

## Chapter 8: Phase Equilibrium

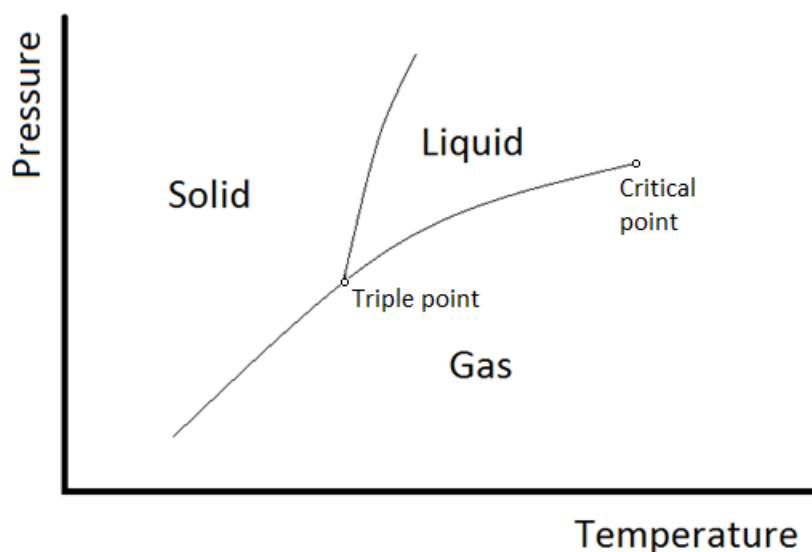
From the very elementary stages of our journey to describe the physical nature of matter, we learn to classify matter into three (or more) phases: solid, liquid, and gas. This is a fairly easy classification system that can be based on such simple ideas as shape and volume.

Phase	Shape	Volume
<b>Solid</b>	Fixed	Fixed
<b>Liquid</b>	Variable	Fixed
<b>Gas</b>	Variable	Variable

As we have progressed, we have seen that solids and liquids are not completely incompressible as they may have non-zero values of  $\kappa_T$ . And we learn that there are a number of finer points to describing the nature of the phases about which we all learn in grade school. In this chapter, we will employ some of the tools of thermodynamics to explore the nature of phase boundaries and see what we can conclude about them.

### Single Component Phase Diagrams

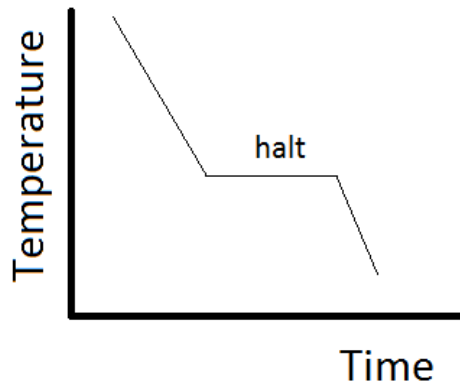
The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. This can be summarized in a phase diagram like the one shown below.



In this diagram, the phase boundaries can be determined by measuring the rate of cooling at constant temperature. A typical cooling curve is shown below. The temperature will decrease

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over time as a sample is allowed to cool. When the substance undergoes a phase change, say



from liquid to solid, the temperature will stop changing while heat is extracted due to the phase change. The temperature at which the halt occurs provides one point on the boundary at the temperature of the halt and the pressure at which the cooling curve was measured.

The same data can be obtained by heating the system using a technique such as scanning calorimetry. In this experiment, heat is supplied to a sample at a constant rate, and the temperature of the sample is measured, with breaks occurring at the phase change temperatures.

## Criterion for Phase Equilibrium

The thermodynamic criterion for phase equilibrium is simple. It is based upon the chemical potentials of the components in a system. For simplicity, consider a system with only one component. For the overall system to be in equilibrium, the chemical potential of the compound in each phase present must be the same. Otherwise, there will be some mass migration from one phase to another, decreasing the total chemical potential of the phase from which material is being removed, and increasing the total chemical potential of the phase into which the material is being deposited. So for each pair of phases present ( $\alpha$  and  $\beta$ ) the following must be true:

$$\mu_{\alpha} = \mu_{\beta}$$

## Gibbs Phase Rule

The **Gibbs phase rule** describes the number of compositional and phase variables that can be varied freely for a system at equilibrium. For each phase present in a system, the mole fraction of all but one component can be varied independently. However, the relationship

$$\sum_i x_i = 1$$

places a constraint on the last mole fraction. As such, there are  $C - 1$  compositional degrees of freedom for each phase present, where  $C$  is the number of components in the mixture. Similarly, all but one of the chemical potentials of each phase present must be equal, leaving only one that can be varied independently, leading to  $P - 1$  thermodynamic constraints placed on each component. Finally, there are two state variables that can be varied (such as pressure and temperature), adding two additional degrees of freedom to the system. The net number of

degrees of freedom is determined by adding all of the degrees of freedom and subtracting the number of thermodynamic constraints.

$$\begin{aligned} F &= 2 + P(C - 1) - C(P - 1) \\ &= 2 + PC - P - PC + C \end{aligned}$$

$$F = 2 + C - P$$

This is the Gibbs phase rule.

**Example:**

Show that the maximum number of phases that can co-exist at equilibrium for a single component system is  $P = 3$ .

**Solution:**

The maximum number of components will occur when the number of degrees of freedom is zero.

$$0 = 2 + 1 - P$$

$$P = 3$$

Note: This shows that there can never be a “quadruple point” for a single component system!

Because a system at its triple point has no degrees of freedom, the triple point makes a very convenient physical condition at which to define a temperature. For example, the International Practical Temperature Scale of 1990 (IPT-90) uses the triple points of hydrogen, neon, oxygen, argon, mercury, and water to define several low temperatures. (The calibration of a platinum resistance thermometer at the triple point of argon, for example, is described by Strouse (Strouse, 2008)). The advantage to using a triple point is that the compound sets both the temperature and pressure, rather than forcing the researcher to set a pressure and *then* measure the temperature of a phase change, introducing an extra parameter than can introduce uncertainty into the measurement.

