4. Advanced chemical thermodynamics

4.0 COLLIGATIVE PROPERTIES

Vapor pressure lowering: Subsection 4.1
Boiling point elevation: Subsection 4.1
Freezing point depression: Subsection 4.2
Osmotic pressure: Subsection 4.3

In dilute mixtures these quantities depend on the number and not the properties of the dissolved particles.

Colligative = depending on quantity

4.1.Vapor pressure lowering and boiling point elevation of dilute liquid mixtures

In a dilute solution Raoult´s law is valid for the solvent (See subsection 3.5)

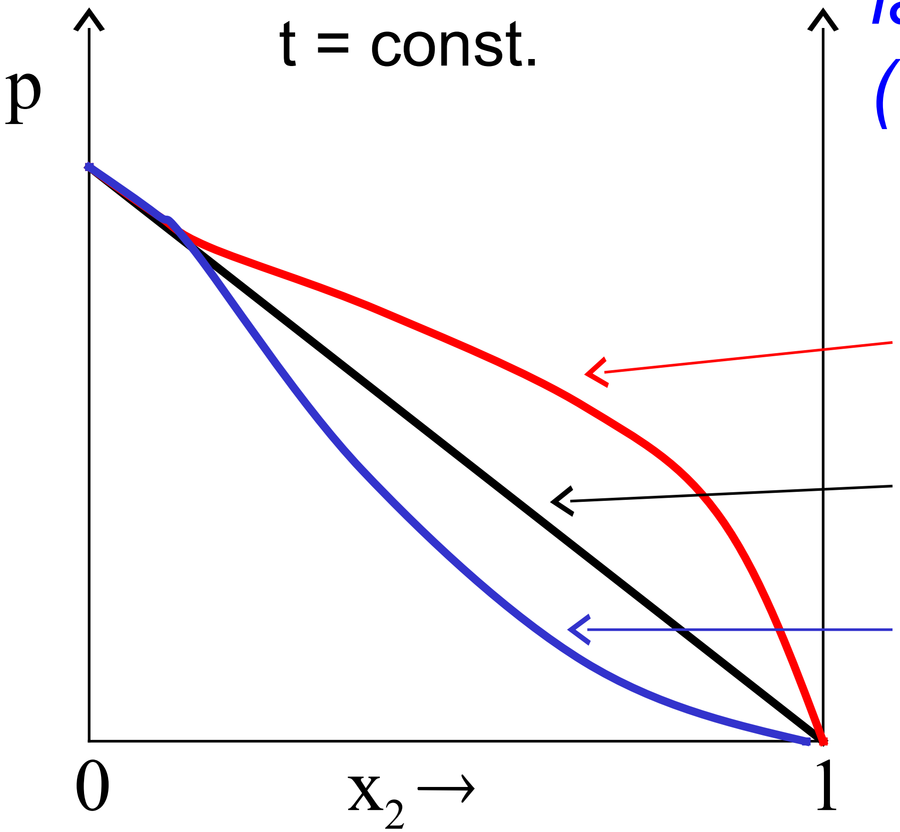


Fig. 4.1

Vapor pressure lowering (if component 2 is non-volatile)

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

$$x_2 = \frac{p_1^* - p_1}{p_1^*} \qquad (4.1)$$

(4.1) gives the relative vapor pressure lowering, see also (3.22)

Fig. 4.2: p-T diagram of the solvent and the solution (see also Fig. 2.4), ΔT_f freezing point lowering, ΔT_b boiling point elevation

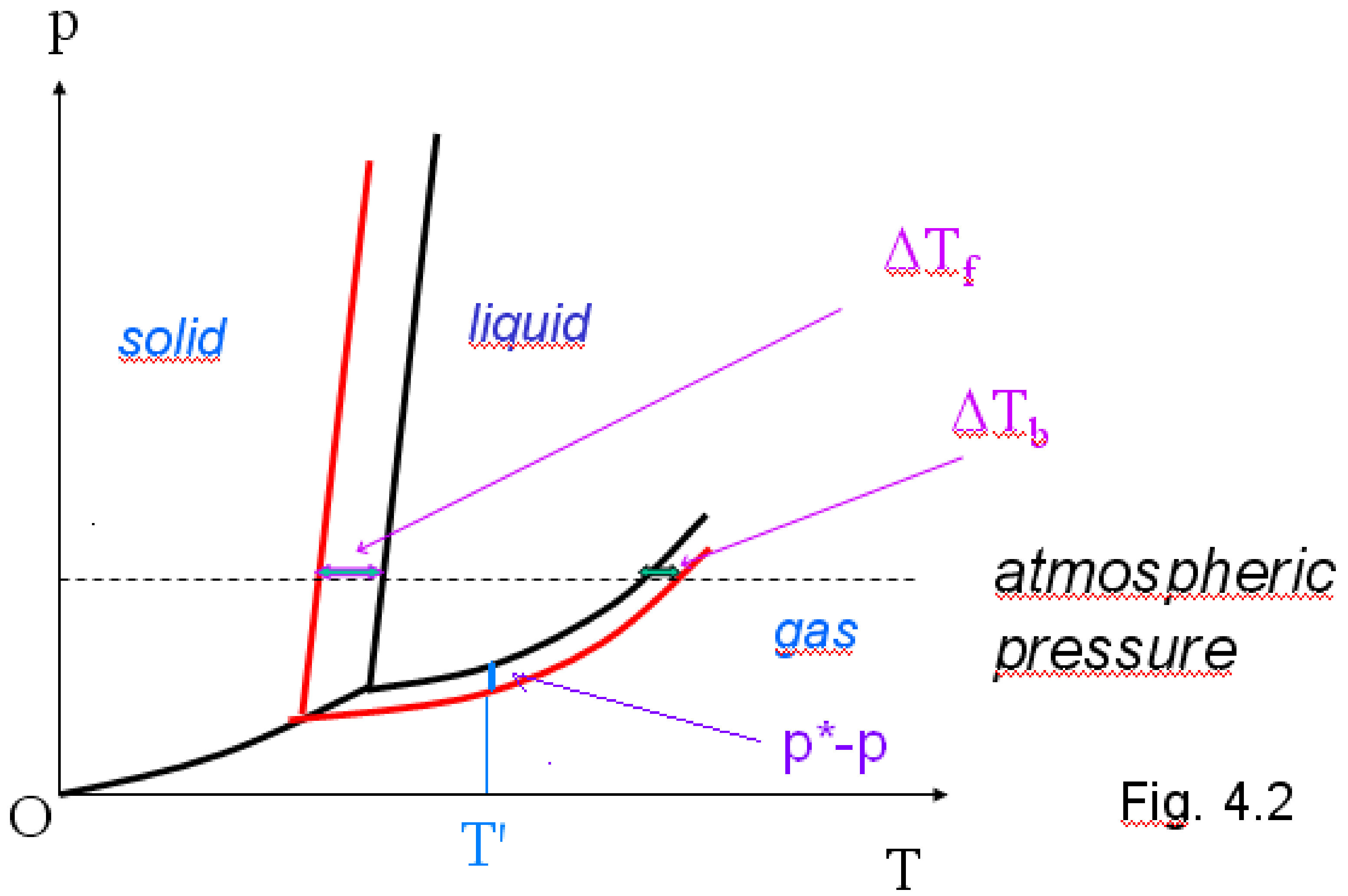


Fig. 4.2

Have a look on Fig. 4.2! There are compared the solvent (black curve) and the solution (red curve) properties in a p-T diagram.

The vapor pressure decreases in comparison of the p-T diagrams of the solvent and the solution. At a constant T' temperature the p-p is observable.*

The boiling point increases (ΔT_b). On the figure you can see it at atmospheric pressure.

In contrary to the behavor of the boiling point the freezing point decreases as effect of the solving (ΔT_f).

Understanding the boiling point elevation based on equivalence of the chemical potentials in equlibrium:

$$\mu_1(g) = \mu_1(l)$$

$$\mu_1^*(g) = \mu_1^*(l) + RT\ln x_1 \qquad (3.24)$$

Molar Gibbs functions

Dilute solution is ideal for the solvent

$$\frac{G_{m1}^*(g) - G_{m1}^*(l)}{RT} = \ln x_1 \qquad (4.2)$$

$$\frac{G^*_{m1}(g) - G^*_{m1}(l)}{RT} = \ln x_1$$

$G = H - TS$ $\quad$ $dG = Vdp - SdT$ $\Rightarrow$ $\left(\frac{\partial G}{\partial T}\right)_p = -S$ $\quad$ (2.19b)

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

$$\left(\frac{\partial \left(G/T\right)}{\partial T}\right)_p = \frac{T\left(\frac{\partial G}{\partial T}\right)_p - G}{T^2} = \frac{-TS - G}{T^2} = -\frac{H}{T^2} \qquad (4.3)$$

This is the Gibbs-Helmholtz equation, see (3.52).

$$\frac{\partial}{\partial T}\left(\frac{G^{*}_{m1}(g) - G^{*}_{m1}(l)}{RT}\right) = \frac{d\ln x_1}{dT}$$

$$\frac{H^{*}_{m1}(l) - H^{*}_{m1}(g)}{RT^2} = \frac{d\ln x_1}{dT}$$

$$\frac{d\ln x_1}{dT} = -\frac{\Delta H_{m1}(vap)}{RT^2}$$

(molar heat of vaporization)

Assume that the molar heat of vaporization is independent of temperature, and integrate from the boiling point of the pure component (T_b) to T.

$$\ln x_1 = \frac{\Delta H_{m1}(vap)}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) \qquad (4.4)$$

Substitute the mole fraction of the solute: $x_1 = 1 - x_2$

Take the power series of ln(1-x_2), and ignore the higher terms since they are negligible (x_2<<1)

$$\ln x_1 = \ln(1 - x_2) \approx - x_2 - \cancel{\frac{x_2^2}{2}} - \cancel{\frac{x_2^3}{3}} - \ldots$$

$$-x_2 = \frac{\Delta H_{m1}(vap)}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)$$

$$x_2 = \frac{\Delta H_{m1}(vap)}{R}\,\frac{T - T_b}{T \cdot T_b} \approx \frac{\Delta H_{m1}(vap)}{R}\,\frac{\Delta T}{T_b^2}$$

$$\Delta T = \frac{RT_b^2}{\Delta H_{m1}(vap)}\,x_2 \tag{4.5}$$

*In dilute liquid solutions molality (**m** = mol solute per kg solvent) or concentration (molarity) (**c** = mol solute per dm^3 solution) are used (instead of mole fraction).*

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{n_2 M_1}{mass\ of\ solvent} = m_2 M_1$$

m_2: *molality of solute*

M_1: *molar mass of solvent*

$$n_1 = \frac{mass\ of\ solvent}{M_1}$$

With this

$$\Delta T = \frac{R T_b^2 M_1}{\Delta H_{m1}(vap)} \cdot m_2 \qquad (4.6)$$

Includes the parameters of the solvent only: K_b

$$\boxed{\Delta T = K_b \cdot m_2} \qquad (4.7)$$

K_b: *molal boiling point elevation*

Examples:

K_b(water) = 0.51 K·kg/mol

K_b(benzene) = 2.53 K·kg/mol

Application: determination of molar mass
determination of degree of dissociation

These measurements are possible since the boiling point elevation depends on the number of dissolved particles.

4.2.Freezing point depression of dilute solutions

The equation of the freezing point curve in dilute solutions has the following form (see equation 3.53):

$$\ln x_1 = \frac{\Delta H_m(fus)}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \qquad (4.8)$$

x_1: mole fraction of solvent

$\Delta H_m(fus)$: molar heat of fusion of solvent

T_0: freezing point (melting point) of pure solvent

T: freezing point of solution

Since $\ln x_1 = \ln(1 - x_2) \approx - x_2$

We have from (4.8)

$$x_2 = \frac{\Delta H_m(fus)}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{\Delta H_m(fus)}{R}\frac{T_0 - T}{T \cdot T_0} \qquad (4.9)$$

Let $T_0 - T = \Delta T$, and $T \cdot T_0 \approx T_0^2$

And so we have from (4.9)

$$x_2 = \frac{\Delta H_m(fus)}{R}\frac{\Delta T}{T_0^2} \qquad (4.10)$$

The freezing point depression is

$$\Delta T = \frac{RT_0^2}{\Delta H_m(fus)} x_2 \qquad (4.11)$$

Since $x_2 \approx m_2 \cdot M_1$, we have

This multipier (K_f) contains solvent parameters only,

$$\Delta T = \frac{RT_0^2 M_1}{\Delta H_m(fus)} \cdot m_2 \qquad (4.12)$$

$$\boxed{\Delta T = K_f \cdot m_2} \qquad (4.13)$$

K_f is molal freezing point depression

The following examples are given in **molality** units

K_f(water) = 1.83 K·kg/mol

K_f(benzene) = 5.12 K·kg/mol

K_f(camphor) = 40 K·kg/mol

Molality unit: moles solute pro 1 kg solvent

4.3. Osmotic pressure

Osmosis: two solutions of the same substance with different concentrations are separated by a semi-permeable membrane (a membrane permeable for the solvent but not for the solute).

Then the solvent starts to go through the membrane from the more dilute solution towards the more concentrated solution.

Why ?

Because the chemical potential of the solvent is greater in the more dilute solution.

The „more dilute” solution may be a pure solvent, component 1.

The effect of osmotic pressure is illustrated on Fig. 4.3.

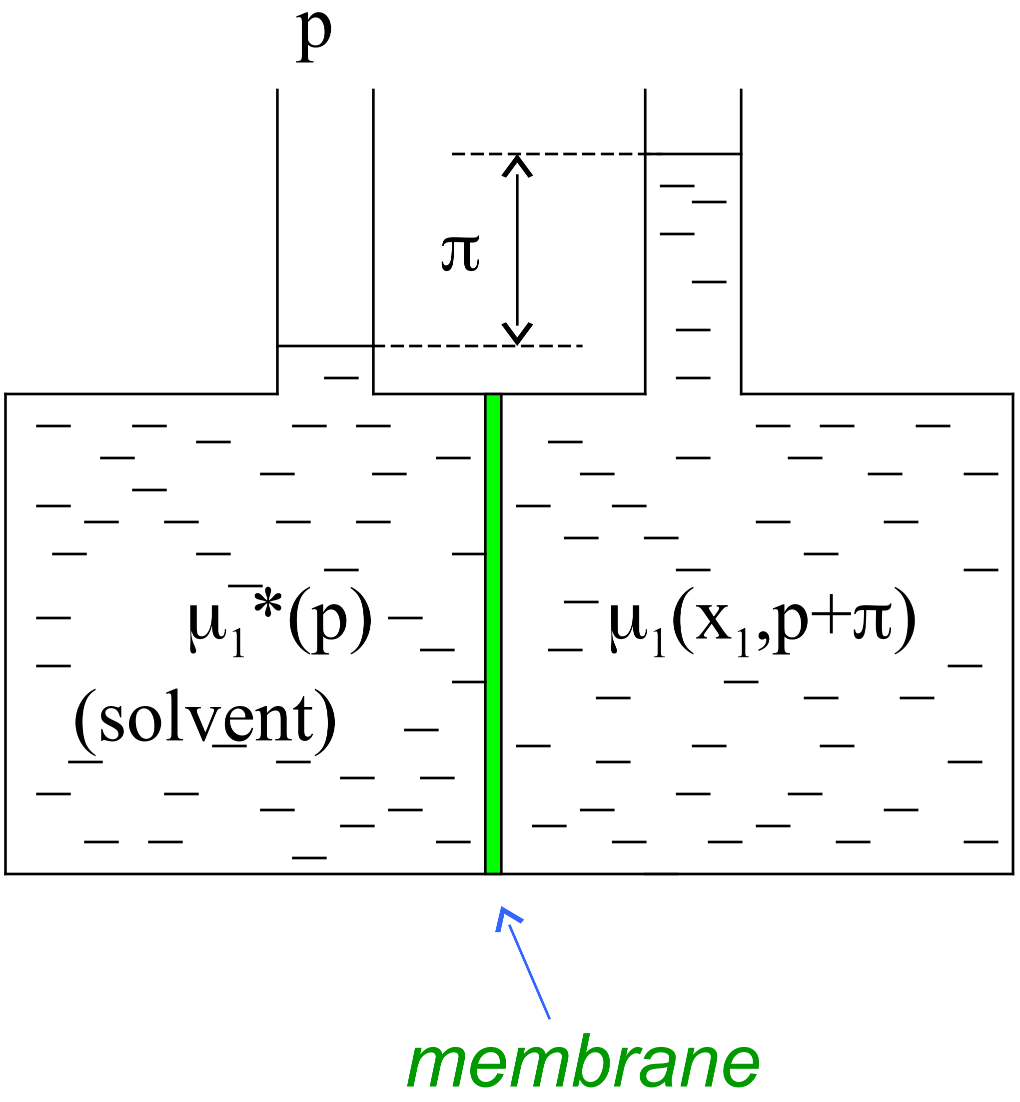


Fig. 4.3

If the more concentrated solution cannot expand freely, its pressure increases, increasing the chemical potential.

Sooner or later an equilibrium is attained. (The chemical potential of the solvent is equal in the two solutions.)

The measured pressure difference between the two sides of the semipermeable membrane is called **osmotic pressure (π)**.

What does osmotic pressure depend on?

van´t Hoff found (1885) for dilute solutions (solute:component 2)

$$\pi V = n_2 RT \quad (4.14)$$

(4.14) is similar to the ideal gas law, see equ. (1.27)

$$\pi = c_2 RT \quad (4.15)$$

Interpretation of Fig. 4.3.

The condition for equilibrium is

$$\mu_1^*(p) = \mu_1(p+\pi, x_2) \qquad (4.16)$$

The right hand side is the sum of a pressure dependent and a mole fraction dependent term:

$$\mu_1^*(p) = \mu_1^*(p+\pi) + \Delta\mu_1(x_1) \qquad (4.17)$$

The chemical potential of a pure substance (molar Gibbs function) depends on pressure

$$\cancel{\mu_1^*(p)} = \cancel{\mu_1^*(p)} + \left(\frac{\partial \mu_1}{\partial p}\right)_T \pi + \Delta\mu_1(x_1)$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$ For μ $$\left(\frac{\partial \mu_1}{\partial p}\right)_T = V_1$$ see (2.19b)

V_1 is the partial molar volume (see equ. 3.5). Its pressure dependence can be neglected. (The volume of a liquid only slightly changes with pressure), so the integral is only $V_1\pi$. So we have

$$0 = \pi V_1 + \Delta\mu_1(x_1)$$

Rearranged $$\boxed{\Delta\mu_1(x_1) = -\pi V_1} \qquad (4.18)$$

This equation is good both for ideal and for real solutions. Measuring the osmotic pressure we can determine μ (and the activity).

In an ideal solution: $\Delta\mu_1(x_1) = RT\ln x_1$ (3.24)

For dilute solution: $-\ln x_1 = -\ln(1-x_2) \approx x_2$

$$\pi V_1 = -RT\ln x_1 \approx RTx_2$$

$$\pi = \frac{RT}{V_1} x_2 = \frac{RT}{V_1} \frac{n_2}{n_1 + \cancel{n_2}} \qquad (4.19)$$

In a dilute solution

a) n_2 can be neglected beside n_1

b) V_1 approaches the molar volume of the pure solvent

c) the contribution of solute to the total volume can be neglected ($V^*_{m1} \cdot n_1 \approx V$).

With this restrictions the result is the van’t Hoff equation for the osmotic pressure, in forms

$$\pi = \frac{RT}{V} n_2 \qquad (4.20a)$$

$$\pi \cdot V = n_2 RT \qquad (4.20b)$$

The osmotic pressure is an important phenomenon in living organisms. Think on the cell – cell membrane – intercellular solution systems.

4.4 Enthalpy of mixing

Mixing is usually accompanied by change of energy.

Mixing processes are studied at constant pressure.

Heat of mixing (Q) = enthalpy of mixing

At constant pressure and constant temperature

$$Q_s = \Delta_{mix} H = H - (n_1 H^*_{m1} + n_2 H^*_{m2}) \qquad (4.21a)$$

$$Q_{ms} = \Delta_{mix} H_m = H_m - (x_1 H^*_{m1} + x_2 H^*_{m2}) \qquad (4.21b)$$

$$H_m = \frac{H}{n_1 + n_2}$$ (molar enthalpy of solution)

Molar heat of mixing (called also integral heat of solution, and molar enthalpy of mixing)

is the enthalpy change when 1 mol solution is produced from the components

at constant temperature and pressure.

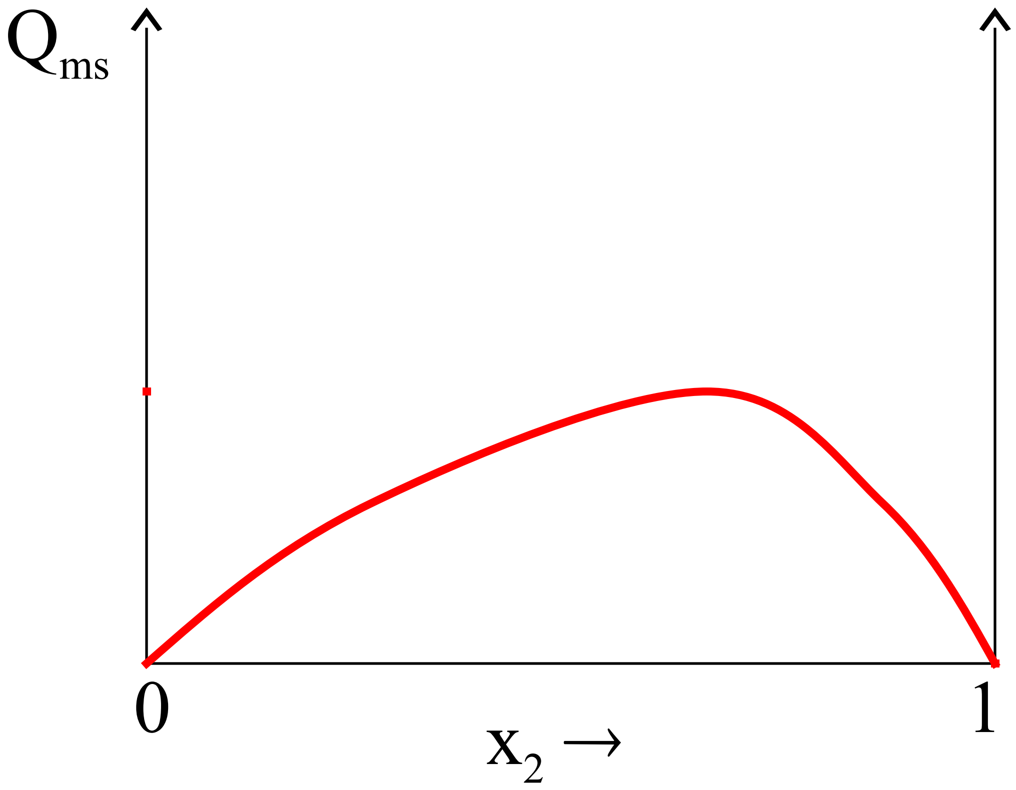
In case of ideal solutions the enthalpy is additive, $Q_{ms} = 0$, if there is no change of state.

In real solutions Q_{ms} (molar heat of fusion) is not zero. The next figures present the deviations from the ideal behavior.

Real solution with positive deviation (the attractive forces between unlike molecules are smaller than those between the like molecules).

$Q_{ms} > 0$ *In an isothermal process we must add heat.*

In an adiabatic process the mixture cooles down.



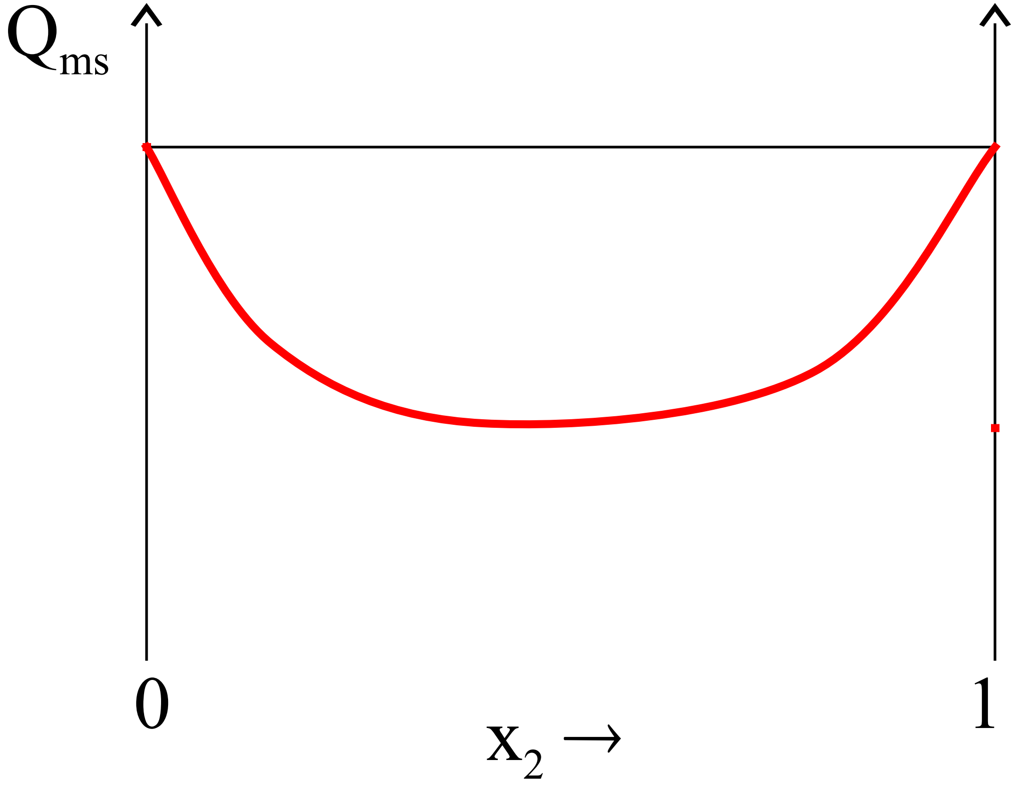
Endothermic process, see section 3.1.

Fig. 4.4

Real solution with negative deviation (the attractive forces between unlike molecules are greater than those between the like molecules).

Q_{ms} < 0 *In an isothermal process we must distract heat.*

In an adiabatic process the mixture warmes up.



Exothermic process, see section 3.1.

Fig. 4.5.

Differential heat of solution is the heat exchange when one mole of component is added to infinite amount of solution at constant temperature and pressure.

Therefore the differential heat of solution is the partial molar heat of solution:

$$Q_{m1} = \left(\frac{\partial Q_s}{\partial n_1} \right)_{p,T,n_2} \qquad Q_{m2} = \left(\frac{\partial Q_s}{\partial n_2} \right)_{p,T,n_1} \qquad (4.22)$$

The determination of the differencial heats of solution is possible e.g. with the method of intercepts, Fig. 4.6 (see also e.g. Fig. 3.8):

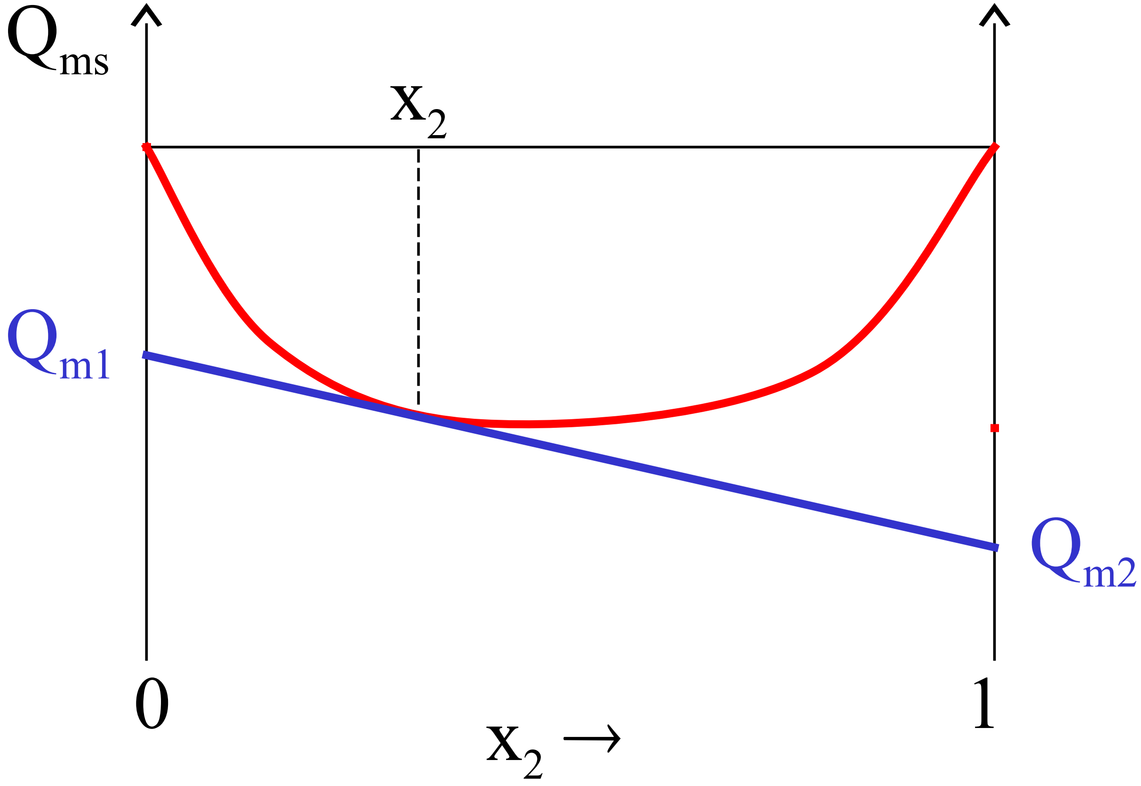


Fig. 4.6

Explanation to Fig. 4.6. [Like (3.2)]:

$$Q_s = H - (n_1 H^*_{m1} + n_2 H^*_{m2})$$

Differentiating with respect to the amount:

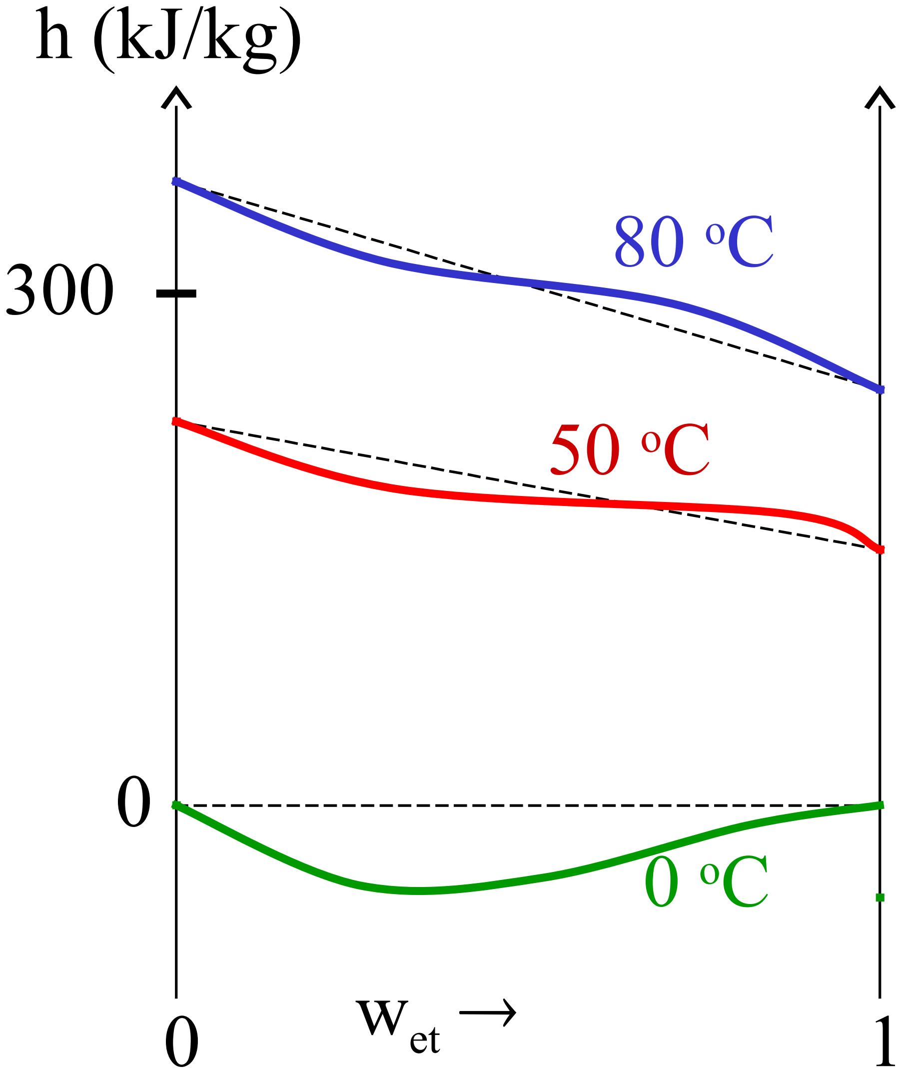
$$Q_{m1} = \left(\frac{\partial H}{\partial n_1}\right)_{p,T,n_2} - \frac{\partial}{\partial n_1}(n_1 H^*_{m1} + n_2 H^*_{m2})$$

$$\boxed{Q_{m1} = H_{m1} - H^*_{m1}} \qquad (4.23)$$

The differencial heat of solution is equal to the partial molar enthalpy minus the enthalpy of pure component.

Enthalpy diagrams: the enthalpy of solution is plotted as the function of composition at different temperatures. These diagrams can be used for the calculation of the heat effects of the solutions.

Fig. 4.7 is a model of a solution enthalpy diagram, the ethanol - water system. Technical units are used!



Compare Fig. 4.7 with Fig. 3.2!

Fig. 4.7

(w: weight fraction)

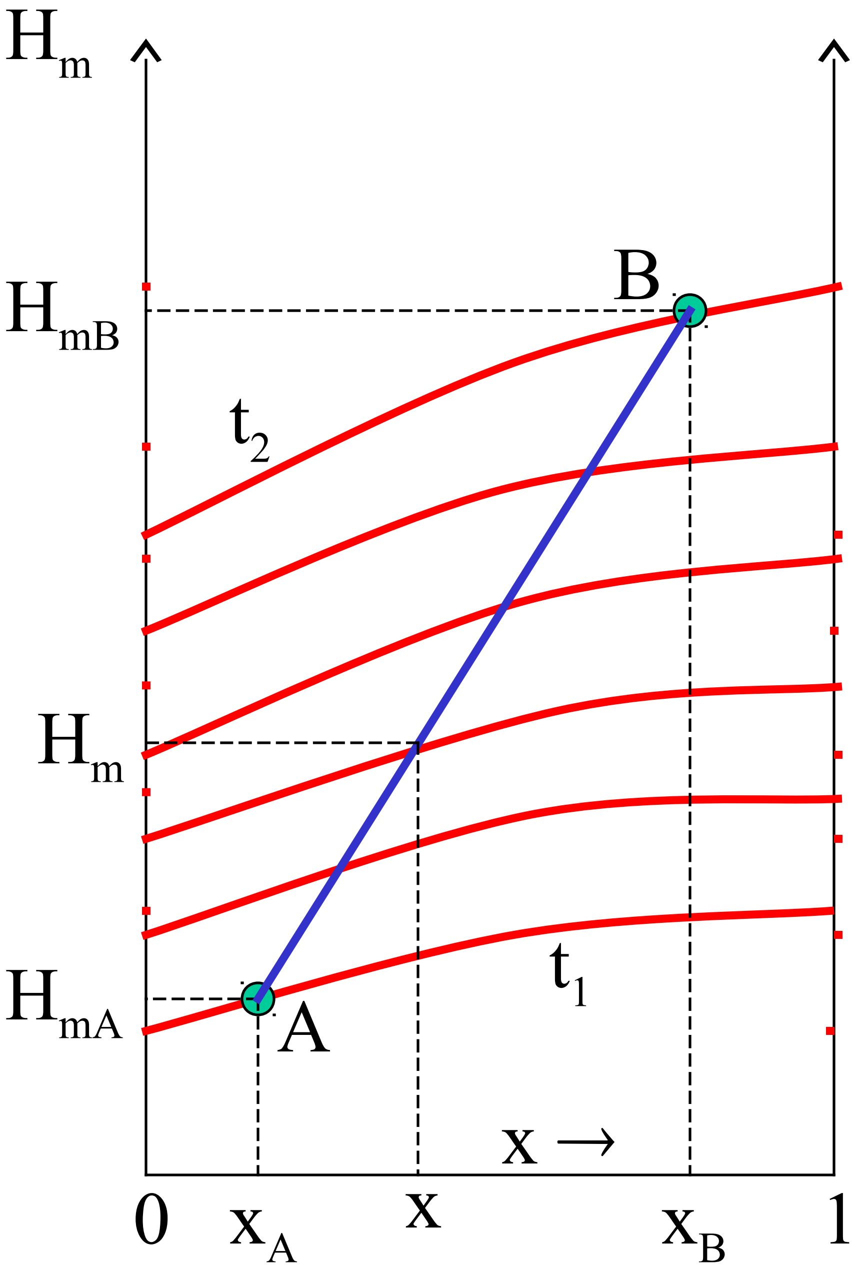
Isothermal mixing: we are on the same isotherm before and after mixing.(see Fig. 4.8). According to (3.2) we have

$$Q_s = (m_1+m_2)h - (m_1h_1+m_2h_2) \qquad (4.24)$$

h, h_1, h_2 can be read from the diagram, using the tangent.

Adiabatic mixing: the point corresponding to the solution is on the straight line connecting the two initial states (see Fig. 4.9). Abbreviatons to the figure:

the mole fraction of the selected component is denoted by x, A an B are the initial solutions: x_A, H_{mA} x_B, H_{mB}, $n_A = n - n_B$.



Material balance:

$$(n-n_B)x_A+n_Bx_B = nx$$ and

$$(n-n_B)H_{mA}+n_BH_{mB} = nH_m$$

Rearranging these equations:

$$n_B(x_B - x_A) = n(x - x_A)$$

$$n_B(H_{mB}-H_{mA}) = n(H_m-H_{mA})$$

Dividing these equations by one another

$$\frac{H_{mB} - H_{mA}}{x_B - x_A} = \frac{H_m - H_{mA}}{x - x_A} \qquad (4.25)$$

(4.25) is a linear equation

Fig. 4.9

At last we have

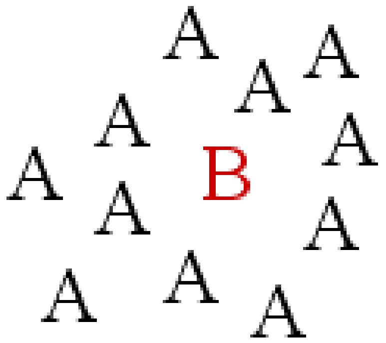
$$H_m - H_{mA} = \frac{H_{mB} - H_{mA}}{x_B - x_A} \cdot (x - x_A) \qquad (4.26)$$

This is a straight line crossing the points (x_1,y_1) and (x_2,y_2) like the algebraic equation

$$y - y_1 = \frac{y_2 - y_1}{x_2 - x_1} \cdot (x - x_1)$$

4.5 Henry's law

In a very dilute solution every dissolved molecule is surrounded by solvent molecules:



A: solvent

B: solute

Fig. 4.10

If a further solute molecule is put into the solution, it will also be surrounded by solvent molecules. It will get into the same molecular environment. So the vapor pressure and other macroscopic properties will be proportional to the mole fraction of the solute: Henry's law.

Henry's law is valid for low mole fractions. Fig 4.11, observe deviations!

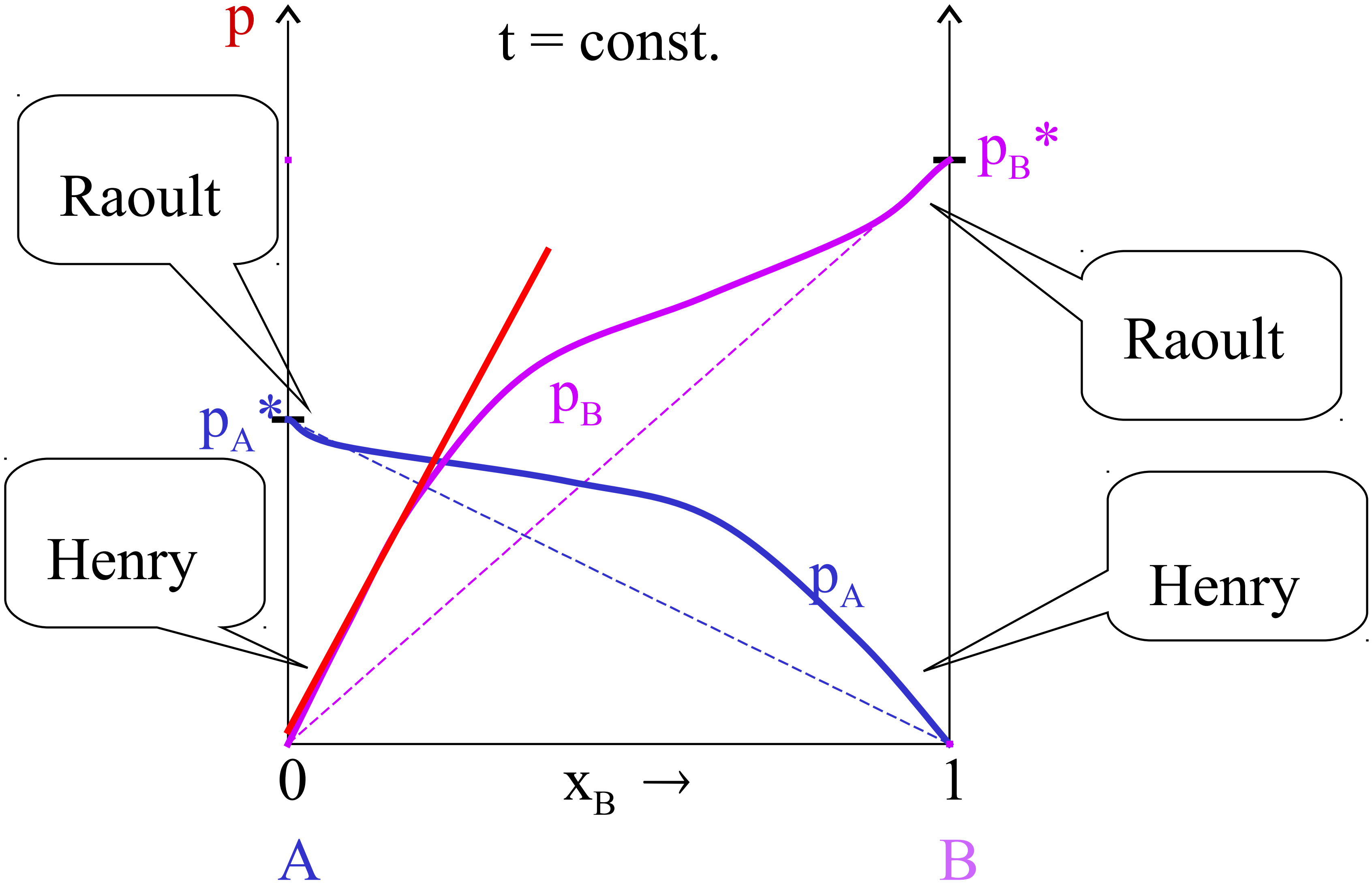


Fig. 4.11

Where component B is the solute, the left hand side of Fig. 4.11):

$$p_B = k_H \cdot x_B \qquad (4.27)$$

k_H *is the Henry constant*

In the same range the Raoult´s law applies to the solvent:

$$p_A = p_A^* \cdot x_A \qquad \text{like } (3.18)$$

The two equations are similar. There is a difference in the constants. p_A^* *has an exact physical meaning (the vapor pressure of pure substance) while* k_H *does not have any exact meaning.*

In a dilute solution the Raoult´s law is valid for the solvent and Henry´s law is valid for the solute.

4.6 Solubility of gases

The solution of gases in liquids are generally dilute, so we can use Henry´s law.

The partial pressure of the gas above the solution is proportional to the mole fraction in the liquid phase.

Usually the mole fraction (or other parameter expressing the composition) is plotted against the pressure. If Henry´s law applies, this function is a straight line. See e.g. the solubilty of some gases on Fig. 4.12!

The solubility of some gases in water at 25 °C

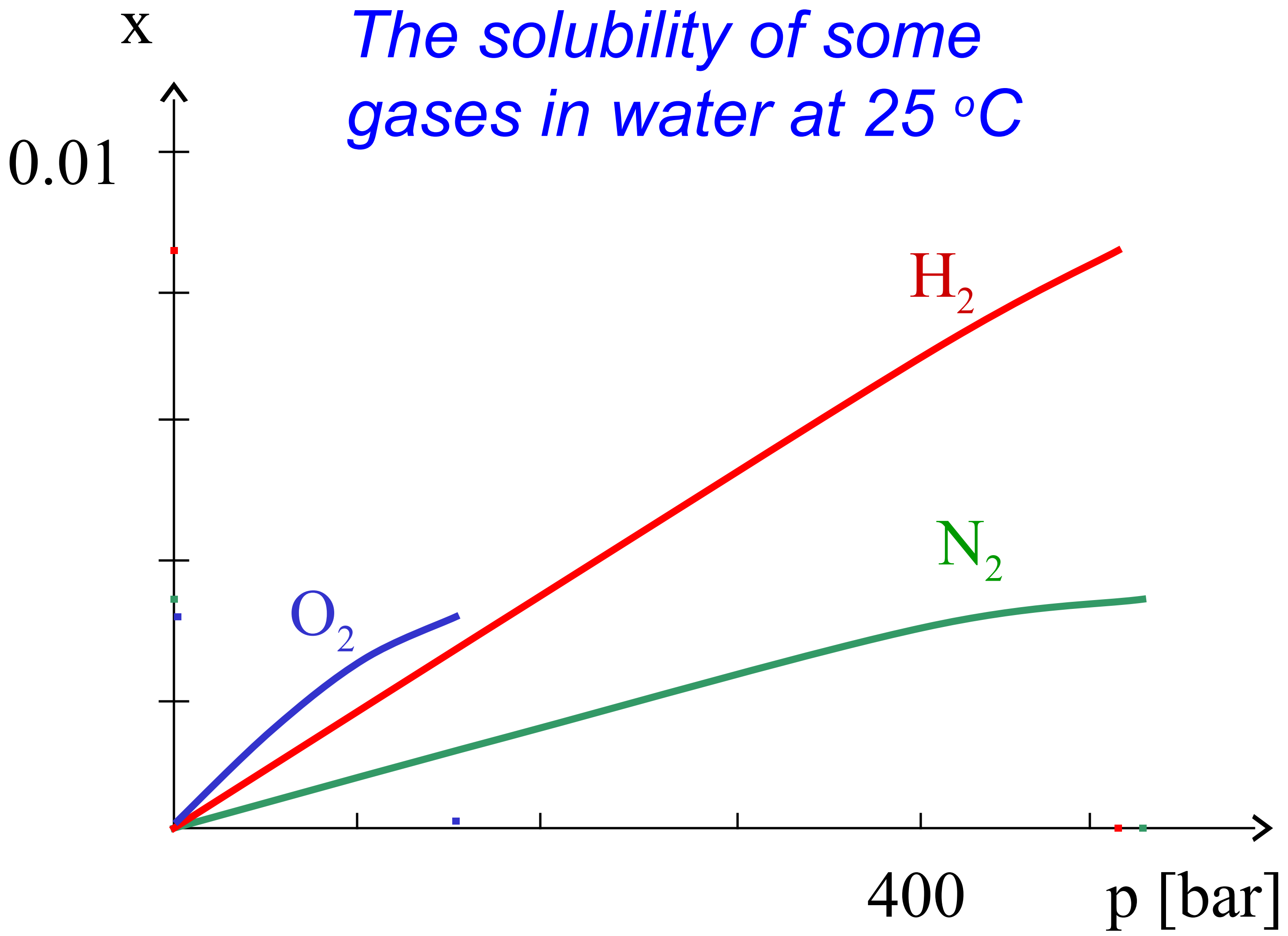


Fig. 4.12

In case of N_2 and H_2 the function is linear up to several hundred bars (Henry´s law applies), in case of O_2 the function is not linear even below 100 bar.

Absorption - desorption

Temperature dependence of solubility of gases

Le Chatelier´s principle: *a system in equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect.*

Solution of a gas *is a change of state: gas → liquid. It is usually an exothermic process.*

Increase of temperature*: the equilibrium is shifted towards the endothermic direction → desorption.*

The ***solubility of gases*** *usually decreases with increasing the temperature.*

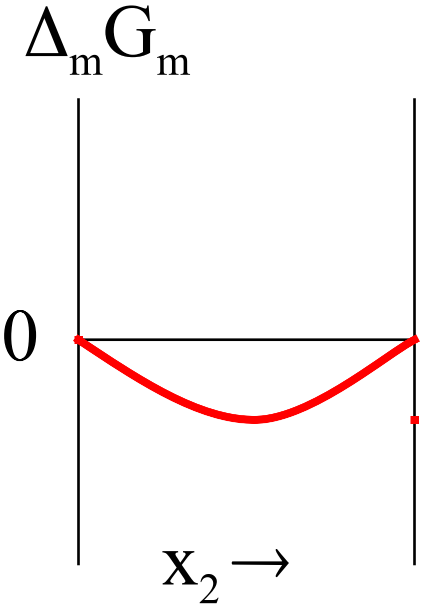
4.7 Thermodynamic stability of solutions

One requirement for the stability is the negative Gibbs function of mixing.

The negative Gibbs function of mixing does not necessary mean solubility (see Fig. 4.13d diagram of the next figure).

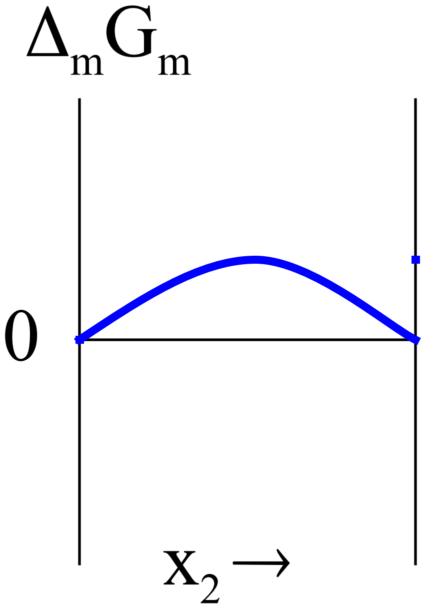
Other requirement: The second derivative of the Gibbs free energy of mixing with respect to composition must be positive.

Some examples of the dependence of molar Gibbs free energy as a function of mole fraction



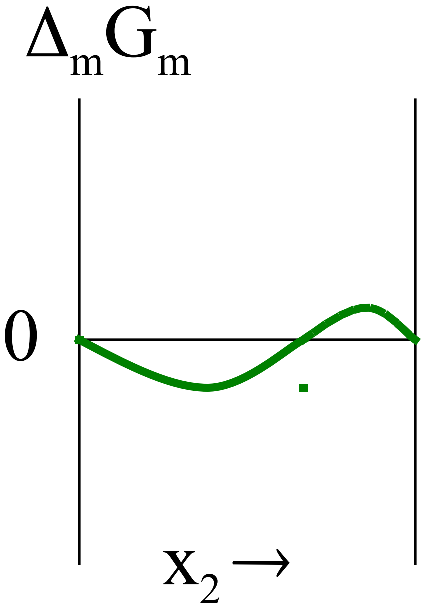
Complete miscibility

Fig. 4.13a



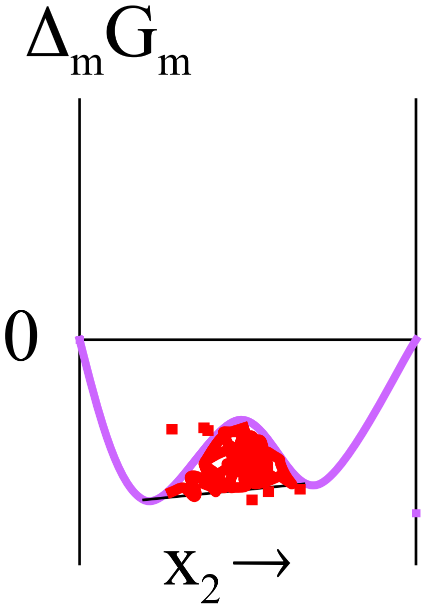
Complete immiscibility

Fig. 4.13b



Partial solubility

Fig. 4.13c



Partial miscibility

Fig. 4.13d

The conditions for stability:

1. $$\Delta_{mix} G_m < 0 \qquad (4.28)$$

2. $$\left(\frac{\partial^2 \Delta_{mix} G_m}{\partial x^2} \right)_{T,p} > 0 \qquad (4.29)$$

Partial miscibility *(diagram 4.13d).*

Chemical potential: partial molar Gibbs function.

Remember! Partial molar quantity of Gibbs function of mixing is the change of chemical potential when mixing takes place: $\Delta\mu_1$, $\Delta\mu_2$. The chemical potential of a component must be the same in the two phases.

Partial miscibility. At the marked points the second derivative changes it sign from negative to positive, according to the requirements of (4.29).

Phase rich in 2

Phase rich in 1

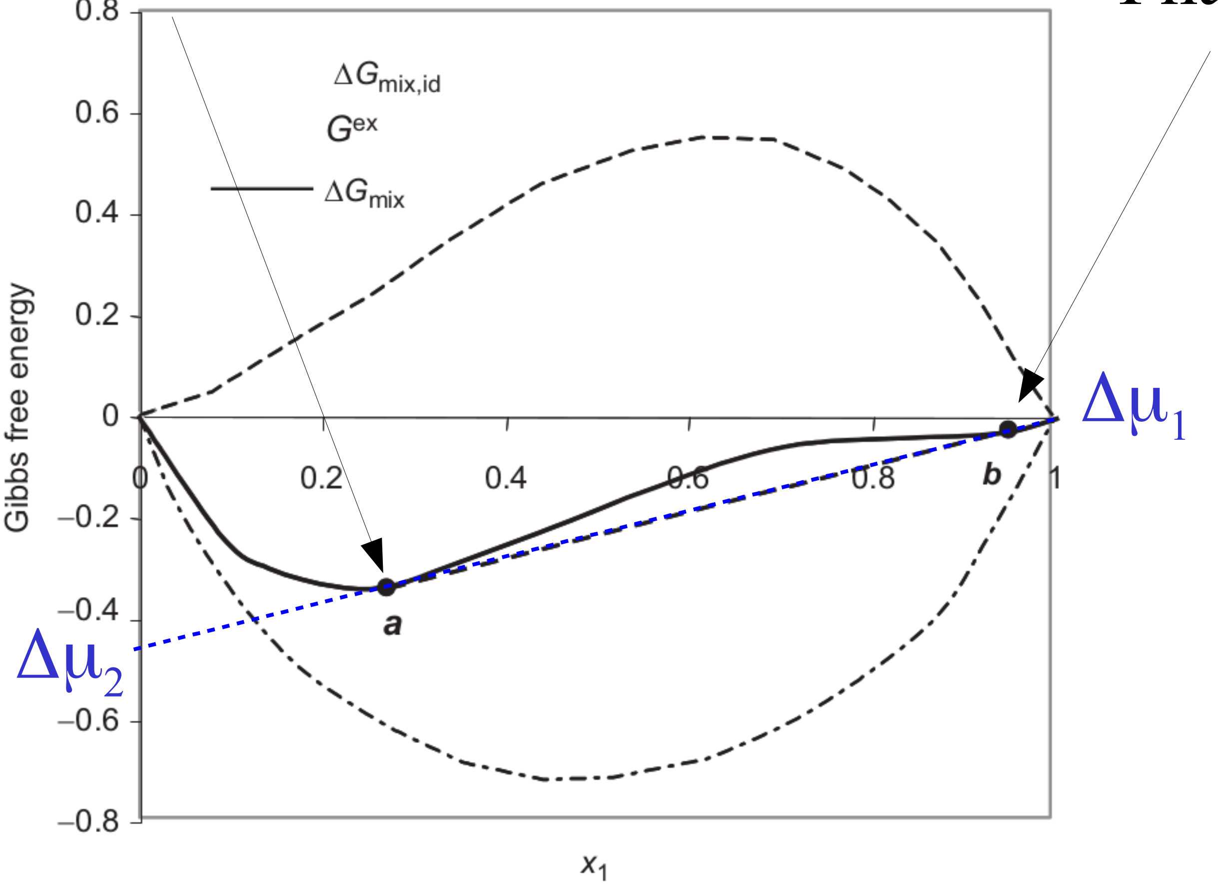


Fig. 4.14

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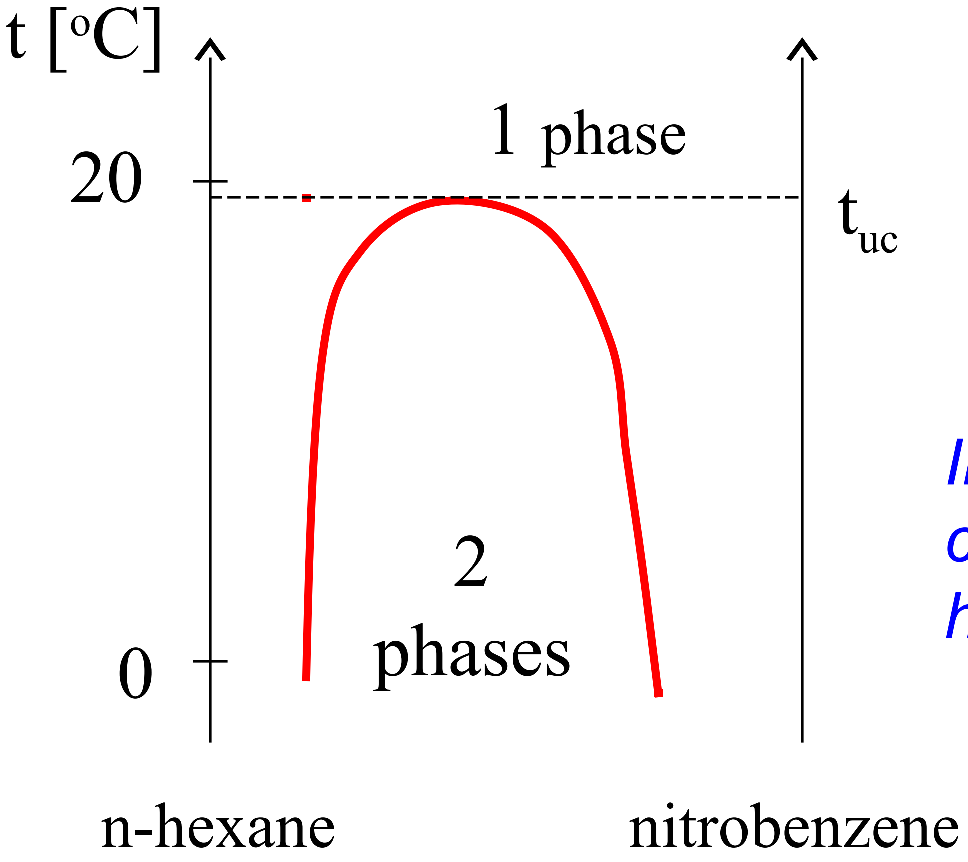
$\Delta\mu_1$ must be the same in the phase rich in 1 as in the phase rich in 2 according to ther requirement of equilibrium. The same applies to $\Delta\mu_2$.

The common tangent of the two curves produces $\Delta\mu_1$ and $\Delta\mu_2$ (method of intercepts). Fig. 4.14.

4.8. Liquid - liquid phase equilibria

The mutual solubility depends on temperature.

In most cases the solubility increases with increasing temperature.



t_{uc} : upper critical solution temperature

u: upper

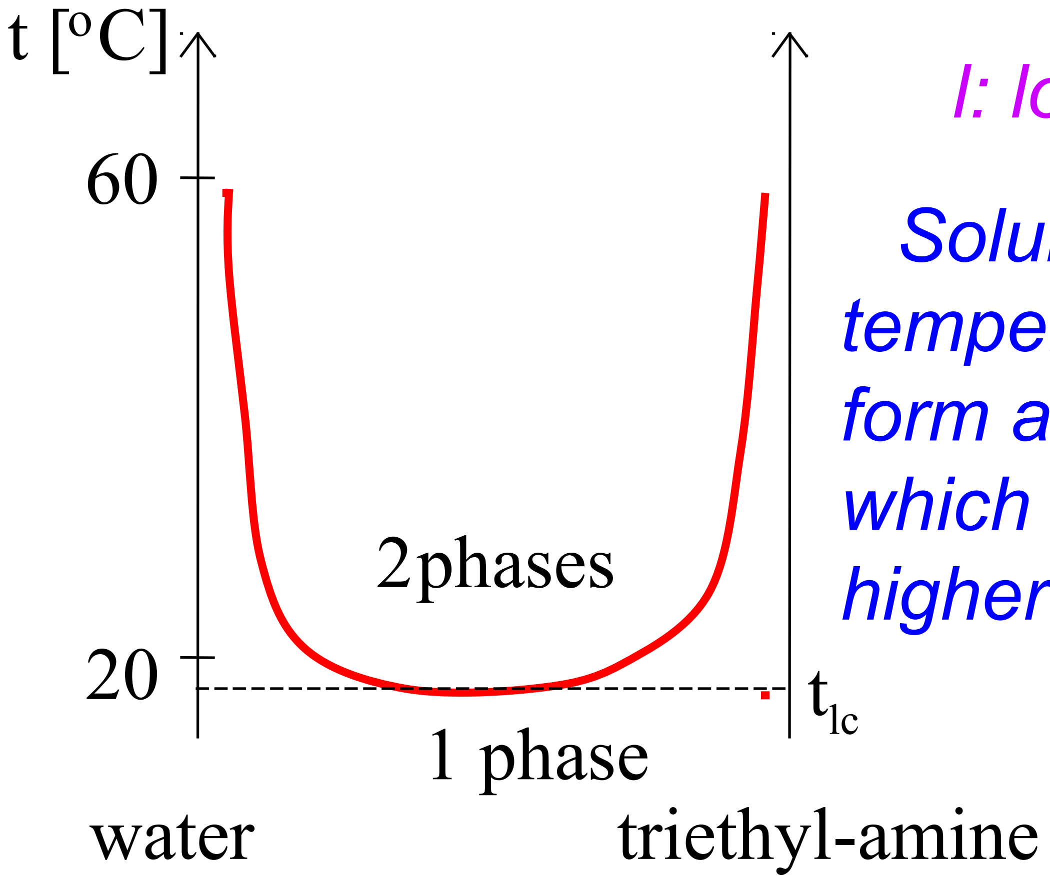
In this case the formed complex decomposes at higher temperatures.

Fig. 4.15

Sometimes the mutual solubility increases with decreasing temperature.

t_{lc} : lower critical solution temperature

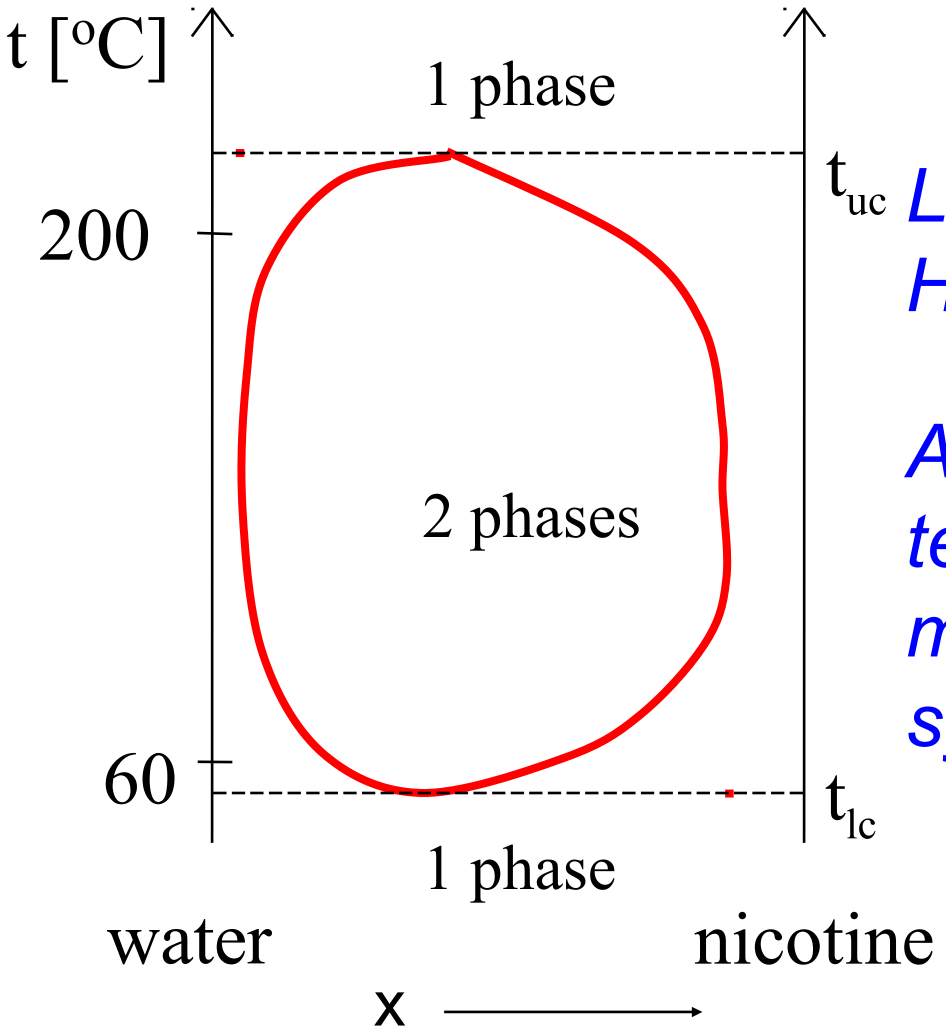
l: lower



Solubility is better at low temperature because they form a weak complex, which decomposes at higher temperatures.

Fig. 4.16

In a special case there are both upper and lower critical solution temperatures.



Low t: weak complexes
Higher t: they decompose

At even higher temperatures the thermal motion homogenizes the system.

Fig, 4.17

4.9 Distribution equilibria

We discuss the case when a solute is distributed between two solvents, which are immiscible.

In equilibrium the chemical potential of the solute is equal in the two solvents (A and B).

$$\mu_i^B = \mu_i^A \qquad (4.30)$$

The chemical potential can be expressed as

$$\mu_i = \mu_i^0 + RT \ln a_i$$

See (3.25)

The activity can be expressed in terms of concentration:

$$a_i = {}^{c}\gamma_i \frac{c_i}{1\,mol/dm^3} \qquad (4.31)$$

See later: "4.11 Activities and standard states"

In this case (when the activites are expressed through the concentration) the standard chemical potential depends on the solvent, too.

$$\mu_i^{0B} + RT\ln a_i^B = \mu_i^{0A} + RT\ln a_i^A \qquad (4.32)$$

Solvent dependent quantities!!!

$$\ln a_i^B - \ln a_i^A = \frac{\mu_i^{0A} - \mu_i^{0B}}{RT}$$

$$\ln \frac{a_i^B}{a_i^A} = \frac{\mu_i^{0A} - \mu_i^{0B}}{RT}$$

The quantities on the right hand side depend on temperature only (i.e. they do not depend on composition).

$$\ln \frac{a_i^B}{a_i^A} = C \longrightarrow \frac{a_i^B}{a_i^A} = K \qquad (4.33)$$

K: *distribution constant (depends on T only).*

In case of dilute solutions (Henry range) we can use concentrations instead of activities.

$$\frac{c_i^B}{c_i^A} = K_c \qquad (4.34)$$

K_c: *distribution constant in terms of concentration*

Processes based on distribution are called ***extraction****.*

Calculation of the efficiency of extraction in a lab

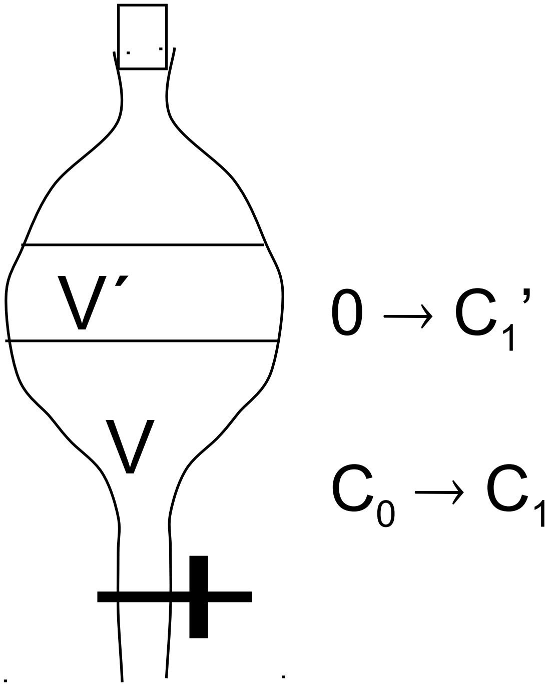


Fig. 4.18

We assume that the solutions are dilute and their volume does not change during extraction. (The two solvents do not dissolve each other at all: Fig. 4.18).

Material balance for the component to be extracted:

$$c_0 V = c_1 V + c_1' V' \qquad \frac{c_1'}{c_1} = K_c$$

$$c_0 V = c_1 V + c_1 K_c V'$$

$$\frac{c_1}{c_0} = \frac{V}{V + K_c V'} = \frac{1}{1 + K_c \dfrac{V'}{V}} \qquad (4.35)$$

Extraction coefficient: $$Q = \frac{K_c V'}{V} \qquad (4.36)$$

$$\frac{c_1}{c_0} = \frac{1}{1+Q} \qquad (4.37)$$

c_1 is the concentration in the mother liquor after the first extraction step.

Repeating the extraction with the same amount of solvent:

$$c_1 V = c_2 V + c_2^{'} V^{'}$$

Similar derivation as before:

$$\frac{c_2}{c_1} = \frac{1}{1+Q}$$

Multiply this formula and the previous one:

$$\frac{c_2}{c_0} = \left(\frac{1}{1+Q} \right)^2$$

If we use N steps with the same amount of solvent:

$$\boxed{\frac{c_N}{c_0} = \left(\frac{1}{1+Q} \right)^N} \qquad (4.38)$$

4.10 Three component phase diagrams

Triangular coordinates are used for phase diagrams of three component systems.

Phase rule: $F = C – P + 2 = 5 – P$ - may be four. If p and T are kept constant, two degrees of freedom still remain: two mole fractions ($x_C = 1 - x_A – x_B$).

An equilateral triangle is suitable for representing the whole mole fraction range.

Each composition corresponds to one point.

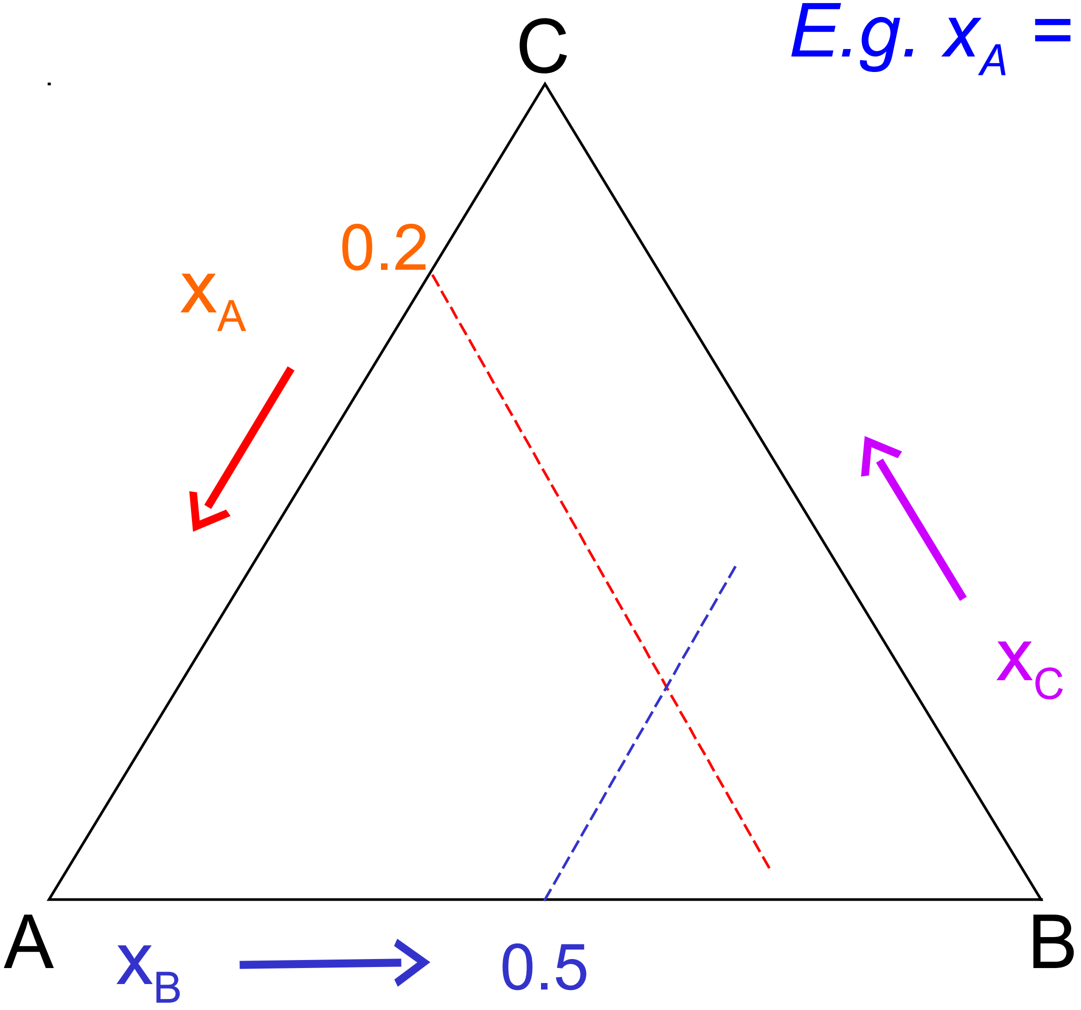


Fig. 4.19

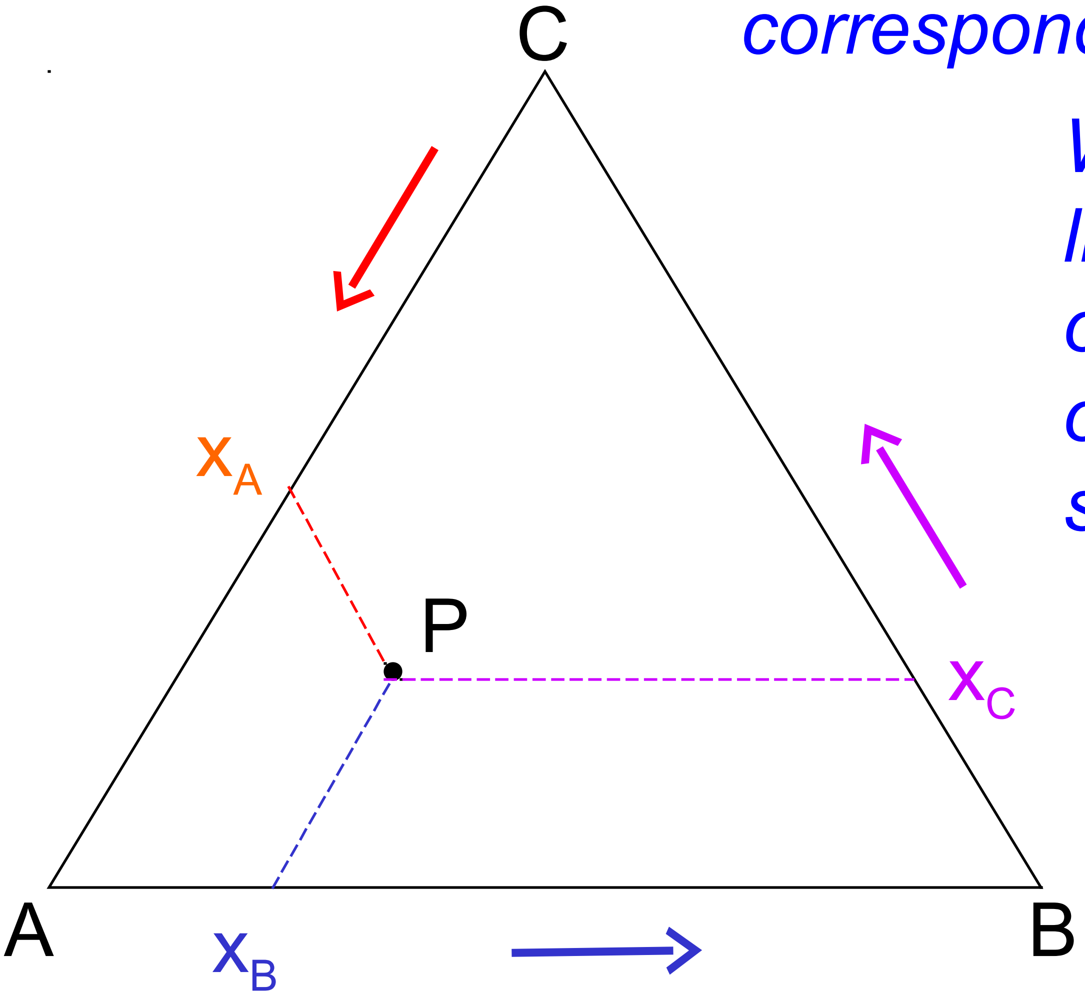
E.g. $x_A = 0.2, \quad x_B = 0.5$

We draw a parallel line with the line opposite the apex of the substance.

The point representing the composition is the crossing point of the two lines

Reading the composition

E.g. read the composition corresponding to point P



We draw parallel lines with the lines opposite the apexes of the corresponding substances.

Where the broken lines cross the axes, we read the mole fractions.

Fig. 4.20

A and B are only partially miscible but both are completely miscible with C.

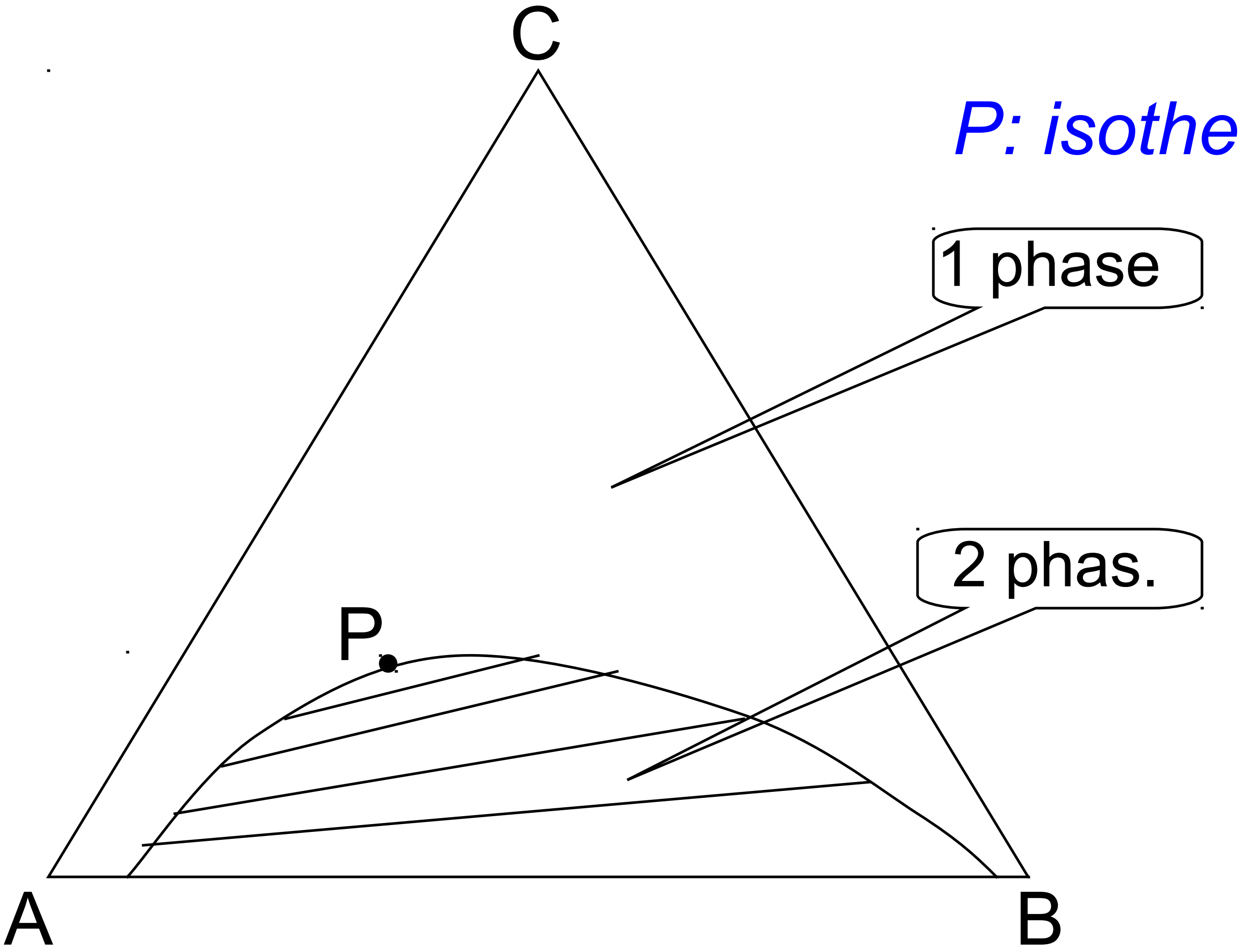


Fig. 4.21

P: isothermal critical point

The lines show the composition of the two phases in those are in equilibrium

A and B are completely miscible but both are partially miscible with C.

a)

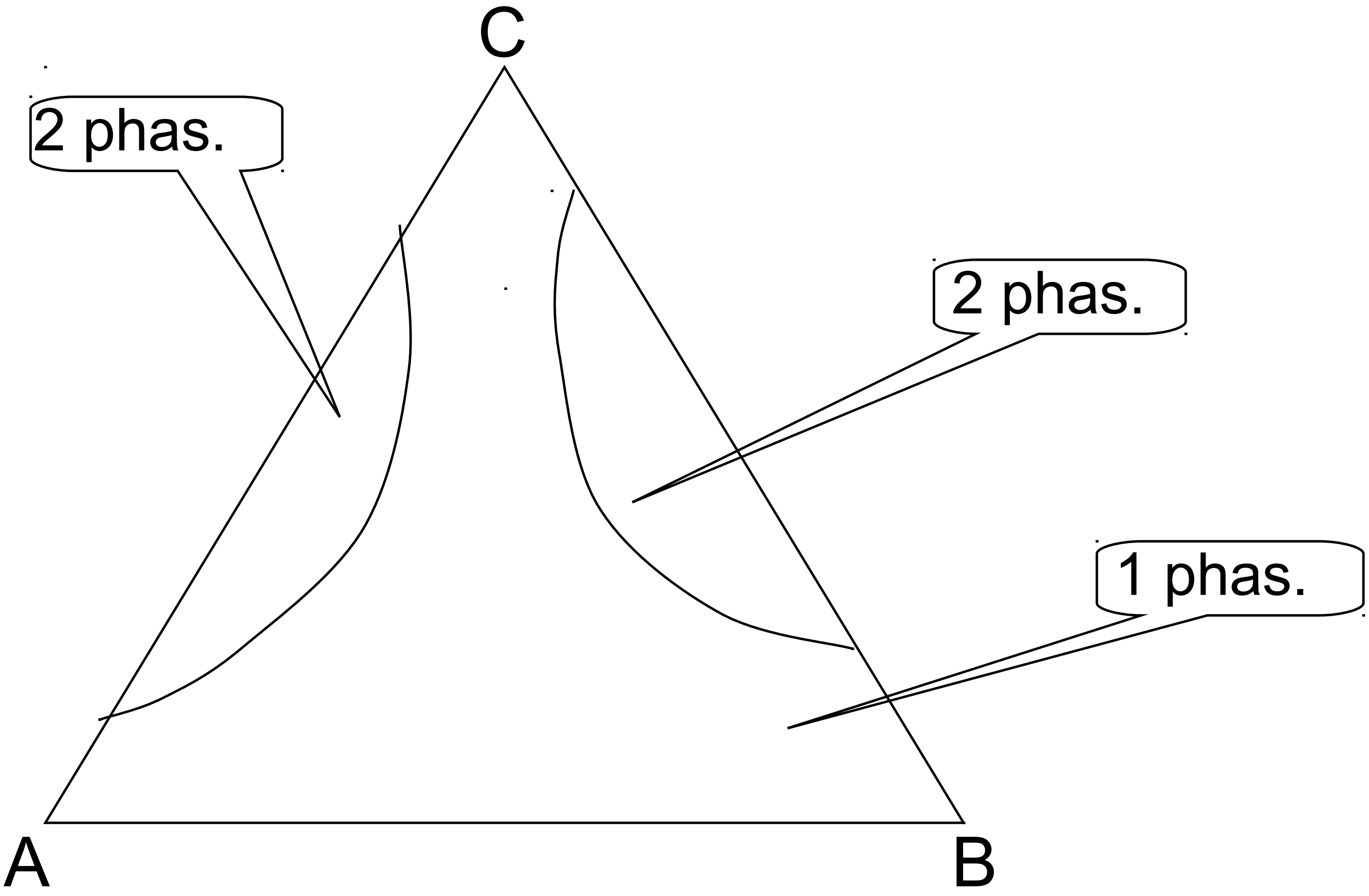


Fig. 4.22

A and B are completely miscible but both are partially miscible with C.

b)

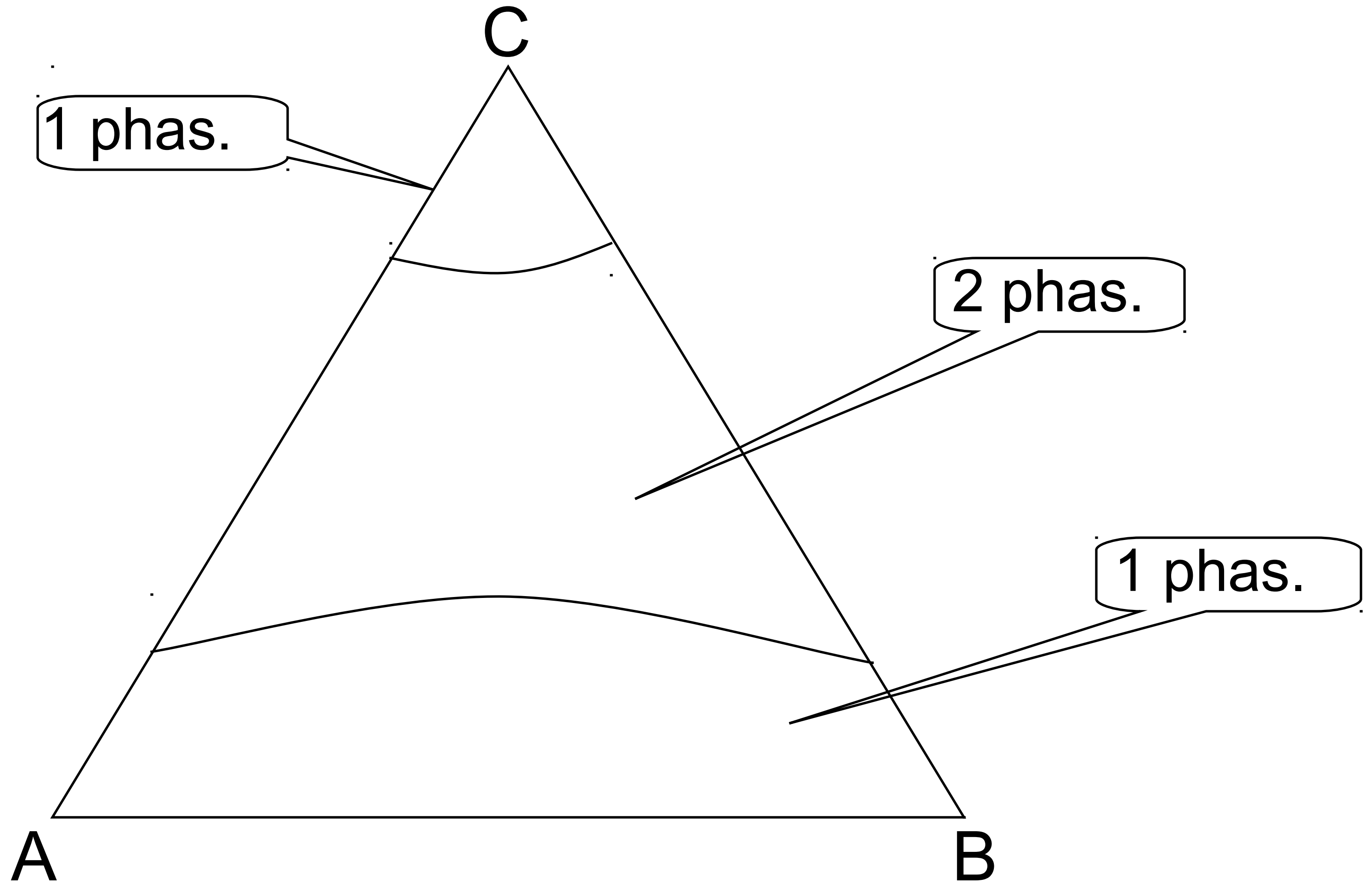


Fig. 4.23

All the three components are partially miscible with one of them

a)

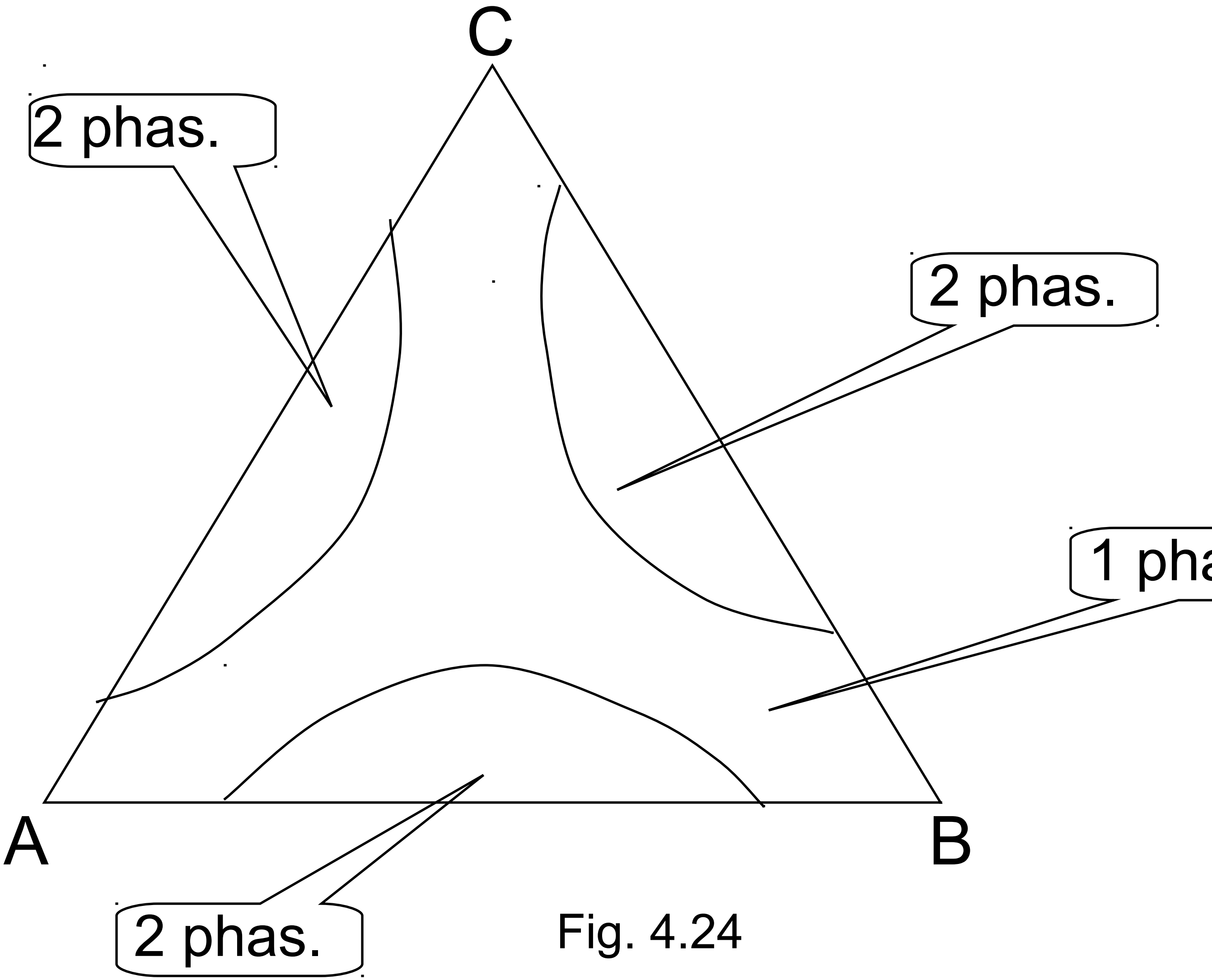


Fig. 4.24

All the three components are partially miscible

b)

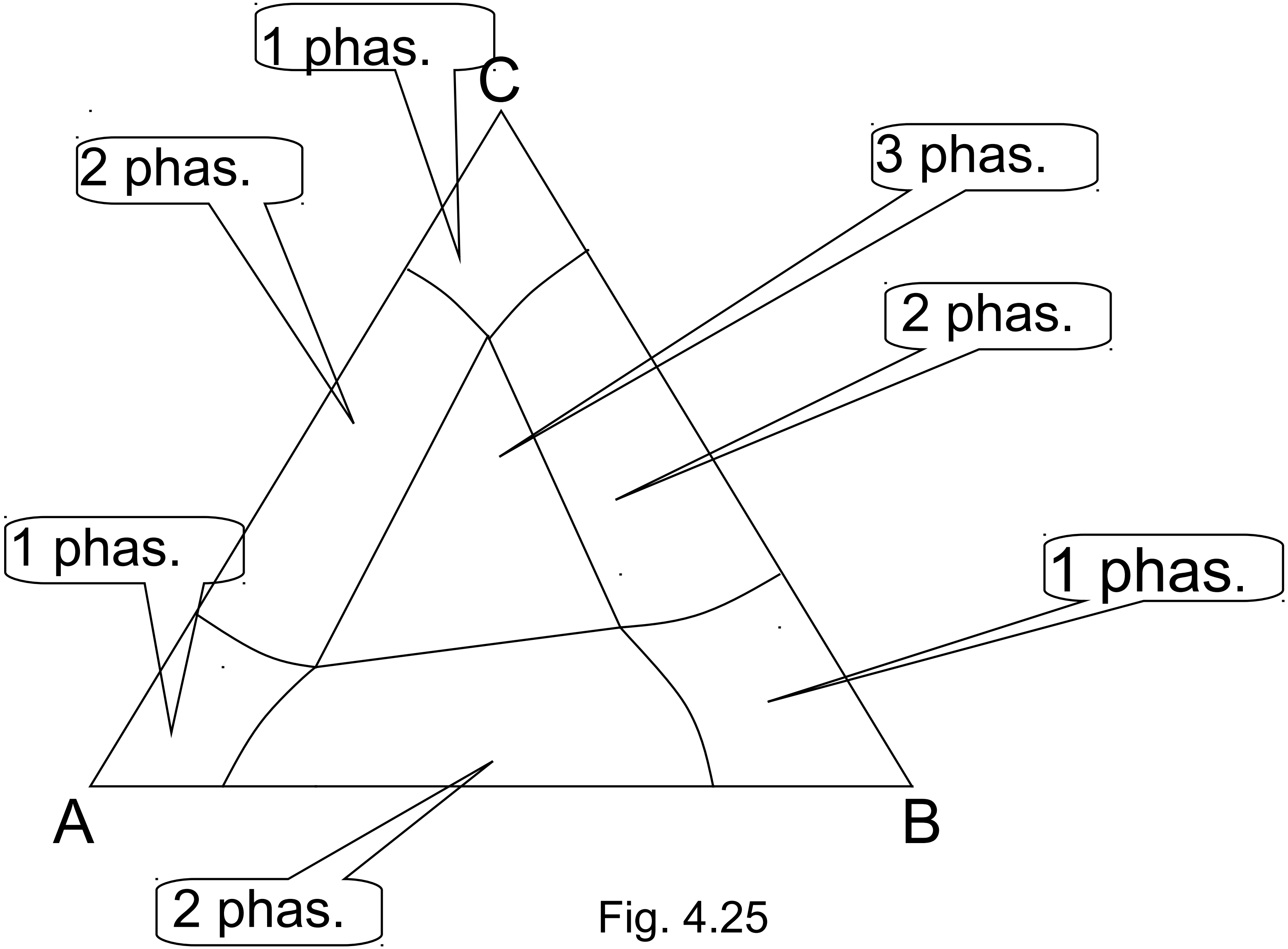


Fig. 4.25

4.11 Activities and standard states

Expression for the chemical potential:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

(see 3.25)

Standard chemical potential

activity (always dimensionless)

1.) Ideal gases

$$a_i = \frac{p_i}{p^0}$$

(partial pressure per standard pressure)

Standard state: p^0 pressure
ideal behavior

2.) **Real gases** (*see subsection 3.7)*

$$a_i = \frac{f_i}{p^0} \qquad (4.39)$$

partial fugacity per standard pressure, see (3.28)

Ideal solution of real gases: *the interaction between molecules cannot be neglected but the same interactions are assumed between unlike molecules as between like molecules.*

Lewis – Randall rule:

$$f_i = \varphi_i \cdot y_i \cdot p \qquad (4.40)$$

fugacity coefficient

mole fraction

total pressure

Standard state: $p \to 1$ bar

$y_i \to 1$

$\varphi_i \to 1$

$f_i \to 1$ bar

The ideal gas state at p^0 pressure (fugacity) is a fictive state. ***The standard chemical potential is the chemical pot. of the ideal gas at standard pressure.***

Expression of the chemical potential for real gases according to (4.40)

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{p^0} = \mu_i^0 + RT \ln \frac{\varphi_i y_i p}{p^0} \qquad (4.41)$$

3.) *Solutions1:* *the component is regarded as solvent. Raoult´s law is applied.*

$$\mu_i = \mu_1^* + RT \ln a_i = \mu_1^* + RT \ln \left({}^x\gamma_i \, x_i \right) \quad (4.42)$$

Standard state $x_i \rightarrow 1$

${}^x\gamma_i \rightarrow 1$

$a_i \rightarrow x_i$

This defines the pure liquid at p^0 pressure

4.) Solutions2: *the component is regarded as solute. Henry´s law is applied. The composition is expressed in terms of concentration or molality.*

A) *concentration,* ***c*** *(mol/dm^3) is applied*

$$\mu_i = \mu_i^0 + RT \ln a_i = \mu_i^0 + RT \ln\left({}^c\gamma_i \frac{c_i}{c^0} \right) \qquad (4.43)$$

$$a_i = {}^c\gamma_i \cdot \frac{c_i}{c^0}$$

${}^c\gamma_i$: *activity coefficient applied to concentration*

c^0: *unit concentration (1 mol/dm^3)*

We cannot choose the infinite dilute solution as standard state because as a_i approaches 0, its logaritm approaches $-\infty$.

The standard state is a state where the activity is 1.

$c_i \rightarrow 1\ mol/dm^3$

${}^c\gamma_i \rightarrow 1$

$a_i \rightarrow c_i/c^0$

This is a hypotetical (fictive) standard state : unit concentration but such behaviour as if the solution was ∞ dilute.

This is a hypotetical (fictive) state.

B) molality (**m**$_i$, mol solute / kg solvent)

$$\mu_i = \mu_i^0 + RT \ln a_i = \mu_i^0 + RT \ln\left({}^m\gamma_i \cdot \frac{m_i}{m^0} \right) \qquad (4.44)$$

${}^m\gamma_i$: activity coefficient applied to molality

m^0: unit molality (1 mol/kg)

The standard state is fictive since unit molality and ideal behavior should be required.

4.12 The thermodynamic equilibrium constant

Chemical affinity is the electronic property by which dissimilar chemical species are capable of forming chemical compounds.

The following considerations are applied.

1.) In equilibrium at a given temperature and pressure the Gibbs function of the system has a minimum.

2.)The Gibbs function can be expressed in terms of chemical potentials: $G = \Sigma n_i \mu_i$

3.) The chemical potentials depend on the composition ($\mu_i = \mu_i^0 + RT \ln a_i$). In a reaction mixture there is one composition, where the Gibbs function has its minimum. This is the equilibrium composition.

Qualitative discussion

Three cases are shown below

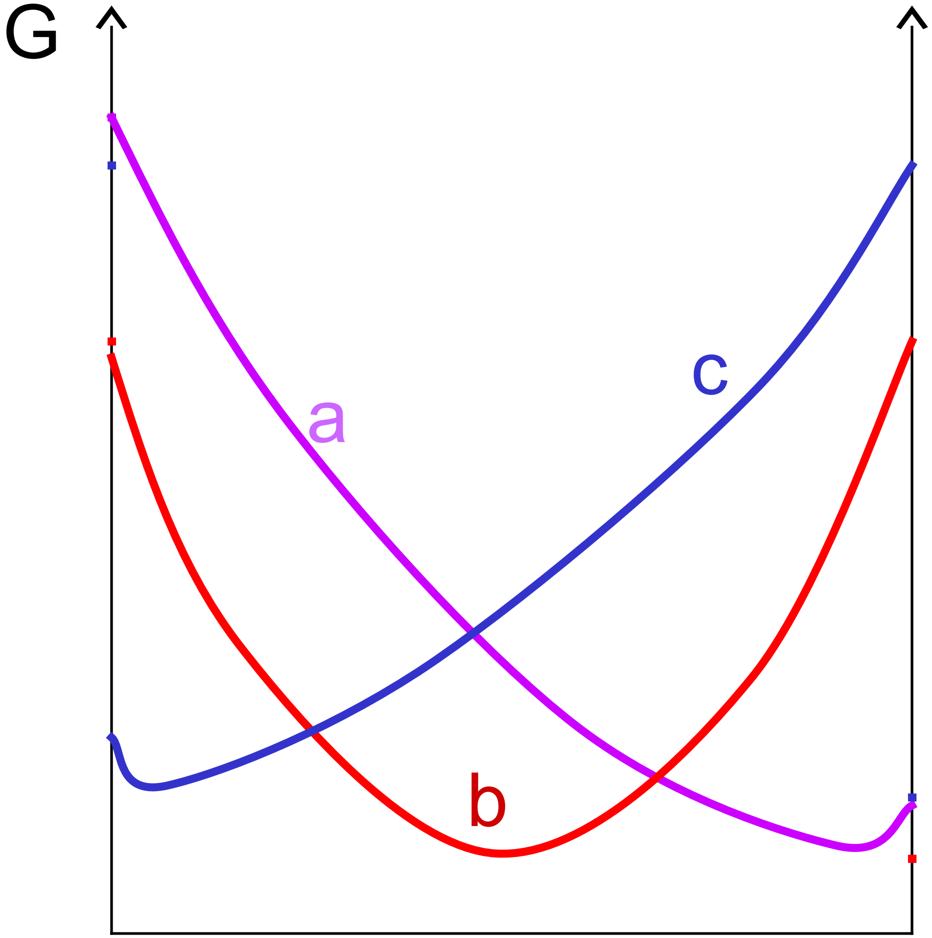


Fig. 4.26

reactants *products*

Conclutions:

a) The equilibrium lies close to pure products. The reaction „goes to completion”.

b) Equilibrium corresponds to reactants and products present in similar proportions.

c) Equilibrium lies close to pure reactants. The reaction „does not go”.

Quantitative discussion

$$\Sigma \nu_A M_A = \Sigma \nu_B M_B \qquad (4.45)$$

e.g. $N_2 + 3H_2 = 2NH_3$

Three cases depending on composition:

1) $$\Sigma \nu_A \mu_A > \Sigma \nu_B \mu_B \qquad (4.46)$$

e.g. $\mu_{N_2} + 3\mu_{H_2} > 2\mu_{NH_3}$

The reaction can go from left to right when G decreases.

2) $\Sigma \nu_A \mu_\mathrm{A} < \Sigma \nu_B \mu_B$ (4.47)

e.g. $\mu_{\mathrm{N}_2} + 3\mu_{H_2} < 2\mu_{NH_3}$

The reaction can go from right to left.

3) $\Sigma \nu_A \mu_\mathrm{A} = \Sigma \nu_B \mu_B$ (4.48)

e.g. $\mu_{\mathrm{N}_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

Equilibrium : $\Sigma \nu_B \mu_\mathrm{B} - \Sigma \nu_A \mu_\mathrm{A} = 0$ (4.49)

Reaction Gibbs function: $\boxed{\Delta_r \mu = \Delta_r G = 0}$ (4.50)

e.g. $\Delta_r G = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2} = 0$

Since $\mu_i = \mu_i^0 + RT\ln a_i$

$$\Sigma\left(\nu_B \mu_B^0 + \nu_B RT\ln a_B\right) - \Sigma\left(\nu_A \mu_A^0 + \nu_A RT\ln a_A\right) = 0$$

Rearranging

$$\Sigma\nu_B \mu_B^0 - \Sigma\nu_A \mu_A^0 + RT\left(\Sigma\ln a_B^{\nu_B} - \Sigma\ln a_A^{\nu_A}\right) = 0$$

Sum of logarithms = logarithm of the product

Difference of logarithms = logarithm of the ratio

Constant times logarithm = logarithm of the power

Now we have

$$\Sigma\nu_B \mu_B^0 - \Sigma\nu_A \mu_A^0 + RT\ln\frac{\Pi a_B^{\nu_B}}{\Pi a_A^{\nu_A}} = 0 \qquad (4.51)$$

As result

$$\Delta_r \mu^0 = \Delta_r G^0 = -RT \ln K \qquad (4.52)$$

standard reaction Gibbs function

The equilibrium constant is

$$\boxed{K = \frac{\Pi\, a_B^{\nu_B}}{\Pi\, a_A^{\nu_A}}} \qquad (4.53)$$

e.g. $N_2 + 3H_2 = 2NH_3 \qquad K = \dfrac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$

The equilibrium constant K depends on temperature only.

K does not depend on either pressure or concentrations. (The concentrations or partial pressures take up values to fulfil the constancy of K).

The equilibrium constant is a very important quantity in thermodynamics that characterizes several types of equilibria of chemical reactions:

in gas, liquid, and solid-liquid phases;

in different types of reactions between

neutral and charged reactants;

The equlibrium constant can be expressed using several parameters like pressure, mole fraction, (chemical) concentration, molality.

4.13 Chemical equilibrium in gas phase

Applications of $K = \dfrac{\Pi a_B^{\nu_B}}{\Pi a_A^{\nu_A}}$

Ideal gases: $a_i = \dfrac{p_i}{p^0}$

Therefore

$$K = \frac{\Pi\left(\dfrac{p_B}{p^0}\right)^{\nu_B}}{\Pi\left(\dfrac{p_A}{p^0}\right)^{\nu_A}} \longrightarrow K = \frac{\Pi p_B^{\nu_B}}{\Pi p_A^{\nu_A}} \cdot \left(p^0\right)^{\sum \nu_A - \sum \nu_B} \qquad (4.54)$$

$$\Delta\nu = \sum \nu_B - \sum \nu_A$$

and $K = K_p \left(p^0\right)^{-\Delta\nu}$ (4.55)

$\Delta\nu$**:** change in number of molecules

e.g. $SO_2 + ½\, O_2 = SO_3$

$\Delta\nu = 1 – 0.5 – 1 = - 0.5$

$$K_p = \frac{\Pi p_B^{\nu_B}}{\Pi p_A^{\nu_A}} \qquad (4.56)$$

K_p is also constant because $(p^0)^{-\Delta\nu}$ is constant for a given reaction. The dimension of K_p is $[\text{pressure}]^{\Delta\nu}$. E.g., $\text{Pa}^{-1/2}$, $\text{bar}^{-1/2}$ (for the previous reaction).

Real gases:

$$a_i = \frac{f_i}{p^0} = \frac{\varphi_i y_i p}{p^0} \qquad (4.57)$$

(4.57) is the Lewis-Randall rule (see also 3.28)

Applying the Lewis-Randell rule

$$K = \frac{\Pi\left[\varphi_B^{\nu_B}\left(y_B p\right)^{\nu_B}\right]}{\Pi\left[\varphi_A^{\nu_A}\left(y_A p\right)^{\nu_A}\right]} \cdot \left(p_0\right)^{\Sigma\nu_A - \Sigma\nu_B} \qquad (4.58)$$

or

$$K = \overbrace{\frac{\Pi \varphi_B^{\nu_B}}{\Pi \varphi_A^{\nu_A}}}^{K_\gamma} \cdot \frac{\Pi (y_B p)^{\nu_B}}{\Pi (y_A p)^{\nu_A}} \cdot \left(p^0\right)^{-\Delta\nu} \qquad (4.59)$$

Extending (4.55) for real gases:

$$K = K_p K_\gamma p_0^{-\Delta\nu} \qquad (4.60)$$

Constant, depends on T only. This is the “true” equilibrium constant.

They depend on pressure but their product does not.

Example: 1/2 N_2 + 3/2 H_2 = NH_3 at 450 ^{0}C

p(bar)	K_φ	$K_p \cdot 10^3$ $(bar)^{-1}$	$K \cdot 10^3$
10	0.995	6.6	6.6
30	0.975	6.8	6.6
50	0.95	6.9	6.6
100	0.89	7.3	6.5
300	0.70	8.9	6.2

Error due to the failure of the ideal mixture of real gases approx

Effect of fugacity coefficient is observed at high pressures.

4.14 Effect of pressure on equilibrium

The equilibrium constant is independent of pressure. On the other hand, the equilibrium composition in a gas reaction can be influenced by the pressure.

Assume that the participants are ideal gases. According to (4.54a)

$$K = \frac{\Pi\left(\frac{p_B}{p^0}\right)^{\nu_B}}{\Pi\left(\frac{p_A}{p^0}\right)^{\nu_A}}$$

We express K with gas mole fractions:

Dalton´s law: $p_i = y_i \cdot p$

$$K = \frac{\Pi\left(\frac{y_B p}{p^0}\right)^{\nu_B}}{\Pi\left(\frac{y_A p}{p^0}\right)^{\nu_A}} = K_y\left(\frac{p}{p^0}\right)^{\Delta\nu} \qquad (4.61)$$

$$K_y = \frac{\Pi y_B^{\nu_B}}{\Pi y_A^{\nu_A}} \qquad (4.62)$$

$$\Delta\nu = \Sigma\nu_B - \Sigma\nu_A \qquad (4.63)$$

K_y: *reaction quotient expressed in gas mole fractions*

$$\boxed{K_y = K \cdot \left(\frac{p}{p^0}\right)^{-\Delta\nu}} \qquad (4.64)$$

K_y is not constant if the number of molecules changes but it is dimensionless.

The effect of pressure on equilibrium composition depends on the sign of $\Delta\nu$.

If $\Delta\nu > 0$ (the number of molecules increases), increasing the pressure, decreases K_y, that is, the equilibrium shifts towards the reactants (-$\Delta\nu$ is exponent!).

If $\Delta\nu < 0$ (the number of molecules decreases), decreasing the pressure, favours the products (K_y increases).

***Principle of Le Chatelier**: a system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect.*

Equilibrium gas reaction: Increasing the pressure, the equilibrium shifts towards the direction where the number of molecules decreases.

Reactions where the volume decreases at constant pressure ($\Delta\nu < 0$) are to be performed at high pressure.

For example

$N_2 + 3\ H_2 = 2NH_3 \qquad \Delta\nu = -2$

Several hundred bars are used.

