sum_j \nu_j z_j + z = 0$, respectively. Equation 14.3.11 becomes

$$\Delta_{\text{r}}G_{\text{cell}} = \Delta_{\text{r}}G - zFE_{\text{j}} \tag{14.3.12}$$

(cell with liquid junction)

where $E_{\text{j}} = \phi^\beta - \phi^\alpha$ is the liquid junction potential.

Finally, in Eqs. 14.3.9 and 14.3.12 we replace $\Delta_{\text{r}}G_{\text{cell}}$ by $-zFE_{\text{cell, eq}}$ (Eq. 14.3.8) and solve for $E_{\text{cell, eq}}$:

$$E_{\text{cell, eq}} = -\frac{\Delta_{\text{r}} G}{zF} \tag{14.3.13}$$
(cell without liquid junction)

$$E_{\text{cell, eq}} = -\frac{\Delta_{\text{r}} G}{zF} + E_{\text{j}} \tag{14.3.14}$$
(cell with liquid junction)

$E_{\text{cell, eq}}$ can be measured with great precision. If a reaction can be carried out in a galvanic cell without liquid junction, Eq. 14.3.13 provides a way to evaluate $\Delta_{\text{r}} G$ under given conditions. If the reaction can only be carried out in a cell with a liquid junction, Eq. 14.3.14 can be used for this purpose provided that the liquid junction potential E_{j} can be assumed to be negligible or can be estimated from theory.

Note that the cell has reaction equilibrium only if $\Delta_{\text{r}} G$ is zero. The cell has thermal, mechanical, and transfer equilibrium when the electric current is zero and the cell potential is the zero-current cell potential $E_{\text{cell, eq}}$. Equations 14.3.13 and 14.3.14 show that in order for the cell to also have reaction equilibrium, $E_{\text{cell, eq}}$ must equal the liquid junction potential if there is a liquid junction, or be zero otherwise. These are the conditions of an exhausted, “dead” cell that can no longer do electrical work.

14.3.3 Standard molar reaction quantities

Consider a hypothetical galvanic cell in which each reactant and product of the cell reaction is in its standard state at unit activity, and in which a liquid junction if present has a negligible liquid junction potential. The equilibrium cell potential of this cell is called the **standard cell potential** of the cell reaction, $E^{\circ}_{\text{cell, eq}}$. An experimental procedure for evaluating $E^{\circ}_{\text{cell, eq}}$ will be described in Sec. 14.5.

In this hypothetical cell, $\Delta_{\text{r}} G_{\text{cell}}$ is equal to the standard molar reaction Gibbs energy $\Delta_{\text{r}} G^{\circ}$. From Eq. 14.3.13, or Eq. 14.3.14 with E_{j} assumed equal to zero, we have

$$\Delta_{\text{r}} G^{\circ} = -zFE^{\circ}_{\text{cell, eq}} \tag{14.3.15}$$

$\Delta_{\text{r}} G^{\circ}$ is the molar reaction Gibbs energy when each reactant and product is at unit activity and, if it is an ion, is in a phase of zero electric potential. Since $\Delta_{\text{r}} G^{\circ}$ is equal to $-RT \ln K$ (Eq. 11.8.10), we can write

$$\ln K = \frac{zF}{RT} E^{\circ}_{\text{cell, eq}} \tag{14.3.16}$$

Equation 14.3.16 allows us to evaluate the thermodynamic equilibrium constant K of the cell reaction by a noncalorimetric method. Consider for example the cell

$$\text{Ag} \mid \text{Ag}^{+}(\text{aq}) \mathrel{\vdots\vdots} \text{Cl}^{-}(\text{aq}) \mid \text{AgCl(s)} \mid \text{Ag} \tag{14.3.1}$$

in which the pair of dashed vertical bars indicates a liquid junction of negligible liquid junction potential. The electrode reactions are

$$\begin{aligned} \text{Ag(s)} &\rightarrow \text{Ag}^{+}(\text{aq}) + \text{e}^{-} \\ \text{AgCl(s)} + \text{e}^{-} &\rightarrow \text{Ag(s)} + \text{Cl}^{-}(\text{aq}) \end{aligned}$$

and the cell reaction is

$$\text{AgCl(s)} \rightarrow \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$$

The equilibrium constant of this reaction is the solubility product K_{s} of silver chloride (Sec. 12.5.5). At $298.15\ \text{K}$, the standard cell potential is found to be $E^{\circ}_{\text{cell, eq}} = -0.5770\ \text{V}$. We can use this value in Eq. 14.3.16 to evaluate K_{s} at $298.15\ \text{K}$ (see Prob. 14.5).

Equation 14.3.16 also allows us to evaluate the standard molar reaction enthalpy by substitution in Eq. 12.1.13:

$$\begin{aligned} \Delta_{\text{r}} H^{\circ} &= RT^2 \frac{\text{d} \ln K}{\text{d}T} \\ &= zF\left(T \frac{\text{d}E^{\circ}_{\text{cell, eq}}}{\text{d}T} - E^{\circ}_{\text{cell, eq}}\right) \end{aligned} \tag{14.3.17}$$
(no solute standard states based on concentration)

Finally, by combining Eqs. 14.3.15 and 14.3.17 with $\Delta_{\mathrm{r}}G^{\circ} = \Delta_{\mathrm{r}}H^{\circ} - T\Delta_{\mathrm{r}}S^{\circ}$, we obtain an expression for the standard molar reaction entropy:

$$\Delta_{\mathrm{r}}S^{\circ} = zF\frac{\mathrm{d}E^{\circ}_{\text{cell, eq}}}{\mathrm{d}T} \qquad (14.3.18)$$

(no solute standard states based on concentration)

Because G, H, and S are state functions, the thermodynamic equilibrium constant and the molar reaction quantities evaluated from $E^{\circ}_{\text{cell, eq}}$ and $\mathrm{d}E^{\circ}_{\text{cell, eq}}/\,\mathrm{d}T$ are the same quantities as those for the reaction when it takes place in a reaction vessel instead of in a galvanic cell. However, the heats at constant T and p are not the same (Sec. 11.3.1). During a reversible cell reaction, $\mathrm{d}S$ must equal $đq/T$, and $đq/\,\mathrm{d}\xi$ is therefore equal to $T\Delta_{\mathrm{r}}S^{\circ}$ during a cell reaction taking place reversibly under standard state conditions at constant T and p.

14.4: The Nernst Equation

The standard cell potential $E^\circ_{\text{cell, eq}}$ of a cell reaction is the equilibrium cell potential of the hypothetical galvanic cell in which each reactant and product of the cell reaction is in its standard state and there is no liquid junction potential. The value of $E^\circ_{\text{cell, eq}}$ for a given cell reaction with given choices of standard states is a function only of temperature. The measured equilibrium cell potential $E_{\text{cell, eq}}$ of an actual cell, however, depends on the activities of the reactants and products as well as on temperature and the liquid junction potential, if present.

To derive a relation between $E_{\text{cell, eq}}$ and activities for a cell without liquid junction, or with a liquid junction of negligible liquid junction potential, we substitute expressions for $\Delta_r G$ and for $\Delta_r G^\circ$ from Eqs. 14.3.13 and Eq. 14.3.15 into $\Delta_r G = \Delta_r G^\circ + RT \ln Q_{\text{rxn}}$ (Eq. 11.8.8) and solve for $E_{\text{cell, eq}}$:

$$E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{RT}{zF} \ln Q_{\text{rxn}} \tag{14.4.1}$$

$$(\text{no liquid junction, or } E_j{=}0)$$

Equation 14.4.1 is the **Nernst equation** for the cell reaction. Here Q_{rxn} is the reaction quotient for the cell reaction defined by Eq. 11.8.6: $Q_{\text{rxn}} = \prod_i a_i^{\nu_i}$.

The rest of this section will assume that the cell reaction takes place in a cell without liquid junction, or in one in which E_j is negligible.

If each reactant and product of the cell reaction is in its standard state, then each activity is unity and $\ln Q_{\text{rxn}}$ is zero. We can see from the Nernst equation that the equilibrium cell potential $E_{\text{cell, eq}}$ in this case has its standard value $E^\circ_{\text{cell, eq}}$, as expected. A decrease in product activities or an increase in reactant activities decreases the value of $\ln Q_{\text{rxn}}$ and increases $E_{\text{cell, eq}}$, as we would expect since $E_{\text{cell, eq}}$ should be greater when the forward cell reaction has a greater tendency for spontaneity.

If the cell reaction comes to reaction equilibrium, as it will if we short-circuit the cell terminals with an external wire, the value of Q_{rxn} becomes equal to the thermodynamic equilibrium constant K, and the Nernst equation becomes $E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - (RT/zF)\ln K$. The term $(RT/zF)\ln K$ is equal to $E^\circ_{\text{cell, eq}}$ (Eq. 14.3.16), so $E_{\text{cell, eq}}$ becomes zero—the cell is “dead” and is incapable of performing electrical work on the surroundings.

At $T{=}298.15\,\text{K}(25.00\,^\circ\text{C})$, the value of RT/F is 0.02569 V, and we can write the Nernst equation in the compact form

$$E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{0.02569\ \text{V}}{z} \ln Q_{\text{rxn}} \tag{14.4.2}$$

$$(T{=}298.15\,\text{K})$$

As an illustration of an application of the Nernst equation, consider the reaction equation

$$\text{H}_2(\text{g}) + 2\,\text{AgCl}(\text{s}) \rightarrow 2\,\text{H}^+(\text{aq}) + 2\,\text{Cl}^-(\text{aq}) + 2\,\text{Ag}(\text{s}) \tag{14.4.1}$$

This reaction takes place in a cell without liquid junction (Fig. 14.1), and the electrolyte solution can be aqueous HCl. The expression for the reaction quotient is

$$Q_{\text{rxn}} = \frac{a_+^2\, a_-^2\, a_{\text{Ag}}^2}{a_{\text{H}_2}\, a_{\text{AgCl}}^2} \tag{14.4.3}$$

We may usually with negligible error approximate the pressure factors of the solids and solutes by unity. The activities of the solids are then 1, the solute activities are $a_+ = \gamma_+ m_+/m^\circ$ and $a_- = \gamma_- m_-/m^\circ$, and the hydrogen activity is $a_{\text{H}_2} = f_{\text{H}_2}/p^\circ$. The ion molalities m_+ and m_- are equal to the HCl molality m_{B}. The expression for Q_{rxn} becomes

$$Q_{\text{rxn}} = \frac{\gamma_+^2 \gamma_-^2 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} = \frac{\gamma_\pm^4 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} \tag{14.4.4}$$

and the Nernst equation for this cell is

$$\begin{aligned} E_{\text{cell, eq}} &= E^\circ_{\text{cell, eq}} - \frac{RT}{2F} \ln \frac{\gamma_\pm^4 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} \\ &= E^\circ_{\text{cell, eq}} - \frac{2RT}{F} \ln \gamma_\pm - \frac{2RT}{F} \ln \frac{m_{\text{B}}}{m^\circ} + \frac{RT}{2F} \ln \frac{f_{\text{H}_2}}{p^\circ} \end{aligned} \tag{14.4.5}$$

By measuring $E_{\text{cell, eq}}$ for a cell with known values of m_{B} and f_{H_2}, and with a derived value of $E^{\circ}_{\text{cell, eq}}$, we can use this equation to find the mean ionic activity coefficient $\gamma_{\pm}$ of the HCl solute. This is how the experimental curve for aqueous HCl in Fig. 10.3 was obtained.

