

Phase diagrams

Here we describe a systematic way of discussing the physical changes mixtures undergo when they are heated or cooled and when their compositions are changed. We see how to use phase diagrams to judge whether two substances are mutually miscible, whether an equilibrium can exist over a range of conditions, or whether the system must be brought to a definite pressure, temperature, and composition before equilibrium can be established. Phase diagrams – have considerable commercial and industrial significance, particularly for semiconductors, ceramics, steels, and alloys; also the basis of separation procedures in the petroleum industry and the formulation of foods and cosmetic preparations.

Phases, components, and degrees of freedom

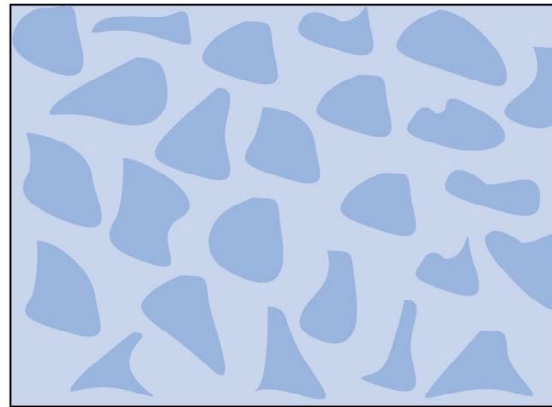
Definitions

Phase – a state of matter that is uniform throughout, not only in chemical composition but also in physical state: solid, liquid, and gas phases, various solid phases. The number of phases in a system – P . A gas, a gaseous mixture, a crystal, two totally miscible liquids – examples of a single phase ($P = 1$). An alloy of two metals – a two-phase system ($P = 2$) if the metals are immiscible, but a single phase system ($P = 1$) if they are miscible. A solution of solid A in solid B – a homogeneous mixture of the two substances – is uniform on a molecular scale: atoms of A are surrounded by atoms of A and B, and any segment cut from the sample, however small, is representative of the composition of the whole.

A dispersion is uniform on a macroscopic scale but not on a microscopic scale – it consists of grains or droplets of one substance in a matrix of the other.



(a)

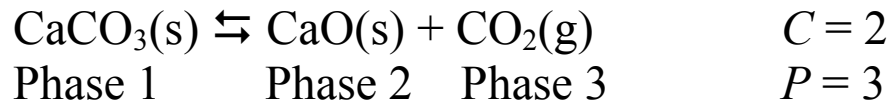


(b)

A small sample could come entirely from of the minute grains of pure A and would not be representative of the whole.

Dispersions are important because in many advanced materials (including steels) heat treatment cycles are used to achieve the precipitation of a fine dispersion of particles of one phase within a matrix formed by a saturated solid solution phase – through this process one can achieve the mechanical properties of the materials desirable for a particular application.

A **constituent** of a system – a chemical species that is present. A mixture of ethanol and water – two constituents. A solution of sodium chloride – two constituents. A **component** – a chemically independent constituent of a system. The number of components, C – the minimum number of independent species necessary to define the composition of all phases present in the system. When no chemical reaction takes place, the number of components is equal to the number of constituents. Pure water is a one-component system ($C = 1$). A mixture of ethanol and water is a two-component system ($C = 2$). When a reaction can occur, we need to decide the minimum number of species that can be used to specify the composition of all phases.



There are three phases, but only two components, CaO and CO₂.
The identity of CaCO₃ can be expressed in term of CaO and CO₂.

Example 1. Counting components

How many components are present in a system in which ammonium chloride undergoes thermal decomposition?

Begin by writing down the chemical equation for the reaction and identifying the constituents of the system (all the species present) and the phases. Then decide whether, under the conditions prevailing in the system, any of the constituents can be prepared from any other constituents. The removal of these constituents leaves the number of independent constituents. Finally, identify the minimum number of these independent constituents that are needed to specify the composition of all the phases.



There are three constituents and two phases (one solid, one gas). However, NH₃ and HCl are formed in fixed stoichiometric proportions by the reaction. Therefore, the compositions of both phases can be expressed in terms of the single species NH₄Cl:

$C = 1$. However, if additional HCl (or NH₃) were supplied to the system, the decomposition of NH₄Cl would not give the correct composition of the gas phase and HCl (or NH₃) would have to be invoked as a second component. A system consisting of hydrogen, oxygen, and water at room temperature has three components: under the conditions prevailing in the system, H₂ and O₂ do not react to form water, so they are independent constituents.

The **variance**, F – the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. In a single-component, single-phase system ($C = 1, P = 1$), the pressure and temperature may be changed independently without changing the number of phases: $F = 2$. Such a system is called **bivariant**, it has two **degrees of freedom**.

If two phases are in equilibrium (a liquid and its vapor) in a single-component system ($C = 1, P = 2$), only the temperature (or the pressure) can be changed independently, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium: $F = 1$.

The phase rule

A general relation between the variance F , the number of components, C , and the number of phases in equilibrium, P , was derived by Gibbs:

$$F = C - P + 2$$

A one components system. The condition of equilibrium: $\mu_j(\alpha) = \mu_j(\beta)$

Each chemical potential is a function of T and p : $\mu_j(\alpha, p, T) = \mu_j(\beta, p, T)$

This equation relates T and p , so only one of these variables is independent and the second can be found from the equation, once we know the value for the first.

Three phases in mutual equilibrium: $\mu_j(\alpha, p, T) = \mu_j(\beta, p, T) = \mu_j(\gamma, p, T)$

We have 2 equations with 2 unknowns, T and p . There is only one solution for T and p , so $F = 0$.

Four phases cannot be in mutual equilibrium in a one-component system, because in that case we have three equations:

$$\mu_j(\alpha, p, T) = \mu_j(\beta, p, T) \quad \mu_j(\beta, p, T) = \mu_j(\gamma, p, T) \quad \mu_j(\gamma, p, T) = \mu_j(\delta, p, T)$$

for only two unknowns – no solution.

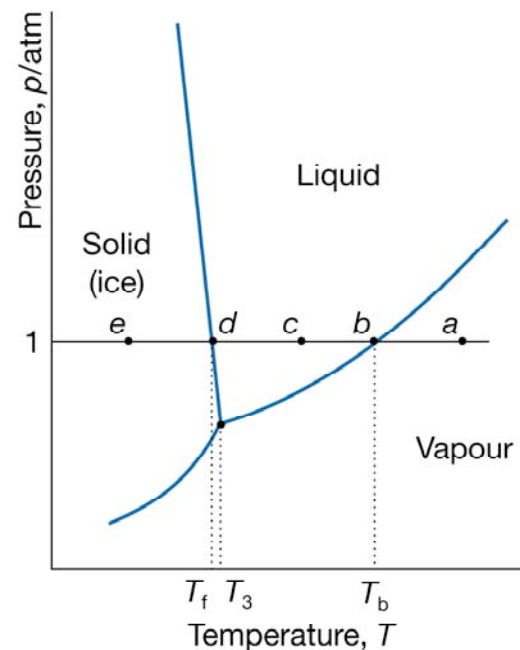
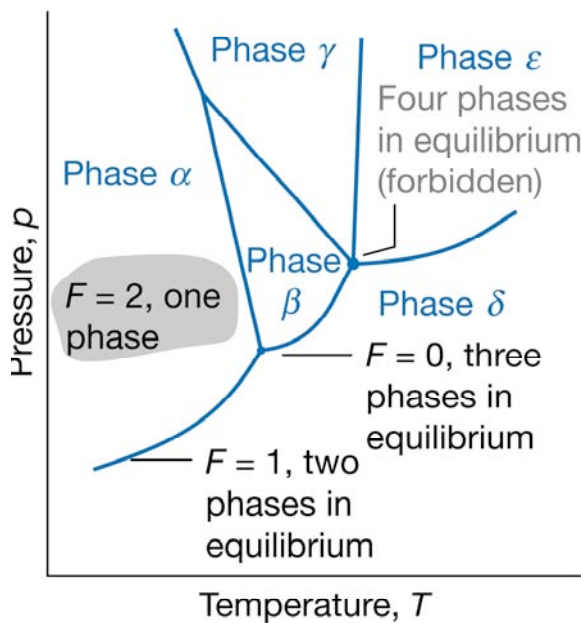
Now consider the general case. Begin by counting the total number of intensive variables: p , T give us 2. The composition of a phase can be specified by giving mole fractions of $C - 1$ components because $x_1 + x_2 + \dots + x_C = 1$. When we have P phases, the total number of mole fractions needed to be specified: $P(C - 1)$. The total number of intensive variables: $P(C - 1) + 2$.

