Chapter 6 – Multiphase Systems

Single-Component Systems

Phase Diagram: a plot that shows conditions under which a pure substance exists in a particular phase – e.g. a liquid, a solid, or a gas. Often, the y-axis indicates pressure and the x-axis the temperature.

On the above phase diagram:
Where does boiling occur?
Where does sublimation occur?
Where does melting take place?
Where can solid, liquid, and gas coexist?
What is the difference between a vapor and a gas?
Where does the substance exist as a single phase?

Vapor-liquid equilibrium (VLE) curve: the locus of points for which liquid and vapor can coexist.

In the above figure, where is the solid-vapor equilibrium curve? And where is the solid-liquid equilibrium curve?

Vapor pressure: the pressure of vapor when it is in equilibrium with the liquid or solid phase. For a point \((T,P)\) on the vapor-liquid equilibrium curve, \(P\) is the vapor pressure of the liquid. For a point \((T,P)\) on the solid-vapor equilibrium curve, \(P\) is the vapor pressure of the solid.
**Boiling point temperature:** for a point \((T,P)\) on the VLE curve, \(T\) is the boiling point of the substance at the pressure \(P\). The *normal boiling point* is the boiling point temperature for \(P = 1\) atm.

**Freezing/melting point temperature:** for a point \((T,P)\) on the solid-liquid equilibrium curve, \(T\) is the freezing (equivalently, melting) temperature of the substance at the pressure \(P\).

**Sublimation point temperature:** for a point \((T,P)\) on the solid-vapor equilibrium curve, \(T\) is the sublimation point temperature of the substance at the pressure \(P\).

**Calculation of vapor pressures**

**Clapeyron equation:** The full derivation of this equation is explained in courses on chemical engineering thermodynamics. Here we only state the result:

\[
\frac{dp^*}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}
\]

where \(p^*\) is the vapor pressure of the pure substance, \(T\) is the absolute temperature, \(\Delta H_v\) is the latent heat of vaporization (i.e. energy required to vaporize one mole of the liquid at a point \((T,P)\) on the VLE curve), and \(V_g\) and \(V_l\) are the specific molar volumes of the gas and liquid phases.

For ideal gases, equation 1 can be simplified using \(V_g = RT/p^*\) using the ideal gas EOS. Note that we are assuming to have a pure vapor in equilibrium with a pure liquid. This substitution yields

\[
\frac{dp^*}{dT} = \frac{\Delta H_v}{T(RT/p^* - V_l)}
\]

Moreover, if one mole of the liquid occupies a much smaller volume that one mole of the gas, the \(V_l\) term in the denominator can be neglected compared to \(RT/p^*\),

\[
\frac{dp^*}{dT} = \frac{\Delta H_v p^*}{RT^2} \quad \text{or} \quad \frac{d\ln p^*}{d(1/T)} = -\frac{\Delta H_v}{R}
\]
From equation (2), how could you determine $\Delta \hat{H}_v$?

If $\Delta \hat{H}_v$ does not strongly depend on $T$, equation (2) can be integrated to give the **Clausius-Clapeyron equation**

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

where $B$ is the constant of integration. $B$ depends on the pure substance considered.

**Cox charts**: these charts plot $\log p^*$ vs $T$. The axes are scaled so as to make the plots come out linear.

**Antoine equation**: An empirical but accurate equation for correlating $p^*(T)$ data. The equation has three parameters ($A$, $B$, and $C$ in eqn 4) that have been tabulated for many substances (e.g. see table B.4 in the text):

$$\log_{10} p^* = A - \frac{B}{T + C}$$

Note that, in Table B.4, $T$ is in degrees Celsius and $p^*$ is in mm Hg. Also, $B$ in equation (4) is different from the $B$ in equation (3).

**Example 6.1-1.** Given the below information on vapor pressure of benzene, estimate $\Delta \hat{H}_v$, $B$, and $p^*(42.2^\circ C)$ using equation (3).