> We can always multiply each of the stoichiometric coefficients of a reaction equation by the same positive constant without changing the meaning of the reaction. How does this affect the Nernst equation for the reaction equation above? Suppose we decide to multiply the stoichiometric coefficients by one-half:
>
> $$\tfrac{1}{2}\text{H}_2(\text{g}) + \text{AgCl(s)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(s)}$$
>
> With this changed reaction equation, the value of z is changed from 2 to 1 and the Nernst equation becomes
>
> $$E_{\text{cell, eq}} = E^{\circ}_{\text{cell, eq}} - \frac{RT}{F}\ln\frac{\gamma_{\pm}^2(m_{\text{B}}/m^{\circ})^2}{(f_{\text{H}_2}/p^{\circ})^{1/2}} \tag{14.4.6}$$
>
> which yields the same value of $E_{\text{cell, eq}}$ for given cell conditions as Eq. 14.4.5. This value must of course be unchanged, because physically the cell is the same no matter how we write its cell reaction, and measurable physical quantities such as $E_{\text{cell, eq}}$ are unaffected. However, molar reaction quantities such as $\Delta_{\text{r}}G$ and $\Delta_{\text{r}}G^{\circ}$ *do* depend on how we write the cell reaction, because they are changes per extent of reaction.

14.5: Evaluation of the Standard Cell Potential

As we have seen, the value of the standard cell potential $E^\circ_{\text{cell, eq}}$ of a cell reaction has useful thermodynamic applications. The value of $E^\circ_{\text{cell, eq}}$ for a given cell reaction depends only on temperature. To evaluate it, we can extrapolate an appropriate function to infinite dilution where ionic activity coefficients are unity.

To see how this procedure works, consider again the cell reaction $\mathrm{H_2(g) + 2\,AgCl(s) \rightarrow 2\,H^+(aq) + 2\,Cl^-(aq) + 2\,Ag(s)}$. The cell potential depends on the molality m_B of the HCl solute according to Eq. 14.4.5. We can rearrange the equation to

$$E^\circ_{\text{cell, eq}} = E_{\text{cell, eq}} + \frac{2RT}{F}\ln\gamma_\pm + \frac{2RT}{F}\ln\frac{m_\mathrm{B}}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{\mathrm{H_2}}}{p^\circ} \tag{14.5.1}$$

For given conditions of the cell, we can measure all quantities on the right side of Eq. 14.5.1 except the mean ionic activity coefficient $\gamma_\pm$ of the electrolyte. We cannot know the exact value of $\ln\gamma_\pm$ for any given molality until we have evaluated $E^\circ_{\text{cell, eq}}$. We do know that as m_B approaches zero, $\gamma_\pm$ approaches unity and $\ln\gamma_\pm$ must approach zero. The Debye–Hückel formula of Eq. 10.4.7 is a theoretical expression for $\ln\gamma_\pm$ that more closely approximates the actual value the lower is the ionic strength. Accordingly, we define the quantity

$$E'_{\text{cell}} = E_{\text{cell, eq}} + \frac{2RT}{F}\left(-\frac{A\sqrt{m_\mathrm{B}}}{1+Ba\sqrt{m_\mathrm{B}}}\right) + \frac{2RT}{F}\ln\frac{m_\mathrm{B}}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{\mathrm{H_2}}}{p^\circ} \tag{14.5.2}$$

The expression in parentheses is the Debye–Hückel formula for $\ln\gamma_\pm$ with I_m replaced by m_B. The constants A and B have known values at any temperature (Sec. 10.4), and a is an ion-size parameter for which we can choose a reasonable value. At a given temperature, we can evaluate E'_{cell} experimentally as a function of m_B.

The expression on the right side of Eq. 14.5.1 differs from that of Eq. 14.5.2 by contributions to $(2RT/F)\ln\gamma_\pm$ not accounted for by the Debye–Hückel formula. Since these contributions approach zero in the limit of infinite dilution, the extrapolation of measured values of E'_{cell} to $m_\mathrm{B}{=}0$ yields the value of $E^\circ_{\text{cell, eq}}$.

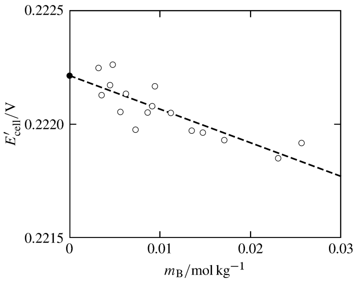

Figure 14.5 E'_{cell} (defined by Eq. 14.5.2) as a function of HCl molality for the cell of Fig. 14.1 at $298.15\,\mathrm{K}$ Data from Herbert S. Harned and Russell W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350–1357, 1932, with $f_{\mathrm{H_2}}$ set equal to $p_{\mathrm{H_2}}$ and the parameter a set equal to $4.3\times10^{-10}\,\mathrm{m}$. The dashed line is a least-squares fit to a linear relation.

Figure 14.5 shows this extrapolation using data from the literature. The extrapolated value indicated by the filled circle is $E^\circ_{\text{cell, eq}} = 0.2222\ \mathrm{V}$, and the uncertainty is on the order of only $0.1\,\mathrm{mV}$.

14.6: Standard Electrode Potentials

Section 14.5 explained how, by measuring the equilibrium cell potential of a galvanic cell at different electrolyte molalities, we can evaluate the standard cell potential $E^\circ_{\text{cell, eq}}$ of the cell reaction. It is not necessary to carry out this involved experimental procedure for each individual cell reaction of interest. Instead, we can calculate $E^\circ_{\text{cell, eq}}$ from standard electrode potentials.

By convention, standard electrode potentials use a standard hydrogen electrode as a reference electrode. A **standard hydrogen electrode** is a hydrogen electrode, such as the electrode shown at the left in Fig. 14.1, in which the species $H_2(g)$ and $H^+(aq)$ are in their standard states. Since these are *hypothetical* gas and solute standard states, the standard hydrogen electrode is a hypothetical electrode—not one we can actually construct in the laboratory.

A **standard electrode potential** E° is defined as the standard cell potential of a cell with a hydrogen electrode at the left and the electrode of interest at the right. For example, the cell in Fig. 14.1 with cell diagram

$$\mathrm{Pt}\,|\,\mathrm{H_2(g)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag}$$

has a hydrogen electrode at the left and a silver–silver chloride electrode at the right. The standard electrode potential of the silver–silver chloride electrode, therefore, is equal to the standard cell potential of this cell.

Since a cell with hydrogen electrodes at both the left and right has a standard cell potential of zero, the standard electrode potential of the hydrogen electrode is *zero* at all temperatures. The standard electrode potential of any other electrode is nonzero and is a function only of temperature.

Consider the following three cells constructed from various combinations of three different electrodes: a hydrogen electrode, and two electrodes denoted L and R.

- We wish to calculate the standard cell potential $E^\circ_{\text{cell, eq}}$ of cell 1 from the standard electrode potentials E°_{L} and E°_{R}.

  If we write the cell reactions of cells 1 and 2 using the same value of the electron number z for both, we find that their sum is the cell reaction for cell 3 with the same value of z. Call these reactions 1, 2, and 3, respectively:

  $$(\text{reaction }1) + (\text{reaction }2) = (\text{reaction }3) \tag{14.6.1}$$

  Equation 14.6.3 is a general relation applicable to any galvanic cell. It should be apparent that we can use the relation to calculate the standard electrode potential of an electrode from the standard electrode potential of a different electrode and the standard cell potential of a cell that contains both electrodes. Neither electrode has to be a hydrogen electrode, which is difficult to work with experimentally.

  Using Eq. 14.6.3 to calculate standard cell potentials from standard electrode potentials saves a lot of experimental work. For example, measurement of $E^\circ_{\text{cell, eq}}$ for ten different cells, only one of which needs to include a hydrogen electrode, provides values of E° for ten electrodes other than $E^\circ{=}0$ for the hydrogen electrode. From these ten values of E°, values of $E^\circ_{\text{cell, eq}}$ can be calculated for 35 other cells without hydrogen electrodes.

14.7: Chapter 14 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

14.1
The state of a galvanic cell without liquid junction, when its temperature and pressure are uniform, can be fully described by values of the variables T, p, and ξ. Find an expression for $\mathrm{d}G$ during a reversible advancement of the cell reaction, and use it to derive the relation $\Delta_r G_{\text{cell}} = -zFE_{\text{cell, eq}}$ (Eq. 14.3.8). (Hint: Eq. 3.8.8.)

14.2
Before 1982 the standard pressure was usually taken as $1\,\mathrm{atm}$. For the cell shown in Fig. 14.1, what correction is needed, for a value of $E^{\circ}_{\text{cell, eq}}$ obtained at $25\,^{\circ}\mathrm{C}$ and using the older convention, to change the value to one corresponding to a standard pressure of $1\,\mathrm{bar}$? Equation 14.3.15 can be used for this calculation.

14.3
Careful measurements (Roger G. Bates and Vincent E. Bower, *J. Res. Natl. Bur. Stand. (U.S.)*, **53**, 283–290, 1954) of the equilibrium cell potential of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2(g)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag}$$

yielded, at $298.15\,\mathrm{K}$ and using a standard pressure of $1\,\mathrm{bar}$, the values $E^{\circ}_{\text{cell, eq}} = 0.22217\,\mathrm{V}$ and $\mathrm{d}E^{\circ}_{\text{cell, eq}}/\,\mathrm{d}T = -6.462\times10^{-4}\,\mathrm{V\,K^{-1}}$. (The requested calculated values are close to, but not exactly the same as, the values listed in Appendix H, which are based on the same data combined with data of other workers.)

