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Phases, components, and degrees of freedom

6.1 Definitions

Phase : a state of matter that is uniform in both chemical composition and physical state

- The number of phases : *P* (See Fig. 6.1)

Constituent : a chemical species (ion or molecule) that is present

- ex) water + ethanol : two constituents

Component : a chemically independent constituent of a system

(= minimum number of independent species to define the composition of all the phases present in the system)

- The number of components : *C*

- ex) water + ethanol : 2 components (no chemical reaction)

$$\underset{\textbf{Phase 1}}{CaCO_3(s)} \leftrightarrow \underset{\textbf{Phase 2}}{CaO(s)} + \underset{\textbf{Phase 3}}{CO_2(g)}$$

→ 3 phases ($P = 3$), 3 constituents and 2 components ($C = 2$)

Degree of freedom (Variance) : the number of intensive variables that can be changed independently without disturbing *P* in equilibrium

- The number of degree of freedom : *F*

- If $F = 2$, it is called, “bivariant” or “ two degrees of freedom”

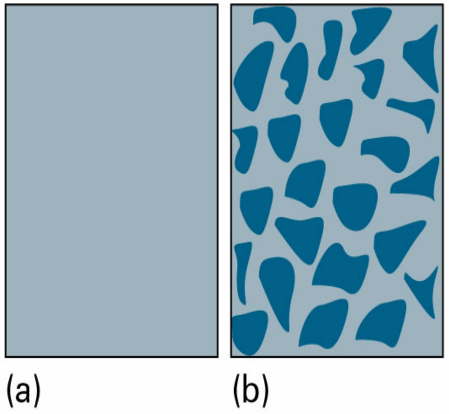


Fig. 6.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

6.2 The phase rule

For a system of any compositions, $F = C - P + 2$ **:** **Phase rule** (by J.W. Gibbs)

Justification 6.1

For two phases in equilibrium, $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T)$: variable is p or $T \rightarrow F = 1$

For three phases in equilibrium, $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T) = \mu_J(\gamma,p,T)$ **:** actually two equations

: $F = 0$ (ex; x+y=2 and 3x-y=4 → single solution : x=3/2 and y=1/2): three phases in mutual equilibrium

Four phases cannot be in mutual equilibrium in a one-component system because the following three equalities, $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T)$ $\mu_J(\beta,p,T) = \mu_J(\gamma,p,T)$ $\mu_J(\gamma,p,T) = \mu_J(\delta,p,T)$ are not consistent for two unknowns (p and T) (ex; x+y=2, 3x-y=4 and x+4y=6 → no solution)

Consider general case for a system of C components and P phases

- The pressure and temperature : 2 variables
- C components : $x_1 + x_2 + \cdots + x_C = 1$, mole fractions specifying the composition of a phase : $C-1$
- Total number of intensive variables : $P(C-1) + 2$
- At equilibrium, the chemical potential of a component J must be the same in every phase

  $\mu_J(\alpha) = \mu_J(\beta) = \cdots$ for P phases

(P-1) equations of this kind have to be satisfied for each component J.

And for C components, the total number of equations = $C(P-1)$, which reduces degree of freedom.

Therefore, the total number of degrees of freedom is,

$$F = P(C-1) + 2 - C(P-1) = C - P + 2 \qquad F' = C - P + 1, \text{ if } p \text{ or } T \text{ is fixed}$$

6.2 The phase rule

(a) One-component systems

For one-component system (see Fig. 6.2)
- ***$F = 3 - P$***
- **If $P = 1$, $F = 2$** : Both p and T are independent variables.
- ***If $P = 2$, $F = 1$*** : p is not freely variable if T is set and vice versa.
- ***If $P = 3$, $F = 0$*** : This can be established only at a definite T and p

Phase diagram for water (see Fig. 6.3)
- At the point b cooled from a : ***$F = 1$*** (two phases of L and V are equilibrium)
- At the temperatures between b and d like c : ***$F = 2$***, the temperature can be varied at will
- At d : ***$F = 1$*** (two phases of S and L are equilibrium)

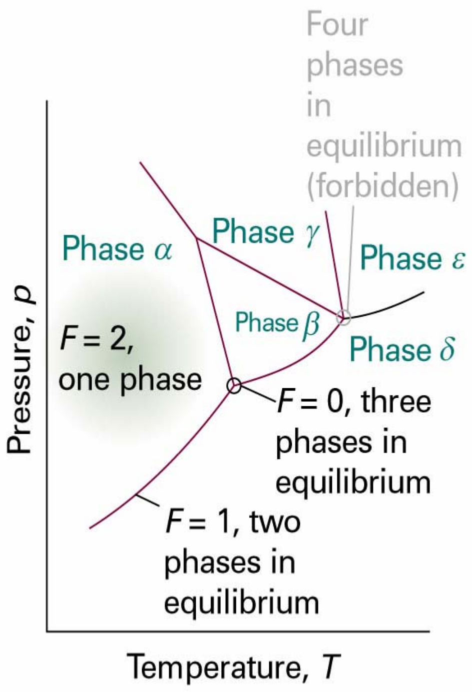


Fig. 6.2 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium.

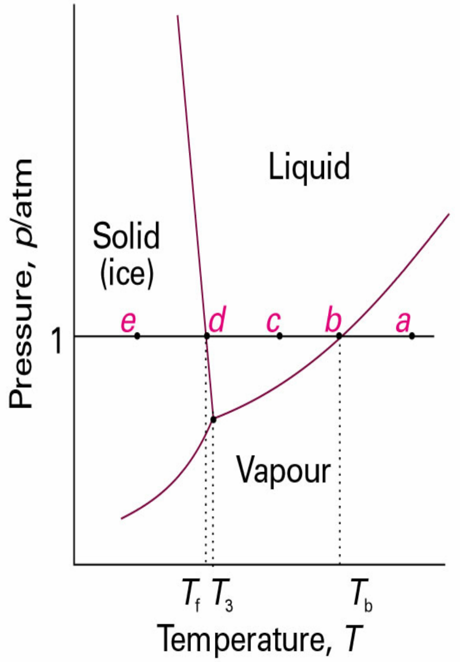


Fig. 6.3 The phase diagram for water, a simplified version of Fig. 4.5. The label T_3 marks the temperature of the triple point, T_b the normal boiling point, and T_f the normal freezing point.