### The Clapeyron Equation

Based on the thermodynamic criterion for equilibrium, it is possible to draw some conclusions about the state variables  $p$  and  $T$  and how they are related along phase boundaries. First, the chemical potentials of the two phases  $\alpha$  and  $\beta$  in equilibrium with one another must be equal.

$$\mu_{\alpha} = \mu_{\beta}$$

Also, any infinitesimal changes to the chemical potential of one phase must be offset by an infinitesimal change to the chemical potential of the other phase that is equal in magnitude.

$$\mu_{\alpha} + d\mu_{\alpha} = \mu_{\beta} + d\mu_{\beta}$$

Taking the difference between these two expressions shows that

$$d\mu_{\alpha} = d\mu_{\beta}$$

And since  $d\mu$  can be expressed in terms of molar volume and molar entropy

$$d\mu = Vdp - SdT$$

It is clear that there will be constraints placed on changes of temperature and pressure while maintaining equilibrium between the phases.

$$V_{\alpha}dp - S_{\alpha}dT = V_{\beta}dp - S_{\beta}dT$$

Gathering pressure terms on one side and temperature terms on the other

$$(V_{\alpha} - V_{\beta})dp = (S_{\alpha} - S_{\beta})dT$$

The differences  $V_{\alpha} - V_{\beta}$  and  $S_{\alpha} - S_{\beta}$  are the changes in molar volume and molar entropy for the phase changes respectively. So the expression can be rewritten

$$\Delta V dp = \Delta S dT$$

or

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

This is the **Clapeyron equation**. This expression makes it easy to see how the phase diagram for water is qualitatively different than that for most substances. Specifically, the negative slope of the solid-liquid boundary on a pressure-temperature phase diagram for water is very unusual, and arises due to the fact that for water, the molar volume of the liquid phase is smaller than that of the solid phase.

Given that for a phase change

$$\Delta S_{phase} = \frac{\Delta H_{phase}}{T}$$

the Clapeyron equation is sometimes written

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

**Example:**

Calculate the magnitude of the change in freezing point for water ( $\Delta H_{\text{fus}} = 6.009 \text{ kJ/mol}$  and the density of ice is  $\rho_{\text{ice}} = 0.9167 \text{ g/cm}^3$  while that for liquid water is  $\rho = 0.9999 \text{ g/cm}^3$ ) for an increase in pressure of 1.00 atm at 273 K.

**Solution:**

The molar volume of ice is given by

$$0.9167 \frac{\text{g}}{\text{cm}^3} \cdot \frac{\text{mol}}{18.016 \text{ g}} \cdot \frac{1000 \text{ cm}^3}{\text{L}} = 50.88 \frac{\text{L}}{\text{mol}}$$

The molar volume of liquid water at 0 °C is given by

$$0.9999 \frac{\text{g}}{\text{cm}^3} \cdot \frac{\text{mol}}{18.016 \text{ g}} \cdot \frac{1000 \text{ cm}^3}{\text{L}} = 55.50 \frac{\text{L}}{\text{mol}}$$

So  $\Delta V$  for the phase change of solid  $\rightarrow$  liquid (which corresponds to an endothermic change) is

$$50.88 \frac{\text{L}}{\text{mol}} - 55.50 \frac{\text{L}}{\text{mol}} = -4.62 \frac{\text{L}}{\text{mol}}$$

To find the change in temperature, use the Clapeyron equation.

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fus}}}{T \Delta V}$$

Separating the variables

$$dp = \frac{\Delta H_{\text{fus}}}{\Delta V} \cdot \frac{dT}{T}$$

Integration (with the assumption that  $\Delta H_{\text{fus}}/\Delta V$  does not change much over the temperature range) yields

$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{\text{fus}}}{\Delta V} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$p_2 - p_1 = \frac{\Delta H_{\text{fus}}}{\Delta V} \ln \left( \frac{T_2}{T_1} \right)$$

Or

$$T_2 = T_1 e^{\frac{\Delta p \Delta V}{\Delta H_{fus}}}$$

So

$$T_2 = 273 \text{ K} \cdot \exp \left\{ \frac{(1.00 \text{ atm}) \left( -4.62 \frac{\text{L}}{\text{mol}} \right)}{6009 \frac{\text{J}}{\text{mol}}} \left( \frac{8.314 \text{ J}}{0.08206 \text{ atm L}} \right) \right\}$$

$$T_2 = 252.5 \text{ K}$$

$$\Delta T = T_2 - T_1 = 252.5 \text{ K} - 273 \text{ K} = -20.5 \text{ K}$$

So the melting point will decrease by 20.5 K. Note that the phase with the smaller molar volume is favored at the higher pressure!

### The Clausius-Clapeyron Equation

The Clapeyron equation can be developed further for phase equilibria involving the gas phase as one of the phases. This is the case for either sublimation (solid  $\rightarrow$  gas) or vaporization (liquid  $\rightarrow$  gas). In the case of vaporization, the change in molar volume can be expressed

$$\Delta V = V_{gas} - V_{liquid}$$

Since substances undergo a very large increase in molar volume upon vaporization, the molar volume of the condensed phase (liquid in this case) is negligibly small compared to the molar volume of the gas. So,

$$\Delta V \approx V_{gas}$$

And if the vapor can be treated as an ideal gas,

$$V_{gas} = \frac{RT}{p}$$

Substitution into the Clapeyron equation yields

$$\frac{dp}{dT} = \frac{p \Delta H_{vap}}{RT^2}$$

Separating the variables puts the equation into an integrable form.

$$\frac{dp}{p} = \frac{\Delta H_{vap}}{R} \frac{dT}{T^2}$$

Noting that

$$\frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

makes the integration very easy. If the enthalpy of vaporization is independent of temperature over the range of conditions,

$$\int_{p_1}^{p_2} \frac{dp}{p} = -\frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This is the Clausius-Clapeyron equation. It can also be used to describe the boundary between solid and vapor phases by substituting the enthalpy of sublimation ( $\Delta H_{sub}$ )

**Example:**

The vapor pressure of a liquid triples when the temperature is increased from 25 °C to 45 °C. What is the enthalpy of vaporization for the liquid?

**Solution:**

The problem can be solved using the Clausius-Clapeyron equation. The following values can be used:

$p_2 = 3 p_1$	$T_2 = 318 \text{ K}$
$p_1 = p_1$	$T_1 = 298 \text{ K}$

Substitution into the Clausius-Clapeyron equation yields

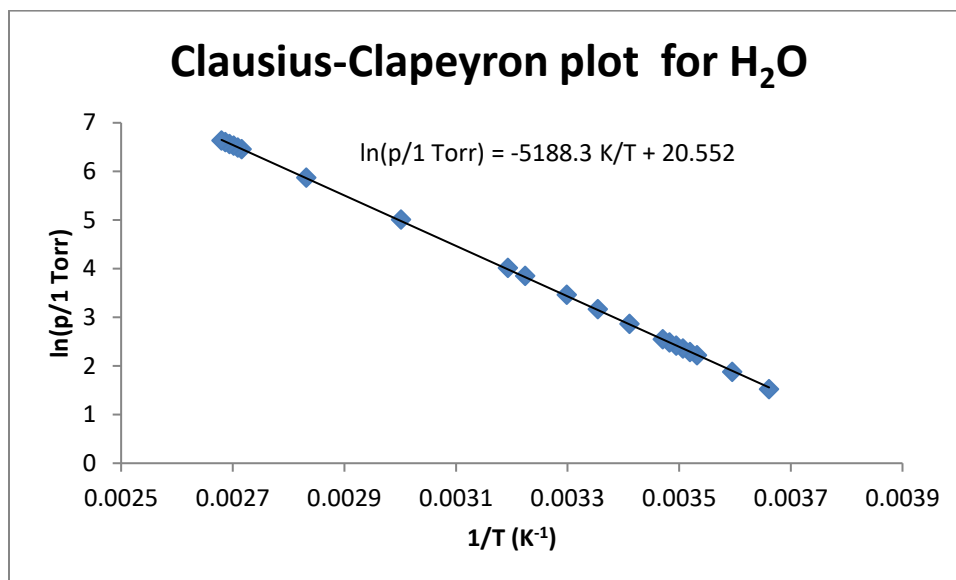
$$\ln\left(\frac{3 p_1}{p_1}\right) = -\frac{\Delta H_{vap}}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{318 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\Delta H_{vap} = 43280 \frac{\text{J}}{\text{mol}} = 43.28 \frac{\text{kJ}}{\text{mol}}$$