At equilibrium, the chemical potential of component J must be the same in every phase:
 $\mu_j(\alpha) = \mu_j(\beta) = \dots$ for P phases

There are $P - 1$ equations to be satisfied for each component J . We have C components, so the total number of equations is $C(P - 1)$. The total number of degrees of freedom equals to the total number of variables minus the total number of equations:

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

One-component systems



$$F = 3 - P$$

Only one phase is present: $F = 2$ – an area on a phase diagram.

Two phases in equilibrium: $F = 1$ – pressure is not freely variable if the temperature is set; at a given temperature a liquid has a characteristic vapor pressure. The equilibrium of two phases is represented by a line in the phase diagram.

We could select the pressure, but then the two phases would be at equilibrium at a single definite temperature.

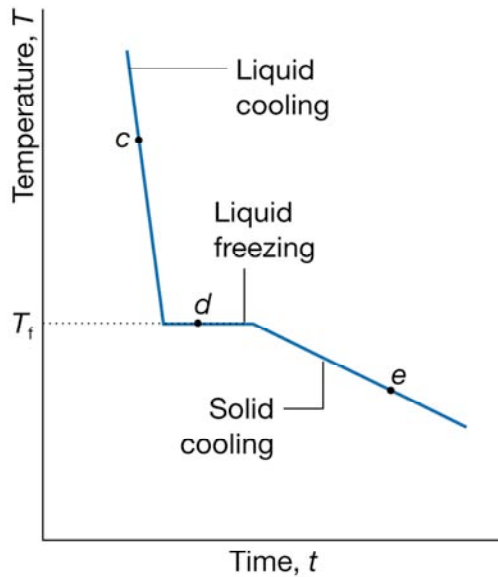
Three phases in equilibrium: $F = 0$ – the system is invariant. This special condition can be established only at a definite temperature and pressure that are characteristic of the substance and outside our control. The equilibrium between three phases – a point (the triple point) on a phase diagram. Four phases cannot be in equilibrium in a one-component system – F cannot be negative.

We can identify the described features in the experimentally determined phase diagram of water. The diagram above summarizes the changes in a sample initially at a and cooled at constant pressure. The sample remains entirely gaseous until the temperature reaches b , when liquid appears. Two phases are now at equilibrium, $F = 1$. Because we have decided to specify the pressure, the temperature of the equilibrium is not under our control. Lowering the temperature takes the system to c in the one-phase liquid region ($F = 2$). When ice appears at d , the variance becomes 1 again.

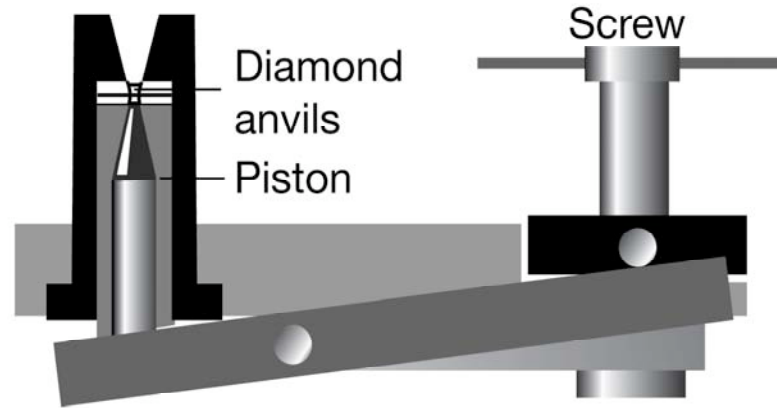
Experimental procedures

Thermal analysis: takes the advantage of the enthalpy change during a first-order transition. A sample is allowed to cool and its temperature is monitored. Heat is evolved and the cooling stops until the transition is complete.

Modern work often deals with systems at very high pressures. Some of the highest pressures are produced in a **diamond-anvil cell**. The sample is placed in a minute cavity between two



Relevant to geology



diamonds, and then pressure is exerted simply by turning the screw – up to 1 Mbar can be reached. The pressure is monitored spectroscopically by the shift of spectral lines in small pieces of ruby added to the sample. One application – to study transitions of covalent

solids to metallic solids: I_2 becomes metallic at ~ 200 kbar.

Two-component systems

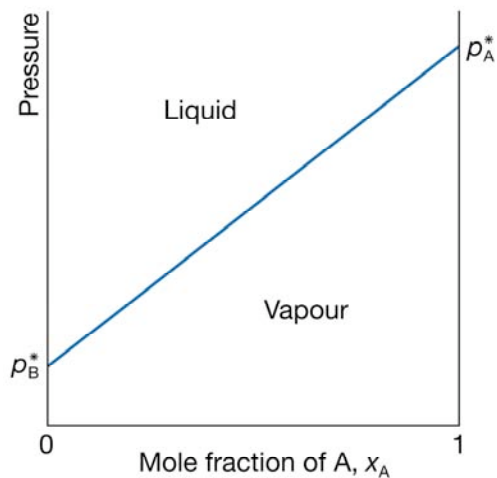
$$C = 2$$

$$F = 4 - P$$

If the temperature is constant, the remaining variance,

$$F' = 3 - P$$

has a maximum value of 2. One of these two remaining degrees of freedom is the pressure and the other is the composition (expressed by the mole fraction of one component. One form of the phase diagram – a map of pressures and compositions at which each phase is stable and the other – a map of temperatures and compositions.



Vapor pressure diagrams

The partial vapor pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law:

$$p_A = x_A p_A^* \quad p_B = x_B p_B^*$$

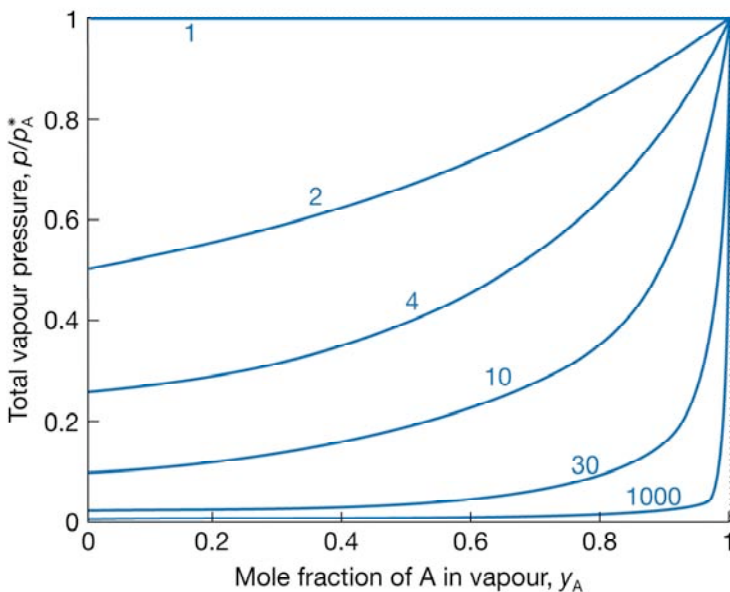
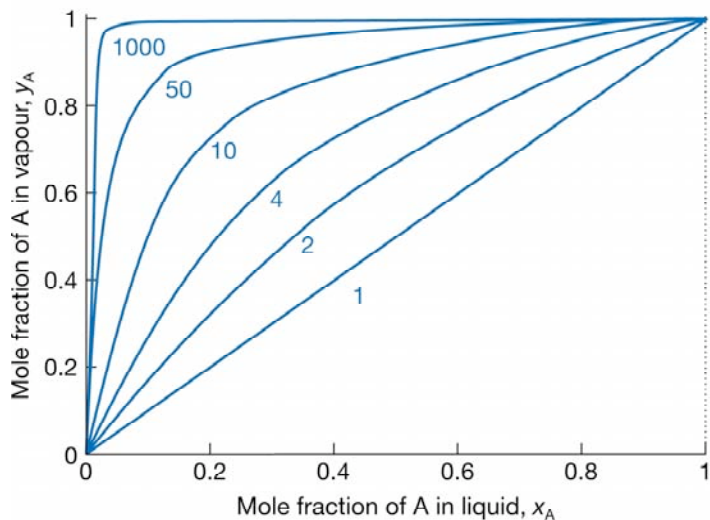
The total pressure:

$$p = p_A + p_B = x_A p_A^* + x_B p_B^*$$

$$p = p_B^* + (p_A^* - p_B^*) x_A$$

The total vapor pressure changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1.

