THE PHASE RULE

Degrees of Freedom:

The number of degrees of freedom (number of variables we can change without affecting the "nature" of the system) is determined by the equation known as the **phase rule**:

$$f = c - p + 2,$$

where f is the no. of degrees of freedom, p is the number of phases present and the "2" represents the two variables temperature and pressure.

Applying this rule to a one-component phase diagram such as that of water, we see that in the interior of the solid, liquid or vapor regions, where only one phase is present, we get two degrees of freedom, since $f = 1 - 1 + 2 = 2$. This means that we can change two variables, in this case temperature and pressure, and still have a system consisting only of one phase.

When we have two phases in equilibrium, the number of degrees of freedom decreases to 1: $f = 1 - 2 + 2 = 1$. This means that if we wish to change the conditions and still retain the equilibrium between the two phases, we can only change one of the variables independently. The other variable is then determined by the equilibrium condition.

When three phases are in equilibrium, as at the triple point, the number of degrees of freedom drops to zero. Therefore, the triple point is a unique point for the system. In some cases, as in the case of sulfur, multiple triple points are present. Each of these are unique points with zero degree of freedom.

Components:

Determining the number of components in a system is not a trivial task. We may make up a formula for this as follows:

$$c = n - e - o,$$

where c is the number of components, n is the number of chemical species present, e is the number of equilibria between them, and o represents any other relationships that may determine the relative amount of one species with respect to another.

6.3. Binary systems involving vapor:

Liquid-vapor systems consisting of two components are commonly represented in pressure-composition diagrams at fixed temperature, or temperature-composition diagrams at fixed pressure.

Two equations govern their behavior. These are derived below. Consider a binary (two-component) system consisting of components 1 and 2. Then

$$y_1 = P_1/P \qquad \text{(Dalton's Law)} \qquad (10)$$

$$P = P_1 + P_2 = x_1P_1^* + x_2P_2^* \qquad \text{(Raoult's Law)}$$

The last equation may be re-written for a binary system as

$$\boxed{P = x_1P_1^* + (1-x_1)P_2^* = P_2^* + (P_1^* - P_2^*)x_1.} \qquad (11)$$

When pressure is lowered on a solution containing x_1 mole fraction of component 1, the first bubble appears when pressure reaches the value predicted by Eq. (11). Therefore, this equation is called the **bubble-point line** equation.

Substituting this expression for the total pressure in Eq. (10), we get

$$y_1 = \frac{P_1}{P_2^* + (P_1^* - P_2^*)x_1} = \frac{x_1P_1^*}{P_2^* + (P_1^* - P_2^*)x_1}$$

which gives the composition of the vapor contained in the bubble.

However, it is more useful to obtain an expression for the variation of total pressure as a function of vapor composition. This is done as follows. From the equation above, we get

$$x_1 = \frac{y_1P_2^*}{P_1^* + (P_2^* - P_1^*)y_1} \qquad (12)$$

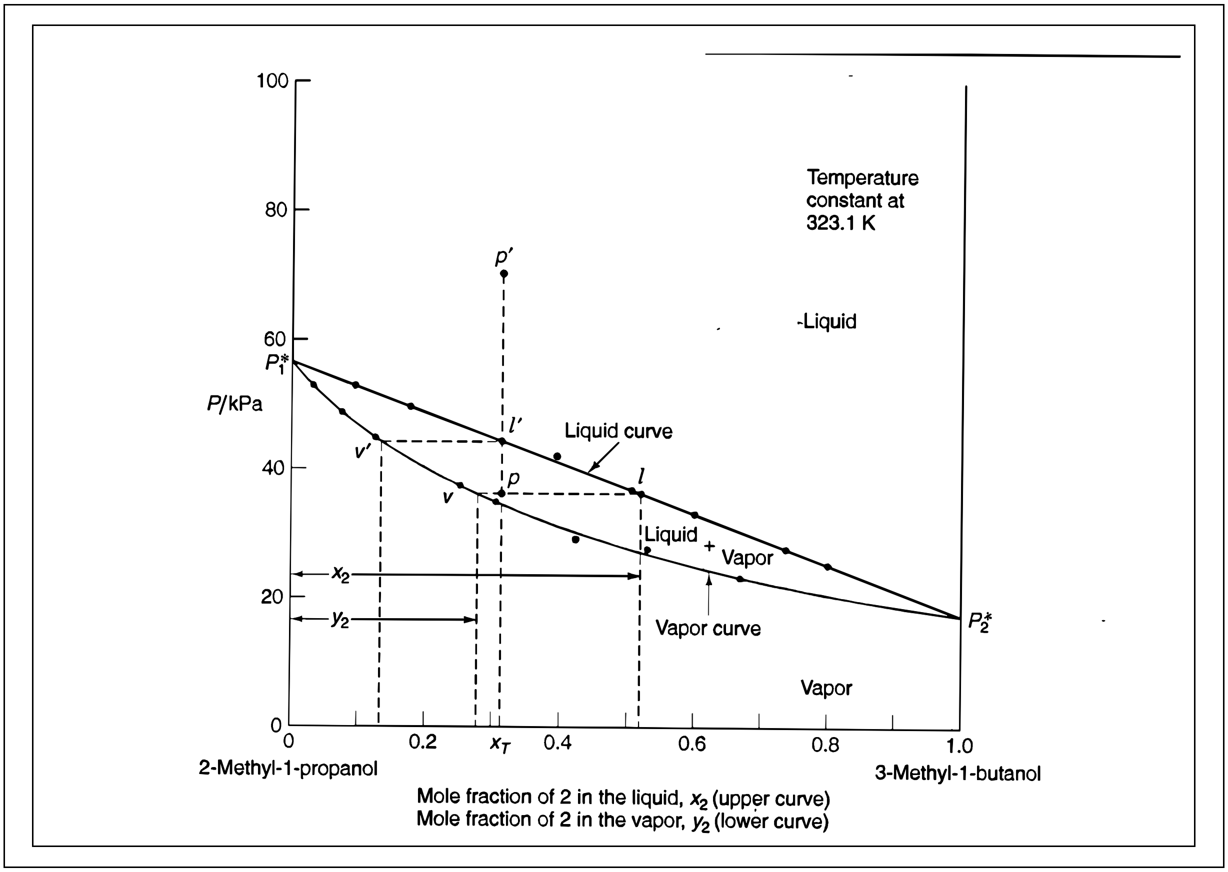
Also, $$y_1P = x_1P_1^*. \qquad (13)$$

Using Eq. (12) to substitute for x_1 in Eq. (13), we get

$$\boxed{P = \frac{P_1^*P_2^*}{P_1^* + (P_2^* - P_1^*)y_1},} \qquad (14)$$

which is the desired equation. This equation is called the **dew-point line** equation because when pressure is increased on a vapor at composition y_1, the first drop of condensate (dew) is formed when the pressure reaches the value predicted by Eq. (14).