<table>
<thead>
<tr>
<th>$T(\circ C)$</th>
<th>$p^*(\text{mm Hg})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>40</td>
</tr>
<tr>
<td>15.4</td>
<td>60</td>
</tr>
</tbody>
</table>
The Gibbs Phase Rule

**Extensive variables:** Extensive variables depend on, and reflect, the size of a chemical “system.” The system could be a liquid solution, for example. Extensive variables include the total volume, the total mass, and the total energy contained in the system, among others.

**Intensive variables:** Variables that do not depend on system size. Examples are temperature, pressure, chemical potential, density, specific volume, viscosity, thermal conductivity, mass fractions, mole fractions, among others.

We will now sketch out a crude derivation of the so-called **Gibbs Phase Rule** for systems in which there are no chemical reactions. For simplicity, we will neglect discussion of the effects of body fields. In thermodynamics it is discussed that if you have a uniform chemical phase (e.g. a gas, a solution, a solid) comprised of \( c \) chemical species, once you specify \( c + 1 \) intensive variables all other intensive variables are fixed. For example, if you specify \( c-1 \) mole fractions, plus \( T \), plus \( P \), the specification of these \( c + 1 \) variables is sufficient to determine the values of all other intensive variables.

If the system contains \( \Pi \) phases, each with its own composition, in principle one would need to specify \( \Pi(c+1) \) intensive variables to completely determine the “intensive” state of each phase and hence the system. However, if the phases are in equilibrium with one another, then the temperatures and pressures of the phases are equal. Otherwise, there would be a flow of heat to even out the temperatures, or movement of matter to even out the pressures. Thus, for phases that are in equilibrium, we only need to specify \( \Pi(c+1) – (\Pi–1) – (\Pi–1) \) intensive variables. Note that equivalency of temperatures and pressures between phases each provides \( (\Pi–1) \) independent equations. For example, if you have two phases, equivalence of temperatures yields the single relation \( T_1 = T_2 \).

After enforcing equivalency of temperatures and pressures between phases, we are left with only \( \Pi(c–1) + 2 \) intensive variables to specify. But we are not done yet, because equilibrium also implies that the chemical potential of each species must be the same in all phases (more on chemical potential next year!). This requirement yields another \( (\Pi–1) \) independent equations for each component, for a total of \( c(\Pi–1) \) constraints. Thus, finally, the degrees of freedom (DF) available before the intensive state of a system with \( \Pi \) phases and \( c \) components is fully specified is
Equation 5 is known as the Gibbs phase rule for nonreactive systems. If chemical reactions occur in the system, at equilibrium each independent reaction contributes another independent constraint; thus, if there are $r$ reactions the DF are further reduced by $r$.

The Gibbs Phase Rule is useful for understanding how many intensive variables must be specified to fully fix, for example, the composition of phases and streams in a process. Applications of it are encountered in chemical engineering separation operations including distillation, absorption/stripping, liquid-liquid extraction, and crystallization (Aside: what phases are contacted in each of these processes?).

**Example 6.2-1.** How many degrees of freedom exist for each of the following scenarios? What intensive variables could be specified to completely determine the intensive state of the system?

(i). Pure liquid water.

(ii) A mixture of liquid, solid, and water vapor of the same species ($c = 1$).

(iii) A vapor-liquid mixture of acetone and methyl ethyl ketone.
Raoult’s Law

**Saturation:** A phase at equilibrium is saturated with a chemical species if it holds as much of the species as it maximally can. For example, air at a given temperature and pressure will only hold so much water vapor. If more water vapor were somehow introduced into the air, **condensation** would occur and the extra water vapor would come out of the air as liquid water. When a gas that is **saturated** with a species A is in contact with a liquid of pure A, the rate at which molecules of A evaporate from the liquid into the gas equals the rate at which molecules of A from the gas condense into the liquid. On the other hand, if the amount of A in the gas is below saturation, the evaporation rate of A will be greater than its rate of condensation. This will continue unless the gas becomes saturated with A and equilibrium is established, at which point the two rates (evaporation and condensation) would become equal. Note that a liquid species that evaporates is referred to as being **volatile,** one that does not is **nonvolatile.**

**Gas-liquid systems with a single condensable component:** These are systems in which a gas phase containing one or more chemical species is contacted with a liquid phase containing just one of those species. That is, only one component in the gas mixture can be induced to condense into liquid by a modest lowering of the temperature. Note that in this scenario the liquid phase consists of one, **pure** component.