The Clausius-Clapeyron equation also suggests that a plot of  $\ln(p)$  vs  $1/T$  should yield a straight line, the slope of which is  $-\Delta H/R$  (provided that  $\Delta H_{vap}$  is independent of temperature over the range of temperatures involved..

$$\ln(p) = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T} \right) + const.$$

This approach is very useful when there are several pairs of measurements of vapor pressure and temperature. Such a plot is shown below for water. The data (between 0 °C and 100 °C) is taken from <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/watvap.html> (Nave).



For water, which has a very large temperature dependence, the linear relationship of  $\ln(p)$  vs  $1/T$  holds fairly well over a broad range of temperatures. So even though there is some curvature to the data, a straight line fit still results in a reasonable description of the data (depending, of course, on the precision needed in the experiment.) For this fit of the data,  $\Delta H_{vap}$  is found to be 43.14 kJ/mol.

For systems that warrant it, temperature dependence of  $\Delta H_{vap}$  can be included into the derivation of the model to fit vapor pressure as a function of temperature. For example, if the enthalpy of vaporization is assumed to take the form

$$\Delta H_{vap} = \Delta H_0 + aT + bT^2$$

the Clausius –Clapeyron equation becomes

$$\frac{dp}{p} = \frac{\Delta H_0 + aT + bT^2}{R} \frac{dT}{T^2}$$

or



$$\frac{dp}{p} = \frac{\Delta H_0}{R} \frac{dT}{T^2} + \frac{a}{R} \frac{dT}{T} + \frac{b}{R} dT$$

And so the integrated form becomes

$$\ln(p) = -\frac{\Delta H_0}{R} \left( \frac{1}{T} \right) + \frac{a}{R} \ln T + \frac{b}{R} T + \text{const.}$$

The results of fitting the Nave (Nave) data to the temperature dependent model are shown in the table below.

$\Delta H_0$ (J mol <sup>-1</sup> )	a (J mol <sup>-1</sup> K <sup>-1</sup> )	b (J mol <sup>-1</sup> K <sup>-2</sup> )	c
43078.99	0.010581	0.000501	20.5042

This results in calculated values of  $\Delta H_{\text{vap}}$  of 43.13 kJ/mol at 298 K, and 43.15 kJ/mol at 373 K. The results are a little bit skewed since there is no data above 100 °C included in the fit. A larger temperature dependence would be found if the higher-temperature data were included in the fit.

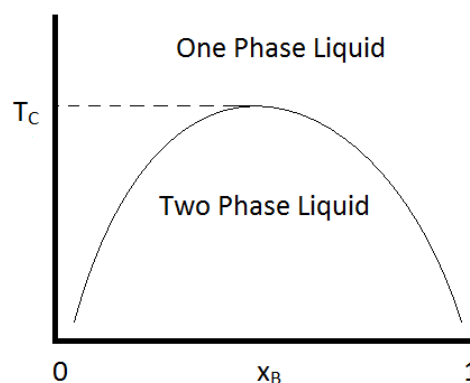
## Phase Diagrams for Binary Mixtures

As suggested by the Gibbs Phase Rule, the most important variables describing a mixture are pressure, temperature and composition. In the case of single component systems, composition is not important so only pressure and temperature are typically depicted on a phase diagram. However, for mixtures with two components, the composition is of vital importance, so there is generally a choice that must be made as to whether the other variable to be depicted is temperature or pressure.

Temperature-composition diagrams are very useful in the description of binary systems, many of which will form two-phase compositions at a variety of temperatures and compositions. In this section, we will consider several types of cases where the composition of binary mixtures are conveniently depicted using these kind of phase diagrams.

### Partially Miscible Liquids

A pair of liquids is considered partially miscible if there is a set of compositions over which the liquids will form a two-phase liquid system. This is a common situation and is the general case for a pair of liquids where one is polar and the other non-polar (such as water and vegetable oil.) Another case that is commonly used in the organic chemistry laboratory is the combination of diethyl ether and water. In this case, the differential solubility in the immiscible solvents allows the two-phase liquid system to be used to

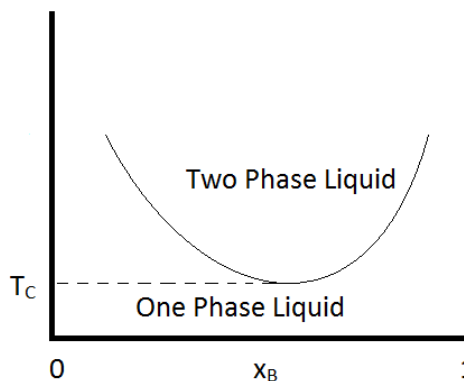


separate solutes using a separatory funnel method.

As is the case for most solutes, their solubility is dependent on temperature. For many binary mixtures of immiscible liquids, miscibility increases with increasing temperature. And then at some temperature (known as the upper critical temperature), the liquids become miscible in all compositions. An example of a phase diagram that demonstrates this behavior is shown to the left. An example of a binary combination that shows this kind of behavior is that of methyl acetate and carbon disulfide, for which the critical temperature is approximately 230 K at one atmosphere (Ferloni & Spinolo, 1974). Similar behavior is seen for hexane/nitrobenzene mixtures, for which the critical temperature is 293 K.

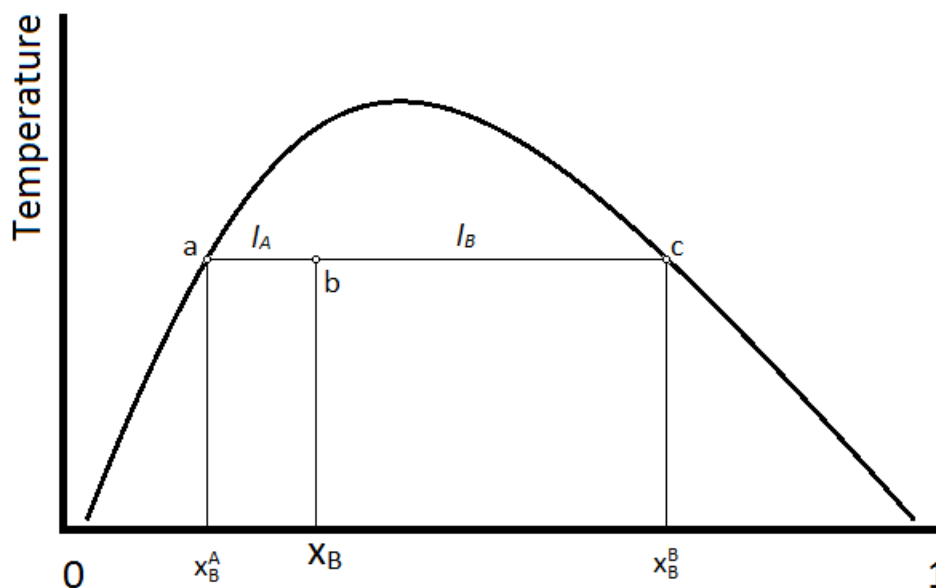
Another condition that can occur is for the two immiscible liquids to become completely miscible below a certain temperature, or to have a lower critical temperature. An example of a pair of compounds that show this behavior is water and trimethylamine. A typical phase diagram for such a mixture is shown to the right.

Some combinations of substances show both an upper and lower critical temperature, forming two-phase liquid systems at temperatures between these two temperatures. An example of a combination of substances that demonstrate the behavior is nicotine and water.



### The Lever Rule

The composition and amount of material in each phase of a two phase liquid can be determined using the **lever rule**. This rule can be explained using the following diagram.



Suppose that the temperature and composition of the mixture is given by point b in the above diagram. The horizontal line segment that passes through point b, is terminated at points a and c, which indicate the compositions of the two liquid phases. Point a indicates the mole fraction of compound B ( $x_B^A$ ) in the layer that is predominantly A, whereas the point c indicates the composition ( $x_B^B$ ) of the layer that is predominantly compound B. The relative amounts of material in the two layers is then inversely proportional to the length of the tie-lines a-b and b-c, which are given by  $l_A$  and  $l_B$  respectively. In terms of mole fractions,

$$l_A = x_B - x_B^A \quad \text{and} \quad l_B = x_B^B - x_B$$

The number of moles of material in the A layer ( $n_A$ ) and the number of moles in the B layer ( $n_B$ ) are inversely proportional to the lengths of the two lines  $l_A$  and  $l_B$ .

$$n_A l_A = n_B l_B$$

Or, substituting the above definitions of the lengths  $l_A$  and  $l_B$ , the ratio of these two lengths gives the ratio of moles in the two phases.

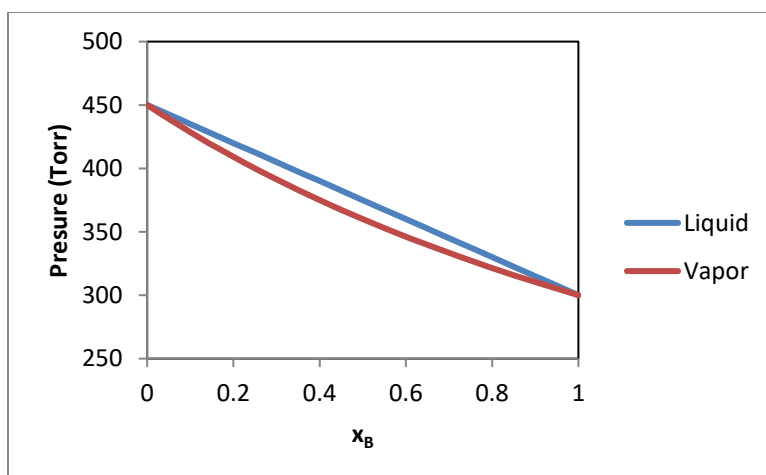
$$\frac{n_A}{n_B} = \frac{l_B}{l_A} = \frac{x_B^B - x_B}{x_B - x_B^A}$$

## Liquid-Vapor Systems

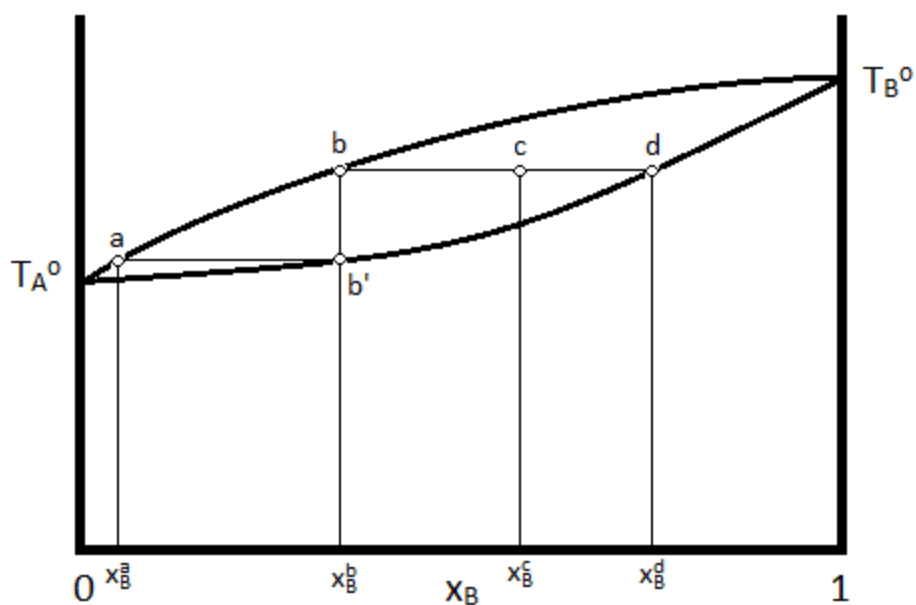
Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value (provided they do not decompose first!) A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using Raoult's Law.

### Raoult's Law

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following theoretical diagram for an ideal mixture of two compounds, one having a pure vapor pressure of  $P_A^o = 450$  Torr and the other having a pure vapor pressure of  $P_B^o = 300$  Torr. In the diagram, the liquid phase is represented at the top of the graph where the pressure is higher.



Oftentimes, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted below for an ideal mixture of two volatile liquids.



In this diagram,  $T_A^\circ$  and  $T_B^\circ$  represent the boiling points of pure compounds A and B. If a system having the composition indicated by  $x_B^c$  has its temperature increased to that indicated by point c, the system will consist of two phases, a liquid phase, with a composition indicated by  $x_B^d$  and a vapor phase indicated with a composition indicated by  $x_B^b$ . The relative amounts of material in each phase can be described by the lever rule, as described previously.

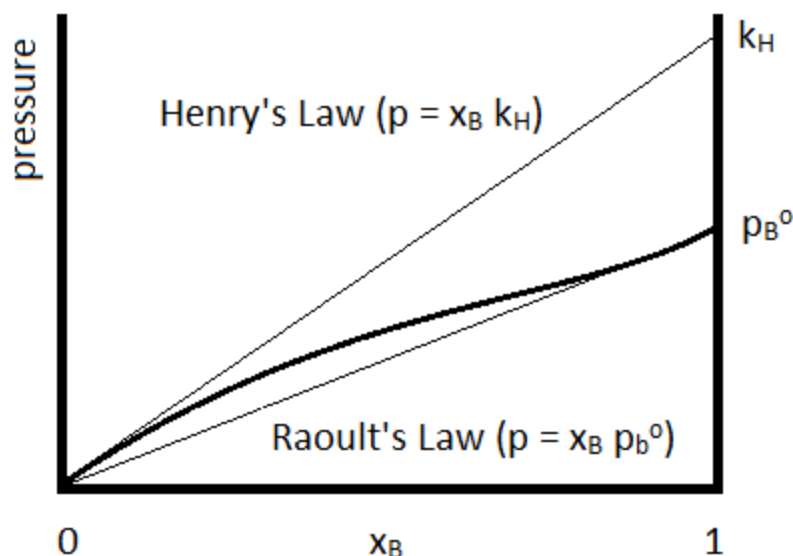
Further, if the vapor with composition  $x_B^b$  is condensed (the temperature is lowered to that indicated by point b') and revaporized, the new vapor will have the composition consistent with  $x_B^a$ . This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as **distillation**.

### Henry's Law

The proceeding discussion was based on the behaviors of ideal solutions of volatile compounds, and for which both compounds follow Raoult's Law. **Henry's Law** can be used to describe these deviations.

$$p_B = k_H p_B^\circ$$

For which the Henry's Law constant ( $k_H$ ) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in the following diagram.



Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

**Example:**

The solubility of  $\text{CO}_2(\text{g})$  in water at  $25^\circ\text{C}$  is  $3.32 \times 10^{-2} \text{ M}$  with a partial pressure of  $\text{CO}_2$  over the solution of 1 bar. Assuming the density of a saturated solution to be  $1 \text{ kg/L}$ , calculate the Henry's Law constant for  $\text{CO}_2$ .

**Solution:**

In one L of solution, there is 1000 g of water (assuming the mass of  $\text{CO}_2$  dissolved is negligible.)

$$(1000 \text{ g}) \left( \frac{\text{mol}}{18.02 \text{ g}} \right) = 55.5 \text{ mol } \text{H}_2\text{O}$$

The solubility of  $\text{CO}_2$  can be used to find the number of moles of  $\text{CO}_2$  dissolved in 1 L of solution also:

$$\frac{3.32 \cdot 10^{-2} \text{ mol}}{\text{L}} \cdot 1 \text{ L} = 3.32 \cdot 10^{-2} \text{ mol } \text{CO}_2$$

And so the mol fraction of  $\text{CO}_2$  is

$$x_B = \frac{3.32 \cdot 10^{-2} \text{ mol}}{55.5 \text{ mol}} = 5.98 \cdot 10^{-4}$$

And so

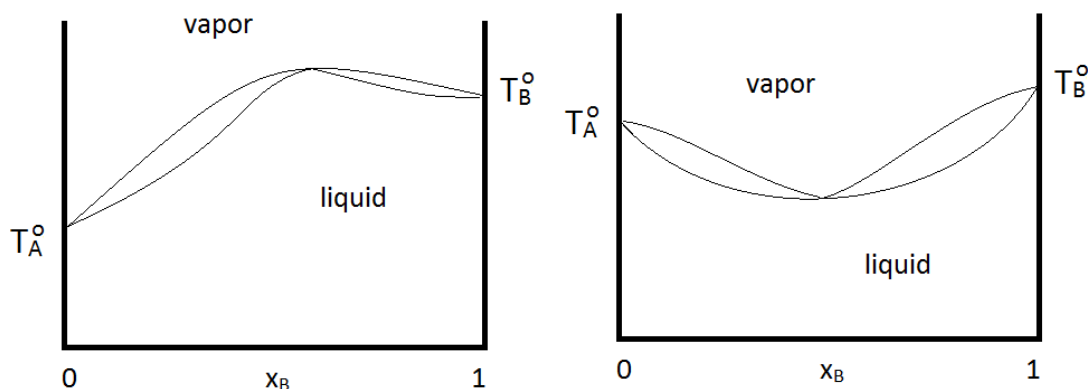
$$10^5 \text{ Pa} = 5.98 \cdot 10^{-4} k_H$$

Or

$$k_H = 1.67 \cdot 10^9 Pa$$

### Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

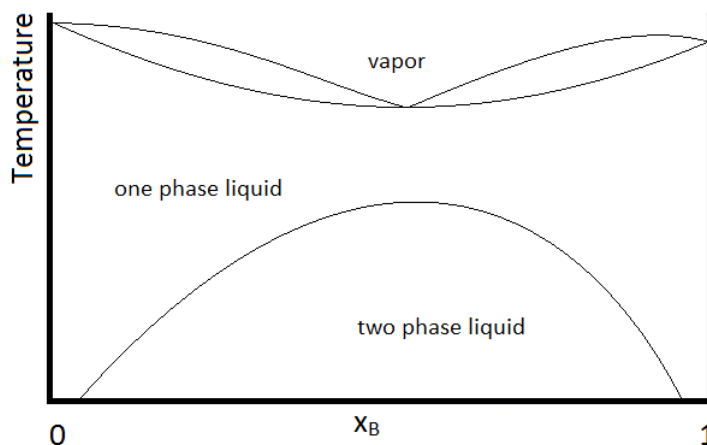


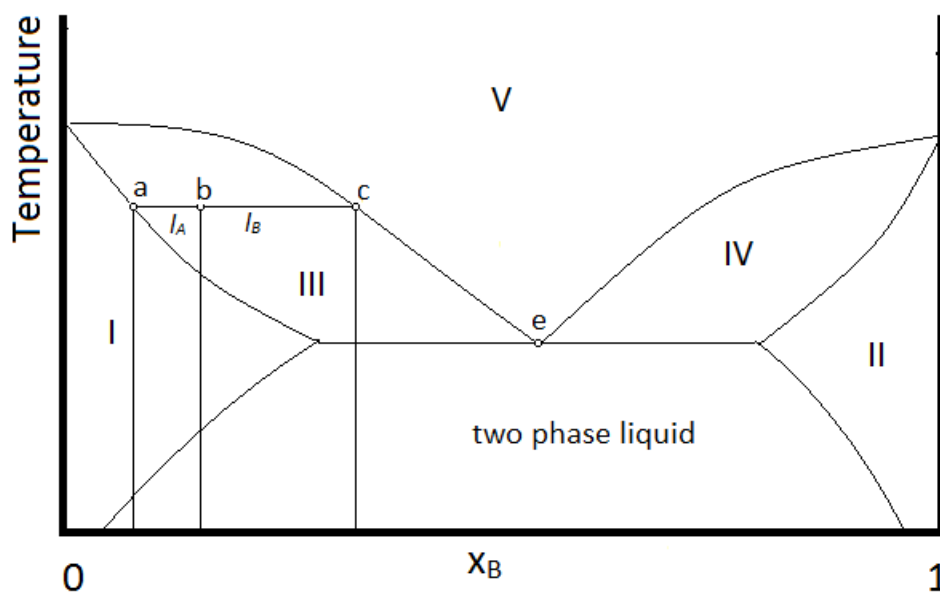
Azeotropes can be either maximum boiling or minimum boiling, as shown in the phase diagrams above. Regardless, distillation cannot purify past the azeotrope point, since the vapor and liquid phases have the same composition.

If a system forms a minimum boiling azeotrope and also has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look as follows:

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look as below.

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.





- I. Single phase liquid (mostly compound A)
- II. Single phase liquid (mostly compound B)
- III. Single phase liquid (mostly A) and vapor
- IV. Single phase liquid (mostly B) and vapor
- V. Vapor (miscible at all mole fractions since it is a gas)

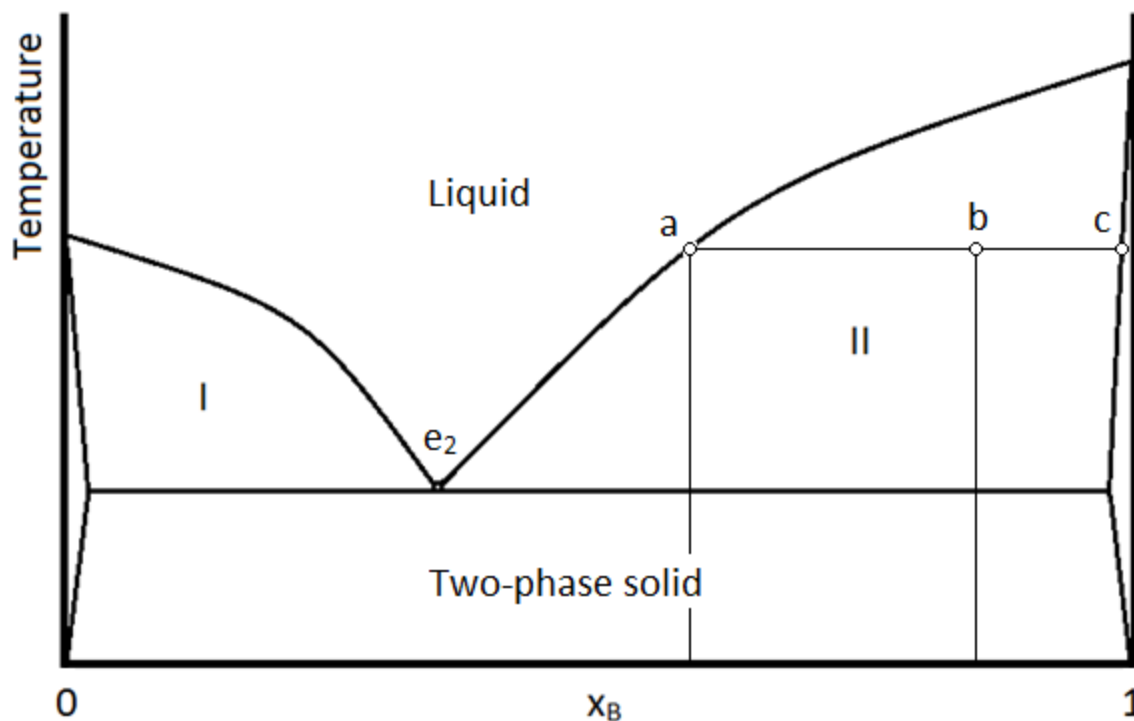
Within each two-phase region (III, IV, and the two-phase liquid region), the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines  $l_A$  and  $l_B$ .

### Solid-Liquid Systems

A phase diagram for two immiscible solids and the liquid phase (which is miscible in all proportions) is shown to the right. The point labeled “ $e_2$ ” is the **eutectic point**, meaning the composition for which the mixture of the two solids has the lowest melting point. The four main regions can be described as below:

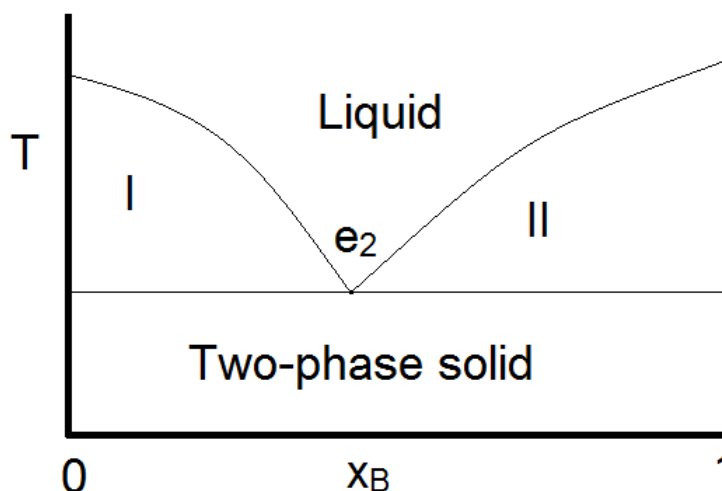
- I. Two-phase solid
- II. Solid (mostly A) and liquid (A and B)
- III. Solid (mostly B) and liquid (A and B)
- IV. Single phase liquid (A and B)





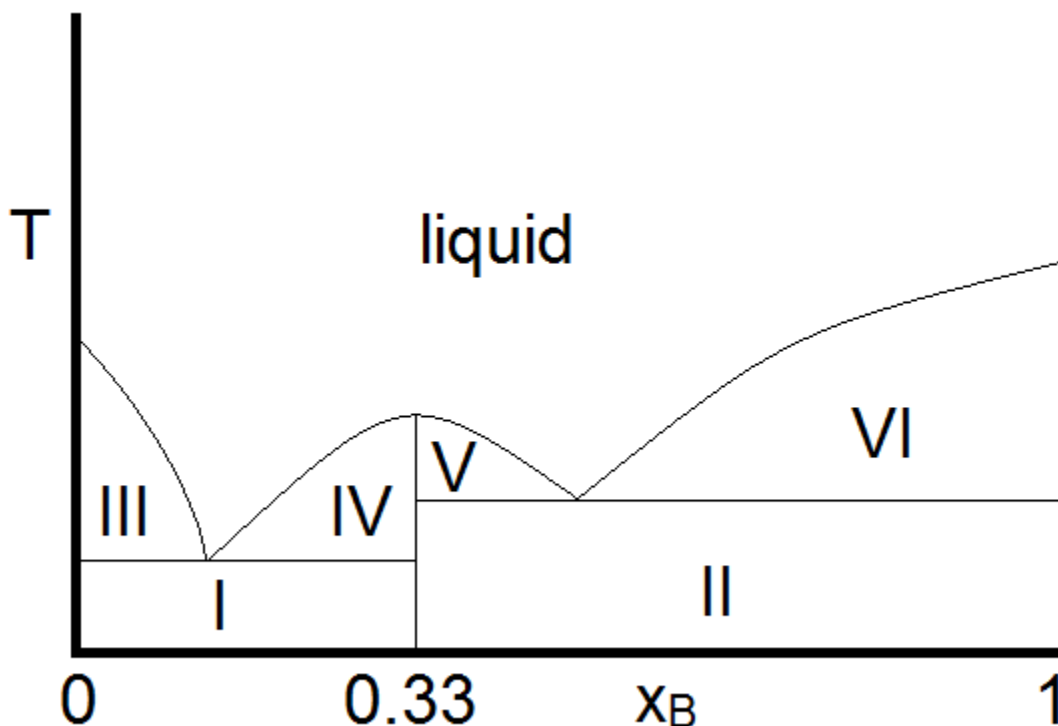
The unlabeled regions on the sides of the diagram indicate regions where one solid is so miscible in the other, that only a single phase solid forms. This is different than the “two-phase solid” region where there are two distinct phases, meaning there are regions (crystals perhaps) that are distinctly A or B, even though they are intermixed within on another. Region I contains two phases: a solid phase that is mostly compound A, and a liquid phase which contains both A and B. A sample in region II (such as the temperature/composition combination depicted by point b) will consist of two phases: 1 is a liquid mixture of A and B with a composition given by that at point a, and the other is a single phase solid that is mostly pure compound B, but with traces of A entrained within it. As always, the lever rule applies in determining the relative amounts of material in the two phases.

In the case where the widths of the small regions on either side of the phase diagram are negligibly small, a simplified diagram with a form similar to that shown to the right can be used. In this case, it is assumed that the solids never form a single phase!



Another important case is

that for which the two compounds A and B can react to form a third chemical compound C. If the compound C is stable in the liquid phase (does not decompose upon melting), the phase diagram will look like the one below.



In this diagram, the vertical boundary at  $x_B = 0.33$  is indicative of the compound C formed by A and B. From the mole fraction of B, it is evident that the formula of compound C is  $A_2B$ . The reaction that forms compound C is



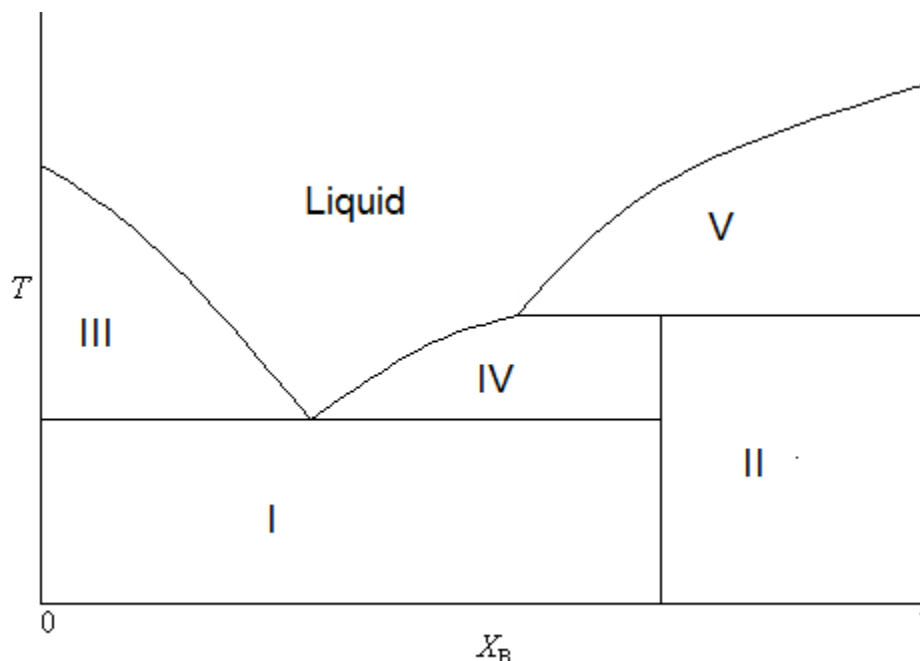
Thus, at overall compositions where  $x_B < 0.33$ , there is excess compound A (B is the limiting reagent) and for  $x_B$  there is an excess of compound B (A is now the limiting reagent.) With this in mind, the makeup of the sample in each region can be summarized as

- I. Two phase solid (A and C)
- II. Two phase solid (C and B)
- III. Solid A and liquid (A and C)
- IV. Solid C and liquid (A and C)
- V. Solid C and liquid (C and B)
- VI. Solid B and liquid (C and B)
- liquid. Single phase liquid (A and C or C and B, depending on which is present in excess)

Zinc and Magnesium are an example of two compounds that demonstrate this kind of behavior, with the third compound having the formula  $\text{Zn}_2\text{Mg}$  (Ghosh, Mezbahul-Islam, & Medraj, 2011).

### Incongruent Melting

Oftentimes, the stable compound formed by two solids is only stable in the solid phase. In other words, it will decompose upon melting. As a result, the phase diagram will take a slightly different form, as is shown in the following diagram.



In this diagram, the formula of the stable compound is  $\text{AB}_3$  (consistent with  $x_B = 0.75$ .) But you will notice that the boundary separating the two two-phase solid regions does not extend all of the way to the single phase liquid portion of the diagram. This is because the compound will decompose upon melting. The process of decomposition upon melting is also called **incongruent melting**. The makeup of each region can be summarized as

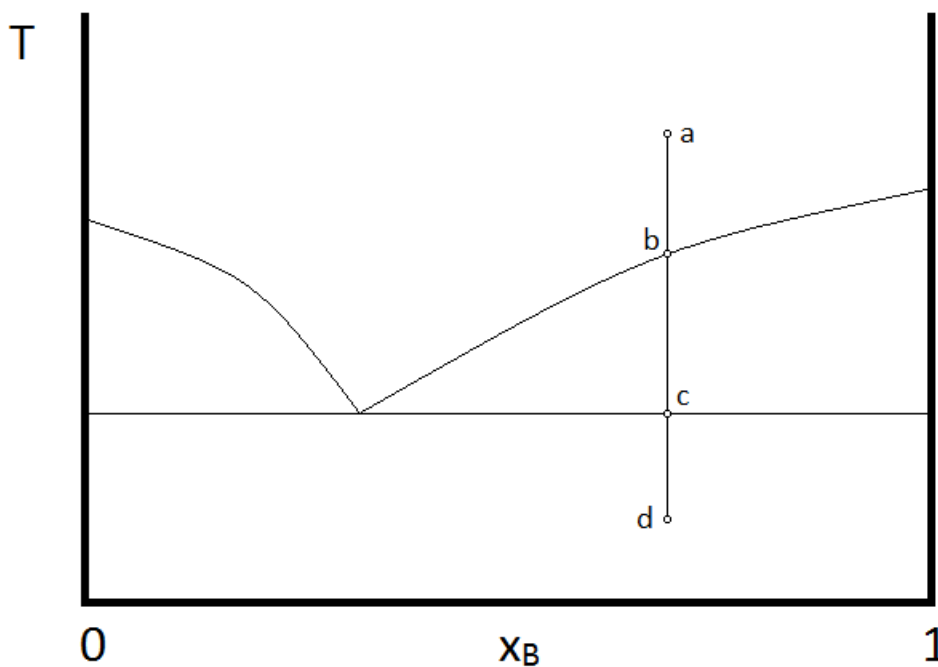
- I. Two phase solid (A and C)
- II. Two phase solid (C and B)
- III. Solid A and liquid (A and B)
- IV. Solid C and liquid (A and B)
- V. Solid B and liquid (A and B)

There are many examples of pairs of compounds that show this kind of behavior. One combination is sodium and potassium, which form a compound ( $\text{Na}_2\text{K}$ ) that is unstable in the liquid phase and so it melts incongruently (Rossen & Bleiswijk, 1912).

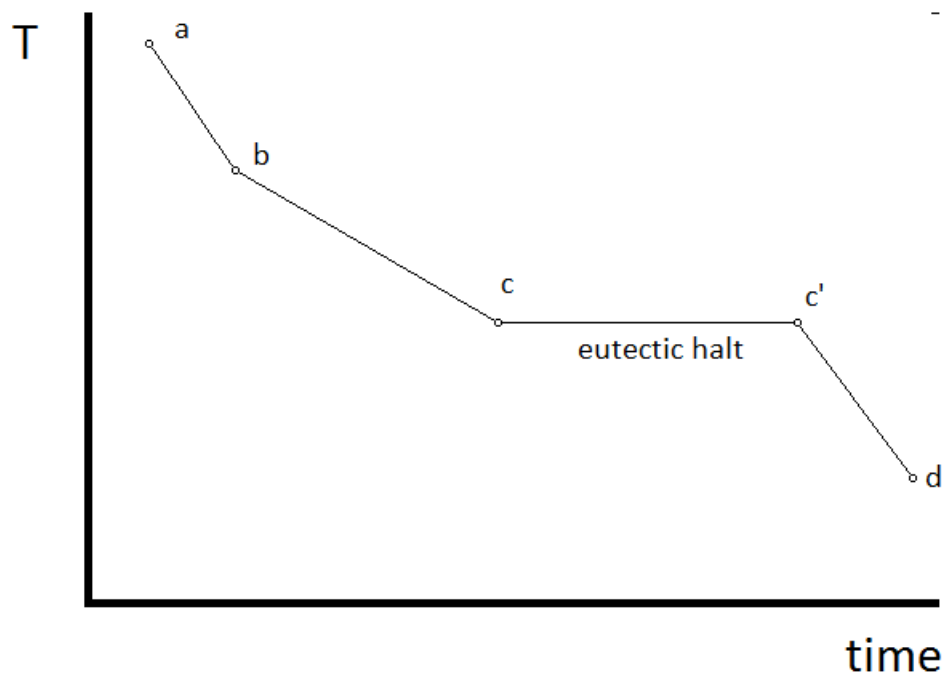
## Cooling Curves

The method that is used to map the phase boundaries on a phase diagram is to measure the rate of cooling for a sample of known composition. The rate of cooling will change as the sample (or some portion of it) begins to undergo a phase change. These “breaks” will appear as changes in slope in the temperature-time curve.

Consider a binary mixture for which the phase diagram is as shown below.



A cooling curve for a sample that begins at the temperature and composition given by point a is shown below.



As the sample cools from point a, the temperature will decrease at a rate determined by the sample composition, and the geometry of the experiment (for example, one expects more rapid cooling if the sample has more surface area exposed to the cooler surroundings) and the temperature difference between the sample and the surroundings.

When the temperature reaches that at point b, some solid compound B will begin to form. This will lead to a slowing of the cooling due to the exothermic nature of solid formation. But also, the composition of the liquid will change, becoming richer in compound A as B is removed from the liquid phase in the form of a solid. This will continue until the liquid attains the composition at the eutectic point (point c in the diagram.)

When the temperature reaches that at point c, both compounds A and B will solidify, and the composition of the liquid phase will remain constant. As such, the temperature will stop changing, creating what is called the **eutectic halt**. Once all of the material has solidified (at the time indicated by point c'), the cooling will continue at a rate determined by the heat capacities of the two solids A and B, the composition, and (of course) the geometry of the experimental set up. By measuring cooling curves for samples of varying composition, one can map the entire phase diagram.

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### Vocabulary and Concepts

azeotrope .....	195	lever rule .....	190
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### Learning Objectives

After mastering the material in this chapter, one will be able to

1. State the thermodynamic criterion for equilibrium in terms of chemical potential.
2. Derive and interpret the Gibbs Phase Rule.
3. Derive the Clapeyron equation from the thermodynamic criterion for equilibrium.
4. Interpret the slope of phase boundaries on a pressure-temperature phase diagram in terms of the relevant changes in entropy and molar volume for the given phase change.
5. Derive the Clausius-Clapeyron equation, stating all of the necessary approximations.
6. Use the Clausius-Clapeyron equation to calculate the vapor pressure of a substance or the enthalpy of a phase change from pressure-temperature data.
7. Interpret phase diagrams for binary mixtures, identifying the phases and components present in each region.
8. Perform calculations using Raoult's Law and Henry's Law to relate vapor pressure to composition in the liquid phase.
9. Describe the distillation process, explaining how the composition of liquid and vapor phases can differ, and how azeotrope composition place bottlenecks in the distillation process.
10. Describe how cooling curves are used to derive phase diagrams by locating phase boundaries.

## Problems