The composition of the vapor



The compositions of the liquid and vapor that are in mutual equilibrium are not necessarily the same. Common sense: the vapor should be richer in the more volatile component. The partial pressures of the components are given by Raoult's law.

From Dalton's law, the mole fractions in gas are:

$$y_A = p_A/p \quad y_B = p_B/p$$

Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in

terms of the mole fractions in the liquid:

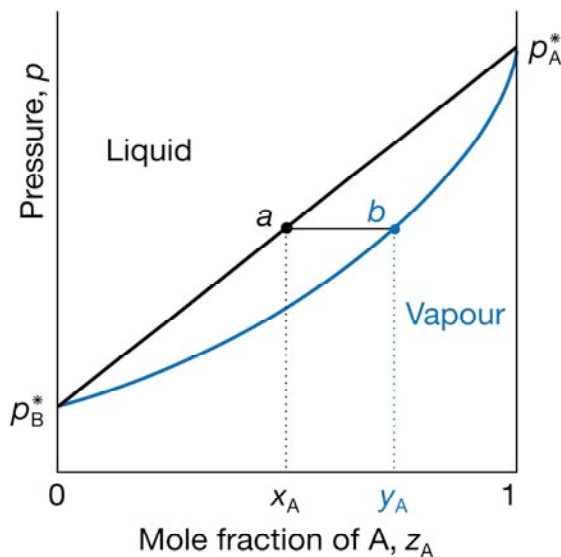
$$y_A = \frac{x_A p_A^*}{p_B^* + (p_B^* - p_A^*)x_A} \quad y_B = 1 - y_A$$

The figure shows the composition of the vapor plotted against the composition of the liquid for various values of $p_A^*/p_B^* > 1$: in all cases $y_A > x_A$ – the vapor is richer than the liquid in the more volatile component. If B is not volatile, $p_B^* = 0$ and $y_B = 0$.

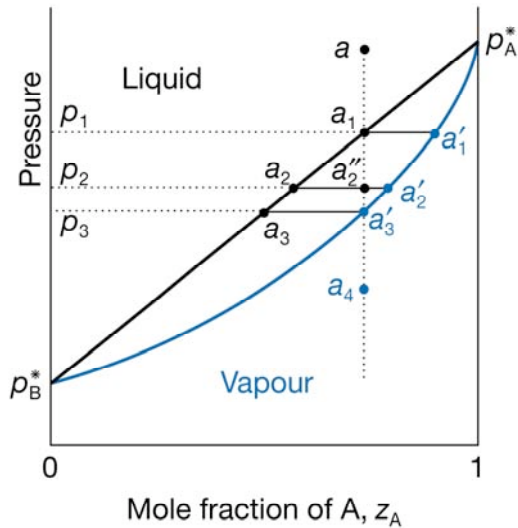
We can relate the total vapor pressure to the composition of the vapor

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$

The interpretation of the diagrams

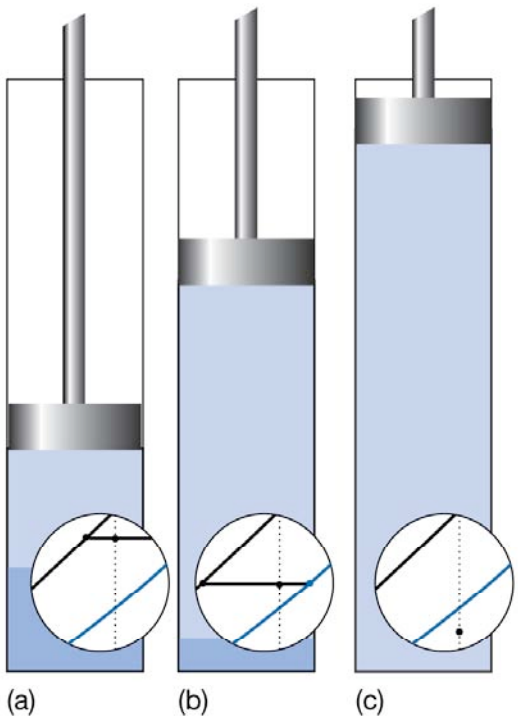


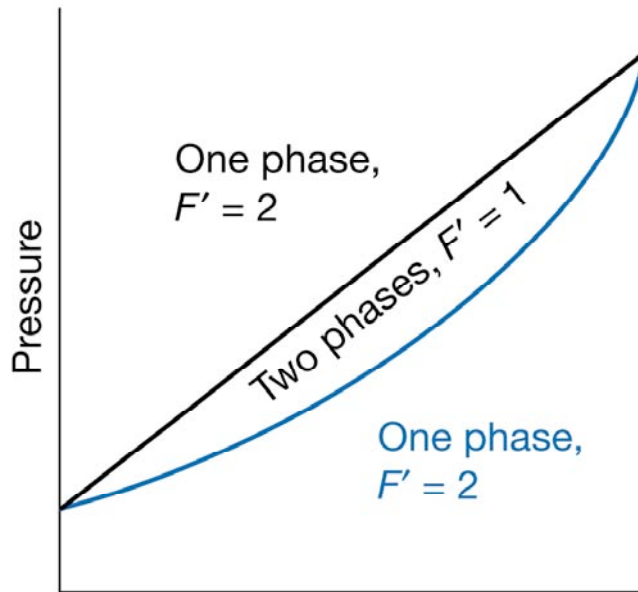
If we are interested in distillation, both the vapor and the liquid compositions are of equal interest and the two preceding diagrams can be combined into one: The point *a* indicates the vapor pressure of a mixture of composition x_A , and the point *b* indicates the composition of the vapor that is in equilibrium with the liquid at that pressure. When two phases are in equilibrium, $P = 2$ and $F' = 1$: if the composition is specified, the pressure at which the two phases are in equilibrium is fixed.



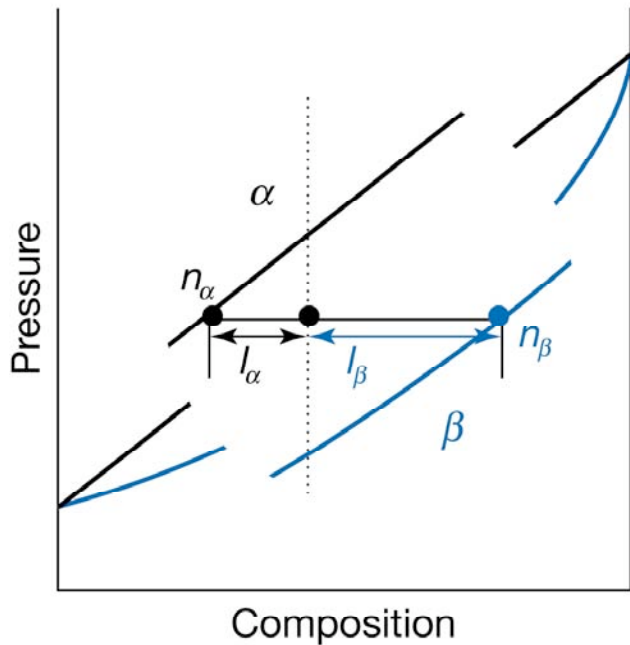
A richer interpretation of the phase diagram: the horizontal axis shows the overall composition of the mixture, z_A . All points above the solid diagonal line correspond to a system that is under such high pressure that it contains only a liquid phase (the applied pressure is higher than the vapor pressure), so $z_A = x_A$, the composition of the liquid. All points below the lower curve correspond to a system that is under such low pressure that it contains only a vapor phase (the applied pressure is lower than the vapor pressure), so $z_A = y_A$.

Points between the two lines: two phases are present, liquid and vapor. The lowering of pressure can be achieved by drawing out a piston. This degree of freedom is permitted by the phase rule because $F' = 2$ when $P = 1$, and even if the composition is selected one degree of freedom remains. The changes do not affect the overall composition, so the state of the system moves down the vertical line via a . This vertical line – **isopleth** (from Greek for ‘equal abundance’) Until a_1 is reached ($p = p_1$), the sample consists of a single liquid phase. At a_1 the liquid can exist in equilibrium with its vapor. The composition of the vapor is given by the point a'_1 . A horizontal line a_1 - a'_1 – a **tie line**. The composition of the liquid is the same as initially (a_1 lies on the isopleth through a) – at this pressure there is virtually no vapor pressure; however, an infinitesimal amount of vapor that is present has the composition a'_1 . Lowering the pressure to p_2 takes the system to a pressure and overall composition a_2 ".