**Raoult’s Law for a single condensable species:** If $i$ is the condensable component, then *at equilibrium* the partial pressure of $i$ in the gas mixture must equal the vapor pressure of the pure $i$ liquid. This is called Raoult’s Law. In equation form,

$$P_i = y_i P = p^*_i \quad (6)$$

Notes:

(i) Only a saturated vapor can condense. If a vapor is present in the gas at a concentration below saturation, the vapor is referred to as **superheated vapor** (since it would have to be cooled to reach saturation and thus enable condensation to take place). For a superheated vapor of species $i$, the partial pressure $P_i$ in the gas mixture is less than its vapor pressure $p^*_i$, $P_i < p^*_i$. If pure liquid $i$ is in contact with a gas mixture containing superheated vapor of $i$, what physical process must be happening?

(ii) If a gas mixture with a single superheated vapor is cooled, the temperature at which the vapor becomes saturated in the gas (and
condensation starts) is called the **dew point**. The difference between the actual temperature and the dew point is called the **degrees of superheat**.

(iii) If the vapor pressure of a liquid of pure \( i \) is below the total pressure of unsaturated gas above it, \( p^*_i < P \), evaporation takes place without formation of bubbles in the liquid. If, however, the liquid’s vapor pressure equals the total pressure \( P \) of the gas, **boiling** takes place and bubbles of \( i \) vapor form in the liquid during the evaporation.

*Example 6.3-2.* Air at 100 °C and 5260 mm Hg contains 10.0 % of water by volume. The Antoine constants for water are \( A = 7.97 \), \( B = 1670 \), and \( C = 228 \), when \( p^* \) is in mm Hg and \( T \) in °C.

a) What are the dew point and degrees of superheat of the air?

b) What is the percentage of the vapor that condenses if the air is cooled to 80 °C (keeping the pressure constant)?
Multicomponent systems: These are systems or processes in which gas and liquid phases that contain multiple chemical species are brought into contact. One usually wants to know how each chemical species distributes itself between the phases; e.g. in order to design a liquid-liquid extraction process you would need to know to what extent the solubility of the extract species varies between the two liquid phases (you want its solubility to be high in the extract phase, and low in the raffinate phase). To determine the compositions of phases in equilibrium, one can resort to tabulated data (if available) or to calculations based on phase-equilibrium thermodynamics.

Raoult’s Law for multicomponent gas-liquid systems: Given a liquid solution (note: we no longer have a pure liquid as in the “single-condensable species” scenario) with one or more volatile components $i$, the partial pressure $P_i$ in a gas that is in equilibrium with the liquid is assumed to be given by

$$P_i = y_i P = x_i p_i^*$$

(7)

where $P$ is the total pressure, $y_i$ is mole fraction of $i$ in the gas phase, $x_i$ is mole fraction of $i$ in the liquid phase, and $p_i^*$ is the vapor pressure of pure liquid $i$. Note that equation 7 is an approximation that has to work well when $x_i$ approaches 1, i.e. when the liquid is almost pure $i$. It may be reasonably accurate for certain mixtures over a larger range in composition, e.g. if the liquid mixture consists of substances of similar polarity and molecular weights.

How could you use physical arguments to motivate the form of equation 7? Think about how it is different from Raoult’s law when the liquid was pure $i$.

