

CHM 3400 – Fundamentals of Physical Chemistry
Chapter 4 - Handout

1. General thermodynamic relationships

One aspect of thermodynamics that makes it such a powerful method for studying systems is the ability to develop general relationships from first principles. Here we will develop three such relationships, for internal energy (U), enthalpy (H), and Gibbs free energy (G), and show a simple example of their use in solving a problem.

According to the first law of thermodynamics

$$dU = \delta q + \delta w \quad (4.1.1)$$

Consider eq 4.1.1 for a reversible process where the only work is mechanical (pressure-volume) work. Since

$$dS = \delta q_{\text{rev}}/T \quad (4.1.2)$$

it follows that

$$\delta q_{\text{rev}} = T dS \quad (4.1.3)$$

For mechanical work, we know that

$$\delta w = - p_{\text{ex}} dV \quad (4.1.4)$$

But for a reversible process $p_{\text{ex}} = p$, and so

$$\delta w_{\text{rev}} = - p dV \quad (4.1.5)$$

If we substitute eq 4.1.3 and 4.1.5 into eq 4.1.1, we get

$$dU = T dS - p dV \quad (4.1.6)$$

Equation 4.1.6 was derived assuming a reversible process. However, every term in the equation is a state function. It follows that if the relationship is true for reversible processes, then it must be true for all processes, reversible or irreversible. Our ability to say this is another example of the importance of state functions in thermodynamics.

Now consider a small change in enthalpy. Since

$$H = U + pV \quad (4.1.7)$$

it follows that

$$dH = dU + p dV + V dp \quad (4.1.8)$$

If we substitute our general expression for dU (eq 4.1.6) into equn 4.1.8, we get

$$dH = T dS - p dV + p dV + V dp \quad (4.1.9)$$

or, after cancellation of terms

$$dH = T dS + V dp \quad (4.1.10)$$

a second general thermodynamic relationship.

Finally, consider the Gibbs free energy. Since

$$G = H - TS \quad (4.1.11)$$

then for a small change we have

$$dG = dH - T dS - S dT \quad (4.1.12)$$

If we substitute eq 4.1.10 into eq 4.1.12, the result is

$$dG = T dS + V dp - T dS - S dT \quad (4.1.13)$$

or, after cancellation

$$dG = V dp - S dT \quad (4.1.14)$$

Equations 4.1.6, 4.1.10, and 4.1.14 are general thermodynamic relationships for internal energy, enthalpy, and Gibbs free energy (there is a fourth relationship for A, the Helmholtz free energy, that we will not discuss). Since these are general results, they can be applied to a variety of problems.

As a simple example, let us consider the change in Gibbs free energy when the pressure on 1.00 mol of an ideal gas is changed from some initial value p_i to some final value p_f by an unspecified isothermal process. Since the process is isothermal, $dT = 0$, and so from eq 4.1.14 it follows that

$$dG = V dp - S dT = V dp \quad (4.1.15)$$

For an ideal gas $V = nRT/p$, and so

$$\int_i^f dG = \Delta G = \int_i^f V dp = \int_i^f (nRT/p) dp = nRT \ln(p_f/p_i) \quad (4.1.16)$$

While the result in 4.1.16 can be derived in other ways, use of the general relationship in eq 4.1.14 is a particularly simple method for finding ΔG for this process. In addition, if our equation of state were more complicated (the equation of state for a van der Waals gas, for example) we could still use eq 4.1.14 to find ΔG in a straightforward manner.

We will make use of the above general thermodynamic relationships, particularly the one given by eq 4.1.14, in some of the material in the remainder of Chapter 4.

2. Phase diagrams and the Gibbs Phase Rule

A phase diagram is a figure indicating which phase or phases are thermodynamically most stable as a function of the intensive variables used to describe a system. The most common phase diagram is one indicating the various stable phases for a pure chemical substance as a function of temperature and pressure, such as the phase diagram for water in Figure 2 of Handout 2. Other types of phase diagrams, including phase diagrams for mixtures of pure chemical substances, can also be given.

Phase diagrams for several pure substances are given below. Figure 1 shows the phase diagram for water at low and intermediate pressures. There are more than a dozen different solid phases for water, of which only two (Ice I and Ice III) are shown. The additional solid phases for water differ in their crystal structure, and are only stable at high values for pressure. Figure 2 shows the phase diagram for carbon dioxide and for elemental carbon. Note that the diamond form of carbon is thermodynamically the more stable phase at high pressures. However, the phase transition $C(s,diamond) \rightarrow C(s,graphite)$ is an extremely slow process, and so the diamond form of carbon is metastable at room temperature and pressure.

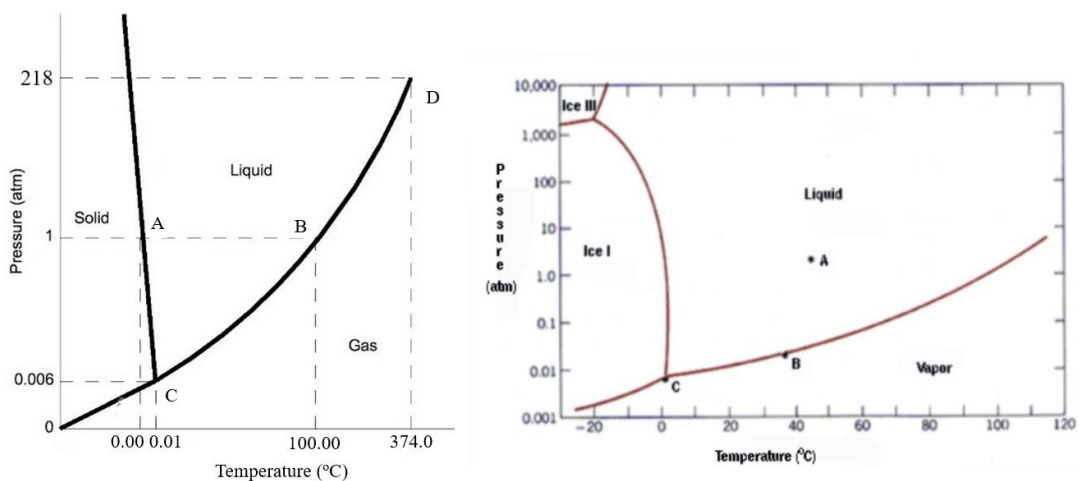


Figure 1. Phase diagram for water. Left – Phase diagram for low pressures. A – normal melting (freezing) point, $p = 1.000 \text{ atm}$, $T = 0.00 \text{ }^\circ\text{C}$; B – normal boiling point, $p = 1.000 \text{ atm}$, $T = 100.00 \text{ }^\circ\text{C}$; C – triple point, $p = 0.006 \text{ atm}$, $T = 0.01 \text{ }^\circ\text{C}$; D – critical point, $p = 218. \text{ atm}$, $T = 374.0 \text{ }^\circ\text{C}$. Right – Phase diagram for high pressures, showing a second solid phase for water (Ice III).

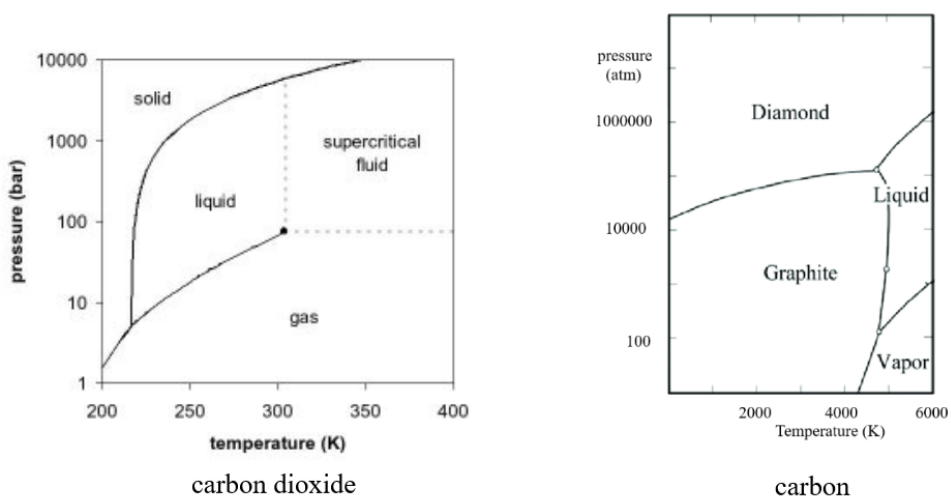


Figure 2. Left – Phase diagram for carbon dioxide. Right – Phase diagram for elemental carbon.