The bubble-point line is a linear equation in pressure-composition space but the dew-point line is nonlinear. The figure below gives good examples of both equations plotted together on the same graph.



Tie-lines:

Horizontal lines (lines drawn at constant pressre in a *P*-*x* diagram or at constant temperature in a *T*-*x* diagram) that connect the compositions of liquid and vapor in equilibrium with each other are called tie-lines.

The lever rule:

The relative amounts of vapor and liquid present at a given *total* composition x_T is given by the lever rule:

$$\frac{n_l}{n_v} = \frac{x_T - y_2}{x_2 - x_T} = \frac{\overline{pv}}{\overline{lp}}.$$

Pressure-composition diagram to Temperature-composition diagram:

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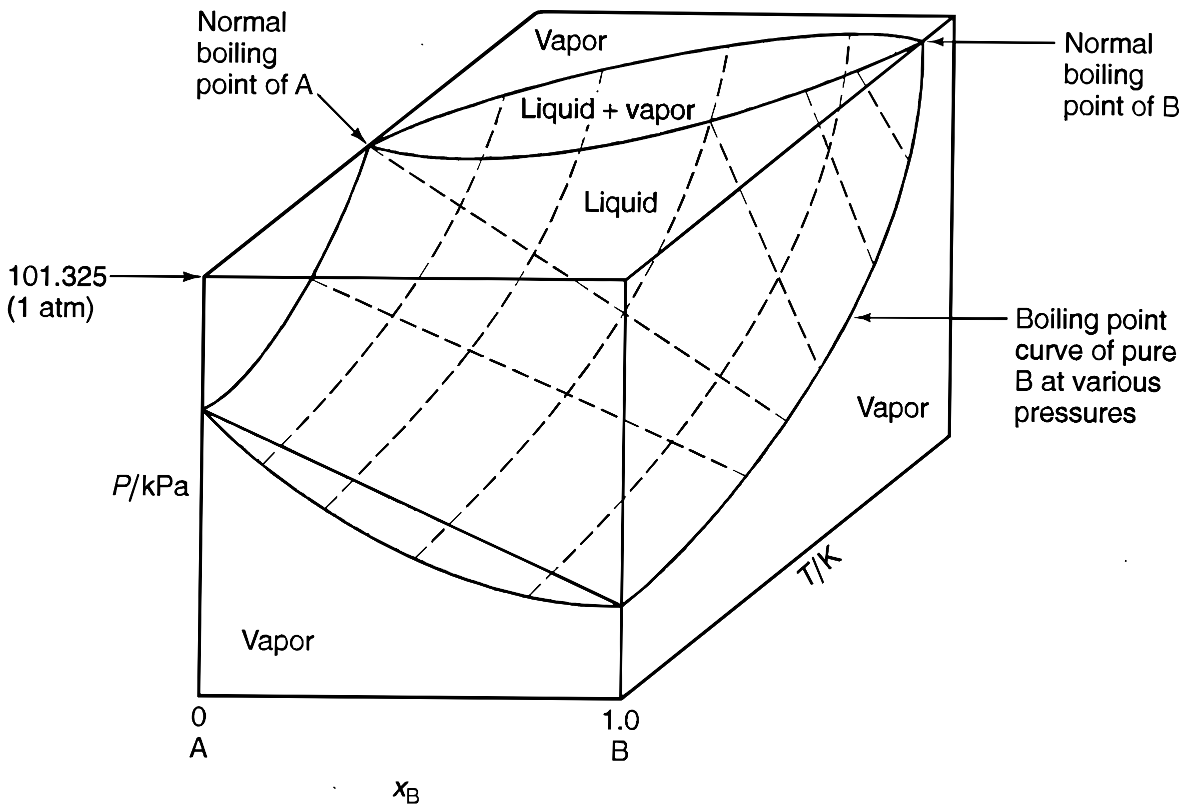
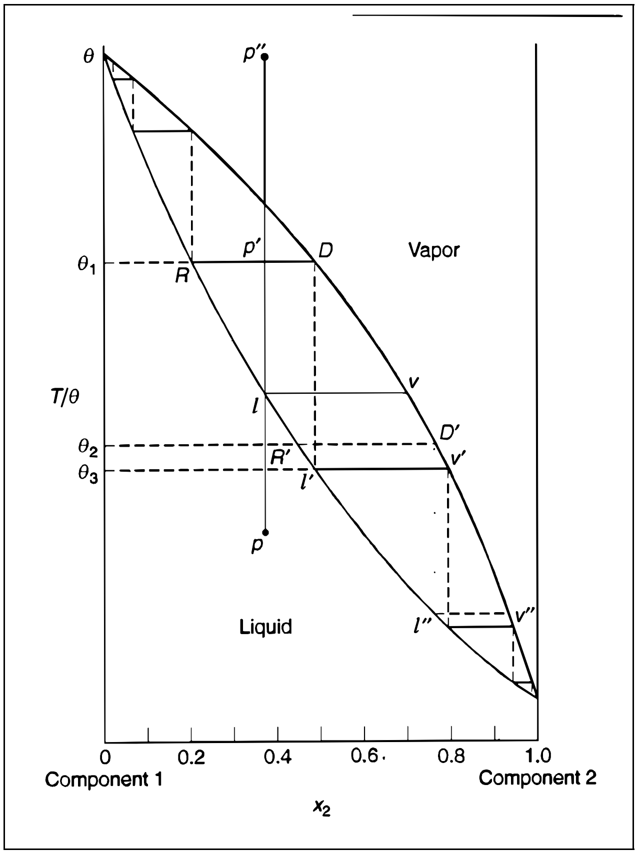


Notes:

Higher vapor pressure ⇒ lower boiling point.

Neither the liquid curve or the vapor curve generally appear as straight lines in temperature-composition space.