Henry’s Law: Henry’s Law is similar in form to Raoult’s Law, except that it applies to vapor-liquid equilibrium when the volatile species $i$ is dilute in the liquid solution. Henry’s Law states that, given a liquid solution with a volatile component $i$, the partial pressure of $i$ in a gas mixture in equilibrium with the liquid is given by

$$P_i = y_i P = x_i H_i$$

(8)

where $H_i$ is the so-called Henry’s Law constant of species $i$. Like $p_i^*$, the vapor pressure of $i$, Henry’s Law constant is also a function of temperature. In contrast to Raoult’s Law, Henry’s Law applies when $x_i$ is close to 0, i.e. when the volatile $i$ component is dilute in the liquid phase. Note that these laws do not work well if species $i$ dissociates – in such a case, the physical picture becomes more complex and its discussion is left to more specialized courses.
Example: The figure below shows an example of a partial pressure curve for a volatile species $i$ (plotted on the y-axis) as a function of its mole fraction in the liquid phase (plotted on the x-axis). In what regimes of $x_i$ do Raoult’s and Henry’s Laws apply? Where on the axes would $p_i^*$ and $H_i$ fall?

![Partial pressure curve](image)

**Bubble-point and Dew-point Calculations**

**Bubble-point:** If pure liquid $i$ is heated its vapor pressure will rise. Eventually, the vapor pressure of the pure liquid equals the external pressure $P$ of the gas above it. At this point, the liquid will start to boil – bubbles of pure $i$ will form and the liquid will be at its boiling temperature at the pressure $P$. As long as $P$ remains constant, the boiling temperature of the liquid will not change.

What happens if a liquid solution, containing multiple chemical species, is heated? Again, eventually a temperature is reached at which bubbles start to form in the liquid solution and boiling sets in. This temperature is called the **bubble-point temperature** $T_{bp}$ (in contrast to boiling point temperature, which is for pure liquids). In the case of a liquid solution, the composition of the vapor in the bubbles that form is not the same as that of the liquid. In fact, the vapor will be more enriched in the more volatile components of the liquid, as you may suspect. In turn, this implies that as these vapor bubbles, enriched in the more volatile species, transport molecules from the liquid to the gas above, the liquid left behind will become progressively depleted in the more volatile species – the composition of the liquid will change. As the liquid composition changes, so will the bubble-point temperature. Thus, in contrast to the boiling of a pure liquid, for which boiling occurs at a fixed $T$ as long as $P$ is fixed, for a liquid solution $T_{bp}$ changes as
boiling proceeds because of the change in the liquid’s composition. Do you think $T_{bp}$ increases or decreases as a liquid solution continues to boil?

What do you think happens if a gas, containing multiple condensable species, is slowly cooled at a constant pressure $P$? As the cooling proceeds, the condensable species will start to leave the gas in the form of a condensed liquid. The liquid droplets will be enriched in the less volatile species of the gas mixture. The temperature at which the first droplets begin to form is the **dew-point temperature** $T_{dp}$ at the pressure $P$. Note that the density of the gas increases if it is cooled at a constant pressure.

What do you think happens if a liquid solution, containing a mixture of volatile species, is subjected to a progressively decreasing pressure $P$ while its temperature $T$ is kept constant?

What if a gas mixture of condensable species is subjected to an increasing pressure $P$ while keeping $T$ constant?

**Calculation of bubble-point and dew-point temperatures and pressures:**
In general, calculation of bubble-point/dew point conditions is a complex task. However, the task simplifies considerably if the composition of the liquid solution is in a regime in which Raoult’s and/or Henry’s Laws apply (i.e. the solution behaves **ideally**).

To illustrate such a calculation, we will assume to have a liquid solution containing $q$ volatile species. We want to calculate its bubble-point when the external pressure of the gas above the solution is $P$. At the bubble point, the sum of the vapor pressures from the $q$ volatile species must sum to $P$ if vapor bubbles are to form. Moreover, the composition of the vapor bubbles that form in the liquid can be assumed to be in equilibrium with the liquid, e.g. as given by Raoult’s or Henry’s laws. For definiteness, we will assume the liquid solution follows Raoult’s law for each of the $q$ volatile species present. Then, the partial pressure $P_i$ of species $i$ in a vapor bubble, formed at the bubble-point temperature $T_{bp}$, is

$$P_i = x_i p_i^* (T_{bp})$$

for $i = 1, 2, \ldots, q$ (9)

where $x_i$ is the mole fraction of $i$ in the liquid solution, and where we explicitly indicated that the vapor pressure $p_i^*$ is to be evaluated at the bubble-point temperature $T_{bp}$. Then, at the bubble-point, we must have
\[ P = \sum_{i=1}^{q} P_i = \sum_{i=1}^{q} x_i p_i^*(T_{bp}) = x_1 p_1^*(T_{bp}) + x_2 p_2^*(T_{bp}) + \ldots + x_q p_q^*(T_{bp}) \]  