6.2 The phase rule

(b) Experimental procedures

Two techniques for detecting a phase change

(1) Thermal analysis

1. Enthalpy change during the first order transition

   - A sample is allowed to cool and its temperature is monitored.
   - At a first-order transition, heat is evolved and the cooling stops until the transition is complete. (see Fig. 6.4)

2. Differential scannning calorimetry (DSC)

   - Measurement of the heat transferred to or from a sample at constant pressure during a physical or chemical change

→ control the electrical power output for the same temperature in the sample and reference

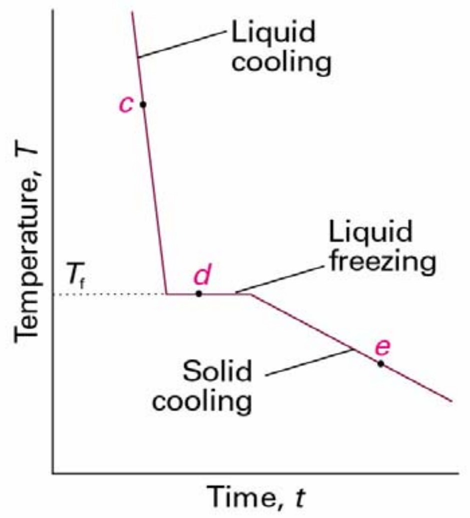
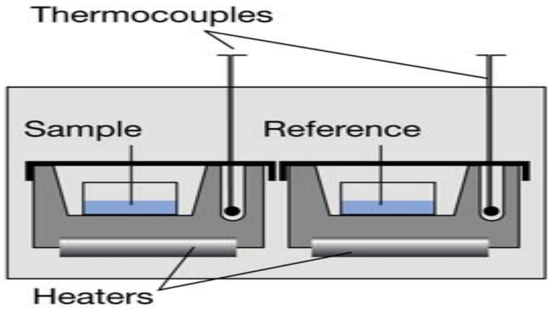


Fig. 6.4 The cooling curve for the isobar *cde* in Fig. 6.3. The halt marked *d* corresponds to the pause in the fall of temperature while the first-order exothermic transition (freezing) occurs. This pause enables T_f to be located even if the transition cannot be observed visually.



6.2 The phase rule

(2) Diamond-anvil cell for a ultrahigh pressure experiment

- Operation : pressure is exerted by turning the screw

→ pressing the sample between two gem-quality diamonds

→ monitoring the pressure spectroscopically by observing the shift of spectral lines in small pieces of ruby added to the sample (see Fig. 6.5)

- Applications : To study the transition of covalent solids to metallic solids

ex) I_2 (Iodine)

200 kbar → metallic

210 kbar → monatomic metallic solid

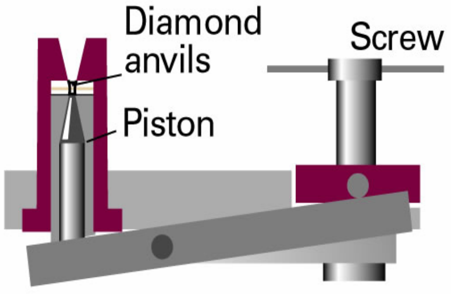


Fig. 6.5 Ultrahigh pressures (up to about 2 Mbar) can be achieved using a diamond anvil. The sample, together with a ruby for pressure measurement and a drop of liquid for pressure transmission, are placed between two gem-quality diamonds. The principle of its action is like that of a nutcracker: the pressure is exerted by turning the screw by hand.

Two-component systems

F* = 4 – *P* or *F'* = 3 – *P

6.3 Vapour pressure diagrams

Partial vapor pressure of an ideal binary solution (obeying Raoult's law) :

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

The total vapour pressure, *p*

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + \left(p_A^* - p_B^*\right)x_A$$

p changes linearly with the composition from p_B* to p_A*
as x_A changes from 0 to 1 (see Fig. 6.6)

(a) The composition of the vapour

- The compositions of the liquid and vapour in mutual equilibrium: not necessarily the same!
- The more volatile component in the liquid: expected to be richer in the vapour.
- From Dalton's law, the mole fractions (y_A, y_B) in the gas are given by

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

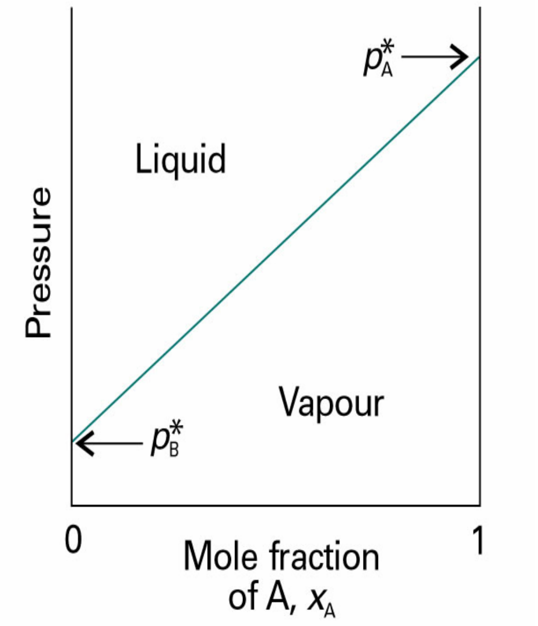


Fig. 6.6 The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult's law is obeyed.

6.3 Vapour pressure diagrams

If $p_A^* > p_B^*$, $y_A > x_A$;
the vapour is richer than the liquid
in the more volatile component
If B is non-volatile (p_B^*=0) :
no contribution to the vapour (y_B = 0)
(see Fig. 6.7)

By relating the composition of the liquid to the composition of the vapour, (see Fig.6.8)

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

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

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

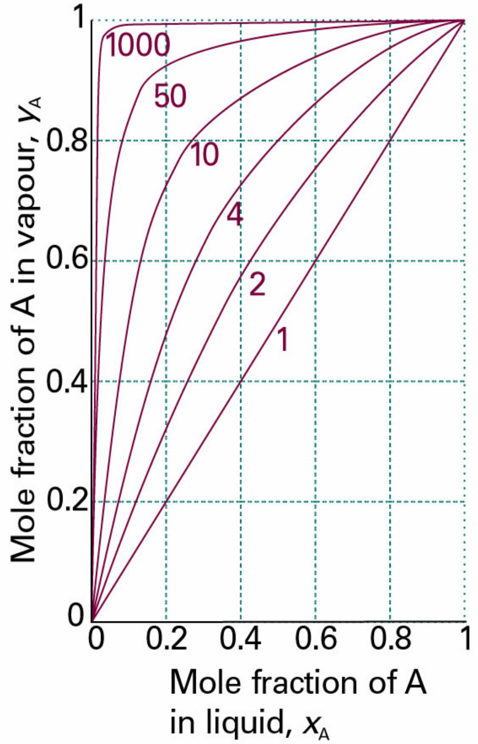


Fig. 6.7 The mole fraction of A in the vapour of a binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn 6.5 for various values of p_A^*/p_B^* (the label on each curve) with A more volatile than B. In all cases the vapour is richer than the liquid in A.