This new pressure is below the vapor pressure of the original liquid, so it vaporizes until the vapor pressure of the remaining liquid falls to p_2 . The composition of such a liquid must be a_2 . The composition of the vapor in equilibrium with that liquid must be given by the point a_2' at the other end of the tie line. Two phases are now in equilibrium, $F' = 1$ for all points between the two lines – for a given pressure (p_2) the variance is zero and the vapor and the liquid phases have fixed compositions. If the pressure is reduced to p_3 , the compositions of the liquid and vapor are represented by the points a_3 and a_3' , respectively. At a_3' the composition of the vapor is the same as the overall composition and the amount of liquid present is now virtually zero, but the tiny amount of liquid present has the composition a_3 . A further decrease in pressure takes the system to a_4 – only vapor is present and its composition is the same as the initial overall composition (the composition of the original liquid).



The lever rule

To find the relative amounts of two phases in equilibrium, we measure the distances l_α and l_β along the horizontal tie line and then use the

lever rule:

$$n_\alpha l_\alpha = n_\beta l_\beta$$

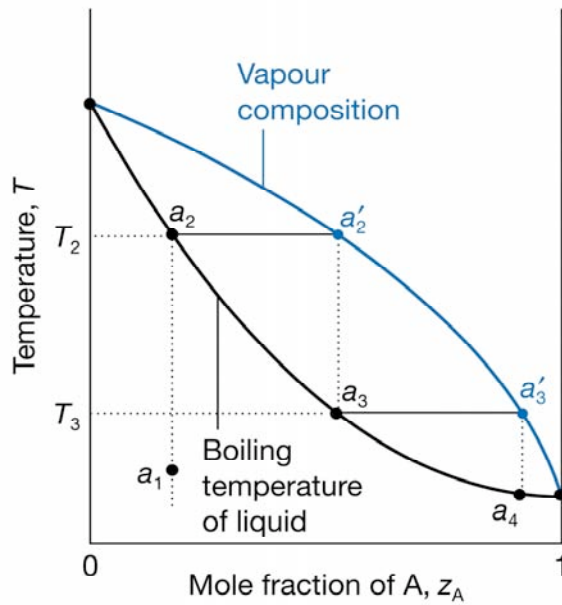
n_α, n_β – the amounts of phases α and β

$n = n_\alpha + n_\beta$, the overall amount is nz_A

$$nz_A = n_\alpha x_A + n_\beta y_A$$

$$nz_A = n_\alpha z_A + n_\beta z_A$$

$$n_\alpha(z_A - x_A) = n_\beta(y_A - z_A)$$



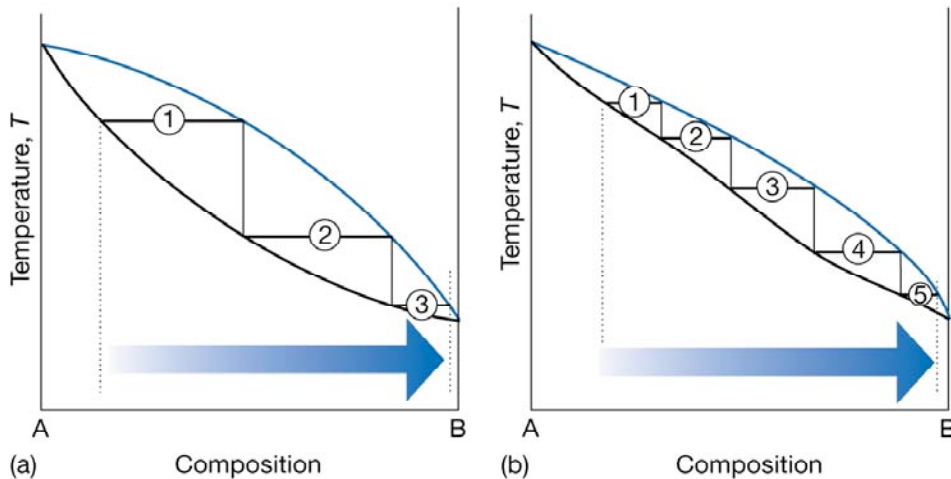
Temperature-composition diagrams

A **temperature-composition diagram** – a phase diagram in which the boundaries show the composition of the phases in equilibrium at various temperatures (at a given pressure, typically, 1 atm). The liquid phase now lies in the lower part of the diagram.

The distillation of mixtures

The region between the lines is a two-phase region with $F' = 1$. The regions outside the phase lines correspond to a single phase and $F' = 2$ (the temperature and composition are both independently variable).

When a liquid of composition a_1 is heated, it boils at the temperature T_2 . Then the liquid has composition a_2 (the same as a_1) and the vapor (present only as a trace) has composition a_2' . The vapor is richer in the more volatile component A (with the lower boiling point). From the



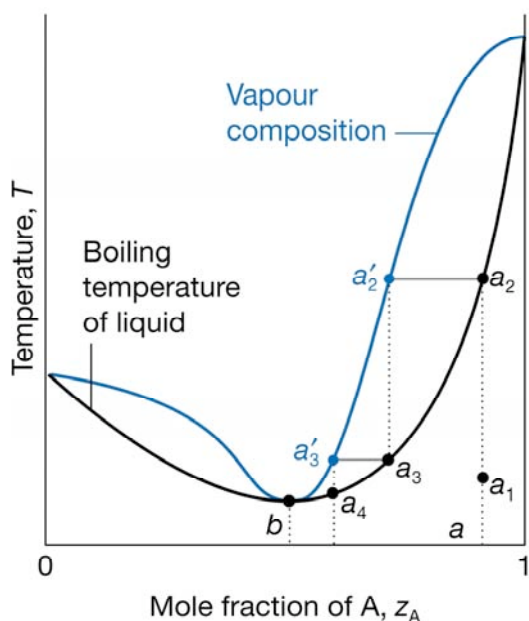
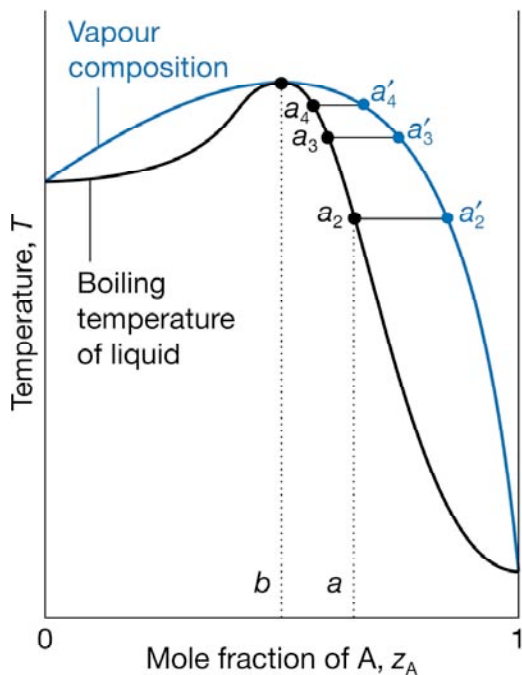
location of a_2 , we can state the vapor's composition at the boiling point, and from the location of the tie line joining a_2 with a_2' we can read off the boiling temperature (T_2) of the original liquid mixture. In a **simple distillation**, the vapor is withdrawn and condensed. In **fractional distillation**, the boiling and condensation cycle is repeated successively until almost pure A is obtained.

The efficiency of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate (three and five for (a) and (b)).

Azeotropes

A maximum in the phase diagram may occur when the favorable interactions between A and B molecules reduce the vapor pressure of the mixture below the ideal value – the A-B interactions stabilize the liquid – G^E is negative. Examples: trichloromethane-propanone, nitric acid-water mixtures. Phase diagram showing a minimum indicate that the mixture is destabilized relative to the ideal solution, with unfavorable A-B interactions. For such mixtures G^E is positive (less favorable mixing than ideal) and there may be contributions from both enthalpy and entropy effects. Examples: dioxane-water and ethanol-water mixtures.