(a) Evaluate $\Delta_r G^{\circ}$, $\Delta_r S^{\circ}$, and $\Delta_r H^{\circ}$ at $298.15\,\mathrm{K}$ for the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{Ag(s)} \tag{14.7.1}$$

(b) Problem 12.18 showed how the standard molar enthalpy of formation of the aqueous chloride ion may be evaluated based on the convention $\Delta_f H^{\circ}(\mathrm{H^+, aq}) = 0$. If this value is combined with the value of $\Delta_r H^{\circ}$ obtained in part (a) of the present problem, the standard molar enthalpy of formation of crystalline silver chloride can be evaluated. Carry out this calculation for $T = 298.15\,\mathrm{K}$ using the value $\Delta_f H^{\circ}(\mathrm{Cl^-, aq}) = -167.08\,\mathrm{kJ\,mol^{-1}}$ (Appendix H).

(c) By a similar procedure, evaluate the standard molar entropy, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of crystalline silver chloride at $298.15\,\mathrm{K}$. You need the following standard molar entropies evaluated from spectroscopic and calorimetric data:

$$\begin{aligned} &S^{\circ}_{\mathrm{m}}(\mathrm{H_2, g}) = 130.68\,\mathrm{J\,K^{-1}\,mol^{-1}} && S^{\circ}_{\mathrm{m}}(\mathrm{Cl_2, g}) = 223.08\,\mathrm{J\,K^{-1}\,mol^{-1}} \\ &S^{\circ}_{\mathrm{m}}(\mathrm{Cl^-, aq}) = 56.60\,\mathrm{J\,K^{-1}\,mol^{-1}} && S^{\circ}_{\mathrm{m}}(\mathrm{Ag, s}) = 42.55\,\mathrm{J\,K^{-1}\,mol^{-1}} \end{aligned} \tag{14.7.2}$$

14.4
The standard cell potential of the cell

$$\mathrm{Ag}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{Cl_2(g)}\,|\,\mathrm{Pt} \tag{14.7.3}$$

has been determined over a range of temperature (G. Faita, P. Longhi, and T. Mussini, *J. Electrochem. Soc.*, **114**, 340–343, 1967). At T=$298.15\,\mathrm{K}$, the standard cell potential was found to be $E^{\circ}_{\text{cell, eq}} = 1.13579\,\mathrm{V}$, and its temperature derivative was found to be $\mathrm{d}E^{\circ}_{\text{cell, eq}}/\,\mathrm{d}T = -5.9863\times10^{-4}\,\mathrm{V\,K^{-1}}$.

(a) Write the cell reaction for this cell.

(b) Use the data to evaluate the standard molar enthalpy of formation and the standard molar Gibbs energy of formation of crystalline silver chloride at $298.15\,\mathrm{K}$. (Note that this calculation provides values of quantities also calculated in Prob. 14.3 using independent data.)

14.5
Use data in Sec. 14.3.3 to evaluate the solubility product of silver chloride at $298.15\,\mathrm{K}$.

14.6
The equilibrium cell potential of the galvanic cell

$$\mathrm{Pt}\,|\,\mathrm{H_2(g},\ f{=}1\ \mathrm{bar)}\,|\,\mathrm{HCl(aq},\ 0.500\ \mathrm{mol\ kg^{-1})}\,|\,\mathrm{Cl_2(g},\ f{=}1\ \mathrm{bar)}\,|\,\mathrm{Pt} \tag{14.7.4}$$

is found to be $E_{\text{cell, eq}} = 1.410\ \mathrm{V}$ at $298.15\ \mathrm{K}$ The standard cell potential is $E^\circ_{\text{cell, eq}} = 1.360\ \mathrm{V}$.

(a) Write the cell reaction and calculate its thermodynamic equilibrium constant at $298.15\ \mathrm{K}$

(b) Use the cell measurement to calculate the mean ionic activity coefficient of aqueous HCl at $298.15\ \mathrm{K}$ and a molality of $0.500\ \mathrm{mol\ kg^{-1}}$.

14.7
Consider the following galvanic cell, which combines a hydrogen electrode and a calomel electrode:

$$\mathrm{Pt}\,|\,\mathrm{H_2(g)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{Hg_2Cl_2(s)}\,|\,\mathrm{Hg(l)}\,|\,\mathrm{Pt} \tag{14.7.5}$$

(a) Write the cell reaction.

(b) At $298.15\ \mathrm{K}$, the standard cell potential of this cell is $E^\circ_{\text{cell, eq}} = 0.2680\ \mathrm{V}$. Using the value of $\Delta_f G^\circ$ for the aqueous chloride ion in Appendix H, calculate the standard molar Gibbs energy of formation of crystalline mercury(I) chloride (calomel) at $298.15\ \mathrm{K}$

(c) Calculate the solubility product of mercury(I) chloride at $298.15\ \mathrm{K}$ The dissolution equilibrium is $\mathrm{Hg_2Cl_2(s)} \rightleftharpoons \mathrm{Hg_2^{2+}(aq)} + 2\,\mathrm{Cl^-(aq)}$. Take values for the standard molar Gibbs energies of formation of the aqueous ions from Appendix H.

14.8
Table 14.1 lists equilibrium cell potentials obtained with the following cell at $298.15\ \mathrm{K}$ (Albert S. Keston, *J. Am. Chem. Soc.*, **57**, 1671–1673, 1935):

$$\mathrm{Pt}\,|\,\mathrm{H_2(g,\ 1.01\ bar)}\,|\,\mathrm{HBr(aq},\ m_\mathrm{B})\,|\,\mathrm{AgBr(s)}\,|\,\mathrm{Ag}$$

Use these data to evaluate the standard electrode potential of the silver-silver bromide electrode at this temperature to the nearest millivolt. (Since the electrolyte solutions are quite dilute, you may ignore the term $Ba\sqrt{m_\mathrm{B}}$ in Eq. 14.5.2.)

14.9
The cell diagram of a mercury cell can be written

$$\mathrm{Zn(s)}\,|\,\mathrm{ZnO(s)}\,|\,\mathrm{NaOH(aq)}\,|\,\mathrm{HgO(s)}\,|\,\mathrm{Hg(l)}$$

(a) Write the electrode reactions and cell reaction with electron number $z = 2$.

(b) Use data in Appendix H to calculate the standard molar reaction quantities $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ for the cell reaction at $298.15\ \mathrm{K}$

(c) Calculate the standard cell potential of the mercury cell at $298.15\ \mathrm{K}$ to the nearest $0.01\ \mathrm{V}$.

(d) Evaluate the ratio of heat to advancement, $đq/\,d\xi$, at a constant temperature of $298.15\ \mathrm{K}$ and a constant pressure of 1 bar, for the cell reaction taking place in two different ways: reversibly in the cell, and spontaneously in a reaction vessel that is not part of an electrical circuit.

(e) Evaluate $\mathrm{d}E^\circ_{\text{cell, eq}}/\,\mathrm{d}T$, the temperature coefficient of the standard cell potential.

CHAPTER OVERVIEW

15: Appendices

15.1: Appendix A- Definitions of the SI Base Units

The official definitions of the base units given in the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, Sec. 3.3) are as follows.

- The **metre** is the length of path traveled by light in vacuum during a time interval of 1/299,792,458 of a second.
  [This e-book uses the alternative spelling *meter*.]
- The **kilogram** is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
  [The international prototype is a platinum-iridium cylinder stored in a vault of the International Bureau of Weights and Measures in Sèvres near Paris, France.]
- The **second** is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom. This definition refers to a caesium atom at rest at a temperature of $0\ \mathrm{K}$.
- The **kelvin**, unit of thermodynamic temperature, is the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water. This definition refers to water having the isotopic composition defined exactly by the following amount-of-substance ratios: 0.000 155 76 mole of $^2\mathrm{H}$ per mole of $^1\mathrm{H}$, 0.000 379 9 mole of $^{17}\mathrm{O}$ per mole of $^{16}\mathrm{O}$, and 0.002 005 2 mole of $^{18}\mathrm{O}$ per mole of $^{16}\mathrm{O}$.
- The **mole** is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is “mol”. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. In this definition, it is understood that unbound atoms of carbon 12, at rest and in their ground state, are referred to.
- The **ampere** is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
- The **candela** is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

15.2: Appendix B- Physical Constants

The following table lists values from *The Nist Reference on Constants, Units, and Uncertainty* of fundamental physical constants used in thermodynamic calculations. Except for those marked “exact,” they are the 2010 CODATA (Committee on Data for Science and Technology) recommended values. The number in parentheses at the end of a value is the standard deviation uncertainty in the right-most digits of the value.

Physical quantity	Symbol	Value in SI units
Avogadro constant	N_{A}	$6.022\,141\,29(27) \times 10^{23}\ \mathrm{mol^{-1}}$
elementary charge	e	$1.602\,176\,565(35) \times 10^{-19}\ \mathrm{C}$
Faraday constant	F	$9.648\,533\,65(21) \times 10^{4}\ \mathrm{C\,mol^{-1}}$
gas constant [a]	R	$8.314\,4621(75)\ \mathrm{J\,K^{-1}\,mol^{-1}}$
magnetic constant [b]	μ_0	$4\pi \times 10^{-7}\ \mathrm{N\,A^{-2}}$ (exact)
electric constant [c]	ϵ_0	$8.854\,187\,817\ldots \times 10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$ (exact)
speed of light in vacuum	c_0	$2.997\,924\,58 \times 10^{8}\ \mathrm{m\,s^{-1}}$ (exact)
standard acceleration of free fall [d]	g_{n}	$9.806\,65\ \mathrm{m\,s^{-2}}$ (exact)

[a] or molar gas constant
[b] or permeability of vacuum
[c] or permittivity of vacuum
[d] or standard acceleration of gravity

15.3: Appendix C- Symbols for Physical Quantities

This appendix lists the symbols for most of the variable physical quantities used in this e-book. The symbols are those recommended in the IUPAC Green Book (Ian Mills et al, *Quantities, Units and Symbols in Physical Chemistry*, 2nd edition, Blackwell, Oxford, 1993) except for quantities followed by an asterisk (*). The first table lists Roman letter symbols, and the second lists Greek letter symbols.

