Chemical Thermodynamics

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Contents

1 Introduction

In this Chapter, we quickly review some basic definitions and concepts from thermodynamics. We then provide a brief description of the first and second laws of thermodynamics. Next, we discuss the mathematical consequences of these laws and cover some relevant theorems in multivariate calculus. Finally, free energies and their importance are introduced.

1.1 Basic concepts

1.1.1 State function versus path function

A *state function* is a function that depends only on the current properties of the system and not on the history of the system. Examples of state functions include density, temperature, and pressure.

A *path function* is a function that depends on the history of the system. Examples of path functions include work and heat.

1.1.2 Intensive property versus extensive property

An *extensive property* is a characteristic of a system that is proportional to the size of the system. That is, if we double the size of the system, then the value of an extensive property would also double. Examples of extensive properties include total volume, total mass, total internal energy, etc. Extensive properties will be underlined. For example, the total entropy of the system, which is an extensive property, will be denoted as $\underline{S}$.

An *intensive property* is a characteristic of a system that does not depend on the size of the system. That is, doubling the size of the system leave the value of an intensive property unchanged. Examples of intensive properties are pressure, temperature, density, molar volume, etc. By definition, an intensive property can only be a function of other intensive properties. It cannot be a function of properties that are extensive because it would then depend on the size of the system.

1.2 Brief review of thermodynamics

1.2.1 The first law of thermodynamics

The first law of thermodynamics is simply a statement of the conservation of energy. Energy can take on a variety of forms, for example kinetic energy, chemical energy, or thermal energy. These different forms of energy can transform from one to another; however, the sum total of all the types of energy must remain constant.

Let's apply the first law of thermodynamics to a closed system (i.e. a system that can exchange heat and work with its surroundings, but not matter). The first law for a closed system can be written as

$$dU = \delta Q - \delta W + \cdots \tag{1.1}$$

where U is the internal energy of the system, δQ is the heat (thermal energy) transferred to the system, and δW is the work performed by the system. Other forms of energy may contribute to the energy balance, such as kinetic energy or potential energy (e.g., from a gravitational or electrostatic field).

1.2.2   The second law of thermodynamics

The second law of thermodynamics formalizes the observation that heat is spontaneously transferred only from higher temperatures to lower temperatures. From this observation, one can deduce the existence of a state function of a system: the entropy S. The second law of thermodynamics states that the entropy change dS of a closed, constant-volume system obeys the following inequality

$$dS \geq \frac{\delta Q}{T} \tag{1.2}$$

where T is the absolute temperature of the system, and δQ is the amount of heat transfered to the system. A process will occur spontaneously in a closed, constant-volume system only if Eq. (1.2) is satisfied. For a reversible process, the equality is satisfied; for an irreversible process, the entropy change is greater than the right-hand side of the relation.

Note that the second law of thermodynamics is unique among the various laws of nature in that it is not symmetric in time. It sets a direction in time, and consequently there is a distinction between running forward in time and running backwards in time. We can notice that a film is being played in reverse because we observe events that seem to violate the second law.

1.3   The fundamental equation of thermodynamics

Now consider a closed system that can alter its volume V. In this case, the work performed by the system is $\delta W = pdV$. Combining the first and the second laws of thermodynamics for a closed system (i.e. inserting the inequality in Eq. (1.2) into Eq. (1.1)), we obtain

$$dU \leq TdS - pdV \qquad \text{for constant } N \tag{1.3}$$

For any spontaneous change (process) in the system, the inequality given in Eq. (1.3) will be satisfied. The equality will be satisfied only in a reversible process.

An isolated system is a system that does not exchange work $\delta W = 0$, heat $\delta Q = 0$, or matter $dN = 0$ with its surroundings. Consequently, the total internal energy and volume remain constant;

that implies that $dU = 0$ and $dV = 0$. Substituting these relations into Eq. (1.3), we find that processes occur spontaneously in an isolated system only if the entropy does not decrease. In this case,

$$dS \geq 0 \tag{1.4}$$

Note that in an isolated system, every spontaneous event that occurs always increases the total entropy. Therefore, at equilibrium, where the properties of a system no longer change, the entropy of the system will be maximized.

For a system where entropy and volume are held fixed (i.e. $dS = 0$ and $V = 0$), a process will occur spontaneously if

$$dU \leq 0 \qquad \text{at constant } S, V, \text{ and } N \tag{1.5}$$

For a reversible process, where the system is always infinitesmally close to equilibrium, the equality in Eq. (1.3) is satisfied. The resulting equation is known as the fundamental equation of thermodynamics

$$dU = TdS - pdV \qquad \text{at constant } N \tag{1.6}$$

1.4   The calculus of thermodynamics

From the fundamental equation of thermodynamics, we can deduce relations between the various properties of the system. To see this, let's consider a function f with independent variables x and y. The differential of f (i.e. the total change in f) can be written as:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{1.7}$$

The first term represents the change in f due to changes in the independent variable x, and the second term representce changes due to the independent variable y. Note that Eq. (1.7) is just a generalization of a first order Taylor series expansion to a function of two variables.

If we consider the internal energy of the system $\underline{U}$ to be a function of the variables $\underline{S}$ and $\underline{V}$, then taking $f \rightarrow \underline{U}$, $x \rightarrow \underline{S}$, and $y \rightarrow \underline{V}$, we find

$$d\underline{U} = \left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} d\underline{S} + \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} d\underline{V} \tag{1.8}$$

Comparing Eq. (1.8) with the fundamental equation of thermodynamics Eq. (1.6), we can make the identifications

$$\left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} = T \tag{1.9}$$

$$\left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} = -p \tag{1.10}$$

Therefore, we see that the temperature and pressure of the system can be related to derivatives of its internal energy.

For most functions, the order of differentiation does not matter. That is

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x \tag{1.11}$$

If we apply Eq. (1.11) to the internal energy, we find

$$\left[\frac{\partial}{\partial \underline{V}}\left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}}\right]_{\underline{S}} = \left[\frac{\partial}{\partial \underline{S}}\left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}}\right]_{\underline{V}}$$

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_{\underline{S}} = -\left(\frac{\partial p}{\partial \underline{S}}\right)_{\underline{V}} \tag{1.12}$$

where we have used Eqs. (1.9) and (1.10). These types of relations are known as Maxwell relations. We will encounter more of these kind of relations later on.

There are three additional relations that need to be mentioned. These relations are useful in converting

properties that depend on "unmeasureable" quantities, such as entropy, to properties that are measure-able, such as temperature or pressure. The first is a generalization of the chain rule to functions of multiple variables

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x \tag{1.13}$$

To determine the other two relations, let's consider a function of three variables that is constrained to be equal to zero. That is

$$f(x, y, z) = 0.$$

This defines a two-dimensional surface embedded in a three-dimensional space. The above equation can be interpreted as defining the functions:

$$x = x(y, z) \quad y = y(x, z) \quad z = z(x, y).$$

Each of these functions can be expanded in terms of its respective independent variables

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{1.14}$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{1.15}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.16}$$

By substituting Eq. (1.15) in to Eq. (1.14) to eliminate the dy term, we find

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{1.17}$$

$$0 = \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right] dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \tag{1.18}$$

This equation should hold for any value of dx and dz. In order for this to be true, the coefficients of the dx and dz must vanish. For the dx coefficient, we find

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1} \tag{1.19}$$

The coefficient of the dz term leads to

$$\left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \tag{1.20}$$

This relation is known as the triple product rule.

1.5 Open systems

We can extend Eq. (1.6) to open systems (i.e. systems in which the number of moles N can vary) by including a term called the chemical potential μ. Mathematically, this quantity represents the increase in the internal energy when a small amount of material is introduced to the system at constant total entropy and volume:

$$\mu = \left(\frac{\partial \underline{U}}{\partial N}\right)_{\underline{S},\underline{V}} \tag{1.21}$$

The fundamental equation of thermodynamics can then be written as

$$d\underline{U} = Td\underline{S} - pd\underline{V} + \mu dN \tag{1.22}$$

Let's determine what the chemical potential is. To do this, we rewrite all total quantities in terms of molar properties. For example, the total internal energy can be written as $\underline{U} = NU$, where U is the molar internal energy of the system, and N is the total number of moles in the system. Substituting

these relations into the fundamental equation, we find

$$d(NU) = Td(NS) - pd(NV) + \mu dN$$
$$NdU + UdN = NTdS + TSdN - NpdV - pVdN + \mu dN$$
$$NdU = N(TdS - pdV) - (U + pV - TS - \mu)dN$$
$$dU = TdS - pdV - \frac{1}{N}(G - \mu)dN \tag{1.23}$$

where in the last line, we have introduced the definition of the molar Gibbs free energy $G \equiv U + pV - TS$.

The molar internal energy U is an intensive property of the system; therefore, it should be independent of extensive properties of the system, in particular, the total number of moles in the system N. In order for this to be true, the chemical potential μ must be equal to the molar Gibbs free energy G. In otherwords:

$$\mu \equiv G \tag{1.24}$$

Note that this derivation is restricted to pure substances. For multicomponent systems, we need to generalize this relation. This will be done later.

1.6   Legendre transforms and free energies

The natural variables of the internal energy U are the entropy S, volume V, and total number of moles N of the system. In many situations, however, these variables are not convenient.

We can easily arrive at a new function that has different natural variables by performing a Legendre transform. For example, to arrive at a new state property that posesses the independent variables T and V, we define the Helmholtz free energy A as:

$$A \equiv U - TS \tag{1.25}$$

Inserting this relation into Eq. (1.3), generalized to open systems, we find

$$dU \leq TdS - pdV + \mu dN$$
$$d(A + TS) \leq TdS - pdV + \mu dN$$
$$dA \leq -SdT - pdV + \mu dN \tag{1.26}$$

From this equation, we see that for a system with the temperature, volume, and total number of moles held fixed (i.e., $dT = 0$, $dV = 0$, and $dN = 0$), a process is spontaneous if it decreases the Helmholtz free energy.

In addition, at equilibrium where the equality holds, we find

$$d\underline{A} = -\underline{S}dT - pd\underline{V} + \mu dN \tag{1.27}$$

From this expression, we see that the natural variables of the Helmholtz free energy $\underline{A}$ are the temperature, volume, and total number of moles of the system.

Similarly, if we define the Gibbs free energy $\underline{G} \equiv \underline{U} - T\underline{S} + p\underline{V}$, then the fundamental equation of thermodynamics becomes

$$d\underline{G} = -\underline{S}dT + \underline{V}dp + \mu dN \tag{1.28}$$

The Gibbs free energy is minimized for a system at constant temperature, pressure, and total number of moles. The Gibbs free energy is important because in most experiments the temperature and pressure are variables that we control. This will become useful to us later when we consider phase equilibria.

The corresponding equation for the enthalpy $\underline{H} \equiv \underline{U} + p\underline{V}$ is

$$d\underline{H} = Td\underline{S} + \underline{V}dp + \mu dN \tag{1.29}$$

As we have seen, free energies such as the internal energy and Gibbs free energy are useful in that they tell us whether a process will occur spontaneously or not. A process in which the requisite free energy decreases will occur spontaneously. A process in which the free energy increases will not occur spontaneously. This does not mean that the process cannot happen; we can force the process to occur by performing work on the system. Therefore, we see that free energies are useful to us, qualitatively, in that they tell us the direction in which things will naturally happen.

Free energies also provide us with quantitative information about processes. The change in the free energy is equal to the maximum work that can be extracted from a spontaneous process, or in the case of a non-spontaneous processes, the minimum amount of work that is required to cause the process to occur.

Free energies also have an additional, fundamental importance. Once the mathematical form of the free energy of a system is known in terms of its natural independent variables (e.g., the Gibbs free energy as a function of T, p, and N), then all the thermodynamic properties of the system can be determined. In the remainder of the course, we will be learning how to both develop approximate models for the free energy and how to use these models to estimate the thermodynamic behavior of various systems.

2   Single component systems

In this Chapter, we describe the basic thermodynamic properties of single component systems. We begin with a qualitative description of their general phase behavior. Then, we discuss the mathematical relations that govern this behavior.

2.1   General phase behavior

Figure 2.1 shows the pressure-temperature projection of the phase diagram for a general one-component system. Depending on the temperature and pressure, the system can exist in either a solid, liquid, or vapor phase. Lines separate the various phases. On the lines, two phases coexist. The line separating the vapor and liquid phases is known as the vapor pressure curve. On crossing this curve, the system will transform discontinuously from a liquid to a vapor (or vice-versa). At high temperatures, the vapor pressure curve ends at a critical point. Beyond this point, there is no real distinction between the vapor and liquid phases. By going around the critical point, a liquid can be continuously transformed into a vapor.

The line separating the solid and liquid phases is known as the melting or freezing curve. The line separating the solid and vapor phases is known as the sublimation curve. The point where the vapor pressure curve, the melting curve, and the sublimation curves meet is the triple point. At these conditions, the solid, liquid, and vapor phases can simultaneously coexist.

In Figure 2.2, we show the temperature-density phase diagram for a general pure substance. As with the pressure-temperature diagram, the temperature-density phase diagram is divided by various curves into vapor, liquid, and solid phases. Outside these curves, the system exists as a single phase.

Inside these curves, multiple phases coexist. For example, if a system is prepared at a state corresponding to point A in the diagram, it will divied into a vapor phase, with density $\rho^{(v)}$, and liquid phase, with density $\rho^{(l)}$. From the phase diagram, we can also determine the relative amounts of the coexisting phases. Let's consider a system consisting of N total moles that are separated into a liquid phase that occupies a volume $\underline{V}^{(l)}$ and a vapor phase that occupies a volume $\underline{V}^{(g)}$. From a mole balance, we have

$$N = \rho^{(l)}\underline{V}^{(l)} + \rho^{(g)}\underline{V}^{(g)}$$
$$\rho(\underline{V}^{(l)} + \underline{V}^{(g)}) = \rho^{(l)}\underline{V}^{(l)} + \rho^{(g)}\underline{V}^{(g)}$$
$$(\rho^{(l)} - \rho)\underline{V}^{(l)} = (\rho - \rho^{(g)})\underline{V}^{(g)}$$
$$\frac{\underline{V}^{(l)}}{\underline{V}^{(g)}} = \frac{\rho - \rho^{(g)}}{\rho^{(l)} - \rho} \tag{2.1}$$

where $\rho = N/(\underline{V}^{(l)} + \underline{V}^{(g)})$ is the overall density of the system. Equation (2.1) is known as the lever rule. It allows us to compute the relative amounts of the two-coexisting phases.
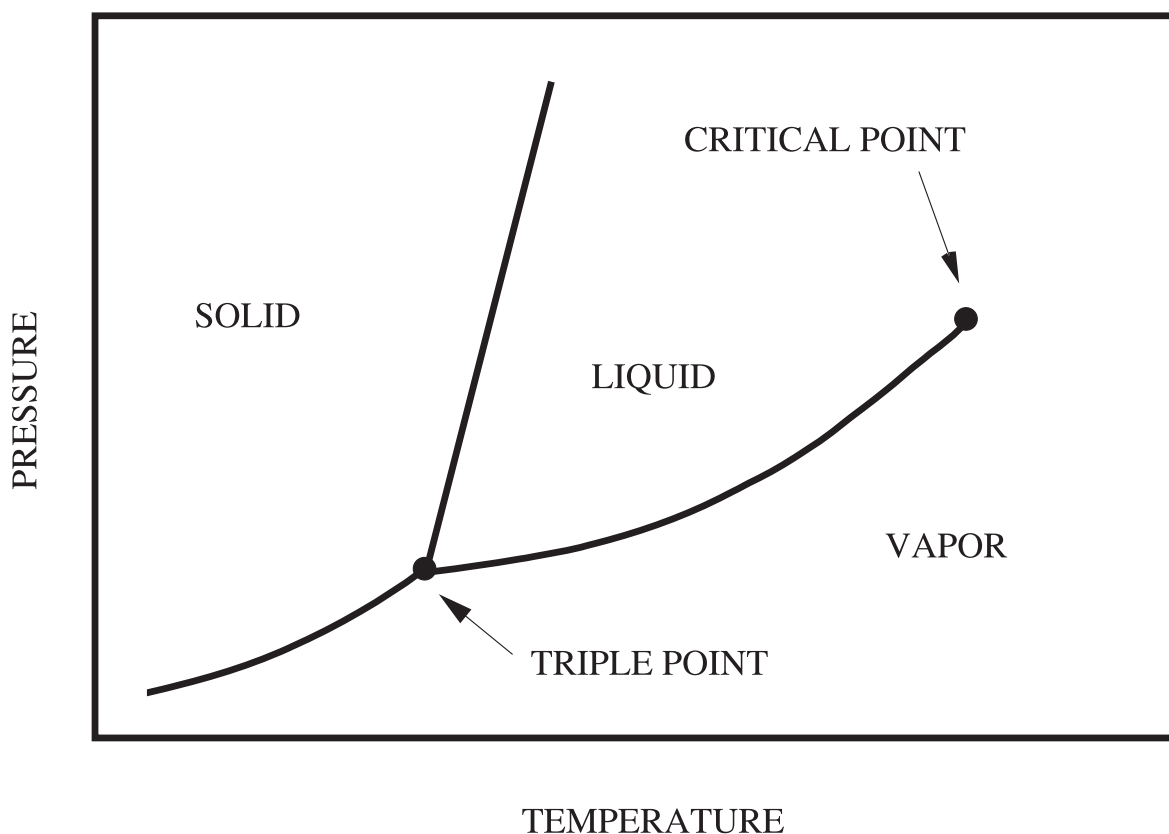
Figure 2.1: Pressure-temperature diagram for a general one-component system.

The dashed-line represents the triple point. Anywhere along the dashed-line, the vapor, liquid, and solid phases can simultaneously exist.

2.2 Conditions for phase equilibrium

Now let's derive the mathematical conditions for equilibrium between two coexisting phases. We consider an isolated system that is separated into two phases, which we label A and B. The volume occupied by each phase can change; in addition, the both phases can freely exchange energy and material with each other. Because the system is isolated, the total energy $\underline{U}$, the total volume $\underline{V}$, and the total number of moles N in the system must remain constant. This leads to the following relations:

$$\underline{U}^{(A)} + \underline{U}^{(B)} = \underline{U} \quad \Longrightarrow \quad d\underline{U}^{(A)} = -d\underline{U}^{(B)} \tag{2.2}$$

$$\underline{V}^{(A)} + \underline{V}^{(B)} = \underline{V} \quad \Longrightarrow \quad d\underline{V}^{(A)} = -d\underline{V}^{(B)} \tag{2.3}$$

$$N^{(A)} + N^{(B)} = N \quad \Longrightarrow \quad dN^{(A)} = -dN^{(B)} \tag{2.4}$$

where $\underline{U}^{(i)}$ is the total energy of phase i, $\underline{V}^{(i)}$ is the total volume of phase i, and $N^{(i)}$ is the total number of moles in phase i.
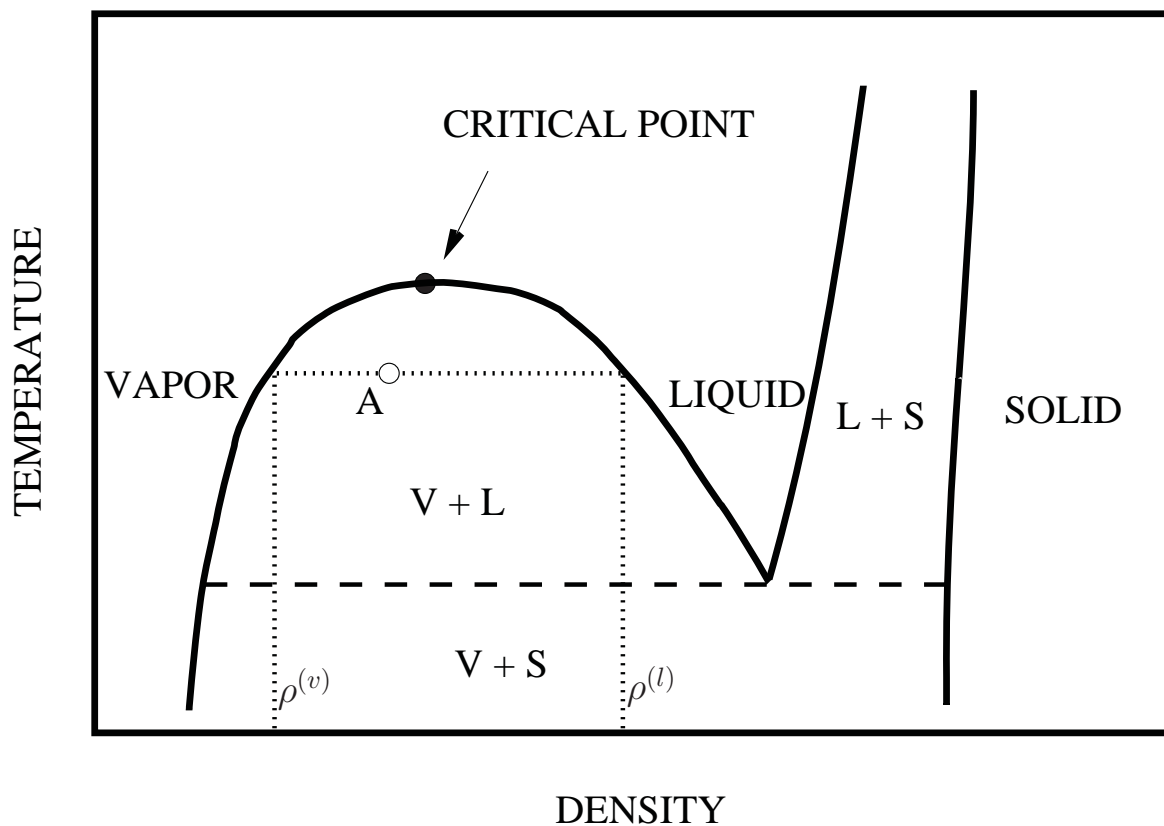
Figure 2.2: Temperature-density diagram for a general pure substance.

The total entropy of an isolated system at equilibrium is maximized. Therefore, we have

$$dS = 0 \tag{2.5}$$

The change in the total entropy of the system is given by the sum of the entropy change in phase A and the entropy change in phase B. This leads to

$$
\begin{aligned}
dS &= dS^{(A)} + dS^{(B)} \\
&= \frac{1}{T^{(A)}} dU^{(A)} + \frac{p^{(A)}}{T^{(A)}} dV^{(A)} - \frac{\mu^{(A)}}{T^{(A)}} dN^{(A)} \\
&\quad + \frac{1}{T^{(B)}} dU^{(B)} + \frac{p^{(B)}}{T^{(B)}} dV^{(B)} - \frac{\mu^{(B)}}{T^{(B)}} dN^{(B)}
\end{aligned}
\tag{2.6}
$$

where we have rearranged Eq. (1.22) to obtain how the entropy of a phase changes with its energy, volume, and number of moles.

Substituting the relations given in Eq. (2.4) into Eq. (2.6), we find

$$
\begin{aligned}
dS &= \frac{1}{T^{(A)}}dU^{(A)} + \frac{p^{(A)}}{T^{(A)}}dV^{(A)} - \frac{\mu^{(A)}}{T^{(A)}}dN^{(A)} \\
&\quad - \frac{1}{T^{(B)}}dU^{(A)} - \frac{p^{(B)}}{T^{(B)}}dV^{(A)} + \frac{\mu^{(B)}}{T^{(B)}}dN^{(A)} \\
0 &= \left(\frac{1}{T^{(A)}} - \frac{1}{T^{(B)}}\right)dU^{(A)} + \left(\frac{p^{(A)}}{T^{(A)}} - \frac{p^{(B)}}{T^{(B)}}\right)dV^{(A)} - \left(\frac{\mu^{(A)}}{T^{(A)}} - \frac{\mu^{(B)}}{T^{(B)}}\right)dN^{(A)}
\end{aligned}
\tag{2.7}
$$

The quantities $dU^{(A)}$, $dV^{(A)}$, and $dN^{(A)}$ on the right-hand side of Eq. (2.7) can be chosen arbitrarily. From Eq. (2.6), we know that the left-hand side of Eq. (2.7) must equal zero. The only manner in which to guarantee the equality between the two sides of Eq. (2.7) is if coefficients of the $dU^{(A)}$, $dV^{(A)}$, and $dN^{(A)}$ terms are each equal to zero. As a result, this implies the relations:

$$
\begin{aligned}
T^{(A)} &= T^{(B)} \\
p^{(A)} &= p^{(B)} \\
\mu^{(A)} &= \mu^{(B)}
\end{aligned}
\tag{2.8}
$$

Therefore, we find that the temperatures, pressures, and chemical potentials are equal for coexisting phases in equilibrium. We will later extend this derivation to multicomponent system.

One interesting point to note is that the labels A and B which we used to derive Eqs. (2.8) do not have to refer to different phases. For example, A and B can refer to different parts of a one phase system. Therefore, Eqs. (2.8) can be interpreted as stating the the temperature, pressure, and chemical potential of a system at equilibrium are uniform (N.B., we did not include the influence of external fields, such as gravitional or electrostatic fields).