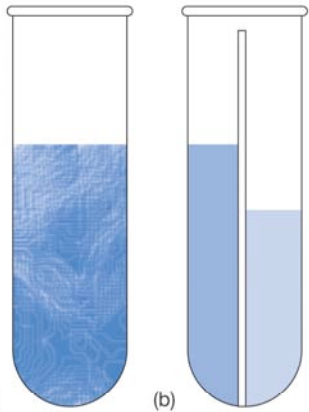
If such a maximum or minimum exists, there are important consequences for distillation. Consider a liquid of composition a on the right of the maximum. The vapor (at a_2') of the boiling mixture (at a_2) is richer in A. If that vapor is removed (and condensed elsewhere), the remaining liquid will move to a composition that is richer in B (at a_3), and the vapor at equilibrium will have composition a_3' . As evaporation proceeds, the composition of the remaining liquid shifts towards B as A is drawn off. The boiling point of the liquid rises and the vapor becomes richer in B. When the liquid has reached the composition b , the vapor has the same composition as the liquid and evaporation occurs without change of composition – the mixture forms an **azeotrope**. When the azeotropic composition has been reached, distillation cannot separate the two liquids. Example: hydrochloric acid-water, azeotropic at 80% by mass of water and boils unchanged at 108.6°C .



The system with a minimum on the phase diagram is also azeotropic but in a different way. We start with a mixture of composition a_1 and follow the changes in the composition of the vapor that rises through a fractionating column (a vertical glass tube packed with glass rings to give a large surface area). The mixture boils at a_2 to give a vapor of composition a_2' . This vapor condenses to a liquid of the same composition (marked a_3). That liquid reaches equilibrium with its vapor at a_3' , which condenses higher up the tube to give a liquid of the same composition (a_4). The fractionation shifts the vapor towards the azeotropic composition at b , but not beyond, and the azeotropic vapor emerges from the top of the column. Example: ethanol-water, boils unchanged when the water content is 4% by mass at 78°C.

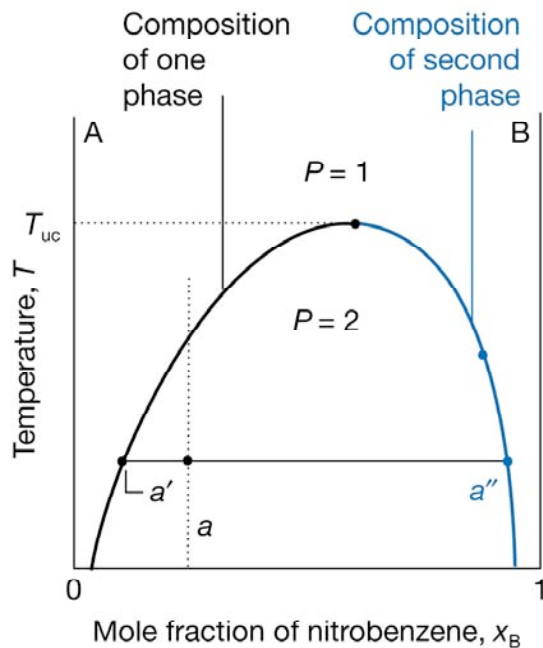
Immiscible liquids

Two immiscible liquids (octane-water): at equilibrium, there is a tiny amount of A dissolved in B and a tiny amount of B dissolved in A. The total vapor pressure is close to $p = p_A^* + p_B^*$. If T is raised at which the total vapor pressure is equal to the atmospheric pressure, boiling occurs and the dissolved substances are purged from their solution. The intimate contact is essential – then the ‘mixture’ boils at lower T than either component would. Boiling begins when the total vapor pressure reaches 1 atm. This is the basis of **steam distillation**, which enables some heat-sensitive, water-insoluble organic compounds to be distilled at a lower temperature than their normal boiling point. The drawback – the composition of the condensate is in proportion to the vapor pressure of the components, so oils of low volatility distil at low abundance.



Liquid-liquid phase diagrams

We consider temperature-composition diagrams of **partially miscible** liquids that do not mix at all proportions at temperatures. When $P = 2$, $F' = 1$, and the selection of a temperature implies that the composition of the immiscible liquid phases are fixed. When $P = 1$ (the liquids are fully mixed), both the temperature and the composition may be adjusted.



Phase separation

Suppose a small amount of B is added to a sample of another liquid A at T' . It dissolves completely – the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium ($P = 2$), the most abundant is A saturated with B and the minor one is a trace of B saturated with A. The compositions of the two phases are represented by a' and a'' and their relative abundances are given by the lever rule. When more B is added, A dissolves in it slightly. The compositions of the two phases remain at a' and a'' ($P = 2$ implies $F' = 0$ when p and T are fixed, so the compositions are invariant). However, the amount of one phase increases at the expense of the other. The compositions of the two phases vary with temperature.

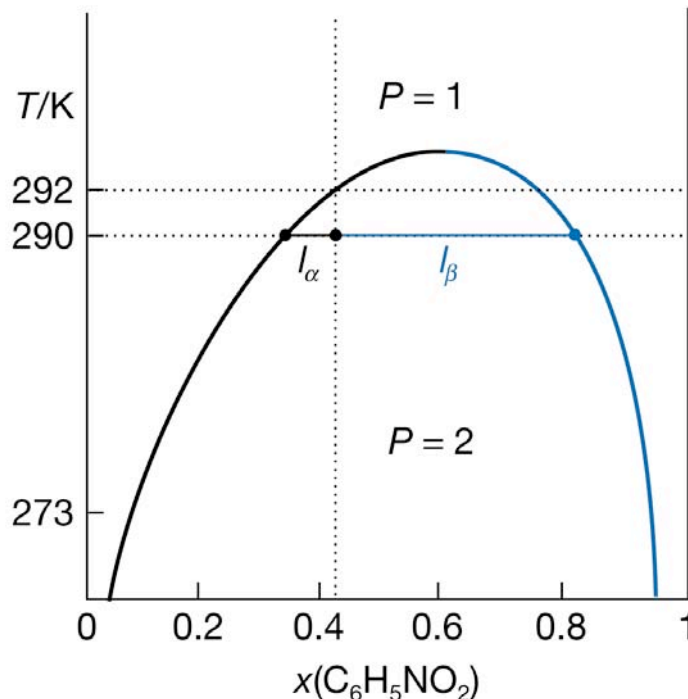
Example 2. Interpreting a liquid-liquid phase diagram

Lever rule: $n'l' = n''l''$

(Amount of phase of composition a'')/(Amount of phase of composition a') = l'/l''

A mixture of 50 g (0.59 mol) of hexane and 50 g (0.41 mol) of nitrobenzene was prepared at 290 K. What are the compositions of the phases, and in what proportions do they occur? To what temperature must the sample be heated to obtain a single phase at 1 atm?

First, we need to identify the tie line corresponding to the temperature specified: the points at its ends give the composition of two phases in equilibrium. Next, we identify the location on the horizontal axis corresponding to the overall composition and draw a vertical line. Where the line cuts the tie line it divides it into the two lengths needed to use the lever rule. Finally, we note the temperature at which the same vertical line cuts through the phase boundary: at that temperature and above, the system consists of a single phase.



$$x_N = 0.41$$

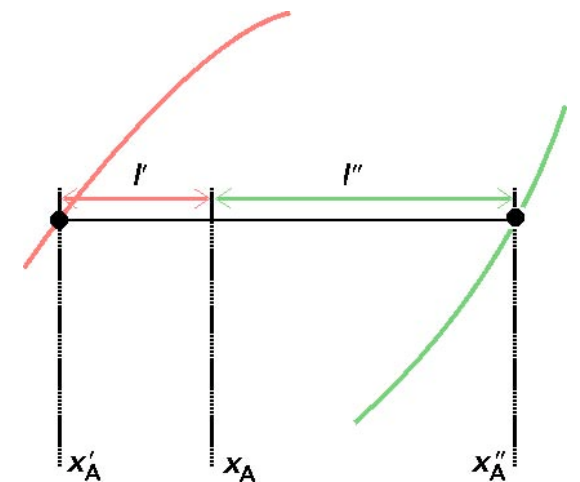
$$x_N' = 0.35$$

$$x_N'' = 0.83$$

$$l''/l' = (0.83 - 0.41) / (0.41 - 0.35) = 7$$

The hexane-rich phase is 7 times more abundant than the nitrobenzene-rich phase.