(10)

If we know the mole fractions, and the vapor pressures \( p^*_i(T) \) of all volatile species \( i = 1, 2 \ldots q \) as a function of temperature, we can solve equation 10 for the temperature \( T_{bp} \) at which the partial vapor pressures sum to the external pressure \( P \). In this manner the bubble-point temperature can be found. (Question: what would happen to equation 10 if some species instead followed Henry's Law?)

How would you determine the bubble-point pressure? This is the pressure at which a liquid solution begins to boil when decompressed at a constant \( T \).

How would you determine the dew-point temperature? Again, let us assume that Raoult’s law holds for all of the condensable components of a gas mixture, and that the gas mixture behaves ideally. The liquid droplets that form will contain the \( q \) condensable species, \( i = 1, 2 \ldots q \). Moreover, the droplets will be in equilibrium with the gas according to Raoult’s Law,

\[ y_i P = x_i p_i^* \quad \text{for} \quad i = 1, 2 \ldots q \]  

(11)

where \( y_i \) are the gas mole fractions and \( x_i \) the liquid mole fractions. Furthermore, at the dew point, we must be able to satisfy the physical constraint

\[ \sum_{i=1}^{q} x_i = 1 \]

which, using equation 11, can be expressed as

\[ \sum_{i=1}^{q} \frac{P y_i}{p_i^*(T_{dp})} = 1 \]  

(12)

If we know the total pressure \( P \), the gas fractions \( y_i \) for all of the \( q \) condensable species, and the vapor pressures \( p_i^*(T) \) of the \( q \) species as a function of
temperature, we could solve equation 12 for the dew-point temperature $T_{dp}$. $T_{dp}$ is that temperature which, when used in equation 12 to evaluate the partial pressures $p_i^\ast$, satisfies the constraint that the summation terms add to unity. Note that any noncondensable species, if present in the gas, are not included in the summation of equation 12. Why not? (Question: what would happen to equation 12 if some species instead followed Henry's Law?)

How would you calculate a dew-point pressure? Dew-point pressure is the pressure at which droplets first form in a gas while the gas is compressed at a constant $T$.

**Txy and Pxy diagrams:** These diagrams are used to correlate bubble-point temperature and bubble-point pressure data for binary (two-component) gas-liquid systems. Examples for the benzene-toluene system are shown below.

![Pxy diagram for benzene-toluene system](image1.png)

![Txy diagram for benzene-toluene system](image2.png)

**Example 6.4-4:**
What is the bubble-point temperature and equilibrium vapor composition for a benzene-toluene liquid solution at 1 atm and with a mole fraction of benzene of 0.80? Note that the x-axis traditionally indicates mole fraction of the more volatile component.
The liquid continues to vaporize until the liquid benzene mole fraction reaches 0.60. What is the temperature at that point?

**Solid-Liquid Systems**

Thus far we discussed situations in which gas and liquid phases are in contact. Now we will consider scenarios when the phases in contact are liquid and solid.

**Solubility:** Solubility is the maximum amount of a solid that can dissolve in a liquid, at equilibrium. Solubility is often expressed as mass of the solid that can dissolve per mass or volume of the liquid; for example, the solubility of sodium chloride (NaCl) in water at 100 °C is 39.12 g/100 cm$^3$. Solubility is often a strong function of temperature, but much less so of pressure.

**Saturated solution:** A saturated solution contains the maximum amount of a solute, as expressed by the solute’s solubility (recall that “solute” is the low concentration species in a solution). A saturated solution is in equilibrium with the solid phase. If a saturated solution is cooled, it is often possible to produce a metastable condition in which the solution holds more than the equilibrium amount of solute; such a solution is referred to as supersaturated. A metastable condition is *NOT* at equilibrium; nevertheless, it can persist for a significant time because the processes that need to occur to reach equilibrium are slow.