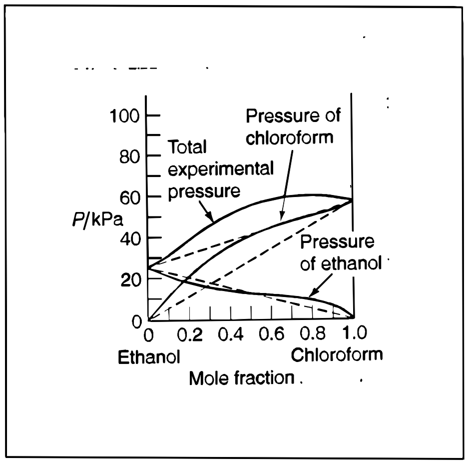
Temperature-Composition or "Distillation" diagrams:

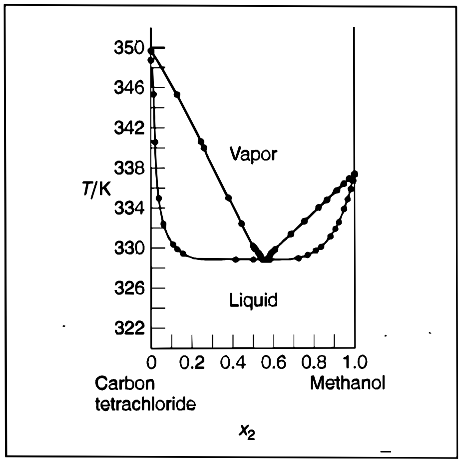


- Temperature-composition diagrams are drawn at fixed pressure, usually 1 atm or 1.013 bar.
- Consider liquid at composition *p*. If we raise the temperature, the liquid will start boiling when it reaches the bubble-point line at that composition, denoted by the point *l*.
- The vapor formed at this temperature has the composition given by the tie-line to the dew-point line, denoted by the point *v*.
- The vapor is richer in the more volatile component. Therefore, the liquid left behind is richer in the less volatile component.
- If this is a sealed system and the vapor is not allowed to escape, the tempearture will remain steady at the boiling point and the liquid and vapor will come to equilibrium.
- On the other hand, if the boiling is allowed to continue and the vapor is continuously removed, the temperature will rise. When it reaches θ_1, the liquid composition is given by the point *R* and the vapor in equilibrium with it will have the composition denoted by the point D.
- If we continue this process of removing the vapor, the liquid will eventually consist of pure component 1, all of component 2 having been removed as vapor.
- If the vapor removed at each stage is allowed to condense to liquid and is boiled again, eventually, the condensate will reach the composition of pure component 2 ($D \rightarrow l' \rightarrow v' \rightarrow l'' \rightarrow v'' \rightarrow$.....)
- This is the principle behind the separation technique known as distillation.

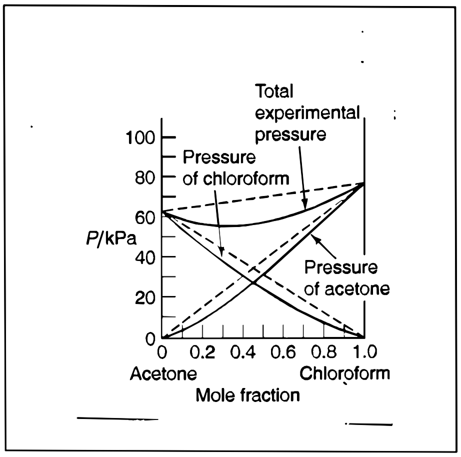
Azeotropes:

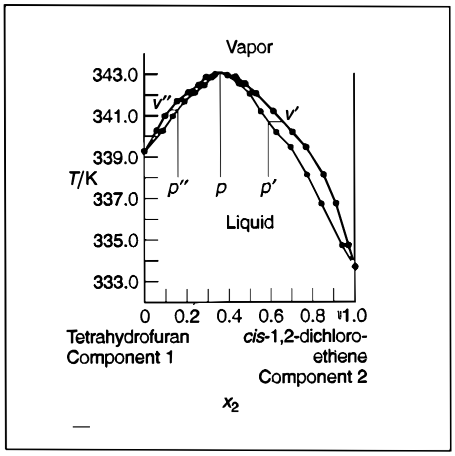
Positive Deviation from Raoult's Law → Minimum boiling point mixtures.





Negative Deviation from Raoult's Law → Maximum boiling point mixtures:





Azeotropes satisfy two conditions:

1. They boil at temperatures less than either of the pure components (positive deviation) or at temperatures greater than either of the pure components (negative deviation).
2. At the maximum or minimum boiling point (eutectic), the liquid and vapor have the same composition.

Distillation of immiscible liquids:

In a system consisting of two liquids that are almost completely immiscible, the two components separate into mutually exclusive layers. In other words, within each layer, the mole fraction of that component is almost 1. Then, we may write

$$P = P_A^* + P_B^*. \tag{15}$$

If n_A and n_B are the compositions of each component in the vapor, we get

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*} \tag{16}$$

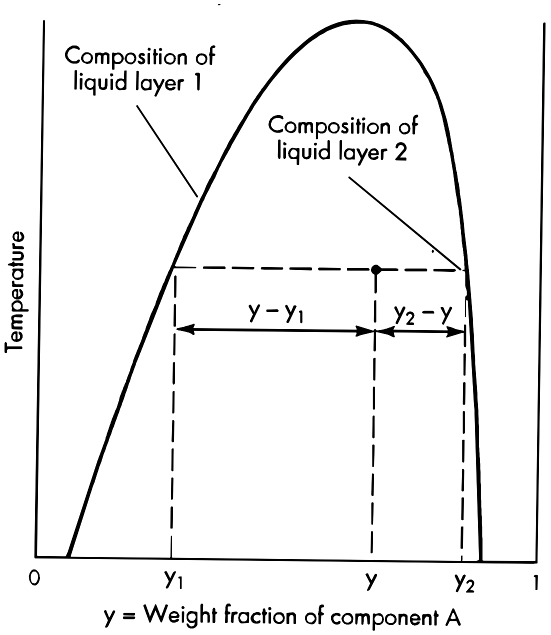
In other words, the vapor contains more of the more volatile component, as we would normally expect.

Since the molar masses are constants, this immediately gives rise to a useful relationship between the masses of the two substances in the vapor:

$$\frac{w_A}{w_B} = \frac{P_A^* M_A}{P_B^* M_B}. \tag{17}$$

Steam distillation is a very useful technique based on these principles for the extraction of organic compounds that are immiscible with water. Since the total vapor pressure of the system is the sum of the two vapor pressures, the liquid mixture boils at temperatures far lower than the boiling points of either liquid. Therefore, it is possible to extract organic compounds that may decompose or undergo reactions if heated to their boiling points.

