Part 1: Equilibrium

8. Phase diagrams

Bilingual Program

8. Phase diagrams

In Chapter 6, we discussed the phase diagrams for pure substances. We shall develop their use systematically and show how they are rich summaries of empirical information about a wide range of systems. To set the stage, we introduce the famous **phase rule of Gibbs**, which shows the extent to which various parameters can be varied yet the equilibrium between phases preserved. With the rule established, we see how it can be used to discuss the phase diagrams that we met in the two preceding chapters.

8. Phase diagrams

Phases, components, and degrees of freedom

8.1 Definitions ▶

8.2 The phase rule

Two-component systems

8.3 Vapour pressure diagrams

8.4 Temperature-composition diagrams

8.5 Liquid-liquid phase diagrams

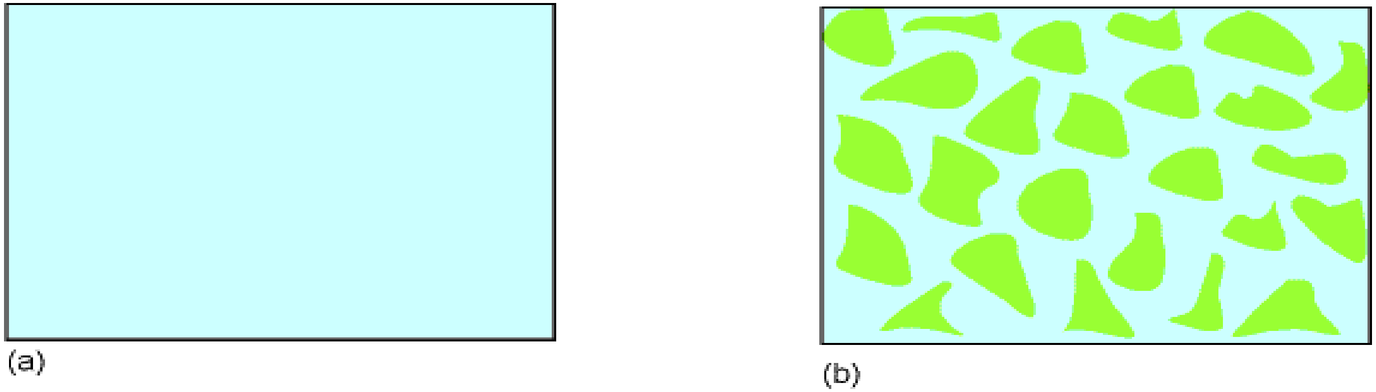
8.6 Liquid-solid phase diagrams

8.7 Ultrapurity and controlled impurity

8.1 Definitions

1). The phase

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.



(a) a single-phase solution, in which the composition is uniform on a microscopic scale.

(b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

8.1 Definitions

1). The phase

The number of phases in a system is denoted *P*.

A gas, or a gaseous mixture, is a single phase.

A crystal is a single phase.

Two totally miscible liquids form a single phase.

Ice is a single phase even though it might be chipped into small fragments.

$$\left.\right\} P = 1$$

Any sample cut from the sample, however small, is representative of the composition of the whole.

8.1 Definitions

1). The phase

A slurry of ice and water is a two-phase system.

An alloy of two metals is a two-phase system if the metals are immiscible.

A dispersion of clays in water is uniform on a macroscopic scale but not on a microscopic scale.

$$\left.\right\} P = 2$$

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

8.1 Definitions

2). Components

A constituent is a chemical species that is present in a system .

A component is a chemically independent constituent of a system.

The number of components, *C*, in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system.

8.1 Definitions

2). The number of components, *C*

- **No chemical reactions**

When no reaction takes place, the number of components is equal to the number of constituents.

The pure water is a one-component system, *C* = 1, because we need only the species H_2O to specify its composition. Similarly, a mixture of ethanol and water is a two-component system, *C* = 2: we need the species H_2O and C_2H_5OH to specify its composition.

8.1 Definitions

- **With chemical reactions**

When a reaction can occur in the system, we need to decide the minimum number of species that can be used to specify the composition of all the phases.

In general:

$$C = K - R$$

where K is the number of constituents and R is the number of independent reactions.

Example

Calculate The number of components, C

At the equilibrium

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

Phase 1 Phase 2 Phase 3

Method: **there are three phases in the system. To specify the composition of the gas phase 3 we need the species CO_2; and to specify the composition of phase 2 we need the species CaO. However, we do not need an additional species to specify the composition of the phase 1 because its identity ($CaCO_3$) can be expressed in terms of the other two constituents by making use of the stoichiometry of the reaction.**

Example

Answer:

At the equilibrium

$$\mathrm{CaCO_3(s)} \leftrightarrow \mathrm{CaO(s)+CO_2(g)}$$

Phase 1	**Phase 2**	**Phase 3**
Cst 1	**Cst 2**	**Cst 3**

The number of components: $C = 2$

The system has three constituents but only two components (C = 2).

8.1 Definitions

3). Degrees of freedom, F

Degrees of freedom ,or the variance of a system, F, is 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 ($C = 1$, $P = 1$), p and T may be changed independently without changing the number of phases, so $F = 2$. We say that such a system is bivariant, or that it has two degrees of freedom.

8.1 Definitions

3). Degrees of freedom, *F*

If two phases are in equilibrium in a single-component system(C = 1, P = 2), T (or p) can be changed at will, but the change in T (or p) demands an accompanying change in p (or T) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to F=1.

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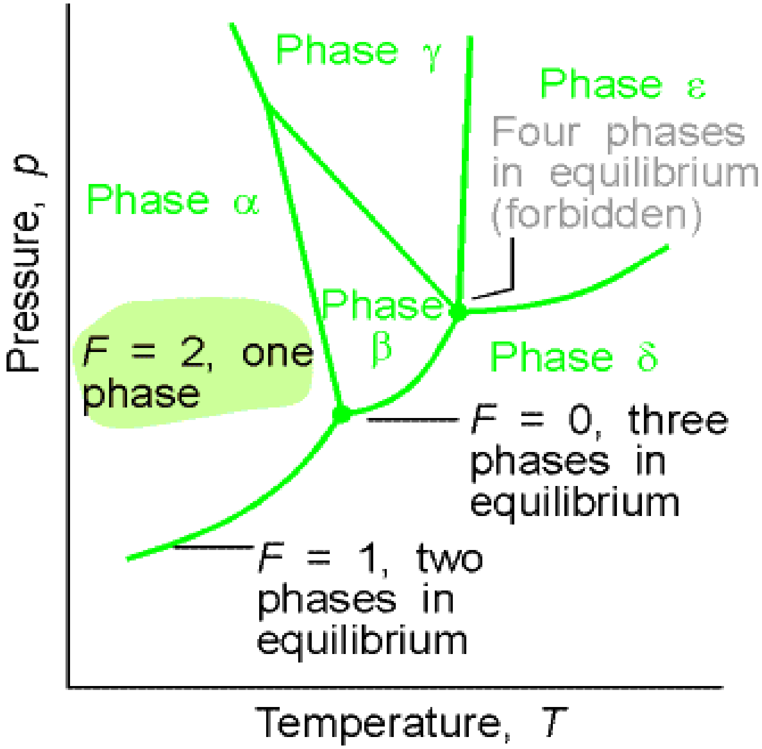
8.2 The phase rule

The phase rule is a general relation between the variance, *F*, the number of components, *C*, and the number of phases at equilibrium, *P*, for a system of any composition:

$$F = C - P + 2$$

8.2 The phase rule

1). One-component systems



The typical regions of a one-component phase diagram.

For a one-component system:

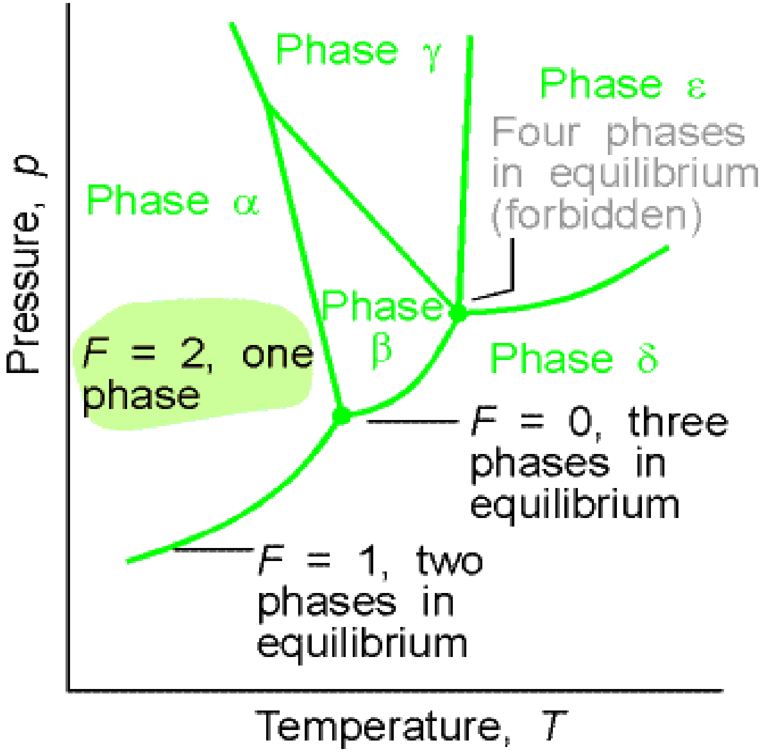
If only one phase is present,

$$F = 1-1+2=2$$

Both *p* and *T* can be varied independently without changing the number of phases. In other words, a single phase is represented by an area on a phase diagram.

8.2 The phase rule

1). One-component systems



The typical regions of a one-component phase diagram.

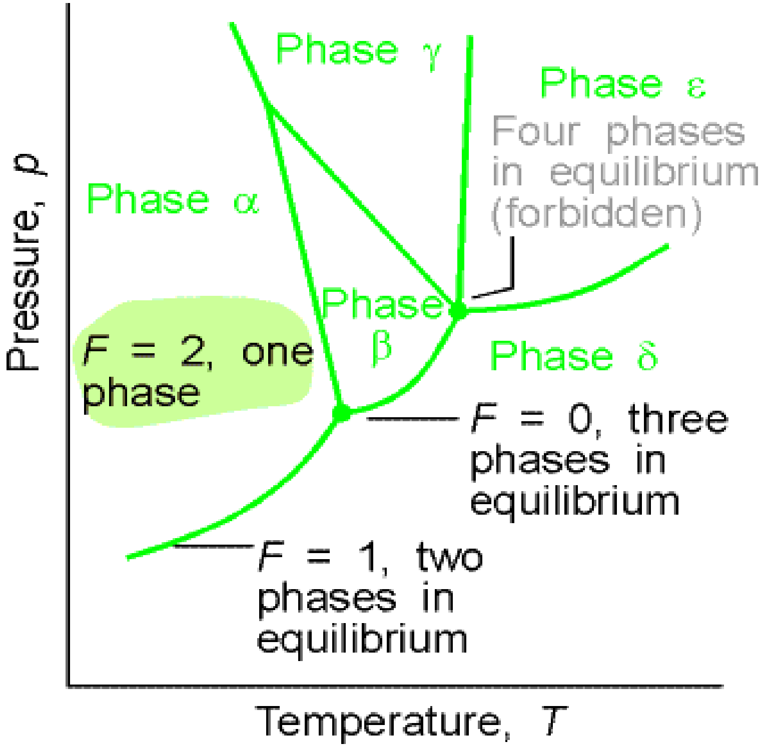
If two phases are in equilibrium

$$F = 1-2+2=1$$

which implies that *p* is not freely variable if the *T* is set. The equilibrium of two phases is represented by a line in the phase diagram. Therefore, freezing (or any other phase transition) occurs at a definite *T* at a given *p*.

8.2 The phase rule

1). One-component systems



The typical regions of a one-component phase diagram.