How many degrees of freedom exist to specify the intensive state of a system that consists of a pure solid phase and a binary liquid phase in equilibrium? The liquid phase is solvent plus dissolved solid.

**Example 6.5-2:** A solution of water and KNO$_3$ salt is cooled in a crystallizer. The solution enters the crystallizer at 80 °C and contains 60.0 wt % KNO$_3$. In the crystallizer, the temperature is lowered to 40 °C. At what point does the solution become saturated, and what fraction of the KNO$_3$ from the feed forms crystals? Solubility data for KNO$_3$ are plotted in the figure below. Assume the solid and liquid phases in the crystallizer are always in equilibrium.
The diagram illustrates the solubility of potassium nitrate (KNO₃) in water as a function of temperature. The solubility increases with temperature, as indicated by the upward curve on the graph. The x-axis represents temperature in degrees Celsius (C), while the y-axis shows the solubility of KNO₃ in grams per 100 grams of water.
Colligative Properties

**Colligative properties**: These are properties of a liquid solution that depend on the concentration of solute, but not on the chemical identity of the solute. Colligative properties include boiling point, freezing point, osmotic pressure, and vapor pressure.

In what follows, we assume we are dealing with a binary solution of a volatile solvent and a nonvolatile solute, and that the solute does not dissociate or otherwise react with the solvent.

**Lowering of solvent vapor pressure and elevation of boiling point**: We will illustrate the effects of vapor pressure lowering and boiling point elevation for the special case when the solution obeys Raoult’s Law. From equation 7 the partial pressure of the solvent $P_{\text{solvent}}$ is (note that the solute vapor pressure is 0 since we assumed it to be nonvolatile)

$$P_{\text{solvent}} = x_{\text{solvent}} p_{\text{solvent}}^*$$

where $x_{\text{solvent}}$ is the mole fraction of solvent and $p_{\text{solvent}}^*$ is the vapor pressure of the pure solvent. Since the solution is binary, $x_{\text{solvent}} = 1 - x_{\text{solute}}$; thus

$$P_{\text{solvent}} = (1 - x_{\text{solute}}) p_{\text{solvent}}^* \quad (13)$$

Equation 13 shows that the effect of the solute is to lower the effective vapor pressure of the solvent by $x_{\text{solute}} p_{\text{solvent}}^*$ from $p_{\text{solvent}}^*$ for the pure solvent to $p_{\text{solvent}}^* - x_{\text{solute}} p_{\text{solvent}}^*$ for the solution; i.e. the solute lowers the effective solvent pressure by $\Delta p_{\text{solvent}}^*$ such that

$$\Delta p_{\text{solvent}}^* = x_{\text{solute}} p_{\text{solvent}}^* \quad (14)$$

Note that the lowering of the effective vapor pressure is independent of the solute’s chemical identity, in keeping with the nature of colligative properties.

A consequence of the vapor pressure lowering is that the solution boiling point is elevated. How can we understand this effect, based on what was already said about the conditions required for boiling to take place?
Lowering of the vapor pressure suggests that the presence of the solute somehow “stabilizes” the solvent in the liquid form – that is, it is harder to transfer solvent particles into the gas phase when the solute is present than it is for a pure solvent. This admittedly vague notion of stabilization is indicated by the elevation of the boiling point. Although we do not attempt to fully explain it here, the idea of stabilization turns out to be essentially correct – the solute increases the disorder (the number of similar arrangements of solvent and solute particles) available to the solution and this makes it more favorable for the solvent molecules to stay in the liquid solution, rather than evaporate.