2.3   The Clapeyron equation

In this section, we derive the Clapeyron equation. This equation relates changes in the pressure to changes in the temperature along a two-phase coexistence curve (e.g., the vapor pressure curve or the melting curve). Note that the condition for equilibrium between two phases is given by

$$
\begin{aligned}
\mu^{(A)} &= \mu^{(B)} \\
G^{(A)} &= G^{(B)} \\
dG^{(A)} &= dG^{(B)} \\
-S^{(A)}dT + V^{(A)}dp &= -S^{(B)}dT + V^{(B)}dp \\
\frac{dp}{dT} &= \frac{S^{(A)} - S^{(B)}}{V^{(A)} - V^{(B)}}
\end{aligned}
\tag{2.9}
$$

This is one form of the Clapeyron equation. It relates the slope of the coexistence curve to the entropy change and volume change of the phase transition.

Entropy is not directly measureable, and, therefore, the Clapeyron equation as written above is not in a convenient form. However, we can relate entropy changes to enthalpy changes, which can be directly measured. At equilibrium, we have

$$\mu^{(A)} = \mu^{(B)}$$

$$G^{(A)} = G^{(B)}$$

$$H^{(A)} - TS^{(A)} = H^{(B)} - TS^{(B)}$$

$$S^{(A)} - S^{(B)} = \frac{1}{T}(H^{(A)} - H^{(B)}) \tag{2.10}$$

Thus, the entropy change of a phase transition, which is not directly measureable, can be determined from the enthalpy change of the phase transition, which is directly measureable.

Substituting this relation into Eq. (2.9), we find

$$\frac{dp}{dT} = \frac{H^{(A)} - H^{(B)}}{T(V^{(A)} - V^{(B)})} \tag{2.11}$$

This is the more commonly used form of the Clapeyron equation.

3 Multicomponent systems

In this section, we examine the thermodynamics of systems which contain a mixture of species. First, we generalize the thermodynamic analysis of the previous section to multicomponent systems, deriving the Gibbs phase rule. Then we describe the general phase behavior of binary and ternary mixtures.

3.1 Thermodynamics of multicomponent systems

3.1.1 The fundamental equation of thermodynamics

In this section, we extend the results of the previous lectures to multicomponent systems. All that needs to be done is to define a chemical potential for each species α in the system

$$dU = TdS - pdV + \sum_\alpha \mu_\alpha dN_\alpha \tag{3.1}$$

where μ_α is the chemical potential of component α. From this, we see that

$$\mu_\alpha \equiv \left(\frac{\partial U}{\partial N_\alpha} \right)_{S,V,N_{\alpha'\neq\alpha}} \tag{3.2}$$

Physically, μ_α is the change in the internal energy of the system with respect to an increase in the number of moles of species α, while holding all number of moles of all other species constant. The other forms of the fundamental equation of thermodynamics can be similarly generalized by performing the Legendre transform:

$$dA = -SdT - pdV + \sum_\alpha \mu_\alpha dN_\alpha$$

$$dG = -SdT + Vdp + \sum_\alpha \mu_\alpha dN_\alpha$$

$$dH = TdS + Vdp + \sum_\alpha \mu_\alpha dN_\alpha \tag{3.3}$$

From these relations, we see that there are the following alternate interpretations of the chemical potential:

$$\mu_\alpha \equiv \left(\frac{\partial A}{\partial N_\alpha} \right)_{T,V,N_{\alpha'\neq\alpha}} \equiv \left(\frac{\partial G}{\partial N_\alpha} \right)_{T,p,N_{\alpha'\neq\alpha}} \equiv \left(\frac{\partial H}{\partial N_\alpha} \right)_{S,p,N_{\alpha'\neq\alpha}} \tag{3.4}$$

3.1.2 Phase equilibria

The conditions for phase equilibria can also be extended to multicomponent systems. Consider an isolated system consisting of ω components and two phases, which we refer to as A and B. The

system is isolated, with a total internal energy of $\underline{U}$, a total volume of $\underline{V}$, and N_α moles of species α. Because the system is isolated, we have the following

$$
\begin{aligned}
\underline{U}^{(A)} + \underline{U}^{(B)} &= \underline{U} &\implies&& d\underline{U}^{(A)} &= -d\underline{U}^{(B)} \\
\underline{V}^{(A)} + \underline{V}^{(B)} &= \underline{V} &\implies&& d\underline{V}^{(A)} &= -d\underline{V}^{(B)} \\
N_\alpha^{(A)} + N_\alpha^{(B)} &= N_\alpha &\implies&& dN_\alpha^{(A)} &= -dN_\alpha^{(B)}
\end{aligned}
\tag{3.5}
$$

where $\underline{U}^{(i)}$ is the internal energy of phase i, $\underline{V}^{(i)}$ is the volume of phase i, and $N_\alpha^{(i)}$ is the number of moles of species α in phase i.

For an isolated system at equilibrium, the total entropy is maximized. Stated mathematically, we have

$$
\begin{aligned}
d\underline{S} &= d\underline{S}^{(A)} + d\underline{S}^{(B)} = 0 \\
&= \frac{1}{T^{(A)}} d\underline{U}^{(A)} + \frac{p^{(A)}}{T^{(A)}} d\underline{V}^{(A)} - \sum_\alpha \frac{\mu_\alpha^{(A)}}{T^{(A)}} dN_\alpha^{(A)} \\
&\quad + \frac{1}{T^{(B)}} d\underline{U}^{(B)} + \frac{p^{(B)}}{T^{(B)}} d\underline{V}^{(B)} - \sum_\alpha \frac{\mu_\alpha^{(B)}}{T^{(B)}} dN_\alpha^{(B)}
\end{aligned}
\tag{3.6}
$$

Inserting the constraint relations given in Eq. (3.5) into Eq. (3.6), we find

$$
d\underline{S} = \left(\frac{1}{T^{(A)}} - \frac{1}{T^{(B)}} \right) d\underline{U}^{(A)} + \left(\frac{p^{(A)}}{T^{(A)}} - \frac{p^{(B)}}{T^{(B)}} \right) d\underline{V}^{(A)} - \sum_\alpha \left(\frac{\mu_\alpha^{(A)}}{T^{(A)}} - \frac{\mu_\alpha^{(B)}}{T^{(B)}} \right) dN_\alpha^{(A)}
\tag{3.7}
$$

This is equal to zero only if all the coefficients of the change terms are zero. As a consequence, we find

$$
\begin{aligned}
T^{(A)} &= T^{(B)} \\
p^{(A)} &= p^{(B)} \\
\mu_\alpha^{(A)} &= \mu_\alpha^{(B)} \quad \text{for all components } \alpha
\end{aligned}
$$

This argument can be generalized to a system containing π phases and ω components. In this case, we have the temperature, pressure, and chemical potentials of each species are equal in each phase.

$$
\begin{aligned}
T^{(A)} &= T^{(B)} = \cdots = T^{(\pi)} \\
p^{(A)} &= p^{(B)} = \cdots = p^{(\pi)} \\
\mu_\alpha^{(A)} &= \mu_\alpha^{(B)} = \cdots = \mu_\alpha^{(\pi)} \quad \text{for all components } \alpha
\end{aligned}
\tag{3.8}
$$

3.1.3 Gibbs phase rule

How many variables need to be specified in order to fix the state of a system? In order to fix the state of a one-phase system, the composition of the phase must be specified as well as two additional

intensive variables (e.g., temperature and pressure). For a phase with ω components, $\omega - 1$ mole fractions are required to specify the composition. Therefore, a total of $\omega + 1$ intensive variables are required to specify the state of a single phase.

For a system with π phases, there are a total of $(\omega + 1)\pi$ unknowns. However, not all of these are independent. The conditions for phase equilibrium (see Eqs. (3.8)) give us $(\omega + 2)(\pi - 1)$ equations that must be satisfied between each of the phases. The difference between the number of unknowns in the system and the number of constraints (or equations) is equal to the number of degrees of freedom f in the system.

$$\begin{aligned} f &= (\omega + 1)\pi - (\omega + 2)(\pi - 1) \\ &= 2 + \omega - \pi \end{aligned} \qquad (3.9)$$

This is known as the Gibbs phase rule. It tells us the number of variables f that must be specified in order to fix the (intensive) state of the system.
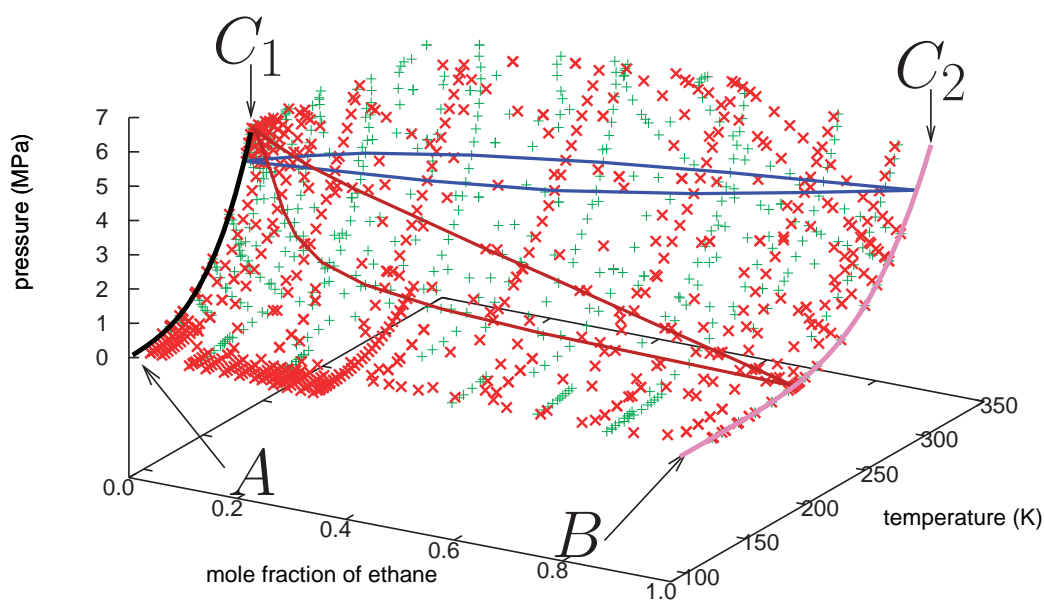
Figure 3.1: Phase diagram for mixtures of methane and ethane. Data taken from a variety of sources.

3.2   Binary mixtures

3.2.1   Vapor-liquid equilibrium

The Gibbs phase rule for a binary mixture simplifies to

$$f = 4 - \pi \tag{3.10}$$

The maximum number of degrees of freedom that a system can have is given when there is only one phase present (i.e., $\pi = 1$). For a binary mixture, we find that there are at most 3 degrees of freedom. This means that we can represent the state of binary mixture using a three dimensional diagram. An example of such a diagram is given in Fig. 3.1, which is for mixtures of methane and ethane.

The key feature of this phase diagram is a solid body in the center of the figure. Within this solid body, the system exists as a two-phase mixture, with a coexisting liquid and vapor phases. Above this body, the system exists as a single liquid phase; below this body, the system is a single vapor phase. The upper surface (marked by red points) that bounds the body is the locus of bubble points (i.e., the points at which bubbles begin to appear in a liquid). The lower surface (marked by green points) is the locus of dew points (i.e., the points at which droplets begin to appear in a vapor).
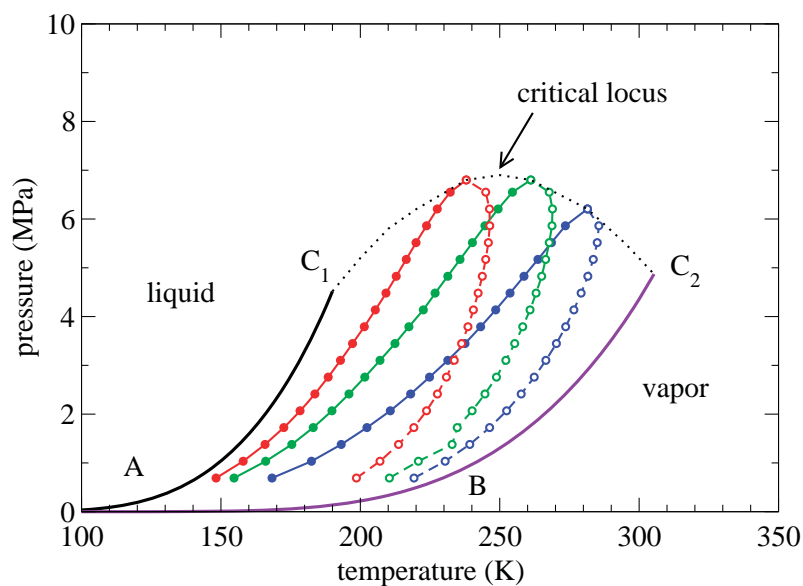
Figure 3.2: Generic pressure-temperature diagram for binary mixtures of methane and ethane: (i) pure methane (black line), (ii) $15\,\mathrm{mol\%}$ ethane (red lines), (iii) $50\,\mathrm{mol\%}$ ethane (green lines), (iv) $70\,\mathrm{mol\%}$ ethane (blue lines), and (v) pure ethane (violet line). The solid lines and filled symbols denote the bubble point curves (saturated liquid), and the dashed lines and open symbols denote the dew point curves (saturated vapor). Data taken from RT Ellington et al., *Pap. Symp. Thermophys. Prop.* **1**, 180 (1959).

The points C_1 and C_2 are the critical points of pure methane and ethane, respectively. The line connecting these two points, which is the intersection of the bubble point and dew point surfaces, is the critical locus. This is the set of critical points for the various mixtures of methane and ethane. The black curve connecting points A and C_1 is the vapor pressure curve of pure methane, and the violet curve connecting points B and C_2 is the vapor pressure curve of pure ethane.

We can represent Fig. 3.1 in a two-dimensional figure by taking various projections. The blue envelope is a horizontal cross-section of the two-phase body; this is a Txy diagram of the methane-ethane mixture taken at constant pressure. The brown envelope is a vertical cross-section of the solid body, taken at constant temperature; this is a pxy diagram.

In Fig. 3.2, we show the pressure-temperature view of the phase diagram for binary mixtures of methane and ethane. The point C_1 represents the critical point of pure methane, and the point C_2 represents the critical point of pure ethane. The curve connecting the points A and C_1 is the vapor pressure curve for pure methane; the curve connecting points B and C_2 is the vapor pressure curve for pure ethane. The dotted curve connecting the points C_1 and C_2 is the critical locus. The critical points of the mixtures, where the coexisting liquid and vapor phases become identical, lie on this critical locus.

For a one component system, the bubble point and the dew point are the same and lie along the vapor pressure curve; however, this is not necessarily the case for a mixture. Within envelopes contained
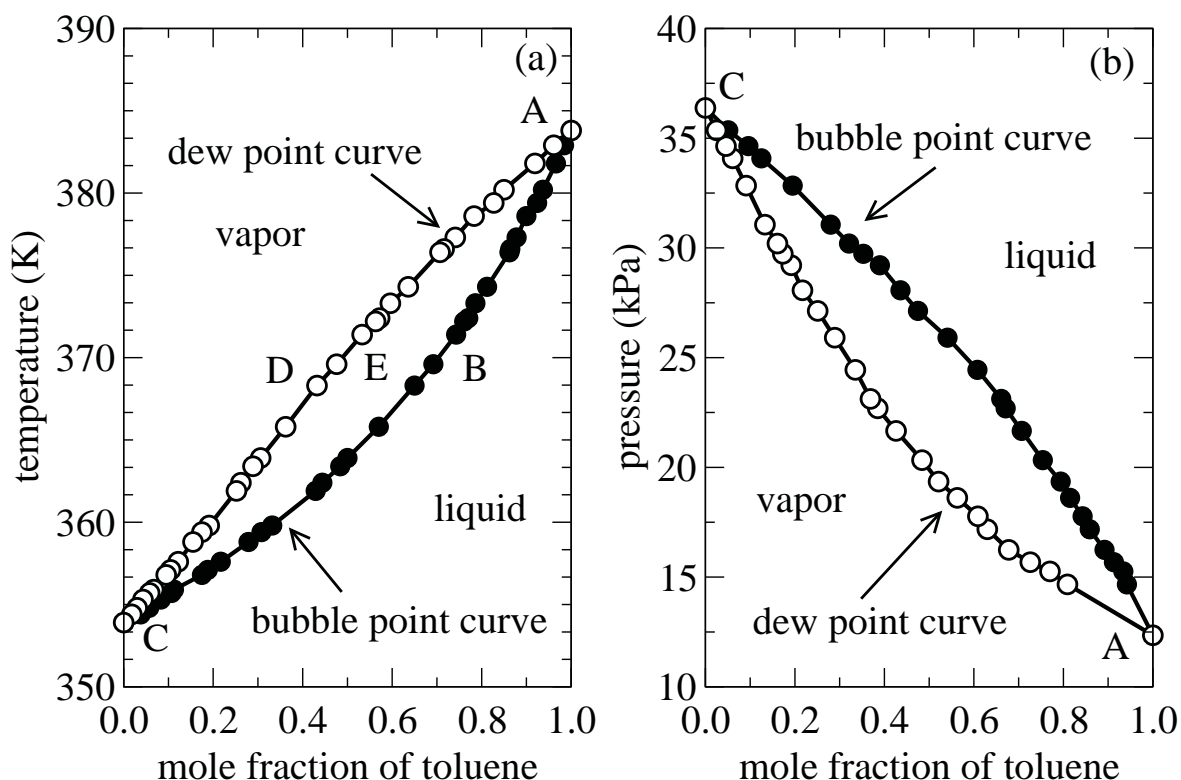
Figure 3.3: Vapor-liquid equilibria of mixtures of cyclohexane and toluene: (a) Txy diagram at a pressure of 1 atm, and (b) pxy diagram at a temperature of $50°$C. The filled symbols denote the bubble point curves (saturated liquid), and the open symbols denote the dew point curves (saturated vapor). Data taken from F Rivenq, *Bull. Soc. Chim. Fr.* **9**, 3034 (1969).

between the vapor pressure curves of the pure components, a mixture consists of a coexisting vapor and liquid phases. The upper part of the envelop (the solid curve with filled symbols) is the bubble point curve; the lower part of the envelop (the dashed curve with open symbols) is the dew point curve. Different envelopes correspond to different mixture compositions.

In Fig. 3.3a, we present the Txy diagram for binary mixtures of cyclohexane and toluene at a pressure of 1 atm, which is below the critical pressure of both pure species. Point A denotes the boiling temperature of pure toluene, and point C is the boiling temperature of pure cyclohexane. Connecting these two points are two curves that form the two-phase envelope. The upper curve (with the open symbols) is the dew point curve, and the lower curve (with the filled symbols) is the bubble point line.

Above the two-phase envelope, the system is a vapor, and below the envelope, the system is a liquid. Within the envelope, the system separates into a coexisting vapor and liquid phase. The composition of the phases is given by the dew point curve and the bubble point curve. For example at point E (mole fraction z_α), the system splits into a vapor phase with a composition corresponding to point D (mole fraction y_α) and a liquid phase with a composition corresponding to point B (mole fraction x_α). The ratio of the total moles of the liquid phase $N^{(1)}$ to the total moles of the vapor phase $N^{(g)}$ is

given by the lever rule:

$$z_\alpha N = x_\alpha N^{(l)} + y_\alpha N^{(g)}$$
$$z_\alpha (N^{(l)} + N^{(g)}) = x_\alpha N^{(l)} + y_\alpha N^{(g)}$$
$$\frac{N^{(l)}}{N^{(g)}} = \frac{z_\alpha - y_\alpha}{x_\alpha - z_\alpha} \tag{3.11}$$

where $N = N^{(l)} + N^{(g)}$ is the total number of moles in the system.

In Figure 3.3b, we show the pxy diagram for binary mixtures of cyclohexane and toluene at $50°$C, which is below the critical temperature of both species. Point A is the boiling pressure of pure toluene, and point C is the boiling pressure of pure cyclohexane. Connecting these two points are the bubble point (upper) and dew point (lower) curves. Above the bubble point curve, the system is entirely in the liquid phase, while below the dew point curve, the system is in the vapor phase. Between these two curves, the system separates into a coexisting liquid and vapor phase. The lever rule, described previously for the Txy diagram, also applies to the pxy diagram and can be used to determine the relative proportions of these phases.

Figure 3.4: Phase diagram for mixtures of methane and ethane. (a) Txy diagram with pressure: (i) 0.101325 MPa (red curves), (ii) 0.6895 MPa (green curves), and (iii) 5.861 MPa (blue curves). (b) pxy diagram with temperature: (i) 172.04 K (red curves), (ii) 199.93 K (green curves), and (iii) 280 K (blue curves). Data taken from RT Ellington et al., *Pap. Symp. Thermophys. Prop.* **1**, 180 (1959).

Now let's consider the variation of the Txy diagram of a binary mixture with pressure. In Figure 3.4a, we show the Txy diagram for mixtures of methane and ethane. At moderately low pressures, we have the standard Txy diagram, which touches the temperature axis at the boiling temperature of each of the pure species. As the pressure increases, the two-phase envelope gradually moves to higher temperatures, due to the fact that boiling temperatures increase with pressure. However, when the pressure of the system becomes higher than the critical pressure of methane (46.0 bar), the two-phase envelope no longer touches the temperature axis at $x_{methane} = 1$. As the pressure further increases beyond the critical pressure of ethane (48.8 bar), then the two-phase envelope also detaches from the temperature axis at $x_{methane} = 0$.

In the systems that we have examined so far, the bubble point and the dew point of the mixture vary monotonically with the composition. This is the case for ideal systems. However, for very non-ideal systems, there may be a maximum or a minimum in the bubble and dew point curves. This is the case for azeotropic systems. An example of a system that exhibits a low-boiling azeotrope is a mixture of n-heptane and ethanol, which is shown in Figure 3.5. For this type of system, both the bubble and dew point temperature curves have a local minimum at the same composition. At this composition, these two curves meet. This point is known as the azeotrope. At the azeotrope, the composition of the coexisting liquid and vapor phases are identical. In this case at the azeotrope, the boiling temperature
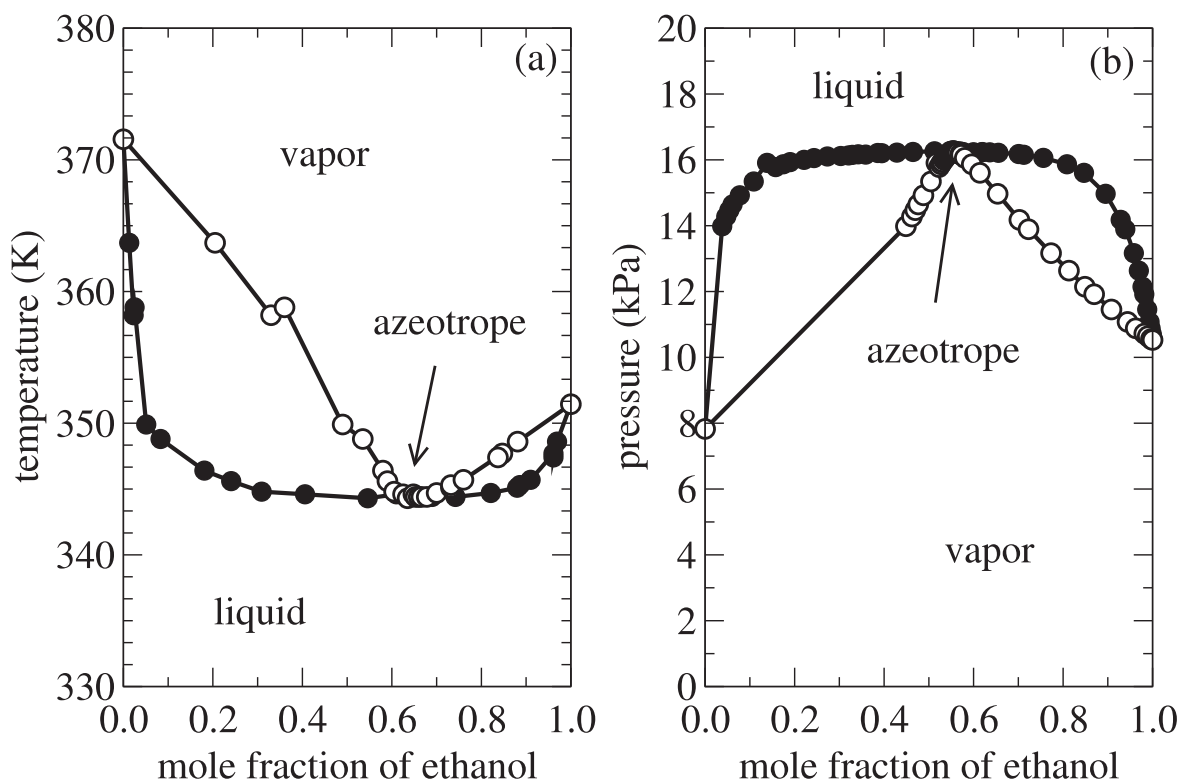
Figure 3.5: Phase diagram for mixtures of n-heptane and ethanol, which exhibits a low boiling azeotrope: (a) temperature-composition diagram at 30.1°C, and (b) pressure-composition diagram at 1 atm. Data taken from JD Raal, RK Code, and DA Best, *J. Chem. Eng. Data* **17**, 211 (1972).

of the liquid is lower than the boiling temperature of either pure components. The corresponding bubble and dew point pressure curves have a maximum at the azeotrope (see Fig. 3.5b).

