3. Solutions

3.1 Quanties of mixing

A **solution** is system where any phase containing more than one component.

A solution may be gas, liquid or solid.

In mixing, extensive quantities are seldom additive. For example, if 1 litre sulphuric acid is mixed with 1 litre water, the volume of the mixture will be about 1.8 litre.

Mass is always **additive**. V, H are **additive in ideal mixtures** (see later, equation 3.8). S, A, G are **never additive**,because entropy of mixing is positive (see subsection 3.8).

Mixtures can be **characterised by the deviation from additivity.** (We define these quantities for two component mixtures). Example:

Volume of mixing (the change of volume in mixing):

$$\boxed{\Delta_{mix} V = V - \left(n_1 V^*_{m1} + n_2 V^*_{m2} \right)} \qquad (3.1)$$

volume of mixture

molar volumes of pure components

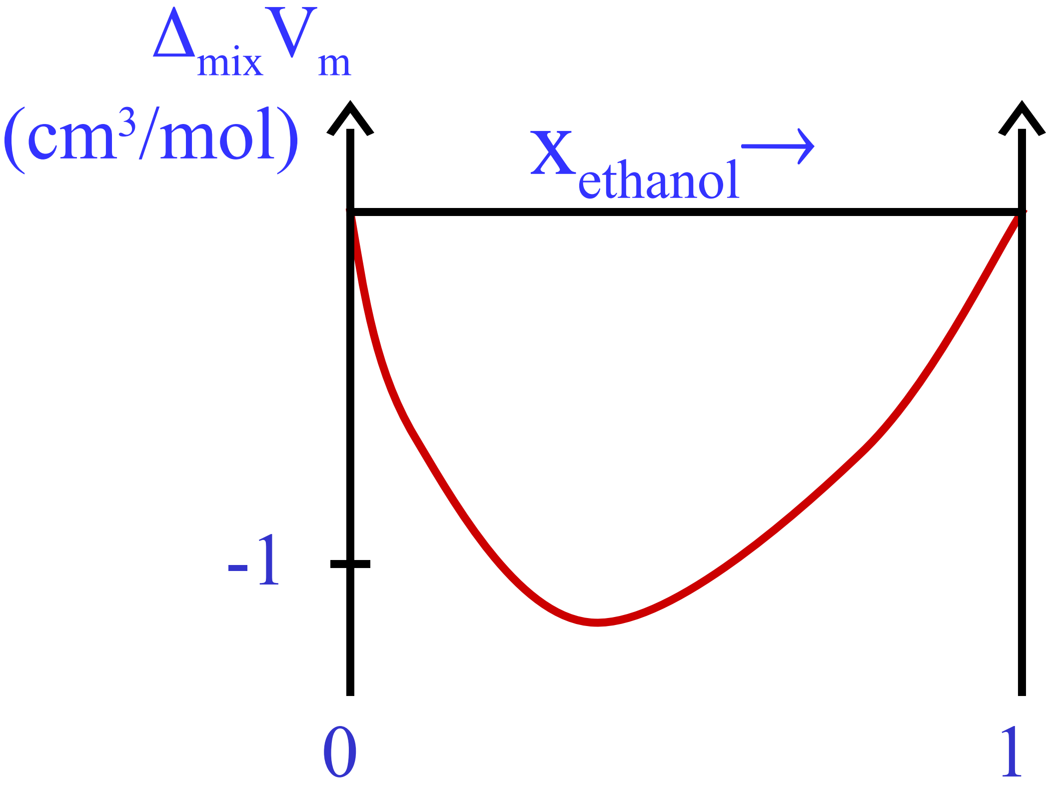
In general: let E any extensive quantity (H, S, G, etc):

$$\Delta_{mix} E = E - \left(n_1 E^*_{m1} + n_2 E^*_{m2} \right) \qquad (3.2)$$

The next definitions are valid for **isothermal-isobaric** processes, i.e. T and p are the same after mixing as before, see Subsection 2.2.

For one mole of mixture - molar volume of mixing (x mole fraction)

$$\Delta_{mix} V_m = \frac{\Delta_{mix} V}{n_1 + n_2} = \frac{V}{n_1 + n_2} - \left(x_1 V^*_{m1} + x_2 V^*_{m2} \right) \qquad (3.2)$$



The reason of the mixing is the intermolecular interaction, i.e. the molecules form associates, e.g. hydrogen bonds.

Fig. 3.1, *mixture: water – ethanol*

Molar enthalpy of mixing (division with $n=n_1+n_2$)

$$\Delta_{mix} H_m = \boxed{\frac{H}{n_1+n_2}} - \left(x_1 \boxed{H^*_{m1}} + x_2 \boxed{H^*_{m2}} \right) \qquad (3.4)$$

molar enthalpies of pure components

molar enthalpy of solution

If $\Delta_{mix}H_m > 0$, endothermic - we must add heat to the system to keep the temperature unchanged

If $\Delta_{mix}H_m < 0$, exothermic - heat is given away by the system.

Weight fractions (mass fractions) are frequently used in techical diagrams.

The specific enthalpy of mixing of water-ethanol system at three temperatures (w: weight fraction):

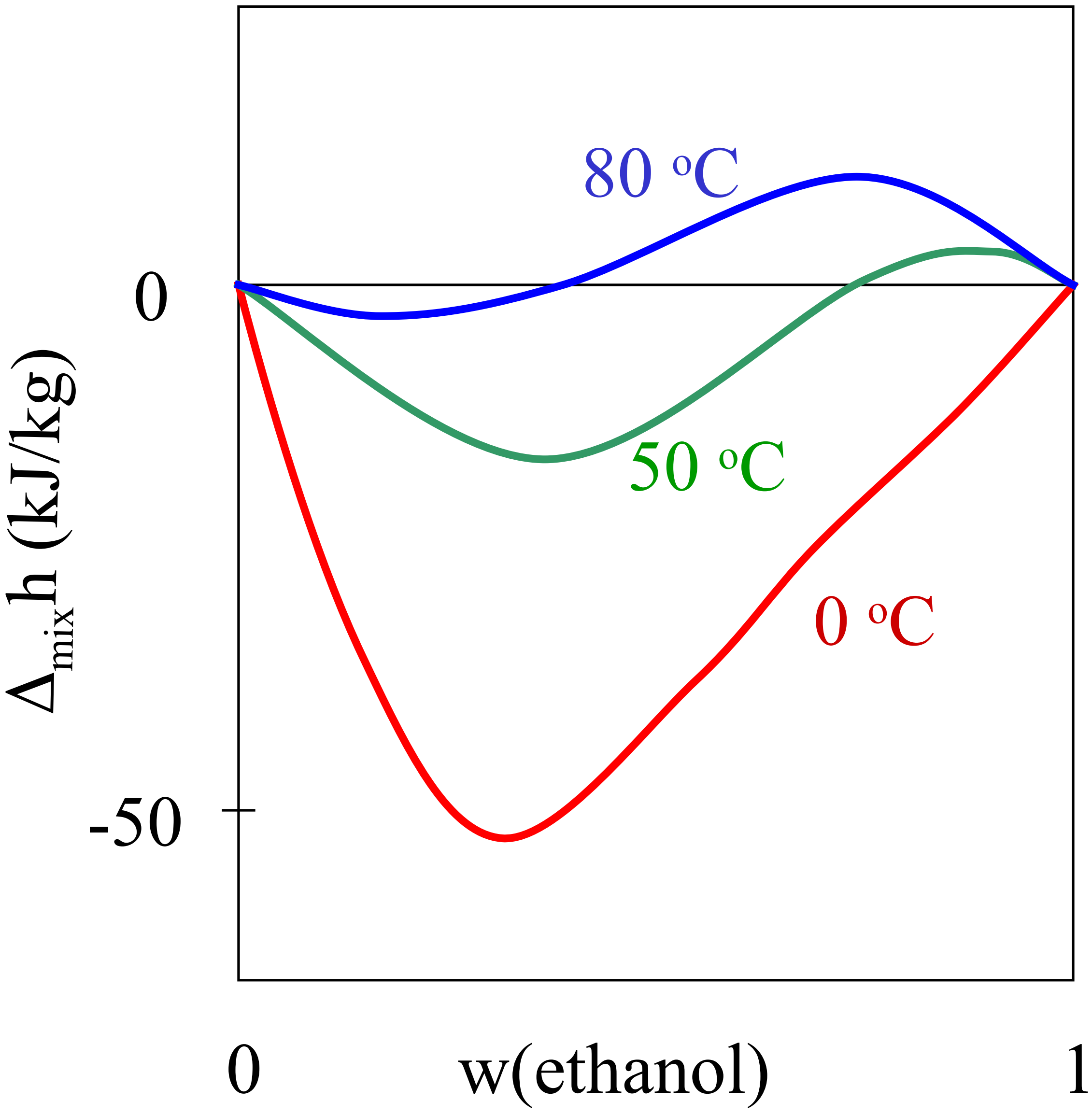


Fig. 3.2

Gibbs free energy of mixing: $\Delta_{mix}G$

In a spontaneous process at constant temperature and pressure G decreases, (2.57) .

Two components are miscible if the Gibbs function of mixing is negative.

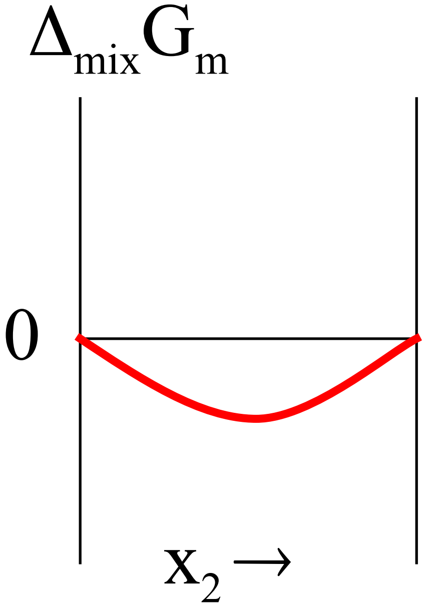
$$\Delta_{mix}G_m = \Delta_{mix}H_m - T\,\Delta_{mix}S_m \tag{3.5}$$

may be negative or positive

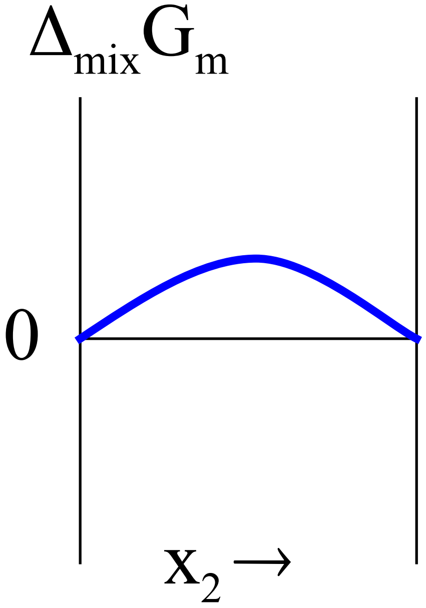
always positive

H and S depend on T, too.

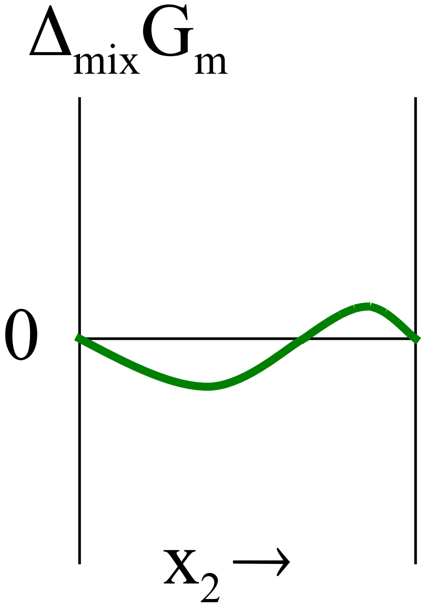
Molar Gibbs function against mole fraction



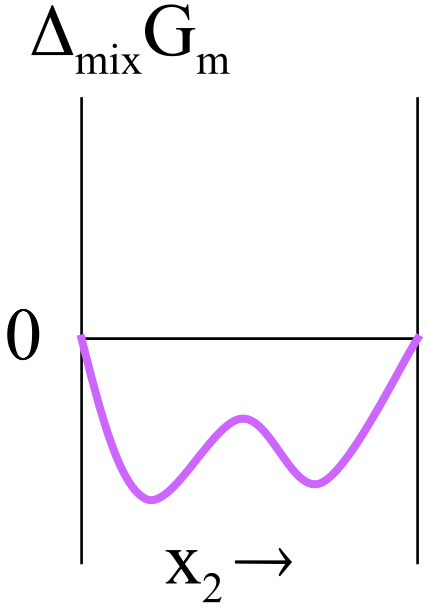
total
miscibility



no
miscibility



partial
solubility



partial
miscibility

3.2 Partial molar quantities

Extensive quantities have partial molar values.

First we discuss partial molar volumes.

If we add one mol (18 cm^3) water to very much water, the volume will increase by 18 cm^3.

If we add one mol (18 cm^3) water to very much ethanol, the volume will increase by 14 cm^3 only.

Explanation: water molecules surrounded by ethanol molecules occupy different volumes than water molecules surrounded by water molecules.

We say that the partial molar volume of water is

18 cm^3/mol in water and
14 cm^3/mol in ethanol.

The partial molar volume is the function of concentrations of the mixture.

The definition of partial molar volumes (in a two component system)

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} \qquad V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} \qquad (3.5)$$

The partial molar volume of a component is the change of volume of the mixture if one mole of a component is added to infinite amount of mixture at constant temperature and pressure.

Infinite: so that the composition (theoretically) does not change (subsection 2.9).

Water-ethanol system

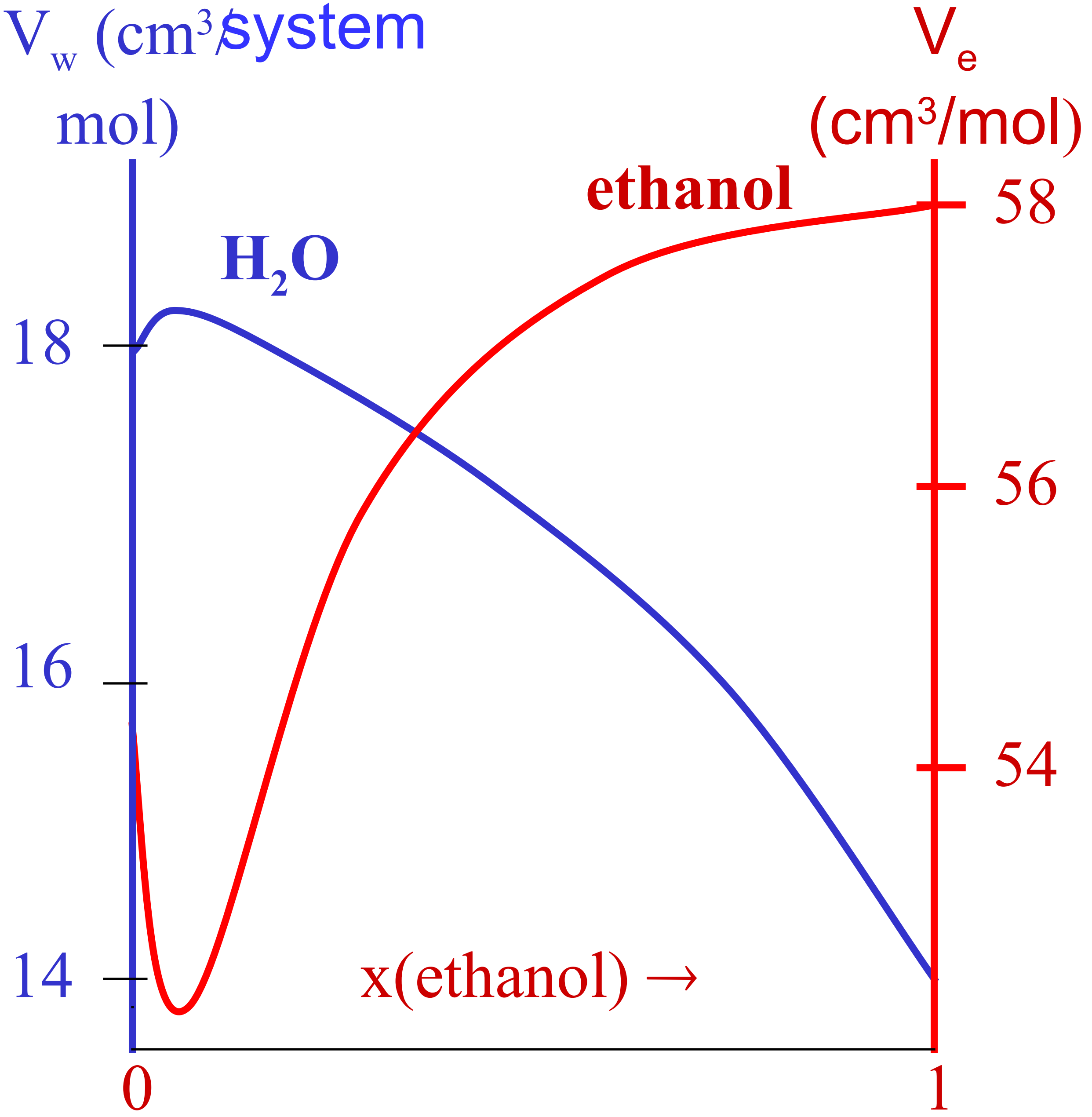


Fig. 3.5

At constant T and p the volume of a two component system depends on the amounts of components only:

$V = V(n_1, n_2)$ *Complete differential:*

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} dn_2 \qquad (3.6)$$

$$dV = V_1 dn_1 + V_2 dn_2$$

Integrate (increase the volume of the mixture at constant composition):

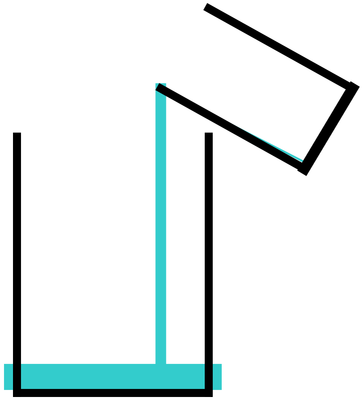


Fig. 3.6

$$\boxed{V = V_1 n_1 + V_2 n_2} \qquad (3.7)$$

The volume of the mixture equals the number of moles of A times the partial volume of A, plus the number of moles of B times the partial volume of B. (It is valid both for ideal and for real solutions.)

In ideal solution:

$$V = V^{*}_{m1} \cdot n_1 + V^{*}_{m2} \cdot n_2 \qquad V^{*}_{m1} = V_1 \quad V^{*}_{m2} = V_2 \quad (3.8)$$

In an ideal mixture the partial molar volume is equal to the molar volume of pure component (the '' superscript refers to the pure component).*

Other extensive parameters (H, G, etc.) also have partial molar quantities.

Denote the extensive quantity by E

$$E_i = \left(\frac{\partial E}{\partial n_i} \right)_{p,T,n_j} \quad j \neq i \tag{3.9}$$

The partial molar value of an extensive quantity is the change of that quantity if one mole of the component is added to infinite amount of mixture at constant temperature and pressure.

In a two component system:

$$dE = E_1 dn_1 + E_2 dn_2 \qquad \boxed{E = E_1 n_1 + E_2 n_2} \qquad (3.10a)$$

In a multicomponent system:

$$dE = \sum E_i dn_i \qquad \boxed{E = \sum E_i n_i} \qquad (3.10b)$$

The extensive quantity of the mixture is the sum of partial molar quantities times the amounts in moles.

The partial molar Gibbs function is chemical potential

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}} \quad j \neq i \qquad (3.11)$$

For a two component system at constant T and p:

$$dG_{p,T} = \mu_1 dn_1 + \mu_2 dn_2 \qquad (3.12a)$$

$$G = \mu_1 n_1 + \mu_2 n_2 \qquad (3.12b)$$

The Gibbs function of the mixture is the sum of chemical potentials times the amounts in moles.

The Gibbs-Duham equation

We derive it for chemical potentials but it is valid for other partial molar quantities, too. Equations (2.44)!

$$dG_{p,T} = \mu_1 dn_1 + \mu_2 dn_2 \qquad (2.44a)$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

The complete differential (at constant p and T) (2.44b)

$$dG_{p,T} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2$$

Subtracting the (2.44a) equation from this one:

$$\boxed{n_1 d\mu_1 + n_2 d\mu_2 = 0}$$

(3.13)

(3.13) is the Gibbs-Duham equation (it is valid when T and p does not change (only the composition changes).

$$n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0$$

I.e., the chemical potentials of the two components are not independent. (If we know the dependence of μ_1 on the composition, we can calculate that of μ_2.)

Since n_1 and n_2 are always positive, if μ_1 increases, μ_2 decreases, and the other way round. Where one of them has a maximum ($d\mu_1 = 0$), the other one has a minimum ($d\mu_2 = 0$, too).

Gibbs-Duhem like equations are valid also for other extensive properites, for volumes:

$$n_1 \, dV_1 + n_2 \, dV_2 = 0 \qquad (3.14)$$

We can interpret the partial molar volume diagram of the water-ethanol system (see Fig. 3.5).