Reactions where the volume increases at constant pressure ($\Delta\nu > 0$) are to be performed at low pressure or in presence of an inert gas.

4.15 Gas - solid chemical equilibrium

Heterogeneous reaction: at least one of the reactants or products is in a different phase.

Gas - solid heterogeneous reactions are very important in industry. For example:

$$C(s) + CO_2\,(g) = 2\,CO\,(g)$$

$$CaCO_3(s) = CaO\,(s) + CO_2\,(g)$$

1. In most cases the solid substance does not have any measurable vapor pressure. The reaction takes place on the surface of the solid phase.

We derive the equilibrium constant in the same way as before but we consider the differences in the expression of chemical potential of gas and solid substances.

$$\Delta_r G = \Sigma \nu_B(g)\mu_B(g) - \Sigma \nu_A(g)\mu_A(g) + \\ + \Sigma \nu_B(s)\mu_B(s) - \Sigma \nu_A \mu_A(s) = 0$$

The **gas components** are assumed ideal gases.

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

*The **solid components** are pure solids, their concentration does not change:* $\mu_i(s) = G_{mi}(s)$

Assume that the molar Gibbs function of a solid does not depend on pressure.

Pressure dependence of G

$$\left(\frac{\partial G_m}{\partial p}\right)_T = V_m$$

$dG = Vdp - SdT$ (see 2.19a)

(see 2.19b)

In case of solids the molar volume (V_m) is small

E.g., C(graphite):

$$V_m = \frac{12\,g/mol}{2.25\,g/cm^3} = 5.33\ cm^3/mol = 5.33\cdot 10^{-6}\,m^3/mol$$

For such kind solid components we neglect the pressure dependence of μ, and we take the chemical potential equal to the molar Gibbs function of pure substance: $\mu_i(s) = G^*_{mi}(s)$

$$\Sigma \nu_B(s) G^0_{mB}(s) - \Sigma \nu_A(s) G^0_{mA}(s) + \Sigma \nu_B(g) G^0_{mB}(g) -$$

$$- \Sigma \nu_A(g) G^0_{mA}(g) + RT \ln \frac{\Pi \left(\frac{p_B}{p^0} \right)^{\nu_B(g)}}{\Pi \left(\frac{p_A}{p^0} \right)^{\nu_A(g)}} = 0$$

$$\Delta_r G^0(s) + \Delta_r G^0(g) = \Delta_r G^0 = - RT \ln K \quad (4.65)$$

So the following rules are used in case of gas - solid heterogeneous reactions:

a) For the calculation of $\Delta_r G^0$ (change of Gibbs free energy during the reaction) the standard molar Gibbs functions of all the participants have to be taken into account.

b) Only the partial pressures of the gas components are included in the equilibrium constant.

Example reaction:

$C(s) + CO_2\,(g) = 2\,CO\,(g)$

$$K = \frac{\left(\frac{p_{CO}}{p_0}\right)^2}{\left(\frac{p_{CO_2}}{p^0}\right)}$$

The change of the Gibbs function in the reaction:

$$\Delta_r G^0 = 2G_m^0(CO) - G_m^0(C) - G_m^0(CO_2)$$

2. *If a solid component has a measurable vapor pressure*

Example: $H_2(g) + I_2\,(s,g) = 2\,HI(g)$ $\Delta\nu=0$

The iodine is present both in the solid and the gas phase (it sublimates)

a) We regard the reaction as homogeneous gas reaction.

$$K = \frac{\left(\frac{p_{HI}}{p_0}\right)^2}{\left(\frac{p_{H_2}}{p^0}\right)\cdot\left(\frac{p_{I_2}}{p^0}\right)}$$

This is also constant (the vapor pressure of solid iodine), so it can be merged into K.

In the vapor phase the partial pressure of iodine is constant as long as solid iodine is present in the system.

b) We regard the reaction as heterogeneous.

$$K' = \frac{\left(\frac{p_{HI}}{p_0}\right)^2}{\left(\frac{p_{H_2}}{p^0}\right)}$$

Therefore the iodine as solid component is left out from the equilibrium constant.

Both methods lead to the same result.

For the calculation of K, the standard chemical potential of gaseous iodine is used.

For the calculation of K´, the standard chemical potential of solid iodine is used.

4.16 Chemical equilibria in liquid state

We study three cases.

1.*The components are present in high concentration (e.g. reactions between organic liquids). Such equilibrium reaction is the formation of esters.*

Equations (4.52) and (4.53):

$$\Delta_r G^0 = -RT \ln K \qquad K = \frac{\Pi a_B^{\nu_B}}{\Pi a_A^{\nu_A}}$$

The composition is expressed in terms of mole fraction.

$$a_i = {}^{x}\gamma_i \cdot x_i \qquad K = \frac{\Pi a_B^{\nu_B}}{\Pi a_A^{\nu_A}} \qquad \mathrm{K} = \mathrm{K}_\gamma \cdot \mathrm{K}_x \qquad (4.66a,b,c)$$

In ideal solutions K_x = const.

In real solutions, too, K_x may be constant if the dependence of activity coefficients on mole fraction is not significant (K_γ = const.).

Example:

$\mathrm{CHCl_2COOH + C_5H_{10} = CHCl_2COOC_5H_{11}}$ at 100^0C

Dichloro acetic acid pentene ester

$$K_x = \frac{x_{ester}}{x_{pentene} \cdot x_{acid}} \qquad (4.67)$$

Varying the acid - pentene molar ratio between 1 and 15, they obtained $K_x \approx 2.25$.

Formation of esters from acids and alcohols are typical equlibrium reactions:

R COOH + R'OH = RCOOR' + H_2O

$$K_x = \frac{x_{ester} \cdot x_{water}}{x_{acid} \cdot x_{alcohol}} \qquad (4.68)$$

2. Reactions in solvents.

The solvent does not take part in the reaction.
Gases and solids, too, can react in the liquid phase.
The composition is expressed in terms of concentration, c or molality, m.

if ***chemical concentrations*** *are used:*

$$\Delta_r \mu^0 = -RT\ln K \qquad \mu_i = \mu_i^0 + RT\ln\frac{{}^{c}\gamma_i c_i}{c^0} \qquad (4.69)$$

$$K = \frac{\Pi\left(\dfrac{\gamma_B c_B}{c^0}\right)^{\nu_B}}{\Pi\left(\dfrac{\gamma_A c_A}{c^0}\right)^{\nu_A}} = \frac{\Pi\gamma_B^{\nu_B}}{\Pi\gamma_A^{\nu_A}} \cdot \frac{\Pi c_B^{\nu_B}}{\Pi c_A^{\nu_A}} \cdot \left(c^0\right)^{\Sigma\nu_A - \Sigma\nu_B}$$

$$K = K_\gamma \cdot K_c \cdot \left(c^0\right)^{-\Delta\nu} \qquad (4.70)$$

$$K_c = \frac{\Pi c_B^{\nu_B}}{\Pi c_A^{\nu_A}} \qquad (4.71)$$

*If **molalities** are used :*

$$\mu_i = \mu_i^0 + RT \ln \frac{{}^m\gamma_i m_i}{m^0} \qquad (4.72)$$

$$K = K_\gamma \cdot K_m \cdot \left(m^0\right)^{-\Delta\nu} \qquad (4.73)$$

In dilute solutions (c < 1 mol/L) K_c , or K_m are practically constant if neutral molecules take part in the reaction.

If ions also take part, the activity coefficients must be taken into account.

3. *Equilibrium in electrolytes.*

Even very dilute solutions cannot be regarded ideal (because of the strong electrostatic interaction between ions). Still K_c can be frequently used as equilibrium constant (it is assumed that the activity coefficients are independent of concentration, so K_γ is taken constant).

Dissociation equilibrium

K^+: cation A^-: anion

$$\mathrm{KA} = \mathrm{K}^+ + \mathrm{A}^- \qquad (4.74)$$

$$c_0(1-\alpha) \qquad c_0\cdot\alpha \qquad c_0\cdot\alpha$$

c_0 : initial concentration

α : degree of dissociation

$$K_c = \frac{\alpha^2 c_0}{1-\alpha} \qquad (4.75)$$

$$0 \le \alpha \le 1$$

The degree of dissociation (α) is the number of dissociated molecules per the number of all molecules (before dissociation).

α depends on concentration (it is higher in more dilute solutions)

Autoprotolytic equilibrium and ionic product of water

$$H_2O+H_2O = H_3O^+ + OH^-$$

$$K_w = a(H_3O^+)\cdot a(OH^-) \quad (4.76)$$

At 25 ^{0}C: $K_w \approx 10^{-14}$

The activity of water is missing because it is in great excess, its concentration is practically constant, and can be merged into the equilibrium constant.

$$pH = -\lg a(H_3O^+) \quad (4.77)$$

Ionization equilibrium of acids

$$HA + H_2O = H_3O^+ + A^- \tag{4.78}$$

Ionization constant:

$$K_a = \frac{a(H_3O^+) \cdot a(A^-)}{a(HA)} \tag{4.79}$$

Its negative decimal logarithm is used:

$$\mathbf{pK_a = -\lg K_a} \tag{4.80}$$

pK_a characterizes the strength of the acid.

Strong acids have small pK_a,

Examples:. for HF it is 3.17, for HNO_3 it is -1.64.

Ionization equilibrium of bases

$$B + H_2O = BH^+ + OH^- \qquad (4.81)$$

The dissociation constant: $$K_b = \frac{a(BH^+) \cdot a(OH^-)}{a(B)} \qquad (4.82)$$

$$\mathbf{pK_b = -\lg K_b} \qquad (4.83)$$

K_a is also frequently used for bases, stronger basis - higher pK_a, it is for CH_3NH_2 10.64, for NH_3 9.23.

The equilibrium: $BH^+ + H_2O = B + H_3O^+$ (4.84)

$$K_a = \frac{a(H_3O^+) \cdot a(B)}{a(BH^+)} \qquad (4.85)$$

The product of the two constants is the ionic product of water: $\mathbf{K_a \cdot K_b = K_w}$ (4.86)

4.17 Temperature dependence of the equilibrium constant

The following equation shows that the equilibrium constant depends on temperature only.

The standard chemical potentials depend on temperature only:

$$\Delta_r G^0 = -RT \ln K$$ (see 4.52)

Derive lnK with respect to temperature

$$\ln K = -\frac{1}{R} \cdot \frac{\Delta_r G^0}{T} \longrightarrow \frac{\partial \ln K}{\partial T} = -\frac{1}{R} \cdot \frac{\partial}{\partial T}\left(\frac{\Delta_r G^0}{T}\right)$$

Derivation of the ratio of two functions

$$\left(\frac{u}{v}\right)' = \frac{u'v - uv'}{v^2}$$

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

Gibbs-Helmholtz equation, (3.52).

We apply this operation to $\Delta_r G^0$, that is we substitute the negative standard reaction enthalpy for the temperature derivative for the standard Gibbs function of reaction.

So the temperature dependence of equilibrium constant is given by the van’t Hoff equation

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta_r H^0}{RT^2}} \qquad (4.87)$$

It is the standard reaction enthalpy that determines the temperature dependence of K.

The sign of dlnK/dT is the same as the sign of dK/dT (because dlnK/dT = 1/K· dK/dT).

In case of endothermic reactions ($\Delta_r H^0 > 0$) the right hand side is positive, so K and lnK increases with increasing temperature (see Fig. 4.27)

In case of exothermic reactions ($\Delta_r H^0 < 0$) K and lnK decrease with increasing temperature (see Fig. 4.27)

Principle of Le Chatelier: The equilibrium shifts towards the endothermic direction if the temperature is raised, and in the exothermic direction if the temperature is lowered,
endothermic: heat is absorbed form the environment,
exothermic: heat is transmitted to the environment.

For exothermic reactions low temperature favours the equilibrium but at too low temperatures the rate of reaction becomes very low. We must find an optimum temperature.

For exact integration of van´t Hoff equation we must know the temperature dependence of the standard enthalpy of reaction.

In a not too large temperature range the reaction enthalpy is assumed constant. Then integration is easy:

$$\ln K = -\frac{\Delta_r H^0}{RT} + const. \qquad (4.88)$$

If we plot the logarithm of the equilibrium constant against the reciprocal of the absolute temperature, we optain a linear function. The slope is determined by the standard reaction enthalpy.

Fig. 4.27 introduces the lnK - 1/T diagram for an endothermic (a) and for an exothermic (b) reaction

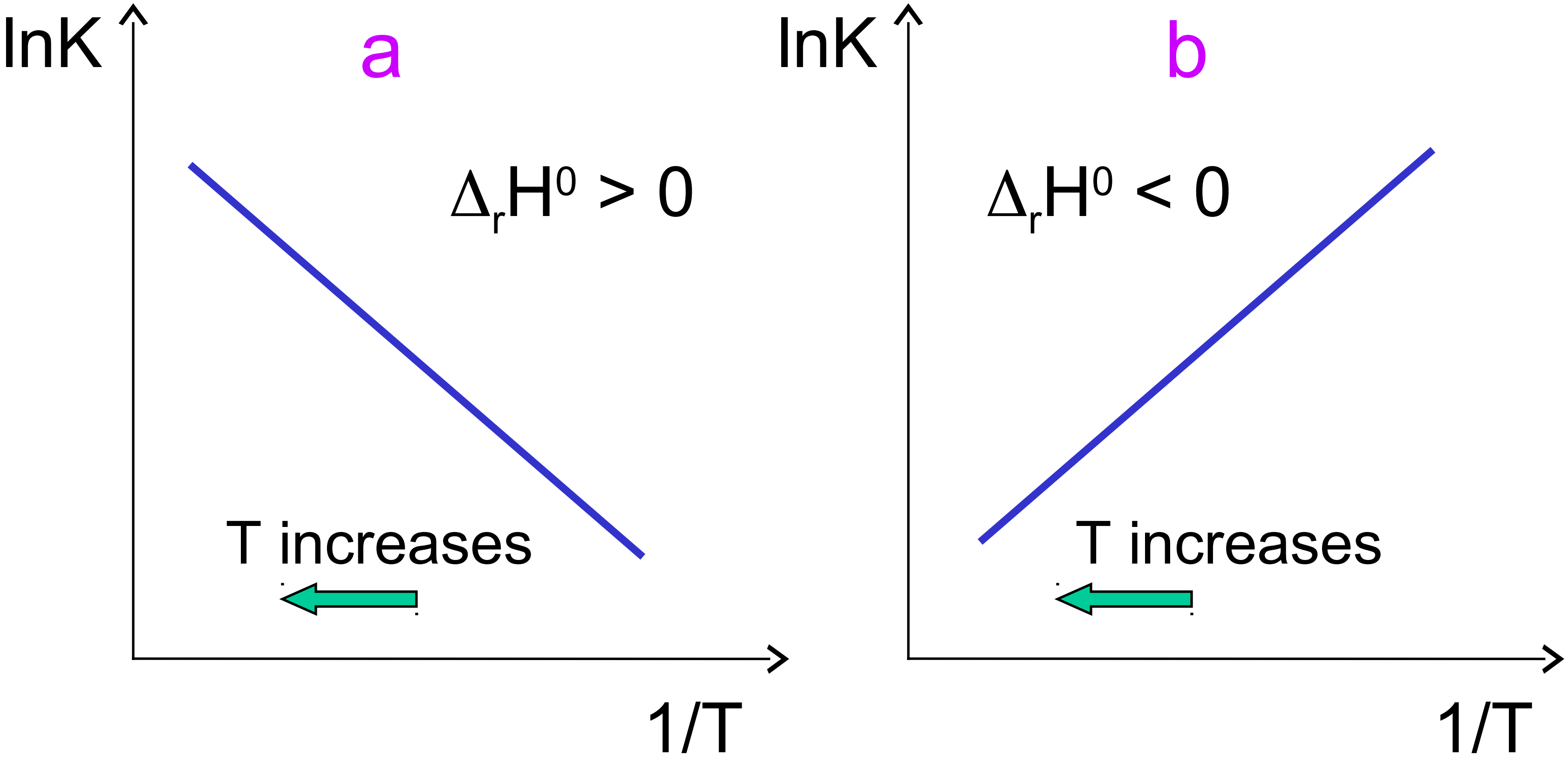


Fig. 4.27