Heating of the sample to 292 K takes it into the single-phase region.



Critical solution temperatures

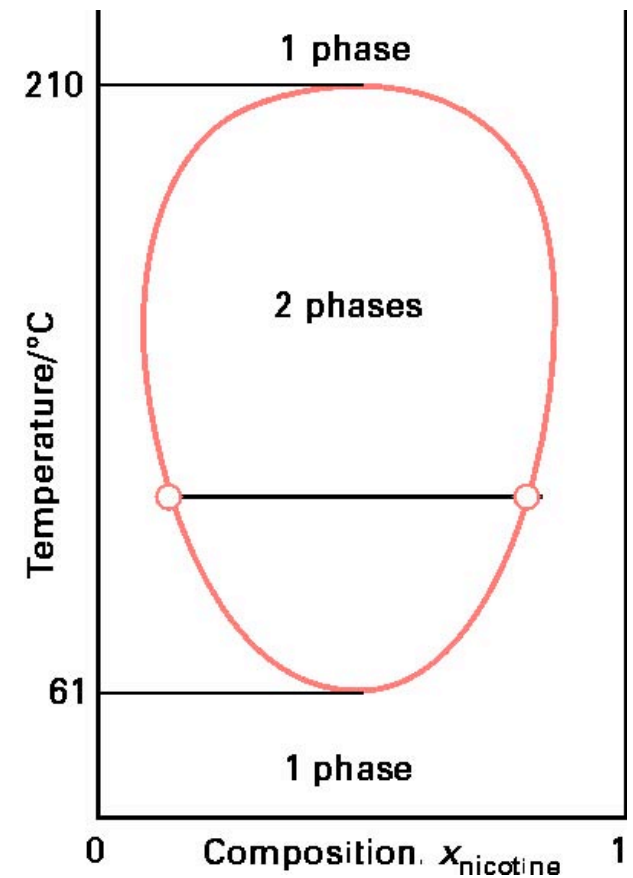
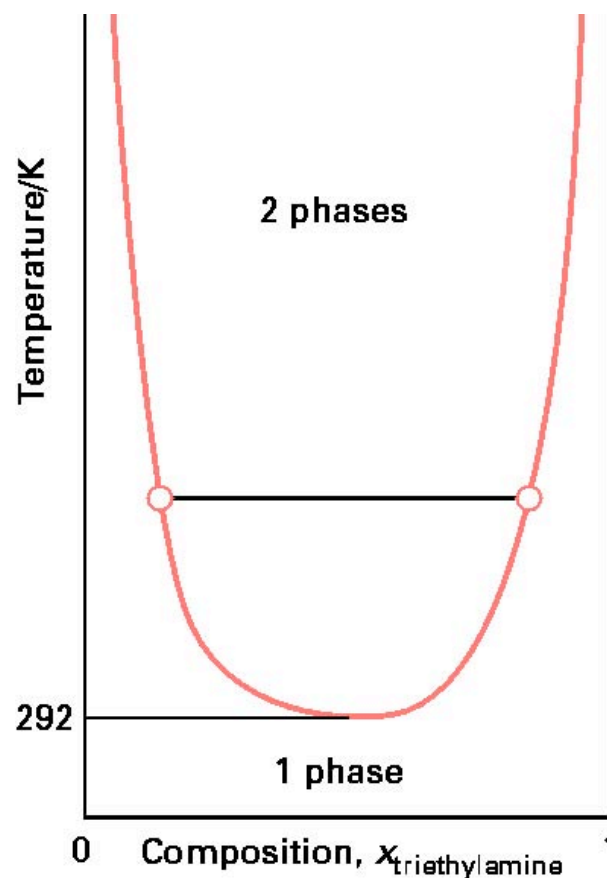
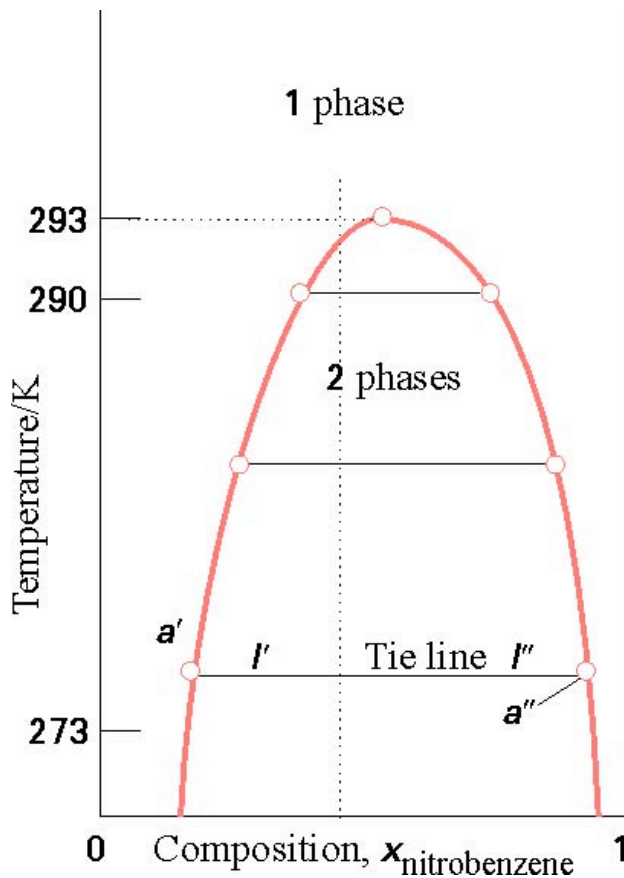
The **upper critical solution temperature**, T_{uc} – the upper limit of temperatures at which phase separation occurs. Above T_{uc} – the two components are fully miscible.

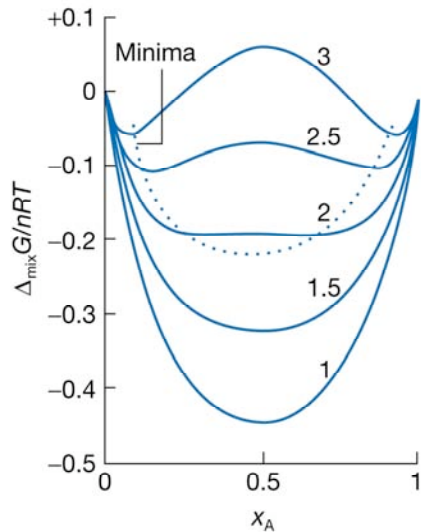
Some systems show a **lower critical solution temperature**, T_{lc} , below which they mix at all proportions and above which they form two phases.

Example: water/triethylamine

A few systems have both upper and lower critical temperatures.

Example: water/nicotine





The thermodynamic interpretation of the upper critical solution temperature – from variation of the Gibbs energy of mixing with temperature. A simple model of a real solution results in a Gibbs energy of mixing that behaves as shown in the figure. Provided the parameter $\beta = w/RT > 2$, the Gibbs energy of mixing has a double minimum – we can expect phase separation to occur.