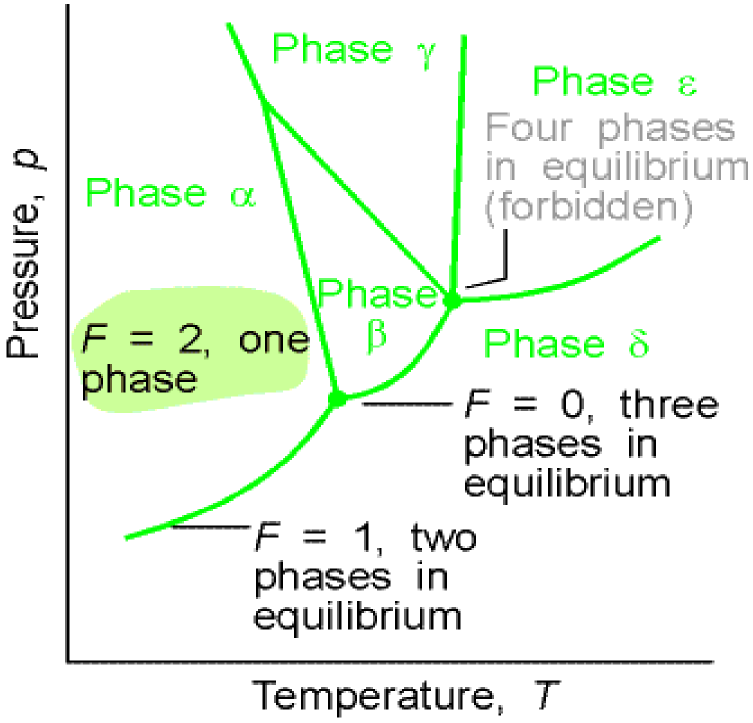
If three phases are in equilibrium

$$F = 1-3+2=0$$

The system is invariant. The special condition can be established only at the definite T and p that is characteristic of the substance and outside our control. The equilibrium of three phases is therefore represented by a point, the triple point, on the phase diagram.

8.2 The phase rule

1). One-component systems



The typical regions of a one-component phase diagram.

For a one-component system

Only one phase, an area:

$C=1, P=1$ ➡ $F=1-1+2=2$

Two phases, The lines:

$C=1, P=2$ ➡ $F=1-2+2=1$

three phases, A point:

$C=1, P=3$ ➡ $F=1-3+2=0$

Four phases cannot mutually coexist in equilibrium

8. Phase diagrams

Phases, components, and degrees of freedom

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8.2 The phase rule

Two-component systems ▶

8.3 Vapour pressure diagrams

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8.6 Liquid-solid phase diagrams

8.7 Ultrapurity and controlled impurity

Two-component systems

If two components are present in a system

$$F = C - P + 2$$

$C = 2$ ➡ $F = 4 - P$

The degree of freedom has a maximum value of 3. The properties of the system depend on *T* , *p* and composition.

Two-component systems

If T or p is constant, the remaining variance is

$$F = 3 - P$$

The remaining degrees of freedom has a maximum value of 2. One is the p (T) and the other is the Composition (c).

1). At constant T, the phase diagram is a map of p and c at which each phase is stable; ▶

2). At constant p, the phase diagram depicted in terms of T and c .

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8.3 Vapour pressure diagrams

1). The composition of the vapour

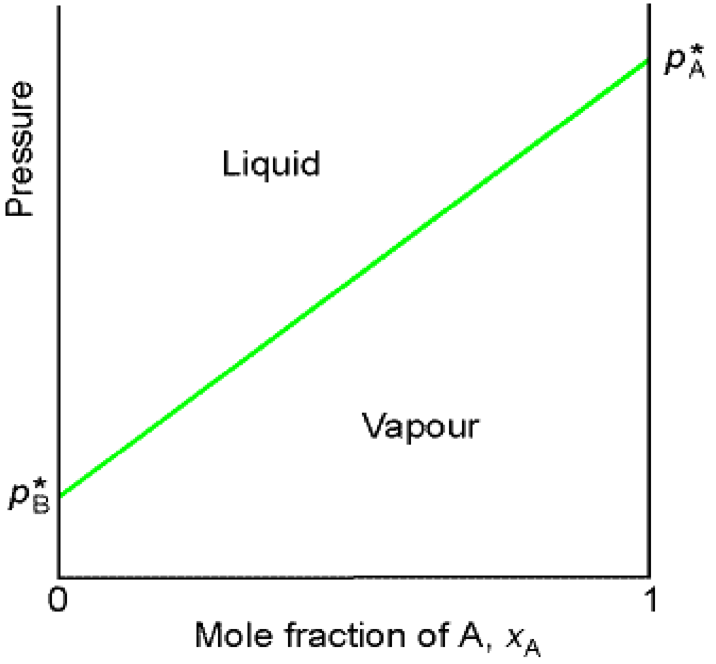
The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law:

$$p_{\mathrm{A}} = x_{\mathrm{A}} p_{\mathrm{A}}^{*} \qquad p_{\mathrm{B}} = x_{\mathrm{B}} p_{\mathrm{B}}^{*}$$

where p^*_{A} is the vapour pressure of pure A and p^*_{B} that of pure B.

8.3 Vapour pressure diagrams

1). The composition of the vapour



The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid.

The total vapour pressure of the mixture:

$$p = p_A + p_B$$

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

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

The total vapour pressure changes linearly with the composition from $p^*{}_B$ to $p^*{}_A$ as x_A changes from 0 to 1.

8.3 Vapour pressure diagrams

1). The composition of the vapour

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. From Dalton's law that the mole fractions in the gas, y_A and y_B, are:

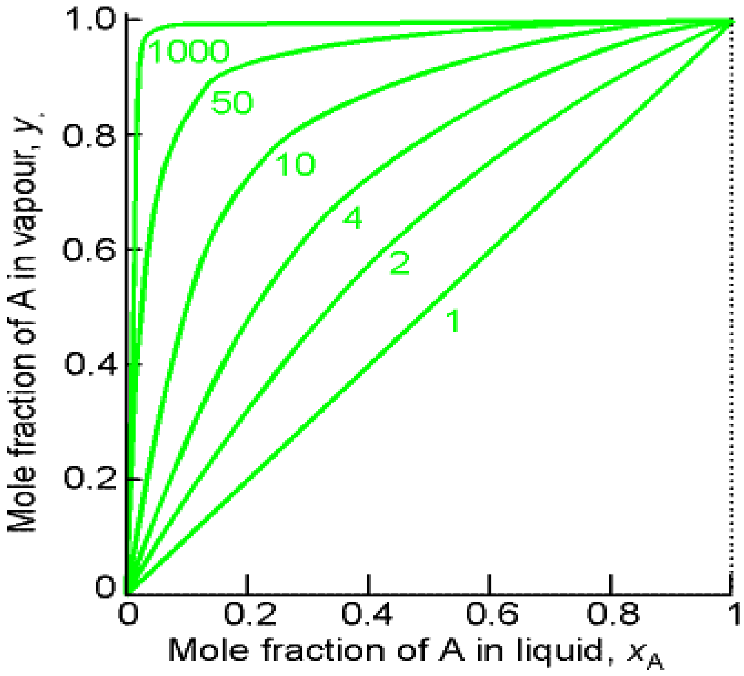
$$y_A = p_A / p \qquad y_B = p_B / p$$

Provided the mixture is ideal, the partial pressure p_i and the total pressure p may be expressed in terms of the mole fractions in the liquid:

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

8.3 Vapour pressure diagrams

1). The composition of the vapour



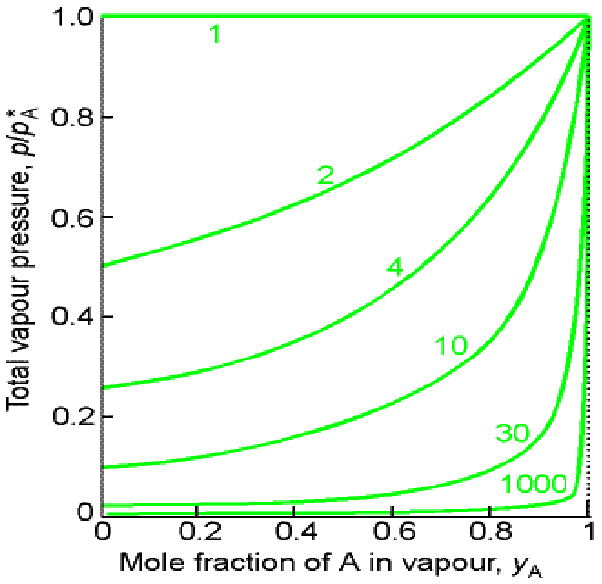
The mole fraction of A in the vapour of a binary ideal solution expressed in terms of its mole fraction in the liquid for various values of p^*_A/p^*_B with A more volatile than B. In all cases the vapour is richer than the liquid in A.

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

It shows that the composition of the vapour plotted against the composition of the liquid for various values of $p_A^*/p_B^* > 1$. In all cases $y_A > x_A$, so the vapour is richer than the liquid in the more volatile component.

8.3 Vapour pressure diagrams

1). The composition of the vapour



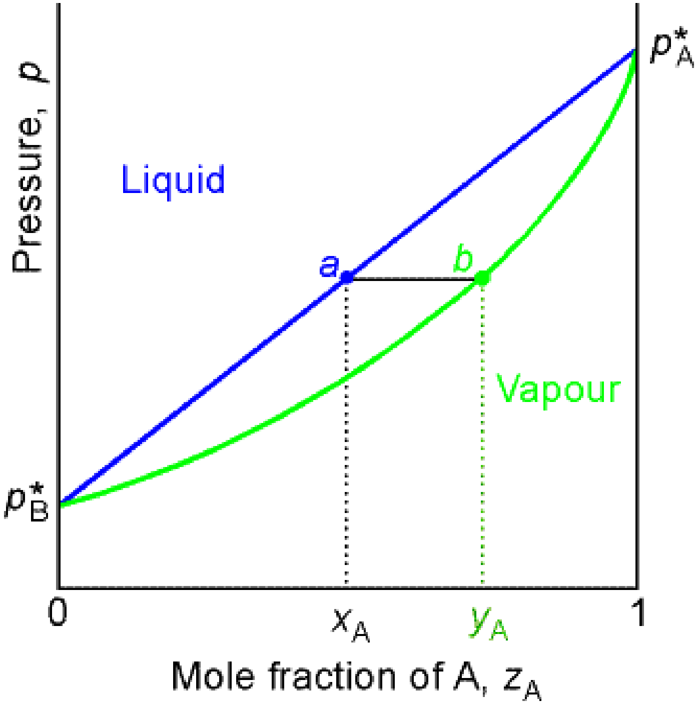
From the relation of the total vapour pressure of the mixture that varies with the composition of the liquid, we can relate the composition of the liquid to the composition of the vapour and relate the total vapour pressure to the composition of the vapour:

The dependence of the vapour pressure of the same system expressed in terms of the mole fraction of A in the vapour. Individual curves are labelled with the value of p^*_A/p^*_B.

$$p = \frac{p^*_A p^*_B}{p^*_A + (p^*_B - p^*_A) y_A}$$

8.3 Vapour pressure diagrams

2). The interpretation of the diagrams

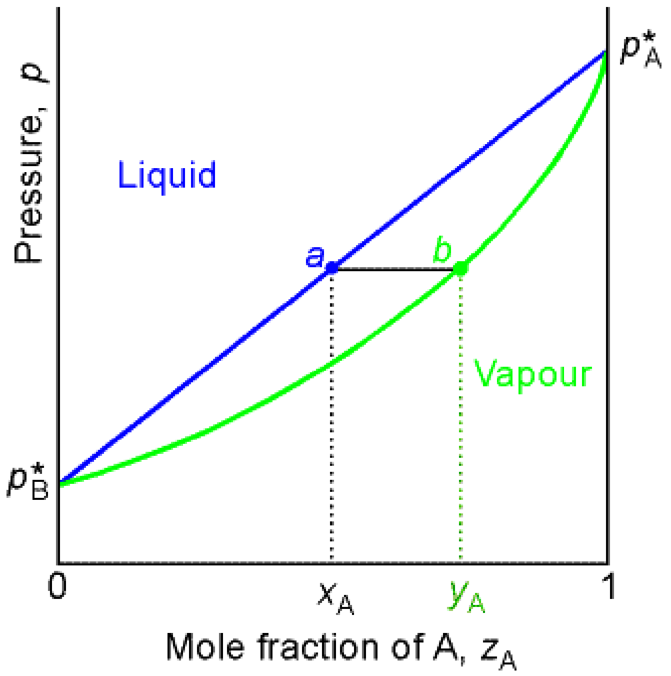


The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

The horizontal axis as shows the overall composition, z_A, of the system. all the points up to the solid diagonal line (blue) in the graph correspond to a system which is under such high pressure that it contains only a liquid phase, so $z_A=x_A$, the composition of the liquid.