For a high boiling azeotropic system, the bubble and dew point temperature curves meet at a maximum in the Txy diagram. Mixtures of nitric acid and water form exhibit a high boiling azeotrope; this system is shown in Fig. 3.6.

3.2.2   Liquid-liquid equilibria

When two liquids are mixed together, they do not always form a single, homogenous liquid phase. In many cases, two liquid phases are formed, with one phase richer in the first component and the other phase richer in the second component. The classic example of a system that exhibits this behavior is a mixture of oil and water.

A typical Txy diagram for a system that demonstrates liquid-liquid phase separation is given in Fig. 3.7, which is for mixtures of phenol and water. Outside the curve, the mixture exists as a single, homogeneous liquid phase. Inside the curve, the system exists as two separate, coexisting liquid phases. Consider the point A, which lies inside the curve. In this case, the system phase separates
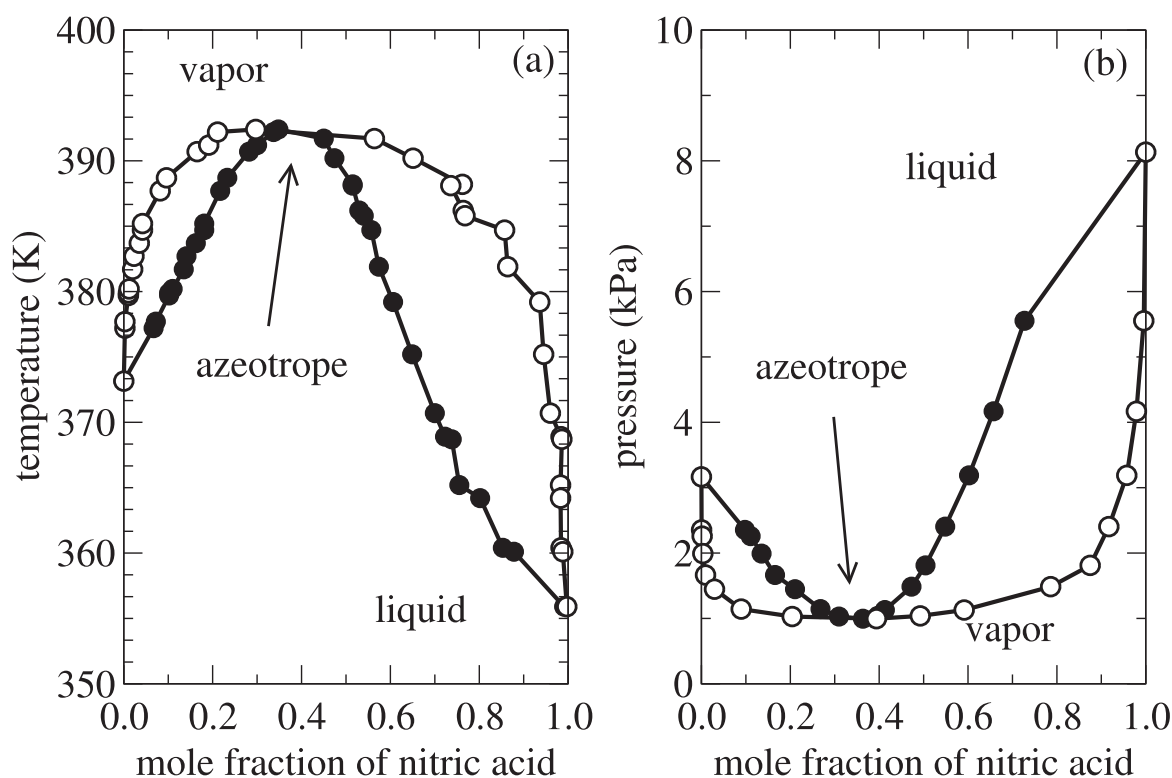
Figure 3.6: Phase diagram for mixtures of nitric acid and water, which has a high boiling azeotrope: (a) temperature-composition diagram at 1 atm, and (b) pressure-composition diagram at 25°C. Data taken from MA Yakimov and VYa Mishin, *Radiokhimiya* **6**, 543 (1964).

into two liquid phases, one with composition x_1' and the other with composition x_1''. The relative amounts of the two phases can be computed using the lever rule, as described previously.

The maximum of the liquid-liquid phase envelope and is known as the critical point of the mixture. Above the critical temperature (i.e., the temperature at the critical point), the system exists as a single liquid phase. Below the critical temperature, the system can split into two coexisting liquid phases, depending on the overall composition.

The basic reason why liquid-liquid phase separation occurs is that the attractive interactions between different molecules are weaker than the attractive interactions beween similar molecules. As a result, similar molecules prefer to be near to each other and than to dissimilar molecules. The consequence of this at a macroscopic level is the formation of two liquid phases.

3.2.3   Vapor-liquid-liquid equilibria

In Figure 3.8, we combine the high temperature and low temperature Txy phase diagrams for a system with a low boiling azeotrope. At high temperatures, the system is a vapor. At lower temperatures, it condenses to become a liquid. Below the critical temperature, liquid can separate to form two
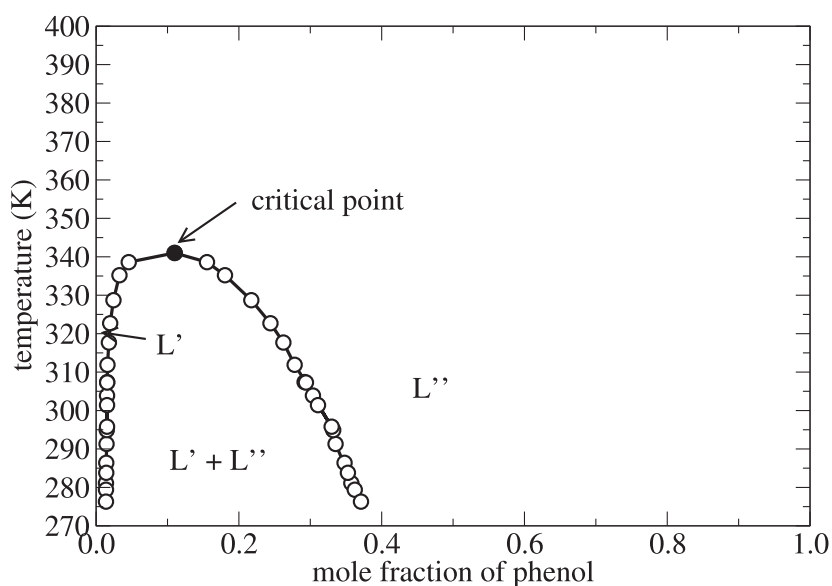
Figure 3.7: Phase diagram of mixtures of phenol and water. Data taken from AN Campbell and AJR Campbell, *J. Am. Chem. Soc.* **59**, 2481 (1937).

coexisting liquid phases.

As the pressure of the system decreases, the boiling temperature decreases, in general. Therefore, we expect the vapor-liquid coexistence envelope to drop to lower temperatures as the pressures decrease. Changes in pressure, however, do not have a strong influence on the phase behavior of liquids. As a result, we do not expect the liquid-liquid phase envelope to change much with pressure. Consequently, we expect that at a low enough pressure, the vapor-liquid coexistence curve will intersect the liquid-liquid coexistence curve. When this occurs, we can have vapor-liquid-liquid equilibria, which is shown in Figure 3.9.
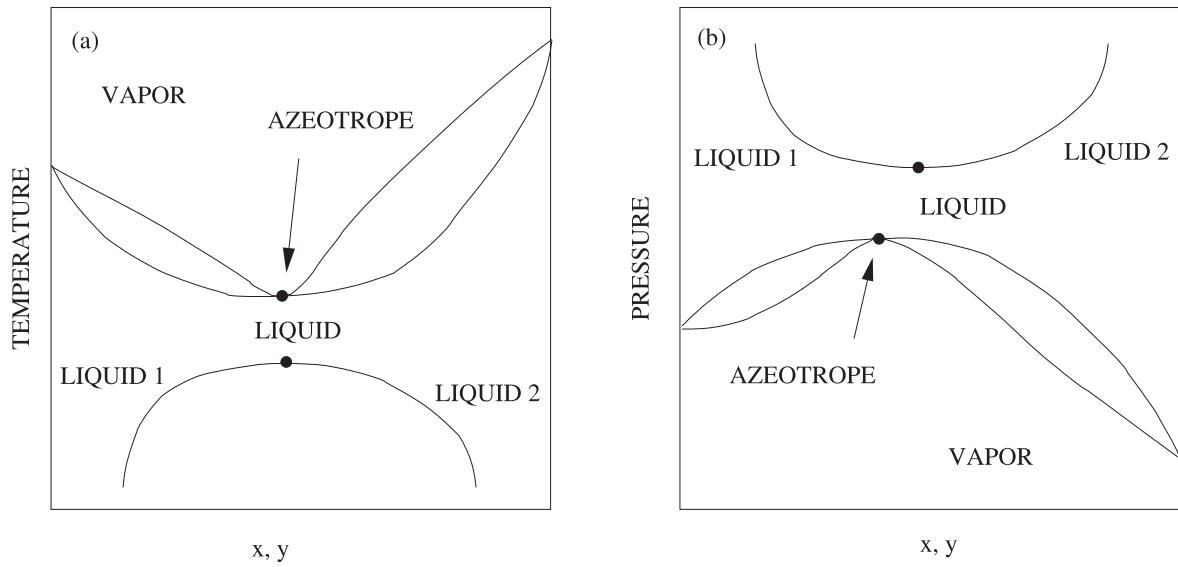
Figure 3.8: Phase diagram for system with a low boiling azeotrope and two liquid phases: (a) temperature-composition diagram, and (b) pressure-composition diagram.
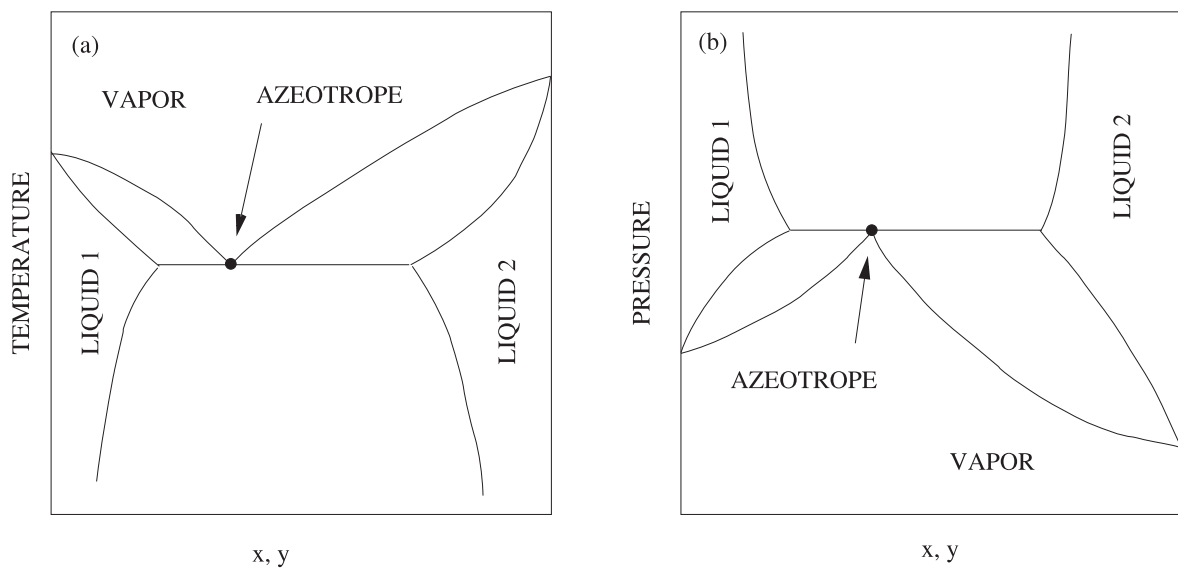
Figure 3.9: Phase diagram for system with a heterogeneous azeotrope: (a) temperature-composition diagram, and (b) pressure-composition diagram.
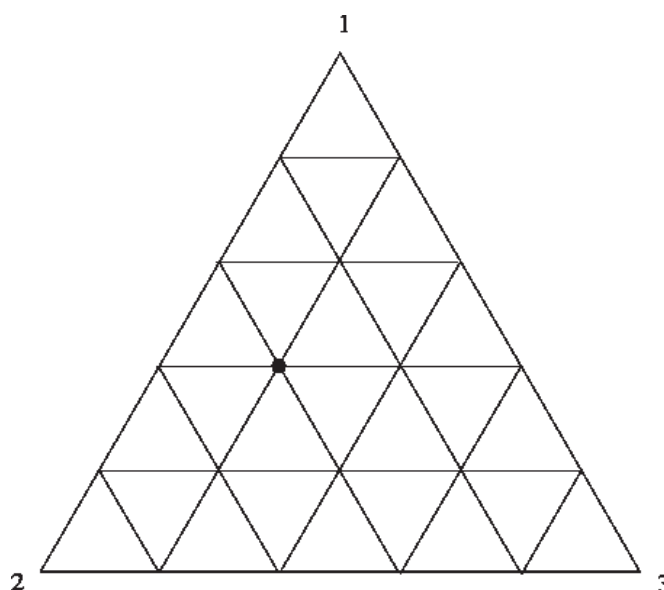
Figure 3.10: Triangular phase diagram representing a ternary mixture. The filled circle represents a 40%, 40%, 20% mixture of components 1, 2, and 3, respectively.

3.3 Ternary mixtures

In this section, we consider the phase behavior of systems with three components. The Gibbs phase rule for a ternary mixture is

$$f = 5 - \pi \tag{3.12}$$

A ternary system can have at most four degrees of freedom, which occurs when there is only one phase present (i.e., $\pi = 1$). At a given temperature and pressure, only the composition of a ternary system needs to specified to fix its state.

In this case, the phase diagram is typically represented on an equilateral triangle, such as the one shown in Figure 3.10. The corners of the triangles represent the pure components. The upper corner is pure 1; the lower left corner is pure 2; and the lower right corner is pure 3. For a general point within the triangle, the mole fraction of a species is equal to the ratio of the distance of the point from the corresponding corner to the height of the triangle. Therefore, the sides of the triangle represent binary mixtures.

Some typical phase behavior that can be exhibited by ternary mixtures is shown in Fig. 3.11. Let us consider a situation where binary mixtures of component 1 and component 2 are only partially miscible, where two coexisting liquid phases may be formed: one rich in 1 and the other rich in 2. This is represented by the base of the ternary phase diagram shown in Fig. 3.11a. In addition, let us assume that components 1 and 3 are completely miscible and components 2 and 3 are also completely miscible. For this case, one might expect that if enough of component 3 is added to the system, then components 1 and 2 can be made to mix with each other, due to their mutual solubility with component 3. This is type I phase behavior.
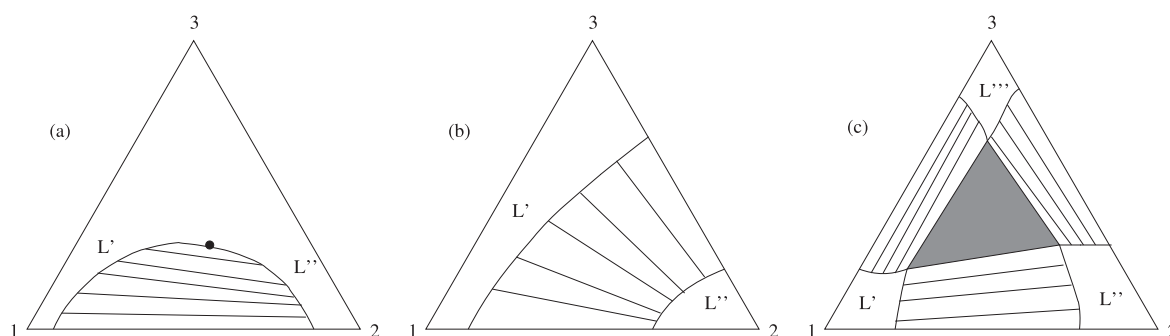
Figure 3.11: Generic phase behavior of ternary mixtures: (a) type I, (b) type II, and (c) type III.

A type II phase diagram, shown in Fig. 3.11b, corresponds to a situation where components 1 and 3 are completely miscible, but both components 1 and 2 and components 2 and 3 are only partially miscible.

Finally, type III phase behavior is shown in Fig. 3.11c. In this case, the various binary mixtures of the three components are each only partially miscible. The shaded triangle in the center of the phase diagram is a region where three phases are in coexistence with each other. Systems with a composition which lies within this shaded triangle will split into three separate phases; the composition of each of these phases corresponds to one of the corners of the triangle. The composition of the individual phases will not vary with the system's location within the triangle (i.e., its overall composition); however, the relative amounts of each of the phases will.

4 The ideal solution model

In many situations, we need to predict the properties of a mixture, given that we already know the properties of the pure species. To do this requires a model that can describe how various components mix. In mathematical terms, this means that we need to relate the Gibbs free energy of a mixture to the Gibbs free energy of the various pure components. One of the simplest models that achieves this is the ideal solution model. In this lecture, we present the ideal solution model. Then we apply this model to describe vapor-liquid equilibria, and as a result, derive Raoult's law.

4.1 Definition of the ideal solution model

For an ideal solution, the Gibbs free energy $\underline{G}$ defined as:

$$\underline{G}(T, p, N_1, N_2, \dots) = \sum_\alpha N_\alpha \mu_\alpha^\circ(T, p) + RT \sum_\alpha N_\alpha \ln x_\alpha \qquad (4.1)$$

where T is the absolute temperature of the system, p is the pressure of the system, R is the ideal gas constant, N_α is the number of moles of component α, x_α is the mole fraction of component α, and $\mu_\alpha^\circ(T, p)$ is the molar Gibbs free energy of pure component α (recall that for pure systems, the molar Gibbs free energy is equal to the chemical potential). The first term on the right-hand side of Eq. (4.1) represents the Gibbs free energy of the system if its components were unmixed. The second term represents the contribution due to the entropy of mixing.

In all calculations involving the ideal solution model, we assume that we know the molar Gibbs free energy of each of the pure species as a function of temperature and pressure. Mathematically, this means that know the form of the functions $\mu_\alpha^\circ(T, p)$. Physically, this means that we know everything about the thermodynamics of the pure species.

Once we know the Gibbs free energy of a system as a function of temperature, pressure, and composition, we know everything about its thermodynamics. For example, the total volume of the system $\underline{V}$ can be derived from the Gibbs free energy:

$$\begin{aligned}
\underline{V} &= \left(\frac{\partial \underline{G}}{\partial p} \right)_{T, N_\alpha} \\
&= \sum_\alpha N_\alpha \left(\frac{\partial \mu_\alpha^\circ}{\partial p} \right)_{T, N_\alpha} \\
&= \sum_\alpha N_\alpha V_\alpha^\circ \qquad (4.2)
\end{aligned}$$

where V_α° is the molar volume of pure species α, and we have used the relation $V_\alpha^\circ = (\partial \mu_\alpha^\circ / \partial p)$. The total volume is equal to the sum of the volumes of the pure components. Therefore, there is no change of volume on mixing for an ideal solution.

The total entropy S of the system is given by

$$
\begin{aligned}
\underline{S} &= -\left(\frac{\partial \underline{G}}{\partial T}\right)_{p,N_\alpha} \\
&= \sum_\alpha N_\alpha S_\alpha^\circ(T,p) - R \sum_\alpha N_\alpha \ln x_\alpha
\end{aligned}
\tag{4.3}
$$

where S_α° is the molar entropy of pure component α, and we have used the relation $S_\alpha^\circ = -(\partial \mu_\alpha^\circ / \partial T)$. Unlike the case for volume, the total entropy of the mixture is not the same as the sum of the entropies of the unmixed systems. In fact, due to the second term in Eq. (4.3), the entropy increases upon mixing.

The total enthalpy $\underline{H}$ of the system is given by

$$
\begin{aligned}
\underline{H} &= \underline{G} + T\underline{S} \\
&= \sum_\alpha N_\alpha \mu_\alpha^\circ(T,p) + RT \sum_\alpha N_\alpha \ln x_\alpha + T\left(\sum_\alpha N_\alpha S_\alpha^\circ(T,p) - R \sum_\alpha N_\alpha \ln x_\alpha\right) \\
&= \sum_\alpha N_\alpha H_\alpha^\circ(T,p)
\end{aligned}
\tag{4.4}
$$

where H_α° is the molar enthalpy of pure α, and we have used the relation $H_\alpha^\circ = \mu_\alpha^\circ + TS_\alpha^\circ$. In this case, we see that the total enthalpy of the system is the same as the sum of the enthalpies of the pure components. No heat is absorbed or released upon mixing an ideal solution.

The chemical potential of species α is given by

$$
\begin{aligned}
\mu_\alpha(T,p,x_2,x_3,\dots) &= \left(\frac{\partial \underline{G}}{\partial N_\alpha}\right)_{T,p,N_{\alpha'\neq\alpha}} \\
&= \mu_\alpha^\circ(T,p) + RT \ln x_\alpha
\end{aligned}
\tag{4.5}
$$

In an ideal solution, we see that the chemical potential of a species depends on its mole fraction and not directly on the composition of the other components in the system. Also, we see that mixing causes the chemical potential of each component to decrease.

4.2   Derivation of Raoult's law

Now we will use the ideal solution model to develop a mathematical description of vapor-liquid equilibrium in a multicomponent solution. We will make the assumption that we have a system that is separated into a coexisting vapor and liquid phase. The vapor phase will be assumed to behave like an ideal gas, while the liquid phase will be assumed to behave as an ideal solution.

The basic condition for equilibrium between phases is

$$\mu_\alpha^{\mathrm{v}}(T, p, y_2, y_3, \dots) = \mu_\alpha^{\mathrm{l}}(T, p, x_2, x_3, \dots) \tag{4.6}$$

where μ_α^{v} is the chemical potential of component α in the vapor phase, μ_α^{l} is the chemical potential of component α in the liquid phase, y_α is the mole fraction of component α in the vapor phase, and x_α is the mole fraction of component α in the liquid phase.

Since the liquid phase behaves as an ideal mixture, we have

$$
\begin{aligned}
\mu_\alpha^{\mathrm{l}}(T, p, x_2, x_3, \dots) &= \mu_\alpha^{\circ,\mathrm{l}}(T, p) + RT \ln x_\alpha \\
&= \mu_\alpha^{\circ,\mathrm{l}}(T, p_\alpha^{\mathrm{vap}}) + \int_{p_\alpha^{\mathrm{vap}}}^{p} dp' \frac{\partial \mu_\alpha^{\circ,\mathrm{l}}(T, p')}{\partial p} + RT \ln x_\alpha \\
&= \mu_\alpha^{\circ,\mathrm{l}}(T, p_\alpha^{\mathrm{vap}}) + \int_{p_\alpha^{\mathrm{vap}}}^{p} dp' V_\alpha^{\circ,\mathrm{l}}(T, p') + RT \ln x_\alpha
\end{aligned} \tag{4.7}
$$

where we have used the relation $(\partial \mu_\alpha^{\circ,\mathrm{l}}/\partial p) = V_\alpha^{\circ,\mathrm{l}}$, and $V_\alpha^{\circ,\mathrm{l}}$ is the molar volume of pure α in the liquid phase. If we assume that the volume of the liquid is nearly independent of pressure, then Eq. (4.7) becomes:

$$\mu_\alpha^{\mathrm{l}}(T, p, x_2, x_3, \dots) = \mu_\alpha^{\circ,\mathrm{l}}(T, p_\alpha^{\mathrm{vap}}) + V_\alpha^{\circ,\mathrm{l}}(T, p)(p - p_\alpha^{\mathrm{vap}}) + RT \ln x_\alpha \tag{4.8}$$

Since the vapor phase can be considered an ideal gas, we have

$$
\begin{aligned}
\mu_\alpha^{\mathrm{v}}(T, p, y_2, y_3, \dots) &= \mu_\alpha^{\circ,\mathrm{v}}(T, p) + RT \ln y_\alpha \\
&= \mu_\alpha^{\circ,\mathrm{v}}(T, p_\alpha^{\mathrm{vap}}) + \int_{p_\alpha^{\mathrm{vap}}}^{p} dp' \frac{\partial \mu_\alpha^{\circ,\mathrm{v}}(T, p')}{\partial p} + RT \ln y_\alpha \\
&= \mu_\alpha^{\circ,\mathrm{v}}(T, p_\alpha^{\mathrm{vap}}) + \int_{p_\alpha^{\mathrm{vap}}}^{p} dp' V_\alpha^{\circ,\mathrm{v}}(T, p') + RT \ln y_\alpha
\end{aligned} \tag{4.9}
$$

where $V_\alpha^{\circ,\mathrm{v}}$ is the molar volume of pure α in the vapor phase. For an ideal gas, we have $V_\alpha^{\circ,\mathrm{v}}(T, p) = RT/p$, and, therefore,

$$
\begin{aligned}
\mu_\alpha^{\mathrm{v}}(T, p, y_2, y_3, \dots) &= \mu_\alpha^{\circ,\mathrm{v}}(T, p_\alpha^{\mathrm{vap}}) + \int_{p_\alpha^{\mathrm{vap}}}^{p} dp' \frac{RT}{p'} + RT \ln y_\alpha \\
&= \mu_\alpha^{\circ,\mathrm{v}}(T, p_\alpha^{\mathrm{vap}}) + RT \ln \frac{p}{p_\alpha^{\mathrm{vap}}} + RT \ln y_\alpha
\end{aligned} \tag{4.10}
$$

Inserting Eqs. (4.8) and (4.10) into Eq. (4.6) yields

$$\mu_\alpha^{\circ,\mathrm{v}}(T, p_\alpha^{\mathrm{vap}}) + RT \ln \frac{p}{p_\alpha^{\mathrm{vap}}} + RT \ln y_\alpha = \mu_\alpha^{\circ,\mathrm{l}}(T, p_\alpha^{\mathrm{vap}}) + V_\alpha^{\circ,\mathrm{l}}(T, p)(p - p_\alpha^{\mathrm{vap}}) + RT \ln x_\alpha$$
$$\tag{4.11}$$

We note that at the vapor pressure of a pure system, the chemical potentials of the liquid and vapor

phases are equal. That is, $\mu_\alpha^{\circ,v}(T, p_\alpha^{vap}) = \mu_\alpha^{\circ,l}(T, p_\alpha^{vap})$. Substituting this relation into Eq. (4.11) gives

$$RT \ln \frac{p}{p_\alpha^{vap}} + RT \ln y_\alpha = V_\alpha^{\circ,l}(T, p)(p - p_\alpha^{vap}) + RT \ln x_\alpha$$

$$y_\alpha p = x_\alpha p_\alpha^{vap} \exp \left[\frac{V_\alpha^\circ(p - p_\alpha^{vap})}{RT} \right] \tag{4.12}$$

The exponential term on the right-hand side of Eq. (4.12) is known as the Poynting factor. For most systems at low to moderate pressures, the Poynting factor is almost equal to one. In the case of water at 25°C:

$$\frac{V_\alpha^\circ(p - p_\alpha^{vap})}{RT} \approx \frac{(10^{-6} \text{ m}^3/\text{g})(18.02 \text{ g/mol})(101325 - 3170) \text{ Pa}}{(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298.15 \text{ K})}$$

$$\approx 7.14 \times 10^{-4} \tag{4.13}$$

This leads to a Poynting factor of 1.000714, which is essentially equal to one. If we assume that the Poynting factor is close to one, we have Raoult's law:

$$y_\alpha p = x_\alpha p_\alpha^{vap}(T) \tag{4.14}$$

5 Partial molar properties

In Chapter 4, we examined the properties of ideal solutions. Many properties of an ideal solution do not change on mixing. For example, the volume of a mixture is equal to the sum of the volume of the original unmixed solutions. In this situation, it is straightforward to assign how much volume is occupied by each component in the system — it is simply the volume occupied by components in their unmixed state.