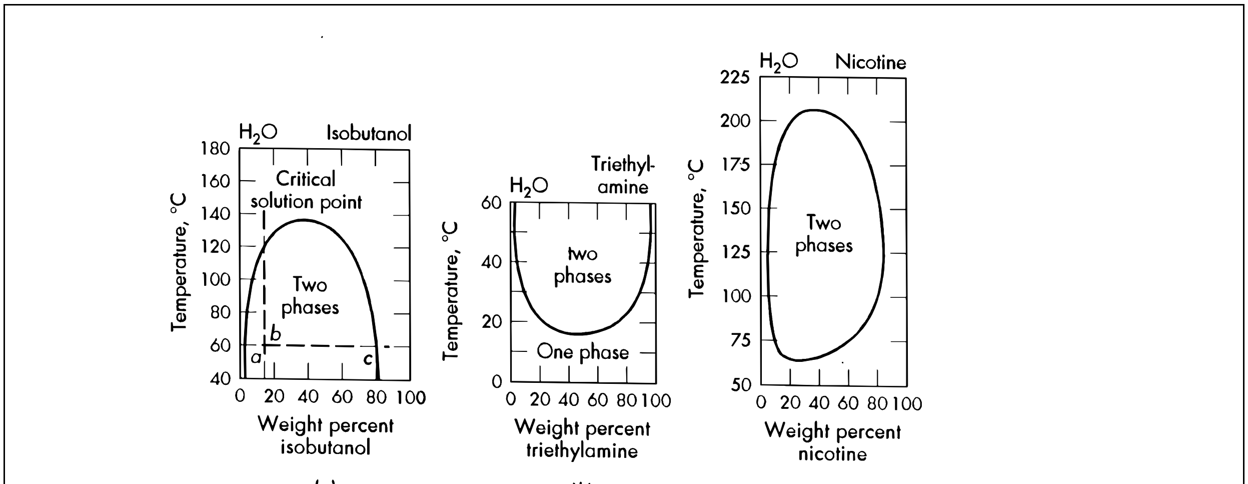
Partially miscible liquids



The figure shows a typical phase diagram for a system of two partially miscible liquids below their boiling points. The region outside the “envelope” consists of a single phase while the region inside the “envelope” represents two phases in equilibrium with each other. Tie lines (as shown) indicate the compositions of the two layers at a given temperature. The relative weights of the two layers can be obtained by using the lever rule (similar to the case of the vapor pressure diagram). Thus, the relative masses of layer 1 (composition y_1) and layer 2 (composition y_2) formed as a result of mixing together the two liquids in the ratio represented by y is given by

$$\frac{w_1}{w_2} = \frac{y_2 - y}{y - y_1}.$$

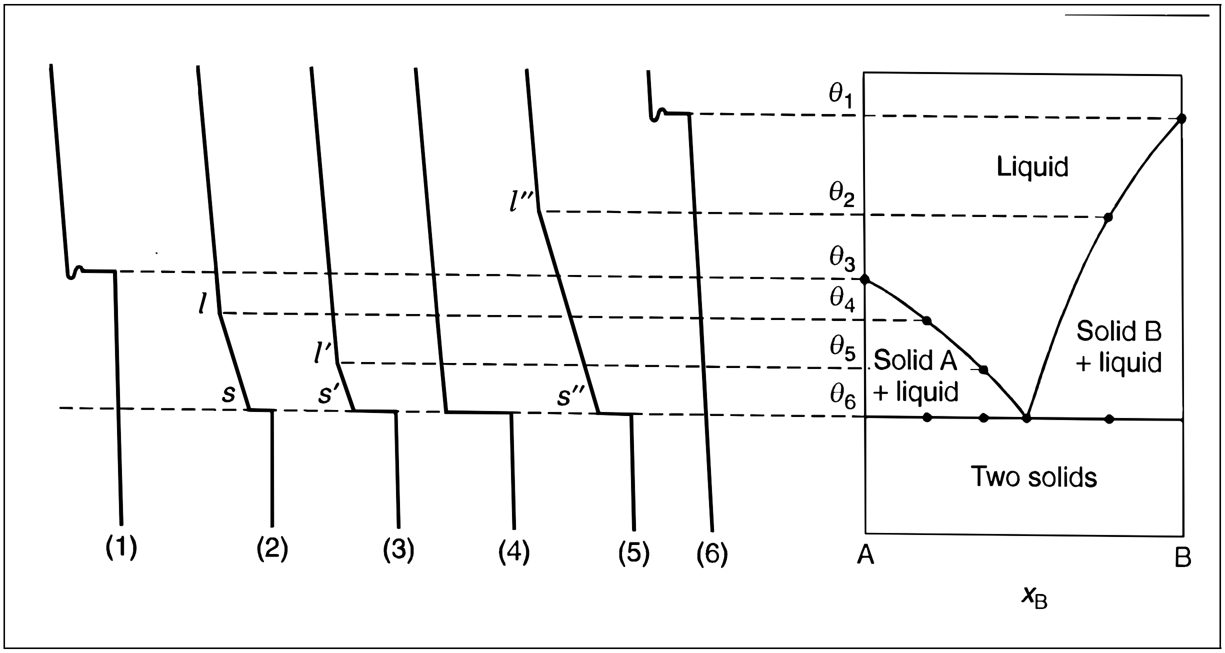
The figure also shows that above at a certain temperature, the system consists of a single layer. This temperature is called the critical solution temperature, T_c. Some systems have a maximum solution temperature (as in the case above), and some have a minimum solution tempearture. Some have *both*! Examples are shown on the next page.