8.3 Vapour pressure diagrams

2). The interpretation of the diagrams



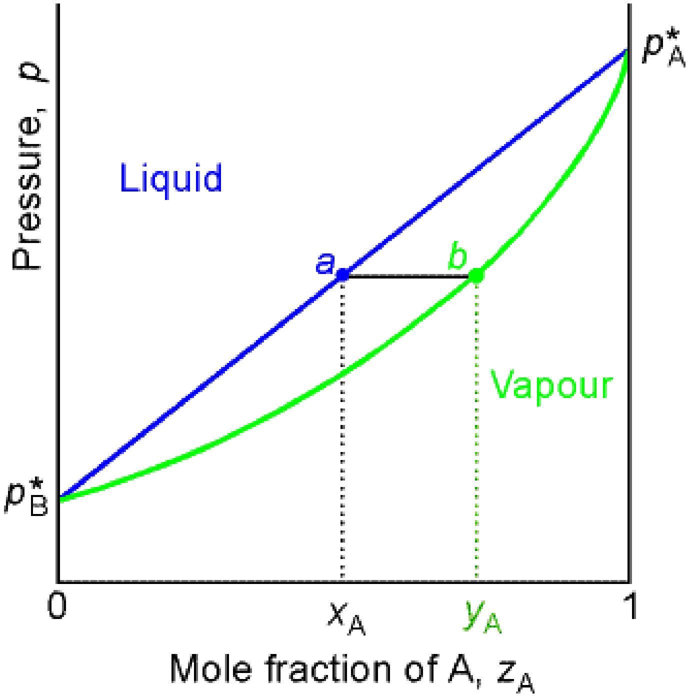
The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

Points that lie between the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour.

The point *a* indicates the vapour pressure of a mixture of composition x_A, and the point *b* indicates the composition of the vapour that is in equilibrium with the liquid at that pressure.

8.3 Vapour pressure diagrams

2). The interpretation of the diagrams

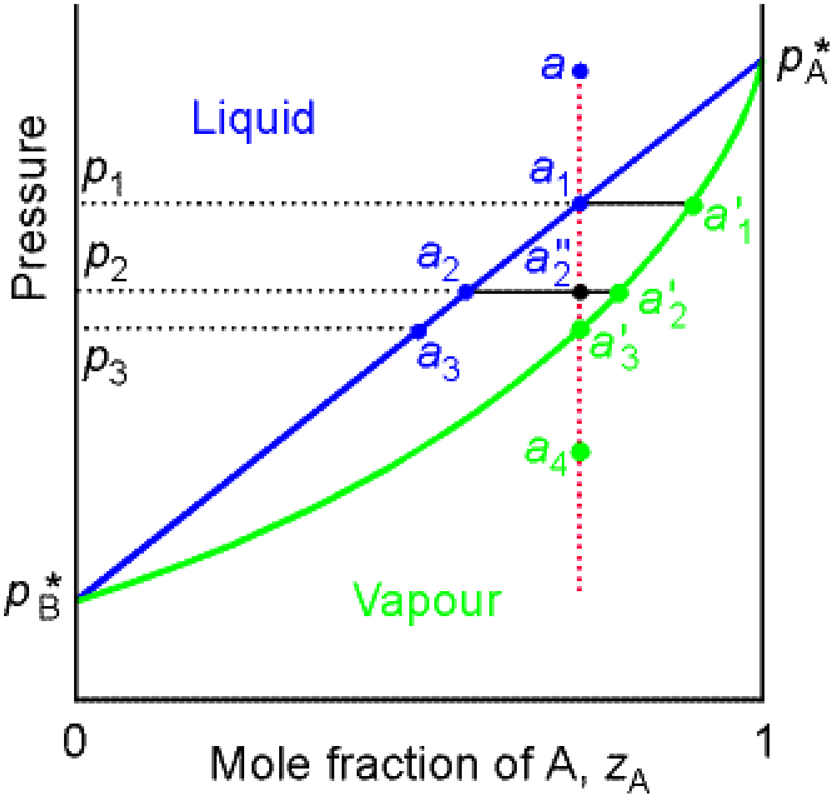


The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

When two phases are in equilibrium, P=2 so F'=l. That is, if the composition is specified, the pressure at which the two phases are in equilibrium is fixed.

8.3 Vapour pressure diagrams

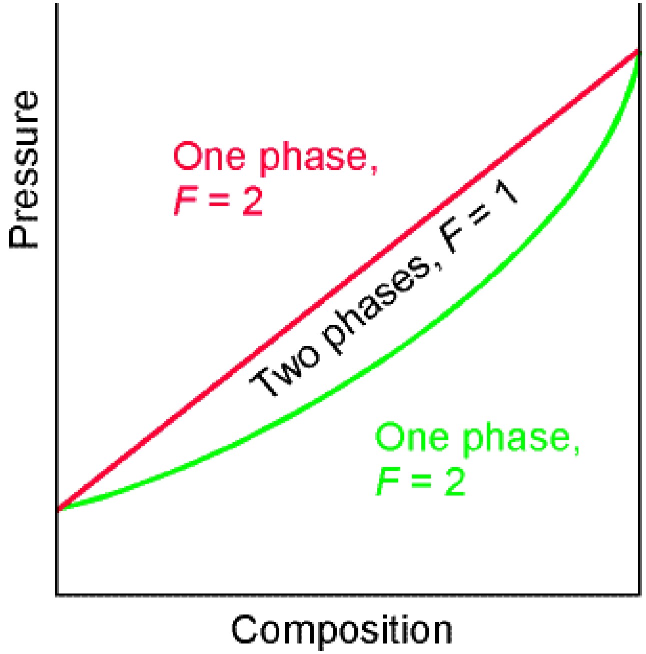
2). The interpretation of the diagrams



The vertical line is called an isopleth. Until point a_1 is reached (p reduced to p_1), the sample consists of a single liquid phase.

8.3 Vapour pressure diagrams

2). The interpretation of the diagrams

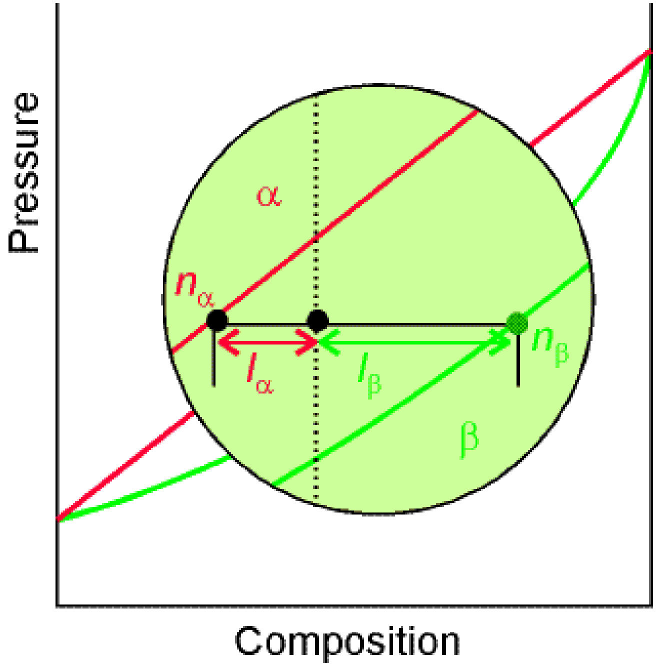


The general scheme of interpretation of a pressure-composition diagram (a vapour pressure diagram).

For all points between the two lines, two phases are in equilibrium, so $F' = 1$. For a given pressure the variance is zero, and the vapour and liquid phases have fixed compositions.

8.3 Vapour pressure diagrams

3). The lever rule



The lever rule. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot($m_\alpha l_\alpha = m_\beta l_\beta$ for balance).

8. Phase diagrams

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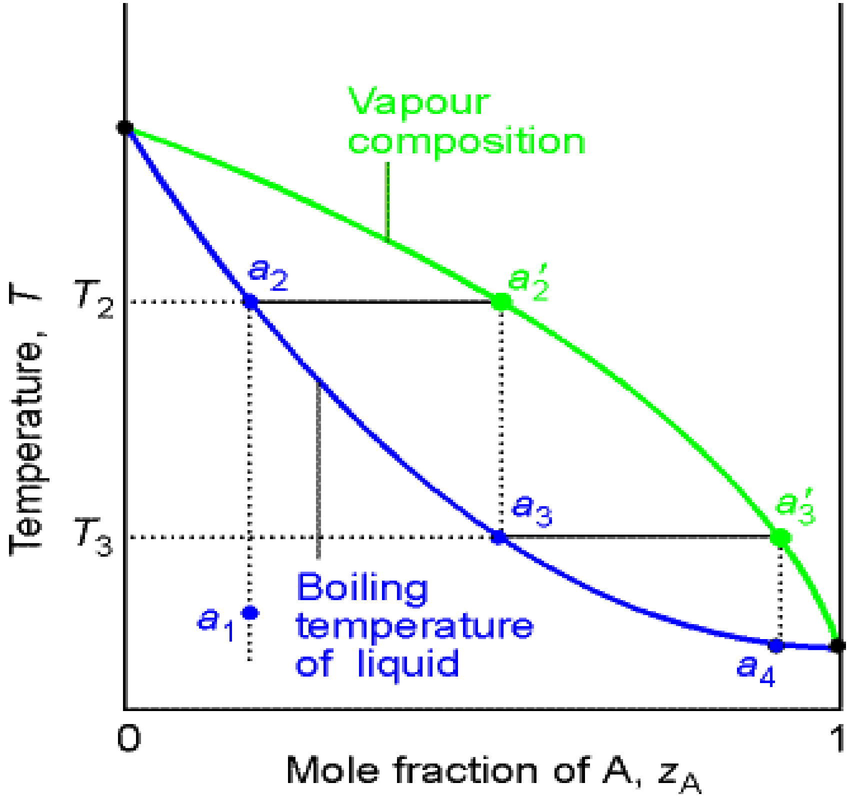
8.4 Temperature-composition diagrams

At constant *p*, the phase diagram depicted in terms of *T* and *C*

A temperature-composition diagram is one in which the boundaries show the compositions of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm).

8.4 Temperature-composition diagrams

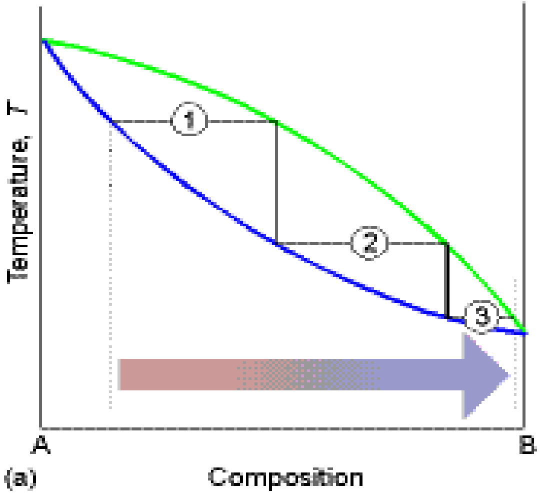
1). The distillation of mixtures

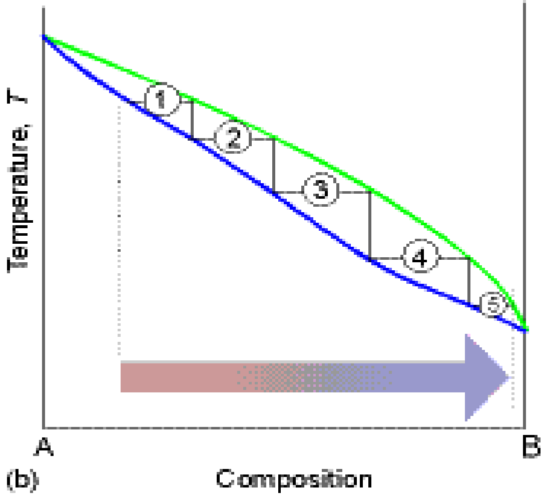


The temperature-composition diagram corresponding to an ideal mixture with the component A more volatile than component B.