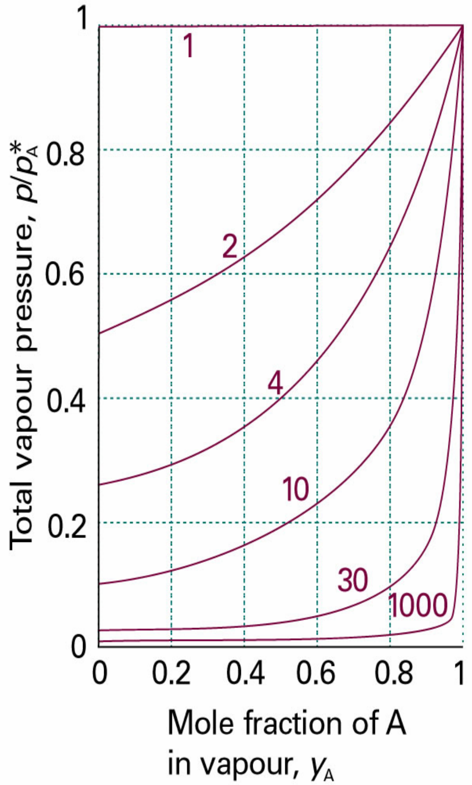


Fig. 6.8 The dependence of the vapour pressure of the same system as in Fig. 6.7, but expressed in terms of the mole fraction of A in the vapour by using eqn 6.6. Individual curves are labelled with the value of p_A^*/p_B^*.

6.3 Vapour pressure diagrams

(b) The interpretation of the diagrams

Combining the two preceding diagrams into one (see Fig. 6.9)

- At the point *a* : the vapor pressure of a mixture of composition x_A
- At the point *b* : the composition of the vapor in equilibrium with the liquid at that pressure
- Two phases in equilibrium on the *a*-*b* line : $P = 2$, $F' = 1$

Let z_A be the overall composition of the system,

$z_A = x_A$ (only liquid phase), where applied $p > p_{\text{vap}}$

$z_A = y_A$ (only vapour phase), where applied $p < p_{\text{vap}}$

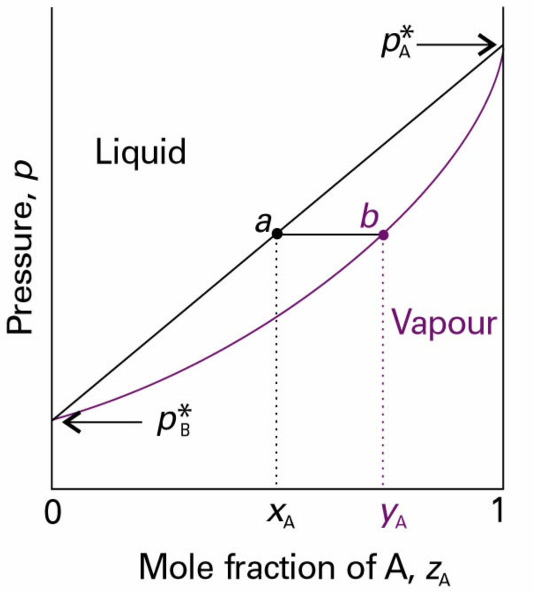


Fig. 6.9 The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system. A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present. The mole fraction of A is denoted z_A, as explained below.

6.3 Vapour pressure diagrams

The effect of lowering *p* on a liquid mixture of overall composition **a** (See Fig. 6.10)

→ $p\downarrow$ by drawing out a piston (See Fig. 6.11)

- For $p > p_1$, $a \rightarrow a_1$: simple liquid phase as $p\downarrow$
- At $p = p_1$, liquid/vapour coexist (in equilibrium)
  liquid comp. = a_1, vapour comp. = a_1'
- At $p = p_2$, overall composition = a_1''
  liquid comp. = a_2, vapor composition : a_2'
  p_2 is lower than the vapor pressure of
  the original liquid (p_1)
  (vaporized until the vapor pressure of the
  remaining liquid falls to p_2)
- F' = 1 if *p* is fixed : no variance (see Fig. 6.12)
- At $p = p_3$, liquid(a_3), vapour(a_3')
- For $p < p_3$, a_4 : vapour phase

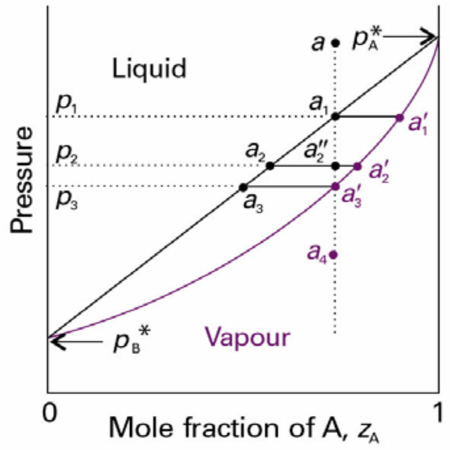


Fig. 6.10 The points of the pressure–composition diagram discussed in the text. The vertical line through *a* is an *isopleth*, a line of constant composition of the entire system.

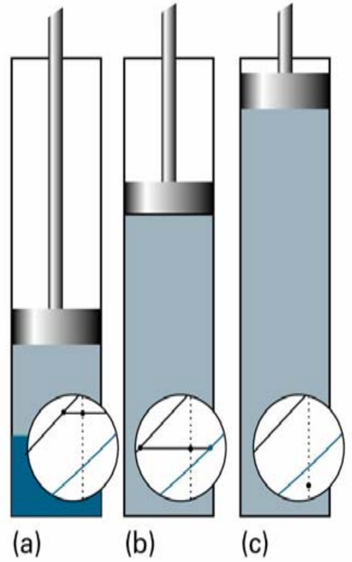


Fig. 6.11 (a) A liquid in a container exists in equilibrium with its vapour. The superimposed fragment of the phase diagram shows the compositions of the two phases and their abundances (by the lever rule). (b) When the pressure is changed by drawing out a piston, the compositions of the phases adjust as shown by the tie line in the phase diagram. (c) When the piston is pulled so far out that all the liquid has vaporized and only the vapour is present, the pressure falls as the piston is withdrawn and the point on the phase diagram moves into the one-phase region.

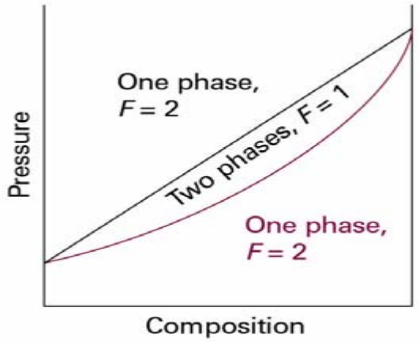


Fig. 6.12 The general scheme of interpretation of a pressure–composition diagram (a vapour pressure diagram).

6.3 Vapour pressure diagrams

(c) The lever rule

The relative proportion of vapor and liquid at some pressure for a given overall composition is determined using the lever rule.

$$\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$$

lever rule

Where, n_α : the amount of phase α

n_β : the amount of phase β

If $l_\beta \approx 2l_\alpha$, the amount of phase α is about twice the amount of phase β (See Fig. 6.13)

Justification 6.2

Let $n = n_\alpha + n_\beta$ and the overall amount of $A = nz_A$

$$nz_A = n_\alpha x_A + n_\beta y_A \quad (1) \qquad nz_A = n_\alpha z_A + n_\beta z_A \quad (2)$$

By eqns. (1) and (2), $n_\alpha (x_A - z_A) = n_\beta (z_A - y_A)$

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

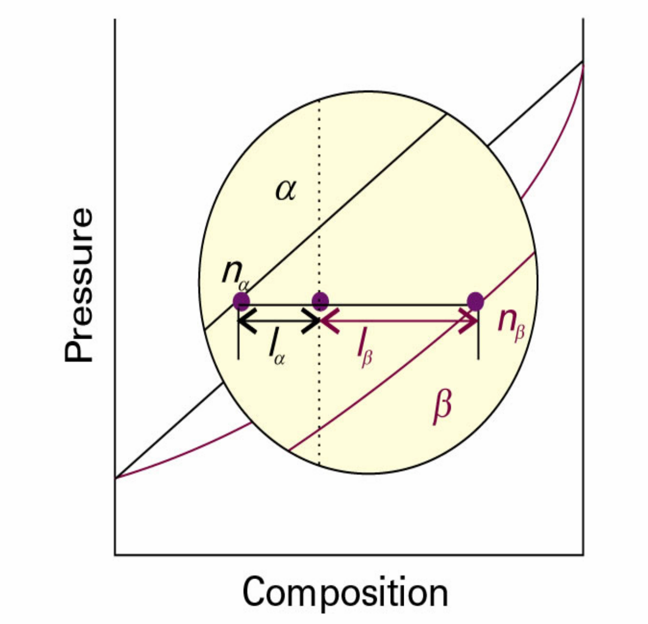


Fig. 6.13 The lever rule. The distances l_α and l_β are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot ($m_\alpha l_\alpha = m_\beta l_\beta$ for balance).

6.4 Temperature-composition diagrams (see Fig. 6.14)

(a) The distillation of mixtures

$F' = 1$→ the compositions of the phases in equilibrium at a given p,T

$F' = 2$→ T and compositions at a given p

When a liquid (a_1) is heated to T_2 (boiling temp. of liquid),
liquid(a_1) and vapour(a_2’) : The vapour is richer in more volatile component A.

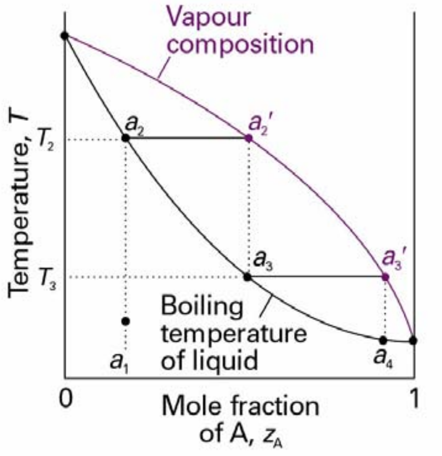


Fig. 6.14 The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

Simple distillation - vapour is withdrawn and condensed

Used to separate volatile liquid from a non-volatile solute or solid.

Fractional distillation – boiling and condensation cycle (repeated)

Used to separate volatile liquids

Theoretical plates (See Fig. 6.15)

- The first condensate a_3→ boiled at T_3 , vapour(a_3’)
  after the vapour is drawn off→a_4

Components in (b) has more similar partial pressures than those in (a)

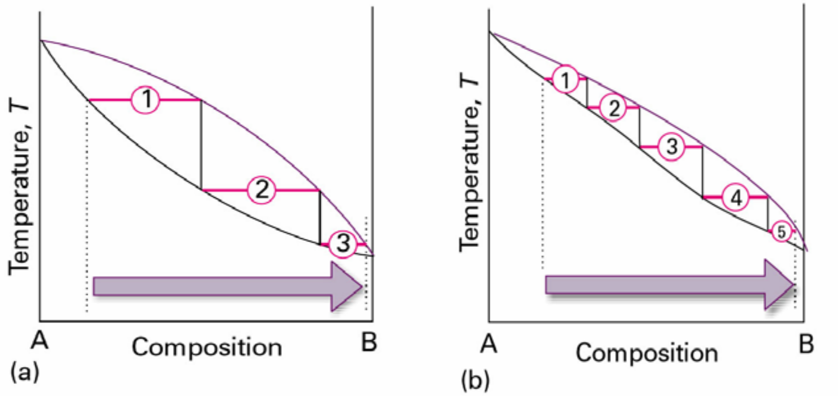


Fig. 6.15 The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) 3, (b) 5 theoretical plates.

6.4 Temperature-composition diagrams (see Fig. 6.14)

(b) Azeotropes

When a maximum in the phase diagram occurs, the favourable interactions between A and B reduce the vapour pressure of the mixture below the idea value (see Fig. 6.16).

- A-B interactions stabilize the liquid → $G^E < 0$

From the composition a, the vapour (at a_2') of the boiling mixture (at a_2) is richer in A

→ if the vapour is removed, liquid ($a_2 \rightarrow a_3$) and vapour ($a_2' \rightarrow a_3'$)

→ as the vapour is removed, liquid ($a_3 \rightarrow a_4$) and vapour ($a_3' \rightarrow a_4'$)

the boiling point of the liquid ↑ → the vapour becomes richer in B

→ when the liquid has reached the composition b, the vapour has the same composition as the liquid → **azeotrope**

Azeotropic composition

- distillation cannot separate the two liquids

(∵ condensate has the same composition as the azeotropic liquid)

Ex) hydrochloric acid/water

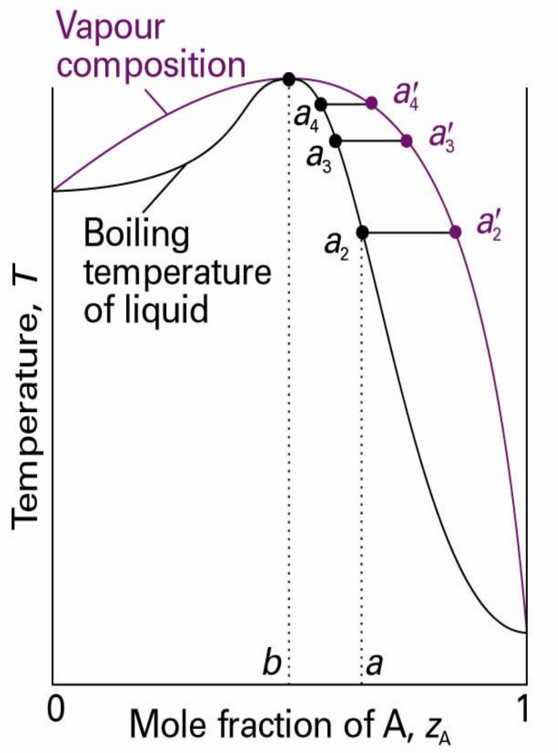


Fig. 6.16 A high-boiling azeotrope. When the liquid of composition *a* is distilled, the composition of the remaining liquid changes towards *b* but no further.

6.4 Temperature-composition diagrams (see Fig. 6.14)

When a minimum in the phase diagram occurs, the unfavourable interactions between A and B increase the vapour pressure of the mixture above the ideal value (see Fig. 6.17).

- A-B interactions destabilize the liquid → $G^E > 0$

From the composition a_1,

- At the boiling temperature, liquid(a_2) and vapour(a_2') in equilibrium

→ this vapour condenses in the column to a liquid ($a_2' \rightarrow a_3$)

→ the liquid is equilibrium with its vapour (a_3') condenses ($a_3' \rightarrow a_4$)

→ final fractionation shift from a_4 to b (azeotropic composition **)**

Ex) ethanol/water

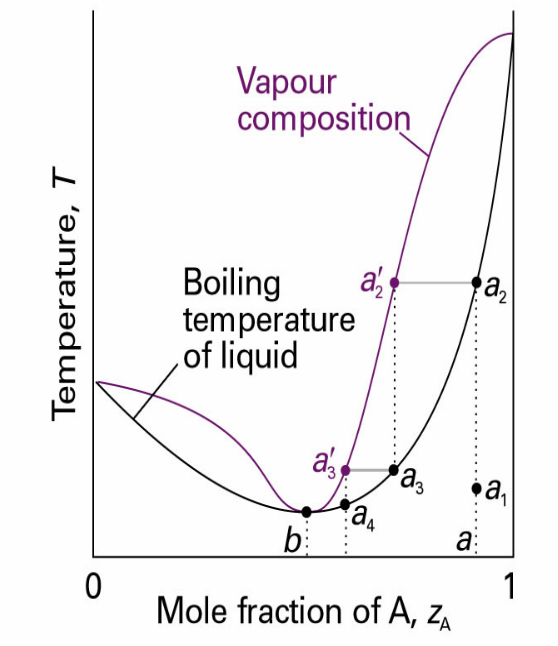


Fig. 6.17 A low-boiling azeotrope. When the mixture at *a* is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards *b* and then remains unchanged.

6.4 Temperature-composition diagrams (see Fig. 6.14)

(c) Immiscible liquids

Consider a mixture of two immiscible liquids.

- At equilibrium, both liquids are saturated with a tiny amount of the other component (see Fig. 6.18a)
  the total vapour pressure, $p = p_A{}^* + p_B{}^*$
- if T ↑ and thus total vapour pressure = atmospheric pressure, boiling commences and dissolved substances are purged from their solution.
- boiling → vigorous agitation of the mixture
  each component is kept saturated in the other component
  purging continues as the very dilute solutions are refilled

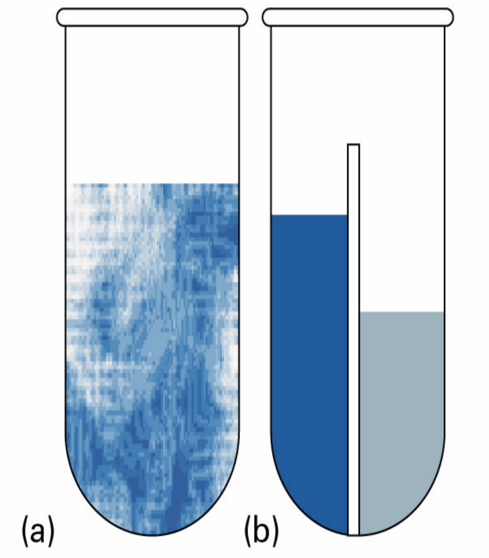


Fig. 6.18 The distillation of (a) two immiscible liquids can be regarded as (b) the joint distillation of the separated components, and boiling occurs when the sum of the partial pressures equals the external pressure.

Two immiscible liquids are heated in a container, (see Fig. 6.18b)

- the mixture boils at a lower T than either component would alone
- boiling begins when the total vapour pressure reaches 1 atm, not when either vapour pressure reaches 1 atm
  → **steam distillation**

6.5 Liquid-liquid phase diagrams

Let's consider temp. – comp. phase diagram for systems composed of two partially miscible liquids

(a) Phase separation

Suppose a small amount of a liquid B is added to another liquid A at *T'*
If B dissolves completely, the binary system remains a single phase
As more B is added, no more B is dissolved, leading to two phases in equilibrium
- Major phase (A saturated with B at a')
- Minor one (B saturated with A at a") (see Fig. 6.19)
  ($F' = 2 - 2 =$ 0 at fixed T and p)

When more B is added, the amount of one phase increases at the expense of the other.

As temperature increase,
- miscibility increases
- two-phase system of less extensive
  (∵ each phase in equilibrium is richer in its minor component)

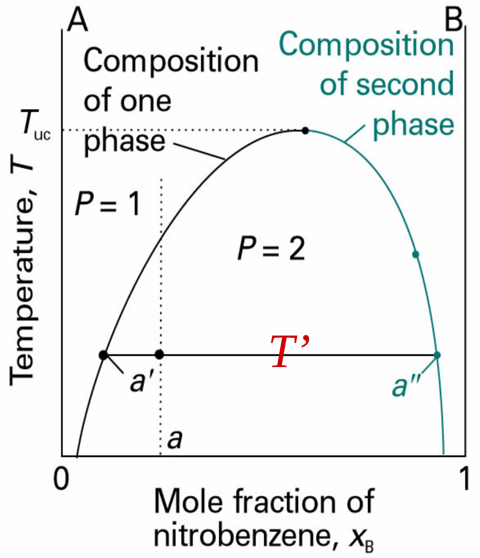


Fig. 6.19 The temperature–composition diagram for hexane and nitrobenzene at 1 atm. The region below the curve corresponds to the compositions and temperatures at which the liquids are partially miscible. The upper critical temperature, T_{uc}, is the temperature above which the two liquids are miscible in all proportions.

6.5 Liquid-liquid phase diagrams

(b) Critical solution temperatures

Upper critical solution temperature (T_{uc})

: the highest temperature at which phase separation occurs

- above T_{uc} : two components are fully miscible
- existence of T_{uc} : the greater thermal motion overcomes any potential energy advantage in molecules of one type being close together

Ex) nitrobenzene/hexane system (see Fig. 6.20)

soild solution (palladium/hydrogen system) (see Fig. 6.21)

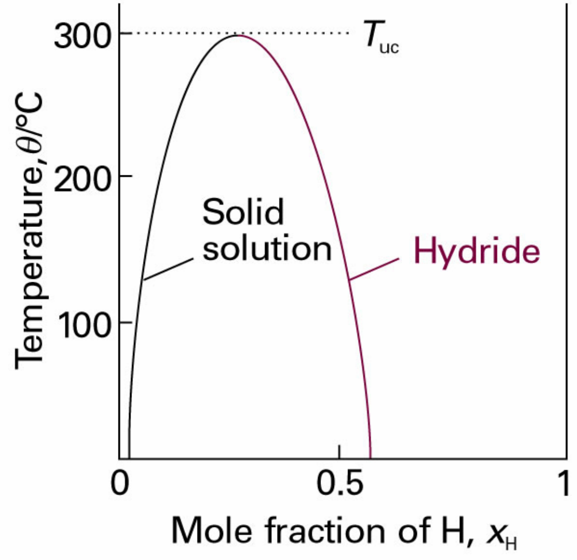


Fig. 6.21 The phase diagram for palladium and palladium hydride, which has an upper critical temperature at 300°C.

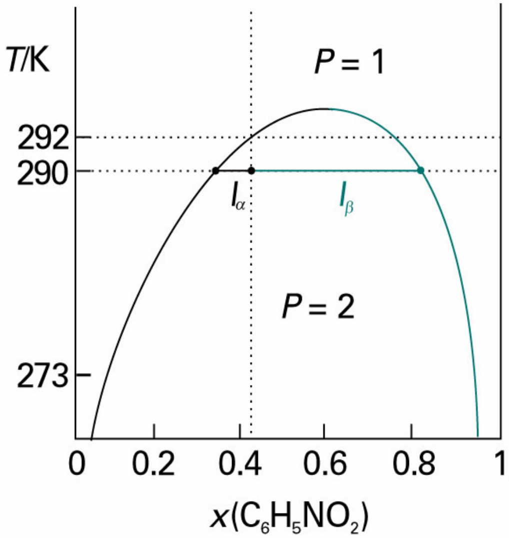


Fig. 6.20 The temperature–composition diagram for hexane and nitrobenzene at 1 atm again, with the points and lengths discussed in the text.

6.5 Liquid-liquid phase diagrams

Thermodynamic interpretation of T_{uc}:
$(\Delta G)_{mix}$ and its variation with T

From Sec. 5.4,

- If β (= w/RT) is greater than 2 (see Fig. 6.22), double minimum in $(\Delta G)_{mix}$ vs x, resulting in the phase separation
- the energy minima at

Since $(\Delta G)_{\mathrm{mix}} = nRT\left(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}} + \beta x_{\mathrm{A}} x_{\mathrm{B}}\right)$

$$\ln \frac{x}{1-x} + \beta(1-2x) = 0 \quad \text{(see Fig. 6.23)}$$

- $\beta \downarrow \rightarrow T \uparrow$ (assuming intermolecular forces and w remain constant)
- $\beta \geq 2$: two minima move together and merge
- $T_{\mathrm{uc}} = w/2R$ for $\beta = 2$

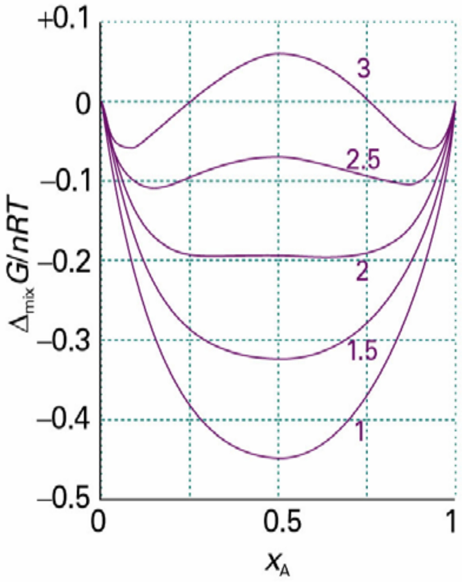


Fig. 6.22 The temperature variation of the Gibbs energy of mixing of a system that is partially miscible at low temperatures. A system of composition in the region $P = 2$ forms two phases with compositions corresponding to the two local minima of the curve. This illustration is a duplicate of Fig. 5.20.

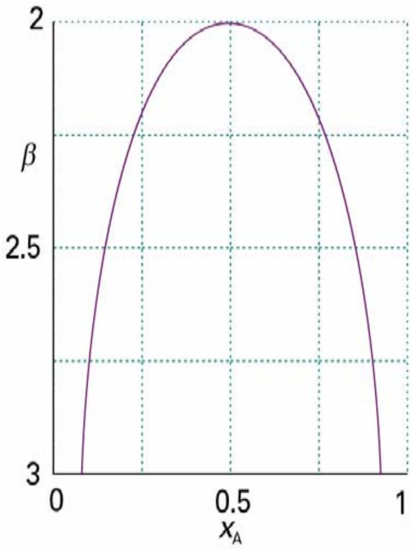


Fig. 6.23 The location of the phase boundary as computed on the basis of the β-parameter model introduced in Section 5.4.

6.5 Liquid-liquid phase diagrams

Lower critical solution temperature (T_{lc})

- $T<T_{lc}$: mixing in all proportions
- $T>T_{lc}$: two phases

ex) water/triethylamine (See Fig. 6.24)

→ low T : more miscible

(∵ a weak complex is formed)

→ high T : less miscible

(∵complexes break up)

Systems having both T_{uc} and T_{lc},

- weak complexes break up

→ partial miscibility (T_{ic} < T <T_{uc})

- homogenizing the mixture again by thermal motion at high ($T > T_{uc}$)

ex) nicotine/water (See Fig. 6.25)

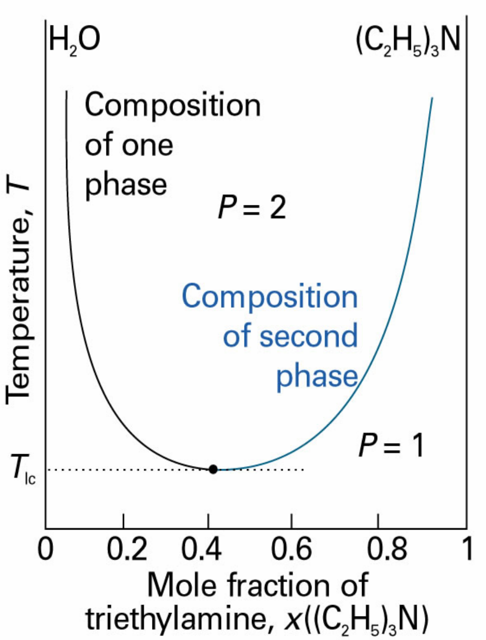


Fig. 6.24 The temperature–composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.

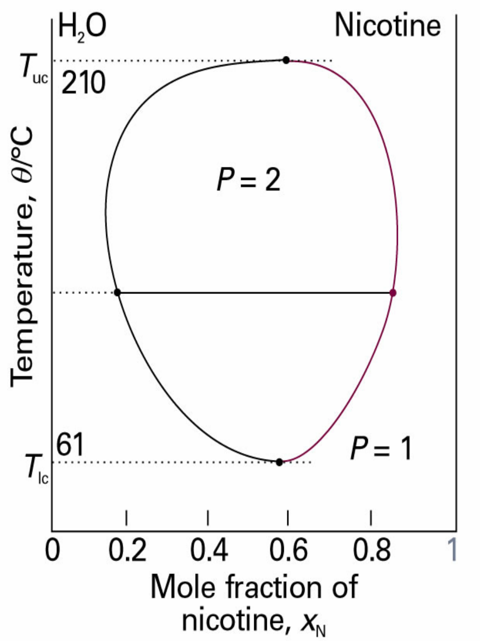


Fig. 6.25 The temperature–composition diagram for water and nicotine, which has both upper and lower critical temperatures. Note the high temperatures for the liquid (especially the water): the diagram corresponds to a sample under pressure.

6.5 Liquid-liquid phase diagrams

(c) The distillation of partially miscible liquids

Consider a pair of of liquids that are partially miscible and form a low-boiling azeotrope. This combination is quite common because both properties reflect the tendency of the two kinds of molecules to avoid each other.

The following two possibilities;

(1) Fully miscible liquids before boiling (See Fig. 6.26)

- Distillation of a mixture of composition a_1 → liquid (a_2) and vapour (b_1) → b_1 condenses to the fully miscible single-phase liquid (b_2) → the distillation is cooled to two phase liquid region (b_3) → phase separation

- If distillation continues, the composition of the remaining liquid changes. In the end, evaporating and condensing → back to a_1

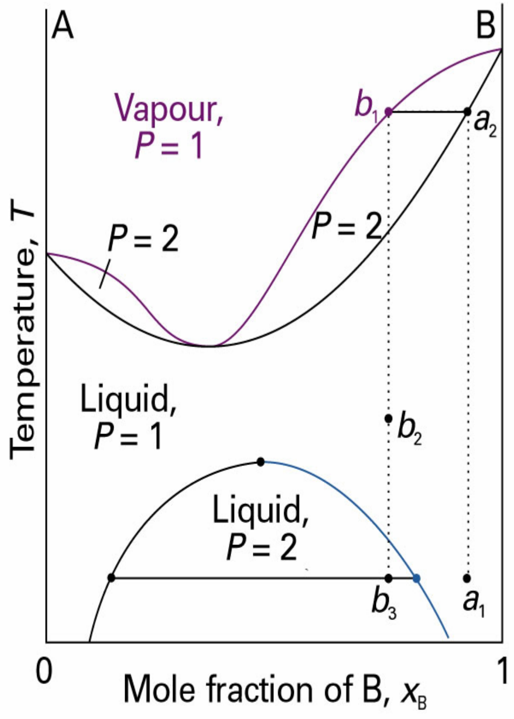


Fig. 6.26 The temperature–composition diagram for a binary system in which the upper critical temperature is less than the boiling point at all compositions. The mixture forms a low-boiling azeotrope.

6.5 Liquid-liquid phase diagrams

(2) Boiling of the liquids before their complete mixing
(See Fig. 6.27)

- no T_{uc} (upper critical solution temperature)

- Distillation of a mixture of composition a_1 → liquid (a_2) and vapour (b_1) → b_1 condenses to the two phase lquid region (b_3) → phase separation (b_3' and b_3")

- For the composition of the isopleth *e*
  vaporizing two phases of e1 overall composition
  → e_2 (boiling point, azeotrope composition)
  condensing a vapour(e_3) → two phase liquid of the same overall composition
  Consequently, at a fixed *T*, the mixture vaporizes and condenses like a single substance.

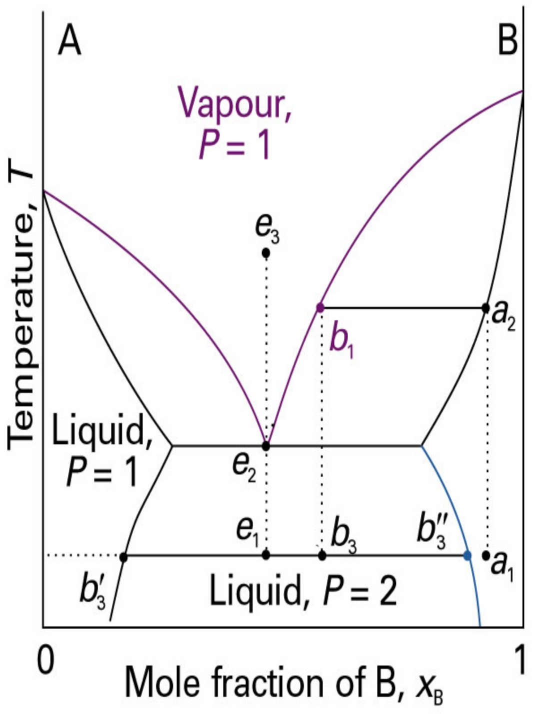


Fig. 6.27 The temperature–composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

6.6 Liquid-solid phase diagrams

Solid and liquid may both be present at T below the boiling point (See Fig. 6.29)

As temperature is decreased along the isopleth a

1. $\boldsymbol{a_1} \rightarrow \boldsymbol{a_2}$ (Liquid + B)
   : pure solid B begins to precipitate
   (liquid phase is richer in A)

2. $\boldsymbol{a_2} \rightarrow \boldsymbol{a_3}$
   : roughly equal amount of liquid and solid (by lever rule)
   (liquid phase is richer in A due to precipitated A)

3. $\boldsymbol{a_3} \rightarrow \boldsymbol{a_4}$
   : less liquid (e) than a_3

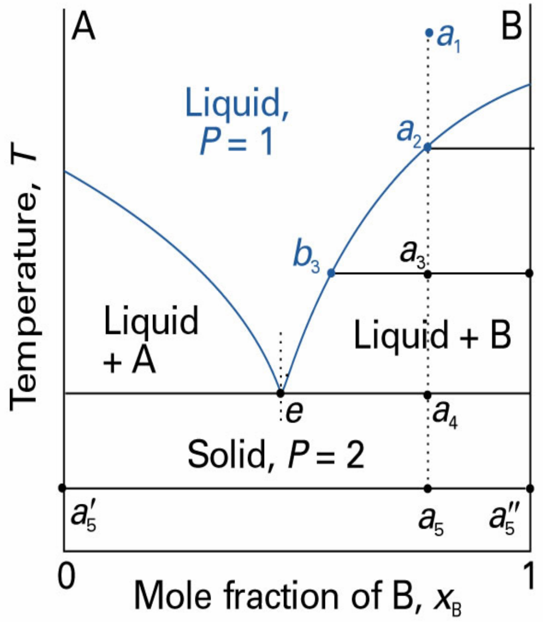


Fig. 6.29 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 6.27. The isopleth through *e* corresponds to the eutectic composition, the mixture with lowest melting point.

6.6 Liquid-solid phase diagrams

(a) Eutectics

Eutectic composition : the isopleth at e in Fig. 6.29

- the mixture with the lowest melting point (single temperature)
- solidified at a single definite temperature ($F' = 0$ when $C = 2$ and $P = 3$)

The cooling curves of isopleth (See Fig. 6.30)

- very useful way of detecting eutectics by thermal analysis
- $a_1 \rightarrow a_2$
  : soild B begins to precipitate
  : cooling is slower
  (∵ B is exothermic and retards the cooling)
- cooling of eutectic composition
  → T remains constant until the whole sample has solidified **: eutectic halt**
- clear indication of the structure of the phase diagram
- the longest eutectic halt
  → the location of the eutectic composition and its melting temperature

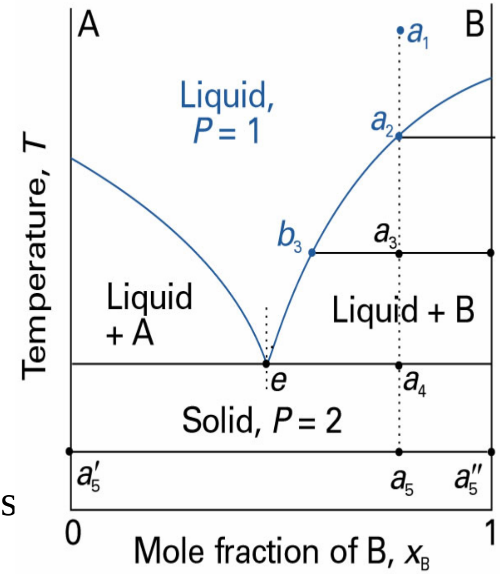


Fig. 6.29 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 6.27. The isopleth through e corresponds to the eutectic composition, the mixture with lowest melting point.