For a general system, however, the volume, as well as other properties, is not additive. That is, the volume of a mixture is not equal to the sum of the volumes of the individual pure components. In this situation, it is not clear how to assign how much volume is occupied of each species. One logical manner to do this is through the use of partial molar properties.

In this Chapter, we define partial molar properties and describe their application. We then discuss their relationship with the change of properties of a system on mixing. Finally, we examine the graphical representation of partial molar properties for binary mixtures.

5.1 Definition

In general for any extensive property $\underline{X}$ of a system, we define a partial molar property of component α as

$$\bar{X}_\alpha \equiv \left(\frac{\partial \underline{X}}{\partial N_\alpha} \right)_{T,p,N_{\alpha'\neq\alpha}}, \tag{5.1}$$

where N_α is the number of moles of species α, T is the temperature, and p is the pressure of the system. Physically, the partial molar quantity $\bar{X}_\alpha$ corresponds to the change of the property $\underline{X}$ with the addition of a small amount of component α, while holding constant the temperature, pressure, and number of moles of all other species. Note that partial molar properties are *intensive* and, therefore, do not depend on the system size.

Examples of partial molar properties include the partial molar enthalpy $\bar{H}_\alpha$, which is defined as

$$\bar{H}_\alpha \equiv \left(\frac{\partial \underline{H}}{\partial N_\alpha} \right)_{T,p,N_{\alpha'\neq\alpha}}, \tag{5.2}$$

and the partial molar volume $\bar{V}_\alpha$, which is defined as

$$\bar{V}_\alpha \equiv \left(\frac{\partial \underline{V}}{\partial N_\alpha} \right)_{T,p,N_{\alpha'\neq\alpha}}. \tag{5.3}$$

Note also that from the relation (see Eq. (3.4))

$$\mu_\alpha \equiv \left(\frac{\partial \underline{G}}{\partial N_\alpha} \right)_{T,p,N_{\alpha'\neq\alpha}}, \tag{5.4}$$

we see that the chemical potential is equal to the partial molar Gibbs free energy.

5.2   Relationship between total properties and partial molar properties

Any extensive property of a system can be written in terms of its partial molar quantities. Recall that an extensive property is a property that scales proportionally with the size of the system. If the system doubles in size, then value of the extensive property should double. If the size of the system increases by a factor t, then the value of the extensive property should increase by a factor t. For example, taking X to be the volume V, then we expect the total volume of the system $\underline{V}$ to increase by a factor t if the number of total moles in the system are increased by a factor t, holding the composition of the system fixed. This feature can be expressed mathematically as

$$tX(T, p, N_1, N_2, \dots) = \underline{X}(T, p, tN_1, tN_2, \dots) \tag{5.5}$$

Taking the derivative of both sides of the Eq. (5.5) with respect to t, while keeping all other variables constant, yields

$$
\begin{aligned}
\underline{X}(T, p, N_1, N_2, \dots) &= \sum_{\alpha} \left(\frac{\partial \underline{X}}{\partial t N_\alpha} \right)_{T, p, t N_{\alpha' \neq \alpha}} \left(\frac{\partial t N_\alpha}{\partial t} \right)_{N_\alpha} \\
&= \sum_{\alpha} \bar{X}_\alpha N_\alpha \\
\underline{X}(T, p, N_1, N_2, \dots) &= \sum_{\alpha} N_\alpha \bar{X}_\alpha
\end{aligned}
\tag{5.6}
$$

The value of any extensive property of a system is equal to the sum of the partial molar properties of each component multiplied by the amount of each component in the system. Therefore, we can "divide" the property of a mixture , such as the volume or enthalpy, between its individual components according to their partial molar properties.

One important example of this, which we will utilize later, is the Gibbs free energy G. In this case, the total Gibbs free energy $\underline{G}$ can be expressed in terms of the chemical potentials μ_α of each component (partial molar Gibbs free energy)

$$\underline{G}(T, p, N_1, N_2, \dots) = \sum_{\alpha} N_\alpha \mu_\alpha \tag{5.7}$$

By dividing both sides of Eq. (5.6) by N, the total number of moles in the system, we find that molar properties are similarly related to partial molar properties

$$X = \sum_{\alpha} x_\alpha \bar{X}_\alpha \tag{5.8}$$

where x_α is the mole fraction of component α.

The derivative of a molar property with respect to x_α can also be written in terms of partial molar properties. To demonstrate this, let us consider that an extensive property $\underline{X}$ is a function of T, p, mole numbers N_α. We can express its differential as

$$dX = \left(\frac{\partial \underline{X}}{\partial T}\right)_{p,N_\alpha} dT + \left(\frac{\partial \underline{X}}{\partial p}\right)_{T,N_\alpha} dp + \sum_\alpha \left(\frac{\partial \underline{X}}{\partial N_\alpha}\right)_{T,p,N_{\alpha' \neq \alpha}} dN_\alpha$$

$$= \left(\frac{\partial X}{\partial T}\right)_{p,N_\alpha} dT + \left(\frac{\partial X}{\partial p}\right)_{T,N_\alpha} dp + \sum_\alpha \bar{X}_\alpha dN_\alpha \tag{5.9}$$

Now, we take the derivative of $\underline{X}$ with respect to x_α, holding T, p, all other mole fractions (with the exception of x_1), and total number of moles N constant:

$$\left(\frac{\partial \underline{X}}{\partial x_\alpha}\right)_{T,p,x_{\alpha' \neq \alpha,1},N} = \sum_{\alpha'} \bar{X}_{\alpha'} \left(\frac{\partial N_{\alpha'}}{\partial x_\alpha}\right)_{T,p,x_{\alpha' \neq \alpha,1},N}$$

$$N \left(\frac{\partial X}{\partial x_\alpha}\right)_{T,p,x_{\alpha' \neq \alpha,1}} = N(\bar{X}_\alpha - \bar{X}_1)$$

$$\left(\frac{\partial X}{\partial x_\alpha}\right)_{T,p,x_{\alpha' \neq \alpha,1}} = \bar{X}_\alpha - \bar{X}_1 \tag{5.10}$$

where we have used the relations $N_\alpha = N x_\alpha$ and $x_1 = 1 - \sum_{\alpha \neq 1} x_\alpha$.

5.3   Properties changes on mixing

Often when pure components are mixed together to form a solution, the properties of the overall system change. For example, if we mix a quantity of pure liquid ethanol with pure liquid water, the volume of the final mixture has a slightly smaller volume than the sum of the volumes of the original pure liquid. This system has a negative volume change on mixing. If a solution of concentrated sulfuric acid is mixed with pure water, then a large amount of heat is released because the enthalpy of the mixture (at equilibrium) is lower than the sum of the enthalpy of the unmixed components. This system has a negative enthalpy of mixing.

To characterize this change, the property change on mixing $\Delta \underline{X}^{\mathrm{mix}}$ is defined as the difference between the property of the mixture and the properties of the pure components:

$$\Delta \underline{X}^{\mathrm{mix}} = \underline{X} - \sum_{\alpha} N_{\alpha} X_{\alpha}^{\circ}$$
$$= \sum_{\alpha} N_{\alpha} (\bar{X}_{\alpha} - X_{\alpha}^{\circ}) \tag{5.11}$$

where X_{α}° is the molar property of pure α. If the property increases on mixing, then $\Delta \underline{X}^{\mathrm{mix}}$ is positive; if the property decreases on mixing, then ΔX^{mix} is negative.

Similarly, the molar change of a property on mixing ΔX^{mix} is given by:

$$\Delta X^{\mathrm{mix}} = \sum_{\alpha} x_{\alpha} (\bar{X}_{\alpha} - X_{\alpha}^{\circ}) \tag{5.12}$$

5.4   Graphical representation for binary systems

The relations derived in this section provide us a means to easily extract the partial molar properties of a system from a graph of the corresponding molar property with repect to composition. A generic plot of the variation of a molar property of a binary mixture with composition is given by the solid line in Fig. 5.1. When $x_2 = 0$, the system consists only of component 1, and the value of the molar property should be equal to the molar property of pure component 1 X_1°. Likewise, when $x_2 = 1$, the system consists only of component 2, and the value of X should be equal to X_2°. The variation of a molar property of an unmixed system composed of pure 1 and pure 2 is given by the thick dashed line in Fig. 5.1.

The distance between the thick dashed line and the solid line represents the difference between a molar property of the mixture and that of the unmixed system. This difference is equal to ΔX^{mix}.

Now consider a line that is tangent to X (i.e., the solid line) at the composition $x_2 = x_2^{\circ}$. This is denoted by the thin dashed line in Fig. 5.1. The intercept of the tangent line at $x_2 = 0$ and $x_2 = 1$ are equal to $\bar{X}_1$ and $\bar{X}_2$, respectively; that is, the intercepts of the tangent line are equal to the partial molar properties of the system at a given composition. To demonstrate this, let's determine the equation for
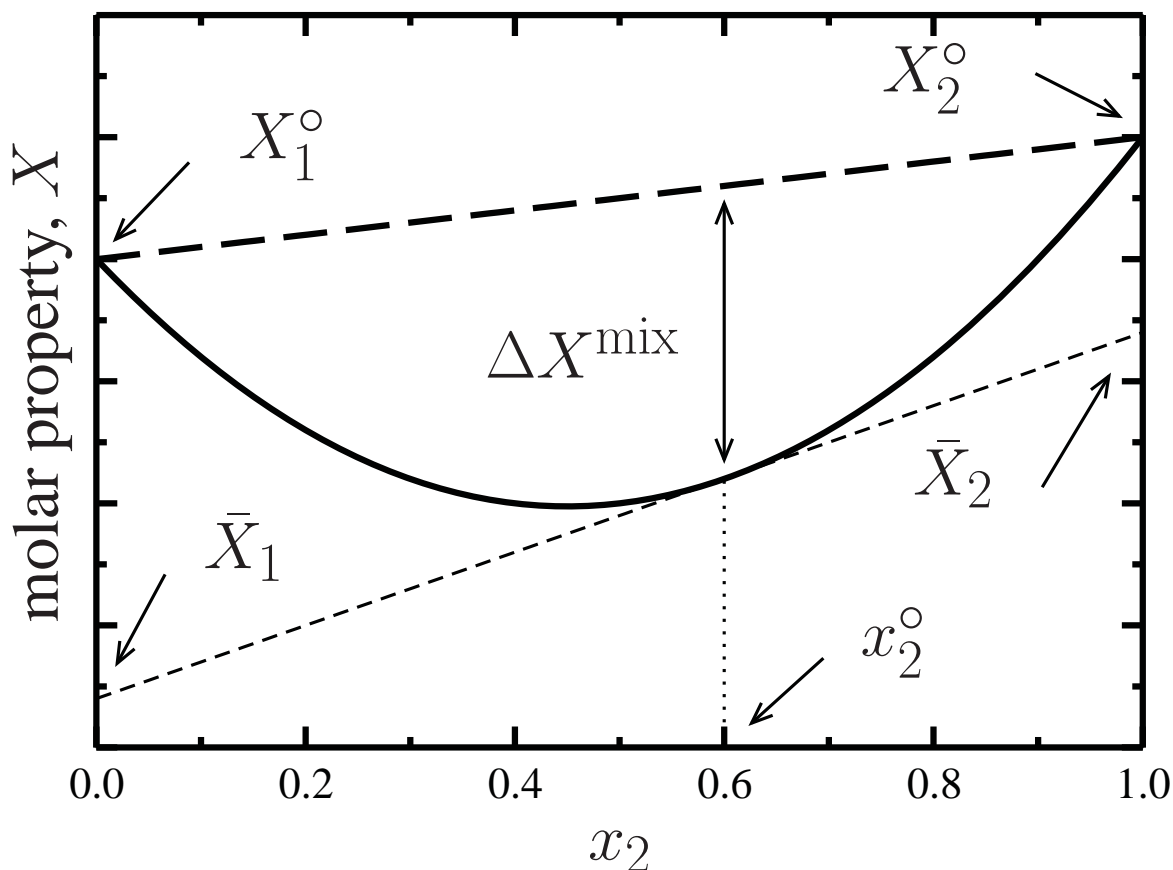
Figure 5.1: Variation of the molar property X (e.g., molar enthalpy or molar volume) of a binary mixture as a function of the mole fraction of component 2 (solid line). The dashed line is the tangent line to X at the composition $x_2 = x_2^\circ$.

the tangent line $y(x_2)$ at $x_2 = x_2^\circ$.

At $x_2 = x_2^\circ$, the tangent must have the value $X(x_2^\circ)$:

$$
\begin{aligned}
y(x_2^\circ) &= X(x_2^\circ) \\
&= x_1^\circ \bar{X}_1(x_2^\circ) + x_2^\circ \bar{X}_2(x_2^\circ) \\
&= \bar{X}_1(x_2^\circ) + x_2^\circ(\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)),
\end{aligned}
\tag{5.13}
$$

where $\bar{X}_\alpha(x_2^\circ)$ is the value of the partial molar property of component α at $x_2 = x_2^\circ$, and we have used Eq. (5.8). Note that the partial molar properties $\bar{X}_1$ and $\bar{X}_2$ are usually functions of composition (i.e., x_2). The slope of the tangent line can be obtained from Eq. (5.10)

$$
\left(\frac{\partial X(x_2^\circ)}{\partial x_2}\right)_{T,p} = \bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ).
\tag{5.14}
$$

Therefore, the slope of the tangent at composition $x_2 = x_2^\circ$ is equal to $\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)$.

Knowledge of both the value of the tangent line at a point and its slope allows us to write the equation

for the tangent line:

$$
\begin{aligned}
y(x_2) &= y(x_2^\circ) + [\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)](x_2 - x_2^\circ) \\
&= \bar{X}_1(x_2^\circ) + x_2^\circ(\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)) + [\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)](x_2 - x_2^\circ) \\
&= \bar{X}_1(x_2^\circ) + [\bar{X}_2(x_2^\circ) - \bar{X}_1(x_2^\circ)]x_2
\end{aligned} \tag{5.15}
$$

From Eq. (5.15), we see that when $x_2 = 0$, the tangent line has a value equal to $\bar{X}_1(x_2^\circ)$, and when $x_2 = 1$, it has a value equal to $\bar{X}_2(x_2^\circ)$. This is shown graphically by the thin dashed line in Fig. 5.1.

For an ideal solution, the molar volume V of a mixture satisfies

$$
V = x_1 V_1^\circ + x_2 V_2^\circ \tag{5.16}
$$

where V_1° and V_2° is the molar volume of pure species 1 and 2, respectively. Therefore, $\Delta V^{\mathrm{mix}} = 0$ for an ideal solution. Similarly, the molar enthalpy H is given by

$$
H = x_1 H_1^\circ + x_2 H_2^\circ \tag{5.17}
$$

where H_1° and H_2° is the molar volume of pure species 1 and 2, respectively. Therefore, $\Delta H^{\mathrm{mix}} = 0$ for an ideal solution.

Equations (5.16) and (5.17) correspond to a straight line connecting the molar properties of the pure components (e.g., the thick dashed line in Fig. 5.1). In this case, we see that the partial molar volumes and partial molar enthalpies of each species are equal to the respective molar quantities in the pure state. We expect ideal behavior when the fluids that are mixed consist of similar molecules.

Most solutions do not exhibit ideal behavior, and the actual curve corresponding to the variation of the molar volume or enthalpy of the mixture deviates from a straight line (e.g., the solid line in Fig. 5.1). When the curve for the molar volume lies above the ideal mixture line, the system expands upon mixing; when the curve lies below the line, the system contracts. In the case of the molar enthalpy, a curve that lies above the ideal mixture line corresponds to the system that absorbs heat (e.g., mixing lead bromide and water); a curve that lies below the line corresponds to the system releasing heat (e.g., mixing sulfuric acid and water). This non-ideal mixing in the case of the molar enthalpy is the principle used in cold packs and heat packs. We will develop mathematical models to describe non-ideal mixtures. We use partial molar properties in more detail later.

6   Nonideal solutions

In Chapter 4, we developed the ideal solution model, which enables the estimation of the properties of mixtures from knowledge of the thermodynamic behavior of the pure species. While the ideal solution model does provide accurate predictions for mixtures of relatively similar substances, many systems do exhibit substantial deviations from the ideal solution model.

In this chapter, we present methods for mathematically describing the properties of non-ideal solutions — mixtures that deviate from the ideal solution model.

6.1   Deviations from Raoult's law and the activity coefficient

As discussed in Chapter 4, the vapor-liquid equilibrium between an ideal gas and an ideal liquid solution is governed by Raoult's law:

$$y_\alpha p = x_\alpha p_\alpha^{\mathrm{vap}}(T),$$

where y_α is the mole fraction of component α in the vapor phase, x_α is the mole fraction in the liquid phase, p is the pressure of the system, and $p_\alpha^{\mathrm{vap}}(T)$ is the vapor pressure of pure component α at the system temperature T.

Raoult's law states that the partial pressure of a species in the vapor phase is proportional to the mole fraction of the species in the liquid phase. The constant of proportionality is the vapor pressure of the pure species. Mathematically, this expressed as

$$p_\alpha = x_\alpha p_\alpha^{\mathrm{vap}}(T). \tag{6.1}$$

This equation is plotted as the solid line in Fig. 6.1.

For most systems, Raoult's law is not obeyed. If we actually measure the partial pressure of a given component above a mixture as a function of its mole fraction, it will most often deviate from a straight line. For example, see the dashed and dotted lines in Fig. 6.1. In order to characterize the deviations from Raoult's law, we define the activity coefficient for component α, which is denoted by γ_α, as:

$$\gamma_\alpha = \frac{p_\alpha}{x_\alpha p_\alpha^{\mathrm{vap}}(T)}. \tag{6.2}$$

Note that in general, the activity coefficient depends on the temperature, pressure, and composition of the system. If the system obeys Raoult's law, $\gamma_\alpha = 1$. When $\gamma_\alpha > 1$, the system is said to exhibit positive deviation from Raoult's law, and when $\gamma_\alpha < 1$, the system is said to exhibit negative deviation from Raoult's law.

Although Raoult's law is not a good approximation for many systems, there are two points at which
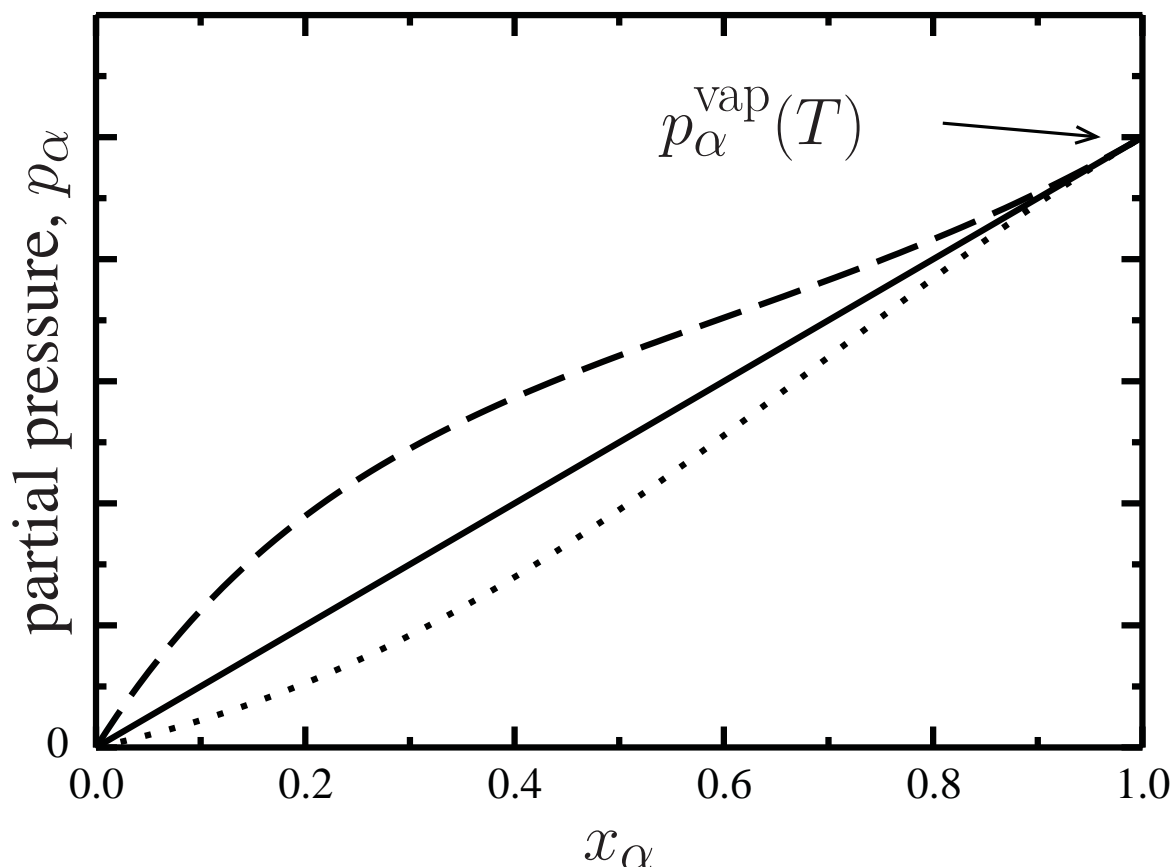
Figure 6.1: Variation of the partial pressure of component α in the vapor phase with its mole fraction in the coexisting liquid phase. The solid line is for a component that obeys Raoult's law, the dashed line is for a component that shows positive deviations from Raoult's law, and the dotted line is for a component that shows negative deviations from Raoult's law.

it is exact: (i) at $x_\alpha = 0$, where the partial pressure of α must equal zero, and (ii) at $x_\alpha = 1$, where the partial pressure of α must be equal to $p_\alpha^{\mathrm{vap}}(T)$. From condition (ii), combined with Eq. (6.2), the activity coefficients must obey: $\gamma_\alpha \rightarrow 1$ as $x_\alpha \rightarrow 1$.

6.2 Modified Raoult's law

As mentioned previously, many systems show significant deviations from Raoult's law. There are even some solutions, such as azeotropic mixtures, that are not even *qualitatively* described by Raoult's law. By rearranging the definition of the activity coefficient γ_α (see Eq. (6.2)), Raoult's law can be generalized to apply to a wider class of mixtures:

$$y_\alpha p = x_\alpha \gamma_\alpha p_\alpha^{\mathrm{vap}}(T). \tag{6.3}$$

This equation is known as the modified Raoult's law.