8.4 Temperature-composition diagrams

1). The distillation of mixtures

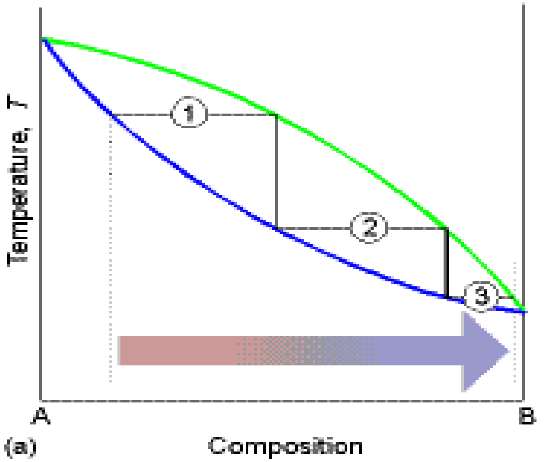




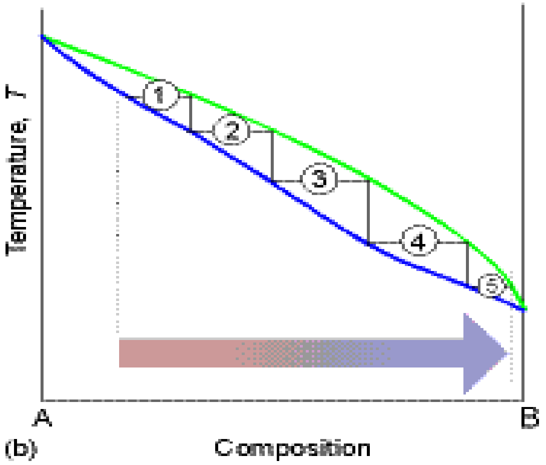
The efficiency of a fractionating column is expressed in terms of the number of theoretical plates, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate.

8.4 Temperature-composition diagrams

1). The distillation of mixtures



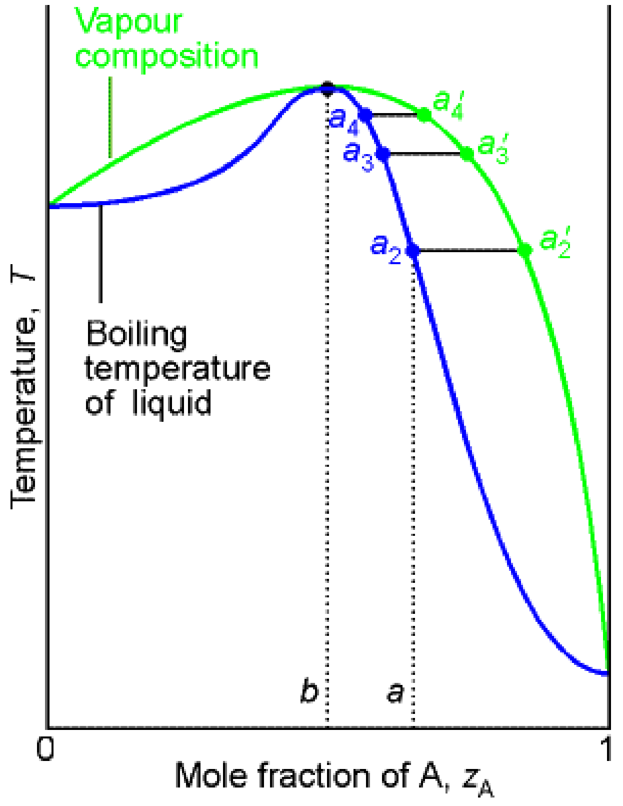
To achieve the degree of separation shown by the dotted lines in Fig. a, the fractionating column must correspond to 3 theoretical plates.



To achieve the same separation for the system shown in Fig b, in which the components have more similar partial vapour pressures, the fractionating column must be designed to correspond to five theoretical plates

8.4 Temperature-composition diagrams

2). Azeotropes

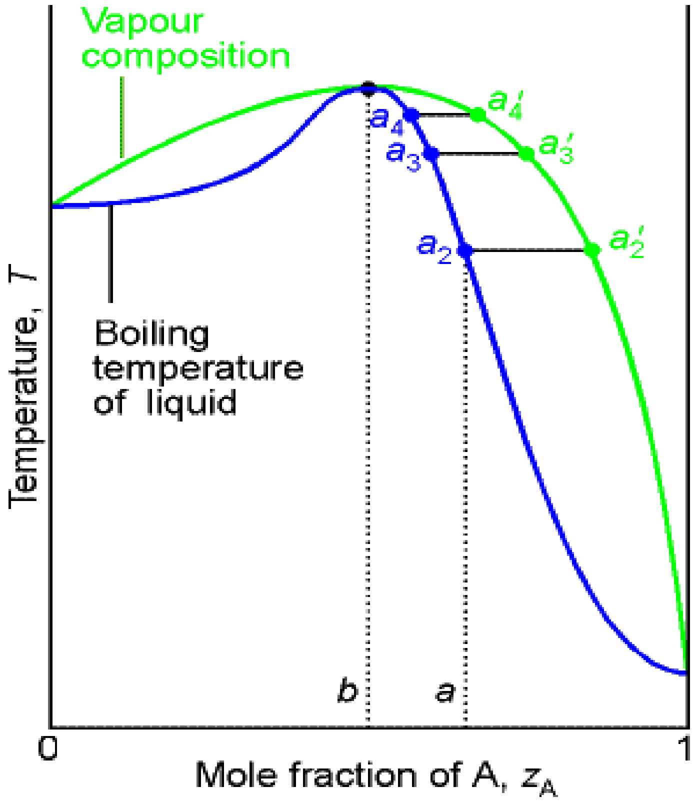


A high-boiling azeotrope

As the evaporation proceeds, the composition of the remaining liquid shifts towards B as vapour is drawn off. The boiling point of the liquid rises, the vapour becomes richer in B. When the liquid has reached the composition *b*, the vapour has the same composition as the liquid. Evaporation then occurs without change of composition. The mixture is said to form an azeotrope (boiling without changing)

8.4 Temperature-composition diagrams

2). Azeotropes

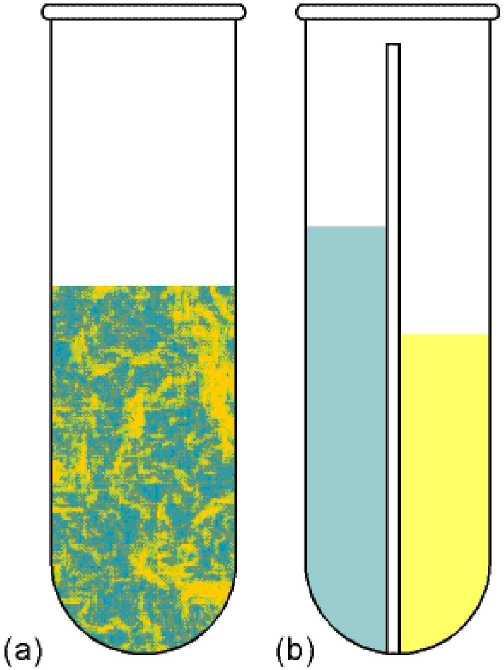


A high-boiling azeotrope

When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid.

8.4 Temperature-composition diagrams

3). Immiscible liquids



The distillation of (a) two immiscible liquids can be regarded as (b) the joint distillation of the separated components,

The immiscible 'mixture' boils at a lower *T* than either component would alone in a container like it shown in Fig.b, because boiling begins when the total vapour pressure reaches 1 atm, not when either vapour pressure reaches 1 atm. This distinction is the basis of steam distillation.

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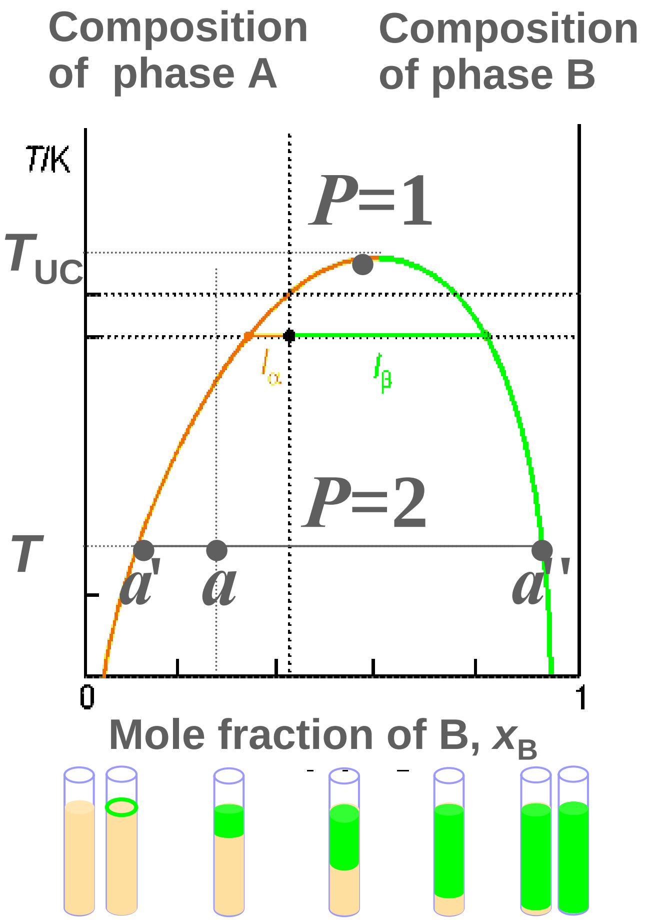
8.5 Liquid-liquid phase diagrams

1). Phase separation

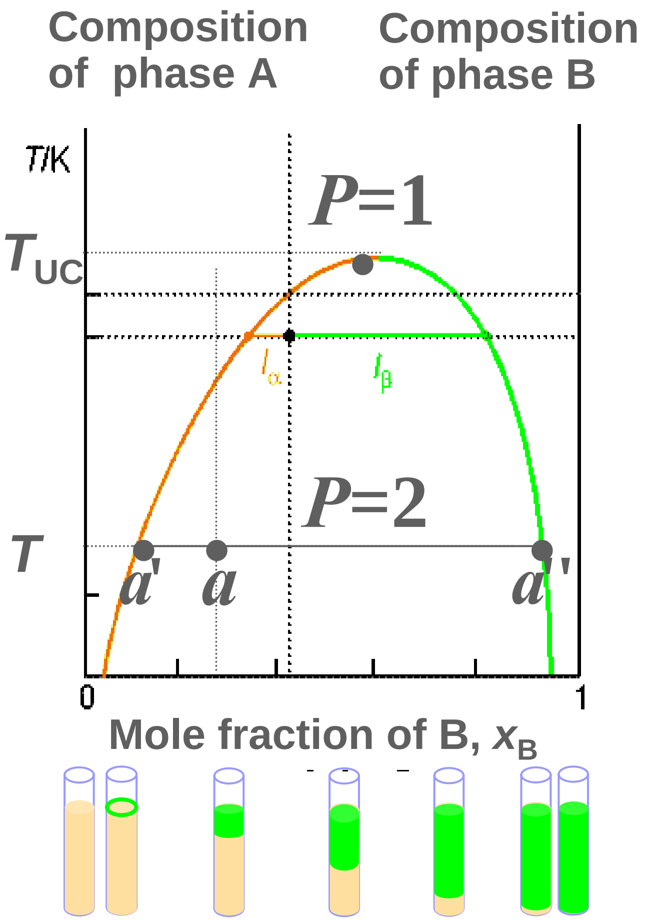


The *T*-*C* diagram for hexane and nitrobenzene at 1 atm

Let a small amount of a liquid B be added to a sample of another liquid A at *T*. It dissolves completely, and the binary system remains a single phase.

8.5 Liquid-liquid phase diagrams

1). Phase separation

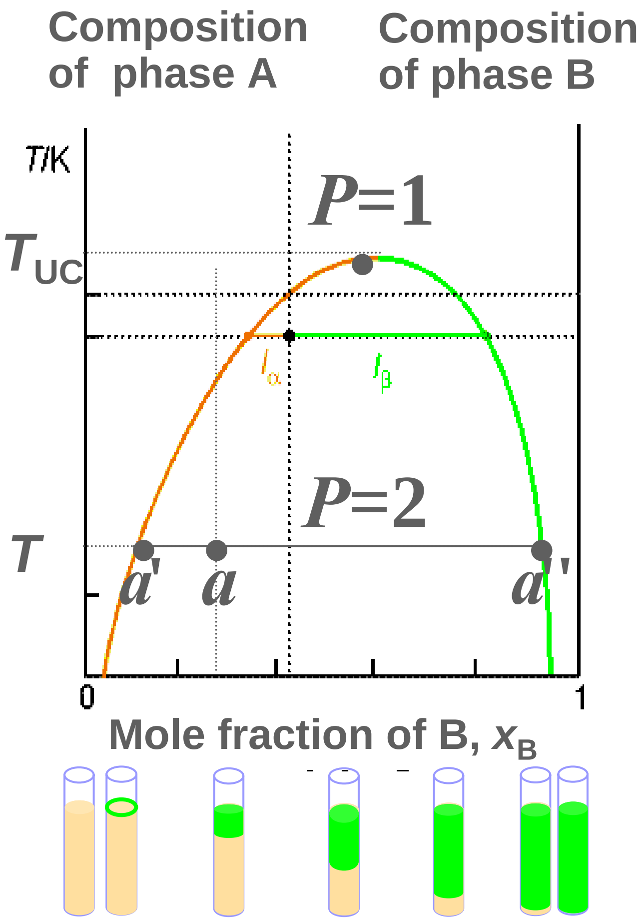


The T-C diagram for hexane and nitrobenzene at 1 atm

As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other (P = 2), the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the diagram, the composition of the former is represented by the point a' and that of the latter by the point a''.