One interesting feature in these sample phase diagrams is that while there can be several different triple points there are no conditions where four or more phases can exist simultaneously at equilibrium. This is a consequence of the Gibbs Phase Rule, which states

$$F = (C - P) + 2 \quad (4.2.1)$$

In this relationship, C is the number of components (pure chemical substances), P is the number of phases, and F is the number of independent intensive variables, called the degrees of freedom, for the system. The phase rule can be proved true but is given here without proof.

For a pure substance, where C = 1, it follows from the phase rule that

$$F = 3 - P \quad (\text{pure substance}) \quad (4.2.2)$$

Examination of the phase diagrams in Figures 1 and 2 shows that they are consistent with the predictions of the phase rule. For example, if we know that only liquid water is present in a system, we need to give both the pressure and temperature to locate where we are at in the phase diagram. If two phases are present, such as solid and liquid water, only a single intensive variable (either pressure or temperature) needs to be given to locate where we are at in the diagram, since the presence of two phases means we must be somewhere on the boundary between phases (so, for example, if we say $p = 1.000$, it follows that $T = 0.00 \text{ }^\circ\text{C}$, the normal freezing point for water). When three phases are present, there are no degrees of freedom, and so we know without any further information our location in the diagram. For example, if for water we have Ice I (the normal solid form of water), liquid, and vapor simultaneously present at equilibrium, the temperature and pressure must be $T = 0.01 \text{ }^\circ\text{C}$ and $p = 0.006 \text{ atm}$, the triple point for water. A hypothetical “quadruple point” would have -1 degrees of freedom, and so cannot occur.

The Gibbs Phase Rule applies to systems of more than one component. It is of use in determining how much information needs to be provided to completely specify the state of a system at equilibrium, and so is of particular interest to chemical engineers and material chemists.

3. Phase transitions, the Clapeyron equation, and the Clausius-Clapeyron equation

Consider a point located on the boundary between two phases, as shown in Figure 3 on the next page. The change in free energy when one mole of substance is transferred from phase 1 to phase 2 is

$$\Delta G_{\text{pt}} = G_2 - G_1 = 0 \quad (4.3.1)$$

where ΔG_{pt} is the change in free energy for the process, and G_1 and G_2 are the free energies of the substance in phase 1 and phase 2. Since at the phase boundary we know the two phases are at equilibrium, it follows that ΔG_{pt} , the change in free energy in going from phase 1 to phase 2, must be equal to zero.

Now, consider changing the temperature of the system by some small amount dT . We also change the pressure by a small amount dp , and do so in such a way that we remain on the boundary between the two phases, as shown in Figure 3. The new value for the change in free energy in going from phase 1 to phase 2 is

$$\Delta G'_{\text{pt}} = G'_2 - G'_1 = 0 \quad (4.3.2)$$

where the ' indicates the new values for ΔG_{pt} , G_1 , and G_2 at the new temperature and pressure. Since the two phases are still in equilibrium, it follows that $\Delta G'_{\text{pt}} = 0$. Since

$$G'_1 = G_1 + dG_1 \quad G'_2 = G_2 + dG_2 \quad (4.3.3)$$

where dG_1 and dG_2 are the change in free energy that occurs when the pressure and temperature are changed as indicated in Figure 3, substitution of these expressions for G'_1 and G'_2 into eq 4.3.2 gives

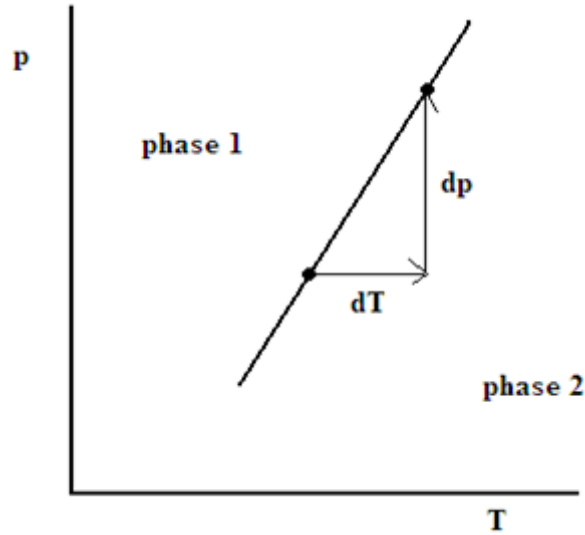


Figure 3. Boundary between two phases.

$$\Delta G'_{pt} = (G_2 + dG_2) - (G_1 + dG_1) = (G_2 - G_1) + (dG_2 - dG_1) = 0 \quad (4.3.4)$$

But the first term on the right in eq 4.3.4 is zero (by eq 4.3.1), and so

$$dG_2 - dG_1 = 0 \quad (4.3.5)$$

However, we have a general expression for dG (eq 4.1.14). Substituting, we get

$$(V_2 dp - S_2 dT) - (V_1 dp - S_1 dT) = 0 \quad (4.3.6)$$

$$(V_2 - V_1) dp - (S_2 - S_1) dT = 0 \quad (4.3.7)$$

$$\Delta V_{pt} dp = \Delta S_{pt} dT \quad (4.3.8)$$

or

$$\frac{dp}{dT} = \frac{\Delta S_{pt}}{\Delta V_{pt}} \quad (4.3.9)$$

Finally, if we recall that at constant pressure and temperature $\Delta S_{pt} = (q_{pt}/T) = (\Delta H_{pt}/T)$, we get as a final result

$$\frac{dp}{dT} = \frac{\Delta H_{pt}}{T \Delta V_{pt}} \quad (4.3.10)$$

the Clapeyron equation. This equation applies to all all simple (first order) phase transitions.

Since when we add heat to a substance to cause a phase transition both ΔH_{pt} and T are positive, the above has an interesting consequence regarding the boundary between phases

If $(dp/dT) > 0$, then $\Delta V_{pt} > 0$ (final state has a larger volume and a smaller density than the initial state)

If $(dp/dT) < 0$, then $\Delta V_{pt} < 0$ (final state has a smaller volume and a larger density than the initial state)

For water, since the liquid phase has a higher density (lower molar volume) than the solid phase, the boundary between the solid and liquid phases has $dp/dT < 0$, and so slopes in the opposite direction from the solid-liquid boundary for most other substances, as can be seen in Figure 1. In addition, for phase transitions where the change in volume is small (such as the $s \rightarrow \ell$ or various $s \rightarrow s$ phase transitions), eq 4.3.10 implies that (dp/dT) will be large. An examination of the phase diagrams that appear in the previous section of this handout confirms this expectation.