3.3 Determination of partial molar quantities

We discuss two methods. Example: partial molar volume.

1. Method of slopes

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1}$$

(3.15)

We put a known amount of component 1 in a vessel then add component 2 in small but known amounts. The volume is measured after each step.

The mole fraction and the slope have to be determined at several points of the curve. We obtains V_2-n_2 data pairs.

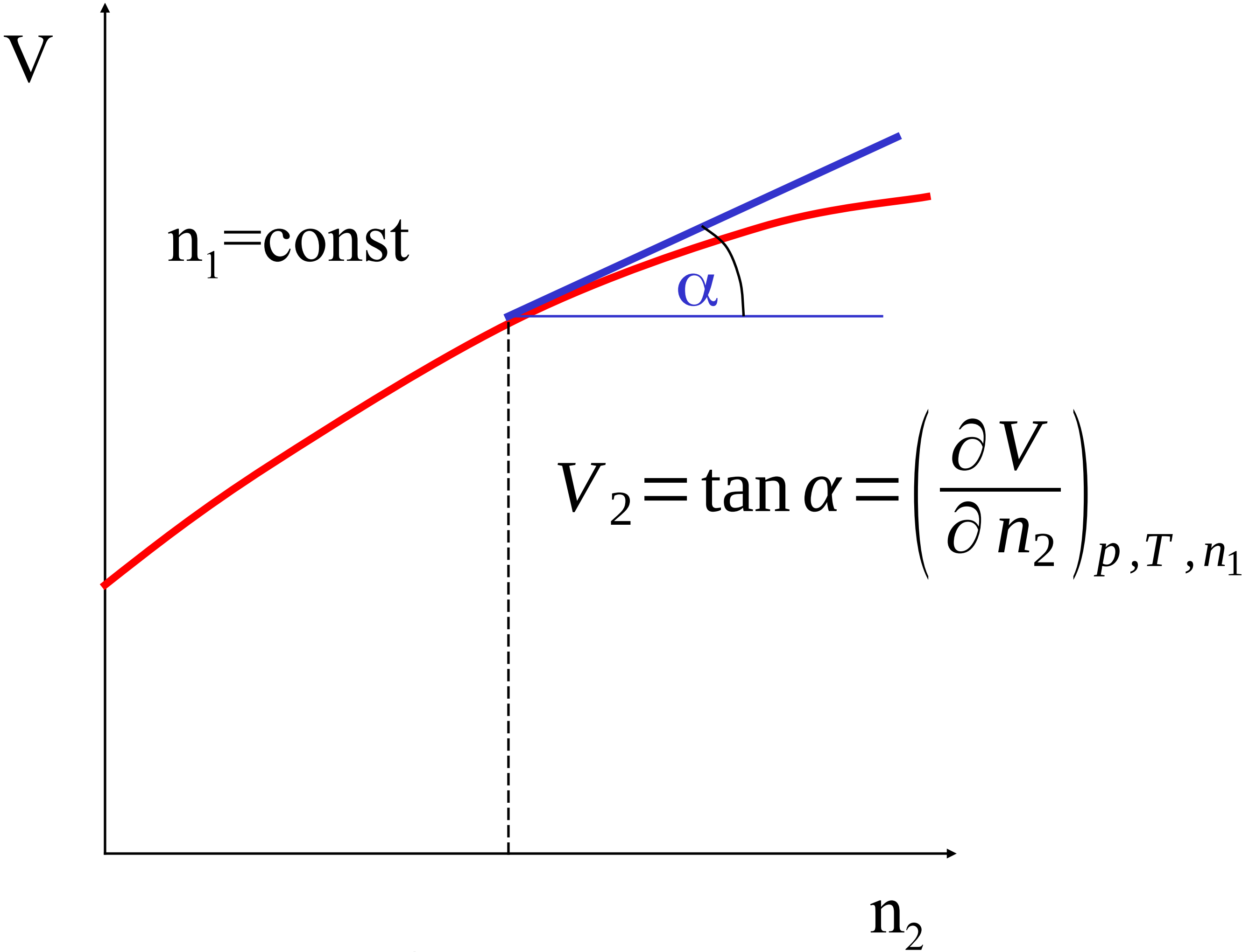


Fig. 3.7

2. The method of intercepts

$$V = V_1 n_1 + V_2 n_2 \qquad dV = V_1 dn_1 + V_2 dn_2$$

Dividing by (n_1+n_2)

$$V_m = V_1 x_1 + V_2 x_2 \qquad dV_m = V_1 dx_1 + V_2 dx_2$$

$$x_1 = 1 - x_2 \qquad dx_1 = -dx_2$$

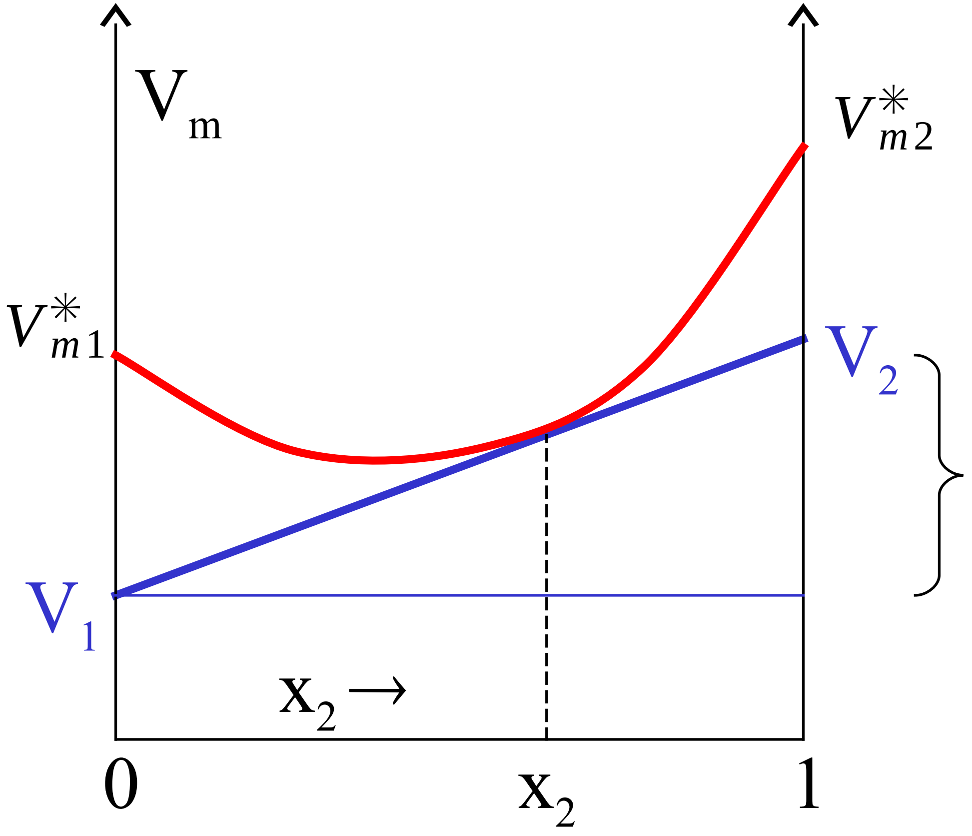
$$V_m = V_1(1 - x_2) + V_2 x_2 \qquad dV_m = (V_2 - V_1)\, dx_2$$

$$V_m = V_1 + (V_2 - V_1)\, x_2 \qquad \boxed{\frac{dV_m}{dx_2}} = (V_2 - V_1)$$

$$\boxed{V_m = V_1 + \frac{dV_m}{dx_2} x_2} \qquad (3.16)$$

$$\boxed{V_m = V_1 + \frac{dV_m}{dx_2} x_2}$$

This is the equation of the tangent of the V_m-x_2 curve.



$$\frac{dV_m}{dx_2} = (V_2 - V_1)$$

Fig. 3.8

The intercepts of the tangents of the V_m-x_2 curve produce the partial molar volumes (see Fig. 3.8).

This method is more accurate than the method of slopes.

3.4 Raoult´s law

The concept of the ideal gas plays an important role in discussions of the thermodynamics of gases and vapors (even if the deviation from ideality is sometimes large).

In case of mixtures it is also useful to define the ideal behaviour. The real systems are characterized by the deviation from ideality.

Ideal gas: complete absence of cohesive forces (Subsection 1.4)

Ideal mixture (liquid, solid): complete uniformity of cohesive forces. If there are two components A and B, the intermolecular forces between A and A, B and B and A and B are all the same.

$$\Longrightarrow \quad \Delta_{mix}V = 0, \quad \Delta_{mix}H = 0 \qquad (3.17)$$

In a mixture of gases, each gas has a partial pressure p_i which is the hypothetical pressure of that gas if it alone occupied the entire volume of the original mixture at the same temperature.

For ideal gases: Dalton's law, $p = \sum_i p_i, \; p_i = p y_i$

The partial vapor pressure of a component is the measure of the tendency of the component to escape from the liquid phase into the vapor phase.

High vapor pressure means great escaping tendency.

Raoult´s law: *In an **ideal liquid mixture** the partial vapor pressure of a component in the **vapor phase** is proportional to its mole fraction (x) in the **liquid phase**.*

$$\boxed{p_i = x_i \cdot p_i^*} \qquad (3.18)$$

For a pure component $x_i = 1$, so $p_i = p_i^*$
p_i^*: vapor pressure of pure component at the specified temperature.

How does the vapor pressure change with the composition in a two component system?

Since $p_1 = x_1 \cdot p_1^*$ and $p_2 = x_2 \cdot p_2^*$

$$p = p_1 + p_2 \qquad (3.19)$$

1. The p(x) diagram for ideal mixture of two volatile components has the shape like Fig. 3.9.

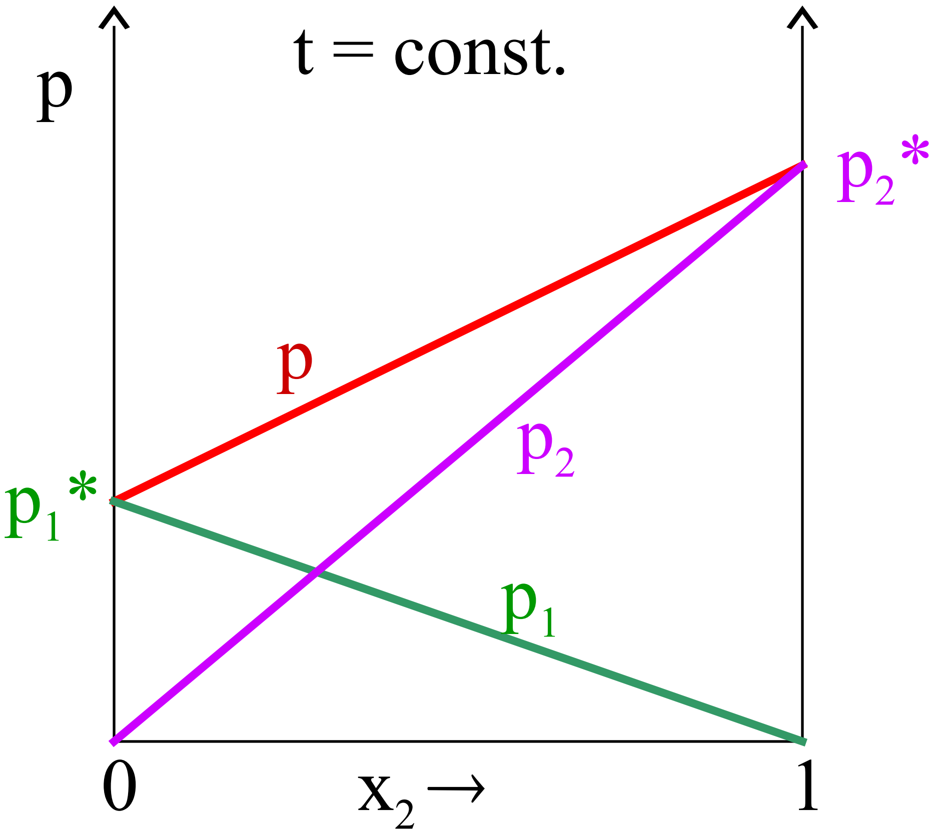
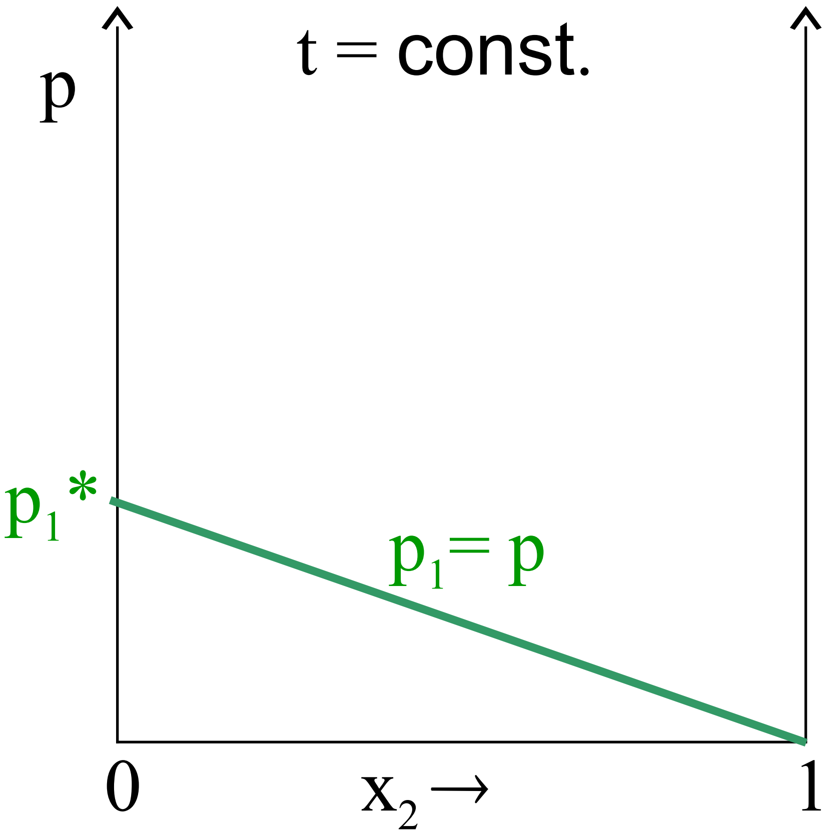


Fig. 3.9

2. If only component (1) is volatile like in solutions of solids, the Fig. 3.9 is modified, see Fig. 3.10.



In this case the vapor pressure is determined only by component 1.

Fig. 3.10

Vapor pressure lowering. Based on equations (3.18) and (3.19):

$$p_1 = x_1 \cdot p_1^* = (1 - x_2) \cdot p_1^* = p_1^* - x_2 \cdot p_1^*$$

$$x_2 = \frac{p_1^* - p_1}{p_1^*} \qquad (3.20)$$

According to (3.20) the relative vapor pressure lowering is equal to the mole fraction of the solute (component 2);

Solute, solvent, solution: see definitions in subsection 3.2.

3.5 Deviations from the ideality

1. Negative deviation: *The cohesive forces between unlike molecules are greater than those between the like molecules in pure liquid („like”: the same component).*

So the „escaping tendency” is smaller than in ideal solution. The activity (a) replaces the mole fraction (3.21).

$\Delta_{mix}V < 0$ *(contraction)*

$\Delta_{mix}H < 0$ *(exotermic solution)*

$p_i < x_i \cdot p_i^*$

$$\boxed{p_i = a_i \cdot p_i^*} \qquad (3.21)$$

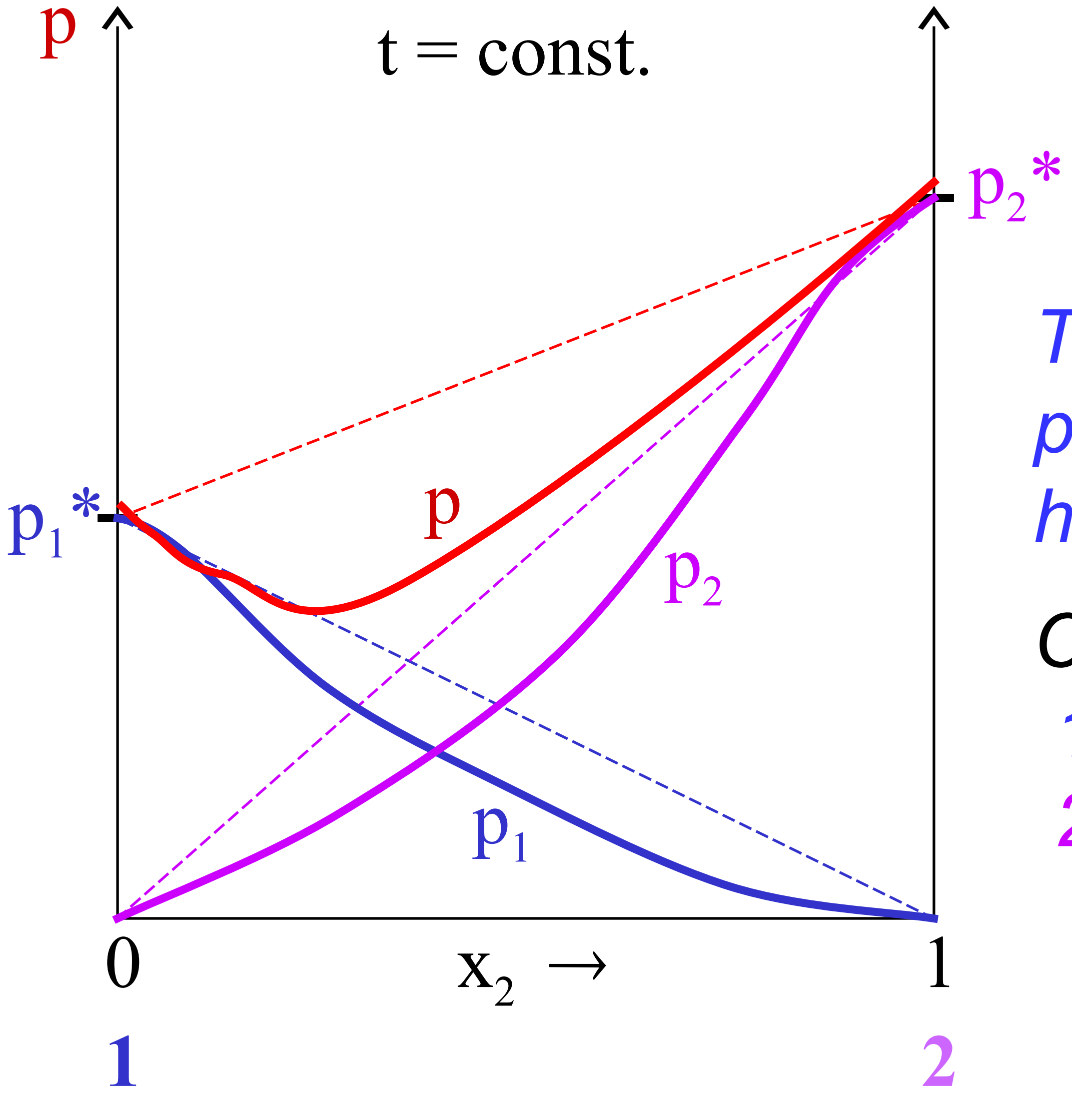
$a_i < x_i$

The activity coefficient represents the deviation (3.22).

$\gamma_i < 1$

$$a_i = \gamma_i \cdot x_i \qquad (3.22)$$

Fig. 3.11 is the isothermal vapor pressure diagram of a two component mixture with negative deviation.



The total vapor pressure may have a minimum.

Components:

1: chloroform

2: acetone

Fig. 3.11

2. Positive deviation: *The cohesive forces between unlike molecules are smaller than those between the like molecules in pure liquids („unlike”: from other component) (see subsection 3.2).*

So the „escaping tendency” is greater than in ideal liquid mixture.

$\Delta_{mix}V > 0$ (expansion)

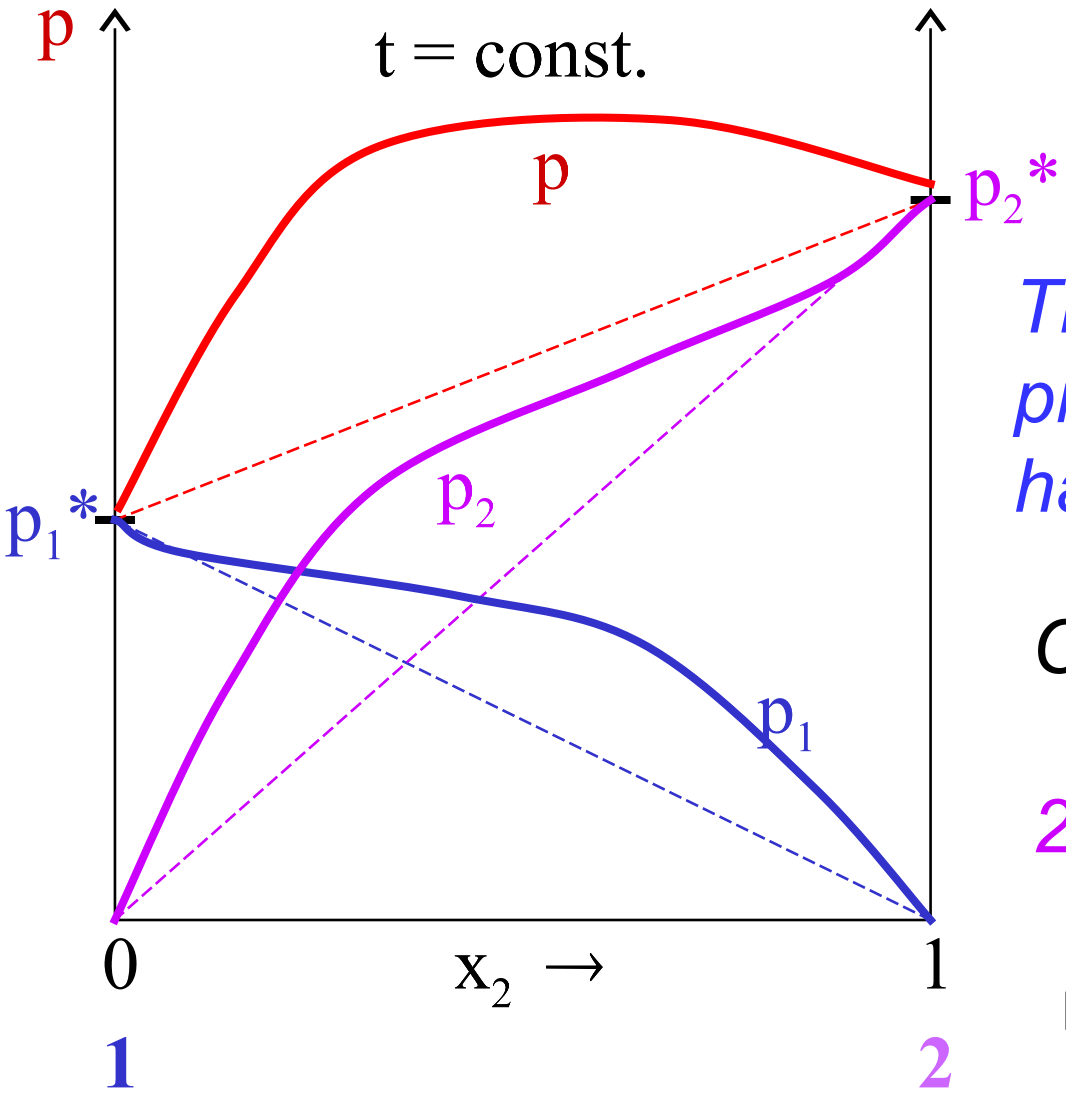
$\Delta_{mix}H > 0$ (endothermic solution)

$p_i > x_i \cdot p_i^*$ $\boxed{p_i = a_i \cdot p_i^*}$ $a_i = \gamma_i \cdot x_i$ (3.21, 3.22)

$a_i > x_i$ activity activity coefficient

$\gamma_i > 1$

Fig. 3.12 is the isothermal vapor pressure diagram of a two component mixture with positive deviation



The deviation character refers always on the vapor pressure diagram!

The total vapor pressure may have a maximum.

Components:

1: water

2: dioxane

Fig. 3.12

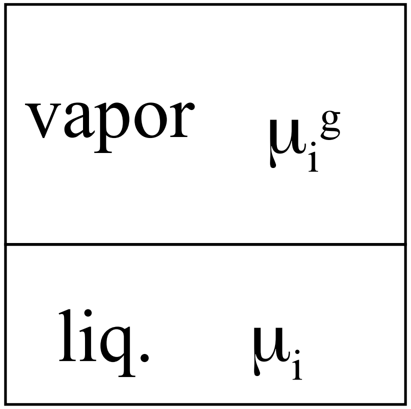
3.6 Chemical potential in liquid mixtures

1. *We derive a formula for calculation of μ.*

2. *We use Raoult´s law.*

In equilibrium the chemical potential of a component is equal in the two phases (see subsection 2.10).

3. *The vapor is regarded as ideal gas (see subsection 1.4).*



vapor μ_i^g

liq. μ_i

$$\mu_i = \mu_i^g = \mu_i^0 + RT\ln\frac{p_i}{p^0} \qquad (3.23)$$

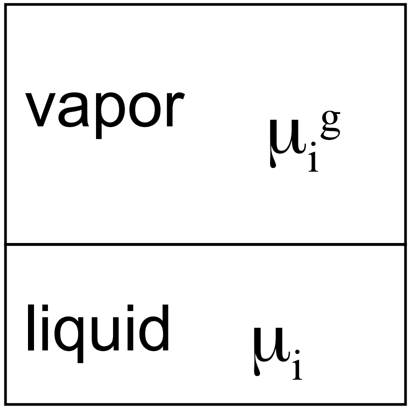
1. Ideal liquid mixture

$$p_i = x_i \cdot p_i^* \qquad \mu_i = \mu_i^0 + RT\ln\frac{x_i \cdot p_i^*}{p^0}$$

$$\mu_i = \mu_i^0 + RT\ln\frac{p_i^*}{p^0} + RT\ln x_i$$

Depends on T only: μ_i^*

$$\boxed{\mu_i = \mu_i^* + RT\ln x_i} \qquad (3.24)$$



$$\mu_i = \mu_i^g = \mu_i^0 + RT \ln \frac{p_i}{p^0}$$

2. Real liquid mixture

$$\mu_i = \mu_i^0 + RT \ln \frac{a_i \cdot p_i^*}{p^0}$$

$$\mu_i = \mu_i^0 + RT \ln \frac{p_i^*}{p^0} + RT \ln a_i$$

Depends on T only: μ_i^*

$$\boxed{\mu_i = \mu_i^* + RT \ln a_i}$$

(3.25)

$$\boxed{\mu_i = \mu_i^* + RT \ln a_i}$$

$$a_i = \gamma_i x_i$$

If $x_i \rightarrow 1$, $\gamma_i \rightarrow 1$, $a_i \rightarrow 1$ (pure substance)

μ_i^*: *the chemical potential of the pure substance at the given temperature and p^0 pressure → standard chemical potential*

$\mu_i^* = G_{mi}^*$ *(because pure substance).* (3.26)

The activity is a function which replaces the mole fraction in the expression of the chemical potential in case of real solutions.

fugacity: “effective” pressure in gas phase

activity: “effective” mole fraction

$$\mu_i = \mu_i^* + RT\ln(\varphi_i y_i) = \underbrace{\mu_i^* + RT\ln y_i}_{\mu_i(id)} + \underbrace{RT\ln\varphi_i}_{\text{deviation from ideality}} \qquad (3.27)$$

y_i: mole fraction in gas phase

For real gas mixtures the f_i fugacity of the component i

$$f_i = \varphi_i \times p_i \qquad (3.28)$$

φ_i is called fugacity coefficient.

$$\mu_i = \mu_i^* + RT \ln\left(\frac{f_i}{p^0}\right) = \mu_i^* + RT \ln\frac{p_i}{p^0} + RT \ln\varphi_i \qquad (3.29)$$

Dependence of the chemical potential on the mole fraction (in an ideal liquid mixture)

$$\boxed{\mu_i = \mu_i^* + RT \ln x_i}$$

(3.24)

As the mole fraction approaches zero, the chemical potential approaches minus infinity (Fig. 3.13)

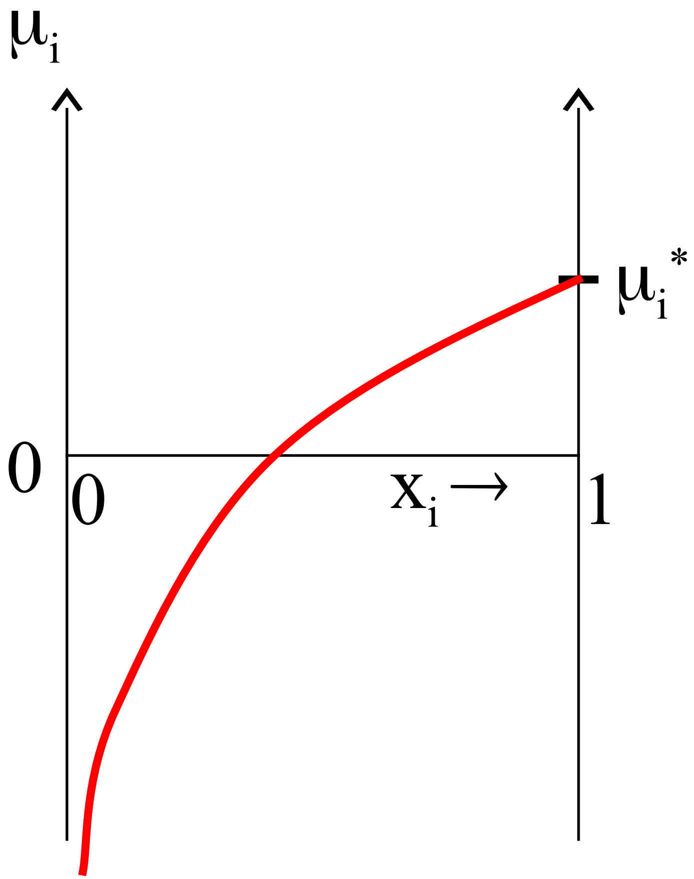


Fig. 3.13

For most substances the standard chemical potential is negative.

$$\mu_i^* = G_{mi}^* = \boxed{H_{mi}^*} - \boxed{TS_{mi}^*} \qquad (3.30)$$

Can be negative or positive

Always positive

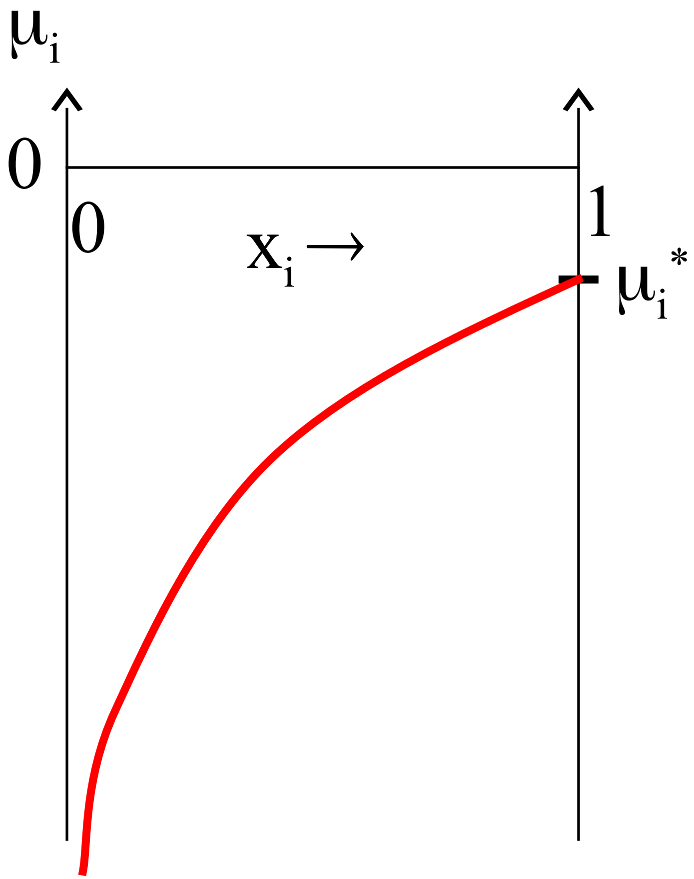
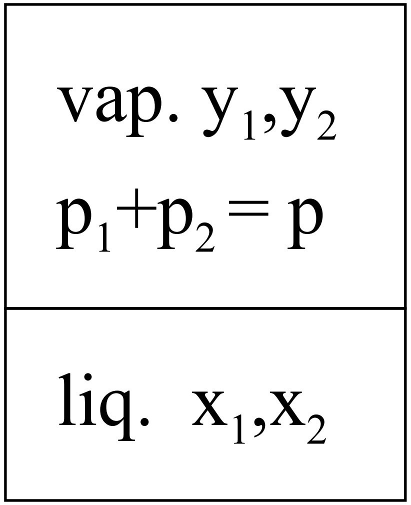


Fig. 3.14

Fig. 3.14 introduces the mole fraction dependence in case of negative chemical potential.

Determination of the activity coefficient from liquid-vapor equilibrium data.

Two-component system. According to Dalton's law if the vapor is an ideal gas $p_i=y_ip$ (3.31)



vap. y_1,y_2

$p_1+p_2=p$

liq. x_1,x_2

$$\underset{\text{Raoult}}{\Downarrow}\qquad\underset{\text{Dalton}}{\Downarrow}$$

$$p_1=\gamma_1x_1p_1^*=y_1p \qquad (3.32)$$

$$p_2=\gamma_2x_2p_2^*=y_2p$$

$$\gamma_1=\frac{y_1p}{x_1p_1^*}\qquad\gamma_2=\frac{y_2p}{x_2p_2^*}\qquad(3.33)$$

The total pressure and the mole fractions in the liquid and vapor phase are measured. If the vapor pressures of the pure components are known, γ-s can be calculated.

3.7 Entropy of mixing and Gibbs free energy of mixing

The quantities of mixing ($\Delta_{mix}V$, $\Delta_{mix}H$, $\Delta_{mix}S$, etc.) are defined at constant temperature and pressure.

We study some important cases:

1. *Mixing of ideal gases*
2. *Ideal mixture of liquids*
3. *Real mixtures*

1. Mixing of ideal gases: The two gas components (1 and 2) are separated by a wall, see Fig. 3.15a.

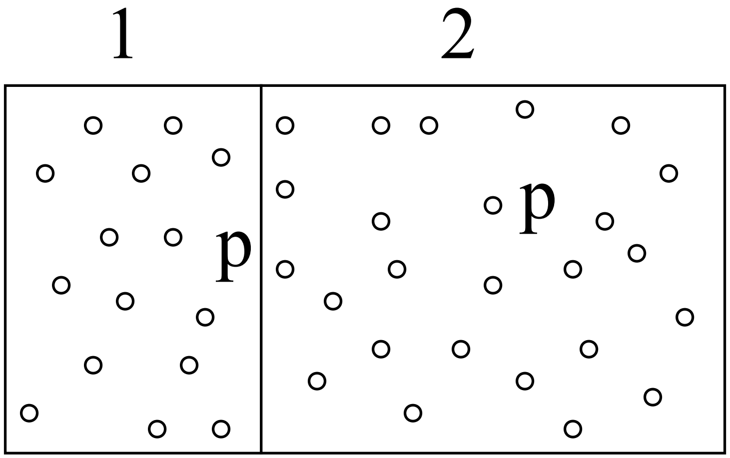


Fig. 3.15a

Then the wall is removed. Both gases fill the space (Fig. 3.15b).

There is no interaction ($\Delta_{mix}H = 0$).

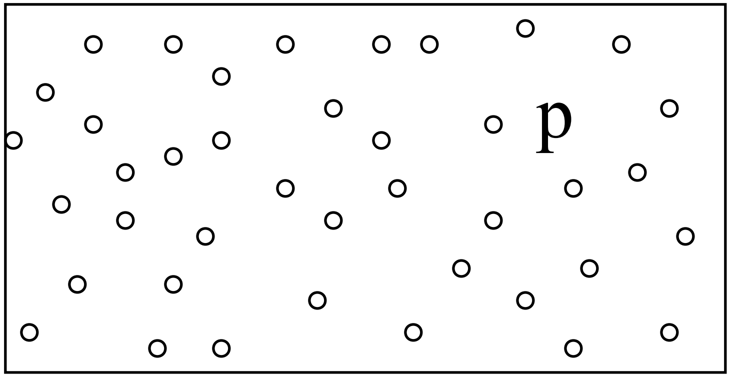


Fig. 3.15b

The pressures of the components are reduced to p_1 and p_2: partial pressures.

$$p_1 = y_1 p \quad p_2 = y_2 p \quad (3.34)$$

Pressure dependence of entropy (at constant temperature):

the entropy of mixing is the sum of the two entropy changes, see (1.71)

$$\Delta S = -nR\ln\frac{p_2}{p_1} \qquad (3.35)$$

$$\Delta_{mix}S = \Delta S_1 + \Delta S_2 = -n_1 R\ln\frac{y_1 p}{p} - n_2 R\ln\frac{y_2 p}{p}$$

$n_1 = n \cdot y_1$ $\quad$ $n_2 = n \cdot y_2$

$$\Delta_{mix}S = -nR\left(y_1\ln y_1 + y_2\ln y_2\right) \qquad (3.36a)$$

For one mol:

$$\Delta_{mix}S_m = -R\left(y_1\ln y_1 + y_2\ln y_2\right) \qquad (3.36b)$$

For more than two components:

$$\boxed{\Delta_{mix} S(id) = -nR \sum y_i \ln y_i} \qquad (3.37)$$

The mole fractions are smaller than 1 so that each term is negative (ln(y)<1).

The entropy of mixing is always positive.

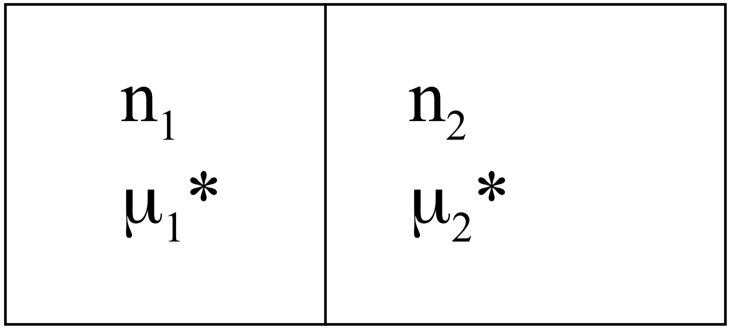
Gibbs function of mixing: $\Delta_{\mathrm{mix}}\mathrm{G} = \underbrace{\Delta_{\mathrm{mix}}\mathrm{H}}_{0} - \mathrm{T}\,\Delta_{\mathrm{mix}}\mathrm{S}$

$$\boxed{\Delta_{mix} G(id) = nRT \sum y_i \ln y_i} \qquad (3.38)$$

It is always negative!

2. Ideal mixture of liquids

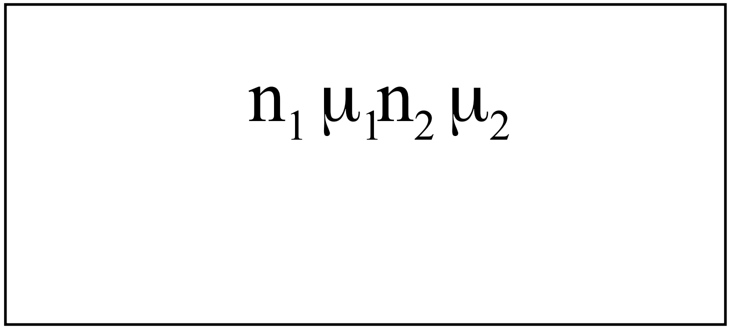
First we calculate the Gibbs function of mixing.



Before mixing:

$$G(initial)=n_1\mu_1^*+n_2\mu_2^*$$

After mixing:



$$\mu_1=\mu_1^*+RT\ln x_1$$

$$\mu_2=\mu_2^*+RT\ln x_2$$

$$G(mixture)=n_1\mu_1+n_2\mu_2$$

$$G(mixture) = n_1 \mu_1^* + n_1 RT \ln x_1 + n_2 \mu_2^* + n_2 RT \ln x_2$$

$$\Delta_{mix} G = G(mixture) - G(initial) = n_1 RT \ln x_1 + n_2 RT \ln x_2$$

$n_1 = n \cdot x_1$ $n_2 = n \cdot x_2$

$$\Delta_{mix} G(id) = nRT\,(x_1 \ln x_1 + x_2 \ln x_2)$$

In case of more than two components:

$$\boxed{\Delta_{mix} G(id) = nRT \sum x_i \ln x_i} \qquad (3.39)$$

$$\Delta_{\mathrm{mix}}G = \underbrace{\Delta_{\mathrm{mix}}H}_{0} - T\,\Delta_{\mathrm{mix}}S \qquad \Delta_{mix}S = -\frac{\Delta_{mix}G}{T}$$

$$\boxed{\Delta_{mix}S(id) = -nR\sum x_i \ln x_i} \qquad (3.40)$$

It is always positive (the disorder increases by mixing).

We obtained the same expressions for ideal gases and ideal liquid mixtures, compare for entropies (3.37) and (3.40), for Gibbs functions (3.38) and (3.39), respectively. All equations contain the sums of mole fractions times logarithms of mole fractions.

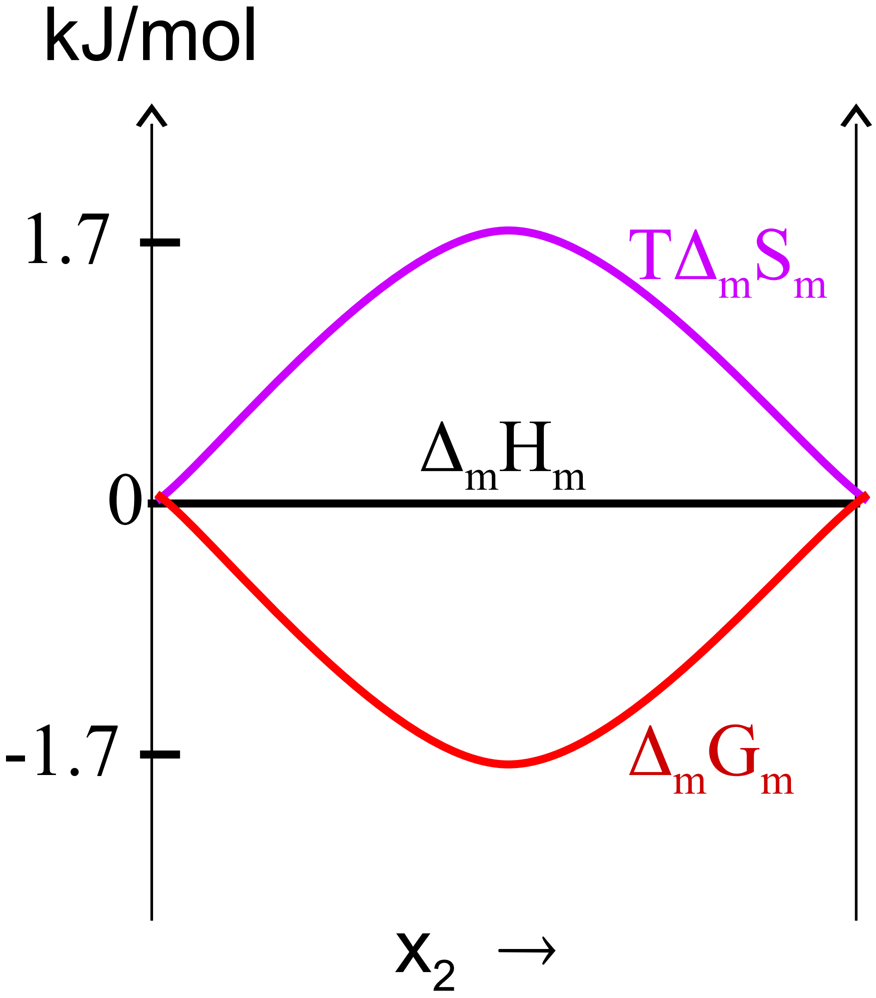


Fig. 3.16

Ideal mixture:

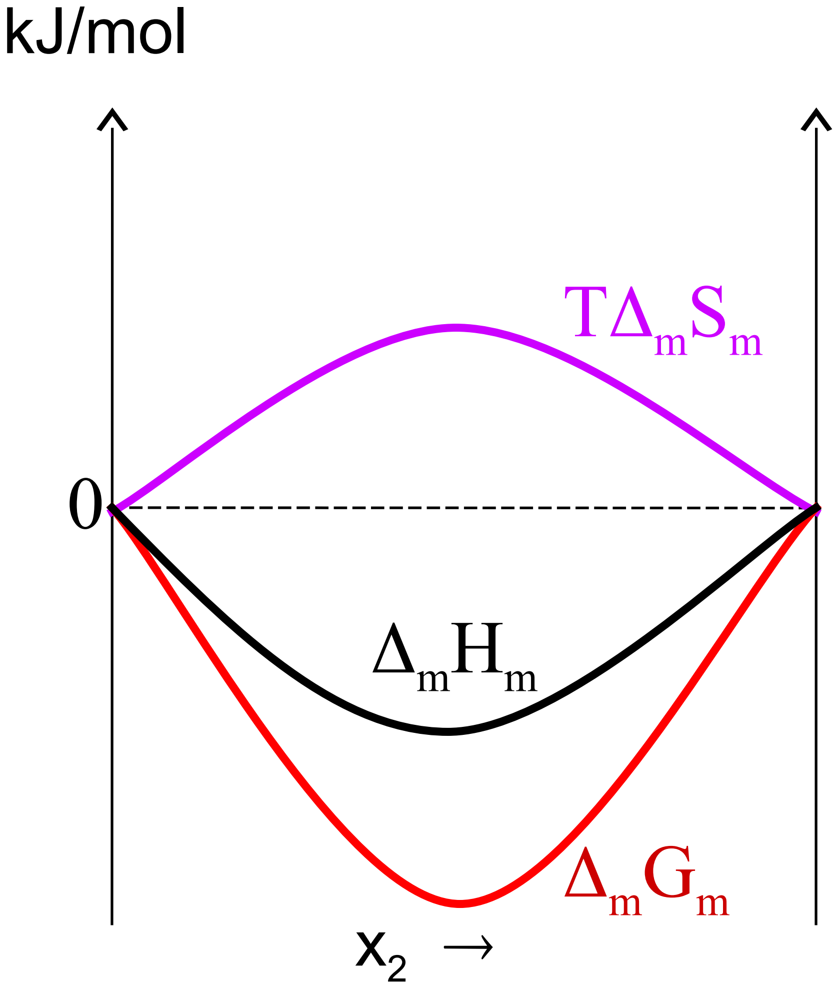
changes of thermodynamic functions as functions of mole fraction at about room temperature (Fig. 3.16)

3. *Studying the real mixtures, the mole fraction dependence of the thermodynamic functions $\Delta_m H_m$, $T\Delta_m S_m$ and $\Delta_m G_m$ depends on the values and signs of the frist two ones. The subscripts 'm' of the Δ-s refer to mixture like in Fig. 3.16.*

The next three figures introduce the three possibilities of the relations between the mentioned functions.

For the better understanding of the properties of mixtures see also subsections 3.1, 3.2 and 3.3.

Real mixture, negative deviation of $\Delta_m H_m$ from the ideal behaviour: $T\Delta_m S_m > \Delta_m G_m$



The entropy of mixing is smaller in real mixtures than in ideal mixtures because there is partial ordering (see subsection 3.2).

Fig. 3.17

There is complete miscibility (compare with Fig. 3.4a).

A

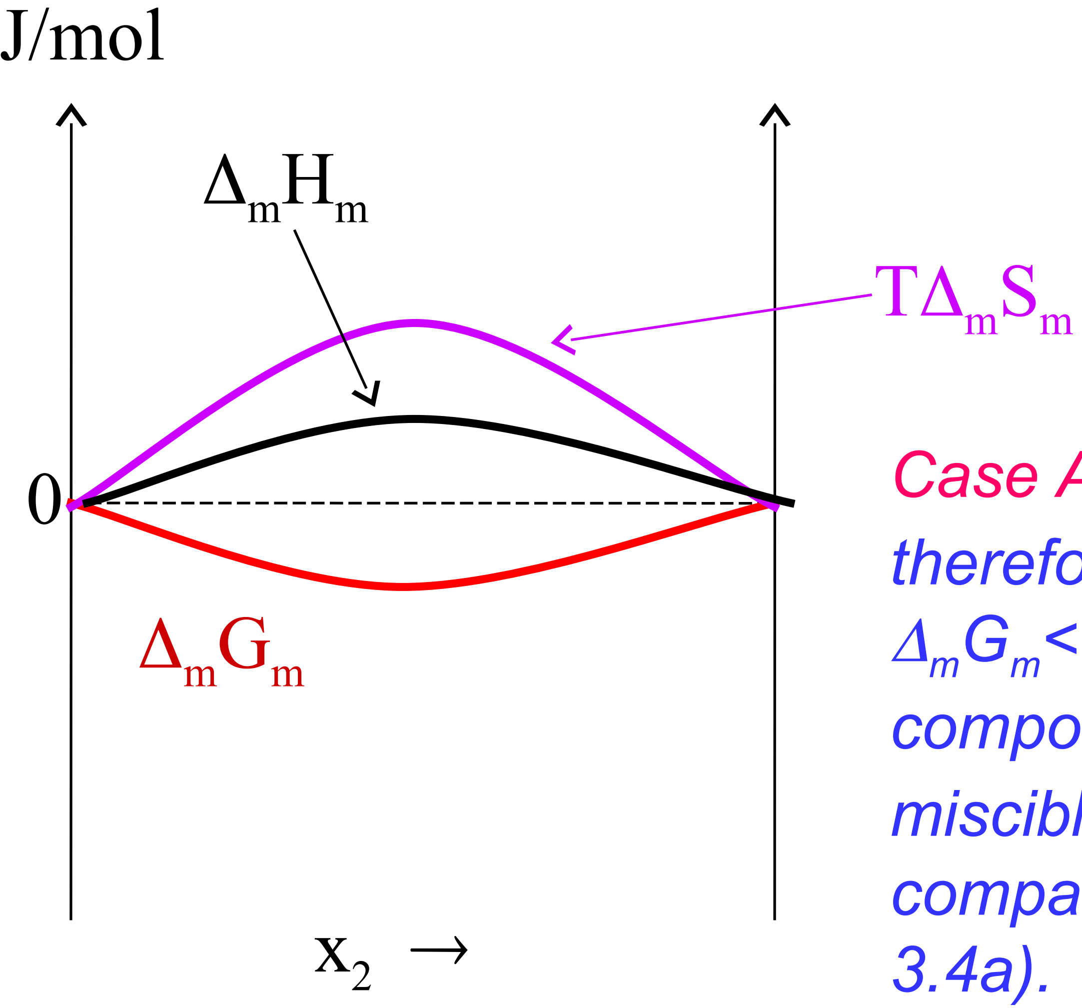


Fig. 3.19

Case A: $\Delta_m H_m < T\Delta_m S_m$, therefore $\Delta_m G_m < 0$. The components are miscible (see Fig. 3.19, compare it with Fig. 3.4a).

If both $\Delta_m H_m > 0$ and $T\Delta_m S_m > 0$, then two cases are possible

B

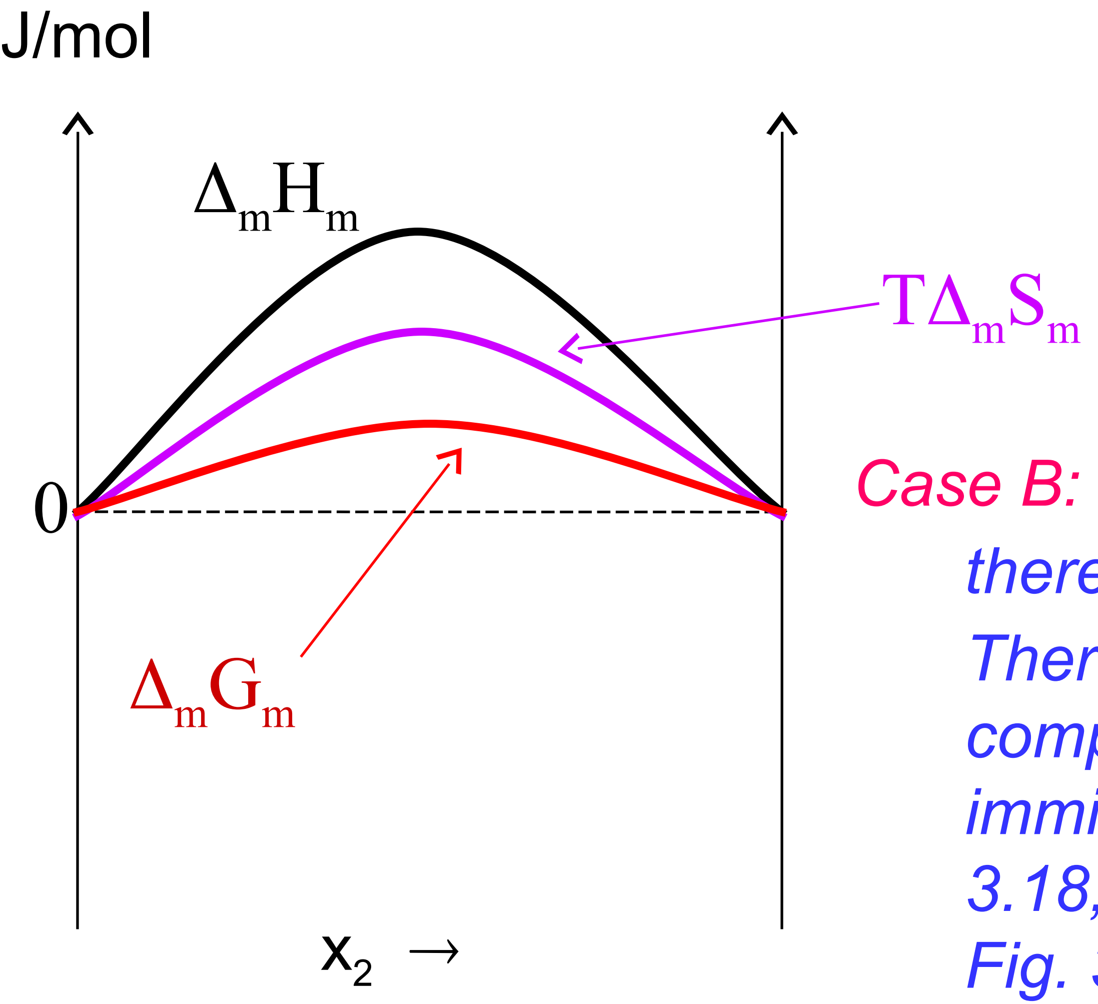


Fig. 3.18

Case B: $\Delta_m H_m > T\Delta_m S_m$,, therefore $\Delta_m G_m > 0$. Therefore the two components are immisible (see Fig. 3.18, compare with Fig. 3.4b)

3.8 Vapor pressure and boiling point diagrams of miscible liquids

Phase rule: F = C - P + 2

In a two component system: F = 4 - P.

In case of one phase there are 3 degrees of freedom.

In case of two phases one parameter has to be kept constant:

Either t = const. (vapor pressure diagram).

Or p = const. (boiling point diagram).

Ideal solution See (3.18) and (3.19)

$$p_1 = x_1 \cdot p_1^* \qquad p_2 = x_2 \cdot p_2^*$$

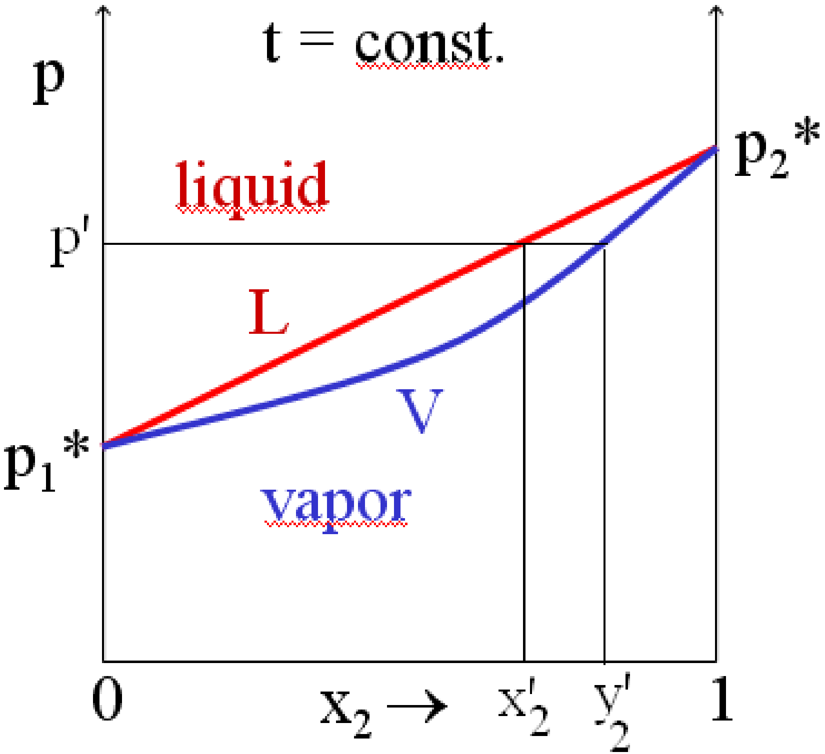
$$p = p_1 + p_2$$

$$y_2 = \frac{p_2}{p} = \frac{x_2 \cdot p_2^*}{p}$$

≥ 1

We assume:

$$p_1^* < p_2^*$$



$$\boxed{y_2 > x_2}$$

(3.41)

First law of Konovalov: $y_2 > x_2$, *i. e., the mole fraction of the more volatile component is higher in the vapor than in the liquid.* It is always true when the vapor pressure does not have a maximum or minimum.

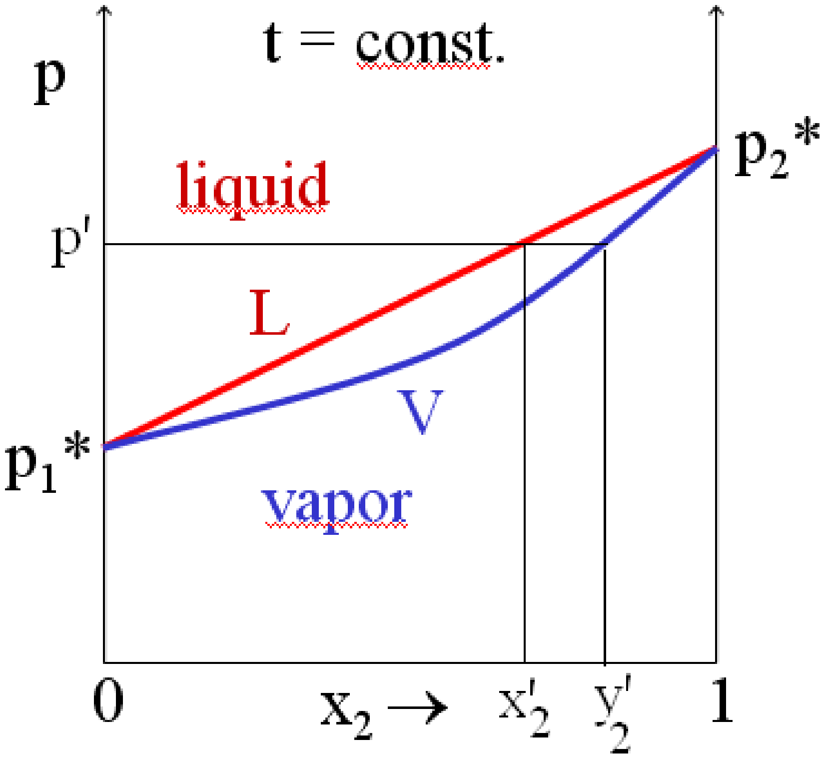


Fig. 3.20

Fig. 3.20: vapor pressure diagram, L: liquid curve, V: vapor curve.

Determination of the vapor pressure diagram:

$$y_2 = \frac{p_2}{p} = \frac{x_2 \cdot p_2^*}{p} \qquad (3.42)$$

Boiling point diagram

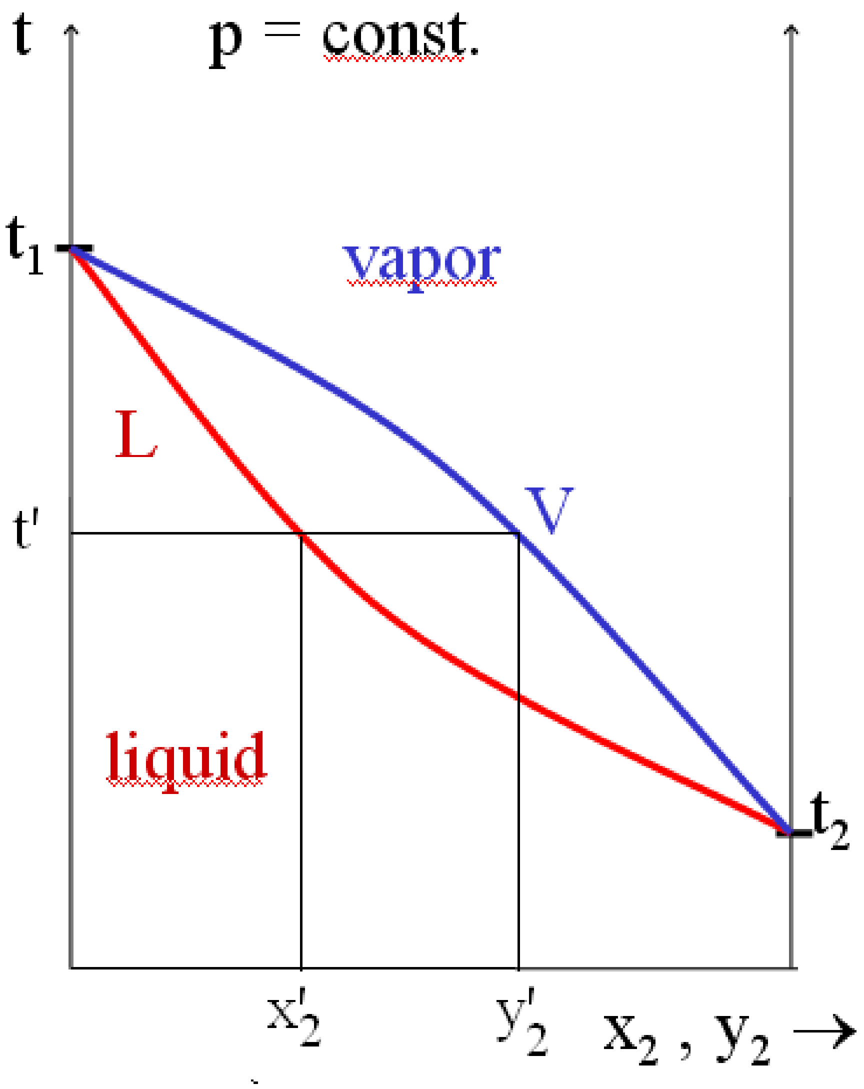


Fig. 3.21

V: vapor curve
(condensation curve)

L: liquid curve
(boiling point curve)

In practice **the boiling point diagram** (temperature-composition diagram) **is more important** than the vapor pressure diagram (pressure-composition diagram). Distillation at constant pressure is more common than distillation at constant temperature.

The boiling point of the more volatile component is lower.

Pálinka distiller

The level rule

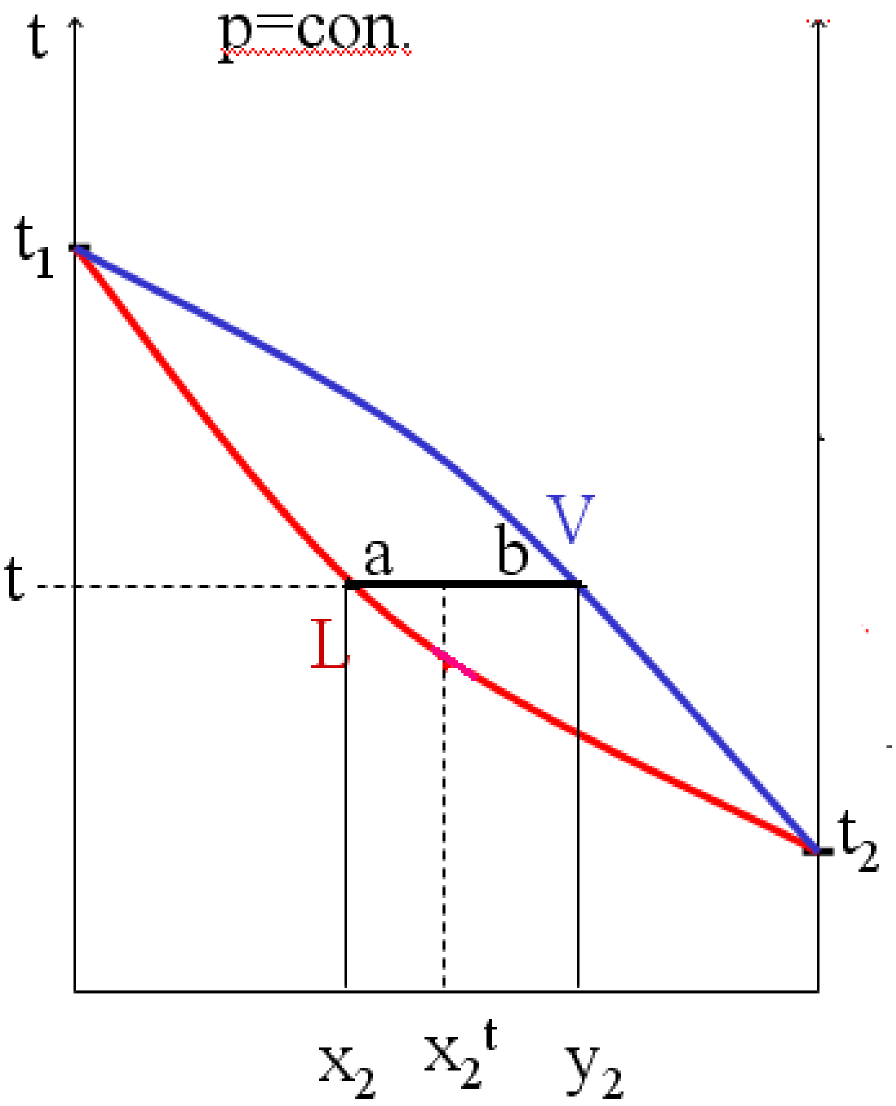


Fig. 3.22

$x^t_2 = x^{tot}_2$

Two phase area:

$$n \cdot x_2^{tot} = n^l \cdot x_2 + n^v \cdot y_2$$

$$n = n^l + n^v$$

$$n^l x_2^{tot} + n^v x_2^{tot} = n^l x_2 + n^v y_2$$

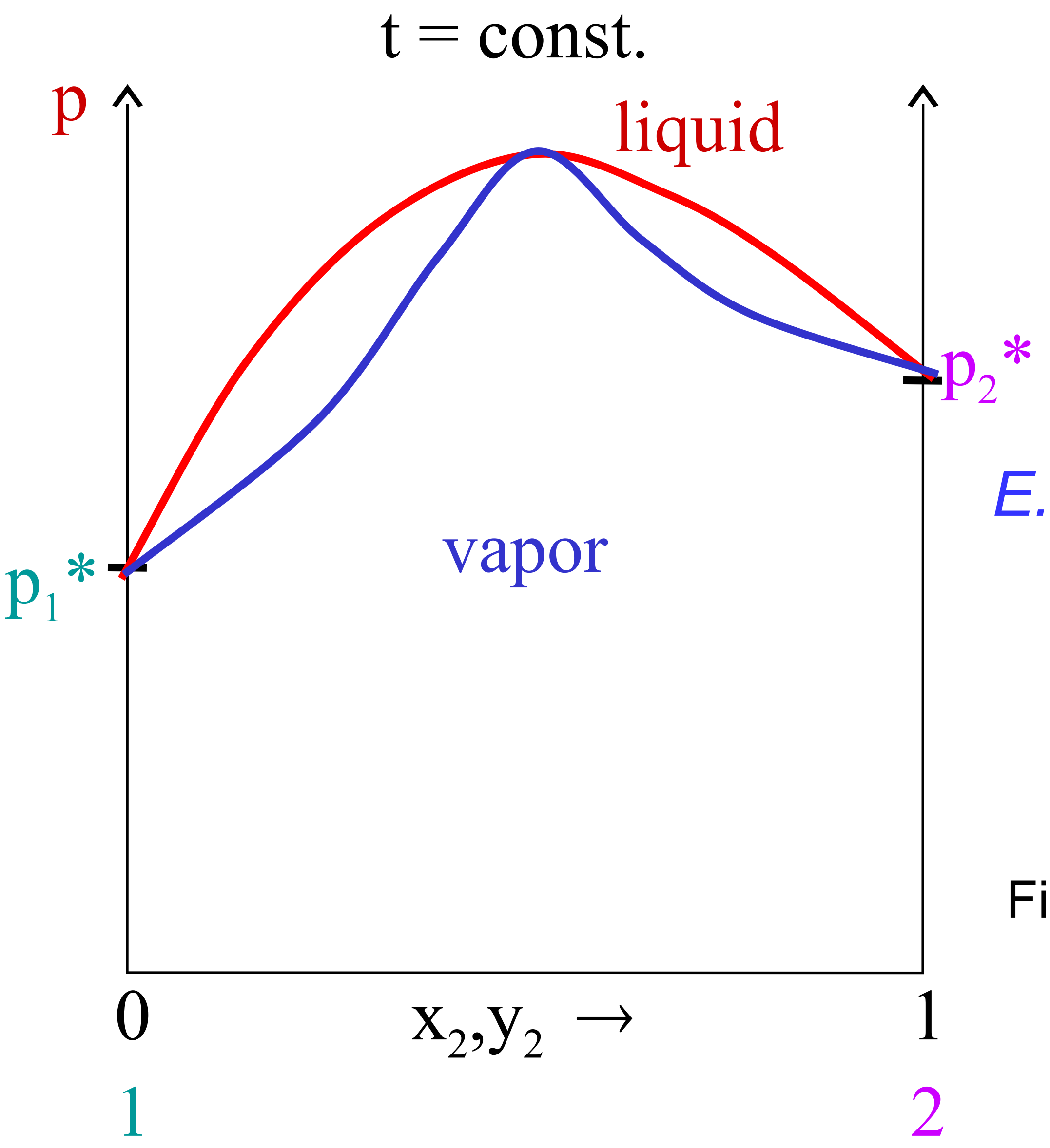
$$n^l \left(x_2^{tot} - x_2 \right) = n^v \left(y_2 - x_2^{tot} \right)$$

$$n^l \cdot a = n^v \cdot b$$

$$\frac{n^v}{n_l} = \frac{a}{b} \qquad (3.43)$$

(3.43): level rule, inverse ratio

Real solution: *Vapor pressure, positive deviation*

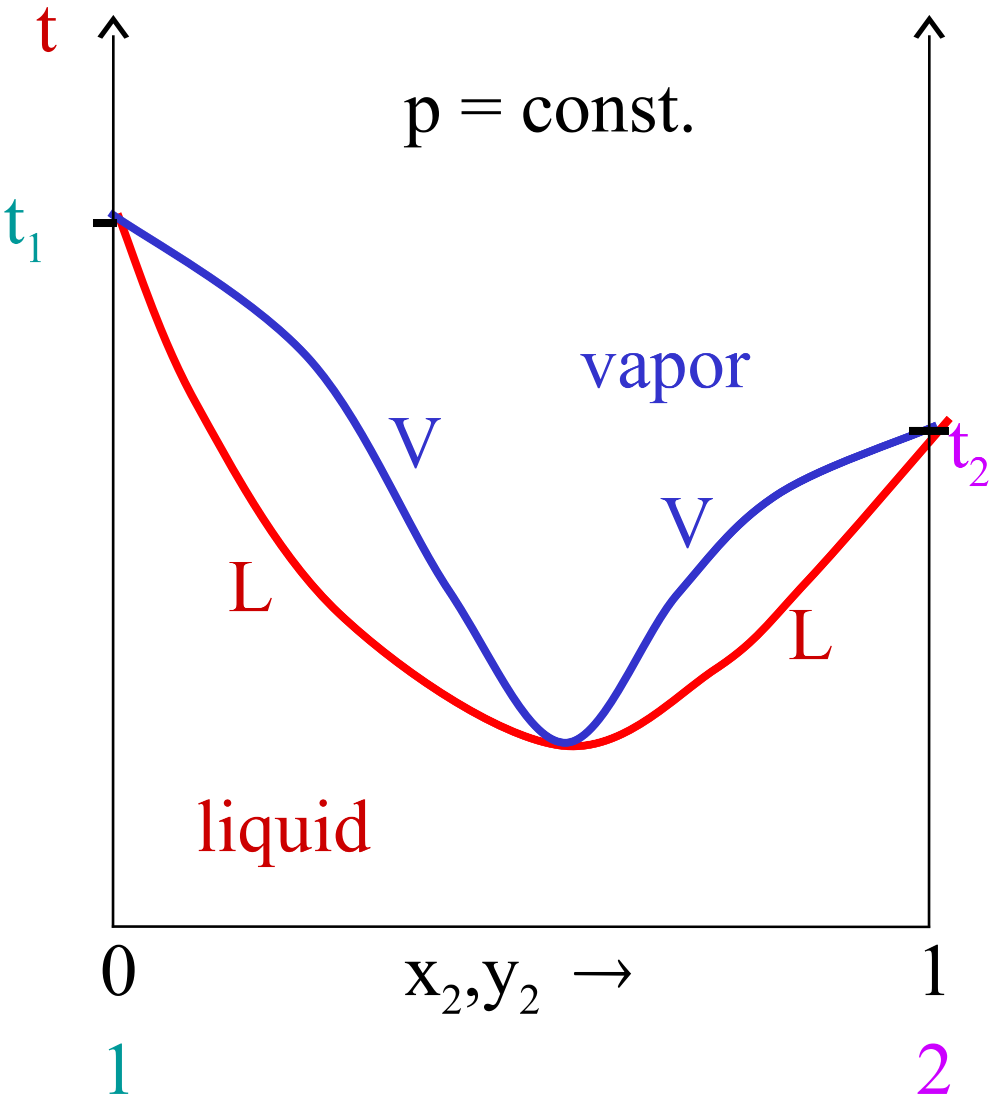


The total vapor pressure may have a maximum: ***azeotrope*** *with maximum*

E.g. Water-dioxane
Water-ethanol

Fig. 3.23

Real solution: *Boiling point diagram, positive deviation*



A low-boiling azeotrope: Fig. 3.24

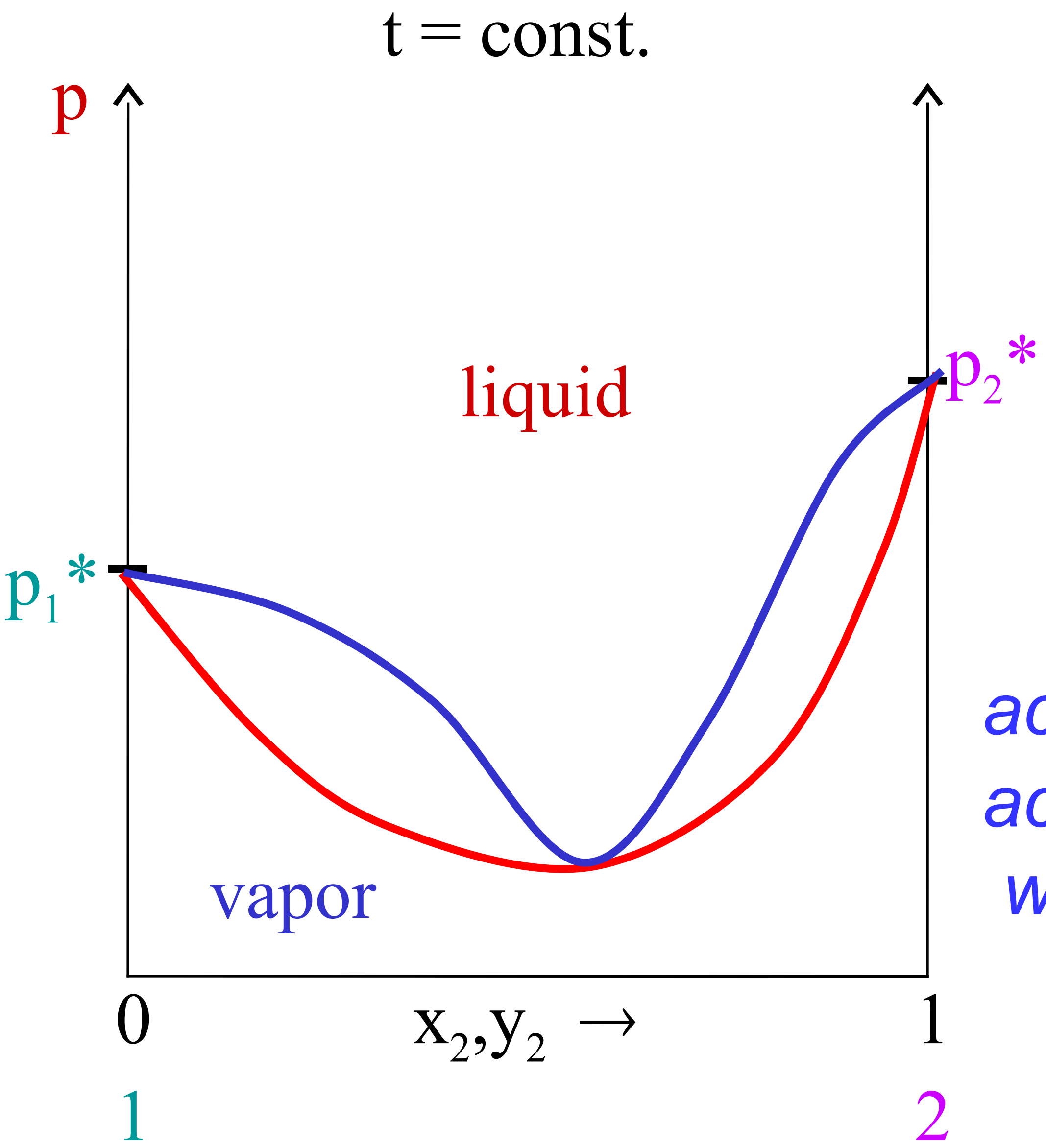
L: boiling point curve

V: condensation curve

E.g. Water-dioxane
Water-ethanol

Fig. 3.24

Real solution: *Vapor pressure, negative deviation*

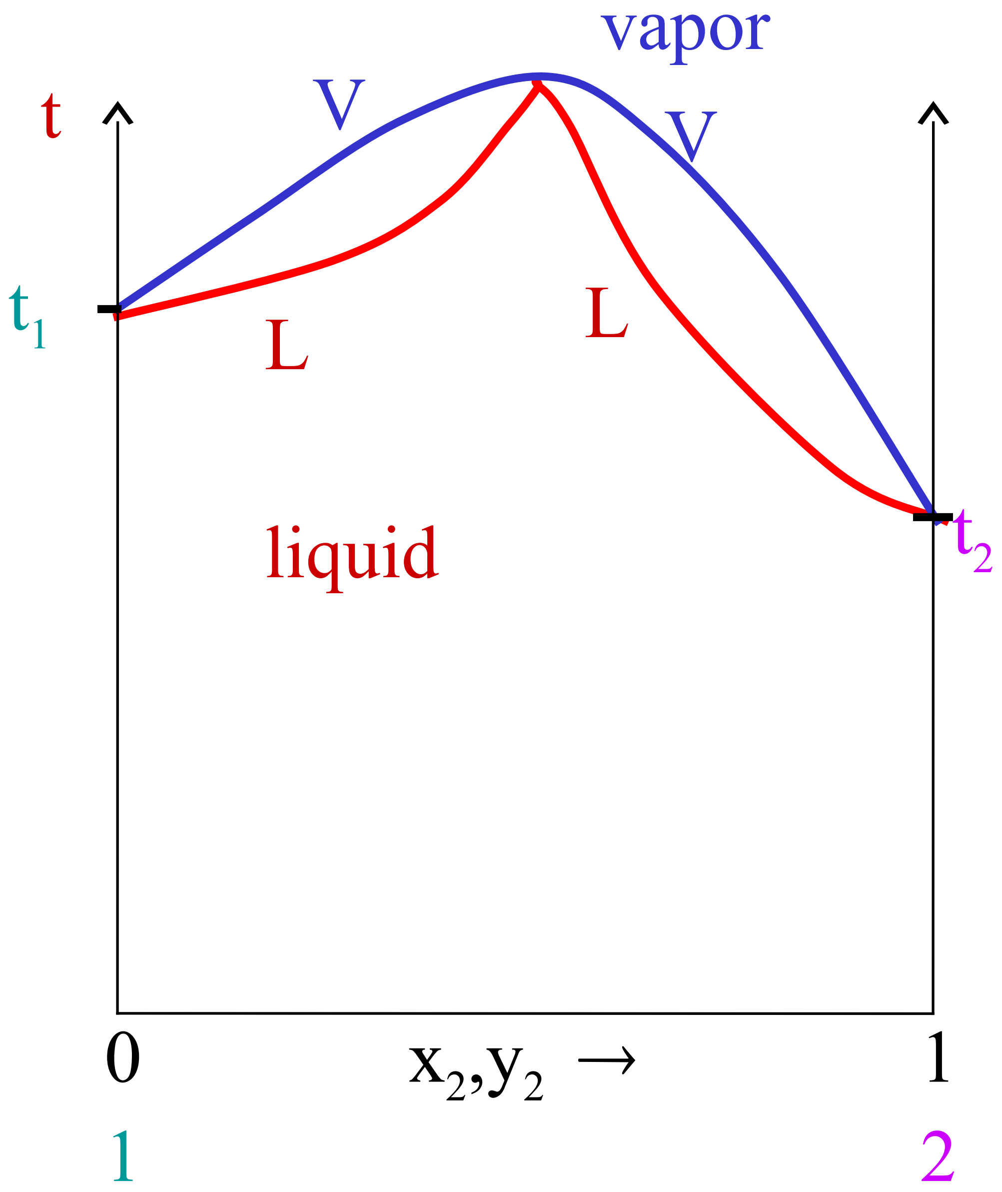


Total vapor pressure may have a minimum: azeotrope with minimum

aceton-methanol
acetone-chloroform
water-nitric acid

Fig. 3.25

Real solution: Boiling point diagram, negative deviation



A high boiling azeotrope.

L: boiling point curve

V: condensation curve

acetone-chloroform
water-nitric acid
aceton-methanol

Fig. 3.26

3.9 Thermodynamic interpretation of azeotropes

1. We start from Gibbs-Duham equation (3.13) (in the liquid phase),

2. The chemical potentials are expressed in terms of vapor pressures

3. The change of total pressure is expressed with respect to mole fraction (dp/dx_2).

$$n_1\,d\mu_1+n_2\,d\mu_2=0$$

(3.13) *Dividing by n:*

$$x_1\,d\mu_1+x_2\,d\mu_2=0$$

At constant T, μ depends on composition only.

$$d\mu_1=\frac{\partial\,\mu_1}{\partial\,x_1}dx_1 \qquad d\mu_2=\frac{\partial\,\mu_2}{\partial\,x_2}dx_2$$

$$x_1\frac{\partial\,\mu_1}{\partial\,x_1}dx_1=-x_2\frac{\partial\,\mu_2}{\partial\,x_2}dx_2$$

$$dx_1 = -dx_2 \qquad x_1 \frac{\partial \mu_1}{\partial x_1} = x_2 \frac{\partial \mu_2}{\partial x_2}$$

In equilibrium the chemical potential of a component is equal in the two phases (2.56):

$$\mu_1 = \mu_1^0 + RT \ln \frac{p_1}{p^0} \qquad \mu_2 = \mu_2^0 + RT \ln \frac{p_2}{p^0}$$

$$\frac{\partial \mu_1}{\partial x_1} = RT \frac{\partial \ln p_1}{\partial x_1} \qquad \frac{\partial \mu_2}{\partial x_2} = RT \frac{\partial \ln p_2}{\partial x_2}$$

$$x_1 \frac{\partial \ln p_1}{\partial x_1} = x_2 \frac{\partial \ln p_2}{\partial x_2} \qquad \frac{x_1}{p_1}\frac{dp_1}{dx_1} = \frac{x_2}{p_2}\frac{dp_2}{dx_2}$$

$$x_1 = 1 - x_2 \qquad dx_1 = -dx_2$$

$$-\frac{1-x_2}{p_1}\frac{dp_1}{dx_2} = \frac{x_2}{p_2}\frac{dp_2}{dx_2}$$

$$\frac{dp_1}{dx_2} = -\frac{x_2}{1-x_2}\frac{p_1}{p_2}\frac{dp_2}{dx_2}$$

$$\boxed{\frac{dp}{dx_2} = \frac{dp_1}{dx_2} + \frac{dp_2}{dx_2} = \left(1 - \frac{x_2}{1 - x_2}\frac{p_1}{p_2}\right)\frac{dp_2}{dx_2}} \tag{3.44}$$

$$\frac{dp_2}{dx_2} > 0$$

(If the mole fraction increases, the partial pressure also increases.)

We study two cases:

$$A) \quad \frac{dp}{dx_2} = 0$$

(The total vapor pressure has a maximum or minimum.)

$$B) \quad \frac{dp}{dx_2} > 0$$

(The increasing amount of

component 2 increases the total pressure.)

$$A)\quad \frac{dp}{dx_2}=0 \qquad\qquad 1-\frac{x_2}{1-x_2}\frac{p_1}{p_2}=0$$

Dalton: $p_1 = y_1p = (1-y_2)p \qquad p_2 = y_2p$

$$\Rightarrow \quad 1-\frac{x_2}{x_1}\frac{y_1}{y_2}=0 \quad \Rightarrow \quad \boxed{\begin{array}{l} y_2=x_2 \\ y_1=x_1 \end{array}}$$

$$\boxed{\begin{array}{l} y_2 = x_2 \\ y_1 = x_1 \end{array}} \qquad (3.45)$$

Third law of Konovalov.

When the total vapor pressure has a maximum or minimum, the composition of the vapor is equal to the composition of the liquid.

This is the azeotrope point.

Azeotrope is not a compound, the azeotrope composition depends on pressure.

$$B)\quad \frac{dp}{dx_2} > 0 \qquad 1 - \frac{x_2}{1-x_2}\frac{p_1}{p_2} > 0$$

Dalton: $p_1 = y_1 p = (1-y_2)p \quad p_2 = y_2 p$

$$1 - \frac{x_2}{1-x_2}\frac{(1-y_2)p}{y_2 p} > 0 \qquad 1 > \frac{x_2}{1-x_2}\frac{1-y_2}{y_2}$$

$$\frac{1-y_2}{y_2} < \frac{1-x_2}{x_2} \qquad \frac{1}{y_2} - 1 < \frac{1}{x_2} - 1$$

$$\boxed{y_2 > x_2}$$

$$\boxed{y_2 > x_2} \qquad (3.46)$$

The second law of Konovalov.

The component has higher mole fraction in the vapor than in the liquid, if its increasing amount increases the total vapor pressure.

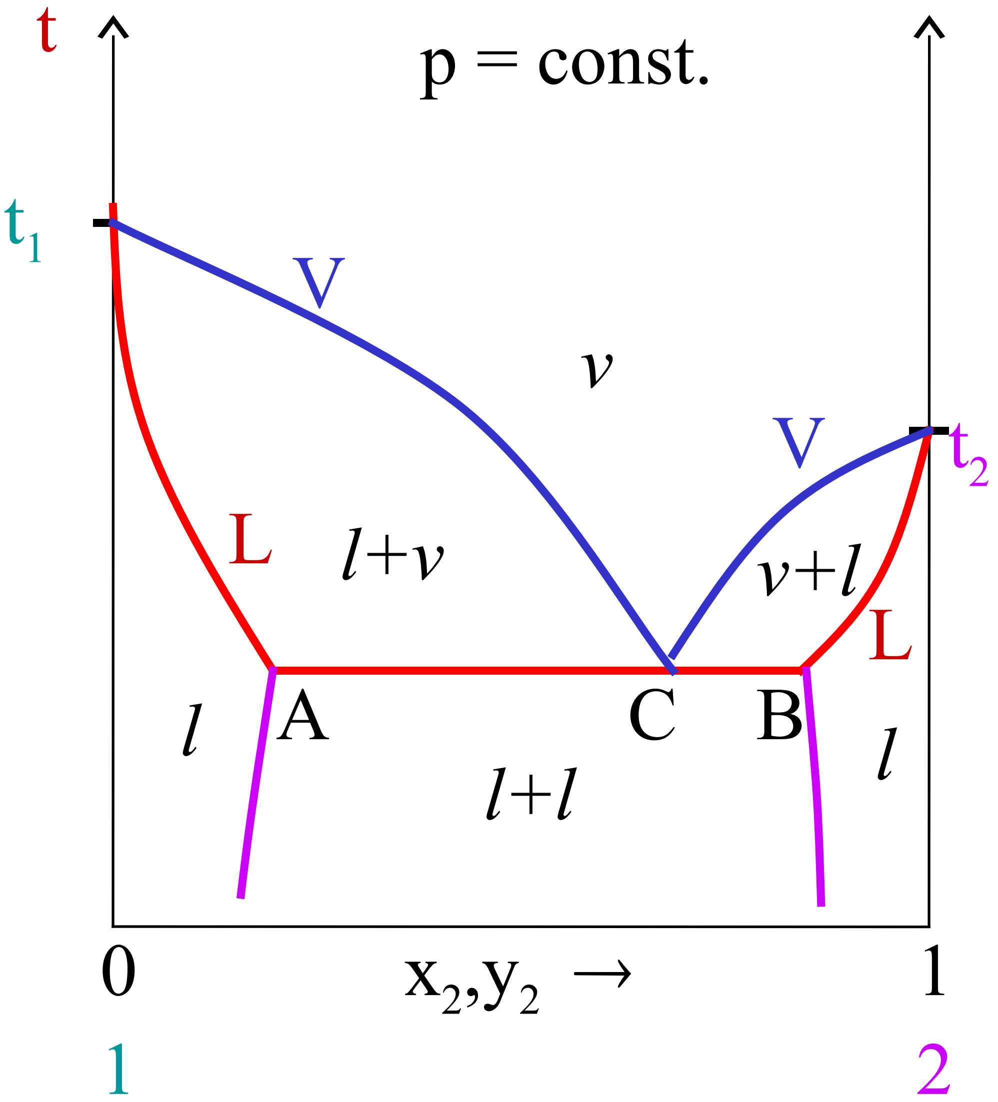
One can control the second law of Konovalov on Figs. 3.23 and 3.25.

3.10 Boiling point diagrams of partially miscible and immiscible liquids

Partial miscibility occurs in case of **positive** deviation. If the attractive forces between A and B molecules are much less than those between A and A molecules and B and B molecules, A and B become partially miscible or immiscible in the liquid phase.

E.g. butanol and water are partially miscible.

Boiling point diagram, partial miscibility in the liquid phase



A-C-B: equilibrium of three phases, degrees of freedom: F=1 (2.58)

A: 1 saturated with 2

B: 2 saturated with 1

C: boiling temperature for two liquid phase region

L: boiling point curve

V: condensation curve

e.g. butanol(1)-water(2)

Fig. 3.27

Calculation of the equilibrium vapor pressure [see also (3.21), (3.22)]:

$$p = \gamma_1^A x_1^A p_1^* + \gamma_2^B x_2^B p_2^* \qquad (3.47)$$

Raoult´s law is conveniently written for the component which behaves as solvent, in our example water.

Other possibility: $$p = \gamma_1^A x_1^A p_1^* + \gamma_2^A x_2^A p_2^*$$

Or: $$p = \gamma_1^B x_1^B p_1^* + \gamma_2^B x_2^B p_2^*$$

In equilibrium the activity (expressed in terms of mole fractions) of a component is equal in all the phases .

Complete immiscibility → *The components keep their phase properties in the mixture.*

E.g. water-toluene mixture

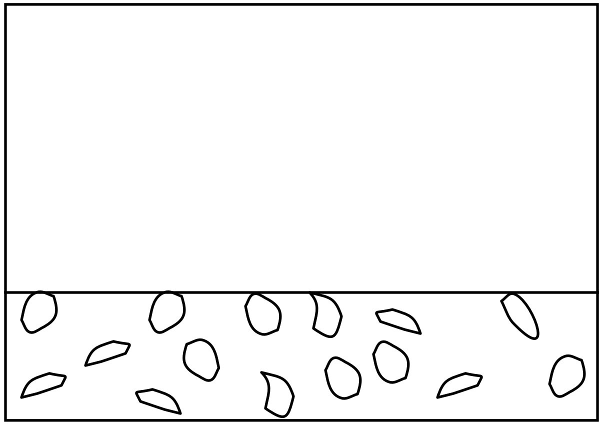


Fig. 3.28

The drops of one component are dispersed in the other component, like on Fig. 3.28.

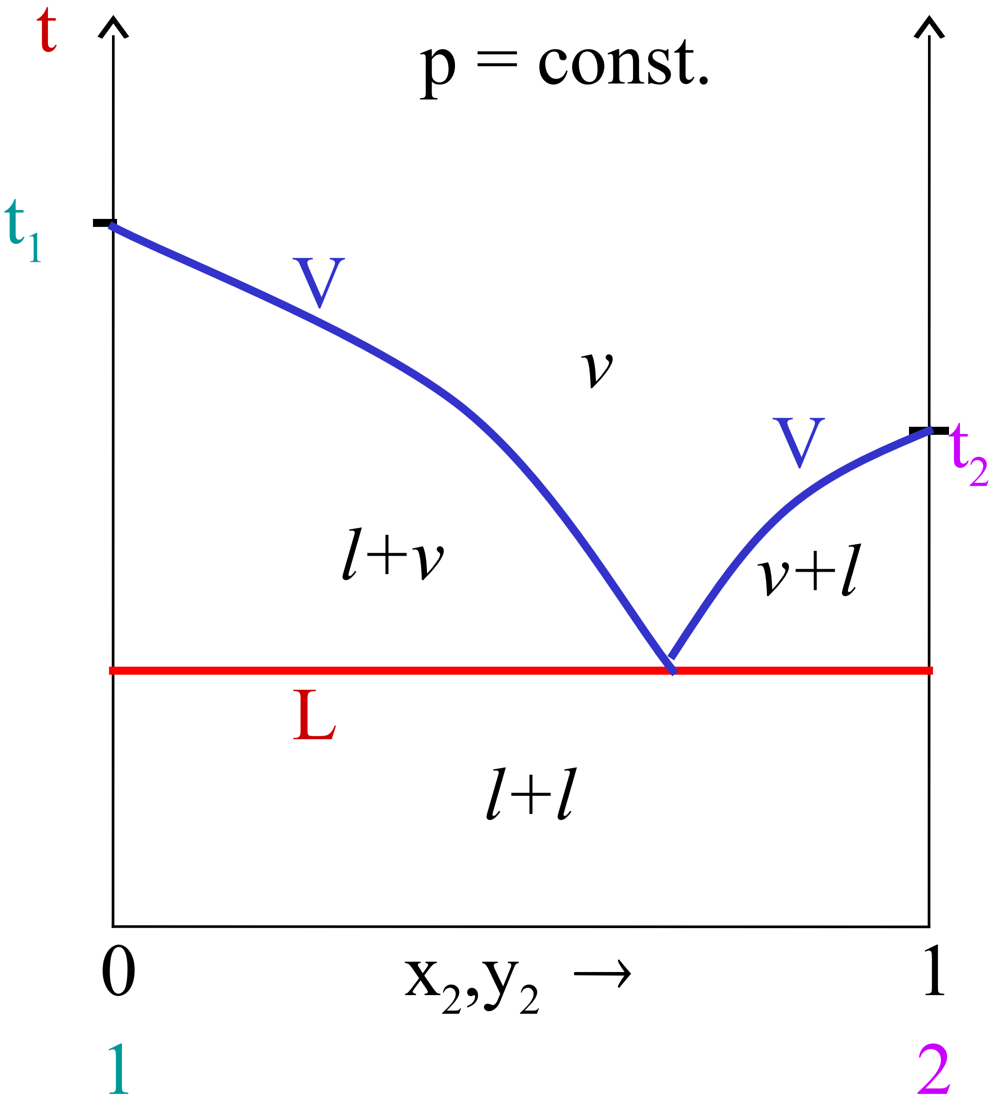
Each component exerts its total vapor pressure, as if it were alone in the system.

$$p = p_1^* + p_2^* \qquad (2.48)$$

*The boiling point is lower than that of any component, i. e., **p** reaches the external pressure at lower **T** than either p_1^* or p_2^*.*

This is the principle of steam distillation.

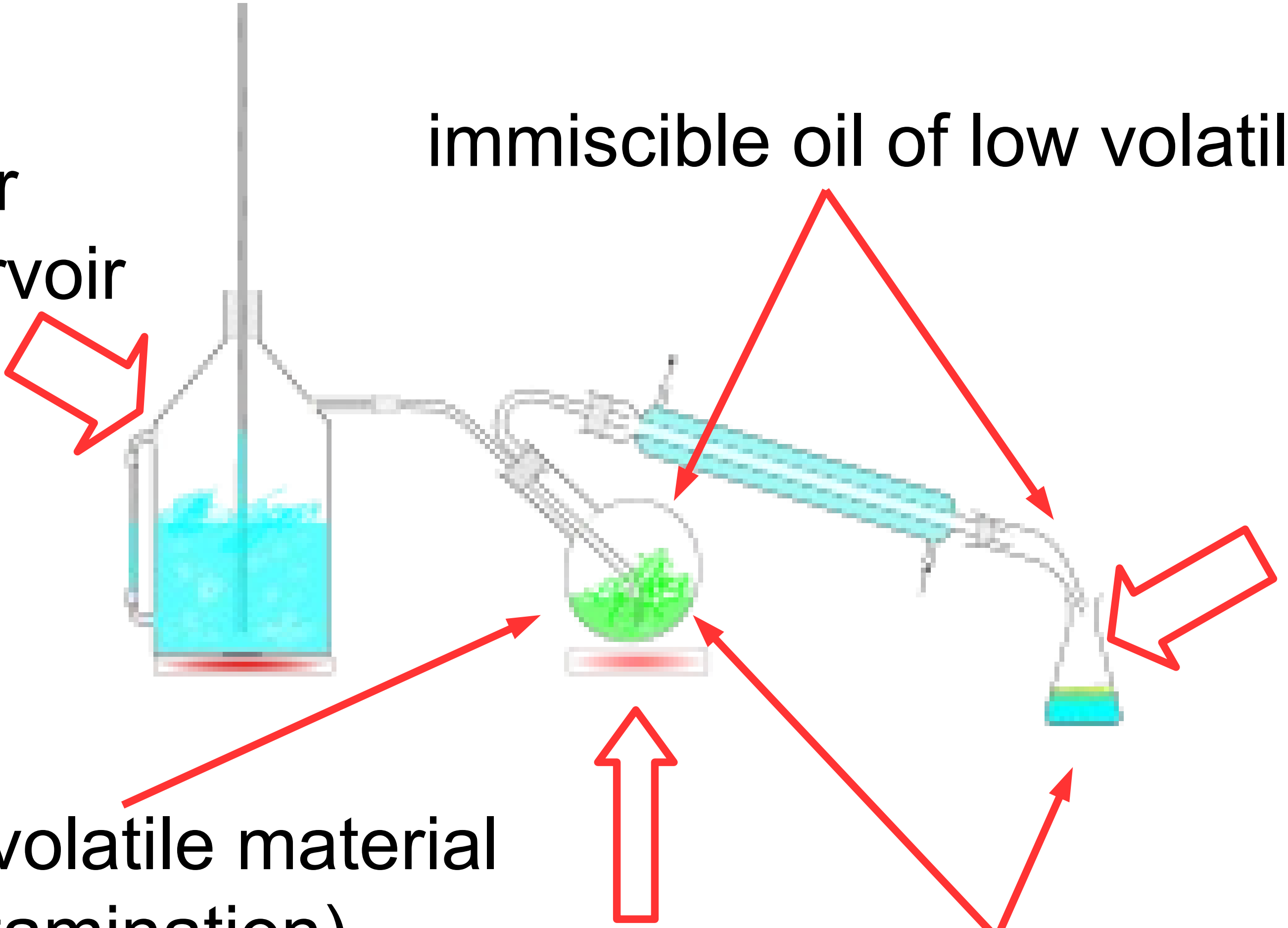
Boiling point diagram, complete immiscibility in the liquid phase



The boiling temperature is independent of the composition of the mixture

Fig. 3.29

Steam distillation


water reservoir

immiscible oil of low volatility

receiving flask

non-volatile material (contamination)

boiling flask

water

Steam distillation - *calculation of molar ratio of the components in the vapor phase*

Dalton´s law.: $p_1 = y_1 p \qquad p_2 = y_2 p$

$$\frac{n_1}{n_2} = \frac{y_1}{y_2} = \frac{p_1}{p_2} = \frac{p_1^*}{p_2^*}$$

E.g.. 1: water
2: organic material

$$\frac{m_1 M_2}{M_1 m_2} = \frac{p_1^*}{p_2^*}$$

m_1:mass of water distilling with m_2 mass of organic material :

$$m_1 = m_2 \frac{p_1^*}{p_2^*} \frac{M_1}{M_2} \qquad (3.49)$$

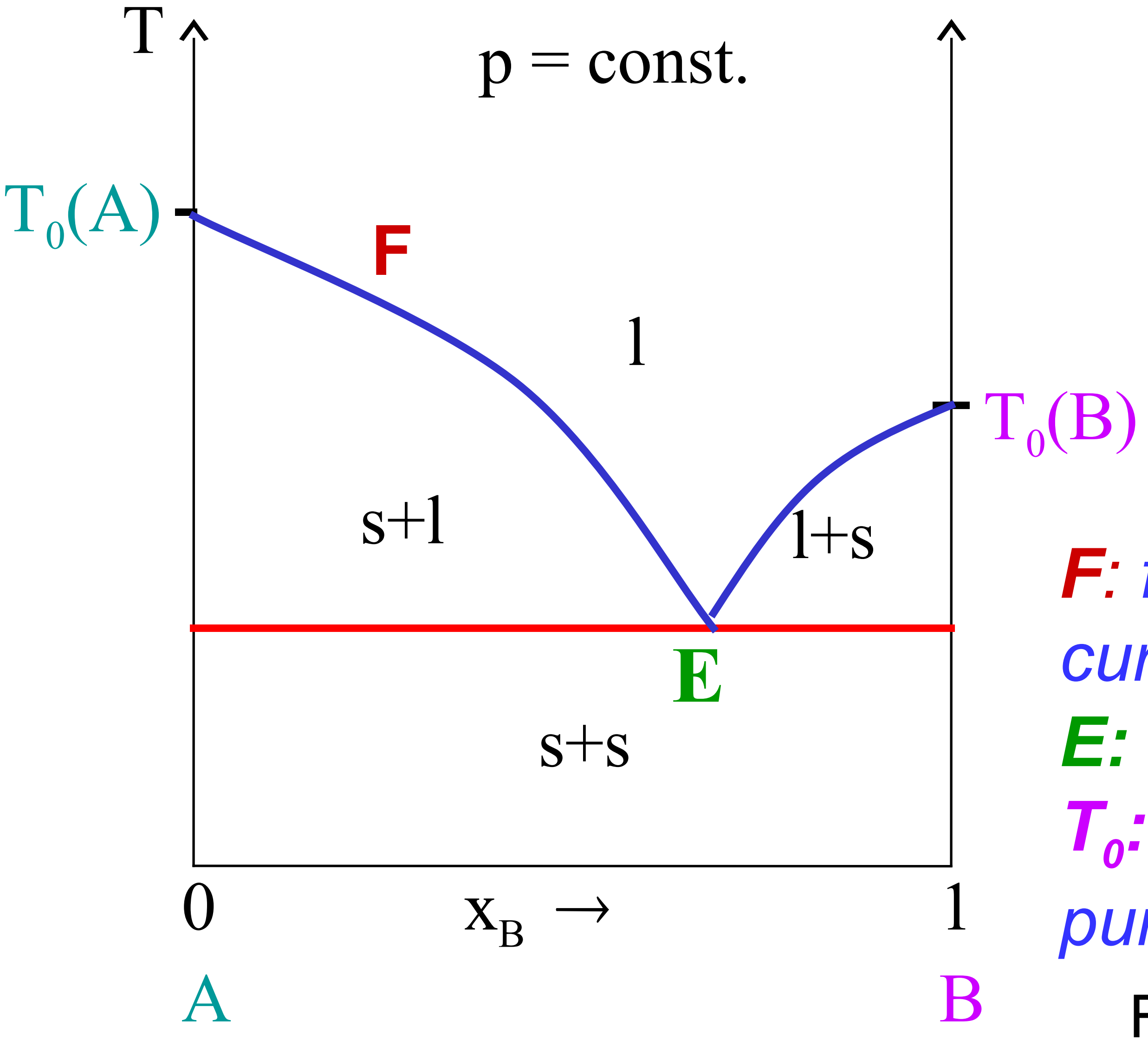
This method is suitable also for determination of molar mass.