Raoult's law was derived under the assumptions that the vapor phase behaved as an ideal gas and

that the liquid phase behaved as an ideal solution. In this section, we will relax the assumption that the liquid behaves as an ideal solution to derive the modified Raoult's law, given in Eq. (6.3). If we re-examine the derivation of Raoult's law, we find that we can arrive at the modified Raoult's law if the chemical potential of the liquid phase can be written as:

$$\mu_\alpha^l(T, p, x_2, x_3, \dots) = \mu_\alpha^{\circ,l}(T, p) + RT \ln x_\alpha \gamma_\alpha \tag{6.4}$$

where $\mu_\alpha^{\circ,l}(T, p)$ is the chemical potential of pure component α. Note that we can divide the chemical potential into an ideal contribution μ_α^{id}, given by the ideal solution model, and a non-ideal contribution (or excess) μ_α^{ex}, which is directly related to the activity coefficient:

$$\mu_\alpha(T, p, x_2, x_3, \dots) = \mu_\alpha^{\mathrm{id}}(T, p, x_2, x_3, \dots) + \mu_\alpha^{\mathrm{ex}}(T, p, x_2, x_3, \dots), \tag{6.5}$$

where

$$\mu_\alpha^{\mathrm{id}}(T, p, x_2, x_3, \dots) = \mu_\alpha^{\circ,l}(T, p) + RT \ln x_\alpha, \tag{6.6}$$

and

$$\mu_\alpha^{\mathrm{ex}}(T, p, x_2, x_3, \dots) = RT \ln \gamma_\alpha(T, p, x_2, x_3, \dots). \tag{6.7}$$

In general, an excess property X^{ex} is defined as the deviation of a property from its ideal solution value:

$$X^{\mathrm{ex}}(T, p, x_2, x_3, \dots) = X(T, p, x_2, x_3, \dots) - X^{\mathrm{id}}(T, p, x_2, x_3, \dots) \tag{6.8}$$

Substituting the expression for the chemical potential given in Eq. (6.4) into Eq. (5.7), we find that the Gibbs free energy of a non-ideal solution can be written as:

$$
\begin{aligned}
G &= \sum_\alpha N_\alpha \mu_\alpha \\
&= \sum_\alpha N_\alpha (\mu_\alpha^\circ + RT \ln x_\alpha \gamma_\alpha) \\
&= \sum_\alpha N_\alpha (\mu_\alpha^\circ + RT \ln x_\alpha) + RT \sum_\alpha N_\alpha \ln \gamma_\alpha \\
G &= G^{\mathrm{id}} + G^{\mathrm{ex}}
\end{aligned}
\tag{6.9}
$$

where G^{id} is the Gibbs free energy of an ideal solution, defined as

$$G^{\mathrm{id}} = \sum_\alpha N_\alpha \mu_\alpha^\circ + RT \sum_\alpha N_\alpha \ln x_\alpha \tag{6.10}$$

and G^{ex} is the excess Gibbs free energy, which is given by

$$G^{\mathrm{ex}} = RT \sum_\alpha N_\alpha \ln \gamma_\alpha \tag{6.11}$$

While the theoretical treatment we have presented for non-ideal solutions are all formally exact, they are of no practical use until we have some kind of model for the variation of the activity coefficients with the system composition, temperature, and pressure. In the next section, we present various models that can be employed to describe the activity coefficients.

6.3   Empirical activity coefficient models

In order to perform quantitative thermodynamic calculations using the Gibbs free energy for a non-ideal solution (see Eqs. (6.9)–(6.11)), we need explicit expressions for the activity coefficients. A few empirical expressions that are typically employed are:

- two-suffix Margules

$$\ln \gamma_1 = A x_2^2$$
$$\ln \gamma_2 = A x_1^2$$
$$\frac{G^{\text{ex}}}{RT} = A x_1 x_2$$

- three-suffix Margules

$$\ln \gamma_1 = [(A + 3B) - 4B x_2] x_2^2$$
$$\ln \gamma_2 = [(A - 3B) + 4B x_1] x_1^2$$
$$\frac{G^{\text{ex}}}{RT} = [A + B(x_1 - x_2)] x_1 x_2$$

- four-suffix Margules

$$\ln \gamma_1 = [(A + 3B + 5C) - 4(B + 4C) x_2 + 12C x_2^2] x_2^2$$
$$\ln \gamma_2 = [(A - 3B + 5C) + 4(B - 4C) x_1 + 12C x_1^2] x_1^2$$
$$\frac{G^{\text{ex}}}{RT} = [A + B(x_1 - x_2) + C(x_1 - x_2)^2] x_1 x_2$$

- van Laar model

$$\ln \gamma_1 = A \left(1 + \frac{A x_1}{B x_2} \right)^{-2}$$
$$\ln \gamma_2 = B \left(1 + \frac{B x_2}{A x_1} \right)^{-2}$$
$$\frac{G^{\text{ex}}}{RT} = \frac{A B x_1 x_2}{A x_1 + B x_2}$$

The parameters A, B, and C in the above models are, in general, functions of temperature and pressure, but are independent of composition. These parameters are typically obtained by fitting experimental data. Given the parameters of these activity coefficient models, we can predict all the thermodynamic properties of the system.

6.4   The Gibbs-Duhem equation

Not all the chemical potentials (and therefore, the activity coefficients) in a mixture are independent of each other. They are all related to one another through the Gibbs-Duhem equation. To derive this equation, we start with the fundamental equation of thermodynamics for the Gibbs free energy, which can be written as

$$dG = -S dT + V dp + \sum_\alpha \mu_\alpha dN_\alpha \tag{6.12}$$

By substituting Eq. (5.7) into Eq. (6.12), we find

$$d\left(\sum_\alpha N_\alpha \mu_\alpha\right) = -S dT + V dp + \sum_\alpha \mu_\alpha dN_\alpha$$

$$\sum_\alpha N_\alpha d\mu_\alpha + \sum_\alpha \mu_\alpha dN_\alpha = -S dT + V dp + \sum_\alpha \mu_\alpha dN_\alpha$$

$$\sum_\alpha N_\alpha d\mu_\alpha = -S dT + V dp \tag{6.13}$$

This relation is known as the Gibbs-Duhem equation. Dividing both sides of the equation by the total number of moles in the system, we find that the Gibbs-Duhem equation can also be written as

$$\sum_\alpha x_\alpha d\mu_\alpha = -S dT + V dp \tag{6.14}$$

The Gibbs-Duhem equation provides a relation between the chemical potentials of each of the chemical species in a given phase. At constant temperature and pressure, this relation simplifies to

$$\sum_\alpha x_\alpha d\mu_\alpha = 0 \tag{6.15}$$

The chemical potential can be written in terms of the activity coefficient (see Eq (6.4)). Subsituting this expression into the Gibbs-Duhem equation, at constant temperature and pressure, we find

$$\sum_\alpha x_\alpha d(\mu_\alpha^\circ + RT \ln x_\alpha \gamma_\alpha) = 0$$

$$RT \sum_\alpha x_\alpha d \ln x_\alpha \gamma_\alpha = 0$$

$$RT \sum_\alpha x_\alpha (d \ln x_\alpha + d \ln \gamma_\alpha) = 0$$

$$\sum_\alpha x_\alpha \left(\frac{dx_\alpha}{x_\alpha} + d \ln \gamma_\alpha\right) = 0$$

$$\sum_\alpha (dx_\alpha + x_\alpha d \ln \gamma_\alpha) = 0$$

$$\sum_\alpha x_\alpha d \ln \gamma_\alpha = 0 \tag{6.16}$$

where in the last line we have used the relationship $\sum_\alpha dx_\alpha = 0$. This equation provides a relationship between the activity coefficients of all of the components in a system. Therefore, not all the activity coefficients in a system are independent. If we know the activity coefficients for all but one of the components in a mixture, we can determine the unknown activity coefficient by using the Gibbs-Duhem equation. We demonstrate this for a binary system.

Suppose we know the activity coefficient of component 1 γ_1 as a function of composition. Then, we can determine the activity coefficient of component 2 γ_2:

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$

$$x_1 \frac{d\ln\gamma_1}{dx_2} + x_2 \frac{d\ln\gamma_2}{dx_2} = 0$$

$$\frac{d\ln\gamma_2}{dx_2} = -\frac{x_1}{x_2}\frac{d\ln\gamma_1}{dx_2}$$

$$\int_1^{x_2} dx_2 \frac{d\ln\gamma_2}{dx_2} = -\int_1^{x_2} dx_2 \frac{x_1}{x_2}\frac{d\ln\gamma_1}{dx_2}$$

$$\ln\gamma_2(x_2) - \ln\gamma_2(x_2 = 1) = -\int_1^{x_2} dx_2 \frac{1-x_2}{x_2}\frac{d\ln\gamma_1}{dx_2}$$

$$\ln\gamma_2(x_2) = -\int_1^{x_2} dx_2 \frac{1-x_2}{x_2}\frac{d\ln\gamma_1}{dx_2} \qquad (6.17)$$

where we have used the fact that $\gamma_2 \to 1$ as $x_2 \to 1$. Given the $\gamma_1(x_2)$, Eq. (6.17) can be used to determine $\gamma_2(x_2)$.

For example, if we are given $\ln\gamma_1(x_2) = Ax_2^2$ (the two-suffix Margules model), then

$$\ln\gamma_2(x_2) = -\int_1^{x_2} dx_2 \frac{1-x_2}{x_2}\frac{d}{dx_2}(Ax_2^2)$$

$$= -\int_1^{x_2} dx_2 \frac{1-x_2}{x_2}(2Ax_2)$$

$$= -2A\int_1^{x_2} dx_2(1-x_2)$$

$$= -2A\left[x_2 - \frac{x_2^2}{2}\right]_1^{x_2}$$

$$= -2A\left[(x_2-1) - \frac{(x_2^2-1)}{2}\right]$$

$$= A(1-x_2)^2 \qquad (6.18)$$

6.5 Azeotropic systems

One of the shortcomings of Raoult's law is that it cannot describe the behavior of azeotropic systems. The modified Raoult's law, however, can describe azeotropic systems as we will demonstrate below.

For a binary mixture, the modified Raoult's law can be written as

$$y_1 p = \gamma_1 x_1 p_1^{\text{vap}}$$
$$y_2 p = \gamma_2 x_2 p_2^{\text{vap}} \tag{6.19}$$

At the azeotrope, the vapor composition is the same as the liquid composition:

$$y_\alpha^{\text{azeo}} = x_\alpha^{\text{azeo}} \tag{6.20}$$

At this point, we can cancel the compositions from both sides of Eq. (6.19), which gives

$$p = \gamma_1 p_1^{\text{vap}}(T)$$
$$p = \gamma_2 p_2^{\text{vap}}(T) \tag{6.21}$$

These two equations can be combined into a single equation that can be used to solve for the azeotropic composition x_2^{azeo}:

$$\gamma_1 p_1^{\text{vap}}(T) = \gamma_2 p_2^{\text{vap}}(T)$$
$$\frac{\gamma_1}{\gamma_2} = \frac{p_2^{\text{vap}}(T)}{p_1^{\text{vap}}(T)}$$
$$\ln \frac{\gamma_1}{\gamma_2} = \ln \frac{p_2^{\text{vap}}(T)}{p_1^{\text{vap}}(T)} \tag{6.22}$$

Given an activity coefficient model, we can use Eq. (6.22) to determine the azeotropic composition. For example, if we use a two-suffix Margules model, where

$$\ln \gamma_1 = A x_2^2$$
$$\ln \gamma_2 = A x_1^2$$

we have

$$
\begin{aligned}
\ln \frac{\gamma_1}{\gamma_2} &= A x_2^2 - A x_1^2 \\
&= A(x_2 + x_1)(x_2 - x_1) \\
&= A(x_2 - x_1) \\
&= A(2x_2 - 1)
\end{aligned}
\tag{6.23}
$$

By substituting Eq. (6.23) into Eq. (6.22), we find

$$
A(2x_2^{\mathrm{azeo}} - 1) = \ln \frac{p_2^{\mathrm{vap}}(T)}{p_1^{\mathrm{vap}}(T)}
$$
$$
x_2^{\mathrm{azeo}} = \frac{1}{2}\left[1 + \frac{1}{A} \ln \frac{p_2^{\mathrm{vap}}(T)}{p_1^{\mathrm{vap}}(T)}\right]
\tag{6.24}
$$

Therefore, if we are given the parameter A, we can determine the azeotropic composition.

On the other hand, if we are given the azeotropic composition, then we can fit the parameter A. Rearranging Eq. (6.24) yields

$$
A = \frac{1}{2x_2^{\mathrm{azeo}} - 1} \ln \frac{p_2^{\mathrm{vap}}(T)}{p_1^{\mathrm{vap}}(T)}
\tag{6.25}
$$

We can also determine what values of the parameter A will lead to an azeotropic system. By noting the restriction $0 \le x_2^{\mathrm{azeo}} \le 1$, a system will have an azeotrope if the A parameter satisfies:

$$
-\ln \frac{p_2^{\mathrm{vap}}(T)}{p_1^{\mathrm{vap}}(T)} < A < \ln \frac{p_2^{\mathrm{vap}}(T)}{p_1^{\mathrm{vap}}(T)}
\tag{6.26}
$$

where we have made the assumption that $p_2^{\mathrm{vap}}(T) > p_1^{\mathrm{vap}}(T)$.

7 Stability

In this Chapter, we consider the mathematical and geometric properties of the free energy of a system which govern its thermodynamic stability. In regions where the free energy satisfies the conditions for stability, the system remains in a single phase; however, if these conditions are violated, then the system can phase separate into two or more coexisting phases. We then discuss how the conditions for stability on the free energy leads to conditions on the value of the parameters in activity coefficient models. Finally, we derive the mathematical equations for the coexistence between two liquid phases.

7.1 Introduction

A system at constant temperature, pressure, and mole numbers tries to decrease its Gibbs free energy. At equilibrium, the Gibbs free energy of the system is minimized.

In Fig. 7.1, the solid line represents the variation of the molar Gibbs free energy of a mixture as a function of composition. The thick dashed line represents the variation of the molar Gibbs free energy of a *completely unmixed* system, with one phase consisting of pure component 1 and the other phase consisting of pure component 2. The distance between the solid line and the dashed line denotes the Gibbs free energy change on mixing. Because the solid line always lies beneath the dashed line, the system possesses a lower Gibbs free energy when mixed than when separated and, therefore, prefers to be mixed. If the opposite were true, then the system would prefer to be phase separated.

The solid line in Fig. 7.2 represents the molar Gibbs free energy of mixture that becomes unstable. The thick dashed line, as in Fig. 7.2, represents the molar Gibbs free energy of a completely unmixed system. The solid line always lies beneath the dashed line, and so the mixture will not phase separate to form two completely demixed phases. However, consider the line joining the points A and B, which lies beneath the solid line. The line $\overline{AB}$ represents the molar Gibbs free energy of a system that is separated into two phases, one with composition x_2' and the other with composition x_2''. This *partially* demixed system has a lower Gibbs free energy than the fully mixed system (solid line), and, therefore, a mixture which is at a composition between x_2' and x_2'' will spontaneously demix to form these two, coexisting phases. Another point to note, is that because the tangent line at x_2' and x_2'' coincide, the chemical potentials in each of the two corresponding phases are identical, which is the criterion for phase equilibrium.

In general, a mixture is unstable when

$$\frac{\partial^2 G}{\partial x_2^2} < 0 \tag{7.1}$$

Graphically, this means that the Gibbs free energy is concave down with respect to x_2 (e.g., see the solid line in Fig. 7.2 between x_2' and x_2''). In this situation, any line that connects two points on the curve will lie below the curve, and thus the mixture will want to phase separate.
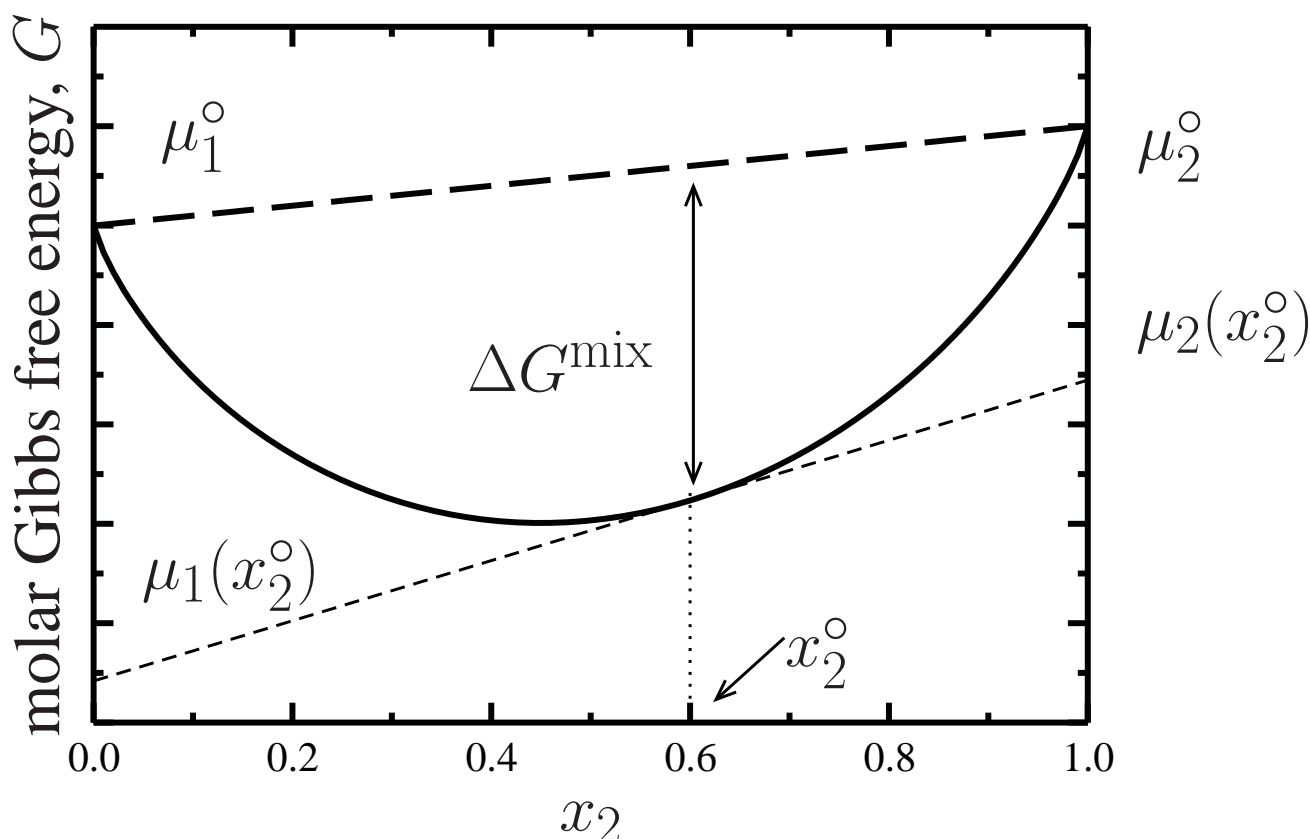
Figure 7.1: The molar Gibbs free energy G of a stable binary mixture as a function of the mole fraction of component 2 (solid line). The dashed line is the tangent line to G at the composition $x_2 = x_2^\circ$.

An ideal solution is never unstable and will always remain as a single phase mixture. To prove this, we need to demonstrate that $\partial^2 G^{\text{id}}/\partial x_2^2$ is always positive. For a binary mixture, the molar Gibbs free energy of an ideal solution is given by

$$
\begin{aligned}
G^{\text{id}} &= x_1 \mu_1^\circ + x_2 \mu_2^\circ + RT x_1 \ln x_1 + RT x_2 \ln x_2 \\
&= (1 - x_2)\mu_1^\circ + x_2 \mu_2^\circ + RT(1 - x_2)\ln(1 - x_2) + RT x_2 \ln x_2
\end{aligned}
\tag{7.2}
$$

Taking the derivative of this, we find

$$
\begin{aligned}
\frac{\partial G^{\text{id}}}{\partial x_2} &= \mu_2^\circ - \mu_1^\circ - RT \ln(1 - x_2) + RT \ln x_2 \\
\frac{\partial^2 G^{\text{id}}}{\partial x_2^2} &= \frac{RT}{1 - x_2} + \frac{RT}{x_2} \\
&= \frac{RT}{x_2(1 - x_2)}
\end{aligned}
\tag{7.3}
$$

For all physical values of x_2 (i.e., $0 \le x_2 \le 1$), we see that $\partial^2 G^{\text{id}}/\partial x_2 > 0$. Therefore, the ideal solution model is always stable.
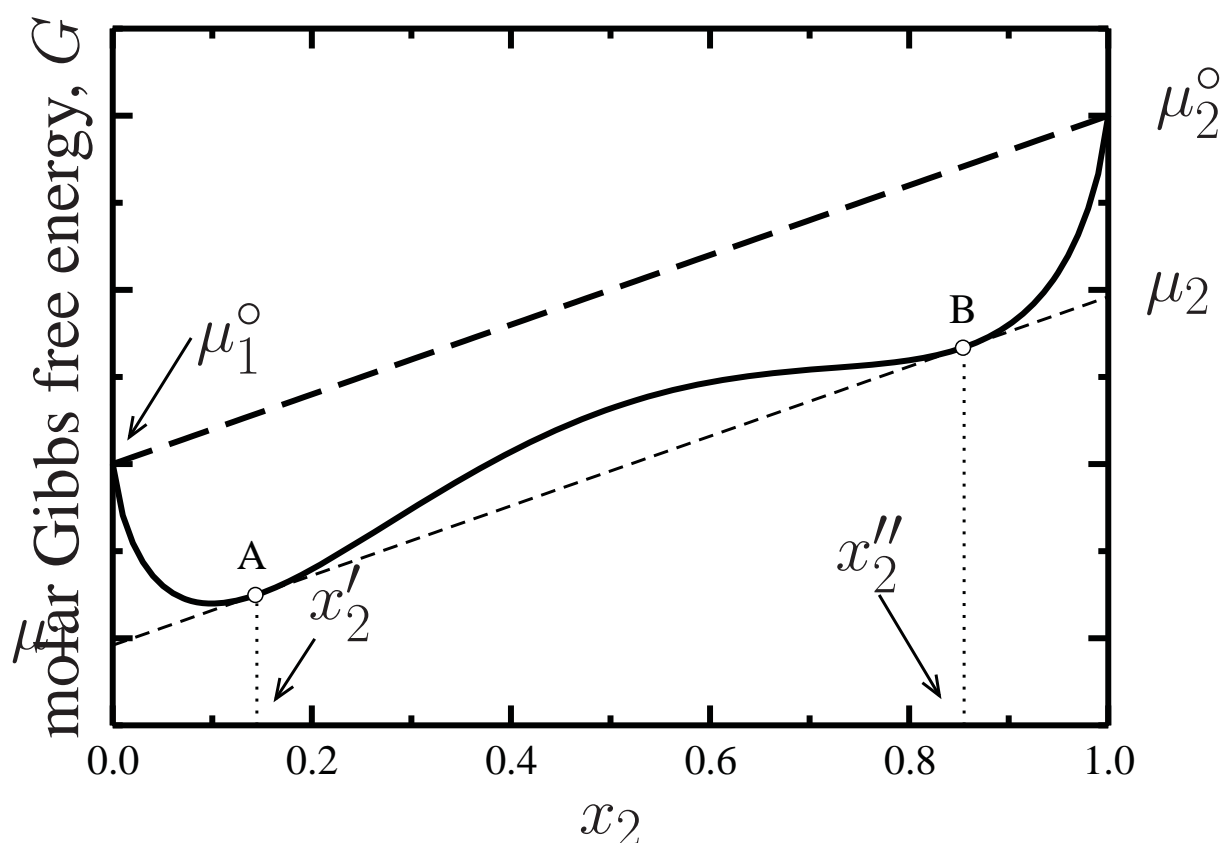
Figure 7.2: Variation of the molar Gibbs free energy G of a binary mixture as a function of the mole fraction of component 2 (solid line). The long-dashed line is the Gibbs free energy for a system of two unmixed pure compounds. The short-dashed line is the tangent line to G at the coexistence compositions $x_2 = x_2'$ and $x_2 = x_2''$.