8.5 Liquid-liquid phase diagrams

1). Phase separation

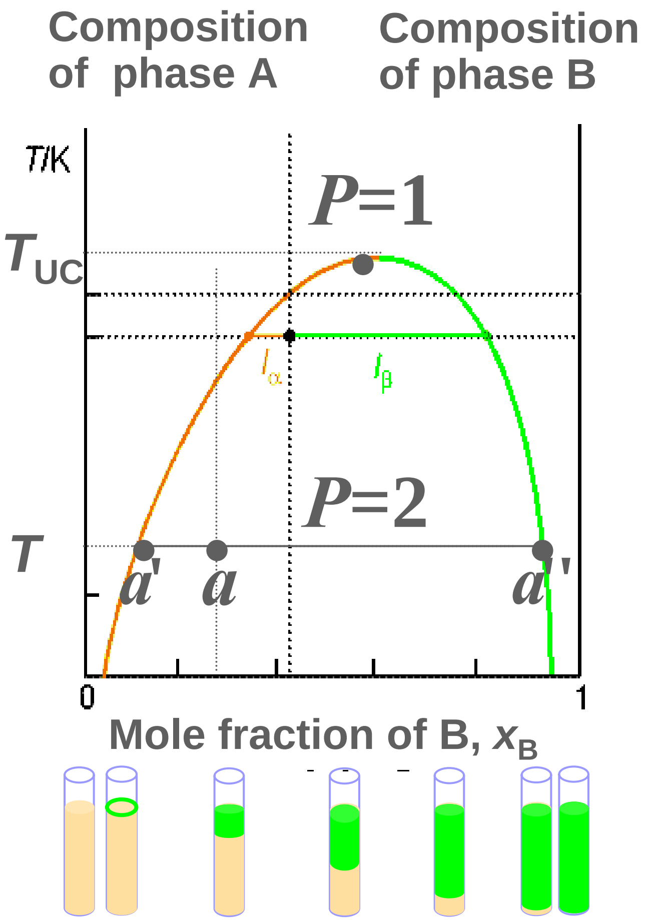


The *T*-*C* diagram for hexane and nitrobenzene at 1 atm

A stage is reached when so much B is present that it can dissolve all the A, and the system reverts to a single phase. The addition of more B now simply dilutes the solution, and from then on it remains a single phase.

8.5 Liquid-liquid phase diagrams

1). Phase separation



The *T*-*C* diagram for hexane and nitrobenzene at 1 atm

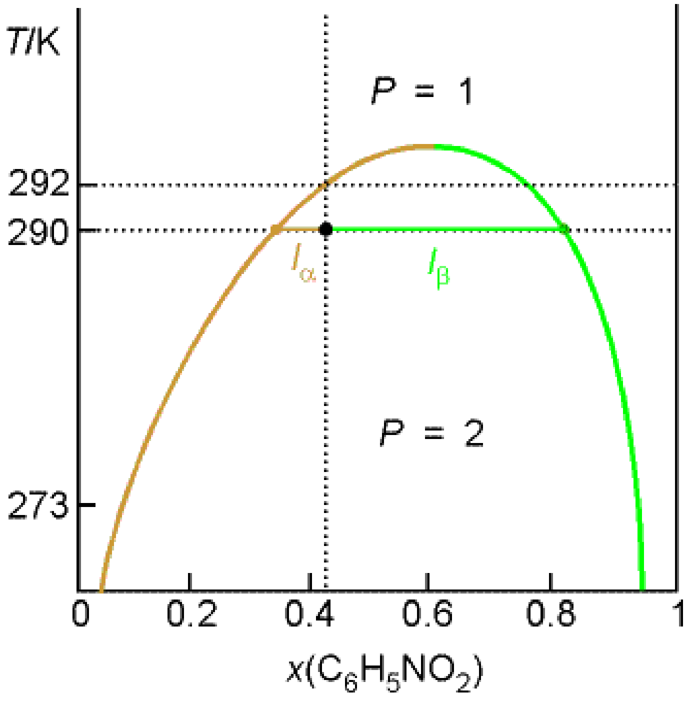
The compositions of the two phases at equilibrium vary with the *T*. The entire phase diagram can be constructed by repeating the observations at different *T* and drawing the envelope of the two-phase region.

Example

Interpreting a liquid-liquid phase diagram

A mixture of 50 g of hexane (0.59 mol C_6H_{14}) and 50 g nitrobenzene (0.41 mol $C_6H_5\,NO_2$) 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 in order to obtain a single phase?

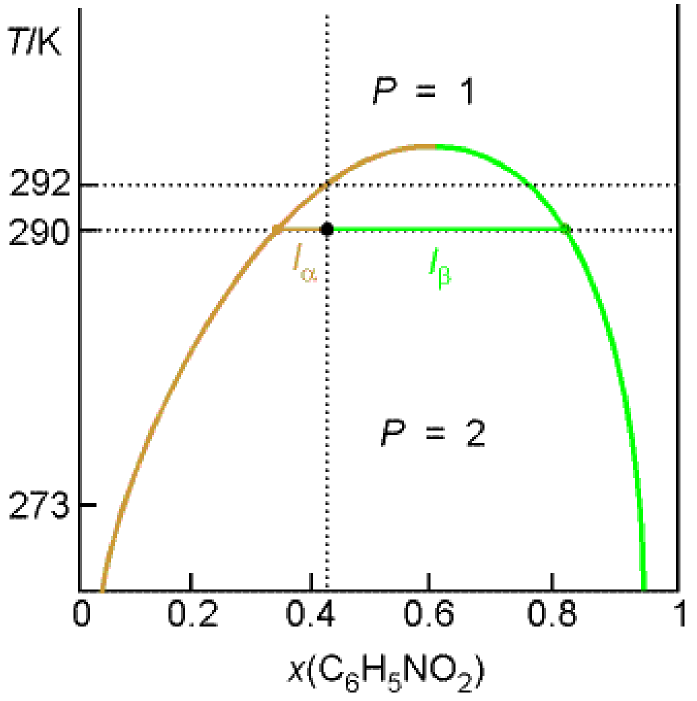
Example



T-C **diagram for hexane and nitrobenzene at 1 atm.**

Method: The compositions of phases in equilibrium are given by the points where the tie line through the point representing the temperature and overall composition of the system intersects the phase boundary. Their proportions are given by the lever rule.

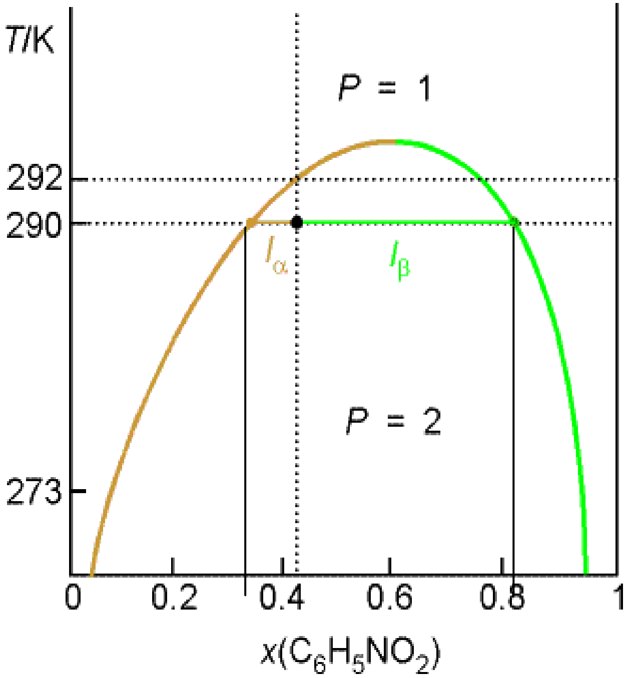
Example



Method: **The temperature at which the components are completely miscible is found by following the isopleth upwards and noting the temperature at which it enters the one-phase region of the phase diagram.**

***T*-*C* diagram for hexane and nitrobenzene at 1 atm.**

Example



T-C diagram for hexane and nitrobenzene at 1 atm.

Answer: **denote hexane by H and nitrobenzene by N;**

The point $x_H = 0.41$, $T = 290$ K occurs in the two-phase region of the phase diagram.

(1)The compositions of the two phases

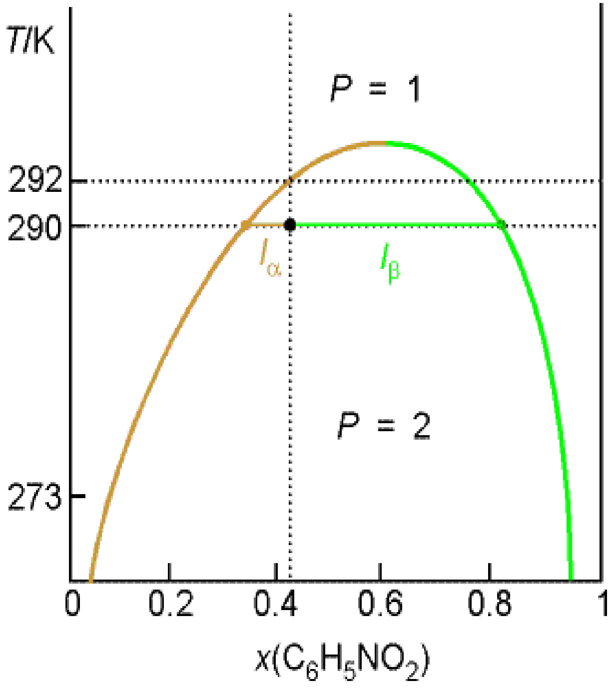
The horizontal tie line cuts the phase boundary at

$x_H = 0.35$ and $x_N = 0.83$,

so those are the compositions of the two phases.

Example

(2). The proportion of the mixture at T=290K



***T-C* diagram for hexane and nitrobenzene at 1 atm.**

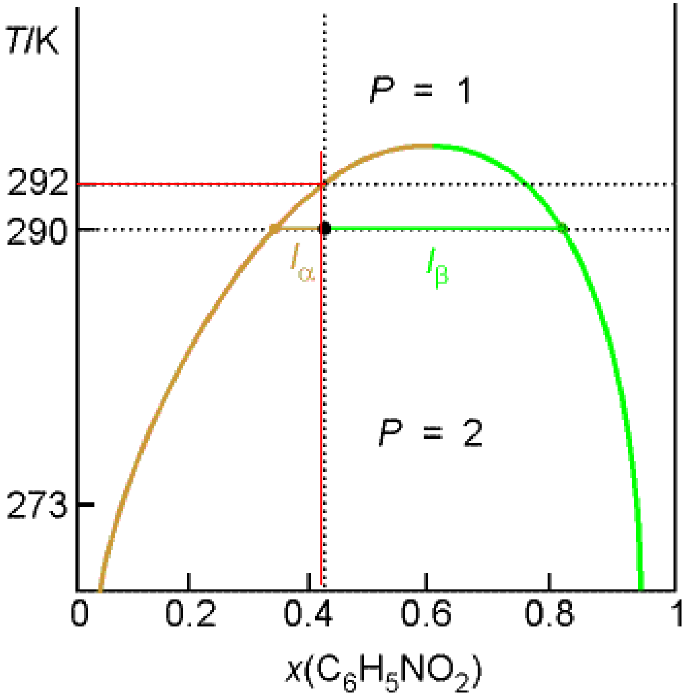
$$n_\alpha l_\alpha = n_\beta l_\beta$$

so the ratio of the amounts of each phase is equal to the ratio of the distances l_α and l_β

$$l_\alpha = 0.41-0.35;\ l_\beta = 0.83-0.41$$

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.83-0.41}{0.41-0.35} = 7$$

Example



T-*C* diagram for hexane and nitrobenzene at 1 atm.