3.11 Solid - liquid equilibria: simple eutectic diagrams

The components are miscible in liquid phase (above the melting points) but they are immiscible in the solid phase (e.g. they have different crystal structure).

E.g. benzene and naphthalene.

Solid-liquid phase diagram, miscible liquids



Find the similarity to the boiling point diagram of immiscible liquids (Fig. 3.29)

***F**: freezing point curve*

***E**: eutectic point*

***T_0**: melting point, pure component*

Fig. 3.30

Derivation of the freezing point curve (F)

$$\mu_A(s) = \mu_A(l) \qquad (3.50)$$

$$\mu_A^*(s) = \mu_A^*(l) + RT\ln a_A \qquad (3.51)$$

molar Gibbs functions

The activity of component A in the solution saturated for A

$$\frac{G_{mA}^*(s) - G_{mA}^*(l)}{RT} = \ln a_A$$

We are going to derive this expression with respect to T

$$\frac{G^*_{mA}(s) - G^*_{mA}(l)}{RT} = \ln a_A$$

G = H - TS dG =Vdp -SdT $\Longrightarrow$ $\left(\frac{\partial G}{\partial T}\right)_p = -S$

Derivative of a ratio: $\left(\frac{u}{v}\right)' = \frac{u'v - uv'}{v^2}$

$$\left(\frac{\partial \left(G/T\right)}{\partial T}\right)_p = \frac{T\left(\frac{\partial G}{\partial T}\right)_p - G}{T^2} = \frac{-TS - G}{T^2} = -\frac{H}{T^2} \qquad (3.52)$$

Gibbs-Helmholtz equation

$$\frac{\partial}{\partial T}\left(\frac{G^*_{mA}(s)-G^*_{mA}(l)}{RT}\right)=\frac{d\ln a_A}{dT}$$

$$\frac{H^*_{mA}(l)-H^*_{mA}(s)}{RT^2}=\frac{d\ln a_A}{dT}$$

$$\frac{d\ln a_A}{dT}=\frac{\Delta H_{mA}(fus)}{RT^2}$$ *(enthalpy of fusion)*

So far we have not used any approximation.

In order to integrate from the melting point of the pure substance A to T, we take the enthalpy of fusion independent of temperature (approximation).

$$\ln a_A = \frac{\Delta H_{mA}(fus)}{R}\left(\frac{1}{T_{0A}} - \frac{1}{T}\right)$$

If the liquid phase is an ideal solution:

$$\ln x_A = \frac{\Delta H_{mA}(fus)}{R}\left(\frac{1}{T_{0A}} - \frac{1}{T}\right) \qquad (3.53)$$

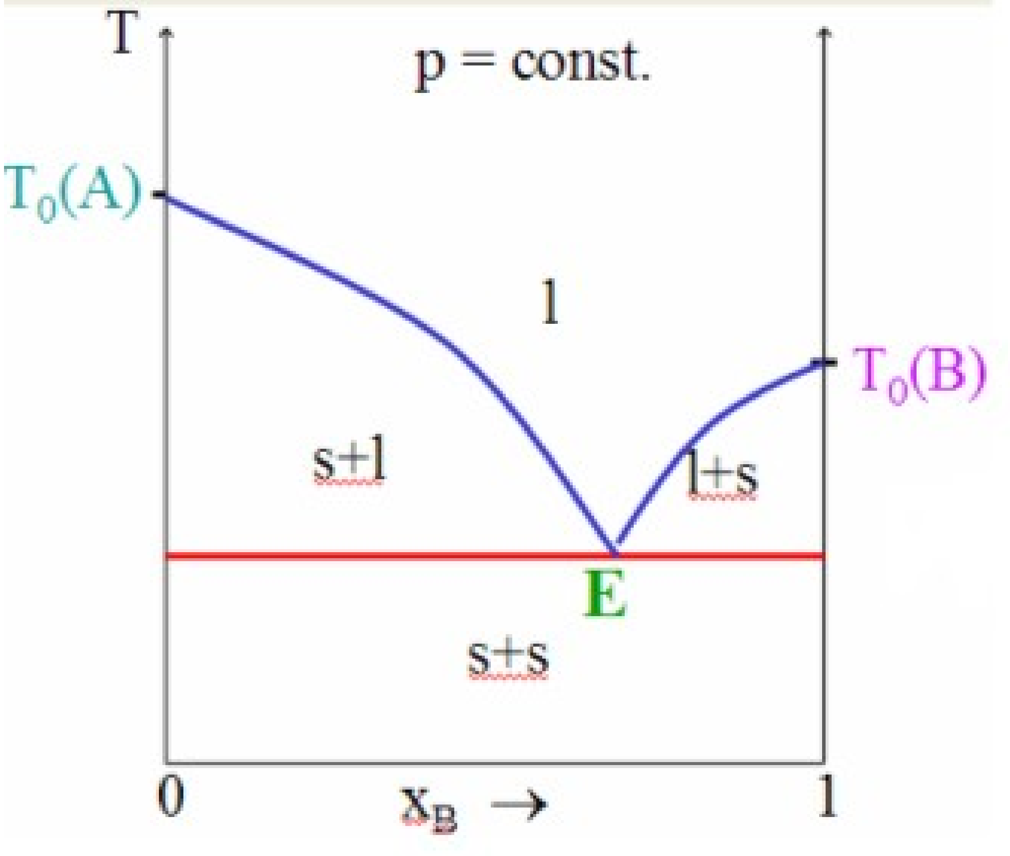
Similarity to the Clausius-Clapeyron equation (2.30)

The temperature as a function of mole fraction:

$$T = \frac{T_{0A}\,\Delta H_{mA}(fus)}{\Delta H_{mA}(fus) - RT_{0A}\ln x_A} = \frac{T_{0A}}{1 - \dfrac{RT_{0A}}{\Delta H_{mA}(fus)}\ln x_A} \qquad (3.54)$$

*The shape of the ideal solubility curve is independent of the other component. The expression for the solubility curve of **A** includes the melting point and enthalpy of fusion of **A**. And the expression for the solubility curve of **B** includes the melting point and enthalpy of fusion of **B**.*

The eutectic point is the crossing point of the two curves.



The mole fraction of the component with lower melting point is used here as abscissa, this choice between the components is arbitrary.

Fig. 3.31

3.12 Solid-liquid phase diagrams

Great similarity to liquid-vapor equilibria. Main types:

1. *Complete miscibility in solid state*
2. *Partial miscibility in solid state*
3. *Complete immiscibility in solid state*
4. *Formation of compounds*

1. Complete miscibility in solid state, compare Fig. 3.32 with Fig. 3.21 or Fig.3.22!

A)

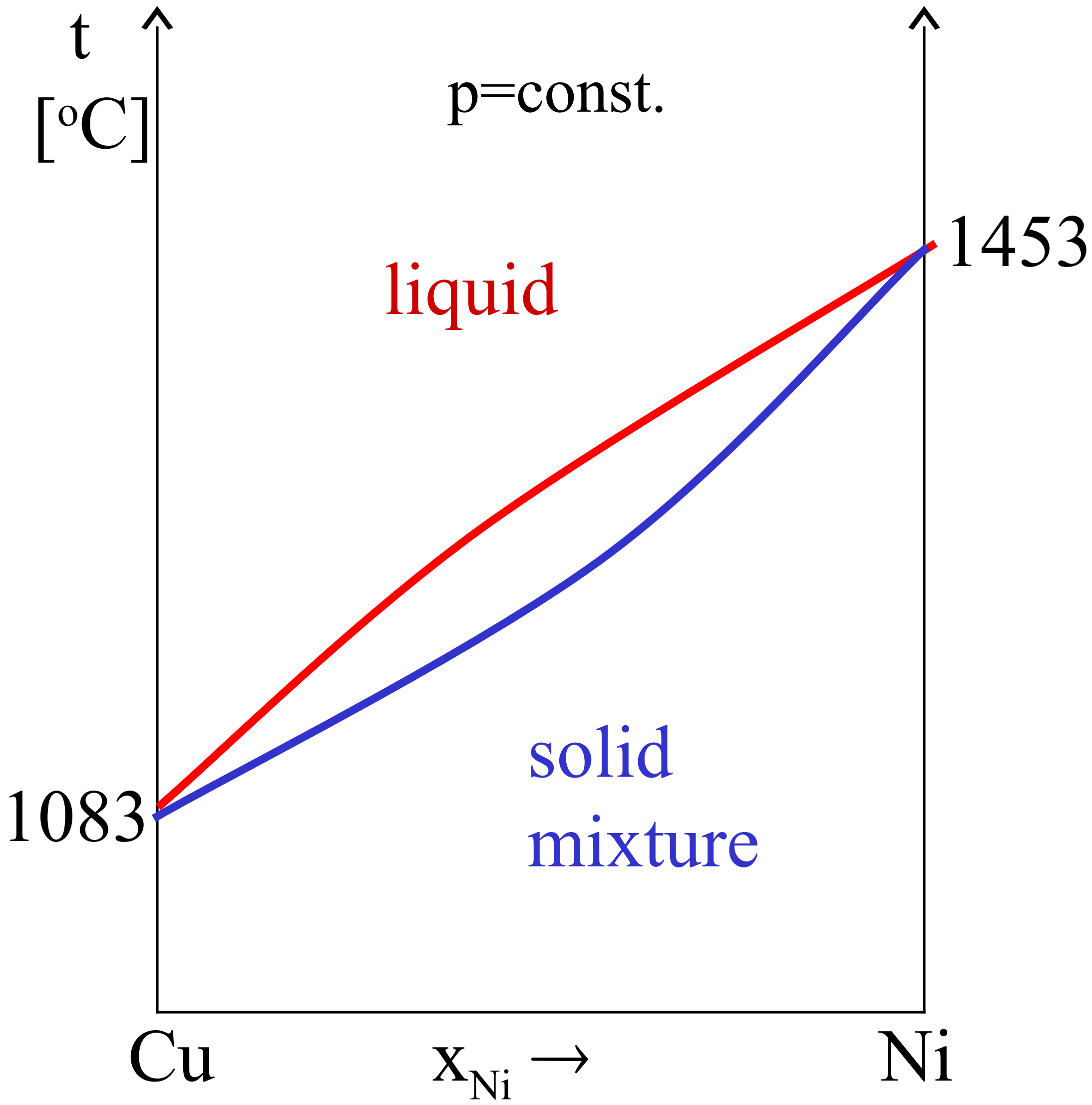


Fig. 3.32

B) *Minimal temperature of melting, compare Fig, 3.33 with Fig. 3.24.*

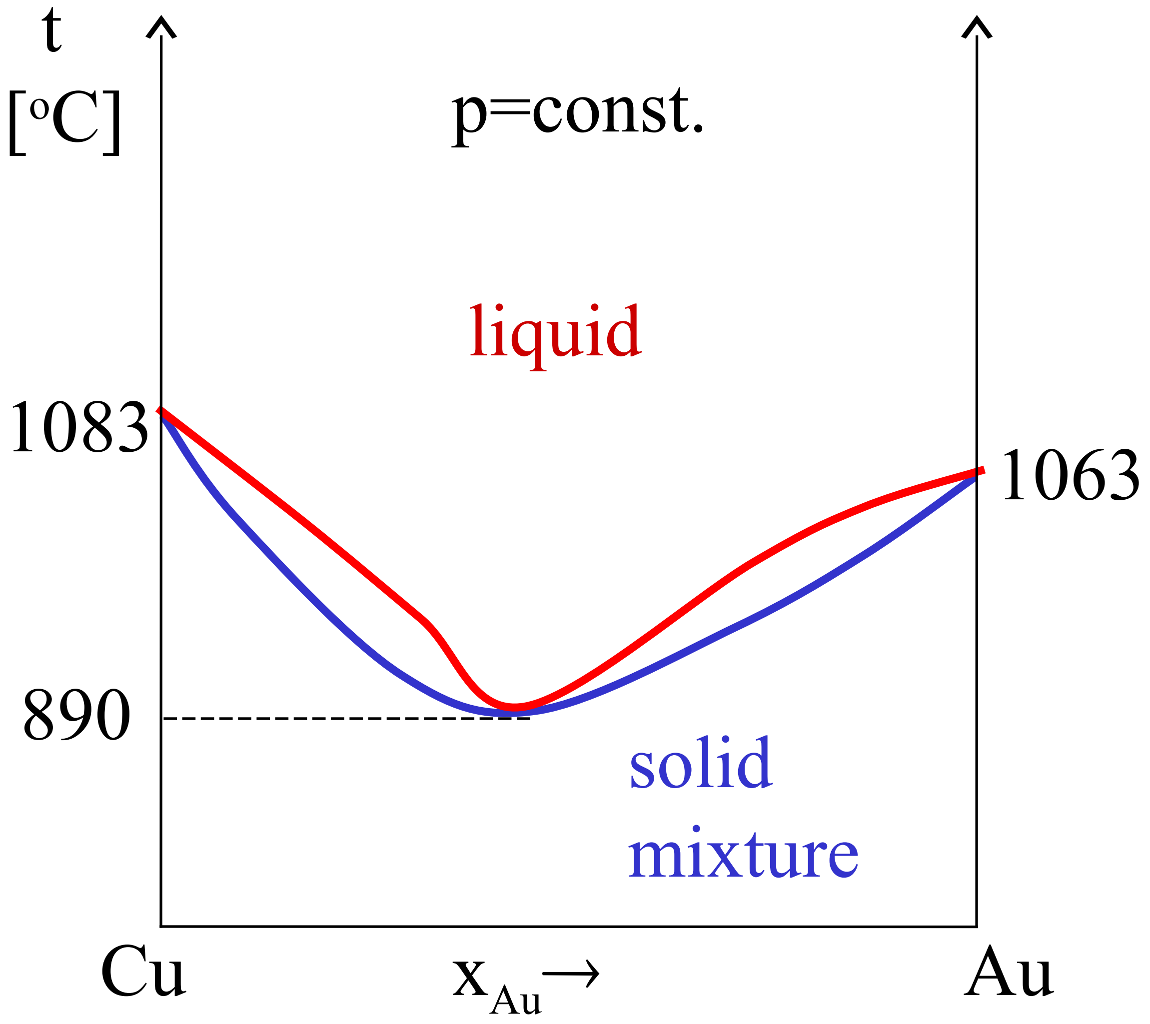


Fig. 3.33

2. Partial miscibility in solid state, compare to Fig. 3.27 (Fig. 3.34)

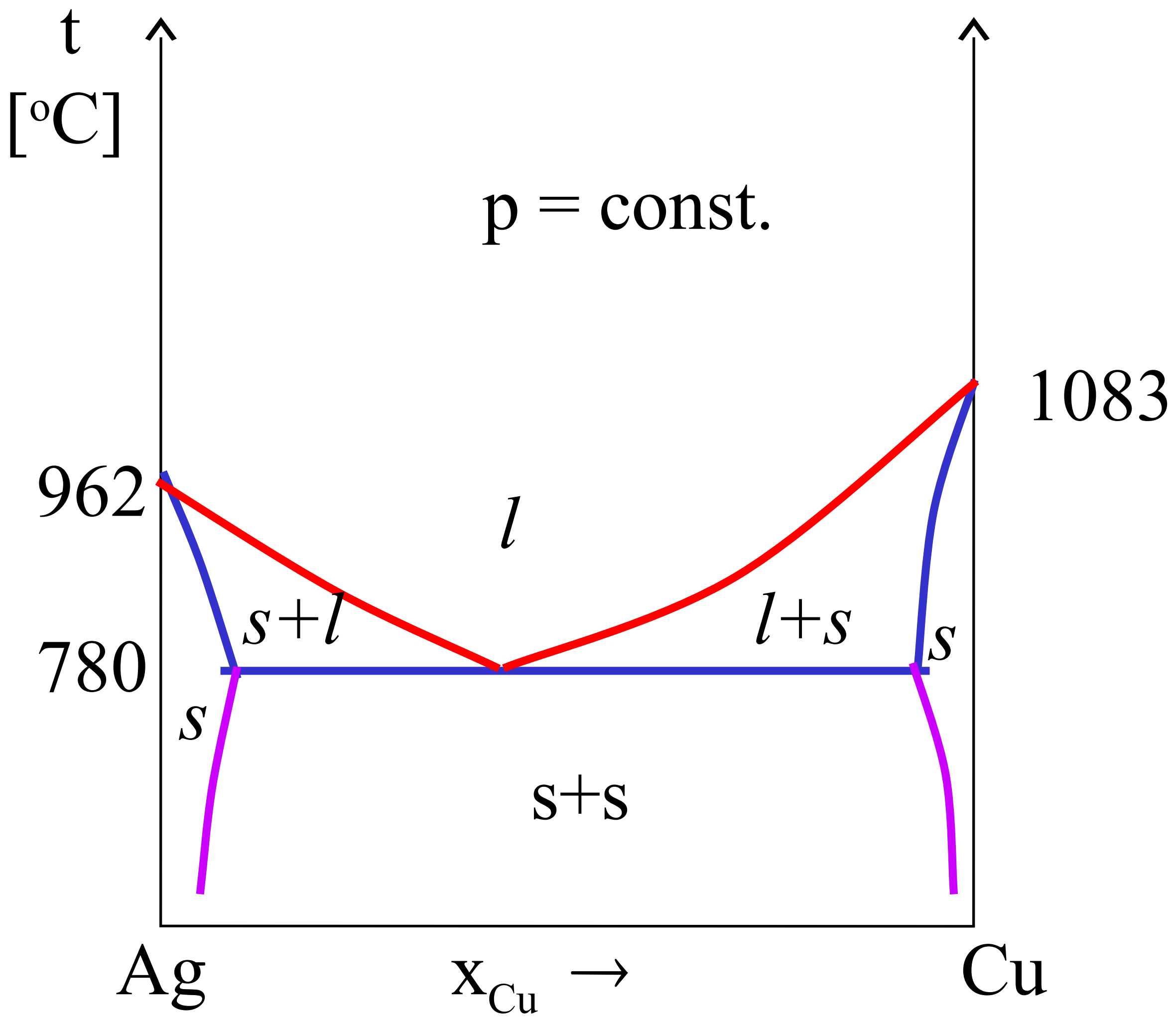
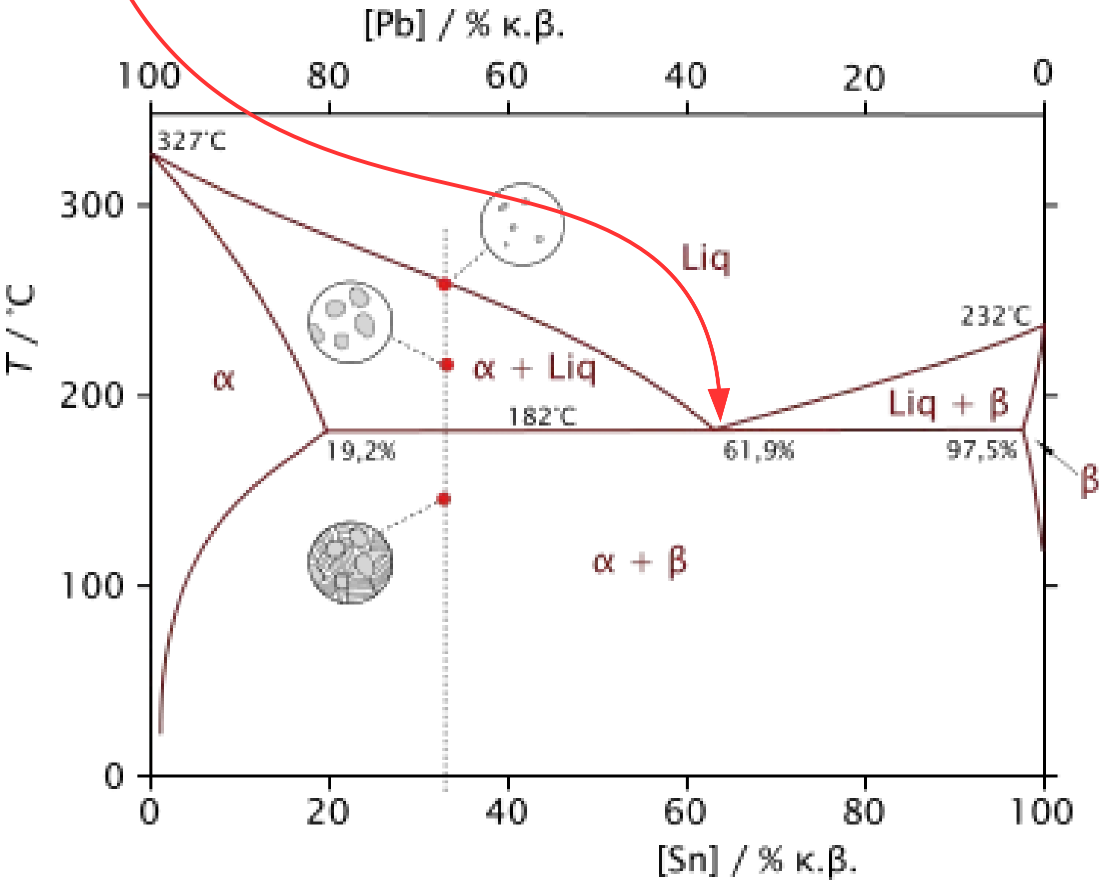
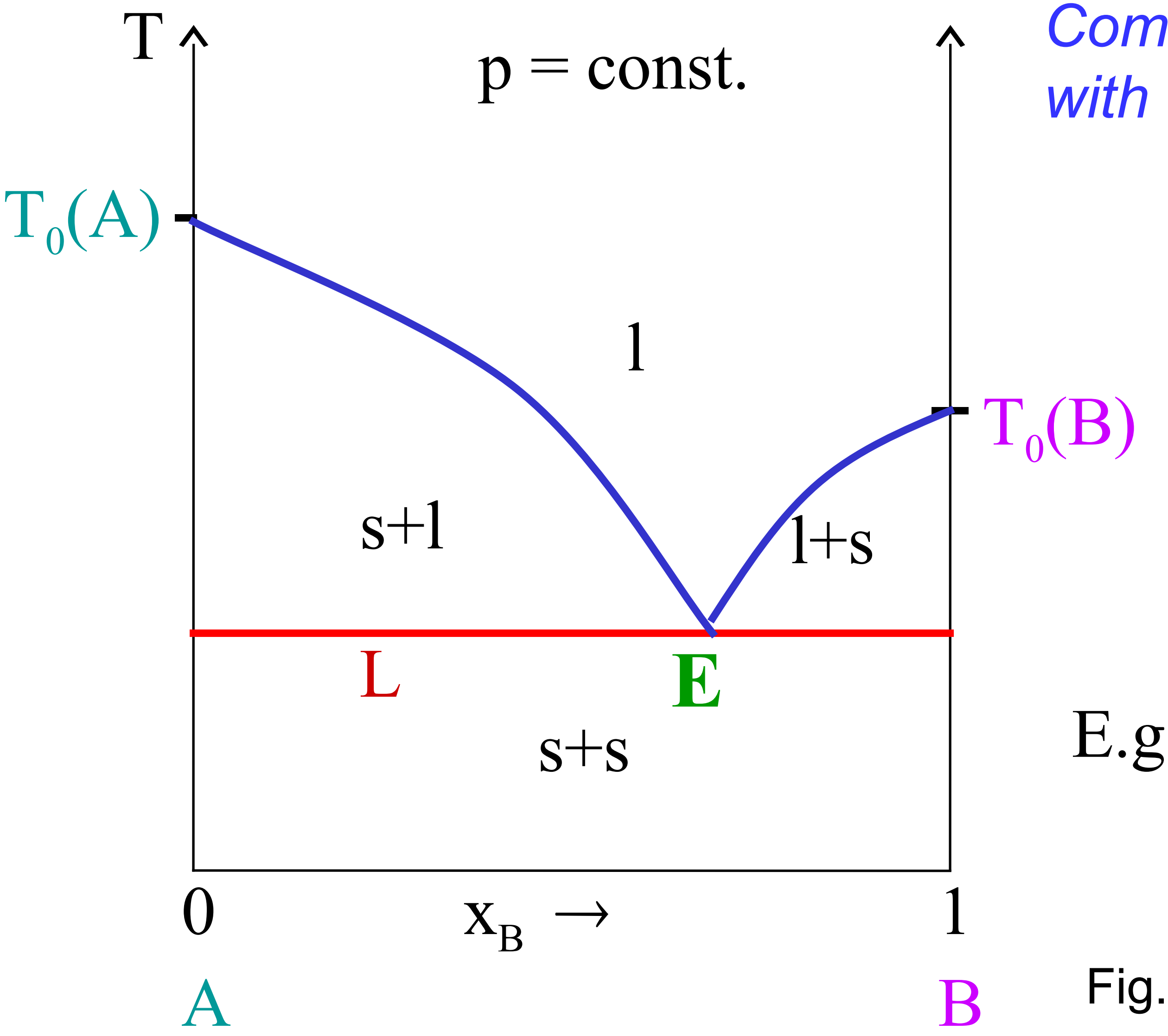


Fig.3.34

- E.g, alloys of lead and tin in soldering (process in which two or more metal surfaces are joined together by melting and putting a filler metal (solder) into the joint)



3. Complete immiscibility in solid state



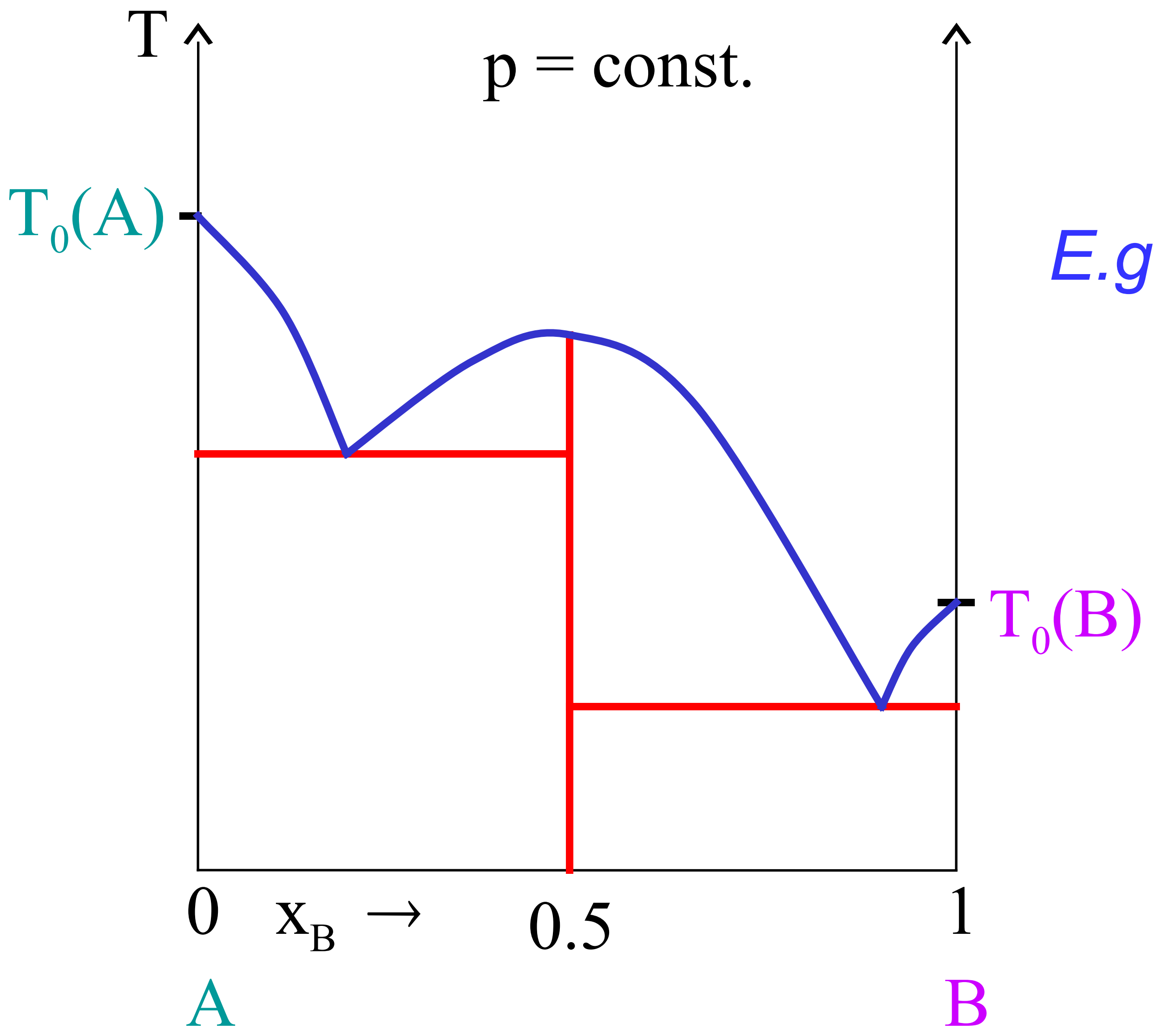
Compare Fig. 3.35 with Fig. 3.29

E.g. naphthalene-benzene

Fig. 3.35

4. Formation of compounds

A) Congruent melting

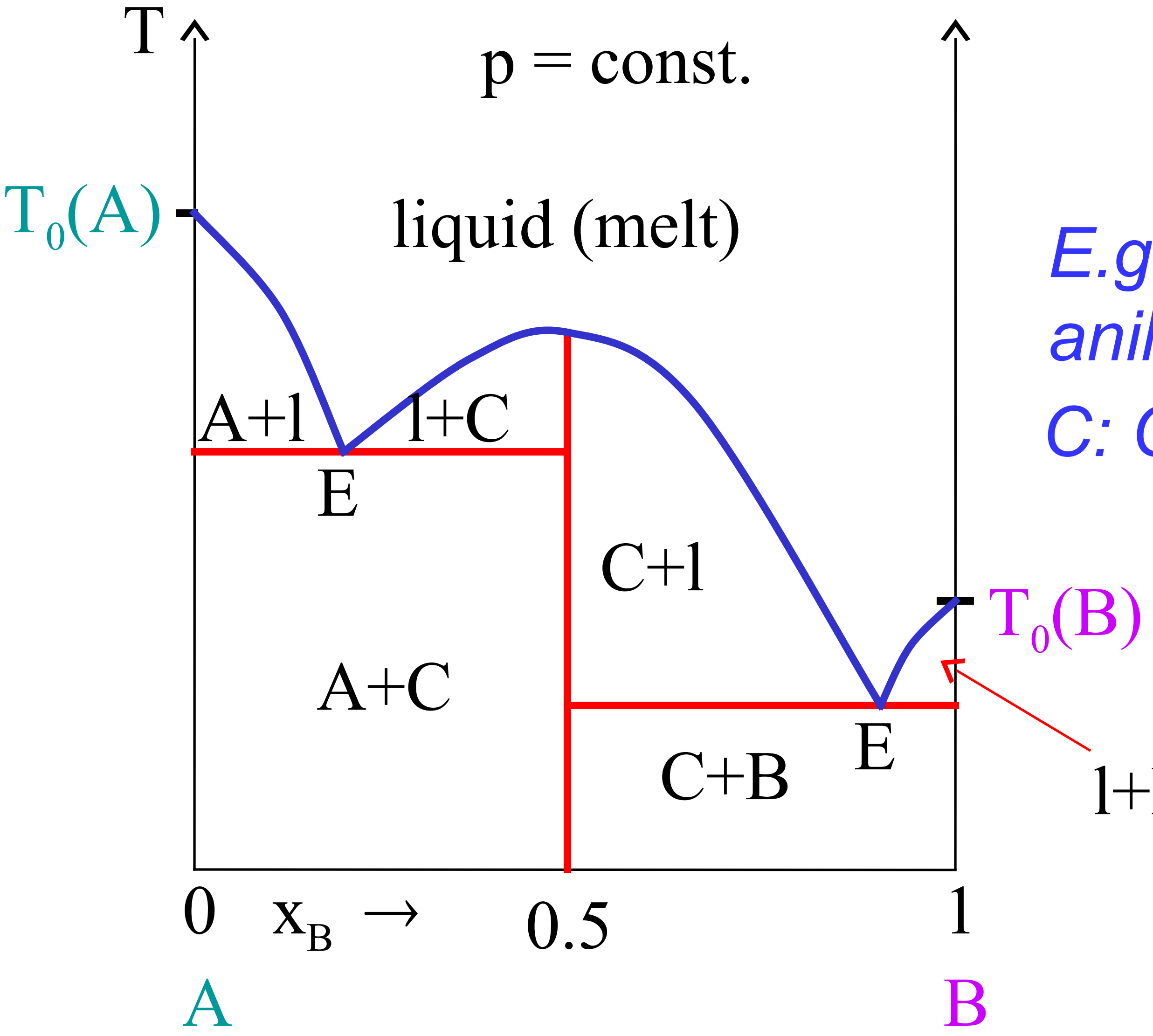


E.g. phenol-aniline

Fig. 3.36

Formation of compounds extended example

Congruent melting

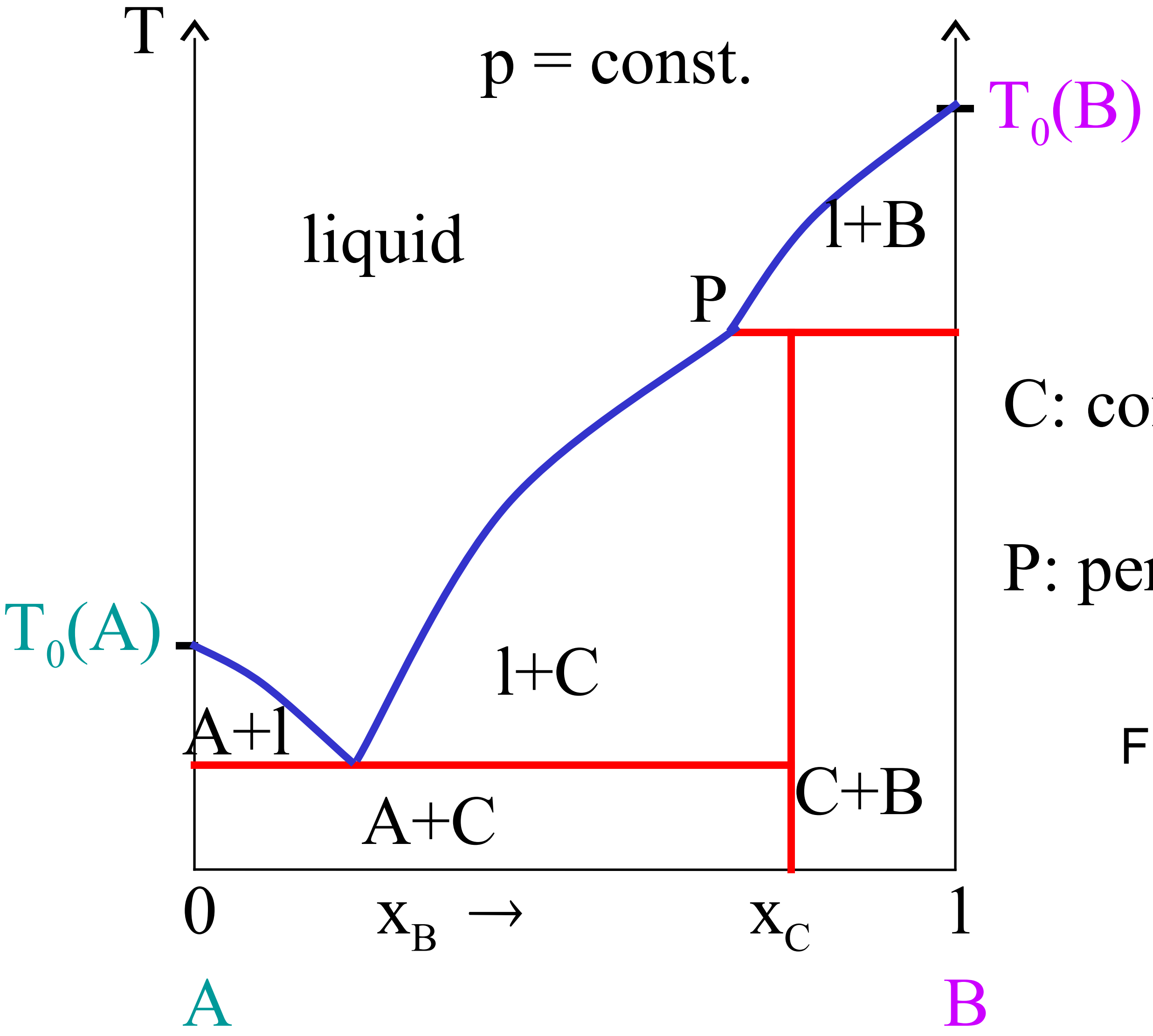


E.g. phenol(A)-aniline (B)

C: Compound

Fig. 3.37

B) Incongruent melting: decomposition during the melt



C: compound

P: peritectic point

Fig. 3.38

The compound C is stable in solid phase only. In liquid phase it decomposes.

By heating the compound of composition x_C, and reaching the peritectic temperature, the compound decomposes to a melt of peritectic composition and to pure solid compound B. Heating further B is gradually melting, as well.

If the melt of composition x_C is cooled, first pure B is precipitated and then, reaching the peritectic temperature, the crystals of the compound of composition x_C is formed (from the crystals of B and from the melt of peritectic composition).

Sodium-potassium incongruent melting: Formation of a compound during the cooling (here:Na_2K). Cooling Na(large amount) + K (small amount): Na deposits, then fromation of Na_2K (peritectic temperature), at last solid Na+Na_2K. Minimum is in the K-Na_2K region: eutectic point. The diagram contains two two-compound solid regions:

K+Na_2K and Na_2K+Na but Na_2K exists only in solid state.

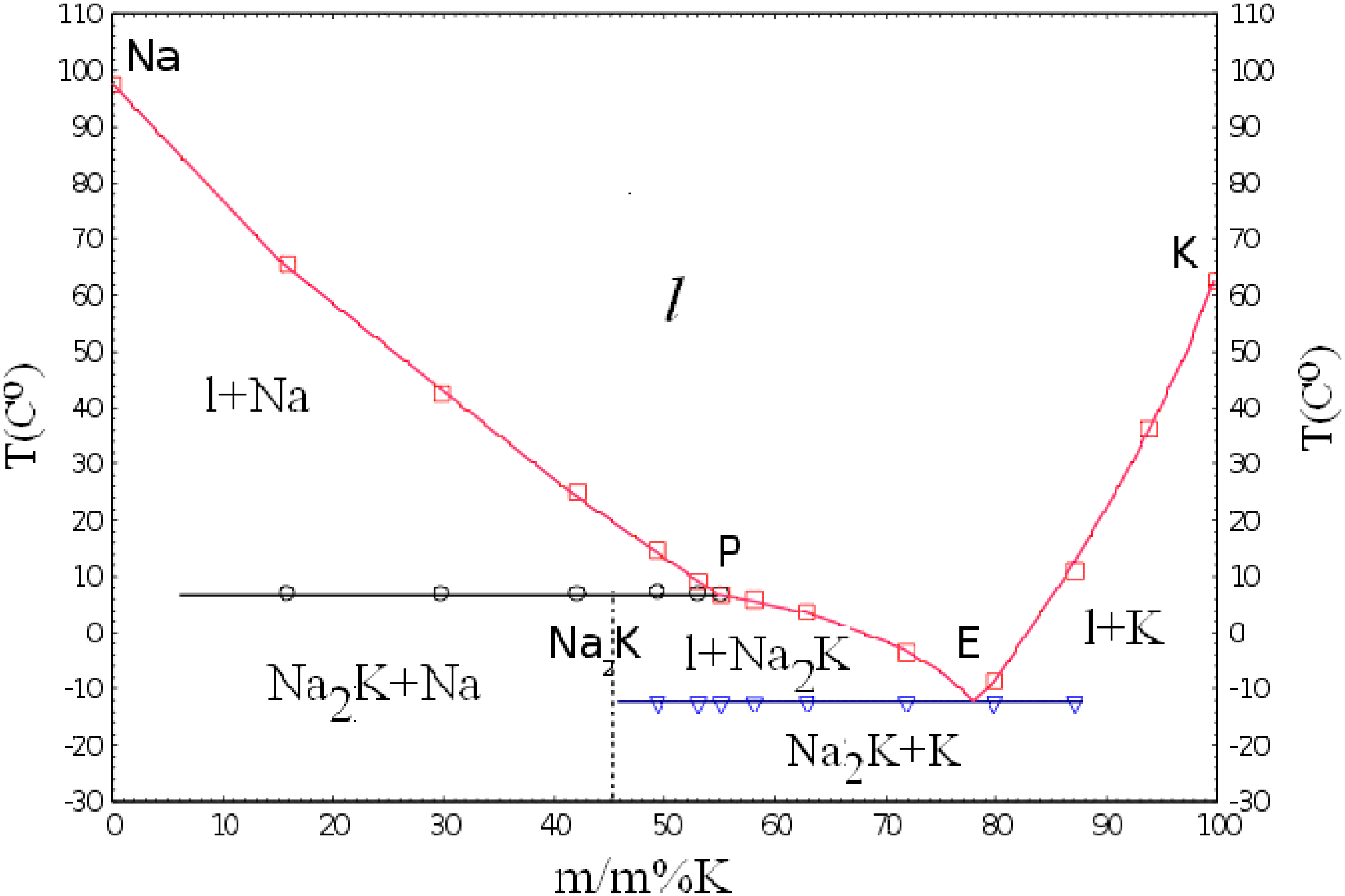


Fig. 3.39

Gold-aluminium phase diagram (no comment)