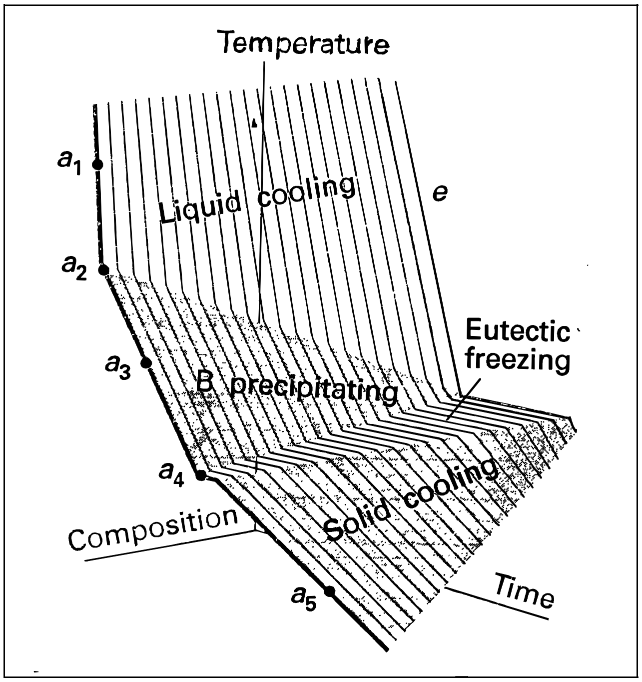


(a) (b) (c)

Solid-liquid systems

Phase diagrams of solid-liquid binary systems are constructed by recording cooling curves. The relationships between different types of cooling curves (qualitatively, there are two types; can you identify them?) and various regions of the phase diagram are illustrated below.

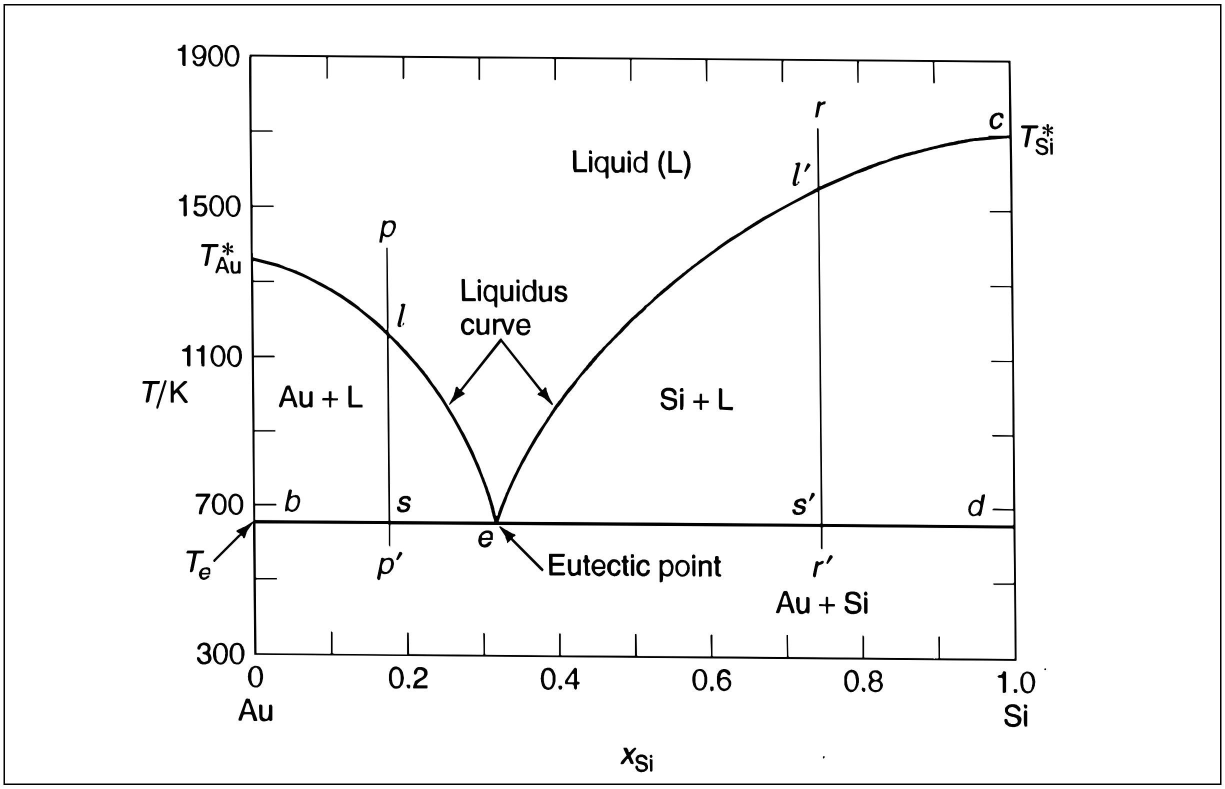




The variation of the length (of time) of the line segments (*l*,*s*), (*l′*,*s′*), and (*l″*,*s″*) are related to the amount of solid that precipitates out of the liquid during cooling. Finally, when the composition of the system reaches the **eutectic point** (the minimum melting point composition), the system behaves like a pure substance. The figure to the left establishes this relationship.

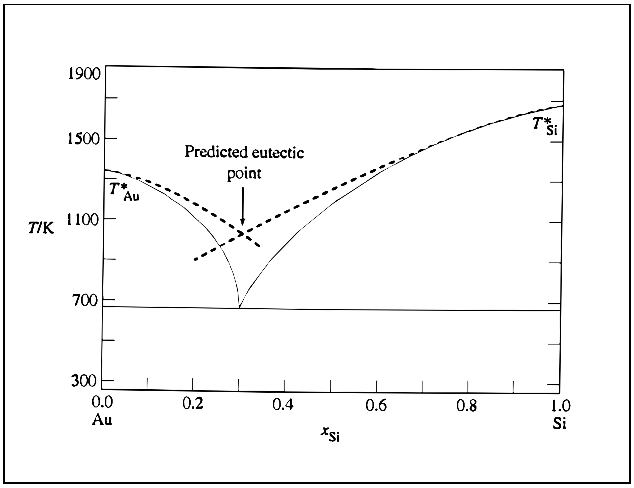
Pure components, eutectics, and compounds yield cooling curves with a single horizontal region. In these cases, the solid that separates out of the liquid has the same composition as the liquid. In other regions, such as those corresponding to cooling curves (2), (3), etc., in the figure above, the solid that separates out has a *different* composition from the liquid. The composition of the solid precipitate can be found by drawing a horizontal tie-line *to the interior of the phase diagram* (into the two-phase region) until it hits a vertical line that marks the composition of a pure component or a compound.

When the liquid and solid have the same composition, they establish an equilibrium with each other and the temperature remains constant until all of the liquid has solidified. The heat being removed by the cooling system (a cold bath, for example) is replaced by the enthalpy of fusion of the solid, which is being released. On the other hand, if the solid that separates has a different composition, the precipitation changes the composition of the liquid phase. Therefore, an equilibrium between the two cannot be established. The liquid cools further but the rate of cooling is slower since the enthalpy of fusion is being released. This leads to the break in the cooling curve followed by a region of slower cooling. Finally, when sufficient solid has separated that the composition becomes identical to the eutectic, all of the liquid solidifies and this results in a horizontal region in the cooling curve.



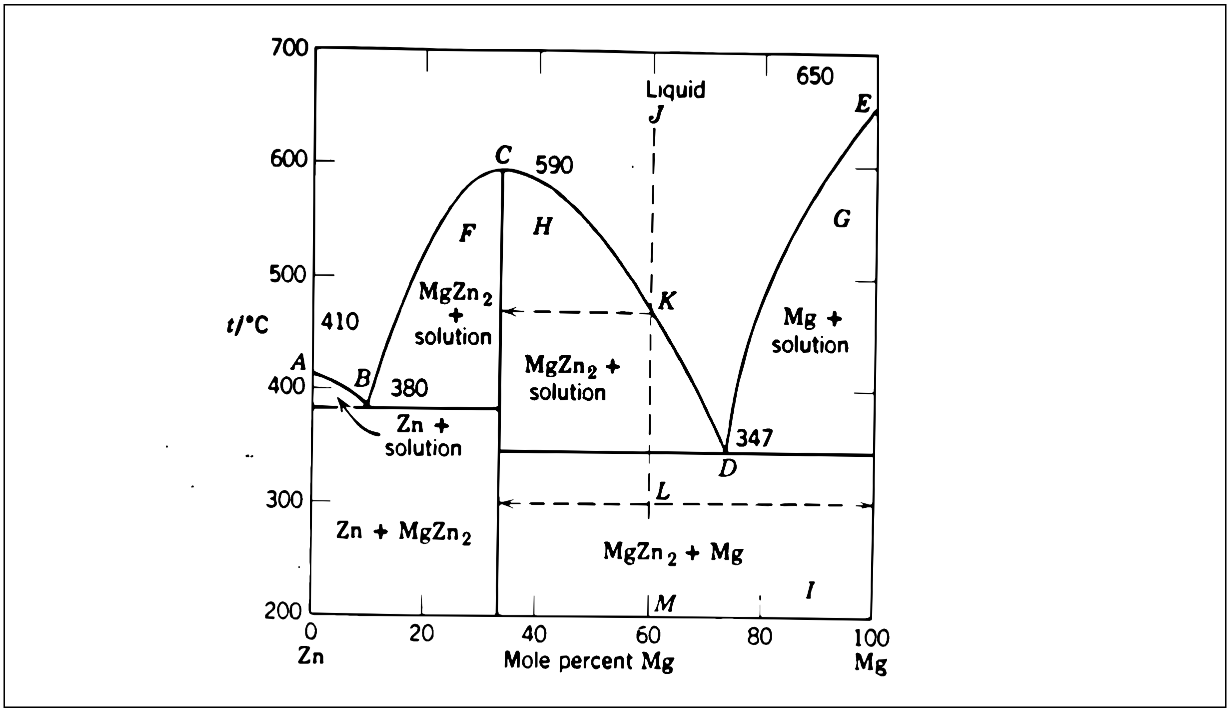
The figure above shows the Au-Si system. Eq. (6), derived earlier, can be used to predict the boundaries between the solid-liquid region [(Au + L) or (Si + L)] and the single phase region:

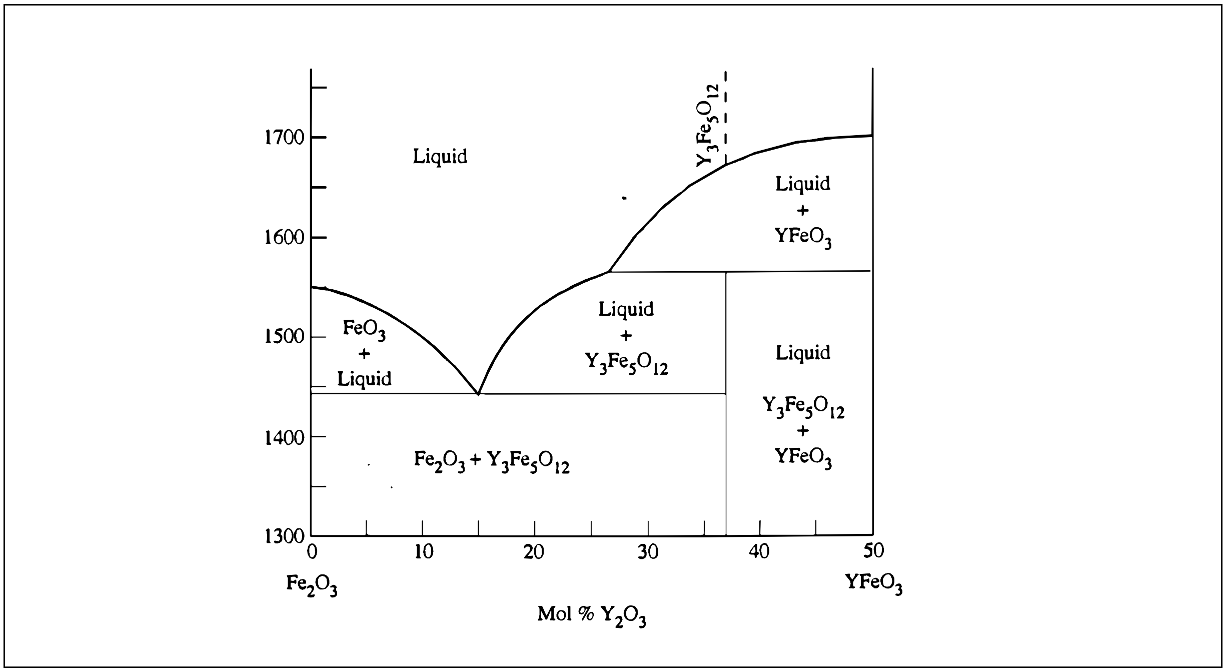
$$\ln x_{\mathrm{Au}} = \frac{\Delta_f H_{Au}}{R}\left(\frac{1}{T^*_{Au}} - \frac{1}{T}\right), \tag{18}$$

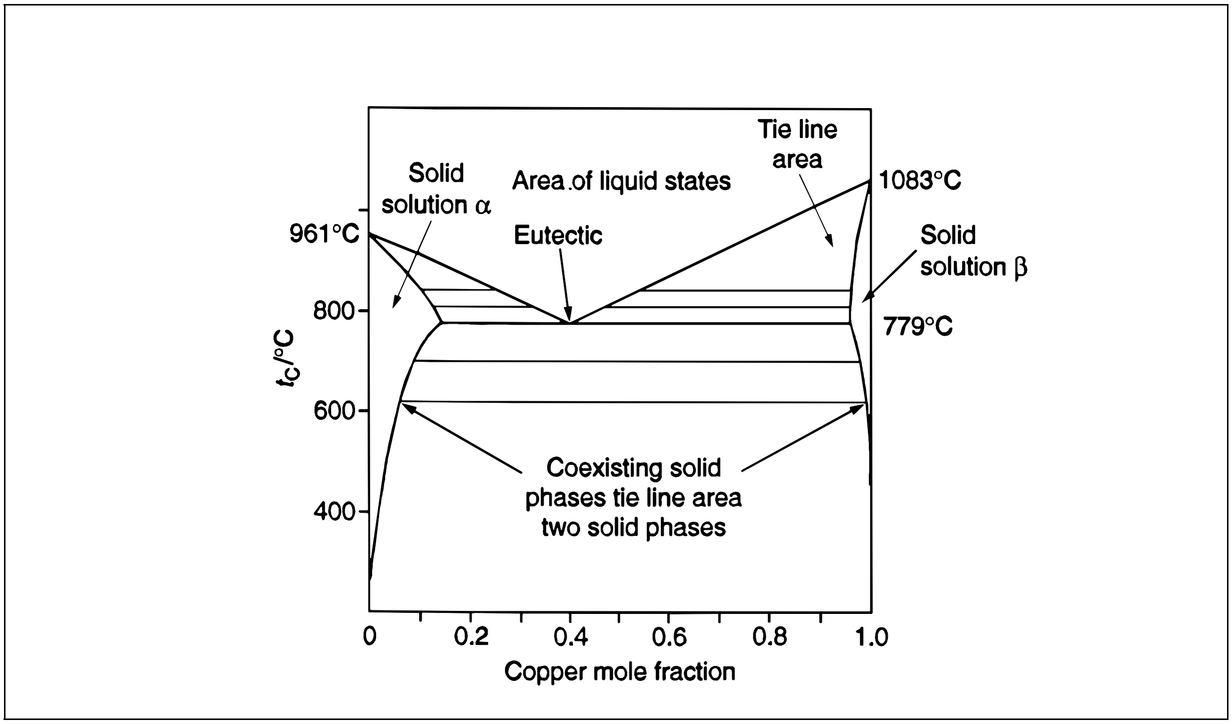


where, if we provide a composition x_{Au}, the equation predicts the temperature at which liquid with that composition is in equilibrium with pure Au(*s*). A similar equation can be written for Si using the enthalpy of fusion of Si and the melting point of pure Si to predict the curve *ce* on the right-hand-side of the equation. The intersection of these two curves will be the eutectic, *e*, *if* the assumptions made in Eq. (18) are valid over the entire range. However, this is not the case. In this particular case, the predictions from Eq. (18) (and one like it for Si) are shown along with the actual curves, on the left.

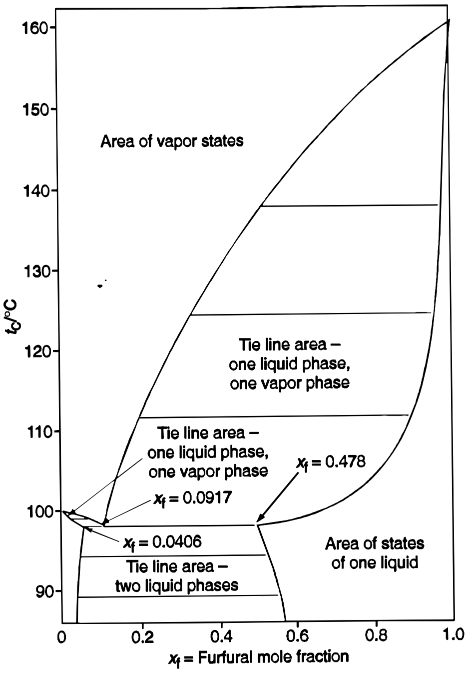
Other interesting artifacts commonly encountered in solid-liquid binary systems are (a) compound formation, (b) incongruent melting points (which occurs when a compound decomporses as it melts, and yields liquid and solid that have different compositions), and (c) solid solutions (which are similar to liquid solutions in that the composition is uniform throughout the solid phase). Examples of these cases are shown below.

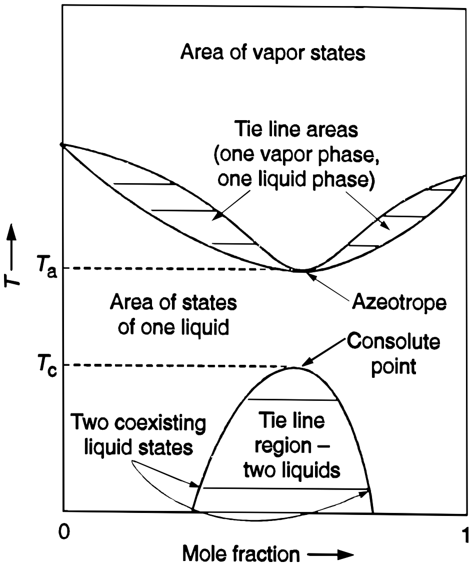






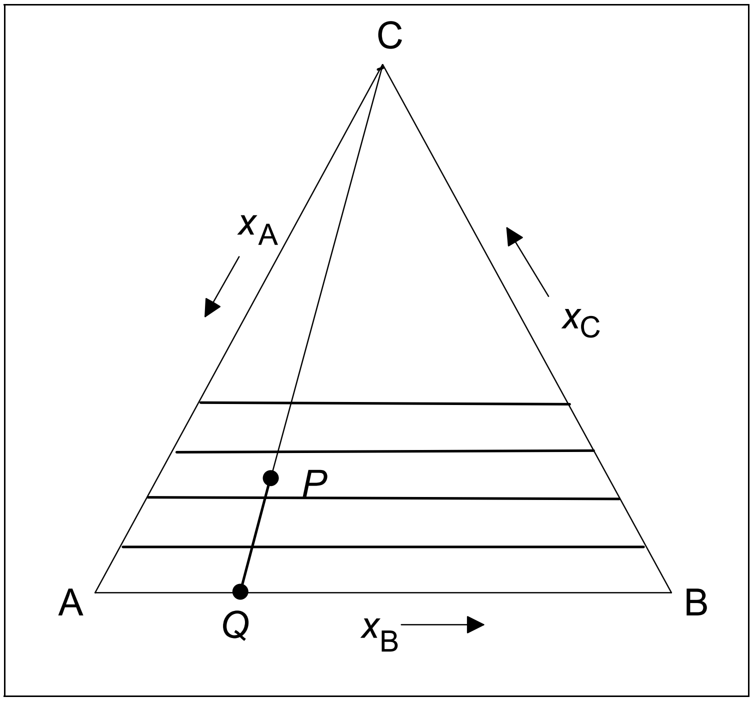
Some of the more exotic phase diagrams involving two immiscible liquids and their vapor are also shown below.