Symbol	Physical quantity	SI unit
A	Helmholtz energy	J
A_s	surface area	$\mathrm{m^2}$
a	activity	(dimensionless)
B	second virial coefficient	$\mathrm{m^3\ mol^{-1}}$
C	number of components *	(dimensionless)
C_p	heat capacity at constant pressure	$\mathrm{J\ K^{-1}}$
C_V	heat capacity at constant volume	$\mathrm{J\ K^{-1}}$
c	concentration	$\mathrm{mol\ m^{-3}}$
E	energy	J
	electrode potential	V
$\boldsymbol{E}$	electric field strength	$\mathrm{V\ m^{-1}}$
E_cell	cell potential	V
E_j	liquid junction potential	V
E_sys	system energy in a lab frame	J
F	force	N
	number of degrees of freedom *	(dimensionless)
f	fugacity	Pa
g	acceleration of free fall	$\mathrm{m\ s^{-2}}$
G	Gibbs energy	J
h	height, elevation	m
H	enthalpy	J
$\boldsymbol{H}$	magnetic field strength	$\mathrm{A\ m^{-1}}$
I	electric current	A
I_m	ionic strength, molality basis	$\mathrm{mol\ kg^{-1}}$
I_c	ionic strength, concentration basis	$\mathrm{mol\ m^{-3}}$
K	thermodynamic equilibrium constant	(dimensionless)
K_a	acid dissociation constant	(dimensionless)
K_p	equilibrium constant, pressure basis	$\mathrm{Pa}^{\sum\nu}$
K_s	solubility product	(dimensionless)
$k_{\mathrm{H},i}$	Henry's law constant of species i, mole fraction basis	Pa
$k_{c,i}$	Henry's law constant of species i, concentration basis*	$\mathrm{Pa\ m^3\ mol^{-1}}$
$k_{m,i}$	Henry's law constant of species i, molality basis*	$\mathrm{Pa\ kg\ mol^{-1}}$
l	length, distance	m
L	relative partial molar enthalpy*	$\mathrm{J\ mol^{-1}}$
M	molar mass	$\mathrm{kg\ mol^{-1}}$
$\boldsymbol{M}$	magnetization	$\mathrm{A\ m^{-1}}$

(15.3.1)

M_r	relative molecular mass (molecular weight)	(dimensionless)
m	mass	kg
m_i	molality of species i	mol kg^{-1}
N	number of entities (molecules, atoms, ions, formula units, etc.)	(dimensionless)
n	amount of substance	mol
P	number of phases *	(dimensionless)
p	pressure	Pa
	partial pressure	Pa
$\boldsymbol{P}$	dielectric polarization	C m^{-2}
Q	electric charge	C
Q_{sys}	charge entering system at right conductor *	C
Q_{rxn}	reaction quotient*	(dimensionless)
q	heat	J
R_{el}	electric resistance*	Ω
S	entropy	J K^{-1}
s	solubility	mol m^{-3}
	number of species *	(dimensionless)
T	thermodynamic temperature	K
t	time	s
	Celsius temperature	°C
U	internal energy	J
V	volume	m^3
v	specific volume	m^3 kg^{-1}
	velocity, speed	m s^{-1}
w	work	J
	mass fraction (weight fraction)	(dimensionless)
w_{el}	electrical work*	J
w'	nonexpansion work*	J
x	mole fraction in a phase	(dimensionless)
	Cartesian space coordinate	m
y	mole fraction in gas phase	(dimensionless)
	Cartesian space coordinate	m
Z	compression factor (compressibility factor)	(dimensionless)
z	mole fraction in multiphase system *	(dimensionless)
	charge number of an ion	(dimensionless)
	electron number of cell reaction	(dimensionless)
	Cartesian space coordinate	m

Symbol	Physical quantity	SI unit
α	degree of reaction, dissociation, etc.	(dimensionless)
	cubic expansion coefficient	K^{-1}
γ	surface tension	$\mathrm{N\,m}^{-1}$, $\mathrm{J\,m}^{-2}$
γ_i	activity coefficient of species i, pure liquid or solid standard state *	(dimensionless)
$\gamma_{m,i}$	activity coefficient of species i, molality basis	(dimensionless)
$\gamma_{c,i}$	activity coefficient of species i, concentration basis	(dimensionless)
$\gamma_{x,i}$	activity coefficient of species i, mole fraction basis	(dimensionless)
$\gamma_{\pm}$	mean ionic activity coefficient	(dimensionless)
$\mathit{\Gamma}$	pressure factor (activity of a reference state) *	(dimensionless)
ϵ	efficiency of a heat engine	(dimensionless)
	energy equivalent of a calorimeter*	$\mathrm{J\,K}^{-1}$
ϑ	angle of rotation	(dimensionless)
κ	reciprocal radius of ionic atmosphere	m^{-1}
κ_T	isothermal compressibility	Pa^{-1}
μ	chemical potential	$\mathrm{J\,mol}^{-1}$
μ_{JT}	Joule–Thomson coefficient	$\mathrm{K\,Pa}^{-1}$
ν	number of ions per formula unit	(dimensionless)
	stoichiometric number	(dimensionless)
ν_+	number of cations per formula unit	(dimensionless)
ν_-	number of anions per formula unit	(dimensionless)
ξ	advancement (extent of reaction)	mol
$\mathit{\Pi}$	osmotic pressure	Pa
ρ	density	$\mathrm{kg\,m}^{-3}$
τ	torque*	J
ϕ	fugacity coefficient	(dimensionless)
	electric potential	V
$\Delta\phi$	electric potential difference	V
ϕ_m	osmotic coefficient, molality basis	(dimensionless)
$\mathit{\Phi}_L$	relative apparent molar enthalpy of solute*	$\mathrm{J}mol^{-1}$
ω	angular velocity	s^{-1}

(15.3.2)

15.4: Appendix D- Miscellaneous Abbreviations and Symbols

D.1 Physical States

These abbreviations for physical states (states of aggregation) may be appended in parentheses to chemical formulas or used as superscripts to symbols for physical quantities. All but “mixt” are listed in the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 54).

$$\begin{array}{ll}
\mathrm{g} & \text{gas or vapor} \\
\mathrm{l} & \text{liquid} \\
\mathrm{f} & \text{fluid (gas or liquid)} \\
\mathrm{s} & \text{solid} \\
\mathrm{cd} & \text{condensed phase (liquid or solid)} \\
\mathrm{cr} & \text{crystalline} \\
\mathrm{mixt} & \text{mixture} \\
\mathrm{sln} & \text{solution} \\
\mathrm{aq} & \text{aqueous solution} \\
\mathrm{aq}, \infty & \text{aqueous solution at infinite dilution}
\end{array} \tag{15.4.1}$$

D.2 Subscripts for Chemical Processes

These abbreviations are used as subscripts to the Δ symbol. They are listed in the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 59–60).

The combination Δ_{p}, where “p” is any one of the abbreviations below, can be interpreted as an operator: $\Delta_{\mathrm{p}} \overset{\text{def}}{=} \partial/\partial\xi_{\mathrm{p}}$ where ξ_{p} is the advancement of the given process at constant temperature and pressure. For example, $\Delta_{\mathrm{c}}H = (\partial H/\partial\xi_{\mathrm{c}})_{T,p}$ is the molar differential enthalpy of combustion.

$$\begin{array}{ll}
\mathrm{vap} & \text{vaporization, evaporation } (\mathrm{l} \rightarrow \mathrm{g}) \\
\mathrm{sub} & \text{sublimation } (\mathrm{s} \rightarrow \mathrm{g}) \\
\mathrm{fus} & \text{melting, fusion } (\mathrm{s} \rightarrow \mathrm{l}) \\
\mathrm{trs} & \text{transition between two phases} \\
\mathrm{mix} & \text{mixing of fluids} \\
\mathrm{sol} & \text{solution of a solute in solvent} \\
\mathrm{dil} & \text{dilution of a solution} \\
\mathrm{ads} & \text{adsorption} \\
\mathrm{dpl} & \text{displacement} \\
\mathrm{imm} & \text{immersion} \\
\mathrm{r} & \text{reaction in general} \\
\mathrm{at} & \text{atomization} \\
\mathrm{c} & \text{combustion reaction} \\
\mathrm{f} & \text{formation reaction}
\end{array} \tag{15.4.2}$$

D.3 Superscripts

These abbreviations and symbols are used as superscripts to symbols for physical quantities. All but $'$, int, and ref are listed as recommended superscripts in the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 60).

$$\begin{array}{ll} {}^{\circ} & \text{standard} \\ {}^{*} & \text{pure substance} \\ {}' & \text{Legendre transform of a thermodynamic potential} \\ \infty & \text{infinite dilution} \\ \text{id} & \text{ideal} \\ \text{int} & \text{integral} \\ \mathsf{E} & \text{excess quantity} \\ \text{ref} & \text{reference state} \end{array} \tag{15.4.3}$$

15.5: Appendix E- Calculus Review

E.1 Derivatives

Let f be a function of the variable x, and let Δf be the change in f when x changes by Δx. Then the **derivative** $\mathrm{d}f/\,\mathrm{d}x$ is the ratio $\Delta f/\Delta x$ in the limit as Δx approaches zero. The derivative $\mathrm{d}f/\,\mathrm{d}x$ can also be described as the rate at which f changes with x, and as the slope of a curve of f plotted as a function of x.

The following is a short list of formulas likely to be needed. In these formulas, u and v are arbitrary functions of x, and a is a constant.

$$\begin{aligned}\frac{\mathrm{d}(u^a)}{\mathrm{d}x} &= au^{a-1}\frac{\mathrm{d}u}{\mathrm{d}x}\\ \frac{\mathrm{d}(uv)}{\mathrm{d}x} &= u\frac{\mathrm{d}v}{\mathrm{d}x}+v\frac{\mathrm{d}u}{\mathrm{d}x}\\ \frac{\mathrm{d}(u/v)}{\mathrm{d}x} &= \left(\frac{1}{v^2}\right)\left(v\frac{\mathrm{d}u}{\mathrm{d}x}-u\frac{\mathrm{d}v}{\mathrm{d}x}\right)\\ \frac{\mathrm{d}\ln(ax)}{\mathrm{d}x} &= \frac{1}{x}\\ \frac{\mathrm{d}(e^{ax})}{\mathrm{d}x} &= ae^{ax}\\ \frac{\mathrm{d}f(u)}{\mathrm{d}x} &= \frac{\mathrm{d}f(u)}{\mathrm{d}u}\cdot\frac{\mathrm{d}u}{\mathrm{d}x}\end{aligned}$$

E.2 Partial Derivatives

If f is a function of the independent variables x, y, and z, the **partial derivative** $(\partial f/\partial x)_{y,z}$ is the derivative $\mathrm{d}f/\,\mathrm{d}x$ with y and z held constant. It is important in thermodynamics to indicate the variables that are held constant, as $(\partial f/\partial x)_{y,z}$ is not necessarily equal to $(\partial f/\partial x)_{a,b}$ where a and b are variables different from y and z.