We can estimate the elevation in boiling point due to the presence of solute particles. At their respective boiling points, the vapor pressures of the solution and the pure solvent must equal the atmospheric pressure, and hence each other. Moreover, the vapor pressure of the solution, from equation 13, is given by \((1 - x_{\text{solute}}) p_{\text{solvent}}^*\) (note that \(p_{\text{solvent}}^*\) refers to the pure solvent). These considerations lead to

\[
(1 - x_{\text{solute}}) p_{\text{solvent}}^*(T_{bs}) = p_{\text{solvent}}^*(T_{b0})
\]

The left hand side is the vapor pressure of the solution at its boiling point \(T_{bs}\), expressed using equation 13 in terms of the pure solvent vapor pressure \(p_{\text{solvent}}^*(T_{bs})\). Under the condition of boiling, this must equal the right hand side, which is just the vapor pressure of the pure solvent at its boiling point, \(T_{b0}\). Equation (15) can be rearranged to

\[
\ln \{(1 - x_{\text{solute}}) p_{\text{solvent}}^*(T_{bs})\} = \ln p_{\text{solvent}}^*(T_{b0})
\]

\[
\ln(1 - x_{\text{solute}}) + \ln p_{\text{solvent}}^*(T_{bs}) = \ln p_{\text{solvent}}^*(T_{b0})
\]

Using the Clausius-Clapeyron equation (equation 3) to relate the \(\ln p_{\text{solvent}}^*\) terms to the latent heat of vaporization and the absolute temperatures \(T_{bs}\) and \(T_{b0}\), we get

\[
\ln(1 - x_{\text{solute}}) - \frac{\Delta H_v}{RT_{bs}} + B = -\frac{\Delta H_v}{RT_{b0}} + B
\]

For dilute solutions, \(x_{\text{solute}}\) is much less than 1 so that the logarithm in equation 16 can be approximated as \(\ln(1 - x_{\text{solute}}) \approx - x_{\text{solute}}\) (you could prove this relation by Taylor series expansion). Equation 16 thus becomes
\[ x_{\text{solute}} \cdot \frac{\Delta \hat{H}_v}{R T_{bs}} + B = \frac{\Delta \hat{H}_v}{R T_{b0}} + B \]

\[ x_{\text{solute}} = \frac{\Delta \hat{H}_v}{R} \left( \frac{1}{T_{b0}} - \frac{1}{T_{bs}} \right) = \frac{\Delta \hat{H}_v (T_{bs} - T_{b0})}{R T_{bs} T_{b0}} \]

what can be rearranged to

\[ T_{bs} - T_{b0} = \frac{R T_{bs} T_{b0} x_{\text{solute}}}{\Delta \hat{H}_v} \]

Approximating the term \( T_{bs} T_{b0} \) as \( T_{b0}^2 \) (recall the temperatures are on absolute scale, and not very different) we arrive at the conventional formula for elevation of the boiling point due to the presence of solute particles,

\[ T_{bs} - T_{b0} = \frac{R T_{b0}^2 x_{\text{solute}}}{\Delta \hat{H}_v} \]  

(17)

As expected of a colligative property, we see that the boiling point elevation \( T_{bs} - T_{b0} \) of the solution relative to the pure solute is independent of the chemical nature of the solute; instead, it only depends on the concentration of solute via its mole fraction \( x_{\text{solute}} \).

Similar arguments as above can be used to derive a formula for the solution’s freezing point \( T_{fs} \) relative to that of the pure solvent \( T_{f0} \),

\[ T_{f0} - T_{fs} = \frac{R T_{f0}^2 x_{\text{solute}}}{\Delta \hat{H}_m} \]  

(18)

where \( \Delta \hat{H}_m \) is the latent heat of fusion (i.e. melting).
Liquid-Liquid Systems

**Fully miscible**: Two liquid solvents are fully miscible if, when combined in any proportion, they yield only a single (mixed) liquid phase.

**Immiscible**: Two liquid solvents, A and B, are immiscible if, when combined in any proportion, they separate into a liquid phase of nearly pure A and a liquid phase of nearly pure B.

**Partially miscible**: The term partially miscible is used to denote two solvents that, when mixed, yield (at least for some proportions of mixing) two liquid phases each of which contains a fraction of both solvents.