(3). to *T* obtain a single phase

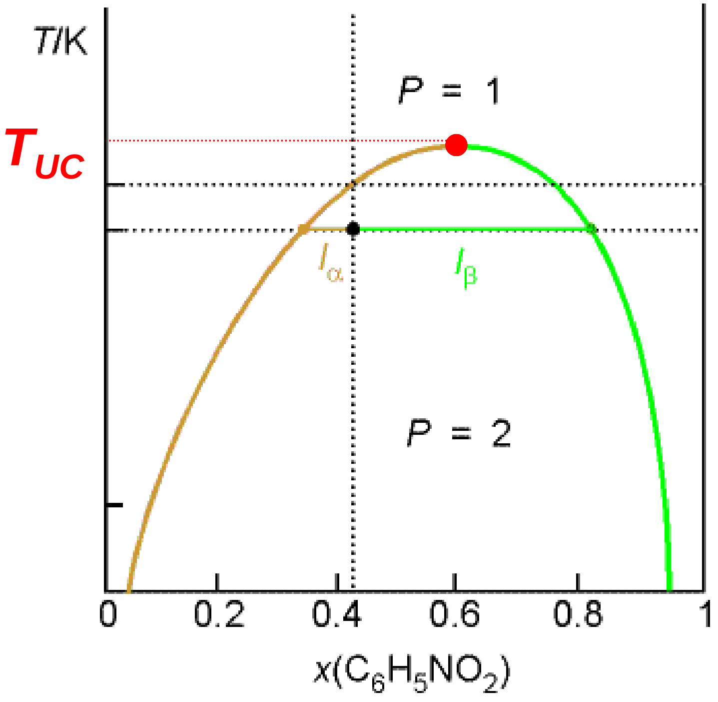
Heating the sample to

***T*=292 K**

takes into the single-phase region.

8.5 Liquid-liquid phase diagrams

2). Critical solution temperatures

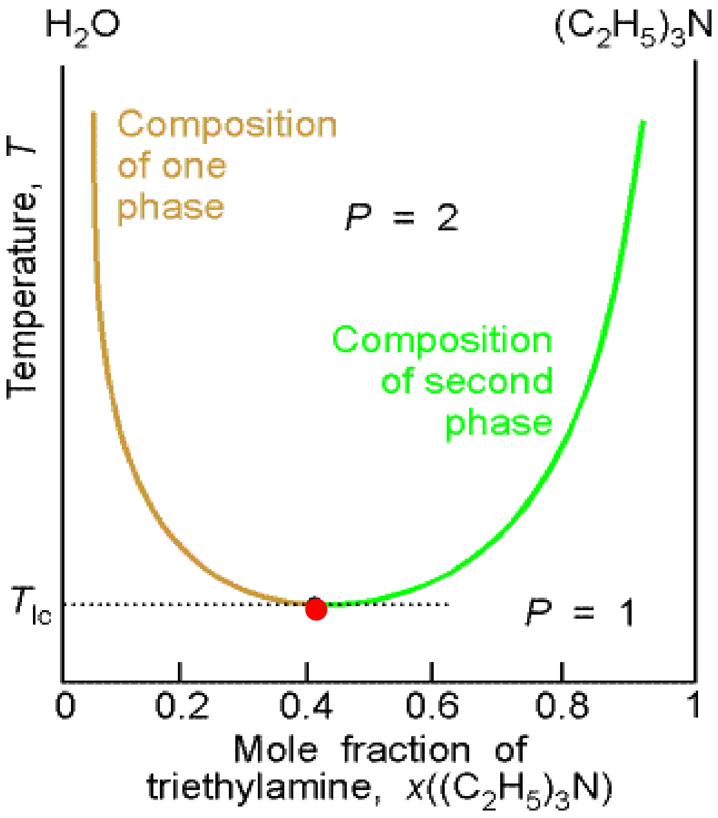


T-C diagram for hexane and nitrobenzene at 1 atm.

The upper critical solution temperature, T_{UC}, is the highest temperature at which phase separation occurs. Above T_{UC} the two components are fully miscible. This temperature exists because the greater thermal motion overcomes any potential energy advantage in molecules of one type being close together.

8.5 Liquid-liquid phase diagrams

2). Critical solution temperatures

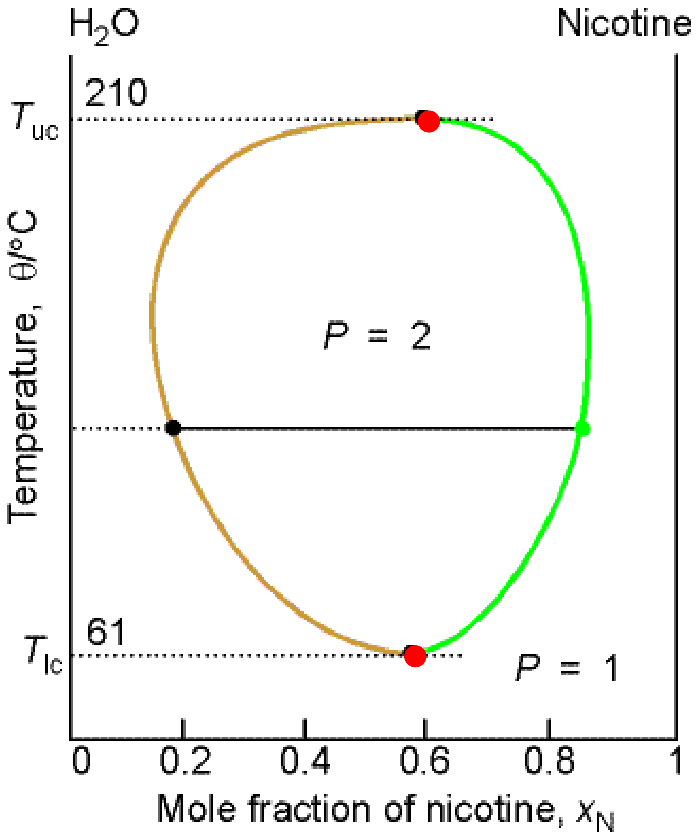


***T-C* diagram for water and trithymine at 292K.**

Some systems show a lower critical solution temperature, *T_{lc}*, below which they mix in all proportions and above which they form two phases. In this case, at low *T* the two components are more miscible because they form a weak complex; at higher *T* the complexes break up and the two components are less miscible.

8.5 Liquid-liquid phase diagrams

2). Critical solution temperatures



The temperature-composition diagram for water and nicotine, which has both upper and lower critical temperatures.

Some systems, like water and nicotine, have both upper and lower critical solution temperatures. They occur because, after the weak complexes have been disrupted, leading to partial miscibility, the thermal motion at higher temperatures homogenizes the mixture again, just as in the case of ordinary partially miscible liquids.

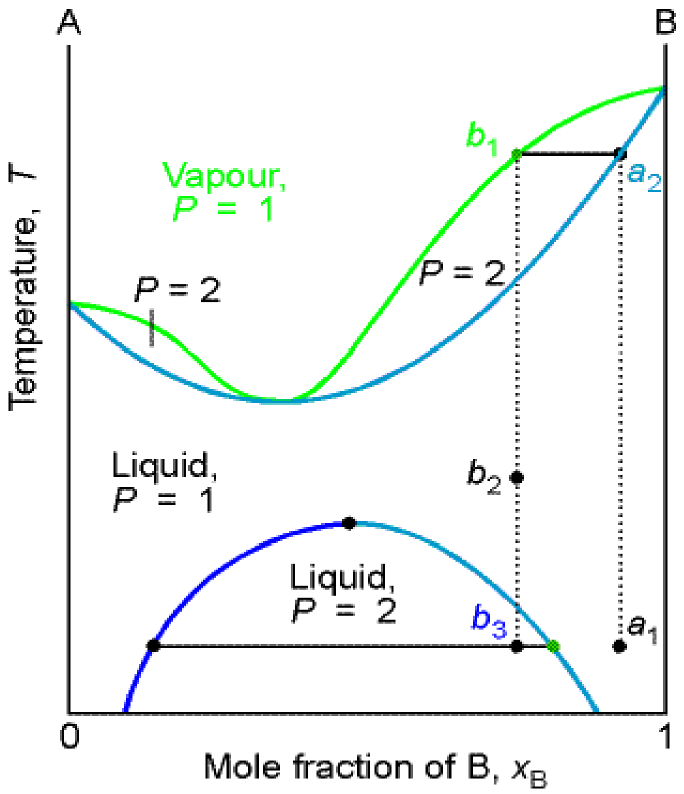
8.5 Liquid-liquid phase diagrams

3). The distillation of partially miscible liquids

A pair of liquids that are partially miscible and form a low-boiling azeotrope is common combination because both properties reflect the tendency of the two kinds of molecule to avoid each other. There are two possibilities: one in which the liquids become fully miscible before they boil, the other in which boiling occurs before mixing is complete.

8.5 Liquid-liquid phase diagrams

3). The distillation of partially miscible liquids



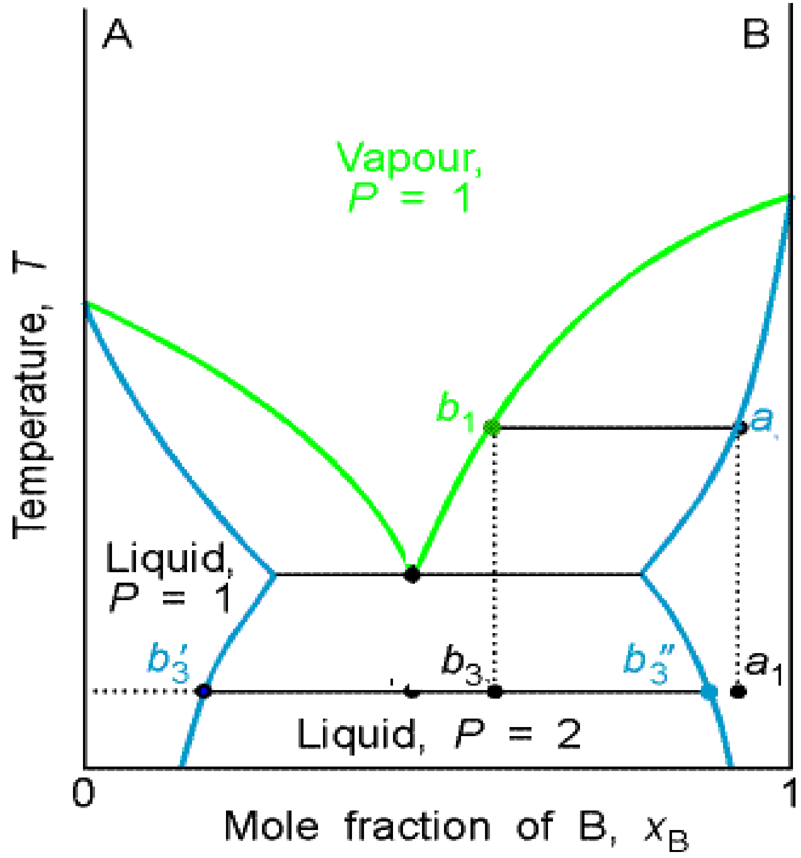
The temperature-composition diagram for a binary system in which the T_{uc} is less than the boiling point at all compositions

The phase diagram for two components that become fully miscible before they boil.

Distillation of a mixture of composition a_1, leads to a vapour of composition b_1, which condenses to the comp-letely miscible single-phase solution at b_2. Phase separation occurs only when cooled to a point in the two-phase liquid region, such as b_3.

8.5 Liquid-liquid phase diagrams

3). The distillation of partially miscible liquids

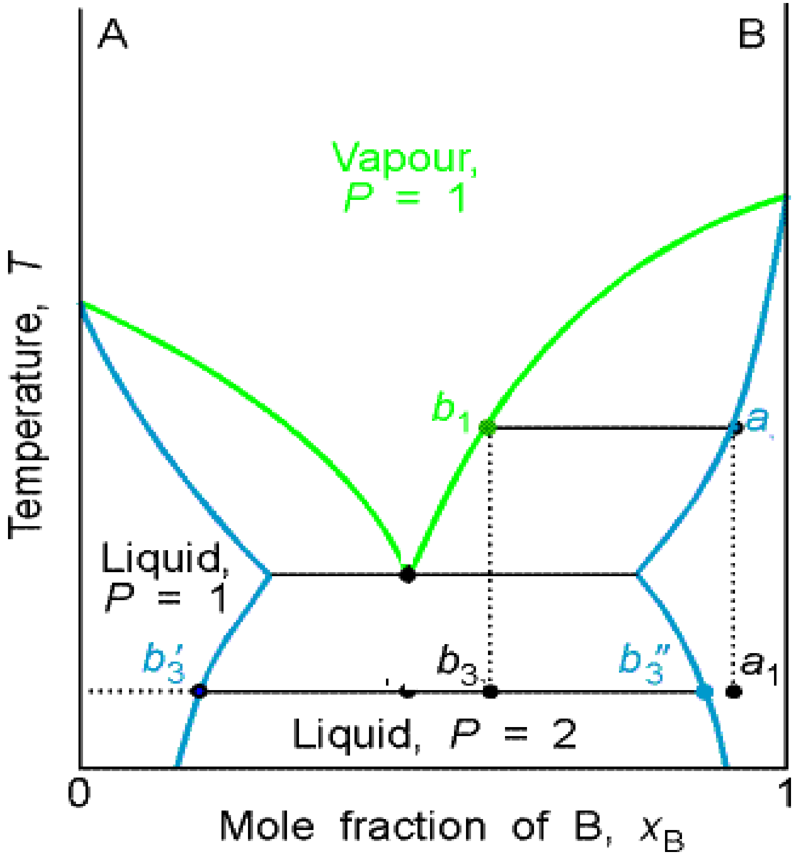


The temperature-composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

It shows the second possibility, in which 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 has composition b''_3.