The variables shown at the bottom of a partial derivative should tell you which variables are being used as the independent variables. For example, if the partial derivative is $\left(\frac{\partial f}{\partial y}\right)_{a,b}$ then f is being treated as a function of y, a, and b.

E.3 Integrals

Let f be a function of the variable x. Imagine the range of x between the limits x' and x'' to be divided into many small increments of size $\Delta x_i (i = 1, 2, \ldots)$. Let f_i be the value of f when x is in the middle of the range of the ith increment. Then the **integral**

$$\int_{x'}^{x''} f\,\mathrm{d}x \tag{15.5.1}$$

is the sum $\sum_i f_i\Delta x_i$ in the limit as each Δx_i approaches zero and the number of terms in the sum approaches infinity. The integral is also the area under a curve of f plotted as a function of x, measured from $x = x'$ to $x = x''$. The function f is the **integrand**, which is integrated over the integration variable x.

This e-book uses the following integrals:

$$\begin{aligned}&\int_{x'}^{x''}\mathrm{d}x = x''-x'\\ &\int_{x'}^{x''}\frac{\mathrm{d}x}{x} = \ln\left|\frac{x''}{x'}\right|\\ &\int_{x'}^{x''} x^a\,\mathrm{d}x = \frac{1}{a+1}\left[(x'')^{a+1}-(x')^{a+1}\right] \qquad (a \text{ is a constant other than } -1)\\ &\int_{x'}^{x''}\frac{\mathrm{d}x}{ax+b} = \frac{1}{a}\ln\left|\frac{ax''+b}{ax'+b}\right| \qquad (a \text{ is a constant})\end{aligned}$$

Here are examples of the use of the expression for the third integral with a set equal to 1 and to -2:

$$\int_{x'}^{x''} x \, \mathrm{d}x = \frac{1}{2}\left[(x'')^2 - (x')^2\right]$$

$$\int_{x'}^{x''} \frac{\mathrm{d}x}{x^2} = -\left(\frac{1}{x''} - \frac{1}{x'}\right)$$

E.4 Line Integrals

A **line integral** is an integral with an implicit single integration variable that constraints the integration to a path.

The most frequently-seen line integral in this e-book, $\int p \, \mathrm{d}V$, will serve as an example. The integral can be evaluated in three different ways:

1. The integrand p can be expressed as a function of the integration variable V, so that there is only one variable. For example, if p equals c/V where c is a constant, the line integral is given by $\int p \, \mathrm{d}V = c\int_{V_1}^{V_2}(1/V)\,\mathrm{d}V = c\ln(V_2/V_1)$.
2. If p and V can be written as functions of another variable, such as time, that coordinates their values so that they follow the desired path, this new variable becomes the integration variable.
3. The desired path can be drawn as a curve on a plot of p versus V; then $\int p \, \mathrm{d}V$ is equal in value to the area under the curve.

15.6: Appendix F- Mathematical Properties of State Functions

A state function is a property of a thermodynamic system whose value at any given instant depends only on the state of the system at that instant (Sec. 2.4).

F.1 Differentials

The **differential** $\mathrm{d}f$ of a state function f is an infinitesimal change of f. Since the value of a state function by definition depends only on the state of the system, integrating $\mathrm{d}f$ between an initial state 1 and a final state 2 yields the change in f, and this change is independent of the path:

$$\int_{f_1}^{f_2} \mathrm{d}f = f_2 - f_1 = \Delta f \tag{F.1.1}$$

A differential with this property is called an *exact* differential. The differential of a state function is always exact.

F.2 Total Differential

A state function f treated as a dependent variable is a function of a certain number of independent variables that are also state functions. The **total differential** of f is $\mathrm{d}f$ expressed in terms of the differentials of the independent variables and has the form

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y + \left(\frac{\partial f}{\partial z}\right)\mathrm{d}z + \dots \tag{F.2.1}$$

There are as many terms in the expression on the right side as there are independent variables. Each partial derivative in the expression has all independent variables held constant except the variable shown in the denominator.

Figure F.1 interprets this expression for a function f of the two independent variables x and y. The shaded plane represents a small element of the surface $f = f(x,y)$.

Consider a system with three independent variables. If we choose these independent variables to be x, y, and z, the total differential of the dependent state function f takes the form

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z \tag{F.2.2}$$

where we can identify the coefficients as

$$a = \left(\frac{\partial f}{\partial x}\right)_{y,z} \qquad b = \left(\frac{\partial f}{\partial y}\right)_{x,z} \qquad c = \left(\frac{\partial f}{\partial z}\right)_{x,y} \tag{F.2.3}$$

These coefficients are themselves, in general, functions of the independent variables and may be differentiated to give mixed second partial derivatives; for example:

$$\left(\frac{\partial a}{\partial y}\right)_{x,z} = \frac{\partial^2 f}{\partial y \partial x} \qquad \left(\frac{\partial b}{\partial x}\right)_{y,z} = \frac{\partial^2 f}{\partial x \partial y} \tag{F.2.4}$$

The second partial derivative $\partial^2 f/\partial y \partial x$, for instance, is the partial derivative with respect to y of the partial derivative of f with respect to x. It is a theorem of calculus that if a function f is single valued and has continuous derivatives, the order of differentiation in a mixed derivative is immaterial. Therefore the mixed derivatives $\partial^2 f/\partial y \partial x$ and $\partial^2 f/\partial x \partial y$, evaluated for the system in any given state, are equal:

$$\left(\frac{\partial a}{\partial y}\right)_{x,z} = \left(\frac{\partial b}{\partial x}\right)_{y,z} \tag{F.2.5}$$

The general relation that applies to a function of any number of independent variables is

$$\left(\frac{\partial X}{\partial y}\right) = \left(\frac{\partial Y}{\partial x}\right) \tag{F.2.6}$$

where x and y are *any* two of the independent variables, X is $\partial f/\partial x$, Y is $\partial_{\mathrm{f}}/\partial y$, and each partial derivative has all independent variables held constant except the variable shown in the denominator. This general relation is the Euler reciprocity relation, or

reciprocity relation for short. A necessary and sufficient condition for $\mathrm{d}f$ to be an exact differential is that the reciprocity relation is satisfied for each pair of independent variables.

F.3 Integration of a Total Differential

If the coefficients of the total differential of a dependent variable are known as functions of the independent variables, the expression for the total differential may be integrated to obtain an expression for the dependent variable as a function of the independent variables.

For example, suppose the total differential of the state function $f(x,y,z)$ is given by Eq. F.2.2 and the coefficients are known functions $a(x,y,z)$, $b(x,y,z)$, and $c(x,y,z)$. Because f is a state function, its change between $f(0,0,0)$ and $f(x',y',z')$ is independent of the integration path taken between these two states. A convenient path would be one with the following three segments:

1. The expression for $f(x,y,z)$ is then the sum of the three integrals and a constant of integration.

   Here is an example of this procedure applied to the total differential

   $$\mathrm{d}f = (2xy)\,\mathrm{d}x + (x^2+z)\,\mathrm{d}y + (y-9z^2)\,\mathrm{d}z \tag{F.3.1}$$

   An expression for the function f in this example is given by the sum

   $$\begin{aligned} f &= \int_0^{x'} (2x\cdot 0)\,\mathrm{d}x + \int_0^{y'} [(x')^2+0]\,\mathrm{d}y + \int_0^{z'} (y'-9z^2)\,\mathrm{d}z + C \\ &= 0 + x^2y + (yz - 9z^3/3) + C \\ &= x^2y + yz - 3z^3 + C \end{aligned} \tag{F.3.2}$$

   where primes are omitted on the second and third lines because the expressions are supposed to apply to any values of x, y, and z. C is an integration constant. You can verify that the third line of Eq. F.3.2 gives the correct expression for f by taking partial derivatives with respect to x, y, and z and comparing with Eq. F.3.1.

   A different kind of integration can be used to express a dependent extensive property in terms of independent extensive properties. An *extensive* property of a thermodynamic system is one that is additive, and an *intensive* property is one that is not additive and has the same value everywhere in a homogeneous region (Sec. 2.1.1). Suppose we have a state function f that is an extensive property with the total differential

   $$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z + \ldots \tag{F.3.3}$$

   where the independent variables $x, y, z, \ldots$ are extensive and the coefficients $a, b, c, \ldots$ are intensive. If the independent variables include those needed to describe an open system (for example, the amounts of the substances), then it is possible to integrate both sides of the equation from a lower limit of zero for each of the extensive functions while holding the intensive functions constant:

   $$\int_0^{f'} \mathrm{d}f = a\int_0^{x'} \mathrm{d}x + b\int_0^{y'} \mathrm{d}y + c\int_0^{z'} \mathrm{d}z + \ldots \tag{F.3.4}$$

   $$f' = ax' + by' + cz' + \ldots \tag{F.3.5}$$

   Note that a term of the form $c\,\mathrm{d}u$ where u is *intensive* becomes *zero* when integrated with intensive functions held constant, because $\mathrm{d}u$ is this case is zero.

F.4 Legendre Transforms

A **Legendre transform** of a state function is a linear change of one or more of the independent variables made by subtracting products of conjugate variables.

To understand how this works, consider a state function f whose total differential is given by

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z \tag{F.4.1}$$

In the expression on the right side, x, y, and z are being treated as the independent variables. The pairs a and x, b and y, and c and z are *conjugate pairs*. That is, a and x are conjugates, b and y are conjugates, and c and z are conjugates.

For the first example of a Legendre transform, we define a new state function f_1 by subtracting the product of the conjugate variables a and x:

$$f_1 \overset{\text{def}}{=} f - ax \tag{F.4.2}$$

The function f_1 is a Legendre transform of f. We take the differential of Eq. F.4.2

$$\mathrm{d}f_1 = \mathrm{d}f - a\,\mathrm{d}x - x\,\mathrm{d}a \tag{F.4.3}$$

and substitute for $\mathrm{d}f$ from Eq. F.4.1:

$$\begin{aligned} \mathrm{d}f_1 &= (a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z) - a\,\mathrm{d}x - x\,\mathrm{d}a \\ &= -x\,\mathrm{d}a + b\,\mathrm{d}y + c\,\mathrm{d}z \end{aligned} \tag{F.4.4}$$

Equation F.4.4 gives the total differential of f_1 with a, y, and z as the independent variables. The functions x and a have switched places as independent variables. What we did in order to let a replace x as an independent variable was to subtract from f the product of the conjugate variables a and x.

Because the right side of Eq. F.4.4 is an expression for the total differential of the state function f_1, we can use the expression to identify the coefficients as partial derivatives of f_1 with respect to the new set of independent variables:

$$-x = \left(\frac{\partial f_1}{\partial a}\right)_{y,z} \qquad b = \left(\frac{\partial f_1}{\partial y}\right)_{a,z} \qquad c = \left(\frac{\partial f_1}{\partial z}\right)_{a,y} \tag{F.4.5}$$

We can also use Eq. F.4.4 to write new reciprocity relations, such as

$$-\left(\frac{\partial x}{\partial y}\right)_{a,z} = \left(\frac{\partial b}{\partial a}\right)_{y,z} \tag{F.4.6}$$

We can make other Legendre transforms of f by subtracting one or more products of conjugate variables. A second example of a Legendre transform is

$$f_2 \overset{\text{def}}{=} f - by - cz \tag{F.4.7}$$

whose total differential is

$$\begin{aligned} \mathrm{d}f_2 &= \mathrm{d}f - b\,\mathrm{d}y - y\,\mathrm{d}b - c\,\mathrm{d}z - z\,\mathrm{d}c \\ &= a\,\mathrm{d}x - y\,\mathrm{d}b - z\,\mathrm{d}c \end{aligned} \tag{F.4.8}$$

Here b has replaced y and c has replaced z as independent variables. Again, we can identify the coefficients as partial derivatives and write new reciprocity relations.

If we have an algebraic expression for a state function as a function of independent variables, then a Legendre transform preserves all the information contained in that expression. To illustrate this, we can use the state function f and its Legendre transform f_2 described above. Suppose we have an expression for $f(x,y,z)$—this is f expressed as a function of the independent variables x, y, and z. Then by taking partial derivatives of this expression, we can find according to Eq. F.2.3 expressions for the functions $a(x,y,z)$, $b(x,y,z)$, and $c(x,y,z)$.

Now we perform the Legendre transform of Eq. F.4.7: $f_2 = f - by - cz$ with total differential $\mathrm{d}f_2 = a\,\mathrm{d}x - y\,\mathrm{d}b - z\,\mathrm{d}c$ (Eq. F.4.8). The independent variables have been changed from x, y, and z to x, b, and c.

We want to find an expression for f_2 as a function of these new variables, using the information available from the original function $f(x,y,z)$. To do this, we eliminate z from the known functions $b(x,y,z)$ and $c(x,y,z)$ and solve for y as a function of x, b, and c. We also eliminate y from $b(x,y,z)$ and $c(x,y,z)$ and solve for z as a function of x, b, and c. This gives us expressions for $y(x,b,c)$ and $z(x,b,c)$ which we substitute into the expression for $f(x,y,z)$, turning it into the function $f(x,b,c)$. Finally, we use the functions of the new variables to obtain an expression for $f_2(x,b,c) = f(x,b,c) - by(x,b,c) - cz(x,b,c)$.

The original expression for $f(x,y,z)$ and the new expression for $f_2(x,b,c)$ contain the same information. We could take the expression for $f_2(x,b,c)$ and, by following the same procedure with the Legendre transform $f = f_2 + by + cz$, retrieve the expression for $f(x,y,z)$. Thus no information is lost during a Legendre transform.

15.7: Appendix G- Forces, Energy, and Work

15.8: Appendix H- Standard Molar Thermodynamic Properties

The values in these tables are for a temperature of 298.15 K (25.00 $^\circ\mathrm{C}$) and the standard pressure $p^\circ = 1\,\mathrm{bar}$. Solute standard states are based on molality. A crystalline solid is denoted by cr.

Most of the values in this table come from a project of the Committee on Data for Science and Technology (CODATA) to establish a set of recommended, internally consistent values of thermodynamic properties. The values of $\Delta_\mathrm{f}H^\circ$ and S°_m shown with uncertainties are values recommended by CODATA (J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp., New York, 1989).

Inorganic substance	$\frac{\Delta_f H^\circ}{\text{kJ mol}^{-1}}$	$\frac{S^\circ_m}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta_f G^\circ}{\text{kJ mol}^{-1}}$
Ag(cr)	0	42.55 ± 0.20	0
AgCl(cr)	-127.01 ± 0.05	96.25 ± 0.20	-109.77
C(cr, graphite)	0	5.74 ± 0.10	0
CO(g)	-110.53 ± 0.17	197.660 ± 0.004	-137.17
CO_2(g)	-393.51 ± 0.13	213.785 ± 0.010	-394.41
Ca(cr)	0	41.59 ± 0.40	0
$CaCO_3$(cr, calcite)	-1206.9	92.9	-1128.8
CaO(cr)	-634.92 ± 0.90	38.1 ± 0.4	-603.31
Cl_2(g)	0	223.081 ± 0.010	0
F_2(g)	0	202.791 ± 0.005	0
H_2(g)	0	130.680 ± 0.003	0
HCl(g)	-92.31 ± 0.10	186.902 ± 0.005	-95.30
HF(g)	-273.30 ± 0.70	173.779 ± 0.003	-275.40
HI(g)	26.50 ± 0.10	206.590 ± 0.004	1.70
H_2O(l)	-285.830 ± 0.040	69.95 ± 0.03	-237.16
H_2O(g)	-241.826 ± 0.040	188.835 ± 0.010	-228.58
H_2S(g)	-20.6 ± 0.5	205.81 ± 0.05	-33.44
Hg(l)	0	75.90 ± 0.12	0
Hg(g)	61.38 ± 0.04	174.971 ± 0.005	31.84
HgO(cr, red)	-90.79 ± 0.12	70.25 ± 0.30	-58.54
Hg_2Cl_2(cr)	-265.37 ± 0.40	191.6 ± 0.8	-210.72
I_2(cr)	0	116.14 ± 0.30	0
K(cr)	0	64.68 ± 0.20	0
KI(cr)	-327.90	106.37	-323.03
KOH(cr)	-424.72	78.90	-378.93
N_2(g)	0	191.609 ± 0.004	0
NH_3(g)	-45.94 ± 0.35	192.77 ± 0.05	-16.41
NO_2(g)	33.10	240.04	51.22
N_2O_4(g)	9.08	304.38	97.72
Na(cr)	0	51.30 ± 0.20	0
NaCl(cr)	-411.12	72.11	-384.02
O_2(g)	0	205.152 ± 0.005	0
O_3(g)	142.67	238.92	163.14
P(cr, white)	0	41.09 ± 0.25	0
S(cr, rhombic)	0	32.054 ± 0.050	0
SO_2(g)	-296.81 ± 0.20	248.223 ± 0.050	-300.09
Si(cr)	0	18.81 ± 0.08	0
SiF_4(g)	-1615.0 ± 0.8	282.76 ± 0.50	-1572.8
SiO_2(cr, α-quartz)	-910.7 ± 1.0	41.46 ± 0.20	-856.3
Zn(cr)	0	41.63 ± 0.15	0
ZnO(cr)	-350.46 ± 0.27	43.65 ± 0.40	-320.48

(15.8.1)

Organic compound	$\Delta_{\mathrm{f}} H^\circ$	S°_{m}	$\Delta_{\mathrm{f}} G^\circ$
	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
CH_4(g)	−74.87	186.25	−50.77
CH_3OH(l)	−238.9	127.2	−166.6
CH_3CH_2OH(l)	−277.0	159.9	−173.8
C_2H_2(g)	226.73	200.93	209.21
C_2H_4(g)	52.47	219.32	68.43
C_2H_6(g)	−83.85	229.6	−32.00
C_3H_8(g)	−104.7	270.31	−24.3
C_6H_6(l, benzene)	49.04	173.26	124.54

(15.8.2)

Ionic solute	$\Delta_{\mathrm{f}} H^\circ$	S°_{m}	$\Delta_{\mathrm{f}} G^\circ$
	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
Ag^+(aq)	105.79 ± 0.08	73.45 ± 0.40	77.10
CO_3^{2-}(aq)	-675.23 ± 0.25	-50.0 ± 1.0	−527.90
Ca^{2+}(aq)	-543.0 ± 1.0	-56.2 ± 1.0	−552.8
Cl^-(aq)	-167.08 ± 0.10	56.60 ± 0.20	−131.22
F^-(aq)	-335.35 ± 0.65	-13.8 ± 0.8	−281.52
H^+(aq)	0	0	0
HCO_3^-(aq)	-689.93 ± 2.0	98.4 ± 0.5	−586.90
HS^-(aq)	-16.3 ± 1.5	67 ± 5	12.2
HSO_4^-(aq)	-886.9 ± 1.0	131.7 ± 3.0	−755.4
Hg_2^{2+}(aq)	166.87 ± 0.50	65.74 ± 0.80	153.57
I^-(aq)	-56.78 ± 0.05	106.45 ± 0.30	−51.72
K^+(aq)	-252.14 ± 0.08	101.20 ± 0.20	−282.52
NH_4^+(aq)	-133.26 ± 0.25	111.17 ± 0.40	−79.40
NO_3^-(aq)	-206.85 ± 0.40	146.70 ± 0.40	−110.84
Na^+(aq)	-240.34 ± 0.06	58.45 ± 0.15	−261.90
OH^-(aq)	-230.015 ± 0.040	-10.90 ± 0.20	−157.24
S^{2-}(aq)	33.1	−14.6	86.0
SO_4^{2-}(aq)	-909.34 ± 0.40	18.50 ± 0.40	−744.00

(15.8.3)

15.9: Appendix I- Answers to Selected Problems

3.3(b)
$q = -w = 1.00 \times 10^5\ \text{J}$

3.4(c)
$w = 1.99 \times 10^3\ \text{J}$, $q = -1.99 \times 10^3\ \text{J}$.

3.5
0.0079%

3.6(c)
$V_2 \to nRV_1/(C_V + nR)$, $T_2 \to \infty$. For $C_V = (3/2)nR$, $V_2/V_1 \to 0.4$.

3.11
$9.58 \times 10^3\ \text{s}\,(2\ \text{hr}\ 40\ \text{min})$

4.4
$\Delta S = 0.054\ \text{J K}^{-1}$

4.5
$\Delta S = 549\ \text{J K}^{-1}$ for both processes; $\int đq/T_{\text{ext}} = 333\ \text{J K}^{-1}$ and 0.

5.4(a)

$$S = nR \ln\left[cT^{3/2}\left(\frac{V}{n} - b\right)\right] + \left(\frac{5}{2}\right) nR$$

5.5(a)
$q = 0$, $w = 1.50 \times 10^4\ \text{J}$, $\Delta U = 1.50 \times 10^4\ \text{J}$, $\Delta H = 2.00 \times 10^4\ \text{J}$

5.5(c)
$\Delta S = 66.7\ \text{J K}^{-1}$

6.1
$S_\text{m} \approx 151.6\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.6(a)
$\alpha = 8.519 \times 10^{-4}\ \text{K}^{-1}$
$\kappa_t = 4.671 \times 10^{-5}\ \text{bar}^{-1}$
$(\partial p/\partial T)_V = 18.24\ \text{bar K}^{-1}$
$(\partial U/\partial V)_T = 5437\ \text{bar}$

7.6(b)
$\Delta p \approx 1.8\ \text{bar}$

7.7(b)
$(\partial C_{p,\text{m}}/\partial p)_T = -4.210 \times 10^{-8}\ \text{J K}^{-1}\ \text{Pa}^{-1}\ \text{mol}^{-1}$

7.8(b)
$8 \times 10^{-4}\ \text{K}^{-1}$

7.11
$5.001 \times 10^3\ \text{J}$

7.12
$\Delta H = 2.27 \times 10^4\ \text{J}$, $\Delta S = 43.6\ \text{J K}^{-1}$

7.13(a)
$C^\circ_{p,\text{m}} = 42.3\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.13(b)
$C_{p,\text{m}} \approx 52.0\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.14(a)
$2.56\ \mathrm{J\ K^{-1}\ g^{-1}}$

7.15(b)
$f = 17.4\ \mathrm{bar}$

7.16(a)
$\phi = 0.739,\ f = 148\ \mathrm{bar}$

7.16(b)
$B = -7.28 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$

8.2(a)
$S^\circ_\mathrm{m}(\mathrm{l}) = 253.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$

8.2(b)
$\Delta_\mathrm{vap}S^\circ = 88.6\ \mathrm{J\ K^{-1}\ mol^{-1}},\ \Delta_\mathrm{vap}H^\circ = 2.748 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.4
$4.5 \times 10^{-3}\ \mathrm{bar}$

8.5
$19\ \mathrm{J\ mol^{-1}}$

8.6(a)
$352.82\ \mathrm{K}$

8.6(b)
$3.4154 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.7(a)
$3.62 \times 10^3\ \mathrm{Pa\ K^{-1}}$

8.7(b)
$3.56 \times 10^3\ \mathrm{Pa\ K^{-1}}$

8.7(c)
$99.60\ {}^\circ\mathrm{C}$

8.8(b)
$\Delta_\mathrm{vap}H^\circ = 4.084 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.9
$0.93\ \mathrm{mol}$

9.2(b)
$V_\mathrm{A}(x_\mathrm{B} = 0.5) \approx 125.13\ \mathrm{cm^3\ mol^{-1}}$
$V_\mathrm{B}(x_\mathrm{B} = 0.5) \approx 158.01\ \mathrm{cm^3\ mol^{-1}}$
$V_\mathrm{B}^\infty \approx 157.15\ \mathrm{cm^3\ mol^{-1}}$

9.4
real gas: $p = 1.9743\ \mathrm{bar}$
ideal gas: $p = 1.9832\ \mathrm{bar}$

9.5(a)
$x_{\mathrm{N_2}} = 8.83 \times 10^{-6}$
$x_{\mathrm{O_2}} = 4.65 \times 10^{-6}$
$y_{\mathrm{N_2}} = 0.763$
$y_{\mathrm{O_2}} = 0.205$

9.5(b)
$x_{\mathrm{N_2}} = 9.85 \times 10^{-6}$
$x_{\mathrm{O_2}} = 2.65 \times 10^{-6}$

$y_{N_2} = 0.851$
$y_{O_2} = 0.117$

9.7(b)
$f_A = 0.03167\,\text{bar}$, $f_A = 0.03040\,\text{bar}$

9.8(a)
In the mixture of composition $x_A = 0.9782$, the activity coefficient is $\gamma_B \approx 11.5$.

9.9(d)
$k_{H,A} \approx 680\,\text{kPa}$

9.11
Values for $m_B/m^\circ = 20$: $\gamma_A = 1.026$, $\gamma_{m,B} = 0.526$; the limiting slopes are $d\gamma_A/d(m_B/m^\circ) = 0$, $d\gamma_{m,B}/d(m_B/m^\circ) = -0.09$

9.13
$p_{N_2} = 0.235\,\text{bar}$
$y_{N_2} = 0.815$
$p_{O_2} = 0.0532\,\text{bar}$
$y_{O_2} = 0.185$
$p = 0.288\,\text{bar}$

9.14(b)
$h = 1.2\,\text{m}$

9.15(a)
$p(7.20\,\text{cm}) - p(6.95\,\text{cm}) = 1.2\,\text{bar}$

9.15(b)
$M_B = 187\,\text{kg mol}^{-1}$
mass binding ratio $= 1.37$

10.2
$\gamma\pm = 0.392$

11.1
$\Delta_r H^\circ = -63.94\,\text{kJ mol}^{-1}$
$K = 4.41 \times 10^{-2}$

11.2(b)
$\Delta_f H^\circ$: no change
$\Delta_f S^\circ$: subtract $0.219\,\text{J K}^{-1}\,\text{mol}^{-1}$
$\Delta_f G^\circ$: add $65\,\text{J mol}^{-1}$

11.3
$p(298.15\,\text{K}) = 2.6 \times 10^{-6}\,\text{bar}$
$p(273.15\,\text{K}) = 2.7 \times 10^{-7}\,\text{bar}$

11.4(a)
$-240.34\,\text{kJ mol}^{-1}$, $-470.36\,\text{kJ mol}^{-1}$, $-230.02\,\text{kJ mol}^{-1}$

11.4(b)
$-465.43\,\text{kJ mol}^{-1}$

11.4(c)
$-39.82\,\text{kJ mol}^{-1}$

11.5
$\Delta H = 0.92\,\text{kJ}$

11.6
$L_A = -0.405\,\text{J mol}^{-1}$

$L_B = 0.810\,\mathrm{kJ\,mol^{-1}}$

11.7(a)
State 1:
$n_{C_6H_{14}} = 7.822 \times 10^{-3}\,\mathrm{mol}$
$n_{H_2O} = 0.05560\,\mathrm{mol}$
amount of O_2 consumed: $0.07431\,\mathrm{mol}$
State 2:
$n_{H_2O} = 0.11035\,\mathrm{mol}$
$n_{CO_2} = 0.04693\,\mathrm{mol}$
\tx{mass of H_2O}=$1.9880\,\mathrm{g}$

11.7(b)
$V_m(C_6H_{14}) = 131.61\,\mathrm{cm^3\,mol^{-1}}$
$V_m(H_2O) = 18.070\,\mathrm{cm^3\,mol^{-1}}$

11.7(c)
State 1: $V(C_6H_{14}) = 1.029\,\mathrm{cm^3}$
$V(H_2O) = 1.005\,\mathrm{cm^3}$
$V^g = 348.0\,\mathrm{cm^3}$
State 2:
$V(H_2O) = 1.994\,\mathrm{cm^3}$
$V^g = 348.0\,\mathrm{cm^3}$

11.7(d)
State 1:
$n_{O_2} = 0.429\,\mathrm{mol}$
State 2:
$n_{O_2} = 0.355\,\mathrm{mol}$
$y_{O_2} = 0.883$
$y_{CO_2} = 0.117$

11.7(e)
State 2:
$p_2 = 27.9\,\mathrm{bar}$
$p_{O_2} = 24.6\,\mathrm{bar}$
$p_{CO_2} = 3.26\,\mathrm{bar}$

11.7(f)
$f_{H_2O}(0.03169\,\mathrm{bar}) = 0.03164\,\mathrm{bar}$
State 1: $f_{H_2O} = 0.03234\,\mathrm{bar}$
State 2: $f_{H_2O} = 0.03229\,\mathrm{bar}$

11.7(g)
State 1:
$\phi_{H_2O} = 0.925$
$\phi_{O_2} = 0.981$
$f_{O_2} = 29.4\,\mathrm{bar}$
State 2:
$\phi_{H_2O} = 0.896$
$\phi_{O_2} = 0.983$
$\phi_{CO_2} = 0.910$
$f_{O_2} = 24.2\,\mathrm{bar}$
$f_{CO_2} = 2.97\,\mathrm{bar}$

11.7(h)
State 1:

$n^{\mathrm{g}}_{\mathrm{H_2O}} = 5.00 \times 10^{-4}\ \mathrm{mol}$
$n^{\mathrm{l}}_{\mathrm{H_2O}} = 0.05510\ \mathrm{mol}$
State 2:
$n^{\mathrm{g}}_{\mathrm{H_2O}} = 5.19 \times 10^{-4}\ \mathrm{mol}$
$n^{\mathrm{l}}_{\mathrm{H_2O}} = 0.10983\ \mathrm{mol}$

11.7(i)
State 1:
$k_{m,\mathrm{O_2}} = 825\ \mathrm{bar\ kg\ mol^{-1}}$
$n_{\mathrm{O_2}} = 3.57 \times 10^{-5}\ \mathrm{mol}$
State 2:
$k_{m,\mathrm{O_2}} = 823\ \mathrm{bar\ kg\ mol^{-1}}$
$k_{m,\mathrm{CO_2}} = 30.8\ \mathrm{bar\ kg\ mol^{-1}}$
$n_{\mathrm{O_2}} = 5.85 \times 10^{-5}\ \mathrm{mol}$
$n_{\mathrm{CO_2}} = 1.92 \times 10^{-4}\ \mathrm{mol}$

11.7(j)
H_2O vaporization: $\Delta U = +20.8\ \mathrm{J}$
H_2O condensation: $\Delta U = -21.6\ \mathrm{J}$

11.7(k)
O_2 dissolution: $\Delta U = -0.35\ \mathrm{J}$
O_2 desolution: $\Delta U = 0.57\ \mathrm{J}$
CO_2 desolution: $\Delta U = 3.32\ \mathrm{J}$

11.7(l)
C_6H_{14}(l) compression: $\Delta U = -1.226\ \mathrm{J}$
solution compression: $\Delta U = -0.225\ \mathrm{J}$
solution decompression: $\Delta U = 0.414\ \mathrm{J}$

11.7(m)
O_2 compression: $\Delta U = -81\ \mathrm{J}$
gas mixture: $\mathrm{d}B/\mathrm{d}T = 0.26 \times 10^{-6}\ \mathrm{m^3 K^{-1}\ mol^{-1}}$
gas mixture expansion: $\Delta U = 87\ \mathrm{J}$

11.7(n)
$\Delta U = 8\ \mathrm{J}$

11.7(o)
$\Delta_{\mathrm{c}} U^\circ = -4154.4\ \mathrm{kJ\ mol^{-1}}$

11.7(p)
$\Delta_{\mathrm{c}} H^\circ = -4163.1\ \mathrm{kJ\ mol^{-1}}$

11.8
$\Delta_{\mathrm{f}} H^\circ = -198.8\ \mathrm{kJ\ mol^{-1}}$

11.9
$T_2 = 2272\ \mathrm{K}$

11.10
$p(\mathrm{O_2}) = 2.55 \times 10^{-5}\ \mathrm{bar}$

11.11(a)
$K = 3.5 \times 10^{41}$

11.11(b)
$p_{\mathrm{H_2}} = 2.8 \times 10^{-42}\ \mathrm{bar}$
$N_{\mathrm{H_2}} = 6.9 \times 10^{-17}$

11.11(c)
$t = 22\ \mathrm{s}$

11.12(b)
$p \approx 1.5 \times 10^4\ \mathrm{bar}$

11.13(c)
$K = 0.15$

12.1(b)
$T = 1168\ \mathrm{K}$
$\Delta_r H^\circ = 1.64 \times 10^5\ \mathrm{J\ mol^{-1}}$

12.4
$K_f = 1.860\ \mathrm{K\ kg\ mol^{-1}}$
$K_b = 0.5118\ \mathrm{K\ kg\ mol^{-1}}$

12.5
$M_B \approx 5.6 \times 10^4\ \mathrm{g\ mol^{-1}}$

12.6
$\Delta_{\mathrm{sol,B}} H^\circ / \mathrm{kJ\ mol^{-1}} = -3.06, 0, 6.35$
$\Delta_{\mathrm{sol,B}} S^\circ / \mathrm{J\ K^{-1}\ mol^{-1}} = -121.0, -110.2, -88.4$

12.7(a)
$m_+^\alpha = m_-^\alpha = 1.20 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$
$m_+^\beta = 1.80 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$
$m_-^\beta = 0.80 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$
$m_P = 2.00 \times 10^{-6}\ \mathrm{mol\ kg^{-1}}$

12.8(a)
$p^l = 2.44\ \mathrm{bar}$

12.8(b)
$f(2.44\ \mathrm{bar}) - f(1.00\ \mathrm{bar}) = 3.4 \times 10^{-5}\ \mathrm{bar}$

12.10(a)
$x_B = 1.8 \times 10^{-7}$
$m_B = 1.0 \times 10^{-5}\ \mathrm{mol\ kg^{-1}}$

12.10(b)
$\Delta_{\mathrm{sol,B}} H^\circ = -1.99 \times 10^4\ \mathrm{J\ mol^{-1}}$

12.10(c)
$K = 4.4 \times 10^{-7}$
$\Delta_r H^\circ = 9.3\ \mathrm{kJ\ mol^{-1}}$

12.13(a)
$p = 92399.6\ \mathrm{Pa},\ y_B = 0.965724$

12.13(b)
$\phi_A = 0.995801$

12.13(c)
$f_A = 3164.47\ \mathrm{Pa}$

12.13(d)
$y_B = 0.965608$

12.13(e)
$Z = 0.999319$

12.13(f)
$p = 92347.7\,\text{Pa}$

12.13(g)
$k_{\text{H,B}} = 4.40890 \times 10^9\ \text{Pa}$

12.15(a)
$\gamma_{x,\text{B}} = 0.9826$

12.15(b)
$x_\text{B} = 4.19 \times 10^{-4}$

12.16
$K = 1.2 \times 10^{-6}$

12.17(a)
$\alpha = 0.129$
$m_+ = 1.29 \times 10^{-3}\ \text{mol kg}^{-1}$

12.17(b)
$\alpha = 0.140$

12.18
$\Delta_\text{f} H^\circ(\text{Cl}^-, \text{aq}) = -167.15\,\text{kJ mol}^{-1}$
$S^\circ_\text{m}(\text{Cl}^-, \text{aq}) = 56.46\,\text{J K}^{-1}\ \text{mol}^{-1}$

12.19(a)
$K_\text{s} = 1.783 \times 10^{-10}$

12.20(a)
$\Delta_\text{r} H^\circ = -65.769\,\text{kJ mol}^{-1}$

12.20(b)
$\Delta_\text{f} H^\circ(\text{Ag}^+, \text{aq}) = 105.84\,\text{kJ mol}^{-1}$

13.1(a)
$F = 4$

13.1(b)
$F = 3$

13.1(c)
$F = 2$

13.10(a)
$x_\text{B}(\text{top}) = 0.02,\ x_\text{B}(\text{bottom}) = 0.31$

13.10(b)
$n_\text{A} = 2.1\,\text{mol},\ n_\text{B} = 1.0\,\text{mol}$

14.3(a)
$\Delta_\text{r} G^\circ = -21.436\,\text{kJ mol}^{-1}$
$\Delta_\text{r} S^\circ = -62.35\,\text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_\text{r} H^\circ = -40.03\,\text{kJ mol}^{-1}$

14.3(b)
$\Delta_\text{f} H^\circ(\text{AgCl, s}) = -127.05\,\text{kJ mol}^{-1}$

14.3(c)
$S^\circ_\text{m}(\text{AgCl, s}) = 96.16\,\text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_\text{f} S^\circ(\text{AgCl, s}) = -57.93\text{\units}\{\text{J K}^{-1}\ \text{mol}^{-1}\}$
$\Delta_\text{f} G^\circ(\text{AgCl, s}) = -109.78\,\text{kJ mol}^{-1}$

14.4(b)
$\Delta_f H^\circ(\text{AgCl, s}) = -126.81\,\text{kJ mol}^{-1}$
$\Delta_f G^\circ(\text{AgCl, s}) = -109.59\,\text{kJ mol}^{-1}$

14.5
$K_s = 1.76 \times 10^{-10}$

14.6(b)
$\gamma_\pm = 0.756$

14.7(b)
$\Delta_f G^\circ = -210.72\,\text{kJ mol}^{-1}$

14.7(c)
$K_s = 1.4 \times 10^{-18}$

14.8
$E^\circ = 0.071\,\text{V}$

14.9(c)
$E^\circ_{\text{cell, eq}} = 1.36\,\text{V}$

14.9(d)
In the cell:
$đq/\,d\xi = 2.27\,\text{kJ mol}^{-1}$
In a reaction vessel:
$đq/\,d\xi = -259.67\,\text{kJ mol}^{-1}$

14.9(e)
$dE^\circ_{\text{cell, eq}}/\,dT = 3.9 \times 10^{-5}\,\text{V K}^{-1}$

Index

Glossary

Sample Word 1 | Sample Definition 1

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    - 3.1: Heat, Work, and the First Law - *CC BY 4.0*
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    - 3.9: Irreversible Work and Internal Friction - *CC BY 4.0*
    - 3.10: Reversible and Irreversible Processes- Generalities - *CC BY 4.0*
    - 3.11: Chapter 3 Problems - *CC BY 4.0*
  - 4: The Second Law - *CC BY 4.0*
    - 4.1: Types of Processes - *CC BY 4.0*
    - 4.2: Statements of the Second Law - *CC BY 4.0*
    - 4.3: Concepts Developed with Carnot Engines - *CC BY 4.0*
    - 4.4: Derivation of the Mathematical Statement of the Second Law - *CC BY 4.0*
    - 4.5: Irreversible Processes - *CC BY 4.0*
    - 4.6: Applications - *CC BY 4.0*
    - 4.7: Summary - *CC BY 4.0*
    - 4.8: The Statistical Interpretation of Entropy - *CC BY 4.0*
    - 4.9: Chapter 4 Problems - *CC BY 4.0*
  - 5: Thermodynamic Potentials - *CC BY 4.0*
    - 5.1: Total Differential of a Dependent Variable - *CC BY 4.0*
    - 5.2: Total Differential of the Internal Energy - *CC BY 4.0*
    - 5.3: Enthalpy, Helmholtz Energy, and Gibbs Energy - *CC BY 4.0*
    - 5.4: Closed Systems - *CC BY 4.0*
    - 5.5: Open Systems - *CC BY 4.0*
    - 5.6: Expressions for Heat Capacity - *CC BY 4.0*
    - 5.7: Surface Work - *CC BY 4.0*
    - 5.8: Criteria for Spontaneity - *CC BY 4.0*
    - 5.9: Chapter 5 Problems - *CC BY 4.0*
  - 6: The Third Law and Cryogenics - *CC BY 4.0*
    - 6.1: The Zero of Entropy - *CC BY 4.0*
    - 6.2: Molar Entropies - *CC BY 4.0*
    - 6.3: Cryogenics - *CC BY 4.0*
    - 6.4: Chapter 6 Problem - *CC BY 4.0*
  - 7: Pure Substances in Single Phases - *CC BY 4.0*
    - 7.1: Volume Properties - *CC BY 4.0*
    - 7.2: Internal Pressure - *CC BY 4.0*
    - 7.3: Thermal Properties - *CC BY 4.0*
    - 7.4: Heating at Constant Volume or Pressure - *CC BY 4.0*
    - 7.5: Partial Derivatives with Respect to \(T\), \(p\), and \(V\) - *CC BY 4.0*
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