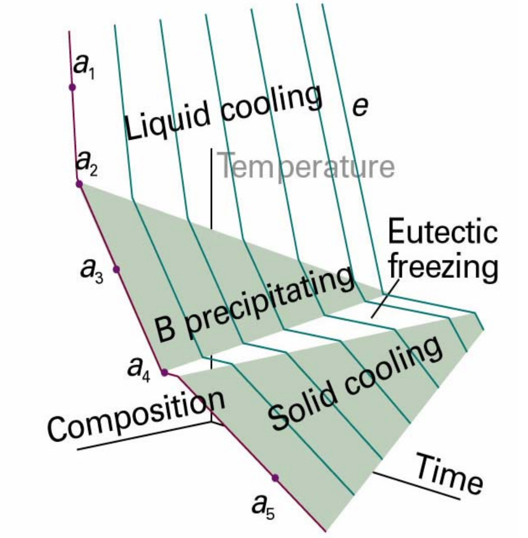


Fig. 6.30 The cooling curves for the system shown in Fig. 6.29. For isopleth a, the rate of cooling slows at a_2 because solid B deposits from solution. There is a complete halt at a_4 while the eutectic solidifies. This halt is longest for the eutectic isopleth, e. The eutectic halt shortens again for compositions beyond e (richer in A). Cooling curves are used to construct the phase diagram.

6.6 Liquid-solid phase diagrams

(b) Reacting systems

A system forms a compound C that also forms eutectic mixtures with A and B (See Fig. 6.31)
ex) Ga + As ↔ GaAs (three constituents/two components)

For the binary system between B and C

→ mixing of C (excess of B with A) and pure B
→ compacting of eutectic phase diagram in Fig. 6.29 into the range of composition C and pure B
→ solid composition precipitated from a_1 : C
→ At T below a_4 : two solid phases (C and B)

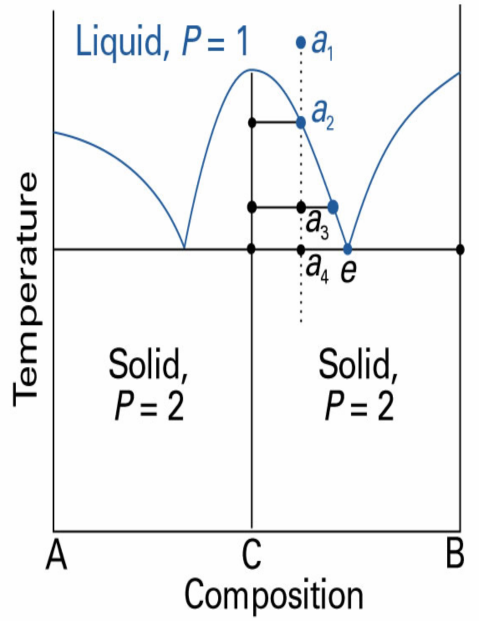


Fig. 6.31 The phase diagram for a system in which A and B react to form a compound C = AB. This resembles two versions of Fig. 6.29 in each half of the diagram. The constituent C is a true compound, not just an equimolar mixture.

6.6 Liquid-solid phase diagrams

(c) Incongruent melting

Compound C is not stable as a liquid
ex) alloy Na_2K (See Fig. 6.32)

- $a_1 \rightarrow a_2$
  : some solid Na begins to precipitate
  : liquid phase is richer in K
  $a_2 \rightarrow$ just below a_3
  : two solids (Na and Na_2K)
- $b_1 \rightarrow b_2$
  : some solid Na begins to precipitate
  $b_2 \rightarrow b_3$
  : solid Na precipitates but at b_3 a reaction occurs to form Na_2K by K atoms diffusing into the solid Na
  $b_3 \rightarrow b_4$
  : solid $Na_2K\uparrow$ until b_4

- No liquid Na_2K forms at any stage : too unstable as a liquid
  → **Incongruent melting** - a compound melts into its components and does not itself form a liquid phase

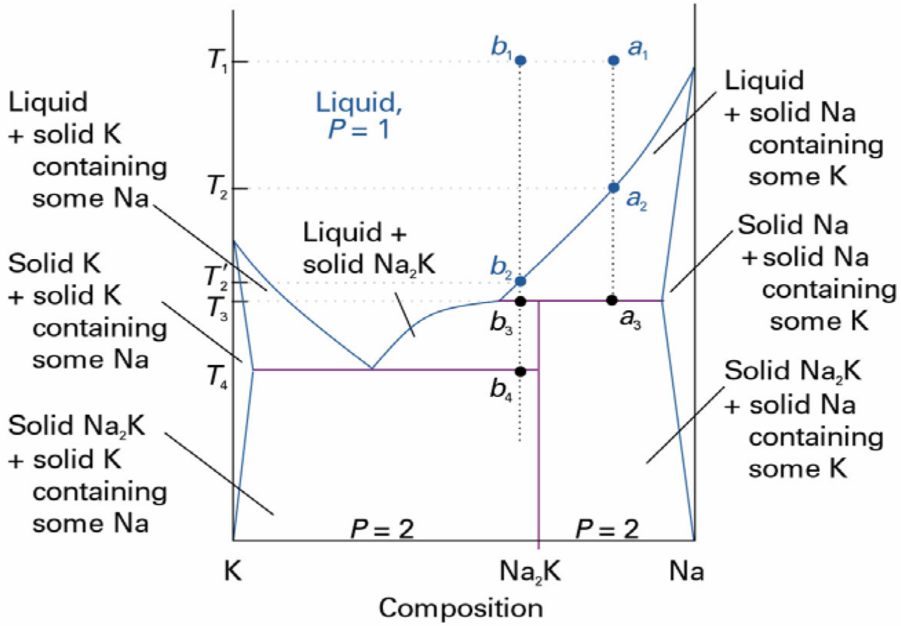


Fig. 6.32 The phase diagram for an actual system (sodium and potassium) like that shown in Fig. 6.35, but with two differences. One is that the compound is Na_2K, corresponding to A_2B and not AB as in that illustration. The second is that the compound exists only as the solid, not as the liquid. The transformation of the compound at its melting point is an example of incongruent melting.