To model a mixture that phase separates into two coexisting liquid phase, we need to add non-ideal terms (activity coefficients) to the ideal solution model. As an example of this, we examine the stability of the two-suffix Margules model, which has a molar Gibbs free energy of

$$G = x_1\mu_1^\circ + x_2\mu_2^\circ + RTx_1\ln x_1\gamma_1 + RTx_2\ln x_2\gamma_2$$
$$= (1-x_2)\mu_1^\circ + x_2\mu_2^\circ + RT(1-x_2)\ln(1-x_2) + RTx_2\ln x_2 + RTA(1-x_2)x_2 \qquad (7.4)$$

The derivatives of the molar Gibbs free energy are:

$$\frac{\partial G}{\partial x_2} = -\mu_1^\circ + \mu_2^\circ - RT\ln(1-x_2) + RT\ln x_2 + RTA(1-2x_2)$$
$$\frac{\partial^2 G}{\partial x_2^2} = \frac{RT}{1-x_2} + \frac{RT}{x_2} - 2RTA$$
$$= \frac{RT}{x_2(1-x_2)} - 2RTA \qquad (7.5)$$

The system is unstable when

$$A > \frac{1}{2x_2(1 - x_2)} \tag{7.6}$$

The right-hand side of Eq. (7.6) is plotted in Fig. 7.3. In Fig. 7.3, the x-axis represents the mole fraction of component 2, and the y-axis represents the value of the parameter A in the Margules model. The shaded region denotes the area where the inequality given in Eq. (7.6) is true, and therefore, the system will undergo liquid-liquid phase separation. Outside this region, the mixture is stable.
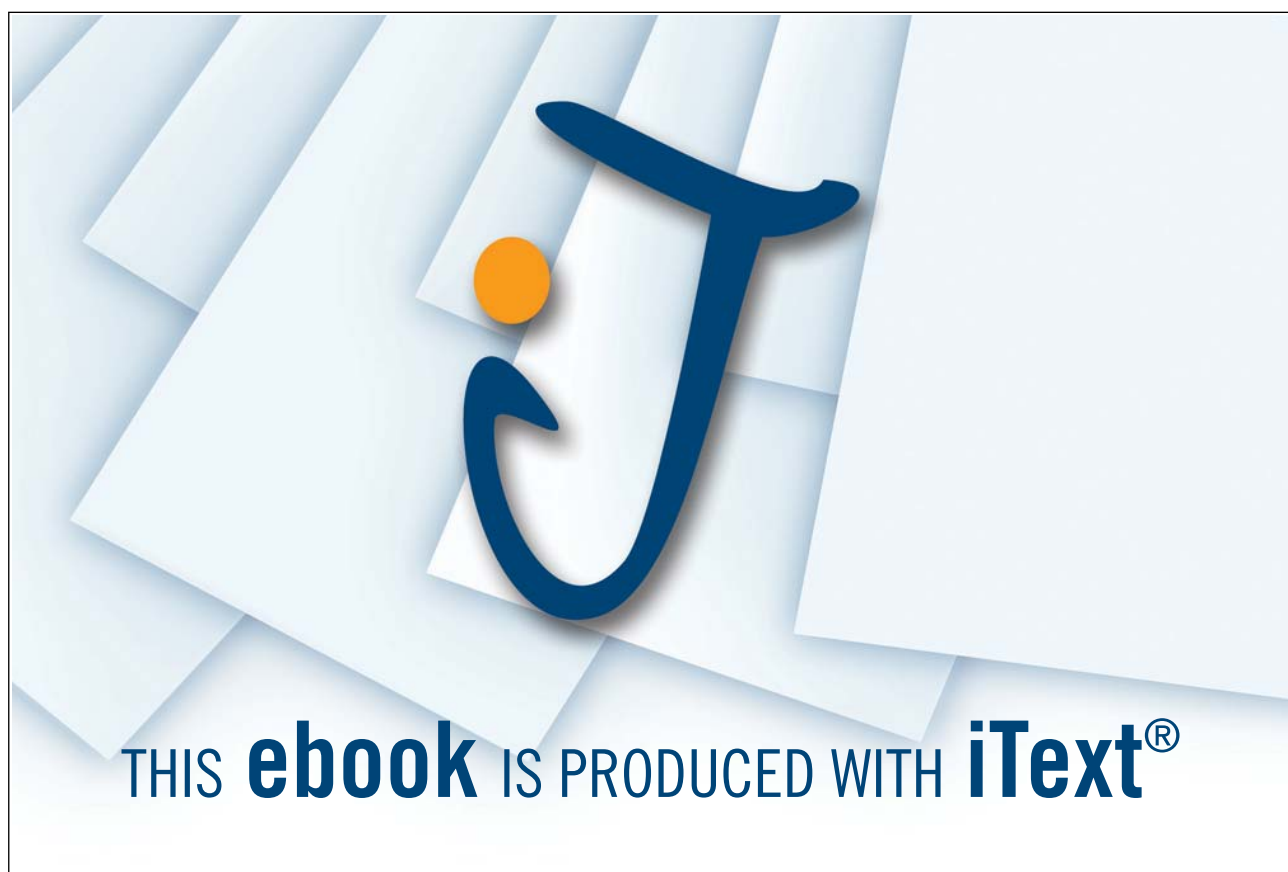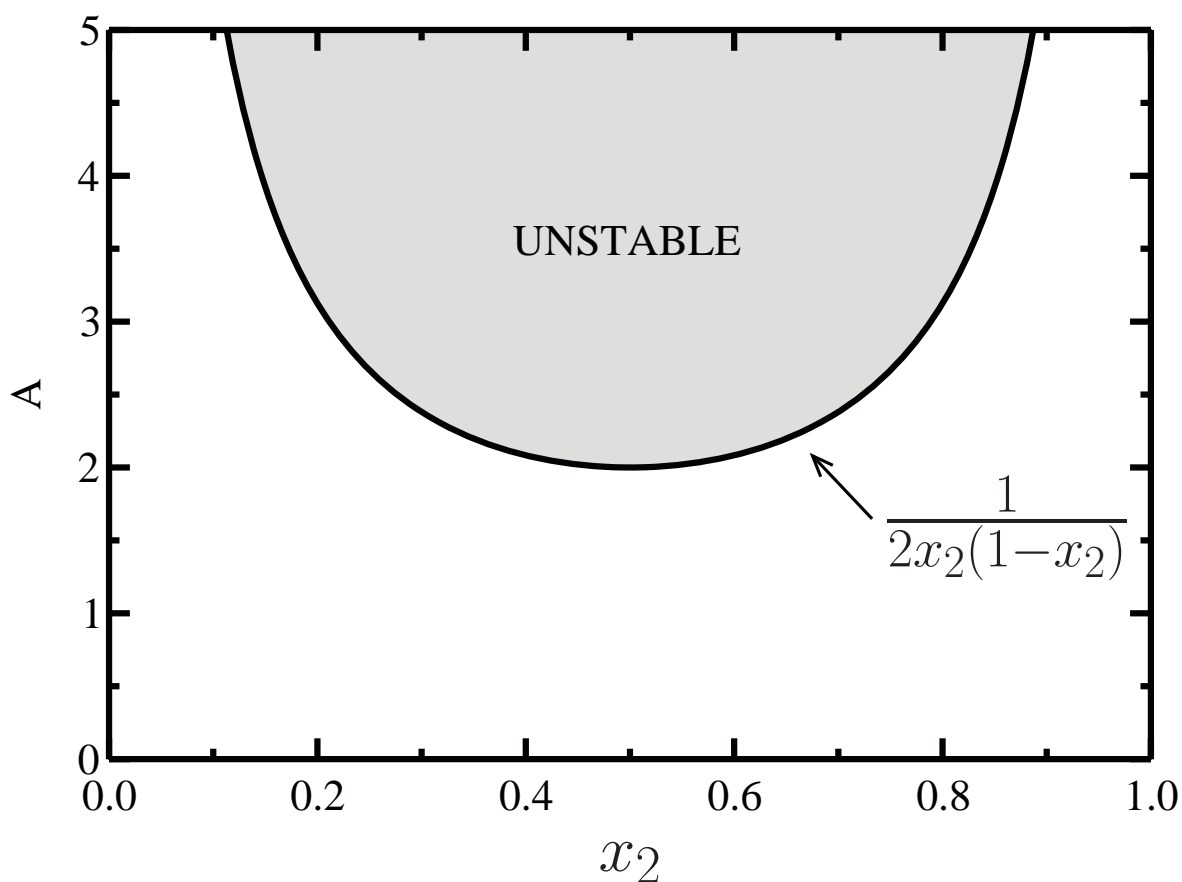
Figure 7.3: Stability diagram for the two-suffix Margules equation. The shaded region represents states where the Margules model predicts that the system is unstable.

7.2 Liquid-liquid equilibrium

When a liquid mixture becomes unstable, it separates into two coexisting liquid phases. We label one of the phases with a $'$ and the other phase with a $''$. The criterion for phase equilibrium is

$$\mu'_\alpha = \mu''_\alpha$$
$$\mu^\circ_\alpha + RT \ln x'_\alpha \gamma'_\alpha = \mu^\circ_\alpha + RT \ln x''_\alpha \gamma''_\alpha$$
$$RT \ln x'_\alpha \gamma'_\alpha = RT \ln x''_\alpha \gamma''_\alpha$$
$$x'_\alpha \gamma'_\alpha = x''_\alpha \gamma''_\alpha \tag{7.7}$$

Given a model for the activity coefficients, Eq. (7.7) yields a set of constraints that can be solved for the compositions of each liquid phase.

Conversely, given the composition of the coexisting liquid phases, Eq. (7.7) can also be used to fit an activity coefficient model. For example, using the two-suffix Margules model for a binary mixture,

we can determine the parameter A

$$\ln \frac{\gamma_1'}{\gamma_1''} = \ln \frac{x_1''}{x_1'}$$

$$Ax_2'^2 - Ax_2''^2 = \ln \frac{x_1''}{x_1'}$$

$$A = \frac{1}{x_2'^2 - x_2''^2} \ln \frac{x_1''}{x_1'} \tag{7.8}$$

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8   Solid-liquid equilibrium

8.1   Introduction

At atmospheric pressure, water will freeze at $0°$C. If a solute is added to water, then the mixture will freeze at a lower temperature. This is known as freezing point depression and occurs with any general mixture. Using a model for the activity coefficients, we can quantitatively predict the magnitude of this effect.

8.2   Phase behavior

To demonstrate the general freezing behavior of a binary mixture, we present the solid-liquid phase diagram for systems of ethanol and water at 1 atm in Fig. 8.1. The solid line with the filled symbols is the freezing curve of water in the mixture. Above the curve the solution is completely liquid; below the curve, it is a liquid mixture coexists with solid water (i.e., ice). At this pressure, pure water freezes at 273.15 K. As ethanol is added to the solution, the temperature at which ice begins to form in gradually decreases.

The dotted line with the open symbols on the right side of the diagram is the freezing curve of ethanol in the mixture. As one passes downward through this curve, solid ethanol precipitates from the solution. Note that the temperature at which ethanol begins to freeze decreases as the amount of water in the solution increases. Therefore, we see that the addition of impurities decreases the freezing temperature of a substance. This phenomena is known as freezing point depression.

The point where the two freezing curves intersect with each other is called the eutectic point. This is the lowest temperature at which a binary mixture can remain in liquid without either of its components precipitating.

Finally, we note that below the dotted line in Fig. 8.1 the system exists as two coexisting solid phases: one consisting of pure ice, and the other composed of pure solid ethanol. The relative amounts of these two phases is given by the lever rule.

8.3   Conditions for equilibrium

In this section, we derive the equation that governs the shape of the freezing curve. Let's consider the freezing of a species in a general multicomponent mixture. We make the assumption that the solid phase consists of pure component α. At equilibrium, the chemical potential of the solid phase is the
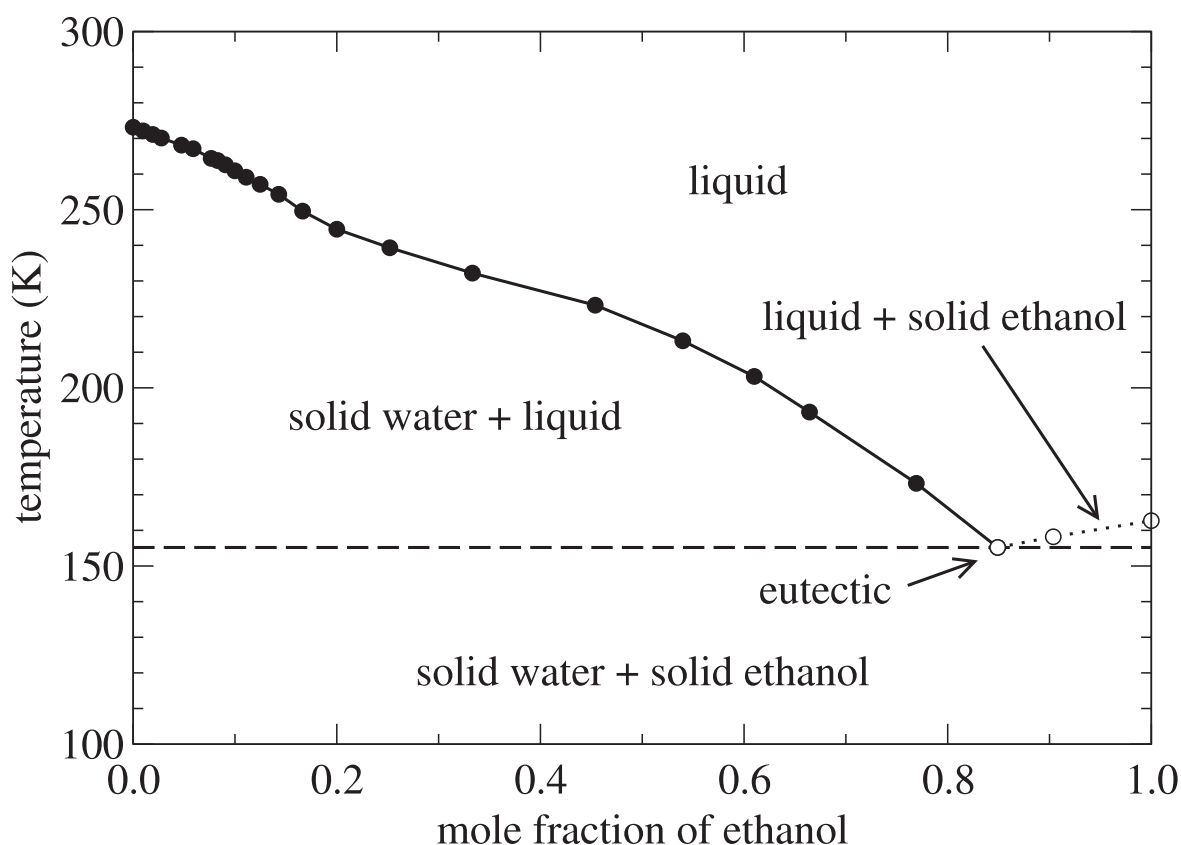
Figure 8.1: Solid-liquid phase diagram for mixtures of ethanol and water at 1 atm. Data taken from SU Pickering, *J. Chem. Soc.* **63**, 998 (1893).

same as that in the liquid phase:

$$\mu_\alpha^{(l)} = \mu_\alpha^{(s)}$$
$$\mu_\alpha^{\circ,(l)}(T,p) + RT \ln x_\alpha \gamma_\alpha = \mu_\alpha^{\circ,(s)}(T,p)$$
$$RT \ln x_\alpha \gamma_\alpha = \mu_\alpha^{\circ,(s)}(T,p) - \mu_\alpha^{\circ,(l)}(T,p)$$
$$\ln x_\alpha \gamma_\alpha = \frac{\Delta G_\alpha(T,p)}{RT} \tag{8.1}$$

where ΔG_α is the difference in the chemical potentials of the solid and liquid phases (i.e., $\Delta G_\alpha(T,p) = \mu_\alpha^{\circ,(s)}(T,p) - \mu_\alpha^{\circ,(l)}(T,p)$). If we knew the composition of the mixture (i.e., x_α), γ_α, and the function ΔG_α, then we could use Eq. (8.1) to predict the freezing temperature T of the mixture.

One method to approximate the function ΔG_α is by using a Taylor series expansion around the temperature T_m, the melting temperature of pure α at pressure p. This yields

$$\Delta G_\alpha(T,p) \approx \Delta G_\alpha(T_m,p) + \frac{\partial \Delta G_\alpha(T_m,p)}{\partial T}(T - T_m) + \cdots \tag{8.2}$$

At the melting temperature T_m, the molar Gibbs free energy of the pure solid phase is equal to the

molar Gibbs free energy of the pure liquid phase. That is

$$\Delta G_\alpha(T_m, p) = 0 \tag{8.3}$$

Therefore, the first term of the Taylor series expansion in Eq. (8.2) vanishes.

From the fundamental equation of thermodynamics, we arrive at

$$\frac{\partial \Delta G_\alpha}{\partial T} = -\Delta S_\alpha \tag{8.4}$$

where ΔS_α is the molar entropy change of freezing. From the relation $G = H - TS$, we can relate the entropy change of freezing to the enthalpy of freezing ΔH_α, which is the heat released by the system when it transforms from a liquid to a solid:

$$\Delta G_\alpha(T_m, p) = \Delta H_\alpha(T_m, p) - T_m \Delta S_\alpha(T_m, p)$$
$$0 = \Delta H_\alpha(T_m, p) - T_m \Delta S_\alpha(T_m, p)$$
$$\Delta S_\alpha(T_m, p) = \frac{1}{T_m} \Delta H_\alpha(T_m, p). \tag{8.5}$$

Combining this with Eq. (8.2) yields

$$\Delta G_\alpha(T, p) \approx -\frac{\Delta H_\alpha(T_m, p)}{T_m}(T - T_m) + \cdots \tag{8.6}$$

Finally, we find:

$$\ln x_\alpha \gamma_\alpha = -\frac{\Delta H_\alpha(T_m, p)}{RTT_m}(T - T_m)$$

$$\ln x_\alpha \gamma_\alpha = -\frac{\Delta H_\alpha(T_m, p)}{RT_m}\left(1 - \frac{T_m}{T}\right) \tag{8.7}$$

This equation allows the prediction of the freezing curve of a mixture. It requires from knowledge of the freezing temperature and enthalpy of melting of the pure component α, as well as a model of the activity coefficients of the liquid mixture. In the absence of information for the activity coefficients, the ideal solution model can be used (i.e., $\gamma_\alpha = 1$); Eq. (8.7) then reduces to the van't Hoff equation.

9   Gas solubility and Henry's law

In order to describe vapor-liquid equilibria, we have been using Raoult's law (see Eq. (6.1)) or the modified Raoult's law (see Eq. (6.3)). One of the required inputs to the modified Raoult's law is the vapor pressure $p_\alpha^{\mathrm{vap}}(T)$ of each component α in the pure state; this is the pressure below which pure liquid α will begin to boil (or vaporize) at a given temperature T. However, the vapor pressure of a substance is only defined at temperatures below its critical temperature. Above the critical temperature, the vapor pressure is undefined (recall that the vapor pressure curve terminates at the critical point). Therefore, Raoult's law and the modified Raoult's law are only applicable if the critical temperatures of all the components in the system are above the system temperature.

This presents difficulties when we want to examine the solubility of gases, such as oxygen which has a critical temperature of $T_c = 154.59\,\mathrm{K}$ and nitrogen which has a critical temperature of $T_c = 126.21\,\mathrm{K}$, in liquids. The critical temperature of these gases are well below ambient temperatures. For these systems, another approach is required to determine the conditions for vapor-liquid equilibrium.

9.1   Henry's law

Let's consider a binary mixture of carbon dioxide and hexane at a temperature of 393.15 K. The critical temperature of hexane is 507.5 K, which is higher than the system temperature, so pure liquid hexane can exist as a liquid. The critical temperature of carbon dioxide is 304.2 K, which is lower than the system temperature. Consequently, pure carbon dioxide does not possess a vapor-liquid transition at this temperature, and its vapor pressure is undefined. Raoult's law cannot be applied to this system.

In Fig. 9.1, we plot the variation of the partial pressure of carbon dioxide with the mole fraction of the gas dissolved in a liquid mixture of carbon dioxide and hexane. When $x_{\mathrm{CO_2}} = 0$, the system consists solely of hexane, and the partial pressure of carbon dioxide is zero. The vapor space consists entirely of hexane at its vapor pressure. As the concentration of carbon dioxide dissolved in the liquid phase increases, the partial pressure of carbon dioxide in the vapor phase also increases. However, for $x_{\mathrm{CO_2}} > 0.7$, the liquid phase no longer exists; above this mole fraction, the system is a one phase vapor (or gas) mixture.

For this system, we cannot apply Raoult's law, as the vapor pressure of carbon dioxide is undefined because the system temperature is above its critical temperature. To overcome this difficulty, for each component that has a critical temperature below the system temperature, we replace Raoult's law with Henry's law, first proposed by J. W. Henry in 1800 to empirically describe the solubility of gases:

$$p_\alpha = K_\alpha(T)x_\alpha, \qquad (9.1)$$

where $K_\alpha(T)$ is known as the Henry's law constant.

The Henry's law constant is equal to the slope of the partial pressure of component α at infinite

Figure 9.1: Variation of the partial pressure of component carbon dioxide in the vapor phase with its mole fraction in the coexisting liquid phase mixture of carbon dioxide and hexane at 393.15 K. The solid line and filled symbols denote the actual variation of the partial pressure. The dotted line is Henry's law. Data taken from YH Li, KH Dillard, and RL Robinson, *J. Chem. Eng. Data.* **26**, 53 (1981).

dilution. Therefore, Henry's law is expected to be accurate where the concentration of α in the liquid mixture is low. $K_\alpha(T)$ plays analogous role as the vapor pressure in Raoult's law (see Eq. (6.1)).

9.2 Activity coefficients

As with Raoult's law, Henry's law is only an approximation. However, we can generalize its range of validity by defining an activity coefficient γ_α^* as

$$\gamma_\alpha^* = \frac{\text{actual } p_\alpha}{\text{ideal } p_\alpha} \tag{9.2}$$

$$\gamma_\alpha^* = \frac{p_\alpha}{K_\alpha x_\alpha} \tag{9.3}$$

Note that Henry's law becomes exact in the limit $x_\alpha \to 0$ and, therefore, we expect that $\gamma_\alpha^* \to 1$ as $x_\alpha \to 0$. This is a different normalization from γ_α.
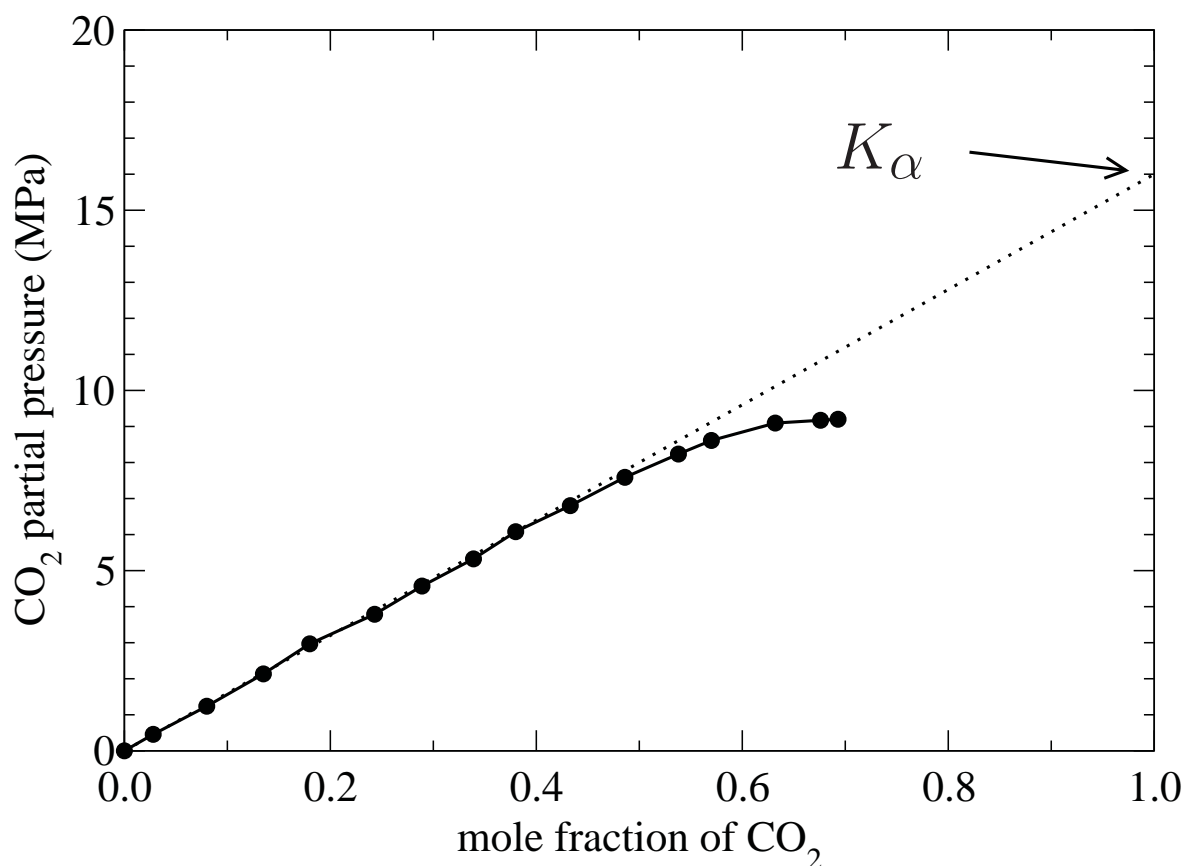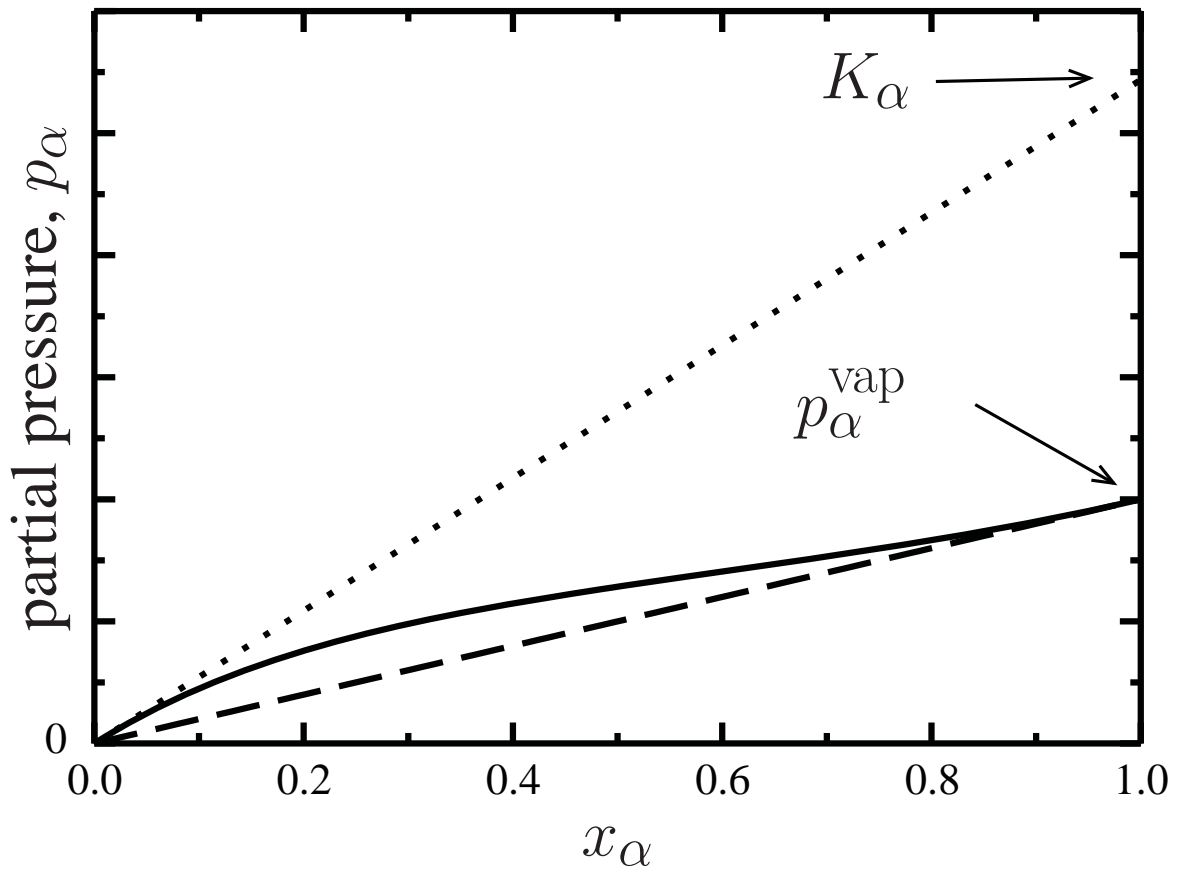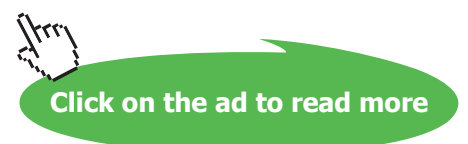
Figure 9.2: Variation of the partial pressure of component α in the vapor phase with its mole fraction in the coexisting liquid phase. The solid line is the actual variation of the partial pressure. The dashed line is the prediction of Raoult's law, and the dotted line is the prediction of Henry's law.

In Fig. 9.2, we plot a schematic drawing of the variation of the partial pressure of a component with its mole fraction in the liquid phase. The solid line represent the experimental variation of the partial pressure, the dashed line is the prediction of Raoult's law, and the dotted line is the prediction of Henry's law.

Even if a component has a vapor pressure at the system temperature (i.e., its critical temperature is greater than the system temperature), we still may prefer to use Henry's law instead of Raoult's law. This is usually done for components that are very dilute, where Henry's law becomes more and more accurate.

If we compare Henry's law and the modified Raoult's law, then we find that Henry's law can be considered as the modified Raoult's law with $\gamma_\alpha = K_\alpha / p_\alpha^{\mathrm{vap}}$.

10 Equations of state

An equation of state (EOS) provides a relation between the pressure, temperature, volume, and composition of a system. Typically, this is given as an explicit function of temperature, molar volume, and composition $p = p(T, V, x_2, x_3, \cdots)$. One example is the ideal gas law, where the pressure is given by

$$p = \frac{RT}{V} \tag{10.1}$$

where R is the universal gas constant.

Real materials have much more complicated equations of state. In this chapter, we present other equations of state that are used to model real systems and demonstrate how to use them to determine various thermodynamics properties from them.

10.1 The principle of corresponding states

The properties of different fluids are in general quite different from each other. In Fig. 10.1, we plot the liquid-vapor coexistence curves for a variety of fluids. However, Guggenheim observed that if the properties of a certain class fluids are plotted in terms of reduced variables, variables divided by their critical values, the data can be collapsed onto a single curve, independent of the identity of the fluid. This can be seen on the right plots in Fig. 10.1. This collapse of the properties is known as the principle of corresponding states.

This observation implies that the thermodynamic properties of all materials are given by a single, "universal" function, independent of the identity of the material. For example, defining the compressibility factor Z as

$$Z = \frac{pV}{RT}, \tag{10.2}$$

the principle of corresponding states implies that

$$Z = Z(T_r, p_r) \tag{10.3}$$

where $T_r = T/T_c$ is the reduced temperature, $p_r = p/p_c$ is the reduced pressure, T_c is the critical temperature of the material, and p_c is its critical pressure.

Guggenheim observed that this principle actually holds very well for many simple fluids, fluids composed of molecules that are roughly spherical. However, in general, this principle does not hold for an arbitrary fluid, in particular, for polar fluids, such as water, and for fluids composed of highly non-spherical molecules, such has n-hexane.

Pitzer noticed that as the molecules in a fluid begin to elongate and deviate from a spherical shape,
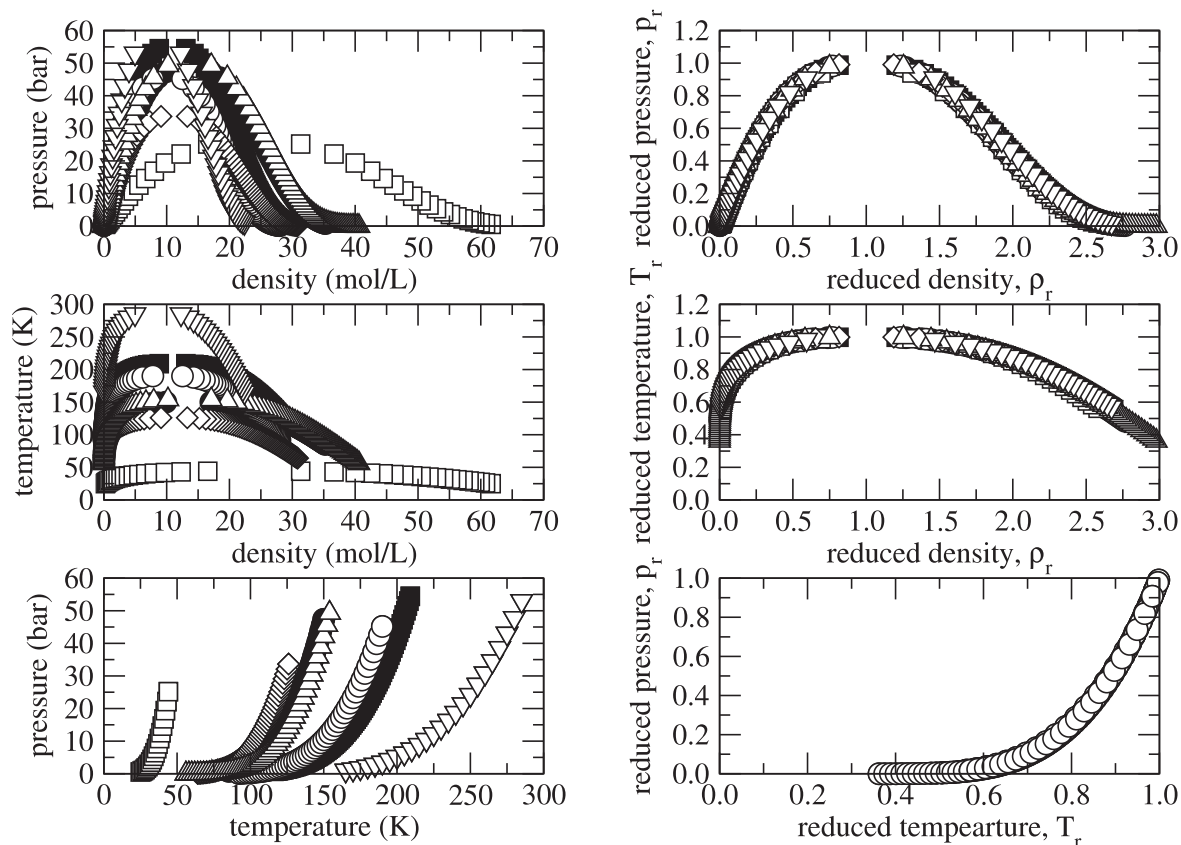
Figure 10.1: Vapor-liquid coexistence curves for neon (open squares), argon (filled circles), krypton (filled squares), xenon (open down-triangles), methane (open circles), nitrogen (open diamonds), and oxygen (open up-triangles). Data taken from the NIST Chemistry Webbook `http://webbook.nist.gov`.

the slope of the vapor pressure curve increased in magnitude. In order to quantify this effect, Pitzer defined the accentric factor ω as

$$\omega = -1 - \log_{10} \frac{p^{\text{vap}}(T = 0.7T_c)}{p_c} \tag{10.4}$$

For spherical molecules, ω is approximately equal to zero.

This generalized principle of corresponding states implies that the compressibility factor of a fluid can be expressed as

$$Z = Z(T_r, p_r, \omega) \tag{10.5}$$

Various approximations for this function have been developed in the literature and are presented in standard reference texts. Therefore, given this function, we can determine the thermodynamic behavior of a compound from knowledge of its critical temperature, critical pressure.

10.2   The van der Waals equation and cubic equations of state

The basic assumption in deriving the ideal gas equation of state is that the interactions between the molecules that compose the gas are negligible. At very low densities, where the average distance between molecules is extremely large compared to the range of the intermolecular interactions (or size of a molecule) and collisions between molecules occur only rarely, this assumption is fairly good. However, for moderately dense gases, this assumption begins to breakdown, as collisions between molecules become more and more frequent. In the case of liquids, this assumption is completely erroneous, as intermolecular interactions dominate the properties of the liquid.

To account for the finite size of molecules in the system. If we consider molecules to be of volume b, then the actual volume available to the system is approximately $V - b$. Therefore, we replace V in the ideal gas equation of state with $V - b$. In addition, at large distances, the molecules in a gas exert an attractive interaction between each other due to dispersion forces. The van der Waals equation of state, which accounts for both the short-ranged repulsions and long-ranged attractions between molecules, is given by

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{10.6}$$

A schematic plot of the variation of the pressure with volume, as predicted by the van der Waals equation of state, at various temperatures is given in Fig. 10.2. At temperatures above the critical temperature, the pressure-volume variation is monotonic and qualitatively similar to that of an ideal gas (see dotted-line). At temperatures below the critical temperature, the pressure-volume curve begins to oscillate, exhibiting a "van der Waals" loop (see dashed-line). This behavior is unphysical, but represents the vapor-liquid transition, and should be replaced by the solid line. The precise location of the solid line is given by the Maxwell construction.

When the temperature is equal to the critical temperature, the pressure-volume curve exhibits a point with the inflection (concavity) of the curve changes sign. This occurs at the critical point, where we have:

$$\frac{\partial p}{\partial V} = 0 \tag{10.7}$$

$$\frac{\partial^2 p}{\partial V^2} = 0 \tag{10.8}$$

Applying Eqs. (10.7) and (10.8) to the van der Waals equation of state, we find

$$\frac{\partial p}{\partial V} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \tag{10.9}$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \tag{10.10}$$
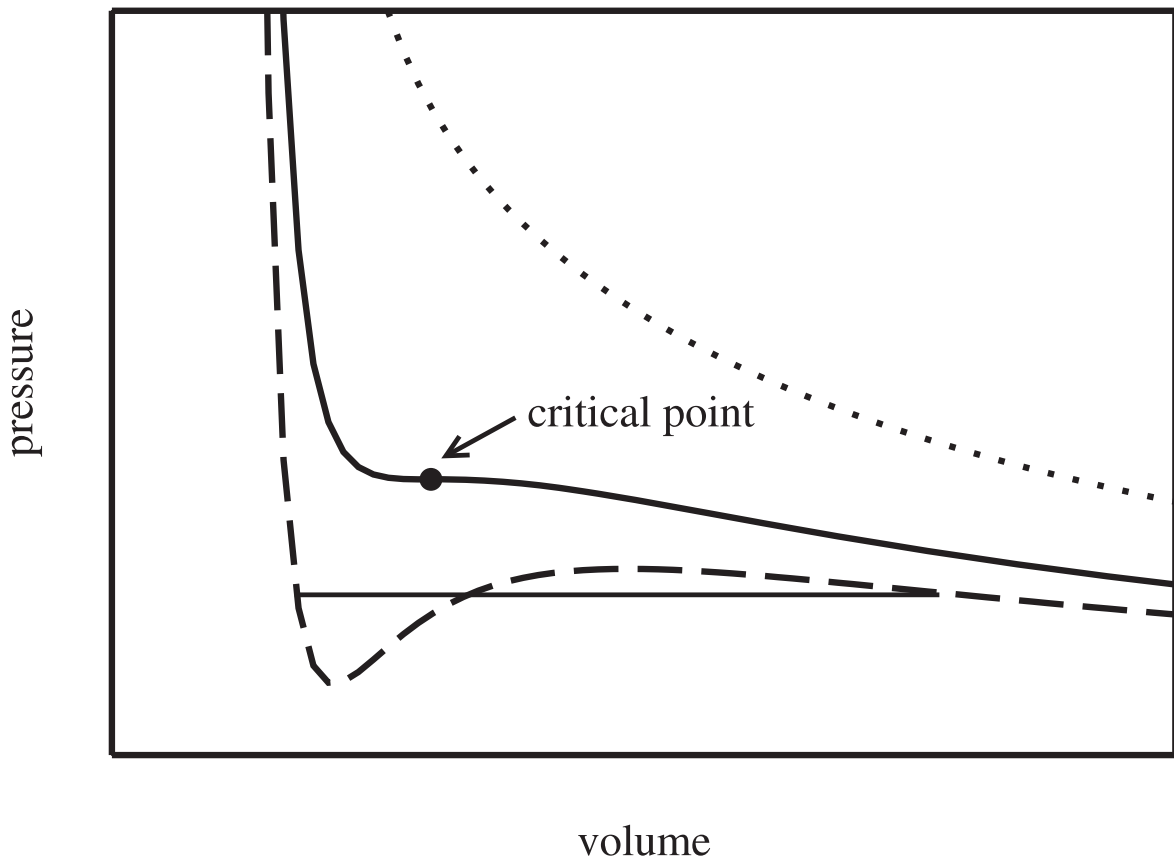
Figure 10.2: Variation of pressure with volume for the van der Waals equation of state for: (i) $T > T_c$ (dotted line), (ii) $T = T_c$ (solid line), and (iii) $T < T_c$ (dashed line).

Multiplying the Eq. (10.9) by $2/(V_c - b)$ and adding it Eq. (10.10) yields

$$-\frac{2RT}{(V_c - b)^3} + \frac{4a}{V_c^3(V_c - b)} + \frac{2RT}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 = 0$$

$$\frac{4a}{V_c^3(V_c - b)} - \frac{6a}{V_c^4} = 0$$

$$2V_c = 3(V_c - b)$$

$$V_c = 3b$$

Substituting $V_c = 3b$ into Eq. (10.9) yields

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$RT_c = \frac{2a(V_c - b)^2}{V_c^3}$$

$$= \frac{2a(3b - b)^2}{(3b)^3}$$

$$= \frac{8}{27}\frac{a}{b} \qquad (10.11)$$

We can compute the critical pressure by substituting T_c and V_c into the equation of state,

$$p_c = \frac{RT}{V_c - b} - \frac{a}{V_c^2}$$

$$= \frac{8a/(27b)}{3b - b} - \frac{a}{(3b)^2}$$

$$= \frac{a}{27b^2} \qquad (10.12)$$

We have shown that, given the parameters a and b of the van der Waals equation of state, one can determine the critical properties of a fluid. However, we can perform the inverse task. That is, given the critical temperature and pressure for a fluid, one can determine the a and b parameters of the van der Waals equation of state. Dividing Eq. (10.11) by Eq. (10.12)

$$\frac{RT_c}{p_c} = \frac{8a/(27b)}{a/(27b^2)}$$

$$b = \frac{RT_c}{8p_c} \qquad (10.13)$$

Inserting the expression for b into Eq. (10.11), we find

$$RT_c = \frac{8}{27}\frac{a}{RT_c/(8p_c)} \qquad (10.14)$$

$$a = \frac{27}{64}\frac{(RT_c)^2}{p_c} \qquad (10.15)$$

Therefore, given the critical temperature and pressure of a fluid, we can use Eqs. (10.13) and (10.15) to determine the parameters for the van der Waals equation. This then allows us to make predictions about the thermodynamic behavior of the fluid at any other state point.

Many other equations of state exist beyond the van der Waals EOS. Some examples include:

- Redlich-Kwong equation of state

$$p = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \tag{10.16}$$

- Soave-Redlich-Kwong equation of state

$$p = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \tag{10.17}$$

where

$$a(T) = a(T_c)\alpha(T) \tag{10.18}$$
$$\alpha(T) = [1 + \kappa(1 - T_r^{1/2})]^2$$
$$\kappa = 0.480 + 1.574\omega - 0.176\omega^2$$

- Peng-Robinson equation of state

$$p = \frac{RT}{V - b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{10.19}$$

where

$$a(T) = a(T_c)\alpha(T)$$
$$\alpha(T) = [1 + \kappa(1 - T_r^{1/2})]^2$$
$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

The relationship between the parameters of these models and the critical temperature and pressure of the fluid are summarized in Table 1.

Table 1: Parameters for various equations of state in terms of the critical temperature and pressure.

	$a(T_c)$	b
van der Waals	$\frac{27}{64}\frac{(RT_c)^2}{p_c}$	$\frac{RT_c}{8p_c}$
Redlich-Kwong	$0.42748\frac{(RT_c)^2}{p_c}$	$0.08664\frac{RT_c}{p_c}$
Redlich-Kwong-Soave	$0.42748\frac{(RT_c)^2}{p_c}$	$0.08664\frac{RT_c}{p_c}$
Peng-Robinson	$0.45724\frac{(RT_c)^2}{p_c}$	$0.07780\frac{RT_c}{p_c}$

10.3 Equations of state for mixtures

Thus far, we have only been considering single component systems. One method of extending an equation of state to mixtures is by making the parameters a and b a function of composition. This is done through the application of mixing rules. For example, we can define the parameter b of the mixture as

$$b = \sum_\alpha y_\alpha b_\alpha \tag{10.20}$$

where b_α is the b parameter for pure α, and y_α is the mole fraction of α in the system.

Similarly, we can define the parameter a of the mixture as

$$a = \sum_{\alpha,\alpha'} y_\alpha y_{\alpha'} a_{\alpha\alpha'} \tag{10.21}$$

where $a_{\alpha\alpha'} = (1 - k_{\alpha\alpha'})(a_\alpha a_{\alpha'})^{1/2}$, a_α is the a parameter of pure α, and $k_{\alpha\alpha'}$ is the binary interaction parameter between species α and α'. The binary interaction parameter $k_{\alpha\alpha'}$ is a purely empirical parameter that is used to obtain better agreement between the predictions of the equation of state and experimental data. Typical values of the parameter are given in Table 2.

Table 2: Typical values of the binary interaction parameters for various mixtures.

mixture	$k_{\alpha\alpha'}$
hydrocarbon/hydrocarbon	~ 0
CO_2/hydrocarbon	~ 0.15
water/hydrocarbon	~ 0.5

11   Thermodynamics from equations of state

Equations of state relate the pressure, temperature, volume, and composition of a system to each other. In this Chapter, we show how to determine other thermodynamic properties of the system from an equation of state. In a typical equation of state, the pressure is given as an explicit function of temperature, volume, and composition. Therefore, the "natural" variables are the temperature, volume, and composition of the system. That is, once given the volume, temperature, and composition of the system, the pressure is readily calculated from the equation of state.

Once one of the free energies of a system is known as a function of its natural variables, then all the other thermodynamic properties of the system can be derived. For these equations of states, the Helmholtz free energy is the relevant quantity. In the following, we demonstrate how to determine the Helmholtz free energy from an equation and then proceed to show how to derive other properties from it.

11.1   The residual Helmholtz free energy

The free energy that has temperature, volume, and mole numbers as its natural variables is the Helmholtz free energy. Before we stated that once the Gibb's free energy of a system is known as a function of temperature, pressure, and mole numbers $G(T, p, N_1, N_2, \dots)$, all the thermodynamics of the system are known. This is equivalent to the statement that once the Helmholtz free energy is known as a function of temperature, volume, and mole numbers of the system $\underline{A}(T, V, N_1, N_2, \dots)$, all the thermodynamics of the system are known. The fundamental equation of thermodynamics can be written in terms of the Helmholtz free energy as

$$dA = -\underline{S}dT - pd\underline{V} + \sum_{\alpha} \mu_{\alpha} dN_{\alpha} \tag{11.1}$$

Given and equation of state, we can determine an explicit expression for the Helmholtz free energy from the fundamental equation of thermodynamics. At constant temperature and mole numbers, we have

$$d\underline{A} = -pd\underline{V} \tag{11.2}$$

By integrating both sides of this equation from a total volume $\underline{V}_1$ to a total volume $\underline{V}_2$

$$\underline{A}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}(T, \underline{V}_1, N_1, N_2, \dots) = -\int_{\underline{V}_1}^{\underline{V}_2} d\underline{V}' p \tag{11.3}$$

For an ideal gas, we have $p = NRT/\underline{V}$, so

$$\underline{A}^{ig}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}^{ig}(T, \underline{V}_1, N_1, N_2, \dots) = -\int_{\underline{V}_1}^{\underline{V}_2} d\underline{V}' \frac{NRT}{\underline{V}'} \tag{11.4}$$

Subtracting Eq. (11.4) from Eq. (11.3), we find

$$[\underline{A}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}(T, \underline{V}_1, N_1, N_2, \dots)]$$

$$-[\underline{A}^{ig}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}^{ig}(T, \underline{V}_1, N_1, N_2, \dots)] = -\int_{\underline{V}_1}^{\underline{V}_2} d\underline{V}' \left(p - \frac{NRT}{\underline{V}'}\right)$$

$$[\underline{A}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}^{ig}(T, \underline{V}_2, N_1, N_2, \dots)]$$

$$-[\underline{A}(T, \underline{V}_1, N_1, N_2, \dots) - \underline{A}^{ig}(T, \underline{V}_1, N_1, N_2, \dots)] = -NRT\int_{\underline{V}_1}^{\underline{V}_2} \frac{d\underline{V}'}{\underline{V}'}(Z - 1) \tag{11.5}$$

$$\underline{A}^{res}(T, \underline{V}_2, N_1, N_2, \dots) - \underline{A}^{res}(T, \underline{V}_1, N_1, N_2, \dots) = -NRT\int_{\underline{V}_1}^{\underline{V}_2} \frac{d\underline{V}'}{\underline{V}'}(Z - 1)$$

where we have defined a residual property $\underline{X}^{res}$ as the difference of the value of the property of the system and that of an ideal gas at the same temperature, volume, and species mole numbers

$$\underline{X}^{res}(T, V, N_1, N_2, \dots) = \underline{X}(T, V, N_1, N_2, \dots) - \underline{X}^{ig}(T, V, N_1, N_2, \dots) \tag{11.6}$$

As the density of the system approaches zero, or the molar volume of the system approaches infinity, the properties of a system approach those of an ideal gas. In particular,

$$\underline{A}(T, V, N_1, N_2, \dots) \rightarrow \underline{A}^{ig}(T, V, N_1, N_2, \dots) \qquad \text{as} \qquad V \rightarrow \infty. \tag{11.7}$$

If we let $\underline{V}_2 = \underline{V}$ and $\underline{V}_1 \rightarrow \infty$ in Eq. (11.6), then we find

$$\underline{A}^{res}(T, \underline{V}, N_1, N_2, \dots) = -NRT\int_{\infty}^{\underline{V}} \frac{d\underline{V}'}{\underline{V}'}(Z - 1)$$

$$= NRT\int_{\underline{V}}^{\infty} \frac{d\underline{V}'}{\underline{V}'}(Z - 1) \tag{11.8}$$

Given an expression for the compressibility factor Z as a function of temperature and volume for a fluid (an equation of state), we can determine the residual Helmholtz free energy of the system.