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}$$

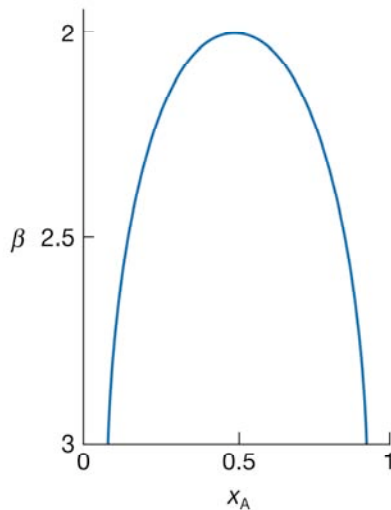
With $x = x_A$,

$$\Delta_{\text{mix}}G = nRT\{x \ln x + (1-x) \ln(1-x) + \beta x(1-x)\}$$

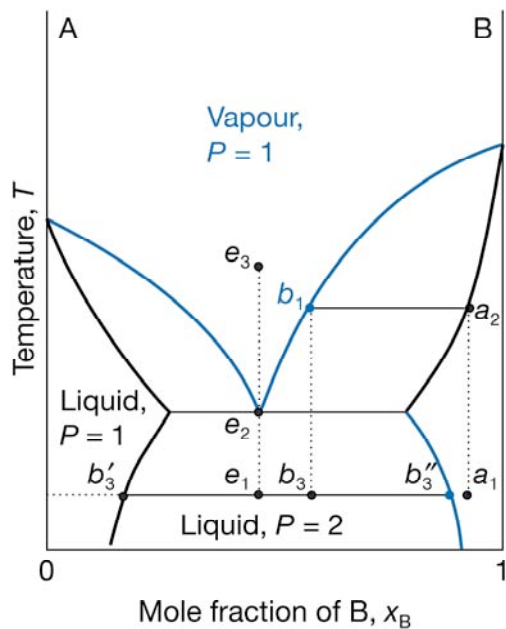
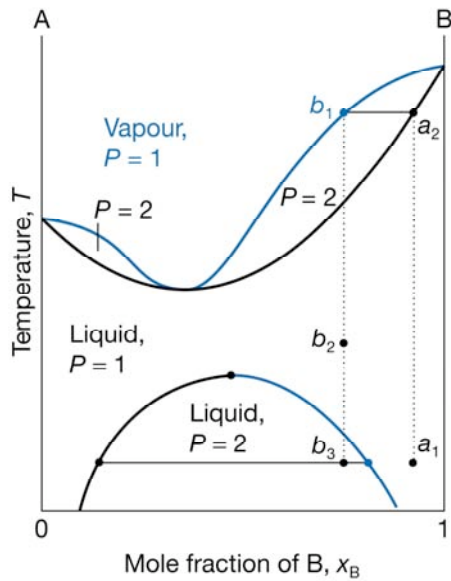
At the minima, $\partial \Delta_{\text{mix}}G / \partial x = 0$:

$$\ln \frac{x}{1-x} + \beta(1-2x) = 0$$

The solutions of this transcendental equation are plotted in the figure. As β decreases, which can be interpreted as an increase in temperature provided the intermolecular forces and w (the energy of AB interactions relative to AA and BB interactions) remain constant, the two minima move together and merge when $\beta = 2$. The upper critical solution temperature is $w/2R$.



The distillation of partially miscible liquids



A pair of liquids can be partially miscible and form a low-boiling azeotrope – a common situation if two kinds of molecules avoid each other. Distillation of a mixture of composition a_1 leads to a vapor of composition b_1 , which condenses to the completely miscible single-phase solution at b_2 . Phase separation occurs only when the distillate is cooled to a point in the two-phase region (b_3).

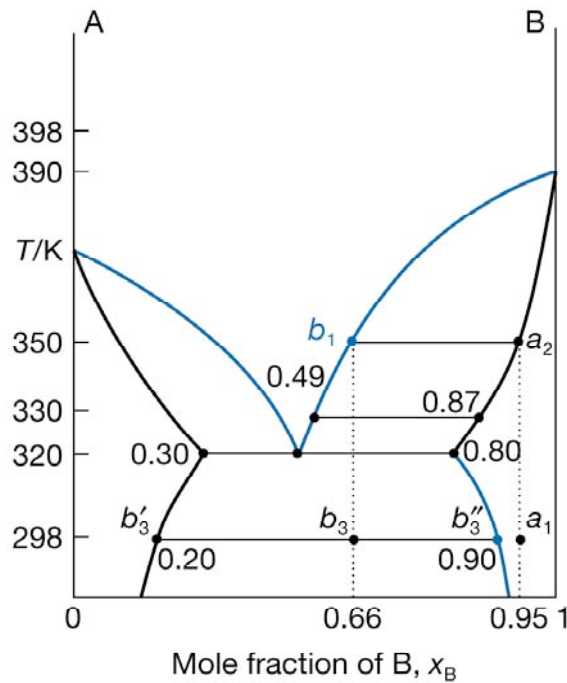
The second possibility – there is no upper critical solution temperature. The distillate obtained from a liquid initially of composition a_1 has composition b_3 and is a two-phase mixture: one phase has composition b_3' and the other b_3'' . The behavior of a system represented by the isopleth e is interesting. A system at e_1 forms two phases, which persist (but with changing proportions) up to the boiling point e_2 . The vapor has the same composition as the liquid (an azeotrope). Condensing a vapor of composition e_3 gives a two-phase liquid of the same overall composition.

Example 3. Interpreting a phase diagram

State the changes when a mixture of composition $x_B = 0.95$ (a_1) is boiled and the vapor condensed.

The area in which the point lies gives the number of phases; the composition of the phases are given by the points at the intersections of the horizontal tie line with the phase boundaries; the relative abundances are given by the lever rule.

a_1 is in the one-phase region. When heated it boils at 350 K (a_2) giving a vapor of composition $x_B = 0.66$. The liquid gets richer in B and the last drop (pure B) evaporates at 390 K. If the initial vapor is drawn off it has $x_B = 0.66$. Cooling the distillate corresponds to moving down the $x_B = 0.66$ isopleth. At 330 K: the liquid has $x_B = 0.87$ and the vapor $x_B = 0.49$, their relative proportions 1:3. At 320 K – three phases, the vapor and two liquids. At 298 K – two liquid phases with $x_B = 0.20$ and 0.90 and the ratio 0.81:1.

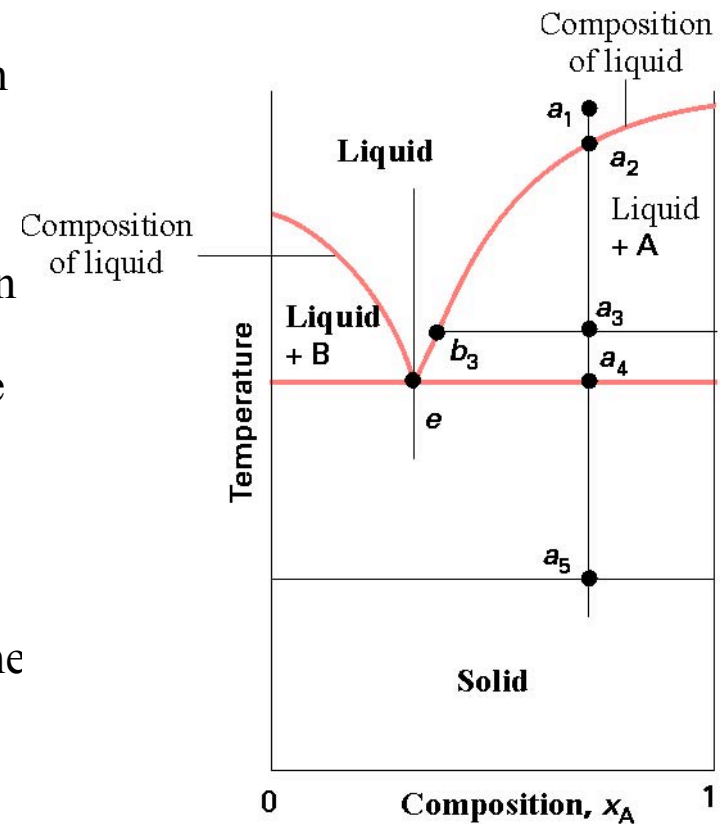


Liquid-solid phase diagrams

Phase diagrams are also used to show the regions of temperature and composition at which solids and liquids exist in binary mixtures. Such diagrams are useful for discussing the techniques used to prepare the high-purity materials and are also of great importance in metallurgy.

Phase diagram for a system of two metals that are almost completely unmiscible up to their melting point. Consider the molten liquid of composition a_1 . When the liquid is cooled to a_2 , the system enters the two-phase region 'Liquid+A'. Almost pure solid A begins to come out of solution and the remaining liquid becomes richer in B. On cooling to a_3 , more of the solid forms, and the relative amounts of the solid and liquid (in equilibrium) are given by the lever rule. The liquid phase is richer in B than before (its composition is given by b_3) because A has been deposited. At a_4 there is less liquid than at a_3 and its composition is given by e . This liquid now freezes to give a two-phase system of almost pure A and almost pure B and cooling down to a_5 leads to no further change in composition.

e – the **eutectic composition**. A solid with the eutectic composition melts, without a change of composition, at the lowest temperature of any mixture. Solutions of composition to the right of e deposit A as they cool, and solution to the left deposit B. Only the eutectic mixture (besides pure A or pure B) solidifies at a single definite temperature without gradually unloading one or other of the components from the liquid.