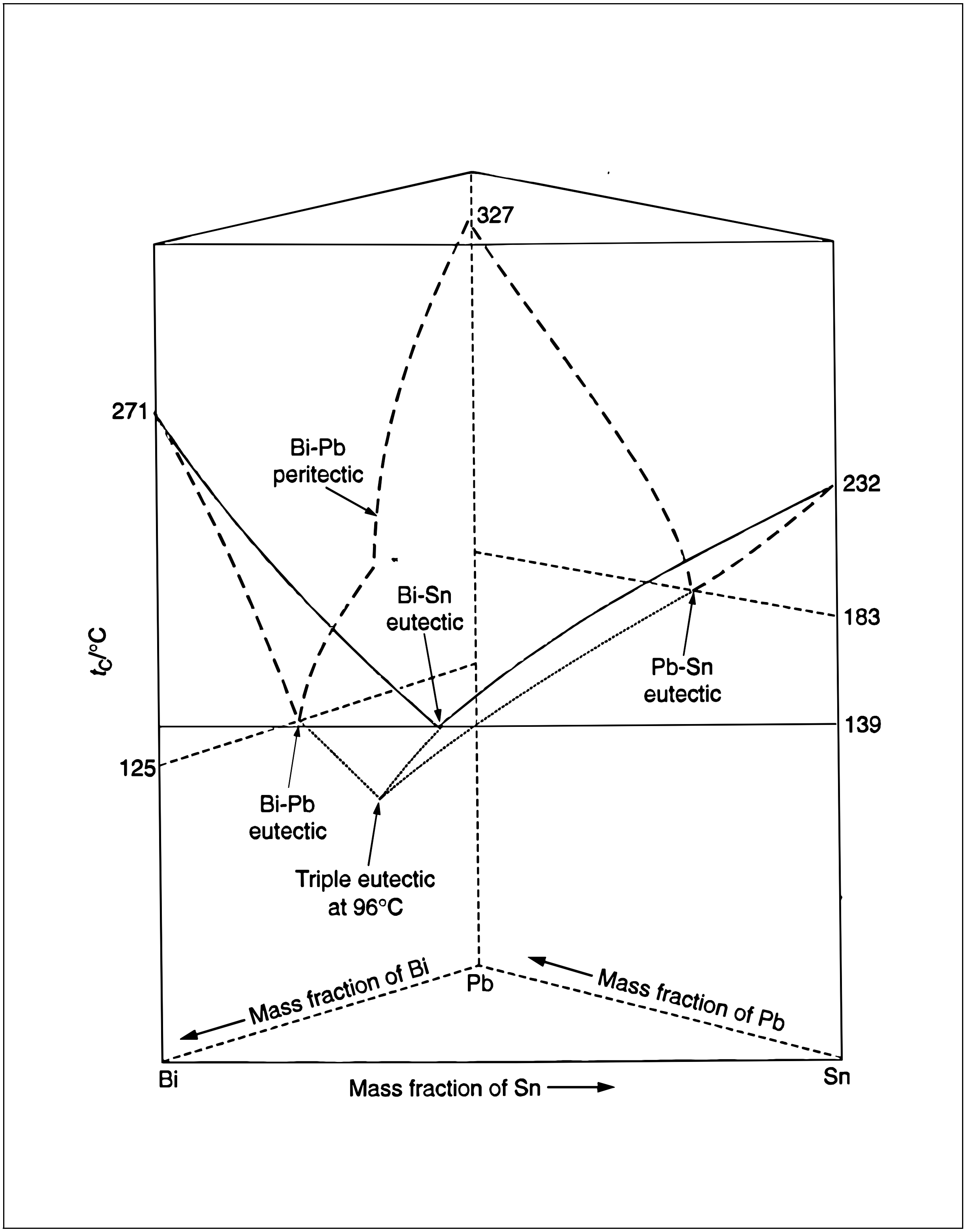
Three-component systems

Three component systems are typically represented on a graph drawn in the shape of an equilateral triangle, which represents the boundaries between regions of one, two, and three phases for fixed temperature and pressure.



Each corner of the triangle represents a pure component. So, the apex of the triangle in the figure to the left, labeled C, corresponds to $x_C = 1$. The side of the triangle opposite to that corner (side AB) corresponds to $x_C = 0$ and is, in fact, the composition axis for a two-component phase diagram for A and B. Lines parallel to the side AB, but closer to the corner C, represent successively increasing concentrations of C. Similarly, the side AC represents $x_B = 0$ and lines parallel to AC, but closer to B represent increasing concentrations of B, and so on. If we prepare a system with the composition *P*, and add pure C to the system (i.e., holding the number of moles of A and B constant), the system moves along the line PC towards the corner C. By the same token, if C is removed from the system, again holding A and B constant, the system will move away from P along the line *PQ*, reaching *Q* when all of C has been removed. Since temperature and pressure are fixed for this diagram, the number of degrees of freedom is given by $f = c - p$. A diagram in which the temperature is also allowed to vary will require four axes, the fourth one representing the temperature. Such a diagram is useful for establishing the presence of **triple eutectics** in alloy systems. An example of such a system is shown on the next page.

Methods of constructing and interpreting three component phase diagrams will be discussed in class.



327
271
232
183
139
125
Bi-Pb peritectic
Bi-Sn eutectic
Pb-Sn eutectic
Bi-Pb eutectic
Triple eutectic at 96°C
t_C/°C
Mass fraction of Bi
Mass fraction of Pb
Mass fraction of Sn
Pb
Bi
Sn