**Distribution coefficient (partition ratio)**: If a solute is added to a system containing two liquid phases (i.e. made from two immiscible or two partially miscible solvents), the solute will distribute its mass between the two phases according to its solubility. The distribution coefficient (also known as the partitioning ratio) is the ratio of the mass fraction of the solute in one phase to its mass fraction in the other, at equilibrium. A distribution coefficient of 1, therefore, would indicate that the solute is equally soluble (on a mass basis) in both phases. If $K$ is the distribution coefficient for solute species $i$, then

$$K = x_i,1/x_i,2$$  \hspace{1cm} (19)

where $x_i,1$ and $x_i,2$ are the mass fraction of species $i$ in phase 1 and phase 2, respectively.

**Liquid extraction**: A process in which a first liquid phase containing a solute is contacted with a second liquid phase in which the solute is more soluble. Therefore, much of the solute is transferred (“extracted”) from the first to the second phase.

*Example 6.6-1*: 200 cm$^3$ of a mixture of acetone (A) and water (W), 10.0 wt% acetone, is mixed with 400.0 cm$^3$ of chloroform (C). Chloroform and water are nearly immiscible. The distribution coefficient is $K = x_{A,C}/x_{A,W} = 1.72$. The densities are $\rho_A = 0.792$ g/cm$^3$, $\rho_C = 1.489$ g/cm$^3$, and $\rho_W = 1.000$ g/cm$^3$.

What fraction of the acetone is transferred from the water phase to the chloroform phase? Assume that equilibrium is reached between the two phases.
**Ternary Phase Diagrams:** A ternary phase diagram represents the solubility behavior of a ternary (i.e. three-component) liquid system. An example is shown in Fig. 6.6-1 in the text.

In Fig. 6.6-1:

a). What is the composition of a system found at the “acetone apex”?

b). What is the composition of a system in the middle of triangle edge $b$?

c). What is the composition of a system at point K?

d). What is the composition of a system at point M?

e). How many liquid phases exist for a system whose composition falls in region A?

f). How many liquid phases exist for a system whose composition falls in region B? What are the compositions of the liquid phases for a system whose composition is given by point M?

g). How many degrees of freedom exist for a system in region A?

In region B?

On triangle edge $a$?

In the middle of triangle edge $c$?
h). How many intensive variables do you think are fixed for the entire phase diagram?

What are they?

*Example 6.6-2:* 1000 kg of a 30.0 wt % solution of acetone in water is fed to a mixer, where it is mixed with a pure stream of MIBK. The mixture then passes to a settler tank where it is allowed to separate into two phases (at 25 °C and 1 atm), a water-rich and a MIBK-rich phase.

How much pure MIBK must be fed to the process in order to reduce the acetone concentration in the water-rich phase to 5 wt%? Assume that equilibrium is achieved between the two liquid phases.
Adsorption on Solid Surfaces

Adsorption: Adsorption is the binding, due to attractive interactions, of a chemical species (the adsorbate) onto a solid surface (the adsorbent). An example is adsorption of water vapor molecules onto the surface of silica particles. The adsorbate could be in a gas or a liquid phase.

Adsorption isotherm: A curve that plots amount of adsorbate bound to an adsorbent surface as a function of free adsorbate concentration in solution. The amount of adsorbate bound increases with its amount in solution. It is called an “isotherm” because such data are customarily obtained at a fixed temperature.

Langmuir isotherm: The Langmuir isotherm assumes that the adsorbed amount of species $i$, $X_i^*$, is related to the solution concentration $c_i$ of free $i$ (i.e. in a gas or a liquid phase) according to

$$X_i^* = \frac{aK_Lc_i}{1 + K_Lc_i}$$

(20)

where $K_L$ is the equilibrium constant for the reaction

adsorbate$_{\text{free}}$ + surface site $\leftrightarrow$ adsorbate$_{\text{bound}}$

In equation 20 $a$ is the maximum possible coverage of adsorbate on the surface ($a = X_{i_{\text{max}}}^*$). Units of $a$ and $X_i^*$ are usually (amount adsorbate) / (area adsorbent); for example: mg/m$^2$, molecules/m$^2$. Sometimes, the units are (amount adsorbate) / (amount adsorbent); for example, g adsorbate/g adsorbent.