For the van der Waals equation of state, the compressibility factor is given by

$$
\begin{aligned}
Z &= \frac{pV}{RT} \\
&= \frac{V}{RT}\left(\frac{RT}{V-b} - \frac{a}{V^2}\right) \\
&= \frac{V}{V-b} - \frac{a}{RTV} \\
Z - 1 &= \frac{b}{V-b} - \frac{a}{RTV}
\end{aligned}
\tag{11.9}
$$

Substituting this expression into Eq. (11.8), we can obtain the residual Helmholtz free energy for the van der Waals equation of state:

$$
\begin{aligned}
\frac{\underline{A}^{res}(T, V, N_1, N_2, \dots)}{NRT} &= \int_V^\infty \frac{dV}{V}\left(\frac{b}{V-b} - \frac{a}{RTV}\right) \\
&= \int_V^\infty dV\left(\frac{1}{V-b} - \frac{1}{V} - \frac{a}{RTV^2}\right) \\
&= \left[\ln\frac{V-b}{V} + \frac{a}{RTV}\right]_V^\infty \\
&= \ln\left(\frac{V}{V-b}\right) - \frac{a}{RTV}
\end{aligned}
\tag{11.10}
$$

The residual chemical potential of species α can be obtained from the residual Helmholtz free energy by differentiating by the number of moles of α (see Eq. (11.1)):

$$
\mu_\alpha^{res} = \frac{\partial \underline{A}^{res}}{\partial N_\alpha}
\tag{11.11}
$$

For the van der Waals equation of state, this becomes

$$
\begin{aligned}
\mu_\alpha^{res} &= \frac{\partial}{\partial N_\alpha}\left\{NRT\left[\ln\left(\frac{V}{V-Nb}\right) - \frac{Na}{RT\underline{V}}\right]\right\} \\
&= RT\ln\left(\frac{V}{\underline{V}-Nb}\right) + \left(\frac{NRT}{V-Nb}\right)\frac{\partial Nb}{\partial N_\alpha} - \frac{1}{V}\frac{\partial N^2 a}{\partial N_\alpha}
\end{aligned}
\tag{11.12}
$$

To obtain the derivative of the a and b parameters with respect to N_α, we need to use the mixing rules given in Eqs. (10.20) and (10.21). This yields

$$
\begin{aligned}
\frac{\partial Nb}{\partial N_\alpha} &= \frac{\partial}{\partial N_\alpha} N \sum_{\alpha'} y_{\alpha'} b_{\alpha'} \\
&= \frac{\partial}{\partial N_\alpha} \sum_{\alpha'} N_{\alpha'} b_{\alpha'} \\
&= b_\alpha
\end{aligned}
\tag{11.13}
$$

and

$$
\begin{aligned}
\frac{\partial N^2 a}{\partial N_\alpha} &= \frac{\partial}{\partial N_\alpha} N^2 \sum_{\alpha',\alpha''} y_{\alpha'} y_{\alpha''} a_{\alpha'\alpha''} \\
&= \frac{\partial}{\partial N_\alpha} \sum_{\alpha',\alpha''} N_{\alpha'} N_{\alpha''} a_{\alpha'\alpha''} \\
&= 2 \sum_{\alpha'} N_{\alpha'} a_{\alpha\alpha'} \\
&= 2N \sum_{\alpha'} y_{\alpha'} a_{\alpha\alpha'}
\end{aligned}
\tag{11.14}
$$

Using these expressions, we find that the residual chemical potnetial for the van der Waals equation of state is given by

$$
\mu_\alpha^{res} = RT \ln \left(\frac{V}{V-b} \right) + \frac{RTb_\alpha}{V-b} - \frac{2}{V} \sum_{\alpha'} y_{\alpha'} a_{\alpha\alpha'}
\tag{11.15}
$$

11.2 Fugacity

An ideal gas is an ideal solution. Thus, the chemical potential of species α in an ideal gas mixture at temperature T, pressure p, and species mole fractions y_1, y_2,... is given by

$$\mu_\alpha^{\text{ig}}(T, p, y_1, y_2, \dots) = \mu_\alpha^{\text{o,ig}}(T, p) + RT \ln y_\alpha \tag{11.16}$$

where $\mu_\alpha^{\text{o,ig}}(T, p)$ is the chemical potential of pure α.

The difference in the chemical potential of an ideal gas at pressure p and mole fractions y_1, y_2, ... and an ideal gas at pressure p' and mole fractions y_1', y_2',... is given by

$$\begin{aligned}
\mu_\alpha^{\text{ig}}(T, p, y_1, y_2, \dots) &= \mu_\alpha^{\text{ig}}(T, p', y_1', y_2', \dots) + RT \ln \frac{y_\alpha p}{y_\alpha' p'} \\
&= \mu_\alpha^{\text{ig}}(T, p', y_1', y_2', \dots) + RT \ln \frac{p_\alpha}{p_\alpha'}
\end{aligned} \tag{11.17}$$

Note that we have made use of the relation In analogy with ideal gases, we define the fugacity of a real gas as

$$\mu_\alpha(T, p, y_1, y_2, \dots) = \mu_\alpha(T, p', y_1', y_2', \dots) + RT \ln \frac{f_\alpha(T, p, y_1, y_2, \dots)}{f_\alpha(T, p', y_1', y_2', \dots)} \tag{11.18}$$

where f_α is a function of temperature, pressure, and the system composition.

The fugacity coefficient ϕ_α is defined as

$$\phi_\alpha = \frac{f_\alpha}{p_\alpha} = \frac{f_\alpha}{y_\alpha p} \tag{11.19}$$

This gives us the difference between the chemical potential of the system and the chemical potential of an ideal gas at the same temperature, pressure, and composition. That is:

$$\mu_\alpha(T, p, y_2, y_3, \dots) - \mu_\alpha^{\text{ig}}(T, p, y_2, y_3, \dots) = RT \ln \phi_\alpha \tag{11.20}$$

The residual chemical potential is equal to the difference between the chemical potential of the system and the chemical potential of an ideal gas at the same temperature, molar volume, and composition. The difference given in Eq. (11.20) is between the system and an ideal gas at the same temperature, *pressure*, and composition. This is not the same as the residual chemical potential. However, the two quantities are related. If we consider an ideal gas with the same molar volume as the system, its pressure will be equal to $p' = RT/V$, which will, in general, *not* be equal to the actual pressure p of

the system.

$$\mu_\alpha^{\text{ig}}(T, p, y_2, y_3, \dots) = \mu_\alpha^{\text{ig}}(T, p' = RT/V, y_2, y_3, \dots) + RT \ln \frac{p}{p'}$$

$$= \mu_\alpha^{\text{ig}}(T, p' = RT/V, y_2, y_3, \dots) + RT \ln \frac{pV}{RT} \tag{11.21}$$

$$= \mu_\alpha^{\text{ig}}(T, p' = RT/V, y_2, y_3, \dots) + RT \ln Z \tag{11.22}$$

where Z is the compressibility factor of the system. Substituting this expression in to Eq. (11.20), we find:

$$RT \ln \phi_\alpha = \mu_\alpha(T, p, y_2, y_3, \dots) - \mu_\alpha^{\text{ig}}(T, p, y_2, y_3, \dots)$$

$$= \mu_\alpha(T, p, y_2, y_3, \dots) - \mu_\alpha^{\text{ig}}(T, p', y_2, y_3, \dots) - RT \ln Z$$

$$= \mu_\alpha^{\text{res}}(T, p, y_2, y_3, \dots) - RT \ln Z \tag{11.23}$$

Therefore, given an equation of state, we can use Eq. (11.23) to obtain an expression for the fugacity coefficient of a system.

11.3 Vapor-liquid equilibrium with a non-ideal vapor phase

Raoult's law assumes that the liquid phase is an ideal solution and the vapor phase is an ideal gas. With an equation of state, such as the van der Waals equation of state, the vapor phase can now described more realistically, and we do not need to make the ideal gas assumption. In this situation, the chemical potential of the vapor phase

$$\mu_\alpha(T, p, y_2, \dots) = \mu_\alpha^\circ(T, p_\alpha^{\text{vap}}) + \mu_\alpha(T, p, y_2, \dots) - \mu_\alpha^\circ(T, p_\alpha^{\text{vap}})$$

$$= \mu_\alpha^\circ(T, p_\alpha^{\text{vap}}) + RT \ln \frac{f_\alpha(T, p, y_2, \dots)}{f_\alpha^\circ(T, p_\alpha^{\text{vap}})} \tag{11.24}$$

where f_α° is the fugacity of pure component α.

Now if we equate the chemical potentials of the liquid and vapor phases, we find

$$\mu_\alpha^g(T, p, y_2, \dots) = \mu_\alpha^l(T, p, x_2, \dots)$$

$$\mu_\alpha^{\circ,g}(T, p_\alpha^{\text{vap}}) + RT \ln \frac{f_\alpha}{f_\alpha^\circ} = \mu_\alpha^{\circ,l}(T, p) + RT \ln \gamma_\alpha x_\alpha$$

$$\mu_\alpha^{\circ,g}(T, p_\alpha^{\text{vap}}) + RT \ln \frac{f_\alpha}{f_\alpha^\circ} = \mu_\alpha^{\circ,l}(T, p_\alpha^{\text{vap}}) + \int_p^{p_\alpha^{\text{vap}}} dp' \frac{\partial \mu_\alpha^{\circ,l}(T, p)}{\partial p} + RT \ln \gamma_\alpha x_\alpha$$

$$RT \ln \frac{f_\alpha}{f_\alpha^\circ} = \int_p^{p_\alpha^{\text{vap}}} dp' V_\alpha^{\circ,l}(T, p) + RT \ln \gamma_\alpha x_\alpha$$

$$RT \ln \frac{y_\alpha p \phi_\alpha(T, p, y_2, \dots)}{p_\alpha^{\text{vap}} \phi_\alpha^\circ(T, p_\alpha^{\text{vap}})} = \int_p^{p_\alpha^{\text{vap}}} dp' V_\alpha^{\circ,l}(T, p) + RT \ln \gamma_\alpha x_\alpha$$

Neglecting the first term on the right side of the above equation is equivalent to assuming that the Poynting factor is equal to one. Making this assumption leads to

$$\frac{y_\alpha p \phi_\alpha(T, p, y_2, \dots)}{p_\alpha^{\text{vap}} \phi_\alpha^\circ(T, p_\alpha^{\text{vap}})} = \gamma_\alpha x_\alpha$$

$$y_\alpha p \frac{\phi_\alpha(T, p, y_2, \dots)}{\phi_\alpha^\circ(T, p_\alpha^{\text{vap}})} = \gamma_\alpha x_\alpha p_\alpha^{\text{vap}} \tag{11.25}$$

If the vapor phase is ideal, then the fugacity coefficients are equal to one, and we see that Eq. (11.25) becomes the modified Raoult's law that we have derived previously.

We do not need to apply an activity coefficient for the liquid phase. In fact, we can, in principle, apply the equation of state to determine the thermodynamics of both phases. In this case, we have

$$\mu_\alpha^g = \mu_\alpha^l$$

$$\mu_\alpha^{\text{ig}}(T, p, y_1, \dots) + RT \ln \phi_\alpha^g = \mu_\alpha^{\text{ig}}(T, p, x_1, \dots) + RT \ln \phi_\alpha^l$$

$$y_\alpha p \phi_\alpha^g = x_\alpha p \phi_\alpha^l \tag{11.26}$$

where we have used Eq. (11.17). Finally, we note that the ratio of the vapor mole fraction to the liquid mole fraction is related to the ratio of the fugacity coefficients:

$$\frac{y_\alpha}{x_\alpha} = \frac{\phi_\alpha^l}{\phi_\alpha^g} \tag{11.27}$$

12 Chemical reaction equilibria

In this section, we discuss the thermodynamics of systems undergoing chemical reactions. First we derive the conditions for equilibrium. Then, we generalize the Gibbs phase rule for reacting systems. Afterwards, we examine the calculation of the and introduce the equilibrium constant. Finally, we examine the influence of pressure and temperature on chemical reaction equilibria.

12.1 Conditions for equilibrium

Let's consider a system that initially contains $N_{N_2}^{(0)}$ moles of nitrogen, $N_{H_2}^{(0)}$ moles of hydrogen, and $N_{NH_3}^{(0)}$ moles of ammonia. This system can undergo the following reversible chemical reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{12.1}$$
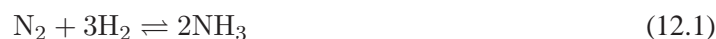
where nitrogen and hydrogen react to form ammonia, or ammonia can decompose to form nitrogen and hydrogen.

If the reaction proceeds forward by ξ moles (i.e., ξ moles of nitrogen combine with 3ξ moles of hydrogen combine to form 2ξ moles of ammonia), then, from a mole balance, the number of moles of each species in the system is given by

$$\begin{aligned} N_{N_2} &= N_{N_2}^{(0)} - \xi \\ N_{H_2} &= N_{H_2}^{(0)} - 3\xi \\ N_{NH_3} &= N_{NH_3}^{(0)} + 2\xi \end{aligned} \tag{12.2}$$

The quantity ξ is known as the extent of reaction. If the system does not react, then the extent of reaction equals zero (i.e., $\xi = 0$), and the mole numbers are equal to their initial value (i.e., $N_\alpha = N_\alpha^{(0)}$). If the reaction proceeds backwards (i.e., ammonia decomposes into nitrogen and hydrogen), then ξ has a negative value.

Note that the coefficient in front of the extent of reaction in the second term on the right side of Eqs. (12.2) is known as the stoichiometric coefficient for the component in the reaction. For a general reaction, we have

$$N_\alpha = N_\alpha^{(0)} + \nu_\alpha \xi \tag{12.3}$$

where ν_α is the stoichiometric coefficient for component α in the reaction. The stoichiometric coefficient is positive for products of the reaction, and it is negative for the reactants of the reaction. The absolute value of the stoichiometric coefficient of a component is equal to the numerical value of its coefficient in the reaction. For example, in the reaction given in Eq. (12.1), we have

$$\nu_{N_2} = -1, \qquad \nu_{H_2} = -3, \qquad \nu_{NH_3} = 2 \tag{12.4}$$

From Eq. (12.3), we directly relate the changes of the number of moles of species α with the change in the extent of reaction:

$$dN_\alpha = \nu_\alpha d\xi \tag{12.5}$$

For an isolated system where the total energy and volume are constant (i.e., $d\underline{U} = 0$ and $\underline{V} = 0$), the total entropy is maximized at equilibrium; therefore, we must have $d\underline{S} = 0$. The change in entropy of a system with respect to changes in the energy, volume, and number of moles of each species is given by (see Eq. (3.1))

$$\begin{aligned}
d\underline{S} &= \frac{1}{T}d\underline{U} + \frac{p}{T}d\underline{V} - \sum_\alpha \frac{\mu_\alpha}{T}dN_\alpha \\
&= \frac{1}{T}\sum_\alpha \nu_\alpha \mu_\alpha d\xi
\end{aligned} \tag{12.6}$$

where we have used Eq. (12.5) to relate changes in the mole numbers to the extent of reaction.

In order to ensure that $d\underline{S} = 0$, the coefficient of the $d\xi$ term must equal zero. Consequently, the criterion for chemical reaction equilibrium is

$$\sum_\alpha \nu_\alpha \mu_\alpha = 0 \tag{12.7}$$

for each chemical reaction that takes place in the system.

12.2   The phase rule for chemically reacting systems

Because the presence of chemical reactions introduces additional constraints on a system, we need to reconsider the Gibbs phase rule. In the absence of chemical reactions, the number of degrees of freedom f in a system is given by

$$f = 2 + \omega - \pi$$

where ω is the number of components, and π is the number of phases.

For a system with chemical reactions, there is one addition equation (see Eq. (12.7)) for every independent chemical reaction in the system. The presence of chemical reactions, therefore, imposes constraints on a system, which decrease its degrees of freedom. The phase rule now becomes:

$$f = 2 + \omega - \pi - r \tag{12.8}$$

where r is the number of independent reactions.

12.3   Gas phase reactions

Now we discuss how to calculate the equilibrium composition of a reacting non-ideal gas mixture. In order to use Eq. (12.7), we need an expression for the dependence of the chemical potential of each species in the system with its composition. In general, this can be expressed as (see Sec. 11):

$$\mu_\alpha(T, p, y_2, y_3, \dots) = \mu_\alpha^{ig,\circ}(T, p_0) + RT \ln \frac{y_\alpha \phi_\alpha p}{p_0} \tag{12.9}$$

where $\mu_\alpha^{ig,\circ}(T, p)$ is the chemical potential of pure α in an ideal gas state at temperature T and pressure p, and p_0 is a reference pressure (typically taken to be either 1 atm or 1 bar). Inserting this expression for the chemical potentials into the condition for chemical reaction equilibrium Eq. (12.7), we find

$$\sum_\alpha \nu_\alpha \mu_\alpha = 0$$

$$\sum_\alpha \nu_\alpha [\mu_\alpha^{ig,\circ}(T, p) + RT \ln y_\alpha \phi_\alpha p] = 0$$

$$RT \ln \prod_\alpha (y_\alpha \phi_\alpha p)^{\nu_\alpha} = -\sum_\alpha \nu_\alpha \mu_\alpha^{ig,\circ}(T, p)$$

$$\prod_\alpha (y_\alpha \phi_\alpha p)^{\nu_\alpha} = K_{\text{eq}}(T, p_0) \tag{12.10}$$

where K_{eq} is the equilibrium constant, defined as:

$$K_{\text{eq}}(T, p_0) \equiv \exp\left[-\frac{\Delta G_{\text{rxn}}(T, p_0)}{RT}\right] \tag{12.11}$$

and $\Delta G_{\text{rxn}}(T, p_0) \equiv \sum_\alpha \nu_\alpha \mu_\alpha^{ig,\circ}(T, p_0)$ is the Gibbs free energy of reaction.

The equilibrium constant and the Gibbs free energy of reaction are *independent* of the composition and pressure of the system but are dependent on the temperature of the system and the choice of the reference pressure. The greater the value of the equilibrium constant (which corresponds to more negative values of the Gibbs free energy of reaction), the further the reaction proceeds to completion. Given a value for the equilibrium constant and the pressure of the system, Eq. (12.10) can be solved to determine the equilibrium composition of the system. In the next section, we discuss how to determine the value of the equilibrium constant.

12.4   The standard Gibbs free energy of formation

In order to determine the equilibrium constant, we need to be able to compute the Gibbs free energy of reaction ΔG_{rxn}. This is dependent on the quantities $\mu_\alpha^{ig,\circ}(T, p_0)$ — the chemical potential of pure species α in an ideal gas state at temperature T and pressure p_0. These can be directly related to the standard Gibbs free energy of formation.

The standard Gibbs free energy of formation of a compound is defined as the Gibbs free energy change for the reaction of forming one mole of the compound from its constituent elements in their standard state at a temperature of 25°C and a pressure of 1 bar (or 1 atm). The standard state of an element is its stable form at 25°C and 1 bar. For example, the standard state for oxygen is the form O_2 in the (ideal) gas state, the standard state for bromine is in the liquid state, and the standard state for carbon is in the form of graphite. The standard Gibbs free energy of formation of elements in their standard state at 25°C and 1 bar is defined to be zero. Tabulations of values for the standard Gibbs free energy of formation for a broad range of compounds can be found in standard references, such as the CRC Handbook of Chemistry and Physics or Perry's Handbook of Chemical Engineering, or on online resource, such as the NIST Chemistry webbook (http://webbook.nist.gov). The standard enthalpy and Gibbs free energy of formation are listed in Table 3.

Table 3: Standard formation enthalpy and Gibbs free energies of various compounds at $T = 25$°C and $p = 1$ bar.

	H_f (kJ mol^{-1})	G_f (kJ mol^{-1})
$H_2(g)$	0.00	0.00
$N_2(g)$	0.00	0.00
$NH_3(g)$	-46.11	-16.45

The Gibbs free energy of the reaction in Eq. (12.1) can be obtained from Table 3

$$\Delta G_{\mathrm{rxn}}(25°C, 1\,\mathrm{bar}) = 2(-16.45) - 1(0.00) - 3(0.00) = -32.9\,\mathrm{kJ\,mol^{-1}},$$

From this, we can compute the corresponding value of the equilibrium constant.

Tables of the standard Gibbs free energy of formation allow the calculation of the equilibrium constant at standard conditions (i.e., $T = 25°C$ and $p = 1\,\mathrm{bar}$). However, in most situations, we require the equilibrium constant at other conditions. In the next section, we discuss how to estimate the equilibrium constant at other temperatures.

12.5   The influence of temperature

Often, we want to know how the equilibrium constant depends on temperature to determine the optimal conditions to perform a reaction. To determine this, we need to know how $\Delta G_{\mathrm{rxn}}/(RT)$ changes with temperature. The variation of the Gibbs free energy with temperature is given by

$$
\begin{aligned}
d\left(\frac{G}{T}\right) &= \frac{dG}{T} - \frac{G\,dT}{T^2} \\
&= \frac{-S\,dT + V\,dp}{T} - \frac{(H - TS)\,dT}{T^2} \\
&= -\frac{H}{T^2}dT + \frac{V}{T}dp \\
&= H\,d\left(\frac{1}{T}\right) + \frac{V}{T}dp
\end{aligned}
\tag{12.12}
$$

which leads to

$$\frac{\partial(G/T)}{\partial(1/T)} = H \tag{12.13}$$

Therefore, we find that the Gibbs free energy of reaction can be obtained directly from the enthalpy of reaction:

$$\frac{\Delta G_{\mathrm{rxn}}(T, p)}{RT} = \frac{\Delta G_{\mathrm{rxn}}(T_0, p)}{RT_0} - \int_{T_0}^{T} dT' \frac{\Delta H_{\mathrm{rxn}}(T', p)}{RT'^2} \tag{12.14}$$

In order to utilize this equation, we need to know how the enthalpy of reaction varies with temperature.

One approximation is to assume that the enthalpy of reaction is approximately independent of temperature. We can now perform the above integration with respect to T' to obtain:

$$\frac{\Delta G_{\mathrm{rxn}}(T, p)}{RT} \approx \frac{\Delta G_{\mathrm{rxn}}(T_0, p)}{RT} - \frac{\Delta H_{\mathrm{rxn}}(T_0, p)}{RT_0}\left(1 - \frac{T_0}{T}\right) + \cdots \tag{12.15}$$

where $\Delta H_{\mathrm{rxn}}(T_0, p)$ is the enthalpy of reaction at a temperature T_0. Note that this relation relies on the enthalpy of reaction being approximately constant in the range of temperatures from T_0 to

T. This condition, however, can be relaxed by incorporating knowledge of the heat capacities of the components involved in the reaction.

With this expression for ΔG_{rxn}, the corresponding expression for the temperature dependence of the equilibrium constant is:

$$K_{\text{eq}}(T) = K_{\text{eq}}(T_0) \exp\left[\frac{\Delta H_{\text{rxn}}(T_0, p)}{RT_0}\left(1 - \frac{T_0}{T}\right)\right] \tag{12.16}$$

For an exothermic reaction, where $\Delta H_{\text{rxn}}(T_0, p) < 0$, an increase in temperature will lead to a decrease in the equilibrium constant, thereby shifting the reaction to the reactants side. For an endothermic reaction, where $\Delta H_{\text{rxn}}(T_0, p) > 0$, an increase in temperature will lead to an increase in the equilibrium constant, thereby shifting the reaction to the products side.

12.6 Liquid phase reactions

For reactions in the liquid phase, the calculations proceed in a manner similar to those for the gas phase. Often for liquids, it is more convenient to express the chemical potential in terms of activity coefficients

$$\mu_\alpha = \mu_\alpha^\circ(T, p) + RT \ln x_\alpha \gamma_\alpha \qquad (12.17)$$

where $\mu_\alpha^\circ(T, p)$ is the chemical potential of pure species α in the liquid state at temperature T and pressure p. If we substitute this expression for the chemical potential into Eq. (12.7), we find

$$\sum_\alpha \nu_\alpha \mu_\alpha = 0$$

$$\sum_\alpha \nu_\alpha (\mu_\alpha^\circ + RT \ln x_\alpha \gamma_\alpha) = 0$$

$$RT \sum_\alpha \nu_\alpha \ln x_\alpha \gamma_\alpha = - \sum_\alpha \nu_\alpha \mu_\alpha^\circ$$

$$\ln \prod_\alpha (x_\alpha \gamma_\alpha)^{\nu_\alpha} = -\frac{1}{RT} \sum_\alpha \nu_\alpha \mu_\alpha^\circ$$

$$\prod_\alpha (x_\alpha \gamma_\alpha)^{\nu_\alpha} = \exp\left[-\frac{\Delta G_{\text{rxn}}(T, p)}{RT} \right] \qquad (12.18)$$

where $\Delta G_{\text{rxn}} = \sum_\alpha \nu_\alpha \mu_\alpha^\circ(T, p)$ is the Gibbs free energy of reaction.

Defining the equilibrium constant K_{eq} as $\ln K_{\text{eq}} = -\Delta G_{\text{rxn}}/(RT)$, we find

$$\prod_\alpha (x_\alpha \gamma_\alpha)^{\nu_\alpha} = K_{\text{eq}}(T, p) \qquad (12.19)$$

This equation is also known as the law of mass action.