Now consider the case of a phase transition from a condensed phase (solid or liquid) to the gas phase. Since $V_g \gg V_s$ or V_ℓ , it follows that

$$\Delta V_{pt} = V_g - V_s \text{ (or } V_\ell) \cong V_g \quad (4.3.11)$$

If we assume ideal behavior for the gas phase (and recall we are considering the conversion of one mole of substance from the initial to the final phase) then

$$\Delta V = V_g = V/n = RT/p \quad (4.3.12)$$

and so

$$\frac{dp}{dT} = \frac{\Delta H_{pt}}{T \Delta V_{pt}} = \frac{\Delta H_{pt}}{T} \frac{p}{RT} = \frac{p \Delta H_{pt}}{RT^2} \quad (4.3.13)$$

Rearranging the above to isolate pressure and temperature on opposite sides of the equation gives

$$\frac{dp}{p} = \frac{\Delta H_{pt}}{R} \frac{dT}{T^2} \quad (4.3.14)$$

But

$$d \ln(p) = \frac{d \ln(p)}{dp} dp = \frac{dp}{p} \quad d(1/T) = \frac{d(1/T)}{dT} dT = -\frac{dT}{T^2} \quad (4.3.15)$$

If we use the relationships in eq 4.3.15 to substitute into eq 4.3.14, we get, after some rearrangement, the result

$$\frac{d \ln(p)}{d(1/T)} = -\frac{\Delta H_{pt}}{R} \quad (4.3.16)$$

the Clausius-Clapeyron equation.

The Clausius-Clapeyron equation may be used to find the enthalpy change for the $s \rightarrow g$ or $\ell \rightarrow g$ phase transitions (sublimation or vaporization) from the slope of a plot of $\ln(p)$ vs $(1/T)$, where p is the vapor pressure of the substance at temperature T . Since ΔH_{pt} is expected to be approximately independent of temperature, eq 4.3.16 implies that a plot of $\ln(p)$ vs $(1/T)$ will give an approximately straight line, from which the enthalpy change for the phase transition can be found. We can, by solving eq 4.3.16 for ΔH_{pt}

$$\Delta H_{pt} = -R (d \ln(p))/(d(1/T)) \quad (4.3.17)$$

use the Clausius-Clapeyron equation as a way of defining the enthalpy of sublimation or enthalpy of vaporization in terms of the derivative $d \ln(p)/d(1/T)$. For precise data, there will be a small amount of curvature in the plot of $\ln(p)$ vs $(1/T)$, in which case the value found for ΔH_{pt} by eq 4.3.17 will exhibit a slight dependence on temperature.

While it is best to find experimental values for ΔH_{sub} or ΔH_{vap} from a plot of $\ln(p)$ vs $(1/T)$, there is a useful equation that can be derived from the Clausius-Clapeyron equation that applies for cases where the vapor pressure is known at two different temperatures

$$\ln(p_2/p_1) = - (\Delta H_p/R) \{ (1/T_2) - (1/T_1) \} \quad (4.3.18)$$

where p_1 is the vapor pressure at a temperature T_1 and p_2 is the vapor pressure at a temperature T_2 . As is the case with the Clausius-Clapeyron equation, the above relationship only applies to phase transitions where the final state is the gas state (that is, sublimation or vaporization).

4. Partial molar quantities

Consider a solution containing two liquids. Let n_A be the moles of A in the solution, and n_B be the moles of B in the solution. We can define the partial molar volume of A ($V_{m,A}$) in terms of the change in the volume of the solution that occurs when a small additional amount of A is added under conditions where pressure, temperature, and the moles of B are kept constant. So

$$V_{m,A} = (\partial V / \partial n_A)_{p,T,nB} \cong (\Delta V / \Delta n_A)_{p,T,nB} \quad (4.4.1)$$

Note that $V_{m,A}$ can be measured experimentally by adding a small amount of A to the solution when pressure, temperature, and the moles of B are kept constant. The partial molar volume of B ($V_{m,B}$) can be defined in a similar manner

$$V_{m,B} = (\partial V / \partial n_B)_{p,T,nA} \cong (\Delta V / \Delta n_B)_{p,T,nA} \quad (4.4.2)$$

Partial molar volumes for cases where there are more than two components can be defined similarly to $V_{m,A}$ and $V_{m,B}$.

For the case of pure liquid A, the partial molar volume of A is simply equal to the molar volume of the pure liquid, which can be found from the density of the liquid. However, the value for partial molar volume usually changes as the composition of a solution changes. For example, if we add 50.0 mL of water to 50.0 mL of ethyl alcohol, the total volume of the solution that forms is not 100.0 mL, but about 96.0 mL. That is because the partial molar volumes for water and ethanol in a water+ethanol solution are different than for the pure liquids. The reason for this is that the intermolecular forces of attraction between water molecules and molecules of ethyl alcohol are different than those of water molecules with other water molecules or ethyl alcohol with other molecules of ethyl alcohol.

The total volume of a solution of two liquids is given by the expression

$$V = n_A V_{m,A} + n_B V_{m,B} \quad (4.4.3)$$

Notice that there is nothing in eq 4.4.3 that requires that the partial molar volume of a component in a solution be a positive number, even though the total volume (V) must be positive. In rare cases negative values for partial molar volume have been found. For example, the partial molar volume of magnesium sulfate ($MgSO_4$) in pure water is $V_m = -0.8$ mL/mol at $T = 25.0$ °C. This occurs because the strong attractive forces between magnesium ions (Mg^{2+}) or sulfate ions (SO_4^{2-}) with water molecules causes the volume to shrink by a small amount when magnesium sulfate is added to water. The partial molar volume of water in the solution is positive, and the total volume, calculated using eq 4.4.3, is also positive.

By analogy with partial molar volume, the partial molar Gibbs free energy of substance A in a solution of A and B ($G_{m,A}$) is defined in terms of the change in free energy of the solution when a small number of moles of A are added under conditions where pressure, temperature, and moles of B are kept constant. So

$$G_{m,A} = (\partial G / \partial n_A)_{p,T,nB} \cong (\Delta G / \Delta n_A)_{p,T,nB} \quad (4.4.4)$$

For B, $G_{m,B}$ is defined as

$$G_{m,B} = (\partial G / \partial n_B)_{p,T,n_A} \cong (\Delta G / \Delta n_B)_{p,T,n_A} \quad (4.4.5)$$

This is more abstract than partial molar volume, and is in fact more difficult to visualize, but it is exactly the same concept used in defining the partial molar volume (or any other partial molar quantity).

The partial molar Gibbs free energy is so important that it is given its own name, chemical potential, and its own symbol μ_A . So

$$\mu_A = G_{m,A} = (\partial G / \partial n_A)_{p,T,n_B} \quad \mu_B = G_{m,B} = (\partial G / \partial n_B)_{p,T,n_A} \quad (4.4.6)$$

As was the case with total volume, the total Gibbs free energy for a solution is given by the expression

$$G = n_A G_{m,A} + n_B G_{m,B} = n_A \mu_A + n_B \mu_B \quad (4.4.7)$$

From now on in discussing the free energy for systems we will use the symbols μ_A and μ_B , and the term chemical potential, rather than the symbols $G_{m,A}$ and $G_{m,B}$, and the term partial molar Gibbs free energy, though these of course mean the same thing.

The advantage of using chemical potential in discussing the thermodynamic behavior of systems is that it gives a simple way of describing the thermodynamic properties of both real and ideal substances. In general, the chemical potential of a substance can be written as

$$\mu_A = \mu_A^\circ + RT \ln(a_A) \quad (4.4.8)$$

where μ_A° is the chemical potential of A for some reference state (chosen for convenience) and a_A , the activity of A, accounts for the difference in chemical potential for a substance if the conditions are not standard conditions and also for any non-ideal behavior for A. For example, we previously showed (eq 4.1.16) that the change in free energy when the pressure of an ideal gas is changed from an initial value p_i to a final volume p_f by an isothermal process is

$$\Delta G_A = \int_i^f V dp = \int_i^f (n_A RT / p) dp = n_A RT \ln(p_{A,f} / p_{A,i}) \quad (4.4.9)$$

where we have modified the result from eq 4.1.16 to apply it to a component in a mixture of ideal gases. If we divide eq 4.4.9 by n_A , we get

$$\Delta G_A / n_A = \mu_A - \mu_A^\circ = RT \ln(p_A / p^\circ) \quad (4.4.10)$$

or

$$\mu_A = \mu_A^\circ + RT \ln(p_A / p^\circ) = \mu_A^\circ + RT \ln(a_A) \quad (4.4.11)$$

where we chosen $p_i = p^\circ = 1.00$ bar as our reference pressure. By comparing eq 4.4.11 to 4.4.8 the activity of A is $a_A = (p_A / p_A^\circ) = (p_A / 1 \text{ bar})$. Note that activity does not have units. Also note that we often write the activity of an ideal gas as $a_A = p_A$, where division by our standard pressure $p^\circ = 1.00$ bar is implied.