8.5 Liquid-liquid phase diagrams

3). The distillation of partially miscible liquids



The temperature-composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

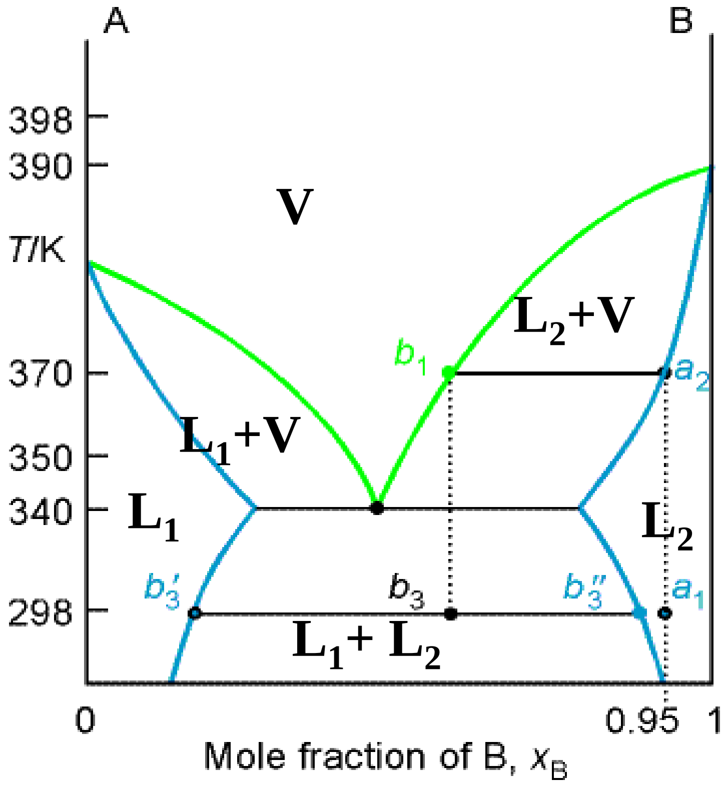
Note the isopleth e.At e_1 forms two phases,which persist up to the boiling point at e_2. The vapour has the same composition as the liquid. Similarly, condensing a vapour of composition e_3 gives a two-phase liquid of the same overall composition. At a fixed *T*, the mixture vaporizes and condenses like a single substance.

Example

Interpreting a phase diagram

State the changes that occur when a mixture of composition $x_B = 0.95$ (a_1) in the figure is boiled and the vapour condensed.

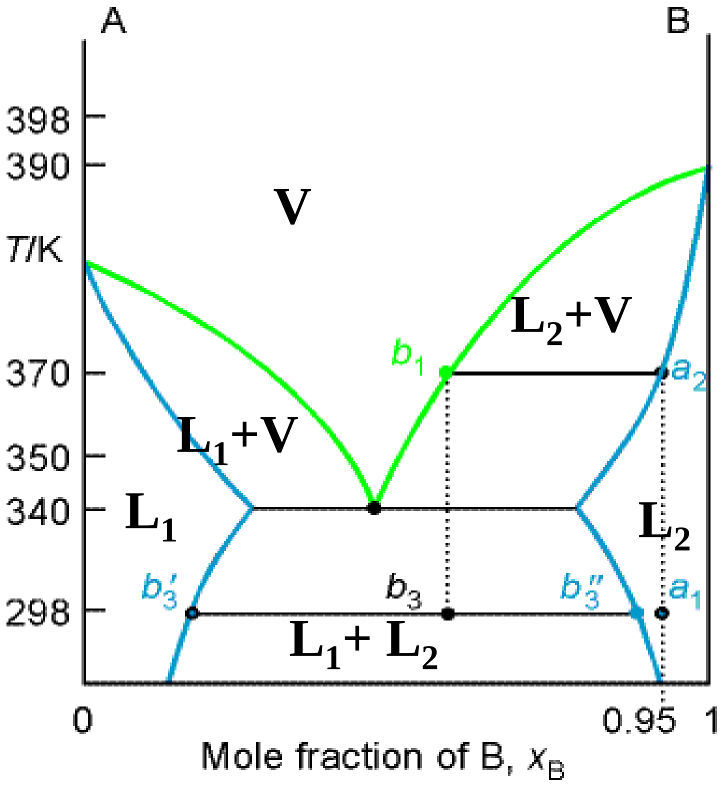
Example



The points of the phase diagram

Method: **The area in which the point lies gives the number of phases; the compositions 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.**

Example



The points of the phase diagram

Answer: The initial point is in the one-phase region. When heated it boils at 370 K (a_2) giving a vapour of composition y_B = 0.66 (b_1). The liquid gets richer in B, and the last drop (of pure B) evaporates at 392 K. The boiling range of the liquid is therefore 370 to 392 K. If the initial vapour is drawn off, it has a composition x_B = 0.66.

Example

Cooling the distillate corresponds to moving down the x_B=0.66 isopleth. At 350 K, for instance, the liquid phase has composition x_B = 0.87, the vapour x_B == 0.49; their relative proportions are 1:3.

At 340 K the sample consists of three phases: the vapour and two liquids. One liquid phase has composition x_B = 0.30; the other has composition x_B = 0.80 in the ratio 0.62:1.

Further cooling moves the system into the two-phase region, and at 298 K the compositions are 0.20 and 0.90 in the ratio 0.82:1.

8. Phase diagrams

Phases, components, and degrees of freedom

8.1 Definitions

8.2 The phase rule

Two-component systems

8.3 Vapour pressure diagrams

8.4 Temperature-composition diagrams

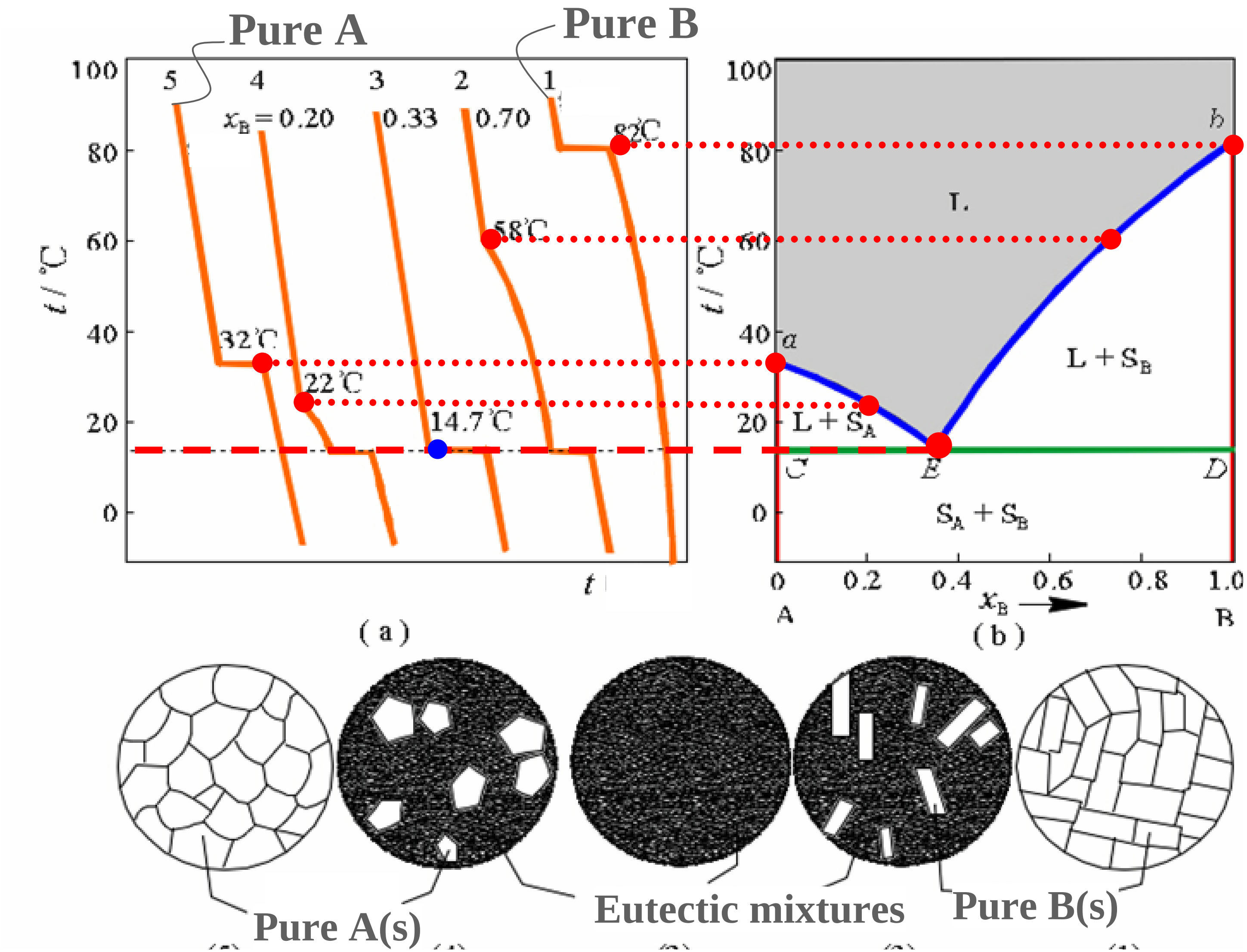
8.5 Liquid-liquid phase diagrams

8.6 Liquid-solid phase diagrams ▶

8.7 Ultrapurity and controlled impurity

8.6 Liquid-solid phase diagrams

The development and establishment of a phase diagram


Pure A

Pure B

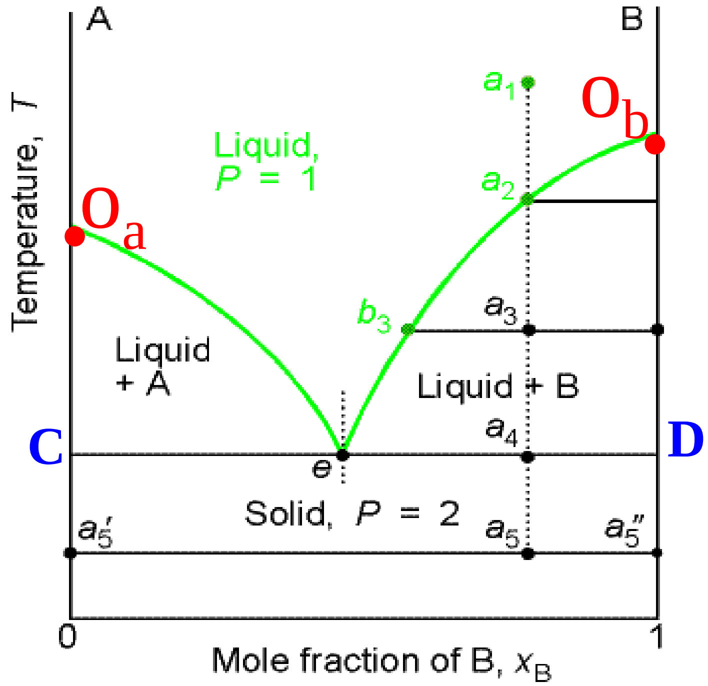
Pure A(s)

Eutectic mixtures

Pure B(s)

8.6 Liquid-solid phase diagrams

1). Eutectics



The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids.

The isopleth through *e* corresponds to the eutectic composition, the mixture with lowest melting point.