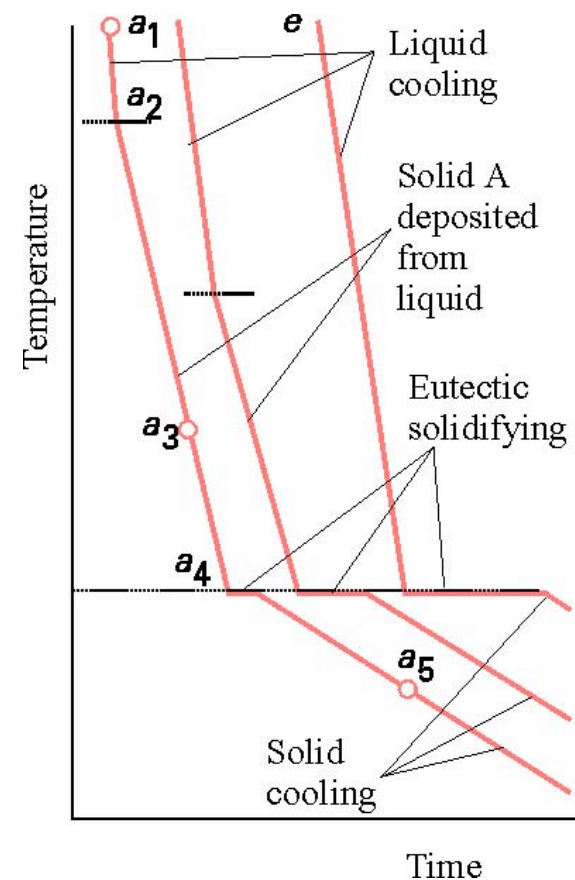


One technologically important eutectic is solder, 67% tin and 33% lead, melts at 183°C. Eutectic formation occurs in the great majority of binary alloy systems. It is of great importance because, although a eutectic solid is a two-phase system, it crystallizes out in a nearly homogeneous mixture of microcrystals. The two microphases can be distinguished by microscopy and X-ray diffraction.

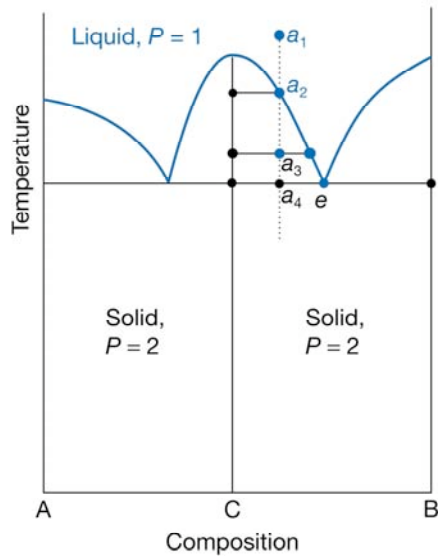
Thermal analysis – a practical way of detecting eutectics.

Consider the rate of cooling down the vertical line at a_1 . The liquid cools steadily until it reaches a_2 , when A begins to be deposited. Cooling is now slower because solidification of A is exothermic and retards the cooling. When the remaining liquid reaches the eutectic composition, the temperature remains constant until the whole sample is solidified: this pause in the decrease of temperature – **eutectic halt**. If the liquid is of the eutectic composition e initially, then the liquid cools steadily down to the freezing temperature of the eutectic, when there is a long eutectic halt as the entire sample solidifies just like the freezing of the pure liquid.

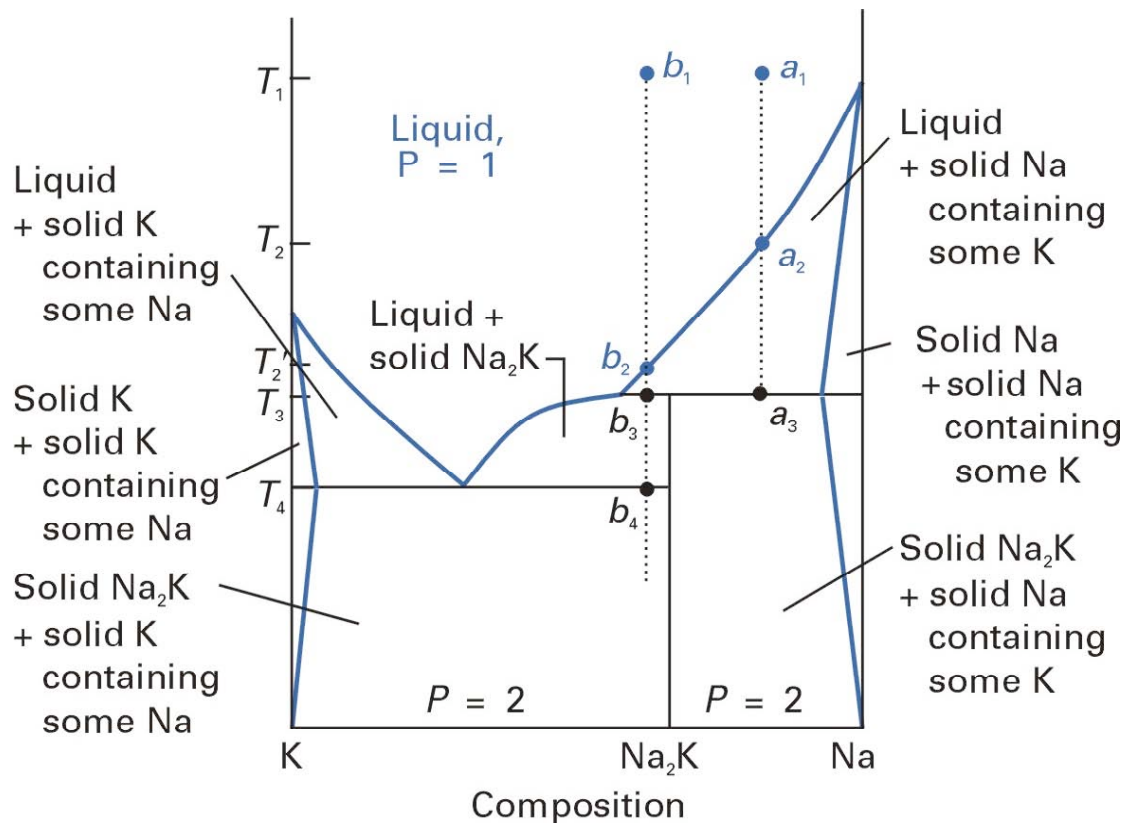
Monitoring the cooling curves at different overall compositions gives an indication of the structure of the phase diagram. The solid-liquid boundary is given by the points at which the rate of cooling changes. The longest eutectic halt gives the location of the eutectic composition and its melting temperature.



Reacting systems



Many binary systems react to produce compounds: III/V semiconductors, such as gallium arsenide system, which forms GaAs. Although three constituents are present, there are only two components – GaAs is formed from the reaction. A system prepared by mixing an excess of B with A consists of C and unreacted B. This is a binary B, C system, which we suppose forms a eutectic. The principal change – the whole of the phase diagram is squeezed into the range of compositions lying between equal amount of A and B ($x_B = 0.5$) and pure B. Otherwise, the interpretation of the diagram is the same as before. The solid deposited on cooling along the isopleth a is the compound C. At temperature below a_4 there are two solid phases, consisting of C and B.



Incongruent melting

In some cases the compound C is not stable as a liquid – the alloy Na_2K survives only as a solid.

Consider the isopleth through a_1 :

$a_1 \rightarrow a_2$ – some solid Na is deposited and the remaining liquid is richer in K.

$a_2 \rightarrow$ just below a_3 – the sample is entirely solid and consists of solid Na and solid Na_2K .

Now consider the isopleth through b_1 :

$b_1 \rightarrow b_2$ – no obvious change occurs until the phase boundary is reached at b_2 when solid Na begins to deposit.

$b_2 \rightarrow b_3$ – solid Na deposits, but at b_3 a reaction occurs to form Na_2K : this compound is formed by the K atoms diffusing into the solid Na. At this stage the liquid Na/K mixture is in equilibrium with a little solid Na_2K , but there is still no liquid compound.

$b_3 \rightarrow b_4$ – as cooling continues, the amount of solid compound increases until at b_4 the liquid reaches its eutectic composition. Then, it solidifies to give a two-phase solid consisting of solid K and solid Na_2K .

If the solid is reheated, the sequence of the events is reversed. No liquid Na_2K forms at any stage because it is too unstable to exist as a liquid. This is called **incongruent melting** – a compound melts into its components and does not itself form a liquid phase.