The chemical potential and activity for a number of common situations are summarized below:

pure solid or pure liquid	$\mu_A = \mu_A^\circ$	$a_A = 1$	
solvent	$\mu_A \cong \mu_A^\circ$	$a_A \cong 1$	
ideal gas	$\mu_A = \mu_A^\circ + RT \ln(a_A)$	$a_A = p_A / p^\circ$	$p^\circ = 1.00 \text{ bar}$
ideal solute (in terms of molarity)	$\mu_A = \mu_A^\circ + RT \ln(a_A)$	$a_A = [A] / [A]^\circ$	$[A]^\circ = 1.00 \text{ mol/L}$

The activity of a pure solid or liquid is 1. Since in a solution the solvent is the major component, it has an activity that is approximately equal to 1. For ideal gases, activity is written in terms of a reference pressure $p^\circ = 1.00 \text{ bar}$ (approximately equal to 1.00 atm), while for solutes, activity is written in terms of a reference concentration $[A]^\circ = 1.00 \text{ mol/L}$. For gases and solutes, we often write $a_A = p_A$ (for an ideal gas) and $a_A = [A]$ (for an ideal solute), where division by standard pressure or standard concentration is implied. Note that in all cases chemical potential is written in terms of a value that applies for a particular reference state, plus an additional terms that in the case of gases or solutes accounts for the conditions being different than those of the reference state, and which can also be used to include non-ideal behavior. Although we will usually assume ideal behavior, one of the main advantages of chemical potential is that it can be used for real systems as well as ideal systems.

5. Thermodynamics of mixing

As an example of the use of chemical potential consider the mixing of two pure ideal gases, as shown in Figure 4. A closed system is divided into two parts using a thin barrier. On the left there are n_A moles of gas A, and on the right there are n_B moles of gas B. Both gases are at the same temperature and pressure. Note that the volumes containing the two gases will in general not be equal.

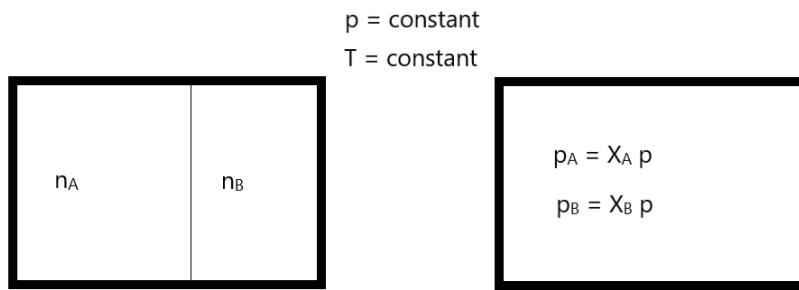


Figure 4. Mixing of ideal gases. The initial state has n_A moles of A and n_B moles of B, at the same pressure and temperature, separated by a thin barrier. After the barrier is removed and sufficient time has passed, the gases will form a homogeneous mixture as their final state.

To allow the gases to mix, the barrier between the gases is removed. The final result will be a homogeneous mixture of A and B. Since the total pressure of gas will be p , the partial pressures of A and B will be given by Dalton's Law

$$p_A = X_A p \qquad p_B = X_B p \qquad (4.5.1)$$

where X_A and X_B are the mole fractions of A and B in the gas mixture.

The change in free energy for the above process, called the free energy of mixing, is

$$\Delta G_{\text{mix}} = G_{\text{final}} - G_{\text{initial}} \qquad (4.5.2)$$

The initial value for free energy is

$$G_{\text{initial}} = G_{\text{initial,A}} + G_{\text{initial,B}} = n_A (\mu_A^\circ + RT \ln p) + n_B (\mu_B^\circ + RT \ln p) \qquad (4.5.3)$$

where we have used eq 4.4.11 for the chemical potential of an ideal gas. The final value for free energy is

$$G_{\text{final}} = G_{\text{final,A}} + G_{\text{final,B}} = n_A (\mu_A^\circ + RT \ln p_A) + n_B (\mu_B^\circ + RT \ln p_B) \qquad (4.5.4)$$

So

$$\begin{aligned} \Delta G_{\text{mix}} = G_{\text{final}} - G_{\text{initial}} = & [n_A (\mu_A^\circ + RT \ln p_A) + n_B (\mu_B^\circ + RT \ln p_B)] \\ & - [n_A (\mu_A^\circ + RT \ln p) + n_B (\mu_B^\circ + RT \ln p)] \end{aligned} \quad (4.5.5)$$

Terms involving μ_A° and μ_B° cancel. We can combine the \ln terms to get

$$\Delta G_{\text{mix}} = n_A (RT \ln p_A/p) + n_B (RT \ln p_B/p) \quad (4.5.6)$$

But for ideal gases, $p_A = X_A p$ and $p_B = X_B p$, and so

$$\Delta G_{\text{mix}} = n_A (RT \ln X_A) + n_B (RT \ln X_B) \quad (4.5.7)$$

Finally, if we multiply and divide each term on the right by $n = n_A + n_B$, the total number of moles of gas, and then factor out nRT from both terms, we get as a final result

$$\Delta G_{\text{mix}} = nRT [X_A \ln X_A + X_B \ln X_B] \quad (4.5.8)$$

Since X_A and X_B must have values between 0 and 1, both \ln terms will be negative, and so ΔG_{mix} will also be negative, as expected, since mixing of ideal gases at constant temperature and pressure is a spontaneous process.

Values for the change in other thermodynamic quantities can also be found. Since enthalpy for an ideal gas only depends on temperature, and since the above mixing process is isothermal, it follows that $\Delta H_{\text{mix}} = 0$. For the entropy change for mixing

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (4.5.9)$$

Solving for ΔS_{mix} , and substituting for ΔG_{mix} and ΔH_{mix} , we get

$$\Delta S_{\text{mix}} = - nR [X_A \ln X_A + X_B \ln X_B] \quad (4.5.10)$$

An important point to note in the above result is that we do not need to know the values for μ_A° and μ_B° , the chemical potential for A and B in our reference state. This is a general result. Because we are always concerned with changes in free energy for various processes, terms involving the free energy for substances in their reference state will always drop out, which means we do not need to know their value.

For liquids that form ideal solutions $\Delta H_{\text{mix}} = 0$, and ΔG_{mix} and ΔS_{mix} are given by eq 4.5.8 and 4.5.10. However, as we will discover in the next section, it is unusual for real liquids to form ideal solutions.

6. Ideal and non-ideal liquid solutions

Consider a pure liquid in equilibrium with its vapor at a particular temperature T . The observed equilibrium pressure is called the vapor pressure of the pure liquid, and given the symbol p_A^* where the $*$ indicates that p_A^* is a property of a pure substance. This vapor pressure is governed by the Clapeyron equation (eq 4.3.10) and, to a good approximation, by the Clausius-Clapeyron equation (eq 4.3.16).

Now consider a homogeneous mixture of two volatile liquids A and B at a particular temperature T , called a binary solution (recall that the term volatile refers to a pure liquid or solid that has a significant vapor pressure). The vapor pressure for A, p_A , is defined as the partial pressure of A above the liquid solution at equilibrium. p_B , the vapor pressure for B, is defined in the same way, as the equilibrium partial pressure of B above the liquid solution.

The dependence of vapor pressure on the composition of the liquid solution is generally complicated, due to the fact that the molecules making up the liquid solution are in close contact with one another. This means that, unlike a mixture of gases, the interaction forces between molecules are important in determining the properties of the solution.

However, there are cases where the behavior of one or both of the components of a liquid solution follows a simple expression, called Raoult's law

$$p_A = X_A p_A^* \quad (4.6.1)$$

In the above equation p_A is the equilibrium vapor pressure of A above a liquid solution of A and B, X_A is the mole fraction of A in the liquid, and p_A^* is the vapor pressure of pure liquid A.

We may use Raoult's law to define an ideal liquid solution. An ideal solution of two liquids is a solution where each component obeys Raoult's law, so that

$$p_A = X_A p_A^* \qquad p_B = X_B p_B^* \quad (4.6.2)$$

In a solution of two liquids there are three types of intermolecular interactions: A•••A interactions, B•••B interactions, and A•••B interactions. For a solution to be close to ideal in behavior we require that both A and B are nonpolar (or slightly polar) molecules, so that all of the interactions are weak. It is also more likely for A and B to form an ideal solution if the molecules have approximately the same size and shape. This means that ideal liquid solutions are relatively uncommon, unlike mixtures of gases, which generally behave ideally at low or moderate pressures.

An example of an ideal solution of two liquids is given in Figure 5, which shows a plot of the partial pressure of benzene (B) and toluene (T) above a liquid solution of the two compounds. For the conditions in the figure benzene and toluene form a nearly ideal solution. One characteristic of an ideal liquid solution is that the partial pressure for each component as a function of mole fraction is a straight line, a consequence of Raoult's law. This behavior is seen in the benzene + toluene solution. From this diagram the values for the vapor pressure of the pure liquids can be found. They are $p_B^* = 72.0$ torr (corresponding to the vapor pressure of benzene when $X_B = 1$) and $p_T^* = 23.5$ torr (corresponding to the vapor pressure of toluene when $X_T = 1$, which occurs when $X_B = 0$).

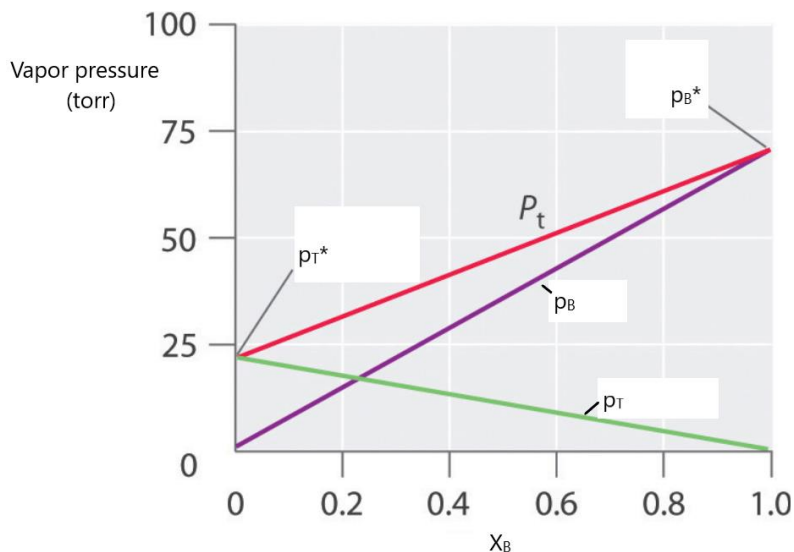


Figure 5. Vapor pressure of benzene ($B = C_6H_6$) and toluene ($T = C_6H_5CH_3$) above a liquid solution of benzene and toluene, at $T = 20.0$ °C. Vapor pressure is given as a function of X_B , the mole fraction of benzene in the liquid phase. The total pressure, p_t , is also shown.

Examples of non-ideal binary liquid solutions are given in Figure 6. In both examples it is clear that non-ideal solutions have formed, as the plots of partial pressure vs mole fraction are curves instead of straight lines. For the carbon disulfide + acetone solution the actual values for partial pressure are larger than those predicted for an ideal solution, indicating that the forces of attraction between carbon disulfide molecules and acetone molecules are weaker than expected for ideal behavior. For the trichloromethane + acetone solution the values for partial pressure are smaller than those predicted for an ideal solution, indicating that the forces of attraction between trichloromethane molecules and acetone molecules are larger than expected for ideal behavior.

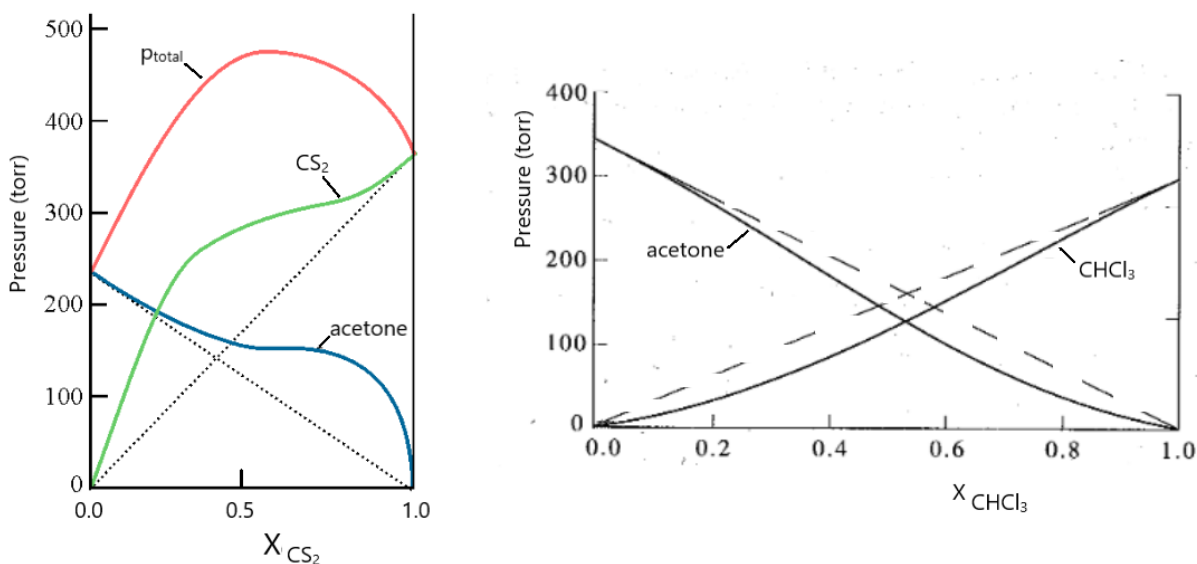


Figure 6. Left – Solution of carbon disulfide (CS_2) and acetone, at $T = 25.0\text{ }^\circ\text{C}$. Right – Solution of trichloromethane (CHCl_3) and acetone, at $T = 25.0\text{ }^\circ\text{C}$. In both figures dashed lines show the behavior that would occur if Raoult's law were obeyed and an ideal solution formed.

Note that even when a solution exhibits non-ideal behavior it is still possible to determine the vapor pressures for the pure liquids from the pressure vs mole fraction plot. For example, for the carbon disulfide + acetone diagram, $p_{\text{CS}_2}^* = 355\text{ torr}$ and $p_{\text{ace}}^* = 225\text{ torr}$.

Binary solutions of volatile liquids are an example of a system where it is relatively easy to find the chemical potential even when non-ideal behavior occurs. The general expression for the chemical potential of a volatile liquid in a binary solution is

$$\mu_A = \mu_A^\circ + RT \ln(a_A) \quad a_A = p_A/p_A^* \quad (\text{real or ideal solution}) \quad (4.6.3)$$

where p_A is the partial pressure of A above the liquid solution, and p_A^* is the vapor pressure of pure A. Equation 4.6.3 is true for both real and ideal solutions.

For an ideal solution $p_A = X_A p_A^*$. Substitution of this result into eq 4.6.3 gives as a result

$$\mu_A = \mu_A^\circ + RT \ln(X_A) \quad (\text{ideal solution}) \quad (4.6.4)$$

There are two additional statements that can be made concerning binary liquid solutions. First, all components in a liquid solution obey Raoult's law in the limit of their mole fraction approaching 1. That means that the behavior of solvents is close to ideal, and approaches ideal behavior as $X_{\text{solvent}} \rightarrow 1$. Second, if there is a solute in a binary mixture of liquids it will obey a relationship called Henry's law

$$p_B = K_H X_B \quad (4.6.5)$$

where p_B is the partial pressure of solute (B) above the solution, X_B is the mole fraction of solute in the liquid phase, and K_H is the Henry's law constant. Values for K_H depend on the solvent, solute, and temperature, and are found experimentally.

There are other ways in which Henry's law can be written. A particularly useful form for finding the concentration of a dissolved gas in a liquid is

$$[B] = K_H' p_B \quad (4.6.6)$$

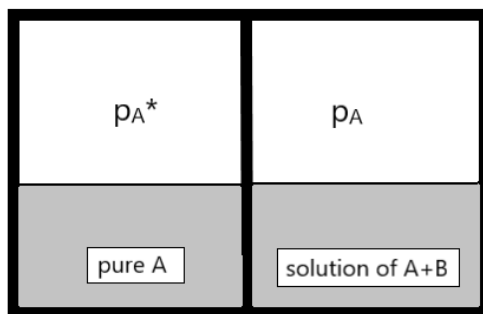
where $[B]$ is the molar concentration of dissolved gas at equilibrium when the partial pressure of the gas is p_B , and K_H' is the Henry's law constant (the symbol K_H' is used because the numerical value and units for this constant will be different from those for K_H in eq 4.6.5). For most gases and solvents the value for K_H' decreases with increasing temperature, indicating the general tendency of gases to become less soluble in liquids as temperature increases. This is the opposite behavior from that normally observed for solids, which usually are more soluble in liquids at high temperature than at low temperature.

7. Colligative properties

The term colligative property refers to a property of a solution of a volatile solvent and a non-volatile solute that at most depends on the physical properties of the solvent and the concentration of solute particles. There are four colligative properties, as discussed below.

Vapor pressure lowering. Consider the system shown in Figure 7. A closed system is divided into two parts. The left side of the system contains pure liquid A in equilibrium with its vapor, while the right side of the system contains a solution of A and a non-volatile solute in equilibrium with its vapor. Both sides of the system are at the same temperature. Since the left side contains pure liquid A, the equilibrium pressure of A is p_A^* , the vapor pressure of the pure liquid. Experimentally it is observed that $p_A^* > p_A$, that is, that the partial pressure of A above the pure liquid is higher than p_A , the partial pressure of A above the solution of A and B. The vapor pressure lowering (Δp_A) is defined as

$$\Delta p_A = p_A^* - p_A \quad (4.7.1)$$



T = constant

Figure 7. Left – Pure A in equilibrium with its vapor. Right – A solution of A and B in equilibrium with its vapor.

For ideal behavior an expression for Δp_A can be found as follows. Since all solvents obey Raoult's law in the limit $X_A \rightarrow 1$, it follows that for dilute solutions $p_A = X_A p_A^*$. Substitution of this result into eq 4.7.1 gives

$$\Delta p_A = p_A^* - p_A = p_A^* - X_A p_A^* = (1 - X_A) p_A^* = X_B p_A^* \quad (4.7.2)$$

where we have used the relationship $X_A + X_B = 1$. Note that since p_A^* is a physical property of the solvent and X_B , the mole fraction of solute, is one way of expressing solute particle concentration, vapor pressure lowering satisfies the definition of a colligative property.

Boiling point elevation and freezing point depression. Figure 8 shows a pure liquid A and a solution of A and B under conditions of constant pressure (usually chosen to be $p = 1.00$ atm). Experimentally, it is observed that the boiling point of the solution is higher than that of the pure liquid, and the freezing point of the solution is lower than that of the pure liquid. We therefore define the **boiling point elevation** (ΔT_b) and **freezing point depression** (ΔT_f) as follows

$$\Delta T_b = T_b - T_b^* \qquad \Delta T_f = T_f^* - T_f \quad (4.7.3)$$

In the above expressions T_b^* and T_f^* are the boiling point and freezing point of pure liquid A (and so are the normal boiling and freezing point if $p = 1.00$ atm), and T_b and T_f are the boiling point and freezing point of the solution of A and B. ΔT_b and ΔT_f have been defined so that both are positive numbers.

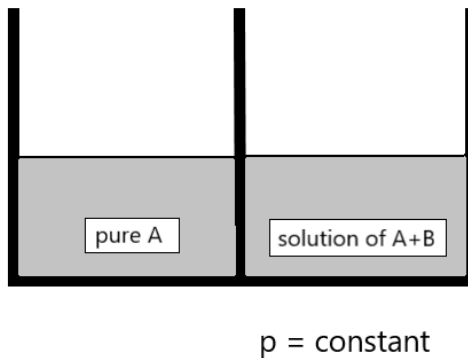


Figure 8. Left – Pure A. Right – A solution of A and B.

Assuming ideal behavior, an expression for ΔT_b and ΔT_f can be derived. The result (not derived) is

$$\Delta T_b = K_b m_B \quad (4.7.4)$$

$$\Delta T_f = K_f m_B \quad (4.7.5)$$

where m_B is the molality of solute particles and K_b and K_f are the **boiling point elevation constant** and **freezing point depression constant**. Values for K_b and K_f are different for different solvents, and are usually found from experiment. However, the derivation of eq 4.7.4 and 4.7.5 gives the following expressions for K_b and K_f

$$K_b = \frac{R (T_b^*)^2 M_A}{\Delta H^\circ_{\text{vap}}} \qquad K_f = \frac{R (T_f^*)^2 M_A}{\Delta H^\circ_{\text{fus}}} \quad (4.7.6)$$

where T_b^* and T_f^* are the boiling point and freezing point temperatures for the pure liquid, and M_A is the molecular weight of the liquid (expressed in units of kg/mol). Values for K_b and K_f calculated using eq 4.7.6 usually agree with those found from experiment to within a few percent, indicating that the assumptions made in deriving eq 4.7.4 and eq 4.7.5 are valid.

Osmotic pressure. Figure 9 shows a sample of pure liquid A and a solution of A and a non-volatile solute, separated by a semipermeable membrane. The membrane allows solvent molecules (A) to pass through, but prevents solute particles from moving from the solution to the pure solvent. The osmotic pressure (Π) of the solution (relative to pure liquid A) is defined as the additional pressure that must be applied on the solution to keep the level of liquids equal on both sides.

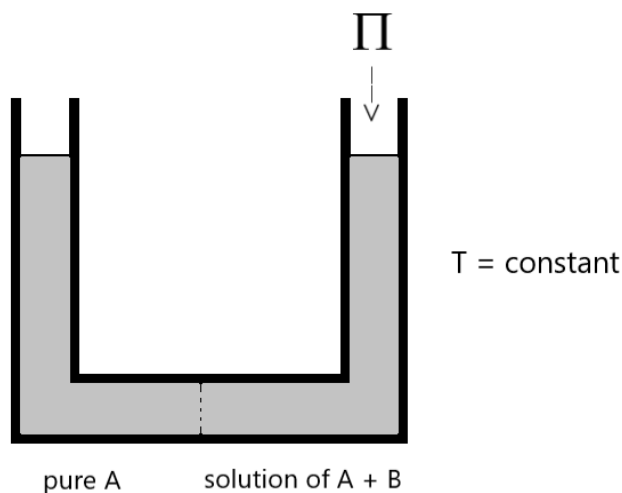


Figure 9. A pure liquid (left) and solution of liquid and non-volatile solute (right) separated by a semipermeable membrane. Π is the osmotic pressure of the solution relative to the pure liquid.

Experimentally, it is found for dilute solutions the osmotic pressure is given by the equation

$$\Pi = [B] RT \quad (4.7.7)$$

where $[B]$ is the molarity of solute particles in the solution (in units of moles/L), R is the gas constant, and T is temperature. As is the case for the other colligative properties, eq 4.7.7 can be derived.

In all of the equations for the colligative properties the concentrations used are the total concentration of solute particles in solution. For example, if a solution of water and sugar contains 0.010 mol/L of glucose and 0.030 mol/L of sucrose, the molarity of solute particles is 0.010 mol/L + 0.030 mol/L = 0.040 mol/L. It is the total molar concentration that is used to find osmotic pressure in eq 4.7.7

One complicating factor in using the equations for the colligative properties is that for soluble ionic compounds (and occasionally for other cases) the number of solute particles will be different than the solute concentration. For example, a 0.200 mol/kg solution of potassium sulfate (K_2SO_4) in water will have a molality of solute particles equal to 0.600 mol/kg. This is because potassium sulfate forms ions when added to water, by the process



Addition of potassium sulfate to water gives three particles per formula unit of compound.

One way of accounting for the difference between the concentration of a solute and the concentration of solute particles is by defining a quantity called the van't Hoff factor (i), given by the expression

$$i = \frac{\text{moles of particles}}{\text{moles of solute}} \quad (4.7.9)$$

For a non-ionizing solute like glucose in water $i = 1$. For an ionic compound dissolved in water the value for the van't Hoff factor will depend on the compound. For example, $i = 2$ for NaCl, $i = 3$ for K_2SO_4 , and $i = 4$ for $Fe(NO_3)_3$. Since the colligative properties all use concentrations of solute particles, ionization or other processes that give a different concentration of particles than the concentration of solute must be taken into account.

Studies of the colligative properties of solutions can be used to find information about non-ideal solution behavior. For example, Table 1 compares the theoretical and experimental values for the van't Hoff factor for sodium chloride in water. For dilute solutions the value for i is close to the theoretical value, indicating that dilute solutions show approximately ideal behavior. As solute concentration increases, the difference between the theoretical and experimental values for the van't Hoff factor increase, indicating that more concentrated solutions are less ideal than dilute solutions. Various models, such as Debye-Huckel theory, have been developed to describe the non-ideal behavior of ions in aqueous solution.

Table 1. Experimental and theoretical values for the van't Hoff factor for NaCl in water, $T = 20.0\text{ }^\circ\text{C}$

m_{NaCl} (mol/kg)	i (theory)	i (experiment)
0.0001	2.000	1.99
0.0010	2.000	1.97
0.0100	2.000	1.94
0.1000	2.000	1.87

For cases where experimental data are available, modified equations for the colligative properties that account for non-ideal behavior can be found using a method similar to that used to develop the virial equations describing the non-ideal behavior of a gas. For example, a modified equation for osmotic pressure can be written as

$$\Pi = [B] RT \{ 1 + a [B] + b [B]^2 + \dots \} \quad (4.7.10)$$

Values for the constants a , b , ... are found by fitting experimental data to eq 4.7.10. Notice that for dilute solutions where $[B] \rightarrow 0$, eq 4.7.10 reduces to eq 4.7.7, the expression for osmotic pressure for ideal solution behavior.

8. Phase diagrams for binary solutions

In section 2 of the Chapter 4 notes we discussed phase diagrams for pure chemical substances. Phase diagrams can also be given for systems containing two or more components (called binary systems). Such diagrams are more complicated than one component phase diagrams, but have a number of important practical applications.

Consider a two component system with a liquid phase and a vapor phase. By the Gibbs Phase Rule (eq 4.2.1) we may say

$$F = (C - P) + 2 = (2 - P) + 2 = 4 - P \quad (4.8.1)$$

Equation 4.8.1 tells us that the number of degrees of freedom (independent intensive variables) depends on the number of phases that are present in the system.

As an example of a two component phase diagram consider the system given in Figure 10 on the next page. The pressure of the system is held constant at $p = 1.00\text{ atm}$. The number of degrees of freedom therefore depends on the number of phases present. In the region below the bottom curve or above the top curve there is a single phase present, and so $F = 4 - 1 = 3$. Specifying the pressure of the system uses one degree of freedom, and so temperature and mole fraction would provided the other two degrees of freedom for the system.

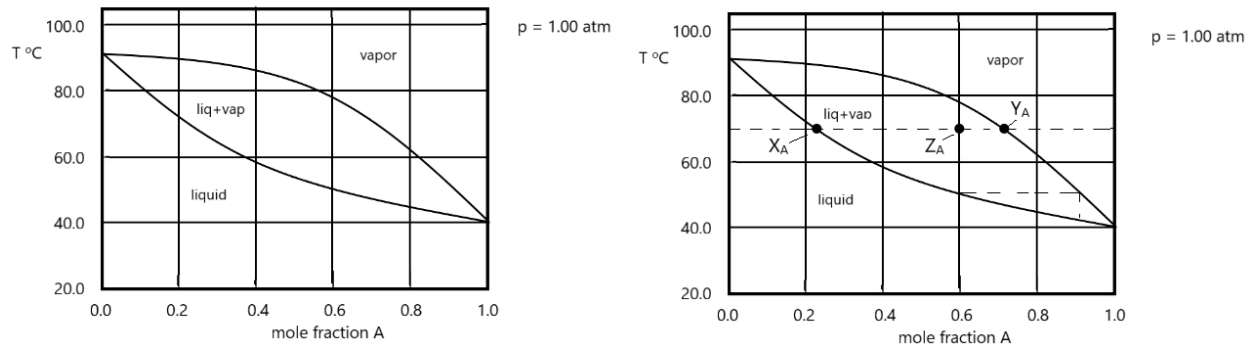


Figure 10. Left - Phase diagram for a two component system. Right – The same phase diagram, indicating the points X_A , Y_A , and Z_A when $T = 70.0\text{ }^\circ\text{C}$, and the composition of the liquid collected from the distillation of a solution with an initial value $X_A = 0.60$.

In the region between the two curved lines there are two phases present, a liquid phase and a vapor phase, and so $F = 4 - 2 = 2$. One degree of freedom is accounted for by specifying the pressure. The second degree of freedom can be accounted for by providing the value for temperature.

Before proceeding, let us define the following terms:

$Z_A =$ mole fraction of A in the system; $Z_A = n_A/(n_A+n_B)$

$X_A =$ mole fraction of A in the liquid phase; $X_A = n_A(\ell)/(n_A(\ell)+n_B(\ell))$

$Y_A =$ mole fraction of A in the gas phase; $Y_A = n_A(g)/(n_A(g)+n_B(g))$

In the two phase region, a vertical line drawn at the temperature of the system will cut the curved lines that represent the boundaries of the two phase region at two points. The point where the line cuts the boundary between the liquid phase and the two phase region occurs at X_A , and represents the composition of the liquid phase. The point where the line cuts the boundary between the vapor phase and the two phase region occurs at Y_A , and represents the composition of the vapor phase. Note that any value of Z_A between these two points will result in two phases in the system. The value for Z_A therefore does not affect the composition of the liquid or vapor phase, but only the relative number of moles of liquid and vapor, which are extensive quantities. Therefore, within the two phase region specifying pressure and temperature is sufficient to describe all of the intensive properties of the system, consistent with the phase rule.

To find the relative number of moles in the liquid and vapor phase in the two phase region, we start by looking at a system whose mole fraction of A is given by Z_A , and which is within the two phase region. The mole fraction of A in the liquid phase is X_A , and the mole fraction in the vapor phase is Y_A , as shown in Figure 10. The total number of moles of A in the system is give by the expression

$$n_A = Z_A n = Z_A (n(\ell) + n(g)) = Z_A n(\ell) + Z_A n(g) \quad (4.8.2)$$

where $n(\ell)$ is the total moles of liquid, $n(g)$ is the total moles of vapor, and $n = n(\ell) + n(g)$ is the total number of moles in the system. But the moles of A in the system is also given by the expression

$$n_A = X_A n(\ell) + Y_A n(g) \quad (4.8.3)$$

Setting eq 4.8.2 and 4.8.3 equal gives

$$Z_A n(\ell) + Z_A n(g) = X_A n(\ell) + Y_A n(g) \quad (4.8.4)$$

$$Z_A n(\ell) - X_A n(\ell) = Y_A n(g) - Z_A n(g) \quad (4.8.5)$$

$$(Z_A - X_A) n(\ell) = (Y_A - Z_A) n(g) \quad (4.8.6)$$

Or, finally

$$\frac{n(\ell)}{n(g)} = \frac{(Y_A - Z_A)}{(Z_A - X_A)} \quad (4.8.7)$$

Since $Y_A - Z_A$ and $Z_A - X_A$ represent the length of the lines connecting Z_A to Y_A or X_A , eq 4.8.7 is often called the lever rule.

Qualitatively, we may say that the shorter lever corresponds to the phase with the larger relative number of moles. For example, in Figure 10 the length of the lever $Y_A - Z_A$ is shorter than the lever $Z_A - X_A$, and so we expect the number of moles of vapor to be larger than the number of moles of liquid.

Figure 10 can also be used to show how it is possible to purify a liquid. Consider a liquid with $Z_A = 0.60$, heated until it just begins to boil. If the vapor is collected and condensed, the liquid formed will have $X_A = 0.92$, a significant enrichment in the mole fraction of A. This process of purification by collecting the vapor produced from boiling a liquid solution is called distillation.

Figure 11 shows an apparatus for carrying out the process of distillation. The liquid being distilled is in the left flask. The vapor produced when the liquid boils is cooled by a water jacketed condenser to convert the vapor into liquid and collected in the right flask. This process is called simple distillation.

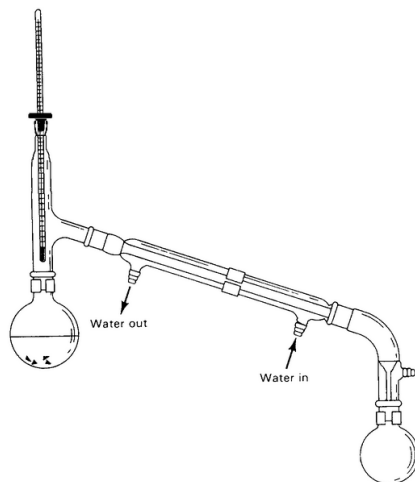


Figure 11. Apparatus for simple distillation of a liquid.

The efficiency of distillation is often discussed in terms of theoretical plates, where one theoretical plate corresponds to the purification achieved by a perfect simple distillation. A more complicated apparatus than the one in Figure 11 can be used to carry out fractional distillation, with a typical purification efficiency of 1-20 theoretical plates. Gas chromatography (GC), a common analytical technique, can have a value of 10^4 or higher theoretical plates. Gas chromatography is a useful technique for separating and analyzing mixtures of substances, but does not usually produce enough product to be a useful purification technique.

Two component solutions can also show more complicated behavior. Figure 12 shows the phase diagram for water + ethyl alcohol. For this system there is an azeotrope, defined as a solution that, like a pure liquid, has a single boiling point temperature. For water + ethyl alcohol, the azeotrope occurs at $X_E = 0.92$ and $T = 78.2^\circ\text{C}$. Since the azeotrope boils at a temperature below that of pure ethyl alcohol ($T = 78.5^\circ\text{C}$) or water ($T = 100.0^\circ\text{C}$), it is termed a low boiling azeotrope. Binary systems with high boiling azeotropes, where the boiling point of the azeotrope is higher than that of either of the pure liquids in the binary solution, also occur. Azeotropes containing three or more substances also exist but will not be discussed here.

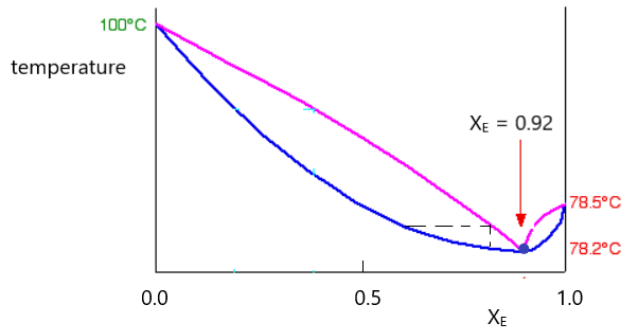


Figure 12. Phase diagram for water + ethyl alcohol. An azeotrope occurs at $X_E = 0.92$, $T = 78.5^\circ\text{C}$.

Formation of an azeotrope has important consequences for purification of liquids by distillation. Consider a solution whose mole fraction ethyl alcohol is $X_E = 0.60$, as shown in Figure 12. A simple distillation will increase the mole fraction of ethyl alcohol to $X_E = 0.80$. Additional distillation will increase the purity, but unlike the example shown in Figure 10, the maximum purity that can be obtained is $X_E = 0.92$, the mole fraction of the azeotrope. Distillation of the azeotropic mixture results in a vapor with the same composition as the liquid, and so no increase in purity. Azeotropic mixtures are common, and other methods have to be used to obtain a pure liquid from an azeotrope.

Note that although the water + ethyl alcohol system shows unusual behavior, the lever rule can still be used to find the relative number of moles of liquid and vapor in the two phase region of the system.

As a final example, the phase diagram for two partially miscible liquids is given in Figure 13. In the region under the curve two liquid phases are present, with composition $X_{A,\text{low}}$ (liquid phase with the lower value for mole fraction A) and $X_{A,\text{high}}$ (liquid phase with the higher value for mole fraction A). Outside of that region only a single liquid phase is present, indicating the formation of a homogeneous mixture (a solution).

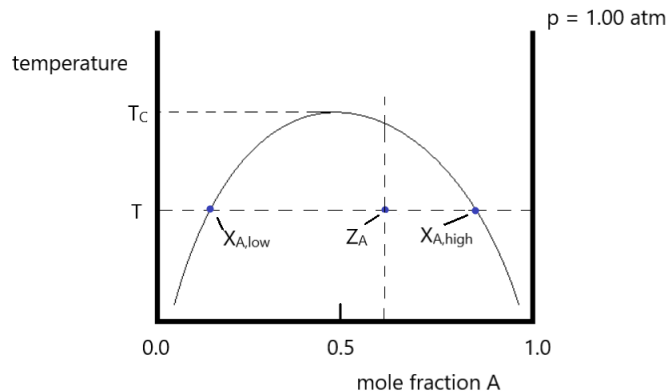


Figure 13. Phase diagram for two partially miscible liquids A and B. $X_{A,\text{low}}$ and $X_{A,\text{high}}$ are the mole fractions of A for the two liquid phases at temperature T . T_C is the critical temperature for the system.

Within the region where two distinct liquid phases exist, the lever rule applies, and can be used to find the relative number of moles of each of the two liquid phases. In the example in Figure 13, the lever going from Z_A to $X_{A,\text{high}}$ is shorter than that going from Z_A to $X_{A,\text{low}}$, and so there will be a larger number of moles of the liquid phase with mole fraction $X_{A,\text{high}}$. Equation 4.8.7, suitably modified, can be used to find the relative number of moles of each of the liquid phases.

At a sufficiently high temperature the two liquids in Figure 13 will always form a single liquid phase. When $T > T_C$, the upper critical temperature, a single liquid phase will form no matter what the value for Z_A . Below T_C , there are values for Z_A that will lead to the formation of two distinct liquid phases. It is also possible for some binary solutions to have a lower critical temperature, meaning that solutions with $T < T_C$ will always form a single liquid phase, while those with $T > T_C$ will sometimes form two distinct liquid phases. There are even a few rare cases where a binary mixture of liquids has both an upper critical temperature and a lower critical temperature.

There are many other examples of phase diagrams for binary systems, such as for systems with a solid and one or more liquid phase. Many of the things we discussed in the examples above, such as the lever rule, can be applied to these systems. Phase diagrams for multicomponent systems can also be given, but are generally much more difficult to represent in simple phase diagrams.