Points, lines, and regions

O_a: freezing point of pure *a*

O_b: freezing point of pure *b*

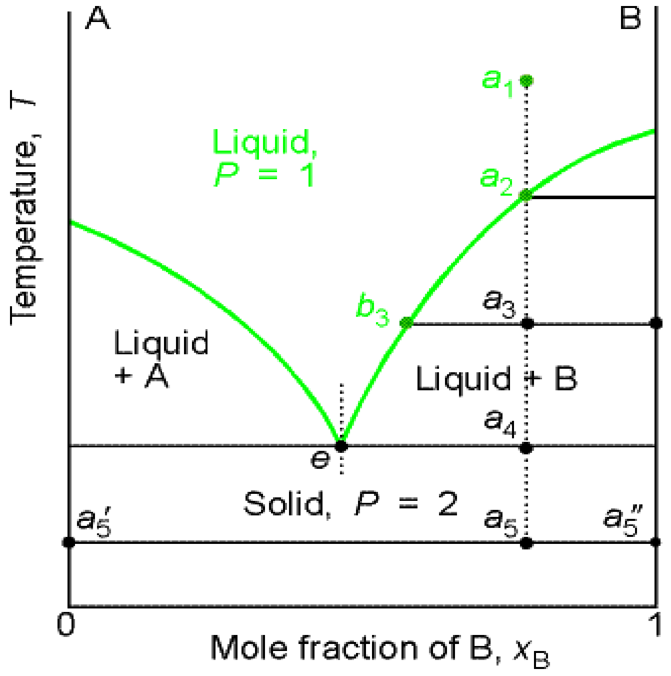
O_a–*e*, O_b–*e* :liquid phase line

O_a–C, O_b–D :solid phase line

C–*e*–D: three phase line

8.6 Liquid-solid phase diagrams

1). Eutectics



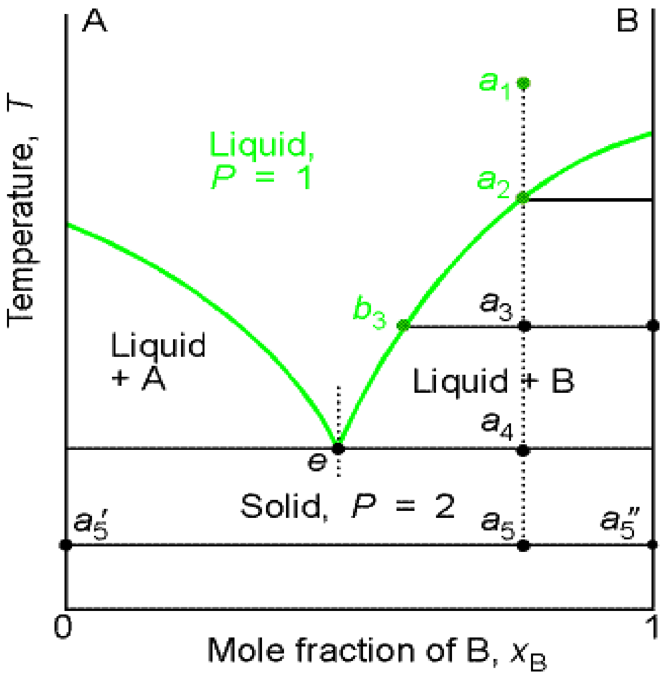
The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids.

(1) $a_1 \rightarrow a_2$

The system enters the two-phase region labelled Liquid + B. Pure solid B begins to come out of solution and the remaining liquid becomes richer in A.

8.6 Liquid-solid phase diagrams

1). Eutectics



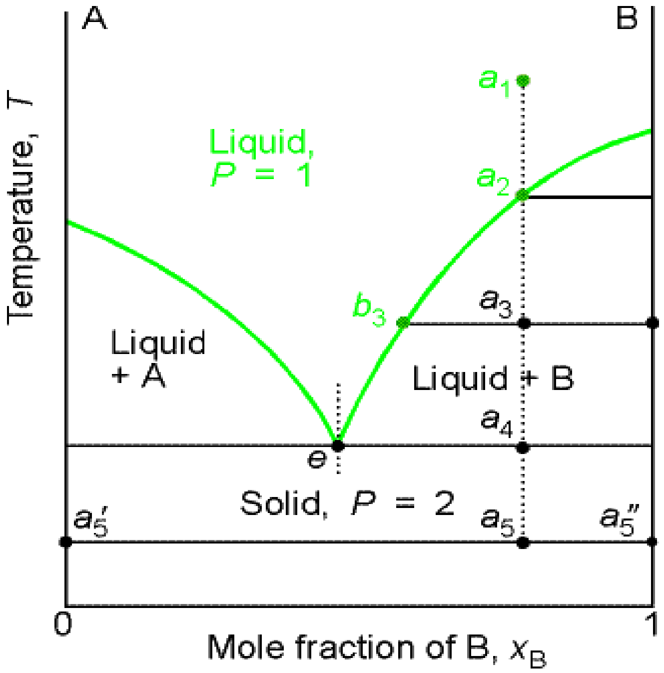
The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids.

(1) $a_2 \rightarrow a_3$

More of the solid forms. The relative amounts of the solid and liquid are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before because some B has been deposited.

8.6 Liquid-solid phase diagrams

1). Eutectics



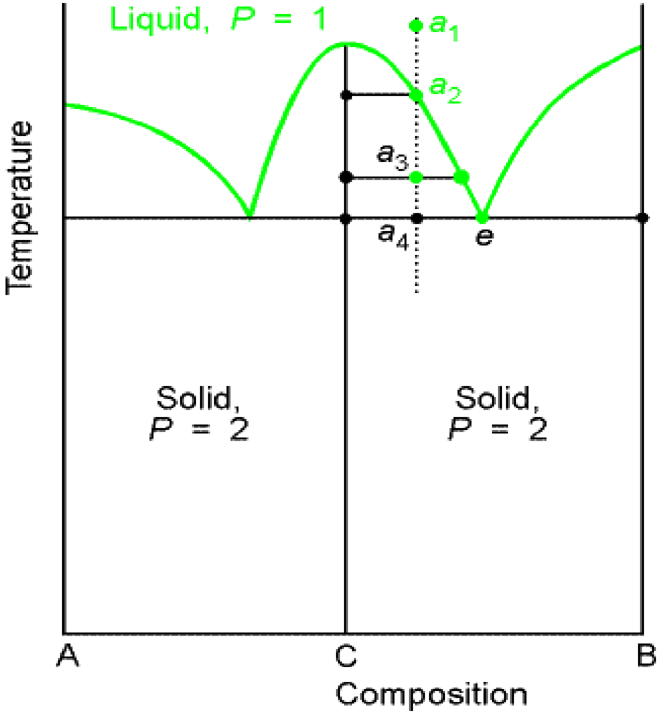
The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids.

(1) $a_3 \rightarrow a_4$

At the end of this step, there are three phases: liquid, solid B and solid A. The liquid composition is given by e. This liquid will freez to give a two-phase system of pure B and pure A.

8.6 Liquid-solid phase diagrams

2). Reacting systems

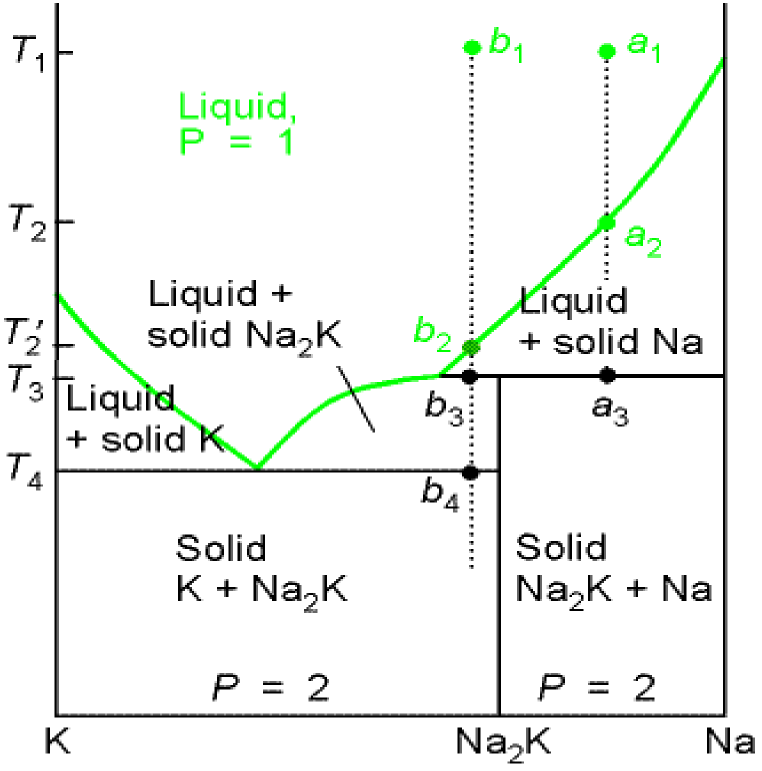


The phase diagram for a system in which A and B react to form a compound C = AB.

Many binary mixtures react to produce compounds, such as the gallium arsenide system, which forms the compound GaAs. Although three constituents are present, there are only two components because GaAs is formed from the reaction Ga+As ↔ GaAs.

8.6 Liquid-solid phase diagrams

3). Incongruent melting



The phase diagram for an actual system

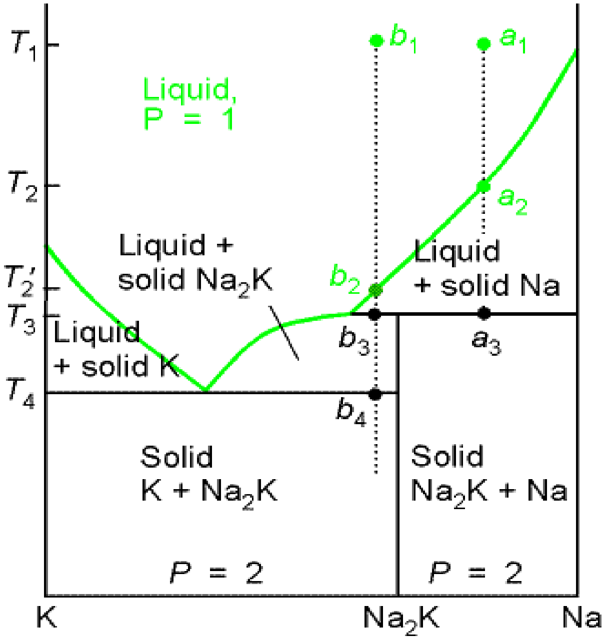
In some cases the compound C is not stable as a liquid. An example is the alloy Na_2K that a liquid at a_1 is cooled:

(1) $a_1 \rightarrow a_2$. Some solid Na is deposited, and the remaining liquid is richer in K.

(2) $a_1 \rightarrow$ Just below a_3. The sample is now entirely solid, and consists of solid Na and solid Na_2K.

8.6 Liquid-solid phase diagrams

3). Incongruent melting



The phase diagram for an actual system

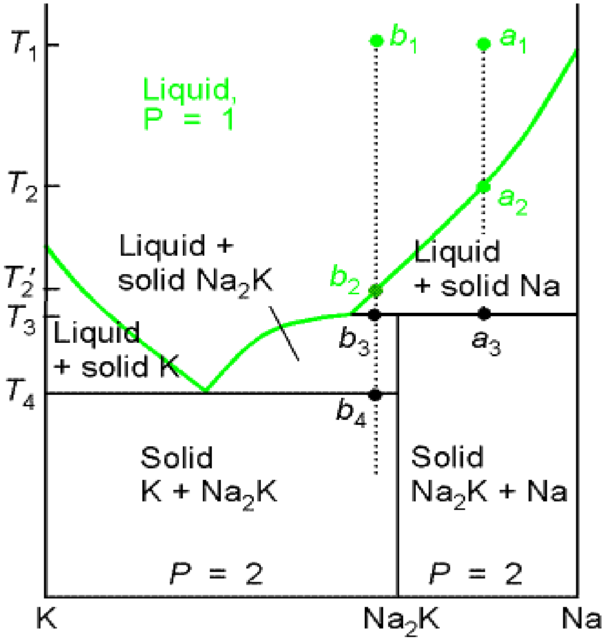
The isopleth through b_1

(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.

(2) $b_2 \rightarrow b_3$. 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 of Na_2K.

8.6 Liquid-solid phase diagrams

3). Incongruent melting



The phase diagram for an actual system

(3) $b_3 \rightarrow b_4$. As cooling continues, the amount of solid compound increases until at b_4 the liquid reaches its eutectic composition. It then solidifies to give a two-phase solid consisting of solid K and solid Na_2K.

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

Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry