BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
DEPARTMENT OF PHYSICAL CHEMISTRY AND MATERIAL SCIENCE

ANDRÁS GROFCSIK – FERENC BILLES

PHYSICAL CHEMISTRY 1
(lecture notes)

TYPOTEX
BUDAPEST
2014

ISBN 978-963-279-812-7

Prepared under the editorship of Typotex Kiadó

Responsible manager: Votisky Zsuzsa

Content

1. BASIC THERMODYNAMICS

1.1. Terms in thermodynamics

System is the part of the world which we have a special interest in, e.g. a reaction vessel, an engine, an electric cell.

There are two points of view for the description of a system:

Phenomenological view: the system is a continuum. This is the method of thermodynamics.

Particle view: the system is regarded as a set of particles, applied in statistical methods and quantum mechanics.

Surroundings: everything outside the system.

Isolated system: neither material nor energy cross the wall (see Fig. 1.1.)

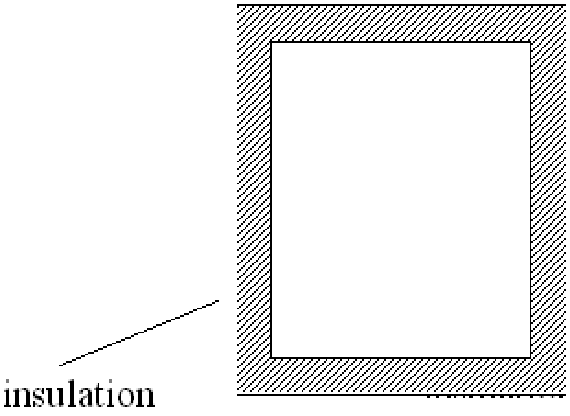


Fig. 1.1.

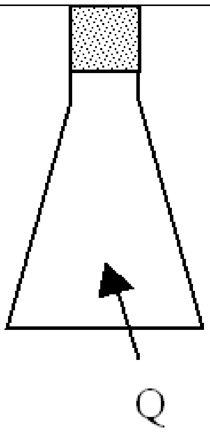
Closed system: energy can cross the wall (see Fig. 1.2), W: work, Q: heat.

Open system: both transport of material and energy is possible (Fig. 1.3).

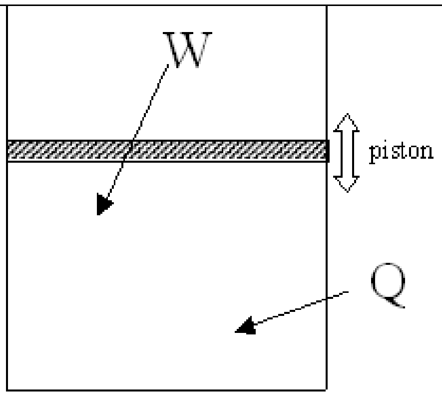
Homogeneous system: macroscopic properties are the same everywhere in the system, see example, Fig. 1.4

Inhomogeneous system: certain macroscopic properties change from place to place; their distribution is described by continuous function. Example:

a copper rod is heated at one end, the temperature (T) changes along the rod, Fig. 1.5.



constant volume
Fig. 1.2a



changing volume
Fig. 1.2b

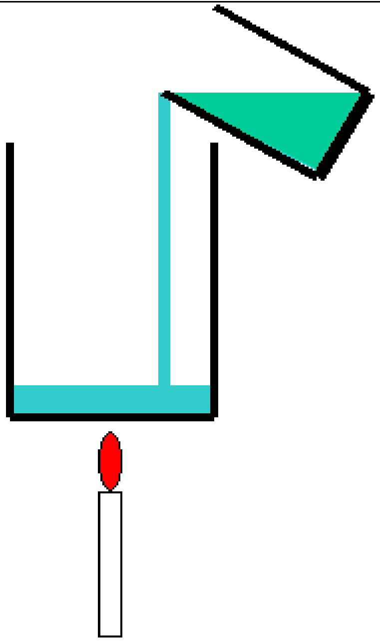


Fig. 1.3

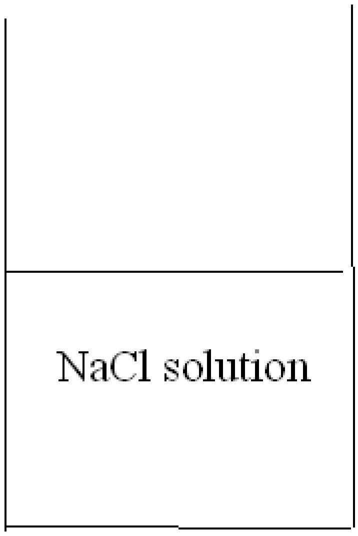


Fig. 1.4

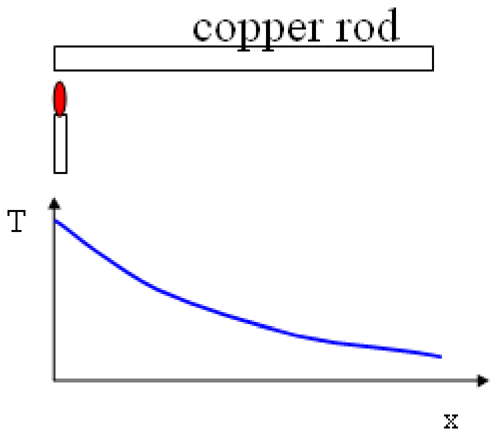


Fig. 1.5

Heterogeneous system: discontinuous changes of macroscopic properties. Example: water-ice system, Fig. 1.6.

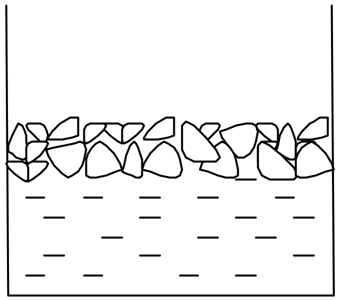


Fig. 1.6

Phase: a well defined part of the system which is uniform throughout both in chemical composition and in physical state. The phase may be a **disperse** one, in this case the parts with the same composition belong to the same phase.

Components: chemical constituents (see subsection 2.11).

Fig 1.6 shows a system with one component but with two phases.

1.2. The state of the thermodynamic system

The state of a thermodynamic system is characterized by the collection of the ***measurable physical properties***. The expression 'measurable' is very important since e.g. the form or the color (white) of the system can characterize the system but they are not measurable.

The macroscopic parameters determined by the state of the system are called ***state functions***.

The basic state functions:

amount of substance: mass (m), chemical mass (n)

volume (V)

pressure (p)

temperature (T)

concentration (c)

A system is in ***thermodynamic equilibrium*** if none of the state functions are changing. In equilibrium no macroscopic processes take place.

In a ***non-equilibrium system*** the state functions change in time**, the system tends to be in equilibrium.**

Meta-stable state: the state is not of minimal energy, energy is necessary for crossing an energy barrier.

A ***reversible change*** is one that can be reversed by an i**nfinitesimal modification** of one variable.

A ***reversible*** **process** is performed through the same equilibrium positions from the initial state to the final state as from the final state to the initial state.

Example: if a ***reversible*** compression of a gas means infinitesimal change of the gas pressure. This causes opposite infinitesimal change of the external pressure, then the system is in ***mechanical equilibrium*** with its environment (Fig. 1.7).

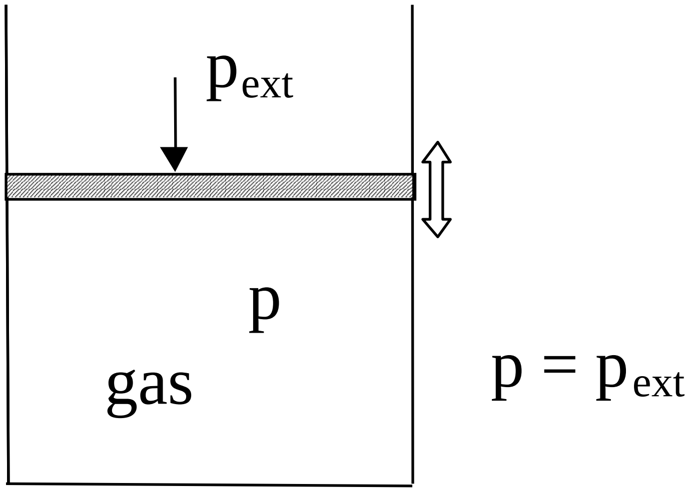


Fig. 1.7

Real processes are sometimes very close to the reversible processes.

The following processes are frequently studied:

isothermal (T = const.)
isobaric (p = const.)
isochoric (V = const.)
adiabatic (Q = 0, Q: heat)

The change of a state function depends only on the initial and the final state of the system. It is ***independent of the path*** between the two states (e.g. potential energy in the gravitation field, or the electrostatic potential).

*Important **state functions** in thermodynamics*:

U – internal energy
H – enthalpy
S – entropy
A – Helmholtz free energy
G – Gibbs free energy

The change of the state functions is labeled with a great Greek delta, *example:* ***ΔU.*** Their ***infinitesimal change*** is an exact differential***, e.g. dU.***

Work and heat are not state functions. They depend on the path between the initial and final state. They are ***path functions.***

For example, an object is moved from A to B along two different paths on a horizontal frictious surface, Fig. 1.8.

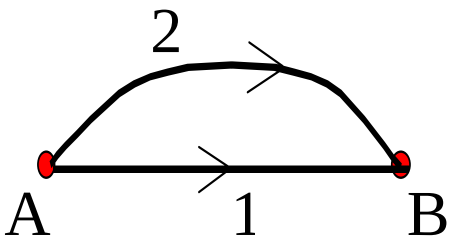


Fig. 1.8

The two works are different:

$W_2 \neq W_1$

We do not use the expression „change" for work and heat (change is labeled by „d" like dH). ***Infinitesimal values of work and heat*** are labeled by **„δ":** δW, δQ, *since they are not exact differentials*. Further parameters have to be given for their integration.

Another type of classification of thermodynamic terms:

Extensive quantities: depend on the **extent of the system** and are additive

mass *(m)*

volume *(V)*

internal energy *(U)*

Intensive quantities*:* **do not depend on the extent of the system** and are not additive*:*

temperature *(T)*

pressure *(p)*

concentration *(c)*

However, at the same time they are also state functions.

Extensive quantities can be converted ***to intensive quantities***, if they are related to unit mass, volume. For example:

Density: $\rho = m/V$

Molar volume: $V_m = V/n$ (subscript m refer to molar)

Molar internal energy: $U_m = U/n$

Equation of state: is a relationship among the state variables of the system in equilibrium.

Example: ***the ideal gas*** is defined according to its equation of state:

$$pV=nRT \tag{1.1}$$

with p[Pa]; V[m^3]; n[mol]; T[K]; R = 8.314 $Jmol^{-1}$ K^{-1} (gas constant)

The equations of states of real materials are given in forms of equation in closed mathematical formulas, as power series, or diagrams and/or tables.

A. Temperature

The temperature scale used at present in science and in every day life at the great part of the world was defined by Anders ***Celsius*** in 1742.

Two basic points: *melting ice*: 0 °C

boiling water (at 1.013 bar): 100 °C

Notice: in an important part of the world the ***Fahrenheit*** scale is used in every day life.

The two basic points are

melting ice: 32 ^{o}F

boiling water (at 1.013 bar): 212 ^{o}F

Several properties of different materials are used for measuring the temperature.

Example: **change of volume of liquids** (mercury or ethanol). They cannot be used in wide temperature range.

If the same thermometer is filled with different liquids, they show *slightly different values at the same temperature*. Reason: thermal expansion is different for the different liquids. For example: with Hg 28.7 °C, with ethanol 28.8 °C is measured.

The pV_m product of an ideal gas has been selected for the basis of temperature measurement. ***All real gases behave ideally if the pressure approaches zero.***

The temperature on the Celsius scale can be expressed as

$$t=\frac{(p\cdot V_m)_t-(p\cdot V_m)_0}{(p\cdot V_m)_{100}-(p\cdot V_m)_0}\cdot 100 \qquad (1.2)$$

*Substituting the **exact values:***

$$t=\frac{(p\cdot V_m)_t}{8.314}-273.15 \qquad (1.3)$$

*On the **absolute temperature scale***:

$$T = 273.15 + t$$

and

$$pV_m = RT \quad \text{or} \quad pV = nRT$$

For the ***definition of thermodynamic temperature scale the triple point of water*** is used (at the triple point the gas, liquid and the solid states are in equilibrium), 0.01°C. One ***Kelvin*** (K) is equal to 1/273.16 times the temperature of the triple point of water on the thermodynamic temperature scale.

The triple point of water is exactly 273.16 K on the thermodynamic temperature scale.

1.3. Internal energy, the first law of thermodynamics

The ***energy*** *(E)* ***of a system*** consists of the kinetic energy (E_{kin}) and the potential energy (E_{pot}) of the system and its internal energy:

$$E = E_{kin} + E_{pot} + U \qquad (1.4)$$

Internal energy, U is *the sum of the kinetic and potential energies of the particles relative to the center mass point of the system.* Therefore it does not include the kinetic and potential energy of the system, i.e. it is assumed in the definition of U that the system itself does neither move, nor rotate.

The idea of ***the internal energy*** covers the following the following energy types.

1. ***Thermal energy*** is connected to the ***motion*** of atoms, molecules and ions (translation, rotation, vibration).
2. ***Intermolecular energy*** *is connected to the* ***forces*** between molecules.
3. ***Chemical energy*** is connected to chemical ***bonds***.
4. ***Nuclear energy*** (nuclear reactions).

Very important is ***Einstein***'s fundamental equation, $\boldsymbol{E = mc^2}$, *the mass is equivalent to energy, e.g. a photon behaves like a wave or like a particle.*

We cannot determine the absolute value of U, only its change, ΔU.

The first law of thermodynamics ***expresses the conservation of energy.***

For *isolated* systems***:*** $\Delta U = 0$ (1.5)

For *closed* system: $\Delta U = W + Q$ (1.6)

Where W: work, Q: heat.

For *infinitesimal* changes***:*** $dU = \delta W + \delta Q$ (1.7)

For *open* systems see Fig. 1.3 and subsection 1.12.

B. Work

The ***mechanical work*** is the scalar product of force (F) and displacement (r)

$$\delta W = \vec{F} \cdot \overrightarrow{dr} \qquad (1.8)$$

Work in changes of volume, ***expansion work*** *(pV work)* plays a special role in thermodynamics. In this case p_{ex} acts on surface A, reversible process in a reversible process:

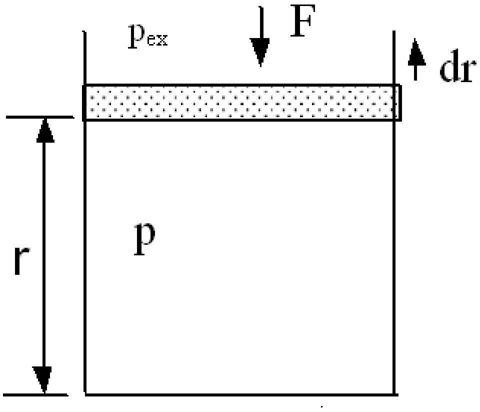


Fig. 1.9

$$\delta W = \vec{F} \cdot \overrightarrow{dr} = p_{ex} \cdot A \cdot dr$$

$$\delta W = -p_{ex} dV$$

$$W = -\int_{V_1}^{V_2} p_{ex} dV \qquad (1.9)$$

Remarks:

a) The change in energy is considered always from the point of view of the system.

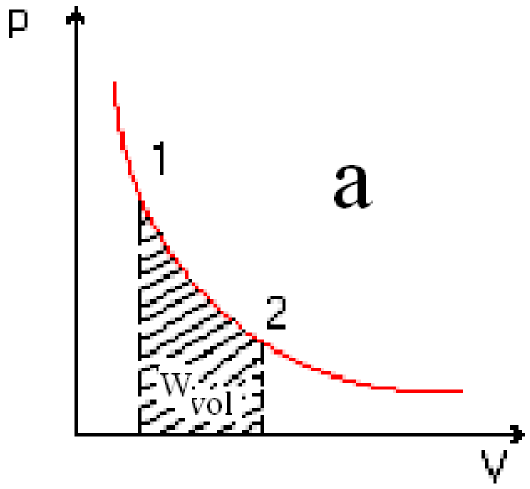
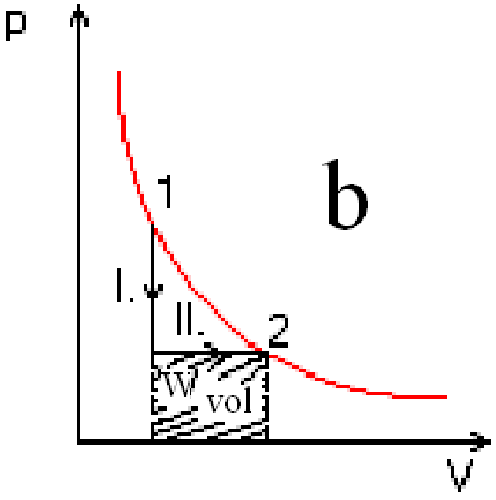
b) The external pressure (p_{ex}) is used, **reversible** change: $p = p_{ex}$.

c) If the **volume increases**, the work is *negative*, if the **volume decreases**, the work is *positive.*

d) If **p = constant**, it is easy to integrate (temperature is changed):

$$W = -p \cdot \int_{V_1}^{V_2} dV = -p \cdot \Delta V \qquad (1.10)$$

The work in changes of volume can be illustrated in ***p-V diagrams***.

 Fig. 10a	 Fig. 10b
Expansion of the gas at constant temperature	I. **Cooling** at constant volume to the final pressure II. **Heating** at constant pressure

Since $W_a \neq W_b$, ***the pV work is not a state function!***

There exist ***other types of work***. *In general the work can be expressed as the product of an intensive quantity and the change of an extensive quantity*.

Work	Intensive quantity	Extensive quantity	Elementary work
pV work	Pressure (-p)	Volume (V)	$\delta W = -pdV$
Surface work	Surface tension (γ)	Surface (A)	$\delta W = \gamma dA$
Electric work	Electric potential (ϕ)	Charge (q)	$\delta W = \phi dq$

The work is an energy transport through the boundary of the system.

The ***driving force*** is the gradient of the intensive parameter (the potential function) belonging to the process. The *temperature driven process* is handled in thermodynamics otherwise (see below, C. Heat).

C. Heat

The heat is the transport of energy (without material transport) through the boundary of a system. The driving force is the gradient of the temperature.

Processes accompanied by heat transfer:

a) Warming, cooling

b) Phase change

c) Chemical reaction

See detailed!

a) Warming, cooling

$$Q = c \cdot m \cdot \Delta T \qquad (1.11)$$

c = *specific heat* [J/kg·K], for water, c = 4.18 kJ/kg·K

Using the *molar heat capacity* C_m [J/mol.K]

$$Q = C_m \cdot n \cdot \Delta T \qquad (1.12)$$

The equations 1.11 and 1.12 are approximations. *The heat capacities are functions of temperature.* For the calculation of the heat C_m must be integrated:

$$Q = n\int_{T_1}^{T_2} C_m(T)dT \tag{1.13}$$

where

$$C_m(T) = \frac{1}{n}\cdot\frac{\delta Q}{dT} \tag{1.14}$$

The heat (like the work) is not a state function. We have to specify the path.

Most frequently *heating and cooling* are performed either at *constant pressure or at constant volume.*

At constant pressure:

$$Q_p = n\int_{T_1}^{T_2} C_{mp}dT \tag{1.15}$$

At constant volume:

$$Q_v = n\int_{T_1}^{T_2} C_{mV}dT \tag{1.16}$$

During heating at constant pressure the volume changes, since pV work is necessary during the heating (expansion or contraction). Therefore $C_{mp} > C_{mV}$.

b) Phase change

Phase changes are isothermal and isobaric processes. That means, both the temperature and the pressure are constant during the phase change.

In case of pure substances either the temperature or the pressure can be freely selected (see section 2.4). For example, as it was already mentioned, at 1.013 bar the boiling point of water is 100 ^{o}C. With changing pressure the boiling point changes, too.

Heat of fusion and heat of vaporization are called **latent heat**, since the temperature does not change during these processes.

c) ***Chemical reaction (see later, Section 1.8)***

D. Enthalpy

$$\Delta U = W + Q$$

According to the first law of thermodynamics

(1.17)

If there is no pV work done (W=0, ΔV=0), the change of internal energy is equal to the heat:

$$\Delta U = Q_v \tag{1.18}$$

Equation 1.18 is valid for processes at constant volume and without pV work. Therefore *processes at constant volume are well characterized by the internal energy*.

In chemistry *constant pressure is more frequent than constant volume.* Therefore we define a similar state function which is suitable for describing processes *at constant pressure, the* ***enthalpy*** **(H):**

$$H = U + pV \tag{1.19}$$

Since this is also an energy function, its unit is Joule (J). In differential from:

$$dH = dU + pdV + Vdp \tag{1.20a}$$

For final change:

$$\Delta H=\Delta U+p\Delta V+V\Delta p \tag{1.20b}$$

At constant pressure*:*

$$\Delta H = \Delta U + p.\Delta V \tag{1.20c}$$

If only pV work is done and the process is reversible*:*

$$dU = -pdV + \delta Q \tag{1.21a}$$

and for finite changes $\Delta U = -p\Delta V + Q$ (1.21b)

Substituting 1.20a for 1.21b we have

$$dH = \delta Q + Vdp \tag{1.22}$$

If the pressure is constant

$$dH = \delta Q_p \tag{1.23a}$$

for finite changes

$$\Delta H = Q_p \tag{1.23b}$$

In an *isobaric process* (if no other than pV work is done) *the change of enthalpy is equal to the heat.* Therefore the enthalpy plays the same role for isobaric processes like the internal energy for isochoric processes.

Calculation of enthalpy change in case of isobaric warming or cooling:

$$\Delta H = n\int_{T_1}^{T_2} C_{mp} dT \tag{1.24}$$

C_{mp} *is* expressed in form of power series, like

$$C_{mp} = a + bT + cT^{-2} + d \cdot T^2 \tag{1.25}$$

Substituting 1.24 for 1.25, the enthalpy change is calculated as

$$\Delta H = n\left[a(T_2 - T_1) + \frac{b}{2}\left(T_2^2 - T_1^2\right) - c\left(T_2^{-1} - T_1^{-1}\right) + \frac{d}{3}\left(T_2^3 - T_1^3\right)\right] \tag{1.26}$$

Phase changes (isothermal and isobaric processes):

ΔH_m (vap): - molar heat of vaporization

ΔHm (fus): - molar heat of fusion

1.4. Ideal gas (perfect gas)

Properties of an ideal gas:

1. There is no interaction among molecules.

2. The size of molecule is negligible.

The ***ideal gas law*** (see equation 1.1)

$$pV = nRT \tag{1.27}$$

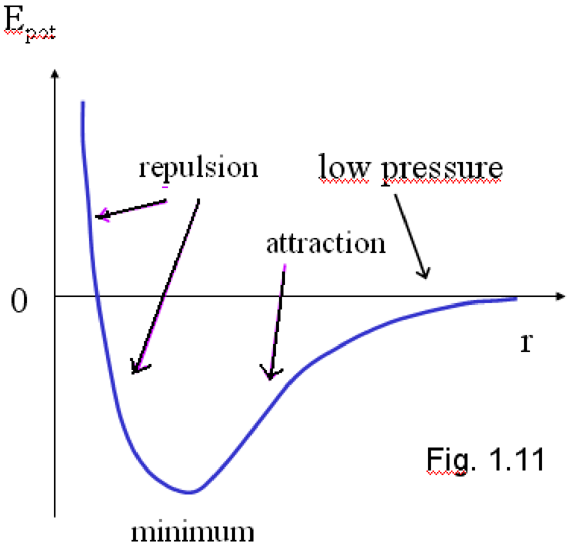


Fig. 1.11

Fig. 1.11 introduces the potential energy between the atoms of a diatomic molecule as function of their distance. At the minimum the sum of forces is zero.

At low pressures real gases approach the ideal gas behaviour.

As it was already mentioned, in ***an ideal gas*** there is no potential energy between molecules. It means that the internal energy does not depend on pressure (or volume). Consequently, the internal energy of an ideal gas depends on temperature only.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{1.28a}$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T = 0 \tag{1.28b}$$

Now looking the temperature dependence of enthalpy! According to the definition of enthalpy (1.19) and the ideal gas law (1.27)

$$H = U + pV = U + nRT$$

Since U depends also on T only,

$$\left(\frac{\partial H}{\partial V}\right)_T = 0 \tag{1.29a}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \qquad (1.29b)$$

1.5. Relation between C_{mp} and C_{mv} (ideal gas)

As it was already mentioned, $C_{mp} > C_{mv}$, because the gas expands when heated at constant pressure -pV work is done. According to equations .15, 1.16, 1.18 and 1.23

$$C_{mv} = \frac{1}{n}\frac{\delta Q_v}{dT} = \frac{1}{n}\cdot\frac{dU}{dT} \qquad (1.30a)$$

and

$$C_{m\,p} = \frac{1}{n}\frac{\delta Q_p}{dT} = \frac{1}{n}\cdot\frac{dH}{dT} \qquad (1.30b)$$

Since H=U+nRT

$$C_{mp} = \frac{1}{n}\cdot\frac{d}{dT}\left(U + nRT\right) = \frac{1}{n}\left(\frac{dU}{dT} + nR\right) \qquad (1.31)$$

$$C_{mp} = C_{mv} + R$$

Therefore for ideal gas

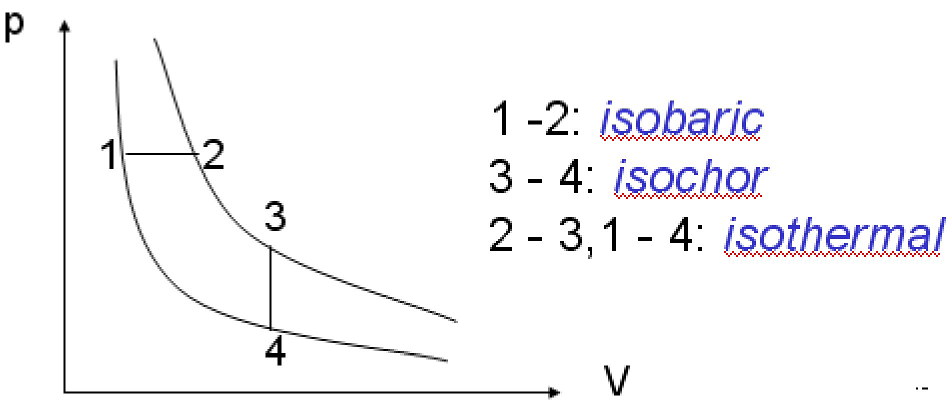
$$C_{mp} - C_{mv} = R \qquad (1.32)$$

1.6. Reversible changes of ideal gases (isobaric, isochor, isothermal)

In case of gases *reversible processes are good approximations* for real (irreversible) processes (this approach is less applicable at high pressures).

Fig. 1.12 shows the isobaric (perpendicular to the ordinate), isochoric (perpendicular to the abscissa) and isothermal (parabola) processes in a p-V diagram.

Fig. 1.12



a. Isobaric process

p-V work:

$$W = -\int p dV = -p\int_{V_1}^{V_2} dV = -p(V_2 - V_1) = -nR(T_2 - T_1) \qquad (133a)$$

$$pdV = nRdT$$

Heat (change of enthalpy, see 1.23b)

$$Q_p = \Delta H = n\int_{T_1}^{T_2} C_{mp} dT \qquad (1.33b)$$

Change of ***internal energy***:

$$\Delta U = W + Q = -nR\int_{T_1}^{T_2} dT + n\int_{T_1}^{T_2} C_{mp} dT = n\int_{T_1}^{T_2}(C_{mp} - R)dT = n\int_{T_1}^{T_2} C_{mv} dT \qquad (1.33c)$$

b. Isochor process

p-V work:

$$W = 0 \qquad (1.34a)$$

Heat (change of internal energy)

$$Q_v = \Delta U = n\int_{T_1}^{T_2} C_{mv} dT \qquad (1.34b)$$

Change of ***enthalpy***

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\int_{T_1}^{T_2} dT = n\int_{T_1}^{T_2}(C_{mv} + R)dT = n\int_{T_1}^{T_2} C_{mp} dT \qquad (1.34c)$$

c. Isothermal process $\Delta U = 0$ $Q = -W$ $\Delta H = 0$

$$W = \int_{V_1}^{V_2} - pdV$$

p-V work:

$$p = \frac{nRT}{V}$$

$$W = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\,ln\frac{V_2}{V_1} = nRT\,ln\frac{V_1}{V_2} \qquad (1.35a)$$

According to ***Boyle's law*** $p_1V_1 = p_2V_2$ and $\frac{V_2}{V_1} = \frac{p_1}{p_2}$

Therefore $W = -nRT\,ln\frac{p_1}{p_2} = nRT\,ln\frac{p_2}{p_1}$ (1.35b)

Heat:

$$W = -nRT\,ln\frac{p_1}{p_2} = nRT\,ln\frac{p_2}{p_1} \qquad (1.35c)$$

***For ideal gases in any process*:**

$$\Delta U = n\int_{T_1}^{T_2} C_{mV} \cdot dT \qquad (1.36a)$$

Fig. 1.13 introduces a process in p-V diagram. Since the internal energy is a state function, we can carry out the process in two parts ΔU is independent of the path.

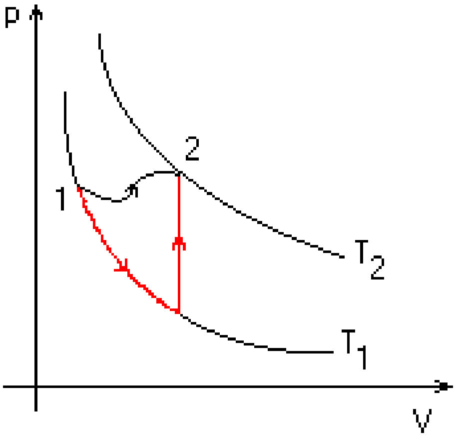


Fig. 1.13

Let us perform the process in two steps (*position 1*: V_1, T_1, p_1)

I. isothermal (expansion to V_2, T_1=const.)

II. isochor (warming to T_2, V_2=const.)

$\Delta U = \Delta U_I + \Delta U_{II}$

$\Delta U_I = 0$

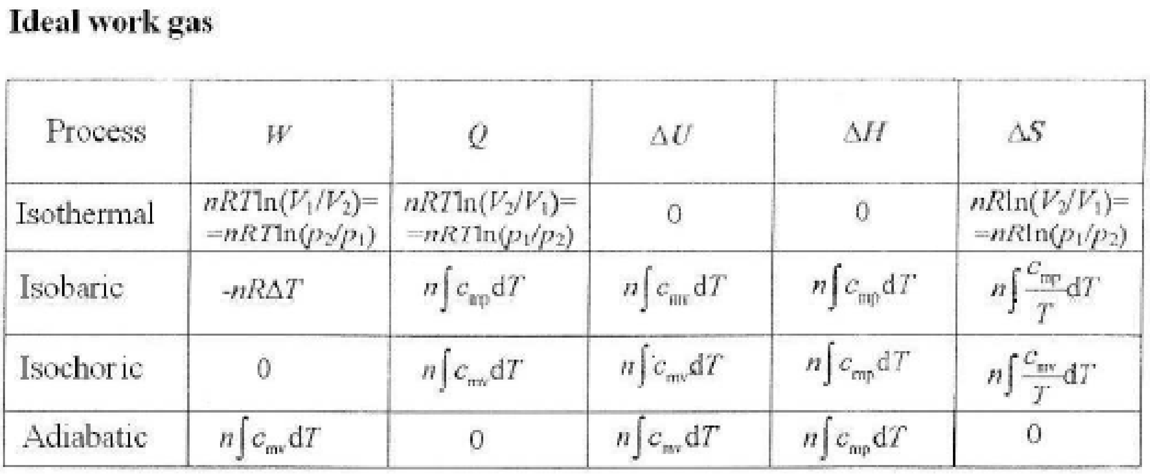
$$\Delta U_{II.} = n\int_{T_1}^{T_2} C_{mV} \cdot dT$$

Similarly, in an ideal gas for any process:

$$\Delta H = n\int_{T_2}^{T_1} C_{mp} dT \qquad (1.36b)$$

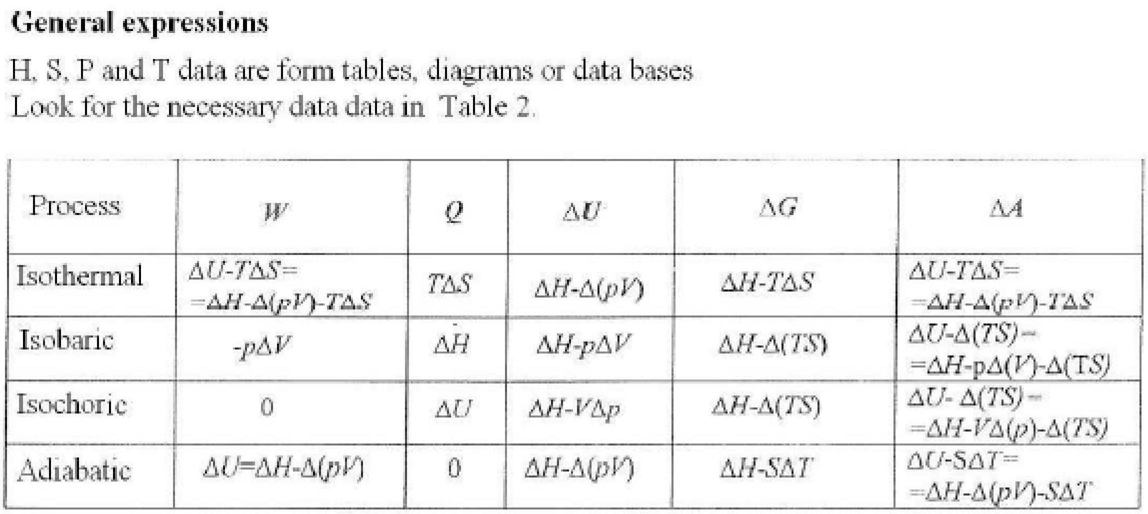
The summary of the equations for the changes of the U, H, W and Q functions for gases during different processes are listed in Table 1.1. For adiabatic reversible processes see also subsection 1.7.

Table 1.1. Calculation of thermodynamic functions of gases



Ideal work gas

Process	W	Q	ΔU	ΔH	ΔS
Isothermal	$nRT\ln(V_1/V_2)=$ $=nRT\ln(p_2/p_1)$	$nRT\ln(V_2/V_1)=$ $=nRT\ln(p_1/p_2)$	0	0	$nR\ln(V_2/V_1)=$ $=nR\ln(p_1/p_2)$
Isobaric	$-nR\Delta T$	$n\int c_{mp}\mathrm{d}T$	$n\int c_{mv}\mathrm{d}T$	$n\int c_{mp}\mathrm{d}T$	$n\int \frac{c_{mp}}{T}\mathrm{d}T$
Isochoric	0	$n\int c_{mv}\mathrm{d}T$	$n\int c_{mv}\mathrm{d}T$	$n\int c_{mp}\mathrm{d}T$	$n\int \frac{c_{mv}}{T}\mathrm{d}T$
Adiabatic	$n\int c_{mv}\mathrm{d}T$	0	$n\int c_{mv}\mathrm{d}T$	$n\int c_{mp}\mathrm{d}T$	0



General expressions

H, S, P and T data are form tables, diagrams or data bases
Look for the necessary data data in Table 2.

Process	W	Q	ΔU	ΔG	ΔA
Isothermal	$\Delta U-T\Delta S=$ $=\Delta H-\Delta(pV)-T\Delta S$	$T\Delta S$	$\Delta H-\Delta(pV)$	$\Delta H-T\Delta S$	$\Delta U-T\Delta S=$ $=\Delta H-\Delta(pV)-T\Delta S$
Isobaric	$-p\Delta V$	ΔH	$\Delta H-p\Delta V$	$\Delta H-\Delta(TS)$	$\Delta U-\Delta(TS)=$ $=\Delta H-p\Delta(V)-\Delta(TS)$
Isochoric	0	ΔU	$\Delta H-V\Delta p$	$\Delta H-\Delta(TS)$	$\Delta U-\Delta(TS)=$ $=\Delta H-V\Delta(p)-\Delta(TS)$
Adiabatic	$\Delta U=\Delta H-\Delta(pV)$	0	$\Delta H-\Delta(pV)$	$\Delta H-S\Delta T$	$\Delta U-S\Delta T=$ $=\Delta H-\Delta(pV)-S\Delta T$

1.7. Adiabatic reversible changes of ideal gases

Adiabatic processes are charcterized by volume changes under the following conditions:

$$Q=0 \tag{1.37a}$$

$$\Delta U=W \tag{1.37b}$$

Volume changes:

Compression, the work done on the system increases the internal energy → T increases.

Expansion, a part of the internal energy is used up for doing work → T decreases.

In adiabatic processes all the three state functions (T, p and V) change.

In a p - V diagram adiabats are steeper than isotherms, look at Fig. 1.14!

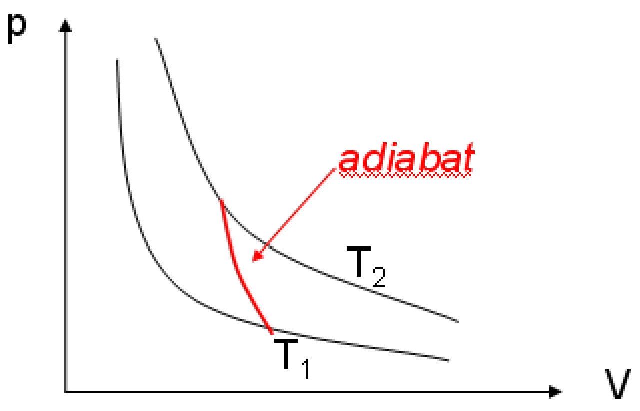


Fig. 1.14.

Derivation of adiabats

a. Relation of V and T

$$dU = \delta W \qquad dU = nC_{mv}dT$$

Reversibility is introduced here: $dW = -pdV$

$$nC_{mv}dT = -pdV$$

Ideal gas: $$p = \frac{nRT}{V}$$

$$nC_{mv}dT = -\frac{nRT}{V}dV$$

$$C_{mv}\frac{dT}{T} = -R\frac{dV}{V}$$

Integrating between initial (1) and final (2) states (We neglect the T-dependence of C_{mv} (and C_{mp}):

$$C_{mv}\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V}$$

$$C_{mv}\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

According to equation 1.32:

$$-R = C_{mv} - C_{mp}$$

So we have

$$C_{mv}\, ln\frac{T_2}{T_1} = \left(C_{mv} - C_{mp}\right) ln\frac{V_2}{V_1}$$

Devided by C_{mv}: $$ln\frac{T_2}{T_1} = \left(1 - \frac{C_{mp}}{C_{mv}}\right) ln\frac{V_2}{V_1}$$

The ***Poisson constant*** $$\frac{C_{mp}}{C_{mv}} = \kappa \qquad (1.37c)$$

$$ln\frac{T_2}{T_1} = \left(1-\kappa\right) ln\frac{V_2}{V_1} = \left(\kappa - 1\right) ln\frac{V_1}{V_2}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\kappa-1} \quad \text{and} \quad T_1V_1^{\kappa-1} = T_2V_2^{\kappa-1}$$

The final relation is

$$TV^{\kappa-1} = const. \qquad (1.37d)$$

To find the relationship between p and V and between p and T we use the ideal gas law (pV = nRT) and equation 1.37d.

b. Relation of p and V

$$T_1V_1^{\kappa-1} = T_2V_2^{\kappa-1} \qquad T_1 = \frac{p_1V_1}{nR} \qquad T_2 = \frac{p_2V_2}{nR}$$

Therefore $$\frac{p_1V_1}{nR}\cdot V_1^{\kappa-1} = \frac{p_2V_2}{nR}\cdot V_2^{\kappa-1}$$

and $$p_1V_1^{\kappa} = p_2V_2^{\kappa}$$

Finally:

$$pV^{\kappa} = const. \qquad (1.37e)$$

c. Relation of p and T

$$p_1V_1^{\kappa} = p_2V_2^{\kappa} \qquad V_1 = \frac{nRT_1}{p_1} \qquad V_2 = \frac{nRT_2}{p_2}$$

Therefore $$p_1\left(\frac{nRT_1}{p_1}\right)^{\kappa} = p_2\left(\frac{nRT_2}{p_2}\right)^{\kappa}$$

$$p_1^{1-\kappa}\cdot T_1^{\kappa} = p_2^{1-\kappa}\cdot T_2^{\kappa}$$

$$T_1 p_1^{\frac{1-\kappa}{\kappa}} = T_2 p_2^{\frac{1-\kappa}{\kappa}}$$

At last we have:

$$Tp^{\frac{1-\kappa}{\kappa}} = const. \tag{1.37f}$$

1.8. The standard reaction enthalpy

In a chemical reaction the molecular energies change during the breaking of old and forming of new chemical bonds.

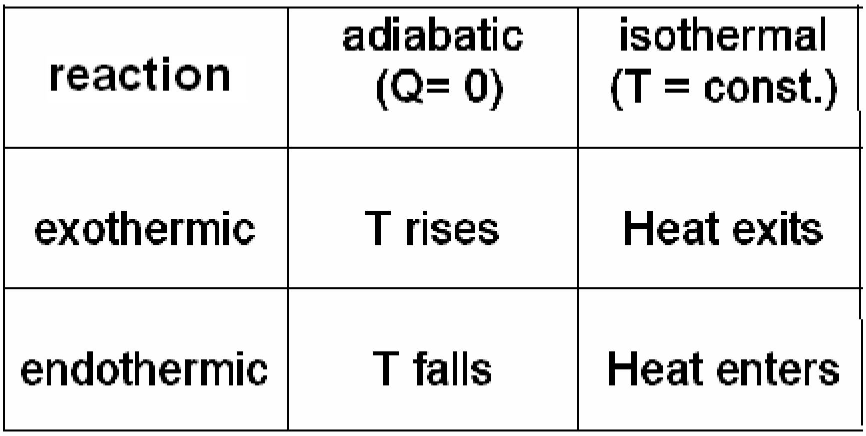
Example: in the reaction $2H_2 + O2 = 2H_2O$ the H-H and O-O bonds break and O-H bonds are formed.

***Exothermic* reaction:** energy is liberated.

***Endothermic* reaction:** energy is needed to perform the reaction at constant temperature.

Table 1.2 introduces the differences in adiabatic and isothermic exothermic and endothermic rections.

Table 1.2. Comparison of the adiabatic and isothermal processes



reaction	adiabatic (Q= 0)	isothermal (T = const.)
exothermic	T rises	Heat exits
endothermic	T falls	Heat enters

Heat of isothermal reaction

Fig. 1.15 intriduces an isothermal reactor.

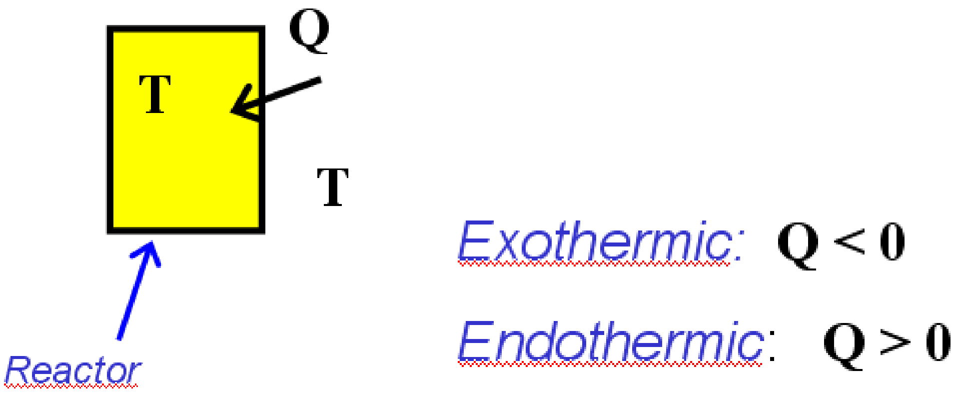


Fig. 1.15.

Heat of reaction is the heat entering the reactor (or exiting from the reactor) if the amounts of substances expressed in the reaction equation react at constant temperature. The *subscript* **r** *refers to „reaction*”.

At *constant volume:* $\Delta_r U$, at *constant pressure:* $\Delta_r H$ is measured.

For example: $2H_2 + O_2 = 2H_2O$

$\Delta_r U = 2U_m(H_2O) - 2U_m(H_2) - U_m(O_2)$

$\Delta_r H = 2H_m(H_2O) - 2H_m(H_2) - H_m(O_2)$

The ***heat of reaction*** *defined this way* ***depends on*** *T, p and the concentrations of the reactants and products.*

Standardization*:* the pressure and the concentrations are fixed but not the temperature.

Standard heat of reaction: is the heat entering the reactor (or exiting from the reactor) if the amounts of substances expressed in the reaction equation react **at *constant temperature***, and both the reactants and the products are pure substances at p^o pressure.

Therefore *standardization* means*: pure substances and* p^o *pressure* (10^5 Pa). *Temperature is not fixed* but most data are available at 25 °C.

The ***standard state*** *will always be denoted by a* ***superscript 0,*** **i.e. standard pressure is denoted with p^0,** 10^5 Pa = 1 bar.

The ***standard heat of reaction*** *is the change of enthalpy* according to the definition of enthalpy ($\Delta H = Q_p$, equ. 1.23).

The general model of a reaction:

$$\sum \nu_A M_A = \sum \nu_B M_B \qquad (1.38)$$

where ν means stoichiometric coefficient, M: molecules, A-s stand for reactants, B-s stand for products.

The standard heat of reaction (enthalpy of reaction):

$$\Delta_r H^0 = \sum_B \nu_B H^0_{mB} - \sum_A \nu_A H^0_{mA} \qquad (1.39)$$

H^0_m is the standard molar enthalpy.

***Example**:* $2H_2 + O_2 = 2H_2O$

Therefore $\Delta_r H^0 = 2H^0_m(H_2O) - 2H^0_m(H_2) - H^0_m(O_2)$

We have to *specify the reaction equation* (very important, see the examples), *the state of the participants and the temperature.*

Example reactions

Standard reaction	*Enthalpy at 25 °C*
$2H_2(g) + O_2(g) = 2H_2O(l)$	*-571,6 kJ*
$H_2(g) + 1/2O_2(g) = H_2O(l)$	*-285,8 kJ*
$H_2(g) + 1/2O_2(g) = H_2O(g)$	*-241,9 kJ*

Compare the first and the second reaction, only the stoichiometric coefficients are different! The comparison of the second and third reaction shows the phase effect.

1.9. Measurement of heat of reaction

Calorimeters are used for measuring heats of reaction. ***Bomb calorimeter*** (Fig. 1.16) is suitable for measuring *heat of combustion.* The substance is burned in excess of oxygen under pressure.

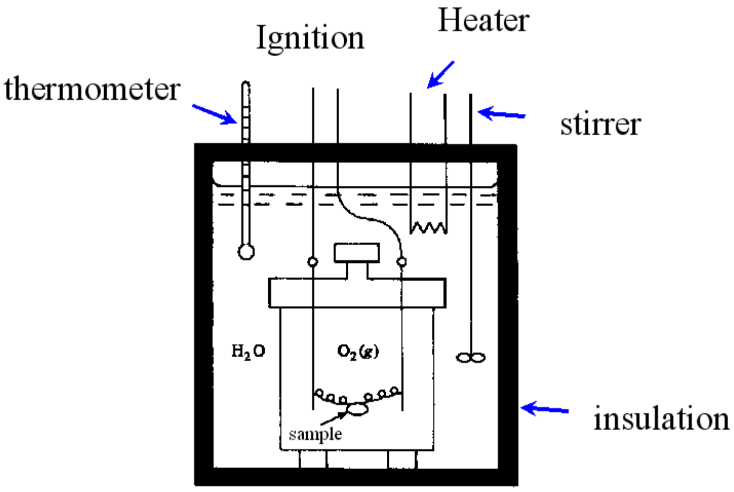


Fig. 1.16

The heat of reaction can be determined from change of the temperature during the reaction (ΔT):

$$q = C\cdot\Delta T \tag{1.40}$$

C *is the* ***heat capacity*** *of the calorimeter* (including everything inside the insulation, wall of the vessel, water, bomb, etc.). Determination of C is possible with known amount of electrical energy, which causes ΔT´ temperature rise:

$$V\cdot I\cdot\Delta t = C\cdot\Delta T' \tag{1.41}$$

V is the power, I is the current and Δt is the time of heating.

In a bomb calorimeter $\Delta_r\mathbf{U}$ is measured because the volume is constant. The *subscript* ***r*** *refers to „reaction*”.

$$H = U + pV$$

$$\Delta_r H = \Delta_r U + \Delta_r(pV) \tag{1.42}$$

The *pV product* changes if the number of molecules of the ***gas phase components*** changes. In ideal gas approximation (pV=nRT)

$$\Delta_r(pV) = \Delta_r n_g RT \qquad (1.43)$$

$\Delta_r n_g$ is the change of the stochiometric coefficients for gaseous components:

$$\Delta_r n_g = \Sigma n_g(\mathit{products}) - \Sigma n_g(\mathit{reactants}) \qquad (1.44)$$

Example:

$C_6H_5COOH(s) + 7.5O2(g) = 7CO_2(g) + 3H_2O(l)$

$\Delta_r n_g = 7 - 7.5 = -0.5$

The difference of $\Delta_r U$ and $\Delta_r H$ is usually small.

1.10. Hess`s law

As it was already defined, enthalpy is a state function. Its change depends on the initial and final states only. (It is independent of the intermediate states). This statement can be applied also for the reaction enthalpy. This theorem can be applied also for the reaction enthalpy.

Example

The reaction enthalpy of the reaction

$C(graphite) + O_2 = CO_2$ (1)

is equal to the sum of reaction enthalpies of the following two reactions:

C(graphite) + 1/2O2 = CO (2)

CO +1/2 O2 = CO2 (3)

We can write:

$\Delta_r H(1) = \Delta_r H(2) + \Delta_r H(3)$

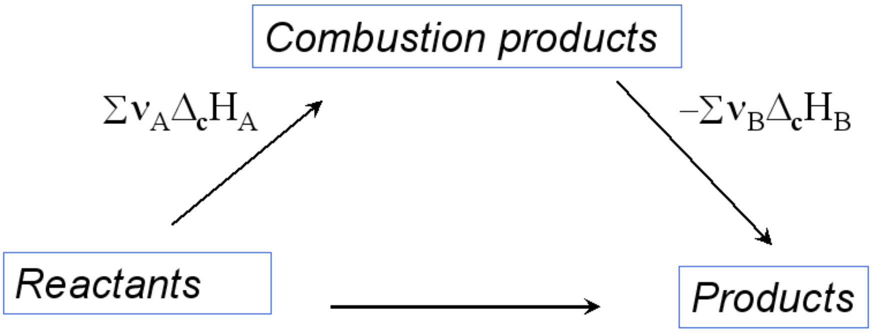
So *if we know two of the three reaction enthalpies, the third one can be calculated. This is* ***Hess's law***. He discovered it in 1840!

The significance of Hess`s law is that reaction enthalpies, which are difficult to measure, *can be determined by calculation.*

The reaction enthalpies can be calculated from ***heats of combustion*** *or* ***heats of formation.***

Calculation of heat of reaction from heats of combustions (subscript c)

Suppose we burn the reactants and then we perform a reverse combustion in order to make the products.



The *heat of reaction* is obtained if we subtract the sum of the heats of combustion of the products from the sum of the heats of combustion of reactants:

$$\Delta_rH = - \Delta_r(\Delta_cH) \qquad (1.45)$$

Example:

$$3C_2H_2 = C_6H_6$$

$$\Delta_rH = 3\Delta_cH(C_2H_2) - \Delta_cH(C_6H_6)$$

The ***heat of formation (enthalpy of formation)*** *of a compound is the enthalpy change of the reaction, in which the compound is formed (from the most stable forms) of its elements.* It is denoted by Δ_fH.

Example:

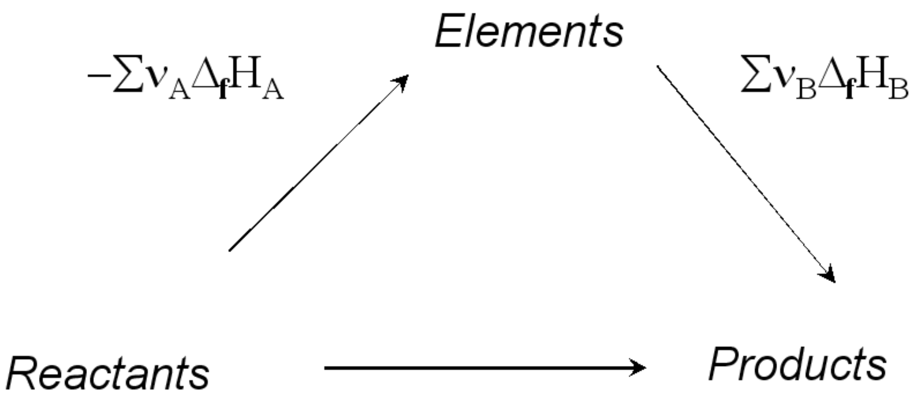
The heat of formation of SO_3 is the heat of the following reaction

$$S + 3/2O_2 = SO_3$$

It follows from the definition that **the heat of formation of an element is zero (at standard temperature).**

Calculation of heat of reaction from heats of formations (subscript f)

Suppose we first decompose the reactants to their elements (reverse of the formation reaction), then we compose the products from the elements.



The heat of reaction is obtained if we subtract the sum of the heats of formation of the reactants from the sum of the heats of formation of the products.

$$\Delta_r H = \Delta_r(\Delta_f H) \tag{1.46}$$

Example:

$3C_2H_2 = C_6H_6$

$\Delta_r H = \Delta_f H(C_6H_6) - 3\Delta_f H(C_2H_2)$

1.11 Standard enthalpies

We do not try to determine the absolute values of enthalpies and internal energies (remember, they have not absolute values).

The standard enthalpies of compounds and elements are determined by international convention.

1. At **298,15 K (25 ^{o}C)** and **$p^o = 10^5$ Pa** the enthalpies of the stable forms of the elements are taken zero:

For elements

$$\mathbf{\Delta H_m^0(298) = 0} \tag{1.47}$$

At temperatures different from 25 ^{o}C the enthalpy is not zero.

The standard molar enthalpy of an element which is solid at 25 ^{o}C but gaseous at T can be calculated as follows:

$$H^0_m(T)=\int_{298}^{\overset{\text{melting point}}{\overset{\downarrow}{T_m}}}\underbrace{C^s_{mp}}_{\substack{\text{Molar heat}\\ \text{capacity of}\\ \text{solid}}}dT+\underbrace{\Delta H^0_m(fus)}_{\substack{\text{Enthalpy}\\ \text{of fusion}\\ \text{of solid}}}+\int_{T_m}^{\overset{\text{boiling point}}{\overset{\downarrow}{T_b}}}\underbrace{C^l_{mp}}_{\substack{\text{Molar heat}\\ \text{capacity of}\\ \text{liquid}}}dT+\underbrace{\Delta H^0_m(vap)}_{\substack{\text{Heat of}\\ \text{vaporization}\\ \text{of liquid}}}+\int_{T_b}^{T}\underbrace{C^g_{mp}}_{\substack{\text{Molar heat}\\ \text{capacity of}\\ \text{gas}}}dT \tag{1.48}$$

The standard enthalpy of a compound ***at 298.15 K (25 ^{o}C)*** *is taken equal to its heat of formation since that of the elements is zero.*

$$H^0_m(298)=\Delta_f H^0 \tag{1.49}$$

At *any other temperature* the enthalpy differs from the heat of formation.

In tables*: standard molar enthalpies at 298 K and molar heat capacity (C_{mp}) functions are given.*

The simplest way is to calculate the ***enthalpy of reaction at T*** *is to calculate the enthalpy of each component at T then take the difference.*

If there is ***no phase change*** from 298 K to T,

$$H^0_m(T)=H^0_m(298)+\int_{298}^{T}C_{mp}dT \tag{1.50}$$

In case of *phase change(s) of elements* use the formula (1.48). *For compounds use a formula similar to (1.48). If the compound is solid at 25 ^{o}C but gaseous at T:*

$$H_m^0(T) = H_m^0(298) + \int_{298}^{T_m} C_{mp}^s dT + \Delta H_m^0(fus) + \int_{T_m}^{T_b} C_{mp}^l dT + \Delta H_m^0(vap) + \int_{T_b}^{T} C_{mp}^g dT \qquad (1.51)$$

1.12. The first law for open systems, steady state systems

In an *open system* (see Fig. 1.3) both material and energy exchange with the surroundings are allowed. Here we deal with open systems since *technological processes are usually performed in open systems.* Fig. 1.17 introduces an open system. A piston compresses with p_{in} prsssure the input V_{in} volume material (cross section A_{in}, length l_{in}) into the system. The V_{out} output (cross section A_{out}, length l_{out}) has p_{out} pressure. The substances entering and leaving the system carry energy. Their transport also needs energy.

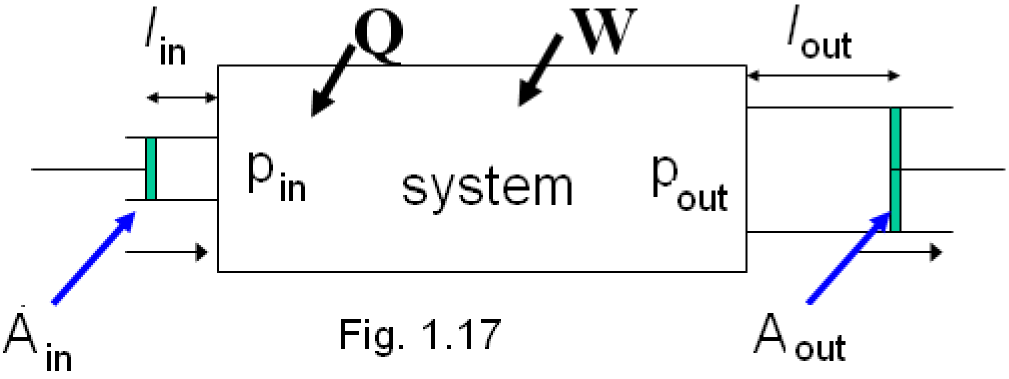


Fig. 1.17

From the *point of view of the system* the input increases, the output decreases its energy. Therefore

$$\Delta U = Q + W + U_{in} - U_{out} + p_{in}V_{in} - p_{out}V_{out}$$

According to the definiton of the enthalpy (H=U+pV)

$$\Delta U = Q + W + H_{in} - H_{out} \qquad (1.52)$$

This equation is the first law of thermodynamics for open systems.

In *technical processes* the inputs are the *volume streams* ($\dot{V}_{in}$ and $\dot{V}_{out}$) substitute the volumes since the processes take place in time. Similarly, the *time derivatives of the energy functions* are used.

A ***steady state system*** *is an open system where the state functions change in space but* ***do not change in time****.* Energy does not come into being and does not disappear:

$$\Delta U = 0 \tag{1.53a}$$

Therefore we have the balance for enthalpy (see 1.52)

$$H_{out} - H_{in} = Q + W \tag{1.53b}$$

The difference between the total exiting and total entering energies (the enthalpy balance) is equal to the heat and the work balance of the steady state system.

If there is ***no chemical reaction****, H_{out} - Hin is the enthalpy change of the substance going through the system:*

$$\Delta H = Q + W \tag{1.54}$$

We shall discuss three examples important in industry:

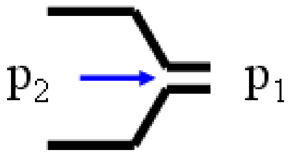
1) Expansion of gases through throttle

2) Adiabatic compressor

3) Steady state chemical reaction

1) Expansion of gases through throttle

The purpose is to reduce the pressure of the gas.

 $p_2 > p_1$ Fig. 1.18	The operation is continuous, the state functions of the gas do not change in time (steady state). *Adiabatic process:* $Q = 0$ (1.55a) *No work done:* $W = 0$ (1.55b) *Therefore (see 1.54)* $\Delta H = 0$ (1.56)

2) Continuous adiabatic compressor

$$Q = 0 \quad \text{(adiabatic)} \qquad (1.57)$$

Acciording to 1.52

$$\Delta H = W \qquad (1.58)$$

W is the work of the compressor.

3) Steady state reactor

Here we can apply equation 1.54:

$$(H_{out} - H_{in}) = \sum n_{out} H_{m,out} - \sum n_{in} H_{m,in} = Q + W \qquad (1.59)$$

1.13. The second law of thermodynamics

I. law: conservation of energy. It does not say anything about the direction of processes.

II. law: it gives information about the direction of processes in nature.

We have also possibility of the thermodynamic definiton of the entropy.

Imagine the following phenomenon: *Heat transfers from the cold table to the hot water (Fig. 1.19):*

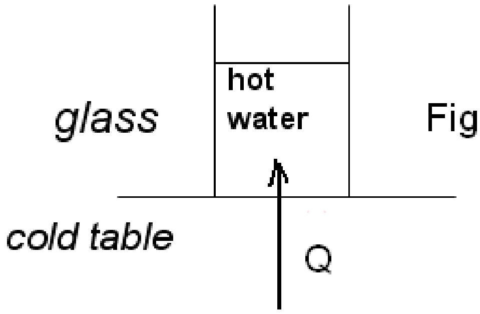


Fig. 1.19

This is not possible. The source of the necessary heat comes from some system of higher temperature than the temperature of the water in the glass.

In ***spontaneous processes*** *heat always goes from bodies of higher temperature to bodies of lower temperature.*

Processes in nature → dissipation of energy

and

Ordered system → disordered system.

Now we try to define the function characterizes the disorder. We use the name ***entropy (S)*** for it. Its most important property must be*:* ***in spontaneous processes (in isolated system) it always increases.***

For definition of entropy consider the first law (Equ. 1.7):

$$dU = \delta W + \delta Q$$

It is valid both for reversible and for irreversible processes**.**

For a **reversible process:**

$$dU = \delta W_{rev} + \delta Q_{rev} \qquad (1.60)$$

For pV work***:***

$$\delta W_{rev} = -p \cdot dV \qquad (1.61)$$

We try to describe the heat similarly to other energy types like pV work. It is straightforward that the *intensive parameter is the temperature*. The corresponding *extensive parameter is the entropy*. For reversible processes we define the elementary heat as

$$\delta Q_{rev} = T \cdot dS \qquad (1.62)$$

From this expression dS is

$$dS = \frac{\delta Q_{rev}}{T} \qquad (1.63)$$

(1.63) is the thermodynamic definition of entropy*. *Entropy is a state function. *Its unit is J/K*. The finite change of entropy is if the system goes from state “A” to state “B”

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T} \qquad (1.64)$$

In **isothermal processes**

$$\Delta S = \frac{1}{T}\int_A^B \delta Q_{rev} = \frac{Q_{rev}}{T} \qquad (1.65)$$

since the temperature is constant.

Applying the expession of the elementary heat (1.62) and the expression of the elementary p-V work (1.61) the equation 1.60 ($dU=\delta W+\delta Q$) contains the entropy in the form

$$dU = -pdV + TdS \qquad (1.66)$$

This is the **fundamental equation for the change of the internal energy in closed systems, the exact differential of U in closed systems.**

1.14. Change of entropy in closed systems

We apply the equation of finite changes of entropy (1.64):

For ***isobaric processes***

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T}$$

$$\delta Q_{rev} = nC_{mp} dT \tag{1.67}$$

Therefore

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{mp}}{T} dT = n\int_{T_1}^{T_2} C_{mp} d\ln T \tag{1.68}$$

Equation 1.68 means, the entropy increases by heating ($T_2>T_1$) and decreases by cooling ($T_2<T_1$).

For isochor processes:

$$\delta Q_{rev} = nC_{mv} dT \tag{1.69}$$

Therefore

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{mv}}{T} dT = n\int_{T_1}^{T_2} C_{mv} d\ln T \tag{1.70}$$

Equation 1.70 means, that also for isochor processes the entropy increases by heating ($T_2>T_1$) and decreases by cooling ($T_2<T_1$).

For isothermal processes

The equation 1.65 is valid:

$$\Delta S = \frac{1}{T}\int_A^B \delta Q_{rev} = \frac{Q_{rev}}{T}$$

For isothermal reversible process in an ideal gas:

since $\Delta U = 0$, therefore $Q = -W$, consequently

$$W = nRT\ln\frac{p_2}{p_1} \quad \text{and} \quad Q = -nRT\ln\frac{p_2}{p_1}$$

So we have

$$\Delta S = -nR\ln\frac{p_2}{p_1} = nR\ln\frac{V_2}{V_1} \tag{1.71}$$

Entropy *increases at expansion, decreases at contraction.*

Changes of entropy in state changes (isothermal, isobaric processes):

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m} \tag{1.72a}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \tag{1.72b}$$

Entropy increases at melting and evaporation, decreases at freezing and condensation.

Change of S in closed systems	
S increases	*S decreases*
warming	Cooling
melting	Freezing
evaporation	Condensation
expansion	Compression
mixing	Separation
dissolving	Precipitation
Disorder increases	***Disorder decreases***

1.15. The second law and entropy

The examination of entropy changes in real (irreversible) processes has practical importance. The following examples will be discussed:

1. *Two bodies of different temperature are in contact.* Heat goes from the body of higher temperature to the body of lower temperature.
2. The temperatures in the two sub-systems are equal, but *the pressures are initially different.*

1. *The two bodies are in thermal contact but together they are isolated from the surroundings.* Look at the model on Fig. 1.20!

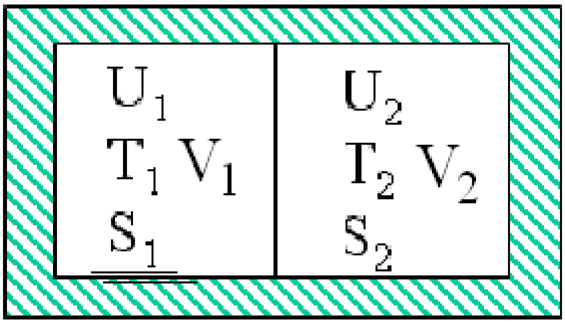


Fig. 1.20

Removing the wall between the two parts of the system: there is no change in the volumes, since $V_1=V_2$, therefore $dV_1=dV_2$. According to the first law of thermodynamics in our isolated system U_1+U_2=const., therefore

$$dU = dU_1 + dU_2 = 0 \quad \text{and} \quad dU_2 = -dU_1.$$

Applying the second law $dU_1 = T_1dS_1$ and $dU_2 = T_2dS_2$.

The overall entropy change:

$$dS = dS_1 + dS_2 = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = \frac{dU_1}{T_1} - \frac{dU_1}{T_2} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \cdot dU_1$$

At last

$$\boldsymbol{dS = \frac{T_2 - T_1}{T_1 \cdot T_2} \cdot dU_1} \qquad (1.73)$$

Discussion of equation 1.73:

a) If body 2 is the warmer:

$T_2-T_1 > 0$

$dU_1 > 0$ (because heat goes **to** body 1)

$dS > 0$

b) If body 1 is the warmer:

$T_2-T_1 < 0$

$dU_1 < 0$ (because heat goes **from** body 1)

$dS > 0$

Since both T_2-T_1 and dU1 have the same, the sign of dS has positive sign in both cases, i.e. the entropy increases:

$$dS > 0 \tag{1.74}$$

Heat goes (spontaneously) from the higher to lower temperature place according to the experience.

2. *The two bodies have the same temperature but their pressure is different (the pressures are changeable with a piston T=const., $p_1 \neq p_2$ Together they are isolated from the surroundings.* Look at the model on Fig. 1.21!

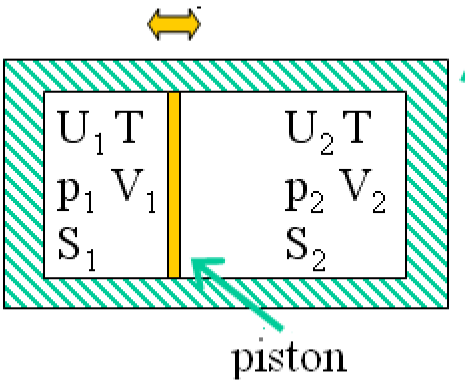


Fig. 1.21

For ideal gas

$dU_2 = -dU_1$ (because of isolation)

$dV_2 = -dV_1$ (the total volume is constant)

Applying second law of thermodynamics:

$dU_1 = -p_1dV_1+TdS_1$ and $dU_2 = -p_2dV_2+TdS_2$

We have

$$dS_1 = \frac{1}{T}dU_1 + \frac{p_1}{T}dV_1$$

$$dS_2 = \frac{1}{T}dU_2 + \frac{p_2}{T}dV_2 = -\frac{1}{T}dU_1 - \frac{p_2}{T}dV_1$$

At last:

$$dS = dS_1 + dS_2 = \frac{1}{T}dU_1 - \frac{1}{T}dU_1 + \left(\frac{p_1}{T} - \frac{p_2}{T}\right)dV_1$$

$$dS = \frac{p_1 - p_2}{T} \cdot dV_1 \tag{1.75}$$

a) If $p_1 > p_2$ and $dV_1 > 0$ (the gas of higher pressure expands)

b) If $p_1 < p_2$ and $dV_1 < 0$

*Since **in both cases** the values have the same sign in (1.75), the entropy increases:*

$$dS > 0 \tag{1.76}$$

Summarizing: *in general, if a macroscopic process takes place in an isolated system, the **entropy increases**. At **equilibrium the entropy has a maximum value.***

According to the **second law** *of thermodynamics* **in an isolated system**

$$\Delta S \geq 0 \tag{1.77}$$

If the **system is not isolated**, the entropy change of the ***surroundings*** must also be ***taken into account***:

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0 \tag{1.78}$$

Macroscopic processes are always accompanied by the increase of entropy.

1.16. Statistical approach of entropy

We stated that the entropy is measure of the disorder (see 1.63):

$$dS = \frac{\delta Q_{rev}}{T}$$

According to this equation if we speak on entropy it is always in contact with heat. We shall discuss whether it is always so.

Examine the expansion of an ideal gas into vacuum:

$$Q = 0 \quad W = 0 \quad \Delta U = 0$$

We expect the increase of S. For the calculation of entropy is this case let us show a model on Fig. 1.22!

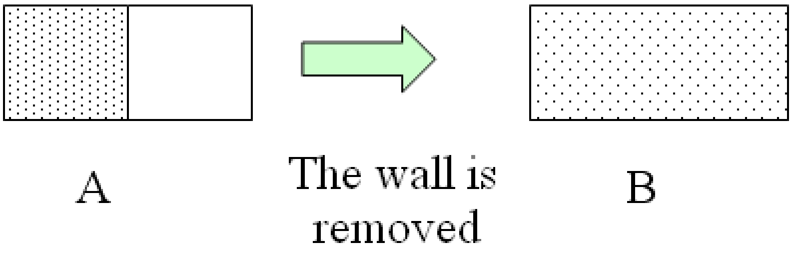


Fig. 1.22

The wall is removed instantly. Therefore we try to expand the gas reversible. On Fig. 1.22 F is the acting force.

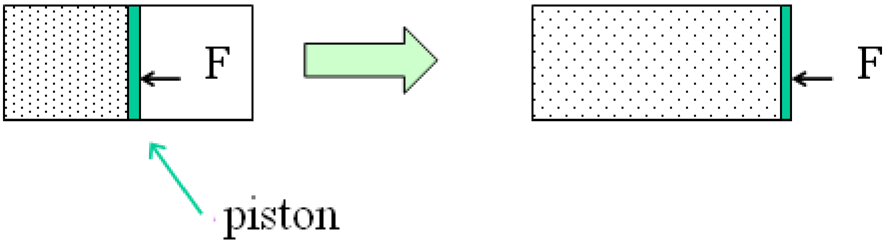


Fig. 1.23

The final state is the same in both cases but the process is performed reversibly ($W \neq 0$, $Q \neq 0$).

Equations for isothermal reversible expansion of an ideal gas:

$$W = nRT \ln \frac{p_2}{p_1} \quad \Delta U = 0, \quad Q = -W, \quad Q = -nRT \ln \frac{p_2}{p_1}$$

The entropy change based on these equations is for isothermal reversible expansion

$$\Delta S = -nR \ln \frac{p_2}{p_1} = nR \ln \frac{V_2}{V_1} \tag{1.79}$$

i. e. the entropy increases.

The process ***A*** $\rightarrow$ ***B*** *(Fig. 1.22) goes spontaneously. The process* ***B*** $\rightarrow$ ***A*** *never goes spontaneously.* For understanding this why it is so, we have to be familiar with some probability calculations, with the ***statistical interpretation of entropy.***

First we discuss the probability of the presence of molecules in a vessel.

If only one molecule exists in the half of the vessel, the probability of its presence in the vessel is ½ (either in one half or in the other half).

If two molecules are present, the probability of their presence in the same half is $\left(\frac{1}{2}\right)^2$ (possible distributions for molecules *a* and *b* are: ab 0, a b, b a, 0 ba, altogether 4 possible distributions).

It we have N molecules, the number of the possible distributions is 2^N, the probability is $\left(\frac{1}{2}\right)^N$. *The probability decreases with increasing number of the molecules.*

*This result means that there exists beside the **thermal disorder** also the **spatial (structural) disorder.***

The thermodynamic definition of the entropy (1.63)

$$dS = \frac{\delta Q_{rev}}{T}$$

does not say about the *spatial disorder* and also about the *absolute value of the entropy* (see subsection 1.18). The *statistical definition of the entropy* helps us:

$$\boldsymbol{S = k \cdot lnW} \tag{1.80}$$

Here *k* is the *Boltzmann constant,* the *ratio of gas constant (R) to the Avogadro constant (N_A)*

$$k = \frac{R}{N_A} = 1.380656 \times 10^{-23}\ J/K$$

W is the *thermodynamic probability*: *the number of possible configurations of the given state.* We calculated similar probabilities for molecules in a vessel the (2^N probabilities for N molecules).

Example 1

Calculate the entropy of 1 mol **CO** at 0 K. There is *no thermal entropy* but there *is structural disorder* (Fig. 1.24).

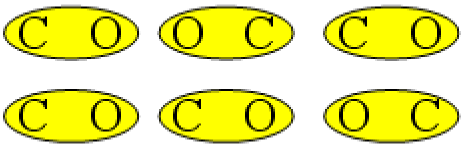


Fig. 1.24

The dipole moment of the CO molecules is small. Each molecule can be oriented two ways in the crystal (Fig. 1.24). In 1 mol there are N^A molecules. The thermodynamic probability is for N_A molecules

$$W = 2^{N_A} \rightarrow \underline{S} = k \cdot \ln 2^{N_A} = k \cdot N_A \cdot \ln 2 = R \cdot \ln 2 = 5.76\ J/K$$

Example 2.

HCl has a large dipole moment. Each molecule is oriented one way.

At 0 K the thermodynamic probability is W = 1, lnW = 0, and therefore $\underline{S = 0}$.

In these examples we calculated the entropy arising from ***structural disorder.***

Thermal disorder

According to quantum theory the energies of particles are quantized.

Example

10 particles, three energy levels, $\varepsilon_0 < \varepsilon_1 < \varepsilon_2$, see Fig. 1.25.

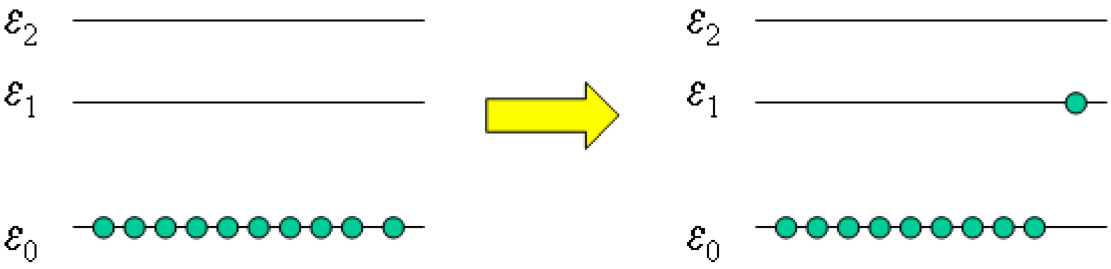


Fig. 1.25

Left figure: at 0 K all molecules are on level ε_0 : W = 1, thermal entropy is 0.

Right figure: If one molecule is on level ε_1, the number of possibilities is 10, the thermal entropy is S= $k \times \ln W = 1.380656 \times 10^{23} \times \ln 10 = 3.1791 \times 10^{23}$J/K. Comparing this result with those for 1 mol CO, this entropy is higher, this system is less ordered.

In case of *N molecules* the number of possibilities is N.

If 2 molecules are on level ε_1, the number of possibilities is N(N-1)/2.

If T increases, more and more molecules get to the higher levels

→ *W increases* → *S increases.*

Some definitions

Microstate: a possible distribution of particles in system under the energy levels.

Macrostate*:* sum of microstates with identical energy.

Thermodynamic probability of a system containing N atoms its energy is distributed under r levels, i=0,1,2,..,r, the energy levels are $\varepsilon_0,\varepsilon_1,.,\varepsilon_r$, indices of N refer on the level:

$$W = \frac{N!}{N_0! \cdot N_1! \cdot N_2! \cdots} \tag{1.81}$$

$$N = \sum_{i=1}^{n} N_i \tag{1.82}$$

For the total energy

$$E = \sum_{i=1}^{n} N_i \varepsilon_i \tag{1.83}$$

This model is analogous to model, where the number of possibilities of putting *N balls in boxes* so that we put N_1 in the first box, N_2 in the second one, and so on.

Example:

$N_0 = 5$, $N_1 = 3$, $N_2 = 2$, $N = 10$. This is a microstate (see Fig. 1.26).

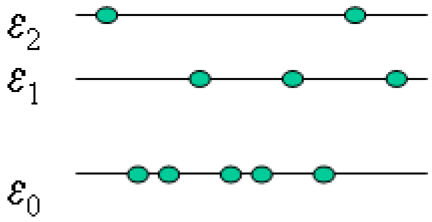


Fig. 1.26

The ***statistical weight of the microstate (configuration)*** **therefore it** ***characterizes the measure of the disorder,*** (remember Eq. 1.80: S=k.lnW) In case of our example:

$$W = \frac{10!}{5!\cdot 3!\cdot 2!} = 2520$$

1.17. T-S diagram

The *p-V diagram* is suitable for illustrating the *changes of state of gases*. *In practice* we need *H or S values*. For *pure substances* we *use tables or diagrams*. For describing the state it is enough to give two (properly chosen) *intensive state parameters*.

In technical diagrams specific units are applied. The state functions in specific values of these functions are labeled by the corresponding low case letters, like **h** *or* **s**. *The applied technical diagrams are* ***t-s, h-p and h-s*** *ones. Enthalpy is used in* kJ/kg units, *entropy in* kJ/kgK, *temperature* in ^{o}C, *pressure* in bar, *volume* m^3/kg units.

Our example is the very important water T-S$_m$ diagram (Fig. 1.27), where the phases and the binary phase area are well observable.

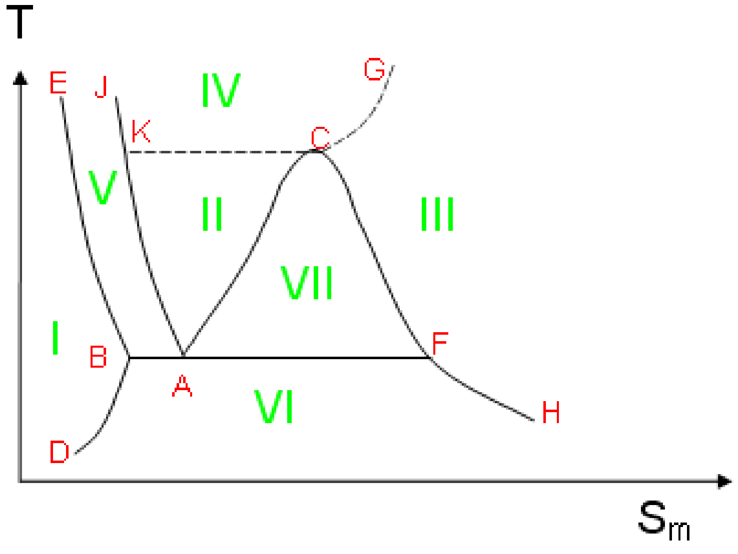


Fig. 1.27

I: solid phase

II: liquid phase

III: gas phase

IV: fluid state

V: solid-liquid

VI: solid-vapor

VII: liquid-vapor

DB: solid (in eq. with vapor)

BAF: ***triple point***

BE: solid (in eq. with liquid)

AJ:liquid (in eq. with solid)

AC: liquid (in eq: with vapor)

CF: vapor (in eq. with liquid)

FH: vapor (in eq. with solid)

C: critical point

KCG: border of fluid state

S_m*: molar entropy* ($Jmol^{-1}K^{-1}$)

The next figure is a part of the t-s diagram of water. The area below the bell curve is the area where liquid and vapor are in equilibrium. For the determination of the *ratio of phases in mixed area use the:* ***lever rule*** (see Fig. 1.29 and text below it).

The isochors are labeled with **v,** the isobars with **p,** the isenthalpic curves with **h** (they characterizes the adiabatic throttles).

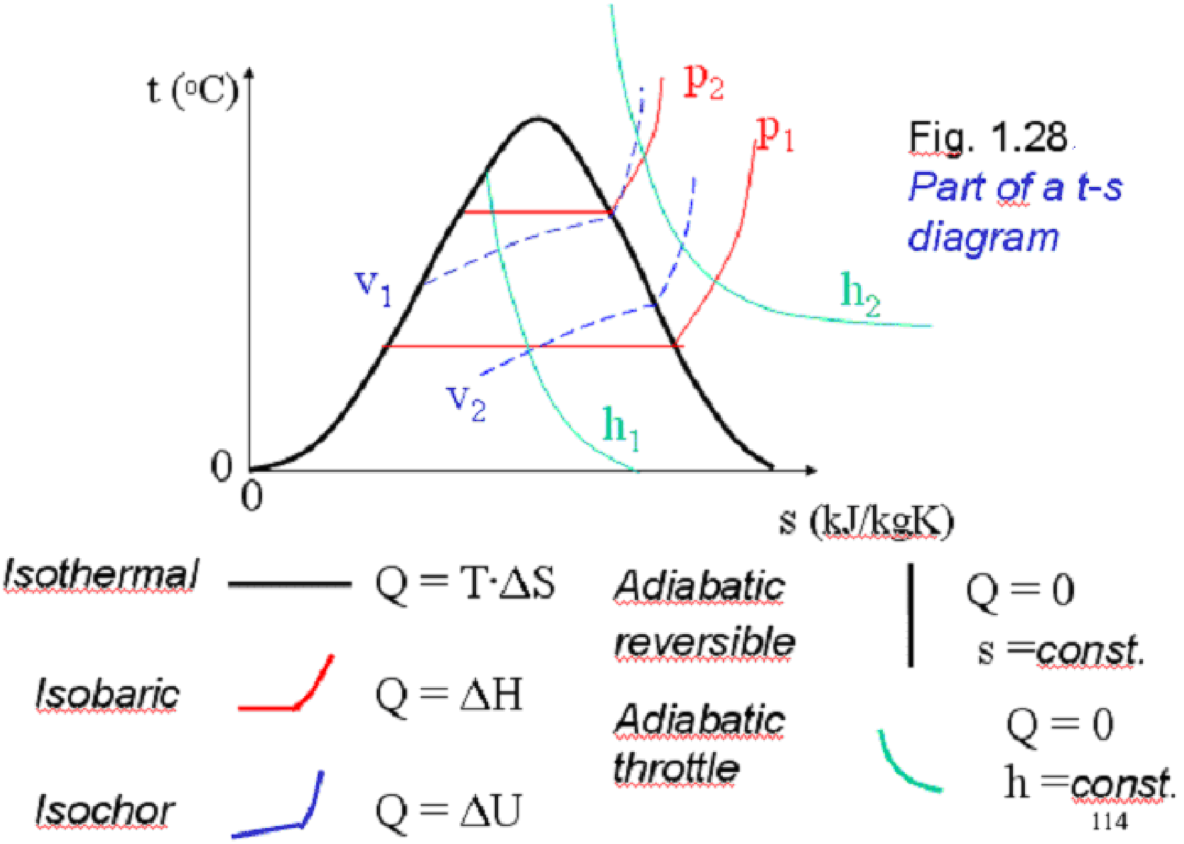


Fig. 1.28 *Part of a t-s diagram*

Calculation of work: $W = \Delta U - Q = \Delta H - \Delta(pV) - Q$ (1.84)

In steady state process: $W = \Delta H - Q$ (1.85)

For the application of the level rule for the determination of the ratio of phases in the mixed are look at Fig. 1.29.

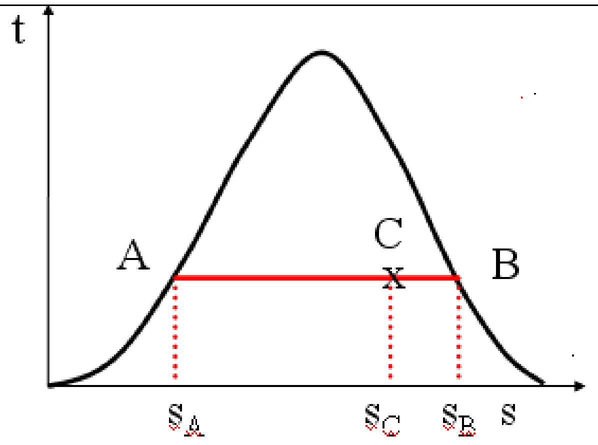


Fig. 1.29

$$\frac{s_C - s_A}{s_B - s_C} = \frac{m_B}{m_A}$$ inverse proportion

How to apply the level rule?

s_A: specific entropy of liquid

s_B: specific entropy of vapor

m: mass

$$m = m_A + m_B$$

$$m s_C = m_A s_A + m_B s_B$$

$$m_A s_C + m_B s_C = m_A s_A + m_B s_B$$

$$m_A(s_C - s_A) = m_B(s_B - s_C)$$

$$m_A \cdot \overline{AC} = m_B \cdot \overline{BC}$$

1.18. The third law of thermodynamics

The third law is in connection with the *absolute zero* (0K) temperature. If we wish to arrive low temperatures special *experiments* are necessary

Joule-Thomson effect (see subsection 2.18)***: expanding of gases through a throtle.*** Usually this is used for cooling down. The following data demonstrate the history of cooling down.

List of liquefied gases in the 19th century*:*

oxygen:	90K
nitrogen	77K
hydrogen	20K
in 1908	
helium	4K

For reaching temperatures below 4K the ***adiabatic demagnetization*** is applied.

Paramagnetic materials: In a magnetic field the particles act as little magnets, and are oriented in the direction of the field → ordered magnetic dipoles.

First step of cooling: the external magnetic field (as magnetic induction, **B**) orders the dipoles. This is an *isothermal step*, the entropy decreases.

Second step of cooling: the magnetic field is switched off, the alignment of little magnets disappears. *Adiabatic step*, therefore the entropy does not change, the *temperature decreases*.

See the method of adiabatic demagnetization on T-S diagram (Fig. 1.30)! One can observe the isothermal 1st step and the isentropic 2nd step.

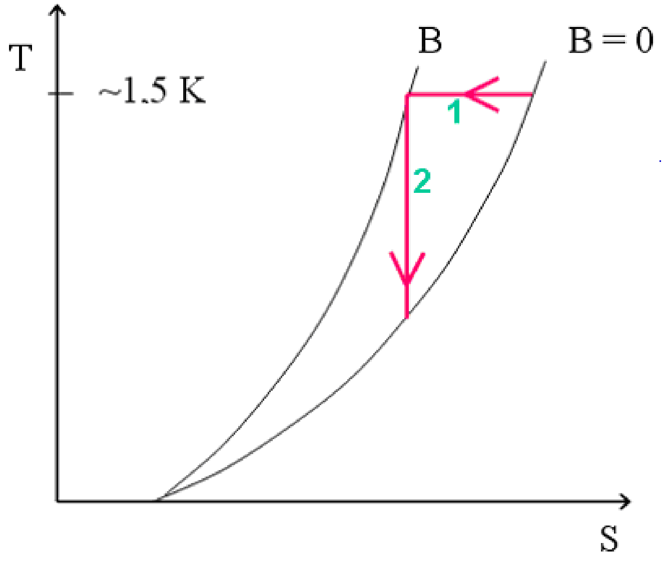


Fig. 1.30

The experiment:

1. The cell containing the *paramagnetic material* (e.g. gadolinium sulfate) is cooled down (by liquid helium) to about 1.5 K. *Magnetic field is switched to the system.*
2. *Helium is pumped out, the magnetic field is slowly reduced to zero.*

The isothermal and adiabatic steps are repeated several times (see Fig. 1.30).

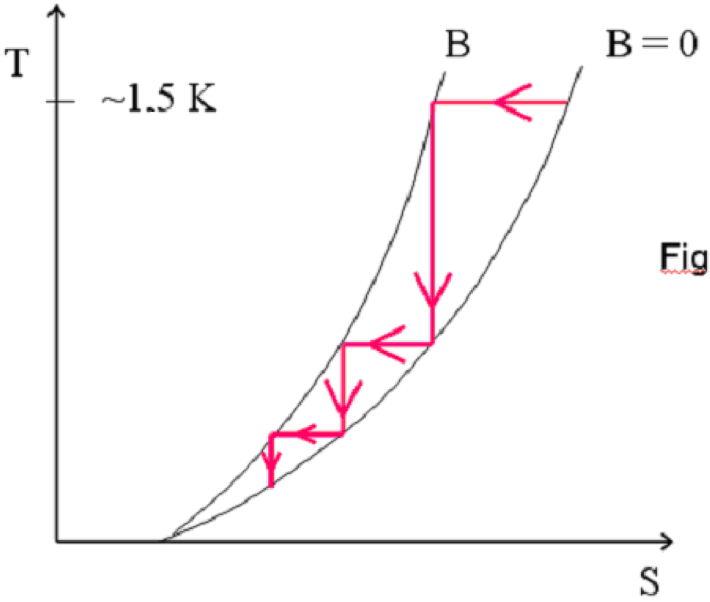


Fig. 1.31

Here you can see some date introducing the development in approaching of the absolute zero:

1933	0.25K
1950	0.0014K
1995	$4\cdot10^{-8}$K
1999	$1\cdot10^{-10}$K

The conclusion of the experiment is one formulation of ***the third law of thermodynamics****:* **it is impossible in any procedure to reduce the temperature of any system to the absolute zero in a finite number of operations.**

Approaching the absolute zero:

If we approach 0 K, ΔS approaches 0. i.e. in isothermal processes (e.g. reactions), if we approach 0 K, $\Delta S \rightarrow 0$.

At 0 K thermal entropy is 0 (should be zero). *The entropy arising from structural disorder may be greater than 0 at 0K.*

Examples*:*

defects in crystals (CO crystal, Fig. 1.24,

mixture of isotopes (e.g. Cl_2*)* .

Another formulation of the ***third law of thermodynamics*****: the zero point entropy of pure, perfect crystals is 0.**

As consequence, in contrast to H and U***, S has an absolute value.***

Therefore we use the ***standard molar entropy*** *of a substance,* which is *in gaseous state at temperature T*

$$S_m^0(T)=S_m^0(0)+\int_0^{T_m}\frac{C_{mp}^s}{T}dT+\frac{\Delta H_{m,fus}}{T_m}+\int_{T_m}^{T_b}\frac{C_{mp}^l}{T}dT+\frac{\Delta H_{m,vap}}{T_b}+\int_{T_b}^{T}\frac{C_{mp}^g}{T}dT \qquad (1.86)$$

2. THERMODYNAMICS OF SYSTEMS

2.1 The Helmholtz free energy (A)

In a not isolated system the entropy increases, considering both the system and ist environment (see 1.78):

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0 \qquad (1.78)$$

The *addition of the surroundings* is important. For example:

During the adsorption of a vapor on an adsorbent, entropy decrease, however, the vapor density decreases, its entropy increases, and consequently, the entropy of the full system increases.

We define two further thermodynamic functions which are suitable for describing processes in closed but not isolated systems:

At *constant T and V:* ***Helmholtz free energy (A)***

At constant T and p: ***Gibbs free energy (G).***

Constant T and V the only *interaction with the surroundings* is the Q *heat exchange*. See Fig. 2.1, there is a closed flask in which a slow process is taking place. The system (1) is taken into a heat bath (2).

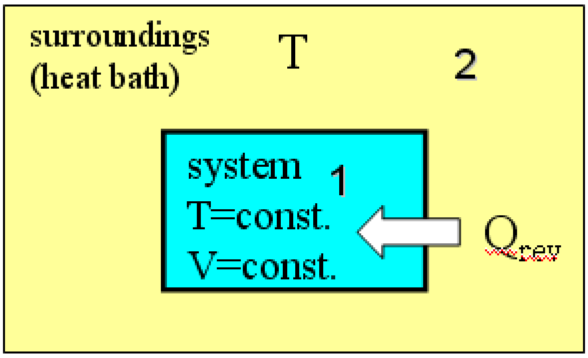


Fig. 2.1

According to 1.78 we have

$$\Delta S_1 + \Delta S_2 \geq 0$$

For the bath $\Delta S_2 = -\frac{Q_{rev}}{T}$ since it losses heat. Substituting it

Rerranging

$$\Delta S_1 - \frac{Q_{rev}}{T} \geq 0$$

$$Q_{rev} - T\Delta S_1 \leq 0$$

At constant volume: $Q_{rev} = \Delta U_1$. Leaving out the subscript 1:

$$\Delta U - T \cdot \Delta S \leq 0 \qquad (2.1)$$

So we can define the **Helmholtz free energy function** which decreases in **isothermal-isochor** processes and has a **minimum at equilibrium**, The Helmholtz

$$\mathbf{A = U - TS} \qquad (2.2)$$

In closed systems the direction of isothermal-isochor processes and the equilibrium can be expressed as follows:

$$\Delta A_{T,V} \leq 0 \ \ (W{=}0) \qquad (2.3a)$$

$$dA_{T,V} \leq 0 \ \ (\delta W{=}0) \qquad (2.3b)$$

According to the 2.3 equations in a closed system of constant temperature and volume (if no work is done) the **Helmholtz free energy** decreases in a spontaneous process and has a minimum at equilibrium.

The differential expression of Helmholtz free energy is using 2.2

$$dA = dU - TdS - SdT \quad \text{since} \quad dU = - pdV + TdS$$

Therefore

$$\mathbf{dA = - pdV - SdT} \qquad (2.4)$$

The change of Helmholtz free energy in an isothermal reversible process is equal to the ***work****.*

We can prove this in the statement following way. At constant temperature

$$dA_T = dU - TdS$$

Since

$$TdS = \delta Q_{rev} \quad \text{and} \quad dU = \delta W_{rev} + \delta Q_{rev}$$

We have

$$\mathbf{dA_T = \delta W_{rev}} \qquad (2.5a)$$

and

$$\mathbf{\Delta A_T = W_{rev}} \qquad (2.5b)$$

This is why **A** is sometimes called the *work function* (**A**rbeit = work in German). It is called also *„free" energy*. Namely, in the expression of internal energy

$$U = A + TS$$

TS cannot converted to work "bound" energy in contrary to ***A***, the „free" work function.

2.2 Gibbs free energy (G)

This function describes systems, which are in thermal and mechanical interaction with the surroundings ($T_1 = T_2$, $p_1 = p_2$). Fig. 2.1 is a closed flask in which a slow process is taking place. The only interaction with the surroundings is the heat (Q) exchange.

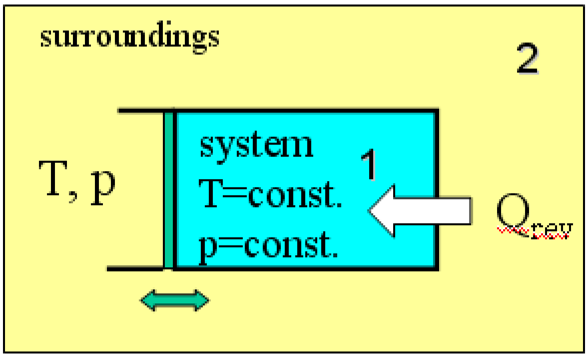


Fig. 2.2

For the entropy one can write

$$\Delta S_1 + \Delta S_2 \geq 0$$

$$\Delta S_2 = -\frac{Q_{rev}}{T}$$

The negative sign indicates the loss of the surroundings. Therefore the sum of the entropy change is

$$\Delta S_1 - \frac{Q_{rev}}{T} \geq 0 \cdot (-T)$$

rearranged

$$Q_{rev} - T\Delta S_1 \leq 0$$

At constant pressure no other work is done,

$$Q_{rev} = \Delta H_1.$$

Leave out the subscript 1:

$$\Delta H - T \cdot \Delta S \leq 0 \qquad (2.6)$$

So we can define a **function** which decreases in **isobar-isochor** processes and has a minimum at equilibrium, the **Gibbs free energy function:**

$$G = H - TS \qquad (2.7)$$

In closed systems the direction of **isobar-isochor processes and the equilibrium** can be expressed as follows:

$$\Delta A_{T,V} \leq 0 \quad \text{(no other than pVwork done)} \qquad (2.8a)$$

$$dA_{T,V} \leq 0 \quad \text{(no other than pV work done)} \qquad (2.8b)$$

In a closed system of constant temperature and pressure, if no other than pV work is done, the **Gibbs free energy decreases in a spontaneous process**, and it has a minimum at equilibrium.

The relationship between G and A is, as follows

$$G = H - TS = U + pV - TS = A + pV \qquad (2.9)$$

In differential form:

$$dG = dU + pdV + Vdp - TdS - SdT \qquad (2.10)$$

If there is pV work only:

$$dG = Vdp - SdT \tag{2.11}$$

At constant temperature and pressure (in a reversible process), if there is no other than pV work:

$$\mathbf{dG_{p,T} = 0} \tag{2.12}$$

If there is other (non-pV) work:

$$dU = \delta W_{other} - pdV + TdS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

As results we have

$$dG_{p,T} = \delta W_{other} \tag{2.13a}$$

$$\Delta G_{p,T} = W_{other} \tag{2.13b}$$

So we can say, *in an isothermal, isobaric reversible process the change of Gibbs free energy is equal to the non-pV work.*

We introduce the idea of the ***chemical potential***. The **chemical potential** of a pure substance (J/mol) is

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} \tag{2.14}$$

Since the chemical potential is some of the central ideas of the chemical thermodynamics, we shall later deal with it in detail (subsection 2.9).

2.3 The first and second derivatives of the thermodynamic functions

Useful relationships can be obtained from the four thermodynamic functions (U, H, A, G) by partial derivation. The relations between the second derivatives are called *Maxwell relations*. The result is independent of the order of derivation, for example:

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \qquad (2.15)$$

Internal energy (U)

$$\mathbf{dU = -pdV + TdS} \qquad (2.16a)$$

The first derivatives:

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \text{And} \qquad \left(\frac{\partial U}{\partial S}\right)_V = T \qquad (2.16b)$$

The second derivatives, based on (2.16b):

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right) = -\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad (2.16c)$$

Enthalpy (H)

$H = U + pV$ (1.19) and $dH = dU + pdV + Vdp$ (1.20a)

Substituting (2.16a) for dU

$$\mathbf{dH = Vdp + TdS} \qquad (2.17a)$$

The first derivatives:

$$\left(\frac{\partial H}{\partial p}\right)_S = V \qquad \text{and} \qquad \left(\frac{\partial H}{\partial S}\right)_p = T \qquad (2.17b)$$

The second derivatives, based on (2.17b)

$$\left(\frac{\partial^2 H}{\partial p \partial S}\right) = \left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \qquad (2.17c)$$

Helmholtz free energy function (A)

$$\mathbf{dA = -pdV - SdT} \qquad (2.18a)$$

The first derivatives:

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \text{and} \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad (2.18b)$$

The second derivatives, based on (2.18b):

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = -\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

Consequently

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (2.18c)$$

Gibbs free energy function (G)

$$\mathbf{dG = Vdp - SdT} \qquad (2.19a)$$

The first derivatives

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{and} \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad (2.19b)$$

The second derivatives, based on (2.19b)

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

So

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (2.19c)$$

Applying the (2.18c) and (2.19c) equations, the **S-V** and the **S-p** functions can be determined **from measurable quantities**, namely from p-T and V-T functions, respectively.

The pressure dependence of enthalpy at constant temperature *can be expressed as*

$$\boldsymbol{H = G + TS}$$

Derivating with respect to T

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial G}{\partial p}\right)_T + T\left(\frac{\partial S}{\partial p}\right)_T$$

Considering (2.19) we have

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{2.20}$$

Using this formula we can prove that the enthalpy of an ideal gas is independent of pressure (at constant temperature).

Thermodynamic functions of state for closed system, pV work only.

Internal energy:	$U = W + Q$	$\Delta U = Q_V$	(2.21a)
Enthalpy:	$H = U + pV$	$\Delta H = Q_p$	(2.21b)
Helmholtz function:	$A = U - TS$	$\Delta A_{T,V} \leq 0$	(2.21c)
Gibbs function:	$G = H - TS$	$\Delta G_{T,p} \leq 0$	(2.21d)

According to the equations (2.21)

$$U = A + TS; \qquad G = A + pV; \qquad H = U + pV = A + TS + pV$$

Therefore **A is the smallest and H is the largest,** see equation 2.22 and the figure 2.3:

$$A < G < U < H \tag{2.22}$$

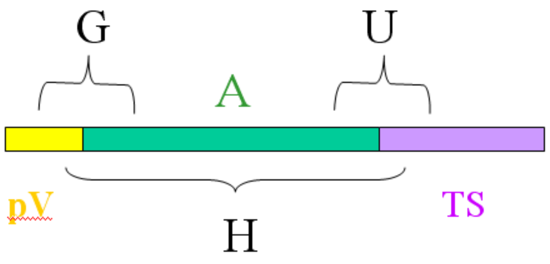


Fig. 2.3

2.4. p-T phase diagram

The p-T phase diagram of a pure compound is presented in Fig. 2.4.

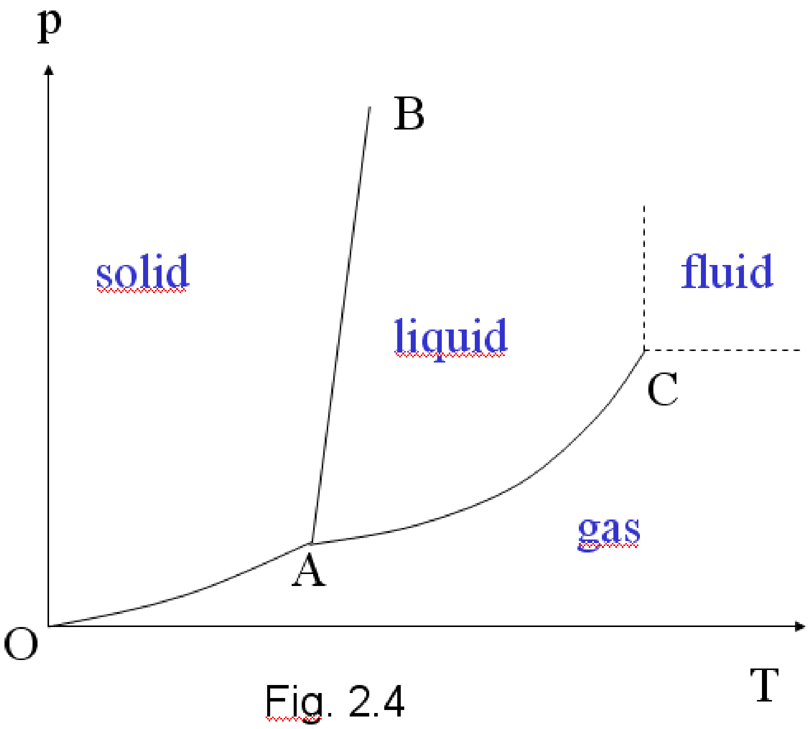


Fig. 2.4

A is the triple point is the only state**,** where all the three phases, solid, liquid and gas are together present and in equilibrium at well defined pressure and temperature. **C** is the **critical point**, at higher presures and temperatures neither liquids nor gases present, the compound is in this case in the very special **fluid state.**

OA is the **sublimation curve,** along this curve **both** solid and gas states are present and are in equilibrium.

AB is the **melting curve,** along this curve both solid and liquid states are present and are in equilibrium.

AO is the **vaporization curve,** along this curve both liquid and gas states are present and are in equilibrium.

Looking at the figure one can find that all these curves have positive slopes. One important exception exists: the melting curve of water has positive slope.

The equlibria of two phases along the mentioned curves mean that p and T are not independent in these cases.

Some *examples:*

The triple point of water is at 6.11 mbar and 273.16K.

The triple point of carbon dioxide is at 5.11 bar and 216.8K.

C: **critical point*:*** The difference between liquid and vapor phase diminishes. At greater temperatures and pressures only one phase exists: **fluid (supercritical) state**.

Let us heat a liquid-vapor system in a vessel of an appropriate volume (Fig. 2.5) We are going from left to right on the vapor pressure curve (Fig. 2.4). It can be observed: *The density of the liquid decreases, the density of the vapor increases*.

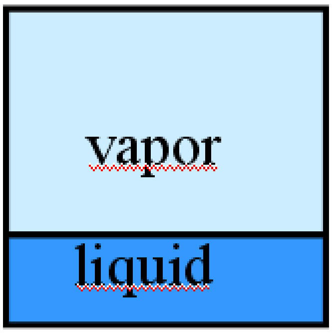


Fig.2.5

Other physical properties (e.g. refractive index) also approach each other. Finally we reach to a point where the difference between the two phases diminishes aproaching the **critical point.**

Critical temperature is thee temperature, above which the gas cannot be liquefied.

Critical pressure, what is necessary to liquefy the gas at the critical temperature yet.

Critical volume, what 1 mole gas occupies at the critical pressure and temperature.

The critical data are characteristic of the substance.

Some *examples* for the critical data*:*

Water: $T_C = 647.4$ K, $p_C = 221.2$ bar

CO2: $T_C = 304.2$ K, $p_C = 73.9$ bar

T_C values below room temperature are: O_2, N_2, CO, CH_4

T_C values above room temperature are: CO_2, NH_3, Cl_2, $C3H_8$. These gases can be liquefied at room temperature.

2.5 Thermodynamic interpretation of the p-T diagram (the Clapeyron equation)

At ***given T and p*** the condition of equilibrium is the minimum of G.

Let have o***ne component, two phases*** (a and b) in a flask (Fig. 2.6)**.**

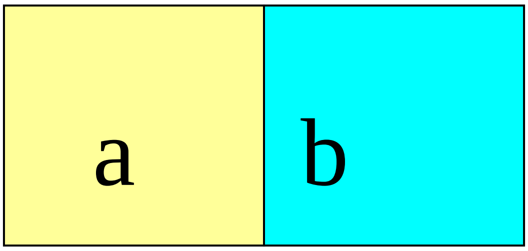


Fig. 2.6

At equilibrium the molar Gibbs free energy of the component must be equal in the two phases. Otherwise there is a flow of the substance from the phase where G_m=G/n is higher to the phase where G_m is lower.

Three cases are possible:

1. $\mathrm{G}_{\mathrm{m}}^{\mathrm{a}} > \mathrm{G}_{\mathrm{m}}^{\mathrm{b}}$ *:* substance goes from a to b

2. $\mathrm{G}_{\mathrm{m}}^{\mathrm{a}} < \mathrm{G}_{\mathrm{m}}^{\mathrm{b}}$ *:* substance goes from b to a

3. $\mathrm{G}_{\mathrm{m}}^{\mathrm{a}} = \mathrm{G}_{\mathrm{m}}^{\mathrm{b}}$ *:* equilibrium

In cases 1 and 2*: macroscopic process takes place,* in case 3*:no macroscopic process take place.*

On the *molecular level there are changes in thermodynamic equilibrium.* The rates of the processes in opposite direction are the same (e.g. in liquid vapor equilibrium the **macroscopic** rates of evaporation and of condensation are equal). However, the *equilibrium is **dynamic*** (and not static at the molecular level)*, **fluctuation*** occurs.

The Clapeyron equation describes the phase equilibrium. We shall derive it using the previous considerations.

In equilibrium

$$G_m^a = G_m^b \tag{2.23}$$

If we change T slightly, p and G also change. The condition of maintaining equilibrium:

$$dG_m^a = dG_m^b$$

Since

$$dG = Vdp - SdT \tag{2.19a}$$

$$V_m^a dp - S_m^a dT = V_m^b dp - S_m^b dT$$

rearranging

$$(V_m^b - V_m^a)dp = (S_m^b - S_m^a)dT$$

Introducing

$$V_m^b - V_m^a = \Delta V_m \qquad S_m^b - S_m^a = \Delta S_m$$

Therefore

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} \qquad \Delta S_m = \frac{\Delta H_m}{T}$$

at last we have the **Clapeyron equation**, *the equation of one component phase equilibrium.*

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \cdot \Delta V_m} \tag{2.24}$$

Nothing was neglected in this derivation. The Clapeyron equation is **valid** for one component *liquid-vapor, liquid-liquid, solid-liquid, solid-vapor and solid-solid equilibria.*

We can obtain the **curves of the p-T diagram** by integration of the Clapeyron equation. For exact integration $\mathbf{\Delta H_m}$ and $\mathbf{\Delta V_m}$ have to be known as functions of temperature.

First approach: the slopes of the phase-phase equilibrium curves in Fig. 2.4 dp/dT.

Some important notes:

1. The melting point curve is the steepest. **Reason:** ΔV_m is small and is in the denominator.

2. Near the triple point the sublimation curve is steeper than the boiling point curve**. Reason:**

$$\Delta H_{m,subl} = \Delta H_{m,fus} + \Delta H_{m,evap} \tag{2.25}$$

ΔV_m (sublimation) is roughly equal to $V_{m,vapor}$.

3. In most cases the melting point curve has a positive slope because ΔV_m is positive (the substance expands at melting). There exists an important *exception*, the *water*: $\Delta V_m < 0$, (see Fig. 2.7), since water contracts until 4 ^oC. The attractive forces are stronger between 0 ^oC and 4 ^oC than the effect of the increasing of the molecular velocities with the temperature.

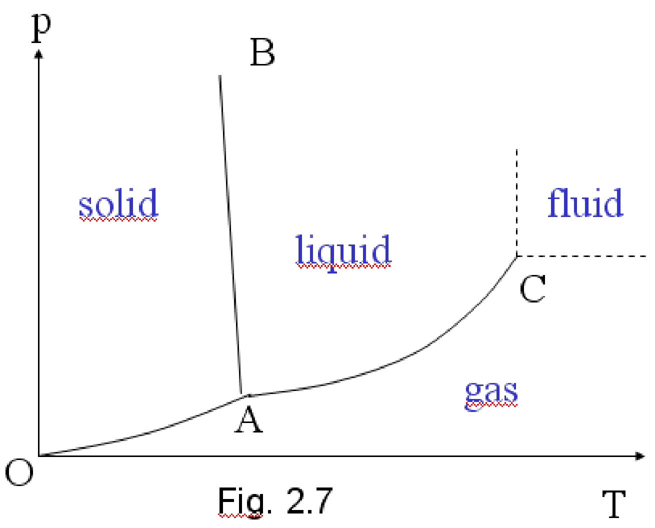


Fig. 2.7

The slope of AB curve is negative. The melting point decreases as the pressure increases (operation of ice-skate).

2.6. One component liquid-vapor equilibria, the Clapeyron Clausius equation

According to the experience the *vapor pressure of a pure liquid depends on temperature only* (Fig. 2.8). The function is exponential.

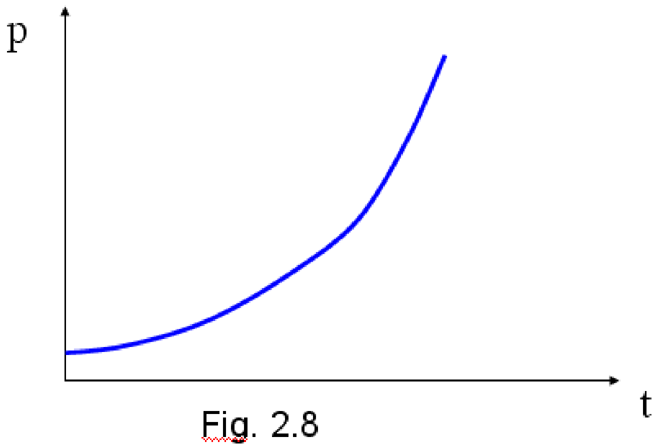


Fig. 2.8

If the logarithm of the vapor pressure is plotted against the reciprocal of temperature, we obtain a straight line (Fig. 2.9).

$$\lg\{p\} = -\frac{A}{T} + B \qquad (2.26)$$

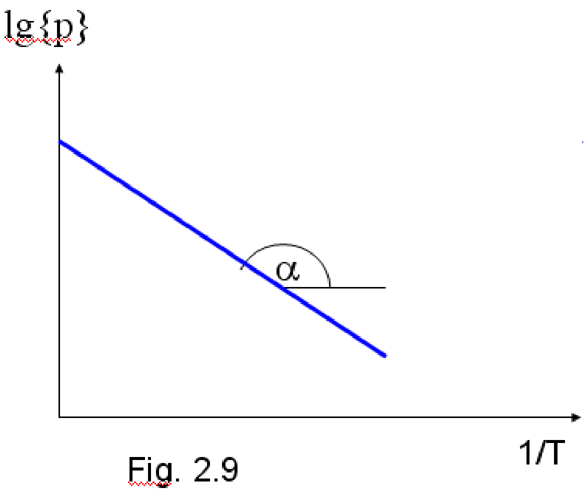


Fig. 2.9

A and **B** are constants, tanα=-A. Since the variable of the *lg* function must be dimensionless, we use for the pressure

$$\{p\} = \frac{p(Pa)}{1\,Pa}$$

This notation does not change the value of the pressure. However, in the practive the *p* notation is used in the same sense.

The **Clapeyron Clausius equation** is suitable for the description of the liquid-vapor equlibrium. We start with the Clapeyron equation (2.24).

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \cdot \Delta V_m} \qquad (2.24)$$

Some neglections are used before the integration of this equation:

1. step: Neglection of the molar volume of the liquid (compared to vapor),

2. step: The vapor is regarded as ideal gas:

$$\Delta V_m \approx V_m(g) = \frac{RT}{p}$$

3.step: ΔH_m will be and **regarded independent of temperature** and denoted by λ.

so
$$\frac{dp}{dT} = \frac{\lambda \cdot p}{RT^2} \qquad (2.27)$$

The expression dp/p = dlnp, because dlnp/dp = 1/p (derivative of ln p), similarly, $dT/T^2 = -d(1/T)$, because $d(1/T)/dT = -1/T^2$. Therefore

$$d\,ln\,p = -\frac{\lambda}{R}d\left(\frac{1}{T}\right)$$

Problem 1. Determination of λ from ln{p}-1/T diagram. Droe the slope of the experimental curve (blue), Fig. 2.10!

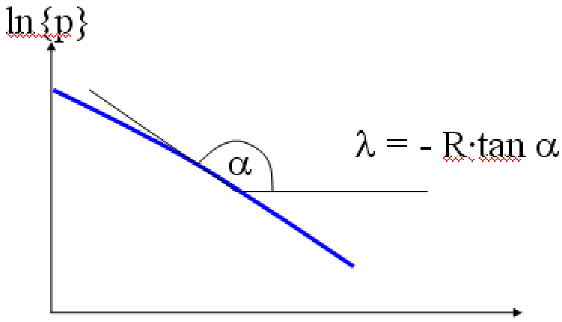


Fig. 2.10

Although

$$\{p\} = \frac{p(Pa)}{1\,Pa}$$

*The **practical unit** is often **kPa*** and

$$ln\{p\} = -\frac{\lambda}{RT} + C \qquad (2.28)$$

Problem 2, integration. Like already mentioned, λ is taken independent of T. Empirical formula

$$lg\{p\} = -\frac{A}{T} + B \qquad (2.29)$$

with

$$A = \frac{\lambda}{2.303R}$$

(2.29) is the Clapeyron Clausius equation with two contants.

Problem 3. Integration between limits:

$$\ln p_2 - \ln p_1 = -\frac{\lambda}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In more paractical form:

$$\ln \frac{p_2}{p_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.30}$$

It is suitable for calculation of pressure p_2 at T_2, if p_1 and T_1 is known. If you know the four mentioned parameters, λ is calculable.

Beside the Clapeyron Clausius equation also other equations are applied but they use more then two constants. One of them is the ***Antoine equation*** with three constants:

$$\lg\{p\} = A - \frac{B}{T + C} \tag{2.31}$$

Here a temperature correction is introduced for straitening the curve on Fig. 2.10.

2.7 Standard Gibbs free energies

The Gibbs free energies are significant in calculation of chemical equilibria. Therefore we deal and shall deal with them later.

*The **standard states are of the Gibbs free energy are fixed*** (similarly to enthalpies, subsection 1.8) *by international conventions:*

Gas: ideal gas at p^0 *(*10^5 *Pa) pressure*

Liquid: pure liquid at p^0 *pressure*

Solid: the most stable crystal state at p^0 *pressure*

The 0 as superscript refer to standard pressure.

In the definition of Gibbs free energy both **enthalpy** and **entropy** take part: G = H – TS (2.7). Remember: The zero level of entropy is fixed by the third law of thermodynamics: the entropy of pure crystalline substance is zero at zero K (subsection 1.18). The zero level of enthalpy is not fixed in the same way.

***By convention*: At 298.15 K (25 °C) and $p^o = 10^5$ Pa pressure the enthalpy of the stable modification of an element is taken zero, that of a compound is taken equal to the enthalpy of formation.**

A similar convention ***for G*** does not exist but ***it is calculated from the standards for H and S*. The standard molar Gibbs free energy is**

$$G_m^0 = H_m - TS_m^0 \tag{2.32}$$

So the **standard molar Gibbs free energy** of the elements at 298 K is **not zero**.

Standard Gibbs free energy of formation: the Gibbs free energy change of the reaction, in which the compound is formed from its elements so that all the reactants are in their standard state. It is denoted by $\Delta_f G^0$.

Standard Gibbs free energy of reaction, $\Delta_r G^0$, can be calculated from the Standard Gibbs free energies of reactants and products:

$$\Delta_r G^0 = \Sigma \nu_B G_{mB}^0 - \Sigma \nu_A G_{mA}^0 \tag{2.33}$$

or from standard Gibbs free energies of formation: this is valid for at any temperature

$$\Delta_r G^0 = \Delta_r \left(\Delta_f G^0\right) \tag{2.34}$$

Example

Reaction: $2SO_2 + O_2 = 2SO_3$

Rection Gibbs free energy: $\Delta_r G^0 = 2\,G_m^0(SO_3) - 2\,G_m^0(SO_2) - G_m^0(O_2)$

Or $\Delta_r G^0 = 2\,\Delta_f G^0(SO_3) - 2\,\Delta_f G^0(SO_2) - \Delta_f G^0(O_2)$

$\Delta_f G^0(O_2) = 0$ since O_2 is an element and threfore its standard free energy of formation is zero.

The standard Gibbs free energies of compounds and elements are given in tables (as functions of temperature). An applied function is

$$-\frac{G^0_{m,T}-H^0_{m,298}}{T} \qquad (2.35a)$$

containing the standard molar enthalpy at 298.15K and the temperature dependence of the standard molar Gibbs free energy.

Another applied function is

$$-\frac{G^0_{m,T}-H^0_{m,0}}{T} \qquad (2.35b)$$

containing ***the standard molar enthalpy at 0* K** (different from the usual convention), the enthalpy of a compound is *taken equal to the enthalpy of formation **at 0 K**.*

***Advantage**: these quantities only slightly depend on temperature.* It is easier to interpolate.

$$dG_m = RT\frac{dp}{p}$$

2.8 Gibbs free energy of an ideal gas

***The pressure dependence** of the molar Gibbs free energy is studied here* (at constant temperature).

The complete differential of the Gibbs free energy has the form (for 1 mol substance):

$$dG_m = V_m dp - S_m dT \qquad (2.36)$$

At **constant temperature** the second term can be neglected, V_m can be expressed from the ideal gas law:

$$V_m = \frac{RT}{p}$$

So integrating from p^0 to p

$$G_m - G_m^0 = RT(\ln p - \ln p^0) = RT \ln \frac{p}{p^0}$$

Rearranging

$$G_m = G_m^0 + RT \ln \frac{p}{p^0} \tag{2.37}$$

Expressing (2.37) with chemical potentials

$$\mu = \mu^0 + RT \ln \frac{p}{p^0} \tag{2.38}$$

Consequence: *The Gibbs free energy (chemical potential, (2.14)) increases with increasing pressure (the entropy decreases).*

2.9 The chemical potential

The idea of chemical potential was introduced by Gibbs in 1875. Like it was already used ((2.14),(2.38)) it is denoted by $\boldsymbol{\mu}$ *[Joule/mol],* The word „potential” refers to physical analogies: masses fall from higher to lower *gravitational potential,* charges move from higher to lower *electric potential.*

The chemical substance moves from place where the chemical potential is higher to a place where it is lower (e. g. by diffusion).

Problem*: What is the advance of the chemical potential? Why is concentration not sufficient to describe the direction of transport of substances?*

Example 1. Two aqueous solutions of NaCl of different concentrations are layered on each other (Fig. 2.11):

$$c_{NaCl}(1) > c_{NaCl}(2) \quad \text{and} \quad \mu_{NaCl}(1) > \mu_{NaCl}(2)$$

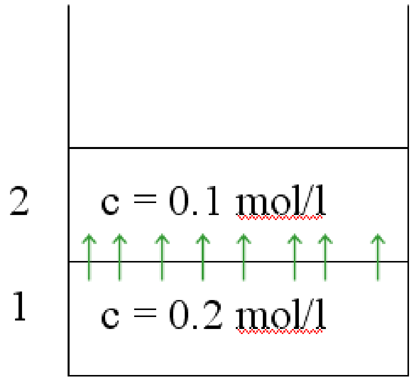


Fig. 2.11

The salt diffuses from the place where the concentration (and the chemical potential) is higher to the place where the concentration (and the chemical potential) is lower.

Consequence: To explain this process we do not needthe chemical potencial.

Example 2. 2. There are two different solvents, water and CCl_4 . The solute is iodine. The concentration of iodine is higher in CCl_4 than in water (Fig. 2.12).

$$c_{\mathrm{iodine}}(1) > c_{\mathrm{iodine}}(2)$$

However, one find that the iodine move in the direction of layer 2, in CCl_4 (extraction). So it must be valid:

$$\mu_{\mathrm{iodine}}(1) < \mu_{\mathrm{iodine}}(2)$$

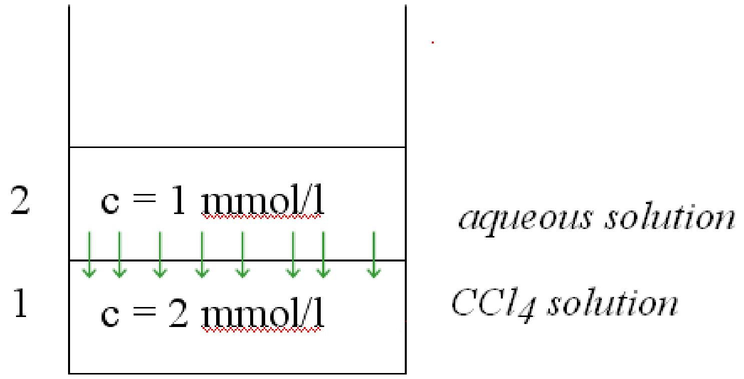


Fig. 2.12

Consequence: Here we need the chemical potential. *The chemical potential is very important when we study solutions.* **The chemical potential considers the effect of chemical environment.**

*So far we have mainly dealt with **closed systems** where the amount of substance does not change.* The complete differentials of the four thermodynamic functions for closed systems if there is only pV work (no other work) are described as follows:

$dG = Vdp - SdT$	$G = G(T,p)$	(2.39a)
$dA = -pdV - SdT$	$A = A(T,V)$	(2.39b)
$dH = Vdp + TdS$	$H = H(p,S)$	(2.39c)
$dU = -pdV + TdS$	$U = U(V,S)$	(2.39d)

*If the amount of substance also changes, **open systems**, the functions of state depend on* n_i*-s, too:*

$$G = G(T,p,n_1,n_2,...)$$

$$A = A(T,V,n_1,n_2,...)$$

$$H = H(p,S,n_1,n_2,...)$$

$$U = U(V,S,n_1,n_2,...)$$

The complete differentials include the amounts of substances, too. For example for the Gibbs function

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i \qquad (2.40)$$

where $n_i = n_1, n_2, n_3$, etc. and $j \neq i$.

This differential has as many terms as the number of components. For a two-component system

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1} dn_2 \qquad (2.41)$$

The derivatives of (2.41) with respect to the amounts of a substance are called ***chemical potentials*** *of the substance in the solution.*

The chemical potential of the component **i** is

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad j \neq i \qquad (2.42)$$

The ***chemical potential of a component*** *is equal to the change of the Gibbs free energy of the system if one mol component is added* ***to infinite amount of substance.*** It is Infinite in the sense that the composition does not change.

The complete differential of G in an **open system** is like (2.41)

In short, considering (2.19a) and (2.19b)

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \qquad (2.43)$$

At constant temperature and pressure:

For many components

$$dG_{p,T} = \sum_i \mu_i dn_i \qquad (2.44a)$$

For two components:

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

Integrating at constant temperature and pressure (see Fig. 2.13, „integration” with increasing the amount of the mixture):

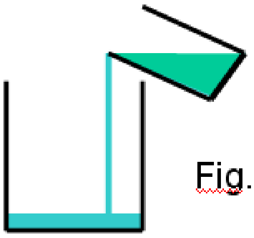


Fig. 2.13

and with integration of (2.44a)

$$G_{p,T} = \sum_i \mu_i n_i \tag{2.44b}$$

For two components

$$G_{p,T} = \mu_1 n_1 + \mu_2 n_2$$

The ***Gibbs free energy of the system*** *can be calculated* ***from the chemical potentials at constant p and T.***

Very important:

$$\mathbf{G \neq \sum G_{mi} \cdot n_i} \tag{2.45}$$

(2.45) means: in solutions S, A and G are not additive from the corresponding values of molar values of the pure components.

The solvent effect leads to

$$G_{mi} \neq \mu_i$$

Detailed:

$$\left(\frac{G_i}{n_i}\right)_{p,T} \neq \left(\frac{\partial G}{\partial n_i}\right)_{n_j,p,T} \quad j = 1,2,..,k \quad j \neq i \tag{2.46}$$

This equation (2.46) means the molar Gibbs free energy of component **i** in the solution is not equal to its partial molar Gibbs free energy (chemical potential) in the same solution.

Relation between μ and Helmholtz free energy:

$$A = G - pV \quad \textit{and} \qquad dA = dG - pdV - Vdp$$

Substituting (2.43)

$$dA = -pdV - SdT + \sum \mu_i dn_i \tag{2.47}$$

Pay attention on the extension of the interpetation of the **idea chemical potential:**

At constant volume and temperature:

$$dA_{V,T} = \sum_i \mu_i dn_i \tag{2.48}$$

Similarly, it can be proved like (2.42) for G

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} \tag{2.49a}$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} \tag{2.49b}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \tag{2.49c}$$

The chemical potential of one component (pure) substances can be expressed since (see also 2.42)

$$G = n \cdot G_m \tag{2.50}$$

We have

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} = G_m \tag{2.51}$$

i.e. the chemical potential of a **pure substance** is equal to the molar Gibbs free energy. If our work material is ideal gas, the chemical potential can calculated as

$$G_m = G_m^0 + RT\ln\frac{p}{p^0} \tag{2.52a}$$

or more simple

$$\mu = \mu^0 + RT\ln\frac{p}{p^0} \tag{2.52b}$$

since

$$\mu = G_m \tag{2.53a}$$

and

$$\mu^0 = G_m^0 \tag{2.53b}$$

The standard chemical potential = standard molar Gibbs free energy, *it is the Gibbs free energy of 1 mol ideal gas at* p^0 *pressure and at the given temperature, see (2.53b).*

2.10. Conditions for phase equilibria

Consider a multicomponent system with several phases!

Our example is the butanol (Bu)-water (W) vapor-liquid system (see Fig. 2.14). There exist two liquid phases since the two liquids mix only limited, in one of the liquid phases the butanol is the majority, in the other one the water. Therefore C = 2 and P = 3 (**P**: number of phases, **C**: number of components). Conclusion: the limited mikxing increases the number of phases.

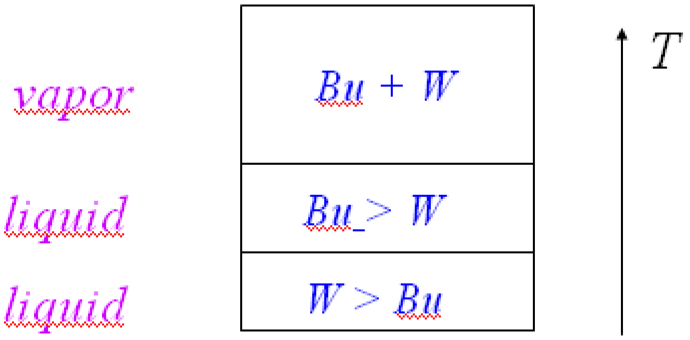


Fig.2.14

In equilibrium the pressure and temperature are equal in all the phases.

$$dG_{p.T} = \sum_i \mu_i dn_i = 0 \qquad i = 1,2,...C \tag{2.54a}$$

Extending (2.54a) for C components and P phases

$$dG_{p,T} = \sum_{j=1}^{P}\sum_{i=1}^{C} \mu_i^j dn_i^j = 0 \tag{2.54b}$$

Suppose that dn_i mol of component **i** goes from phase **j** to phase **k**) at constant pressure and temperature (the amounts of all the other components remain unchanged):

$$dn_i^k = dn_i \qquad dn_i^j = -dn_i$$

therefore

$$dG = dn_i^k \mu_i^k + dn_i^j \mu_i^j$$

so

$$dG = dn_i \mu_i^k - dn_i \mu_i^j$$

Now we have the result

$$dG = dn_i\left(\mu_i^k - \mu_i^j\right) \tag{2.55}$$

Consequences of (2.55):

1. In equilibrium dG = 0, $dn_i \neq 0$, therefore

$$\mu_i^k = \mu_i^j \tag{2.56a}$$

*The chemical potential of component **i** is equal in the two selected phases.*

This equation is valid for any phases (P phases):

$$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^j = \ldots\mu_i^P = \mu_i \tag{2.56b}$$

In equilibrium the chemical potential of a component is equal in all the phases which are in contact (see also 2.23).

2. No equilibrium. Spontaneous process:

$$dG_{p,T} < 0 \tag{2.57}$$

In a spontaneous process any component goes from the phase where its chemical potential is larger to the phase where its chemical potential is smaller:

$$dn_i\left(\mu_i^k - \mu_i^j\right) < 0 \qquad dn_i > 0 \qquad \mu_i^j > \mu_i^k$$

Substance **i** goes from phase **j** to phase **k**, since its chemical potential in phase j is higher than in phase k.

2.11 The phase rule

*The **phase rule** determines the number of parameters that can be independently varied in equilibrium systems. This number depends on the number of phases and the number of components.*

Phase: a state of matter that is uniform throughout, not only in chemical composition but also in physical state.

The number of ***Components:*** the minimum **number of independent species** necessary to define the composition of all the phases present in the system.

For example, the NaCl - water system has two components. The number of the Na^+ and the Cl^- ions is not independent. Because of electroneutrality their numbers must be equal.

The $CaCO_3$, CaO *and* CO_2 *system has two components, too.*

Three chemical substances but one reaction between them:

$$CaCO3 = CaO + CO_2$$

This is an equilibrium!

It was mentioned already the dependence of the phases at the mixing of the components (mixed phases, see Fig. 2.14).

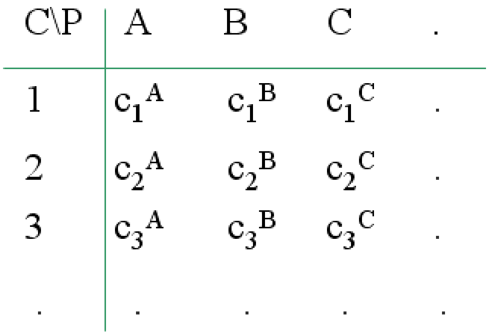
The number of degrees of ***Freedom*** (*variance*): is the number of **intensive variables** that can be **changed independently** without changing the number of phases.

The phase rule is

$$\mathbf{F = C - P + 2} \tag{2.58}$$

Derivation of (2.58): pressure + temperature: 2 degrees, the rest (C-P) is the number of concentrations varied independently (see the mentioned examples of their dependence).

In case of P phases and C components C·P concentration data exist but not all of them are independent:



C\P	A	B	C	.
1	c_1^A	c_1^B	c_1^C	.
2	c_2^A	c_2^B	c_2^C	.
3	c_3^A	c_3^B	c_3^C	.
.	.	.	.	.

In each phase C-1 concentrations are sufficient. For example the vapor-liquid methane-ethane-propane gas mixture. If we know the mole fraction of the first two, the third one can be calculated:

$$y_{pr} = 1 - (y_m + y_e) \qquad \text{(y: mole fraction)}$$

In case of

$$P(C-1) \tag{2.59}$$

concentrations are sufficient.

In equilibrium the concentrations of a component in different phases (A, B, C, …) are not independent (distribution in equilibrium, see also equation 2.56b):

$$\mu_1^A = \mu_1^B = \mu_1^C = \ldots \qquad = \mu_2^A = \mu_2^B = \mu_2^C = \ldots$$

This equation means P-1 relationships for each component. For **C** components C(P-1) has to be subtracted from (2.59):

$$\mathbf{F} = 2 + P(C-1) - C(P-1) = \mathbf{C-P+2} \tag{2.60}$$

or

$$F + P = C + 2$$

For **one component systems** (Fig. 2.15) the degrees of freedom are

P	F
1	2 (T and p
2	1 (T or p)
3	0 (triple point)

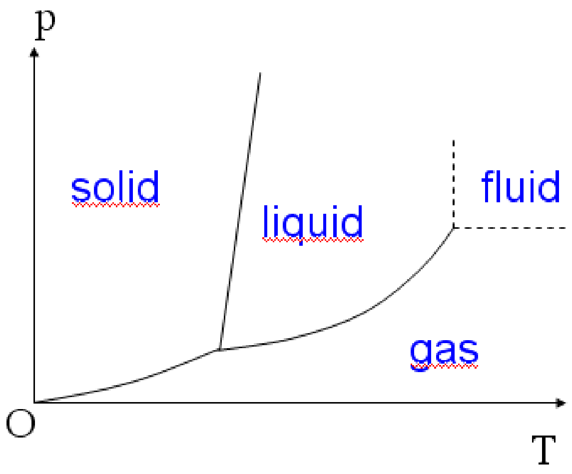


Fig. 2.15

Two component systems

With increasing of the number of components F increases, in this case the concentration as the mole fraction of one component (x) is added:

P	F
1	3 (T, p and x)
2	2 (two of them)
3	1 (one of them)

For plotting in two dimensions a vapor-liquid equilibrium of a two component system one parameter has to be kept constant (p or T), Fig. 2.16 (the temperature in ^{o}C is often labeled with ’t’).

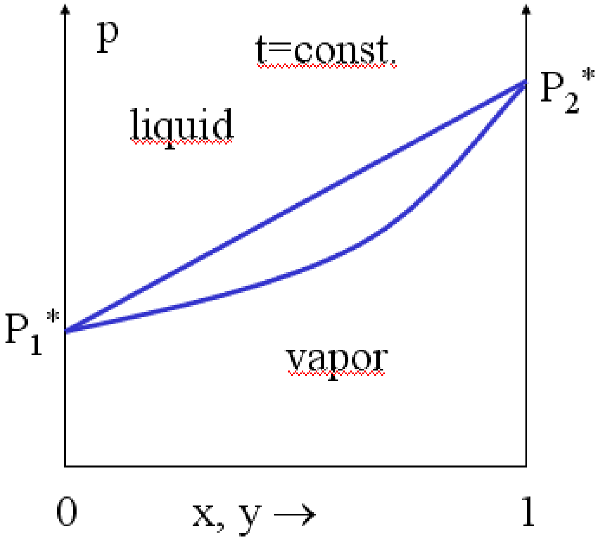


Fig. 2.16

2.12 Equation of state for real gases

Ideal gas, see subsection 1.4:

1. No interaction between molecules (the potential energy of interaction is 0).
2. The molecules are mass points.

We study in this subsection the **real gas equations**:

1. the van der Waals and
2. the virial equations of state.

The potential energy between two molecules as the function of distance **r** is plotted in Fig. 2.17 (see also the similar figure 1.11).

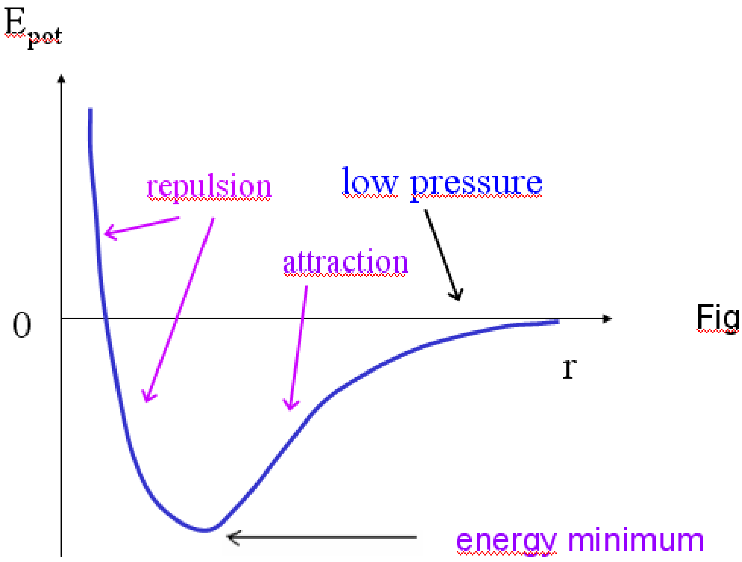


Fig. 2.17

1. **The van der Waals equation of state**

Van der Waals modified the ideal gas law with two constants in order to include the molecules' own sizes and the (attractive) interactions.

According to the ideal gas law is

$$p = \frac{RT}{V_m}$$

Correction of volume: because of the size of the molecules the volume available for motion is smaller: negative correction of V_m, 'b':

$$p = \frac{RT}{V_m - b} \tag{2.61a}$$

Correction of pressure: Because of attractive forces molecule pairs are formed temporarily (decreasing the pressure). If it is an equilibrium reaction:

$$(M + M = M_2) \rightarrow [M_2] = K[M]^2 \tag{2.61b}$$

The decrease of pressure is proportional to the concentration. The concentration is the reciprocal of the molar volume, correction with ’a’. Summarizing the 2.61 equations:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Rearranging this equation we have the **van der Waals equation of state**:

$$\left(p + \frac{a}{V_m^2}\right) \cdot (V_m - b) = RT \tag{2.62}$$

Other forms of the van der Waals equation:

$$\left(p + \frac{a \cdot n^2}{V^2}\right) \cdot \left(\frac{V}{n} - b\right) = R \cdot T \tag{2.63a}$$

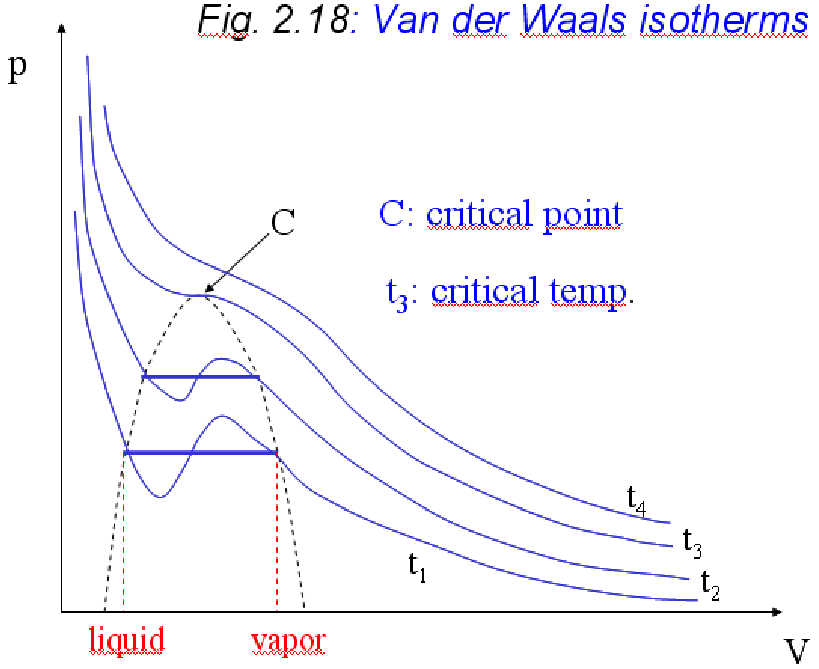
For n moles

$$\left(p + \frac{a \cdot n^2}{V^2}\right) \cdot (V - n \cdot b) = n \cdot R \cdot T \tag{2.63b}$$

The van der Waals equation is cubic for V.

That means, in a certain range three different volumes belong to one pressure. These parts of the isotherms have no physical reality, see Fig. 2.18.

Fig. 2.18: Van der Waals isotherms



***Advantage** of the van der Waals equation:* it has two constants only. It is simple in comparison of a lot of other types of real gas equations.

***Disadvantage*:** it is not accurate enough, look at the maxima of the isotherms, consider the physical irreality since in some cases three different volumes can belong to the same pressure.

2. The virial equation of state

The virial equation of state (2.64) is basically a power series of the concentration ($1/V_m$). B(T), C(T) and D(T) are the second, third and fourth ***virial coefficients***.

$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \ldots \qquad (2.64)$$

Substituting **V/n** for $\mathbf{V_m}$ we have

$$\frac{pV}{nRT} = 1 + \frac{n \cdot B(T)}{V} + \frac{n^2 \cdot C(T)}{V^2} + \frac{n^3 \cdot D(T)}{V^3} + \ldots \qquad (2.65)$$

2.13 The principle of corresponding states

The ***deviation from the ideal gas law*** can be expressed with the ***compressibility factor:***

$$z = \frac{pV_m}{RT} \tag{2.66}$$

The z value characterizes the compressibility of the gas:

$z = 1$ → ideal gas

$z > 1$ → less compressible than the ideal gas - repulsive forces dominate. (at higher pressures are higher temperatures)

$z < 1$ → more compressible than the ideal gas - attractive forces dominate. (at intermediate pressures are lower temperatures)

The compressibility depends on p and T and on the material

$$z = z(p,T, \text{material}) \tag{2.67}$$

The behavior of real gases is found very similar if their properties are studied as functions of reduced pressure. The pressure divided by the critical pressure is the reduced pressure (π), the reduced temperature (ϑ) is the temperature divided by the critical temperature and the volume divided by the critical volume is the reduced volume (φ):

$$\pi = \frac{p}{p_C} \qquad \vartheta = \frac{T}{T_C} \qquad \varphi = \frac{V_m}{V_C} \tag{2.68}$$

Law of corresponding states: *if two reduced parameters of two different gases are equal then the third ones are equal, too.* In short, for gases A and B

if $\pi_A = \pi_B$ *and* $\vartheta_A = \vartheta_B$ *then* $\varphi_A = \varphi_B$.

In this case the two gases are in **"corresponding state".** Their compressibility factors are nearly the same. If the reduced pressures and reduced temperatures of two gases are the same (i.e. they are in corresponding state) then their compressibility factors are the same, too. Therefore *if* $\pi_A = \pi_B$ *and* $\vartheta_A = \vartheta_B$ *then* $z_A = z_B$

This is ***not a strict law****, rather an* ***empirical rule for practical use****.*

We can plot a ***general reduced compressibility diagram*** valid for all the gases (see Figs. 2.19a and b). Fig. 19a introduces the structure of such a diagram, Fig. 19b is a diagram for the practice, abscissa: reduced pressure (p_r), ordinate: compressibility factor (z), the reduced isotherms (T_r) are plotted.

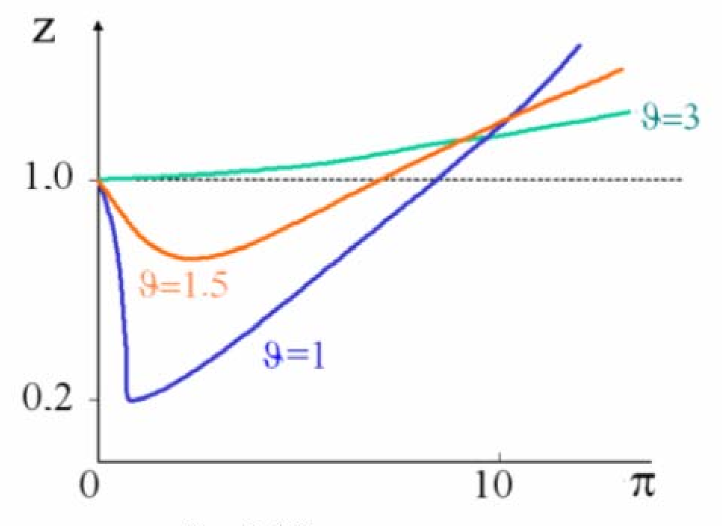


Fig. 2.19a

Near π=0 each curve approaches z=1 (ideal gas).

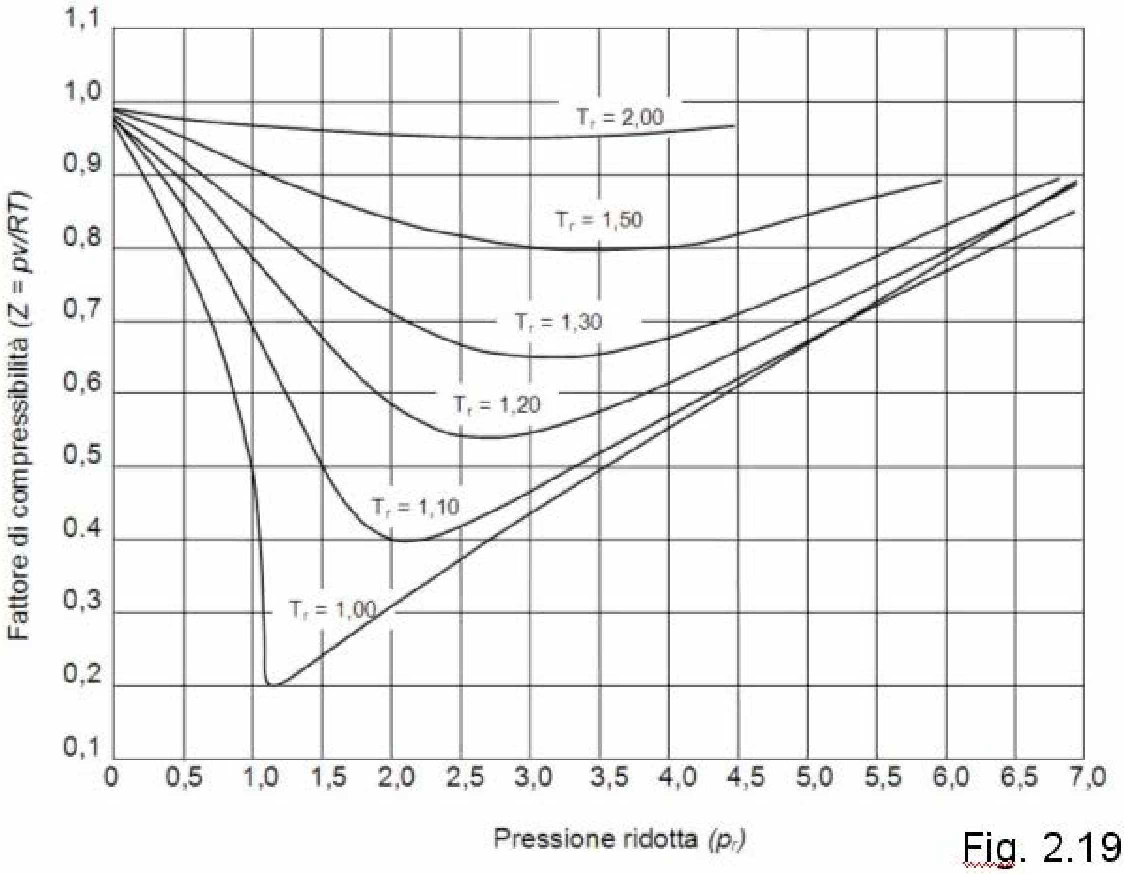


Fig. 2.19b

There exist two types of problems with these diagrams.

A) *p and T are known and* $\mathbf{V_m}$ *has to be determined*.

1. step: calculate $\vartheta = T/T_C$, and select the corresponding isotherm;
2. step: at $\pi = p/p_C$ read z (look at Fig. 2.20);
3. step: calculate $$V_m = \frac{zRT}{p} \qquad (2.69)$$

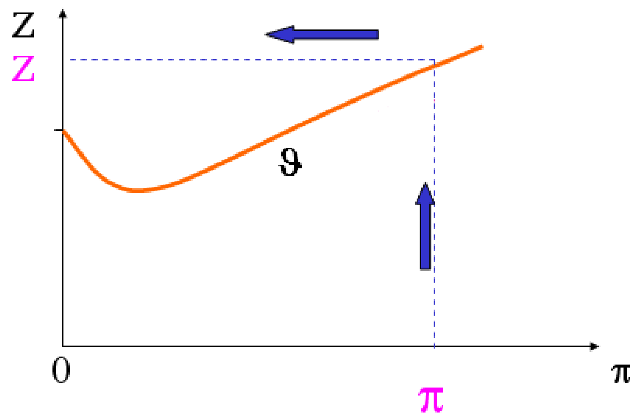


Fig. 2.20

B) *V_m and T are known and p has to be determined*

Both p and z are unknown. Applying the definition of π (2.68):

$$z = \frac{pV_m}{RT} = \frac{p_C V_m}{RT} \cdot \pi \qquad (2.70)$$

This is a linear equation. The slope is z/π (Fig. 2.21):

$$\frac{z}{\pi} = \tan(\alpha) = \frac{p_C V_m}{RT}$$

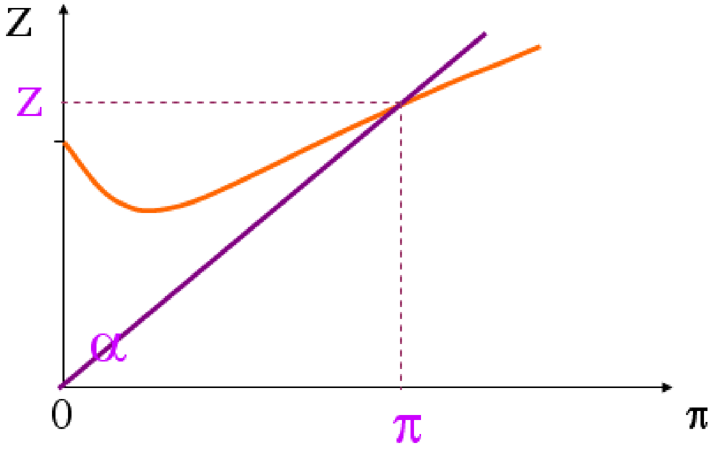


Fig. 2.21

Where the straight line crosses the corresponding isotherm, we can read both z and π, since

$$p = p_C \cdot \pi \quad \text{or}$$

$$p = \frac{zRT}{V_m}$$

2.14 The Joule-Thomson effect

The expansion of gases through throttles it is frequently applied in industry. For example, in *chemical works* high pressure steam network are used often. On the site of application reduced pressure is needed.

If high pressure gases are expanded adiabatically through a throttle, the temperature usually changes. Most frequently the temperature drops, this is the basis of liquefying gases. A well known application is the production of *dry* *ice* in a lab (see Fig. 2.22). The expanding gas cools down so that a part of it gets frozen. The pressure of its triple point is higher than atmospheric pressure, therefore CO_2 does not exist in liquid state on atmospheric pressure (see subsection 2.14).

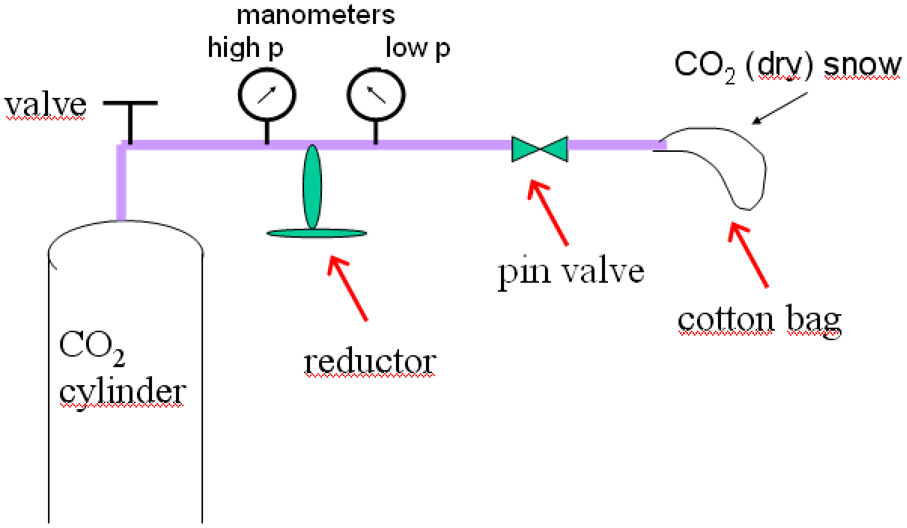


Fig. 2.22

Now we discuss the experiment of Joule and Thomson. The scheme of the experiment is presented in Fig. 2.23.

A) We apply the first law for the **throttle** as an open system (see subsection 1.12).

$$\Delta U = Q + W + H_{in} - H_{out} \qquad (1.52)$$

Since this is a steady state system, $\Delta U=0$ and also adiabatic, therefore $Q=0$. Besides, no work done in the throttle, $W = 0$. As a consequence, $\Delta H=0$.

B) We apply the first law for the whole system including the cylinders, the gas and the pistons. This is regarded as a closed system, $\Delta U = W + Q$. Since it is adiabatic $Q=0$.

Follow Fig. 2.23!

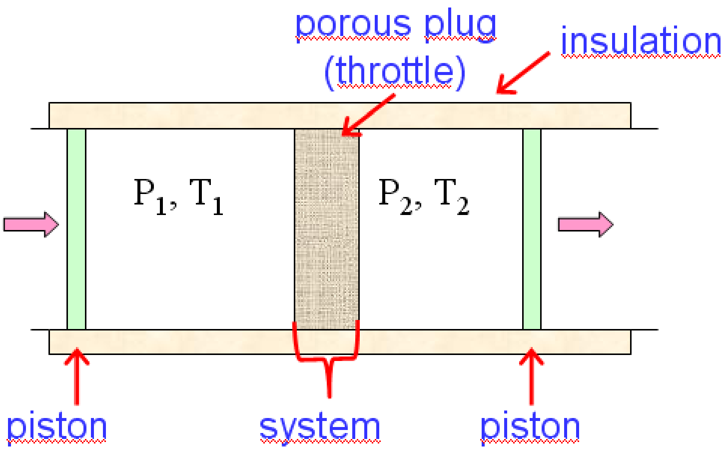


Fig. 2.23

Initial state (state 1), all the gas is in the left hand side.

Final state (state 2), all the gas is in the right hand side.

Since Q=0, ΔU=W. Therefore the work is

$$W=U_2 - U_1 = p_1V_1 - p_2V_2 \tag{2.71}$$

Namely, in the left hand side, work is done **on** the system, while in the right hand side, work is done **by** the system. Rearranging (2.71)

$U_2+p_2V_2=U_1+p_1V_1$ that means $H_1=H_2$, so *if a gas gets through a throttle adiabatically, its enthalpy does not change,* **ΔH=0.**

In contrary to the enthalpy the ***temperature can change*** *during this process*.

In case of an **ideal gas** T does not change. Enthalpy depends on T only, if H does not change, T does not change either.

For **real gas** the Joule-Thomson coefficient is defined:

$$\mu_{JT} = \lim_{\Delta p \to 0} \frac{\Delta T}{\Delta p} = \left(\frac{\partial T}{\partial p}\right)_H \tag{2.72}$$

This coefficient can be positive, zero and negative.

$\mu_{JT} > 0$: the gas cools down (dp is always negative!*)*;

$\mu_{JT} < 0$: the gas warms up;

$\mu_{JT} = 0$: the temperature does not change.

This last case is possible since there are certain temperatures and pressures for real gases, too, where we cannot find a temperature change when performing the Joule-Thomson experiment.

Fig. 2.24 can explain the situation. The inversion curve is the border between warming and cooling area. Practically, at higher temperature and pressure the gas wars up. Cooling is possible between limited temperatures and lower pressures.

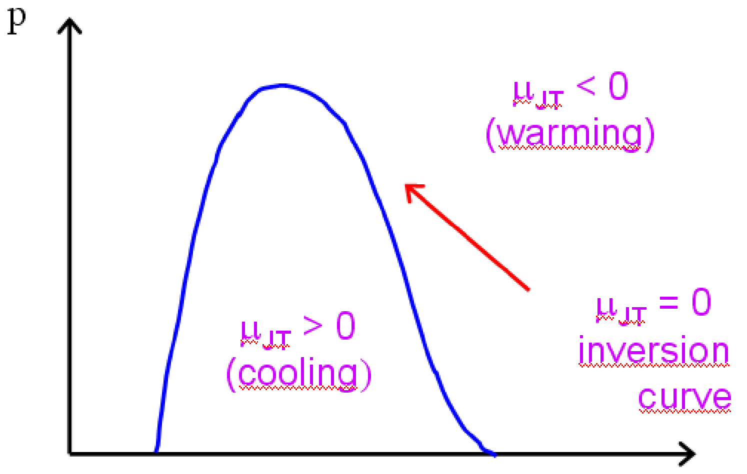


Fig. 2.24

Isothermal Joule-Thomson effect

This is expansion without a throttle. The isothermal compressibility of a gas is characterized by the *isothermal compressibility coefficient:*

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2.73}$$

The negative sign expresses that the volume increases with decreasing pressure. Substituting the equation of the state of the ideal gas (1.1) for equation (2.73) we have

$$\kappa_T = \frac{1}{p} \tag{2.74}$$

i.e. the higher pressure the lower the compressibility in the isothermal process.

The **work of the expansion** for the ideal gas is

$$U_2 - U_1 = W = p_1V_1 - p_2V_2 \tag{2.71}$$

For the **expansion of a real gas** we have

$$Q_T = U_2 - U_1 - p_1V_1 + p_2V_2 = H_2 - H_1 \tag{2.75}$$

An interesting application of the isothermal JT effect is the air sampling for environmental analysis. On the spot a balloon is filled under a little higher pressure than the atmospheric. It is locked up with a valve.

In the lab a little sample is added to the chromatographic carrying gas stream (lower pressure), or into a vacuum cell of an IR spectrometer. For the analysis of such kind samples GC-MS or GC-IR coupled methods are applied.

3. MIXTURES

3.1 Quanties of mixtures

A mixture is system where any phase containing more than one compon*ent. A mixture 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). A and 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). Le tus see an example.

Volume of mixing, that is the change of volume in mixing:

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

V is the volume of the mixture, V_{m1} and V_{m2} are the molar volumes of componets 1 and 2, respectively. In general, rewriting (3.1), let E any extensive property (H, S, G, A, etc.)

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

The followig 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 – i.e. the molar volume of mixing (x is the mole fraction).

$$\Delta_{mix}V_m = \frac{\Delta_{mix}V}{n_1 + n_2} = \frac{V}{n_1 + n_2} - \left(x_1 V^*_{m1} + x_2 V^*_{m2}\right) \tag{3.3}$$

The reason of the mixing is the intermolecular interaction, i.e. the molecules form associates, e.g. hydrogen bonds (see subsection 3.2.). This is demostrated in Fig. 3.1.

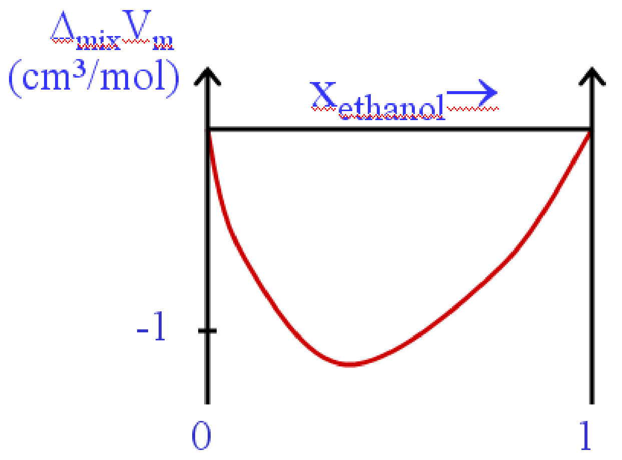


Fig. 3.1, *mixture: water – ethanol*

We can form the **molar enthalpy of mixing** (division by $n=n_1+n_2$) substituting V in (3.2) for H:

$$\Delta_{mix}H_m = \frac{H}{n_1+n_2} - \left(x_1H^*_{m1} + x_2H^*_{m2}\right) \tag{3.4}$$

The first term on the right side is the molar *entahalpy of the mixture*:

$$H_m = \frac{H}{n_1+n_2}$$

the starred quantities refer to the pure component.

If ***$\Delta_{mix}H_m > 0$*, *the mixing is endothermic***, the mixture cools down during the mixing, - we must add heat to the system to keep the temperature unchanged

If ***$\Delta_{mix}H_m < 0$*, *the mixing is exothermic,*** the mixture warm up during the mixing, heat is given away by the system.

In physical chemistry mole fractions are applied in diagrams (see e.g. Fig. 3.1), however, in technical diagrams *weight fractions (mass fractions)* are prefered, look e.g. at Fig. 3.2. Besides, mass units (kg) are used in these diagrams. In this figure the specific enthalpy of mixing of water-ethanol system at three temperatures (w: weight fraction). The changes reflect the changes in intermolecular interactions with heating.

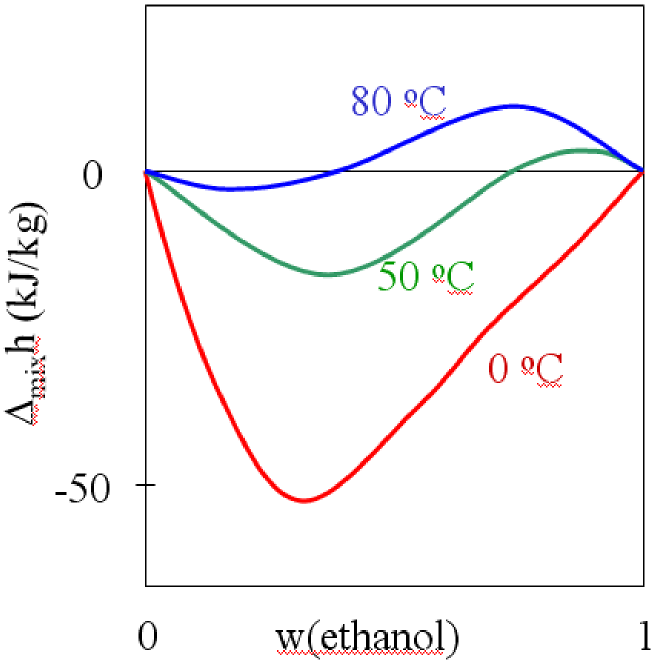


Fig. 3.2

3.2 Intermolecular interactions

The intermolecular interactions maybe

- *electrostatic*, e.g. benzene-toluene mixture;
- *dipole-dipole*, e.g. acetone-thiophene;
- hydrogen bond, e.g. ethanol-water.

It is possible also that

- only molecules of one component build associates (*selfassociation*), and
- the interaction with the molecules of the other component(s) is weak.

We shall study the hydrogen bond interaction on the ethanol-water liquid mixture, on some models. Starred atoms or electron pairs can participate in H-bonds.

The components are

$C_2H_5-\overset{*}{\underset{*}{O}}-H^{*}$

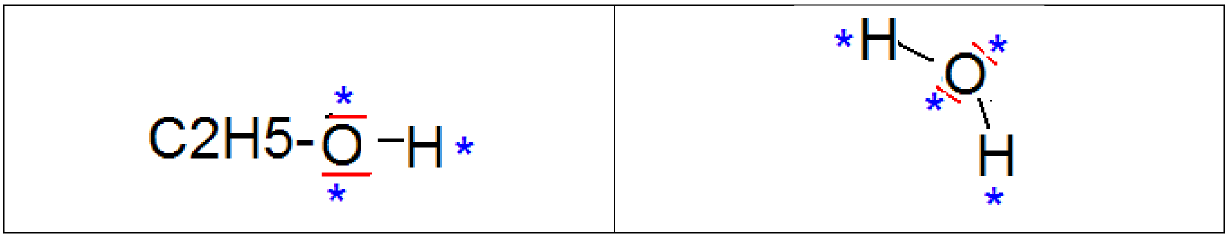


Fig. 3.3.a

Below you can see two different models for the ethanol-water interactions.

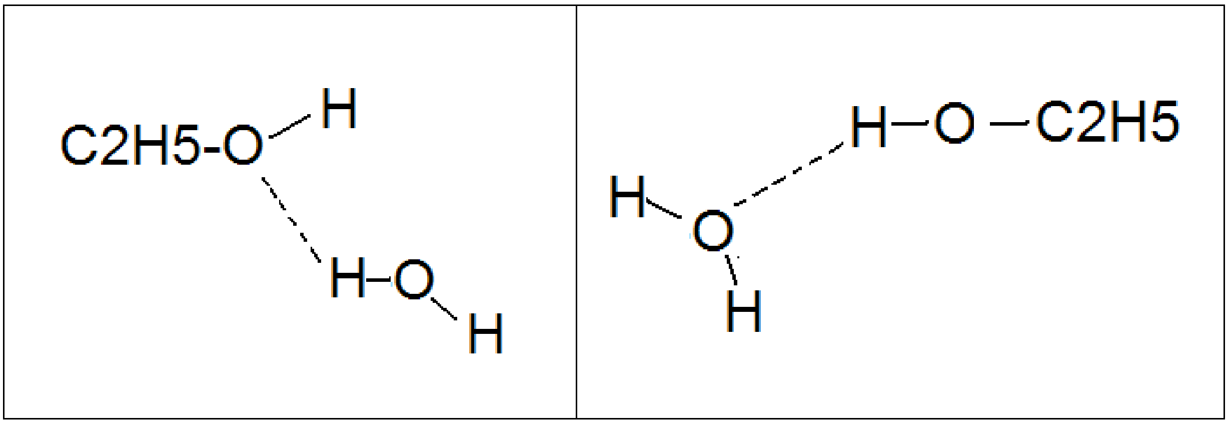


Fig. 3.3b

There are some different definition in the field of mixtures. *Pay attention!* The **solution** is a mixture. The mixture is called **solution** if one component is the bulk of the mixture, this is the **solvent.** All other components in smaller concentrations are the **solutes.**

The form of theGibbs free energy of mixing $\Delta_{mix}G$ is similar to other functions of mixing (see e.g. equation 3.4).

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

The first term may be negative or positive, the second term is always positive.

In a spontaneous process at constant temperature and pressure G decreases, (2.57). Both enthalpy and entropy depend on temperature but here we assume constant temperature.

The mixture building is a spontaneous process. Therefore *the entropy will be increase during mixing.*

Remember: **S=k*lnW** (Subsection 1.16 and Equ.1.80)

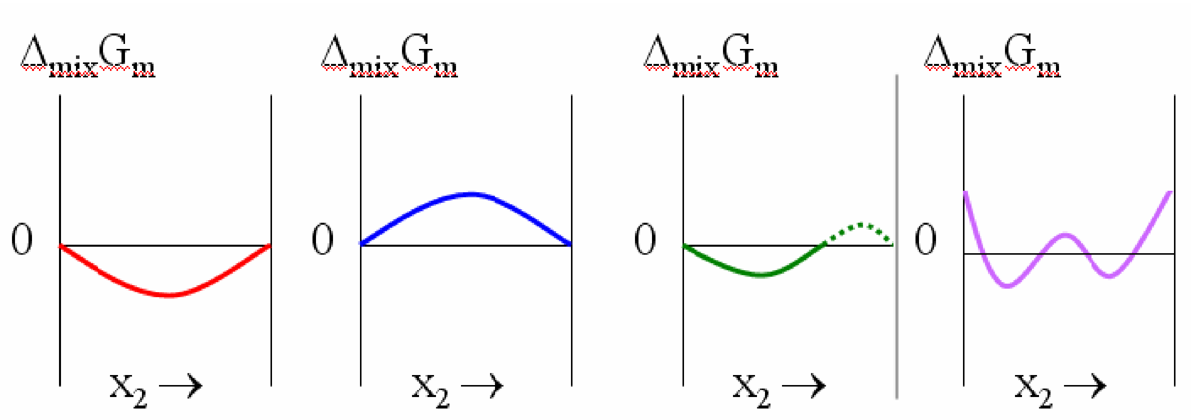
k: Boltzmann constant

W: Thermodynamic probability: number of microstates belonging to system with N atom.

Microstate: a possible distribution of particles under the energy levels of the system.

On Figs. 3.4 you will find diferent types of *dependence of the molar Gibbs function from the mole fraction.*

total miscibility	total immisibility	patly miscibility	partly miscibility



a total miscibility

b total immiscibility

c partly miscibility

d partly miscibility

Fig. 3.4

*The **partial molar volume** is the function of concentration, function of the intermolecular interactions in the mixture.*

Example: the partial molar volume of water is

18 cm^3/mol in water and

14 cm^3/mol in ethanol.

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

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} \quad \text{and} \quad V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} \qquad (3.6a)$$

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 (see subsection 2.9).

Fig. 3.5 introduces the changes of the partial molar voluimes as function of the mole fraction on the water-ethanol liquid system.

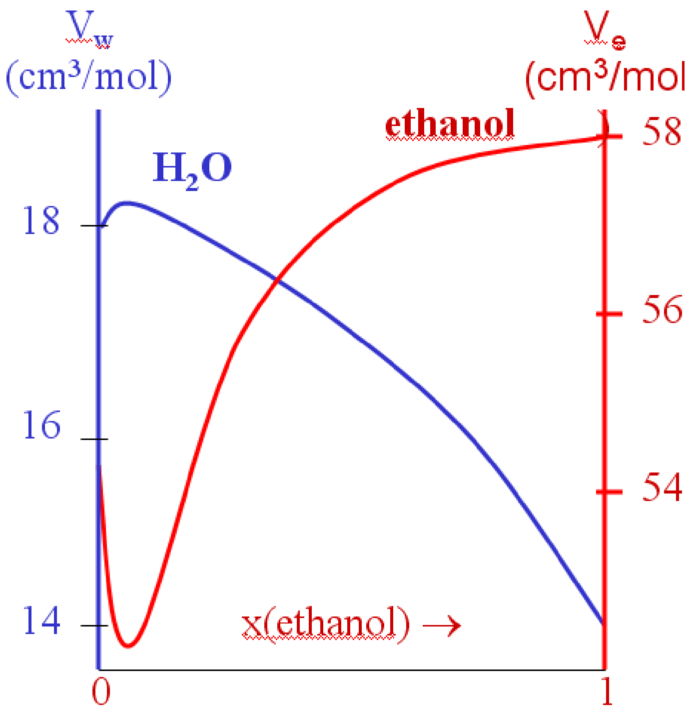


Fig. 3.5

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

$$V = V(n_1, n_2)$$

The complete differential is

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

The short form of (3.6b) is

$$dV = V_1 dn_1 + V_2 dn_2 \qquad (3.6c)$$

Integrating (3.6b) means the increase the mixture volume at constant composition:

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

Technically is this integrating very simple (Fig. 3.6):

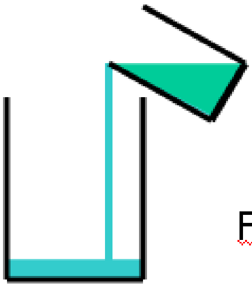


Fig. 3.6

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.

We can rewrite (3.7) for ideal solution

$$V = V_{m1}^{*} \cdot n_1 + V_{m2}^{*} \cdot n_2 \qquad (3.8)$$

The quantities with starred subscripts refer to the pure components, since in ideal mixtures the partial molar volume is equal to the molar volume of the pure component in the full mole fraction region.

Other extensive parameters (H, G, etc.) also have partial molar quantities. In general, let E an extensive quantity

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

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

$$dE = E_1 dn_1 + E_2 dn_2 \qquad (3.10a)$$

Integrating (3.10a)

$$E = E_1 n_1 + E_2 n_2 \qquad (3.10b)$$

For a multicomponent system:

$$dE = \sum E_i dn_i \tag{3.10c}$$

Integrating (3.10c)

$$E = \sum E_i n_i \tag{3.10d}$$

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:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \tag{3.11}$$

The Gibbs function is for a two component system at constant temperature and pressure

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

the integrated form

$$G = \mu_1 n_1 + \mu_2 n_2 \tag{3.12b}$$

(3.12b) means the Gibbs function of the mixture is the sum of chemical potentials times the amounts in moles.

The Gibbs-Duham equation

Here it is derived for chemical potentials but it is valid for other partial molar quantities, too**.** The equations (2.44) will be applied.

According to (3.12a)

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

The corresponding integrated form is (3.12b)

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

The complete differential of (3.12b) is at constant p and T

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

Subtracting (3.12b) from this equation the result is the Gibbs-Duhem equation:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{3.13}$$

The Gibbs-Duham equation is valid when T and p does not change, i.e. only the composition changes. The consequence of this equation is that *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 properties, e.g. for volumes:

$$n_1 dV_1 + n_2 dV_2 = 0 \tag{3.14}$$

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

3.4 Determination of partial molar quantities

We shall discuss *two methods* on the example the ***partial molar volume***.

1. ***Method of slopes***

We introduce the method as example on the partial molar volume (3.15):

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1} \tag{3.15}$$

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 obtain V_2-n_2 data pairs. Look at Fig. 3.7!

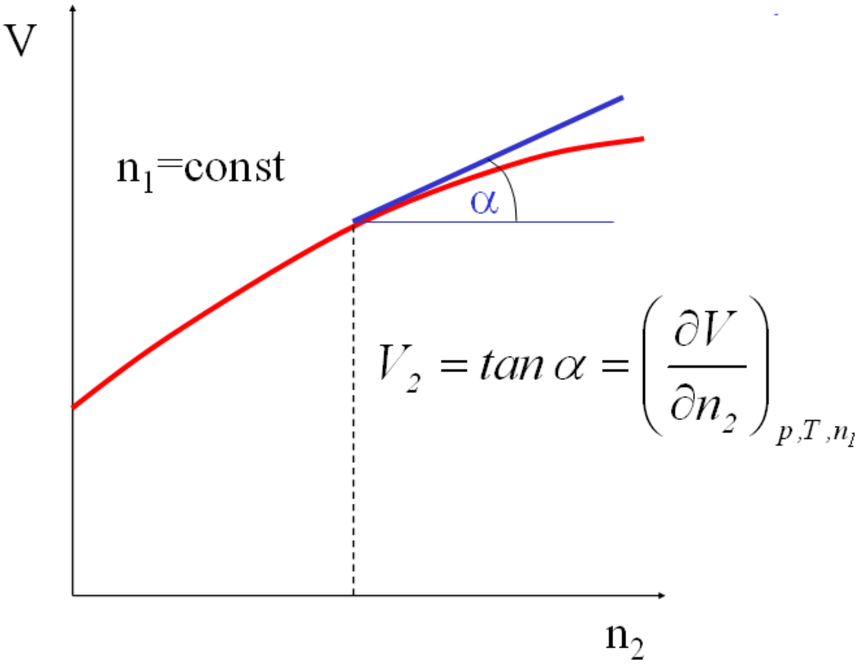


Fig. 3.7

2. The method of intercepts

Follow the derivation of the necessary equation (3.16)!

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

Dividing by n_1+n_2

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

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

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

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

Substituting the differential quotient for the volume difference we have the result

$$V_m = V_1 + \frac{dV_m}{dx_2} x_2 \tag{3.16}$$

This is the equation of the tangent of the V_m-x_2 curve. The intercepts of the tangents of the V_m-x_2 curve produce the partial molar volumes See Fig. 3.8!

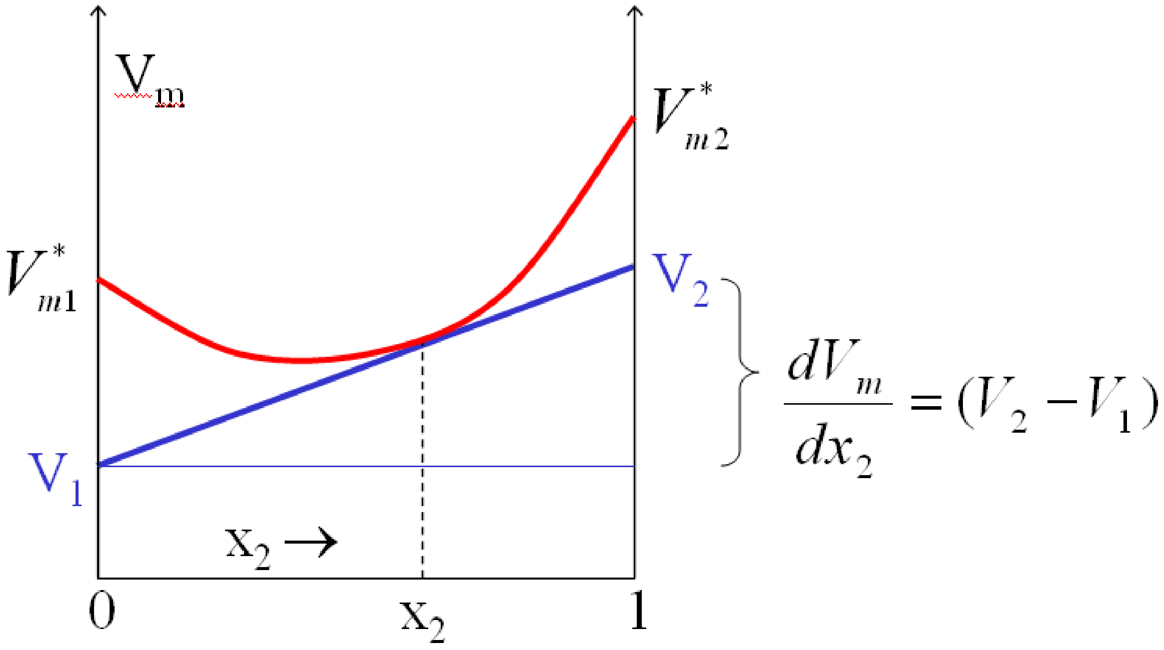


Fig. 3.8

This method is more accurate than the method of slopes.

However, the *measurement itself needs attention and high precision. One has* to *consider and analyze the possible error sources of the measurement.*

3.5 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 behavior. 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. This means

$$\Delta_{mix}V = 0, \quad \Delta_{mix}H = 0 \tag{3.17}$$

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, and high chemical potential. The other way round: small chemical potential in liquid phase means small partial pressure in the vapor phase.

***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** (3.18):*

$$p_i = x_i \cdot p_i^* \tag{3.18}$$

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

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

$$p = p_1 + p_2 \tag{3.19}$$

The p(x) diagram for ideal mixture of two volatile components has the shape like Fig. 3.9. Look at the straight lines and their additivity!

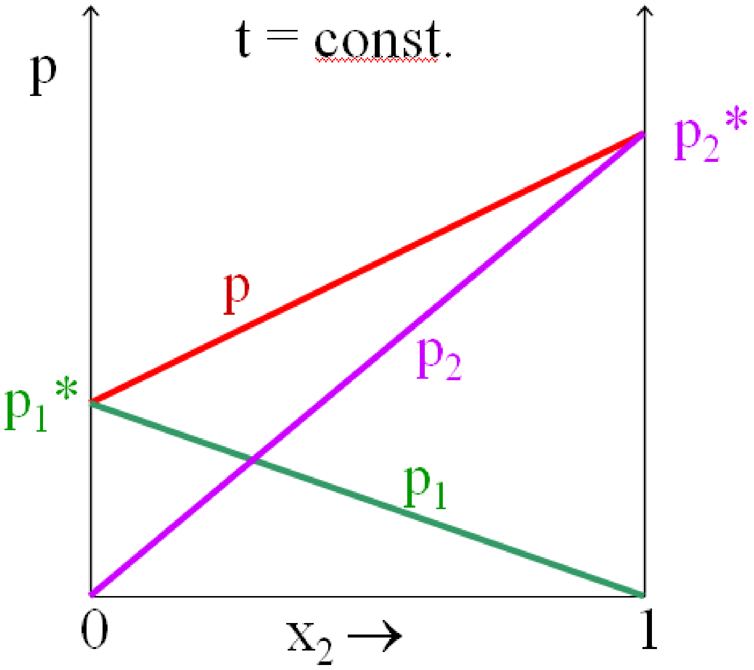


Fig. 3.9.

If *only component (1) is volatile* like in solutions of solids, Fig. 3.9 is modified, see Fig. 3.10. In this case the vapor pressure is determined only by component 1.

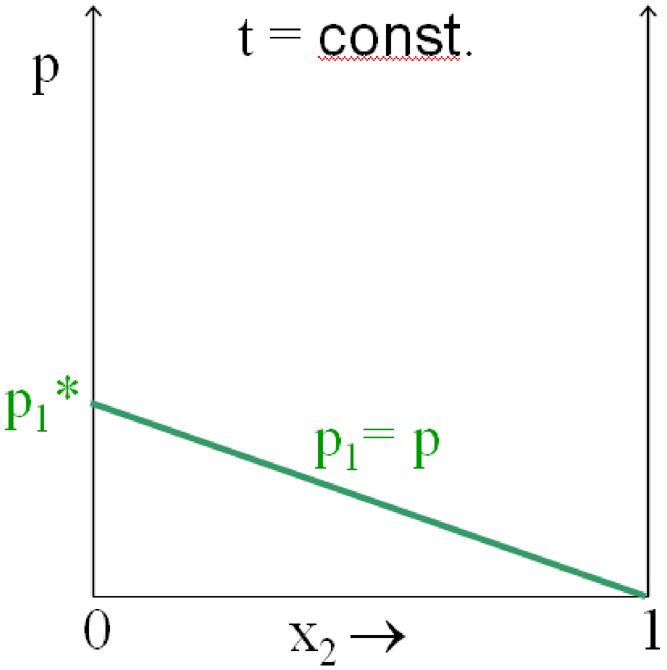


Fig. 3.10

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!

3.6 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).

Contraction: $\Delta_{mix}V < 0$

Exothermic solution: $\Delta_{mix}H < 0$

Activity must be used: $p_i = a_i \cdot p_i^*$ (3.21)

i.e. $p_i < x_i \cdot p_i^*$,

The activity coefficient represents the deviation (3.22):

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

In this case $\gamma_i < 1$.

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.

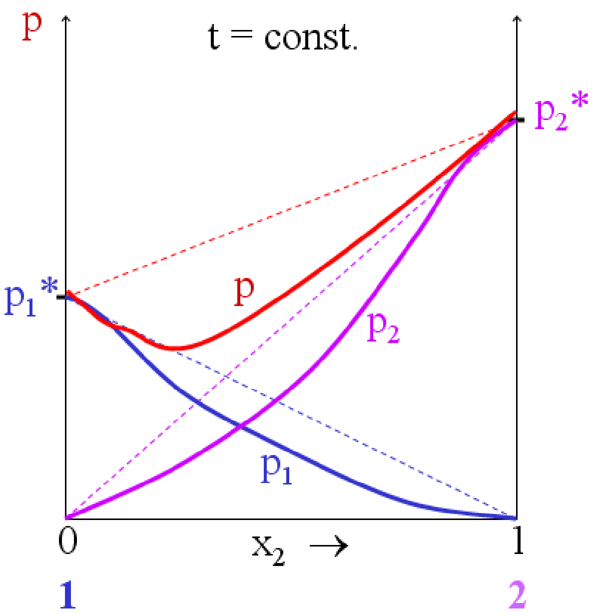


Fig. 3.11

Components: 1: chloroform, 2: acetone.

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.

Expansion: $\Delta_{mix}V > 0$

Endothermic solution: $\Delta_{mix}H > 0$

Activity must be used: $p_i = a_i \cdot p_i^*$ (3.21)

i.e. $p_i > x_i \cdot p_i^*$,

The activity coefficient represents the deviation (3.22):

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

In this case $\gamma_i > 1$.

Fig. 3.12 is the isothermal **vapor pressure** diagram of a two component mixture with ***positive deviation. The total vapor pressure may have a maximum.***

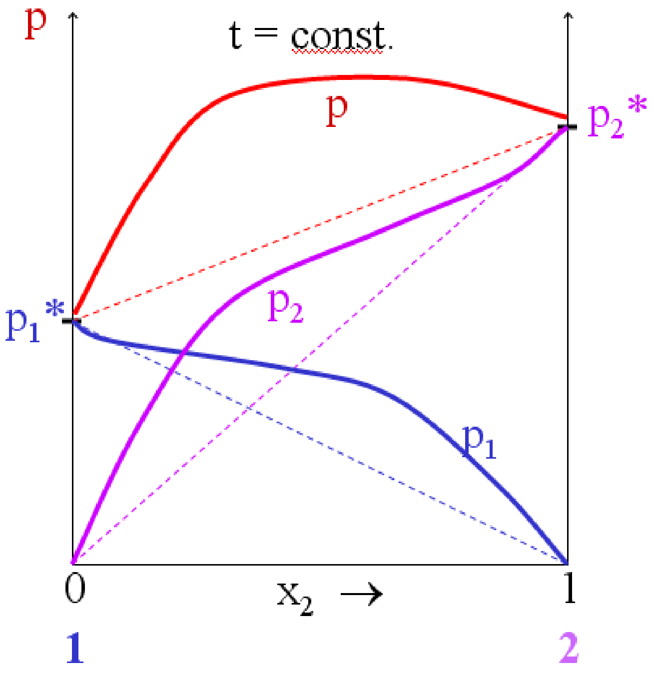


Fig. 3.12

Components: 1: water, 2: dioxane.

3.7 Chemical potential in liquid mixtures

In this subsection

1. We derive a formula for calculation of the chemical potential.

2. We use *Raoult´s law* (see subsection 3.5). In equilibrium the chemical potential of a component is equal in all phases (see subsection 2.10).

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

Let us denote the component **i** in gas (vapor) phase as μ_i^g, in liquid phase as μ_i. In equilibrium

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

1. Ideal liquid mixture

Since $p_i = x_i \cdot p_i^*$ we have from (3.23)

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

rearranged

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

where the first two terms depend only on temperature. Labeling the first to terms as

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

we have now

$$\mu_i = \mu_i^* + RT\, ln\, x_i \qquad (3.24)$$

2. Real liquid mixture

Since $p_i = a_i \cdot p_i^*$ we have from (3.23)

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

rearranged

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

where the first two terms depend only on temperature. Labeling the first to terms similarly as

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

we have now

$$\mu_i = \mu_i^* + RT\, ln\, a_i \qquad (3.25)$$

with $a_i = \gamma_i \cdot x_i$.

For a pure substance both x_i and γ_i are 1, and therefore also a_i is 1.

μ_i^* is the chemical potential of the pure substance at the given temperature and p^0 pressure, the ***standard chemical potential.*** For a pure substance

$$\mu_i^* = G_{mi}^* \qquad (3.26)$$

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

As long as the activity is the “effective” mole fraction, the ***fugacity** is the “effective” pressure in gas phase:*

$$\mu_i = \mu_i^* + RT\,ln(\varphi_i y_i) = \mu_i^* + RT\,ln\,y_i + RT\,ln\,\varphi_i \qquad (3.27)$$

Here φ_i is the *fugacity coefficient,* y_i is the mole fraction in gas phase. The fugacity is

$$f_i = \varphi_i . x_i \qquad (3.28)$$

The first two term on the right hand side of (3.27) describe the ideal behavior, $\mu_i(\mathrm{id})$ the third term expresses the deviation from the ideality

$$\mu(\mathrm{real}) - \mu(\mathrm{id}) = RT\,ln\,\varphi_i \qquad (3.29)$$

Dependence of the chemical potential on the mole fraction in an ideal liquid mixture is (3.24), $\mu_i = \mu_i^* + RT\,ln\,x_i$ Fig. 3.13 introduces this function. As the mole fraction approaches zero, the chemical potential approaches minus infinity. *The infinite chemical potential has not any physical meaning!*

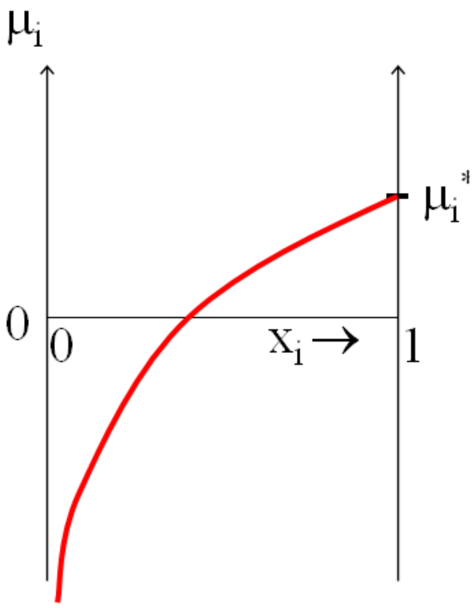


Fig. 3.13

For most substances the *standard chemical potential* (3.30) is negative.

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

The first term on the right hand side of (3.30) may be either positive or negative, while the standard molar entropy is always positive (the mixing increases the disorder).

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

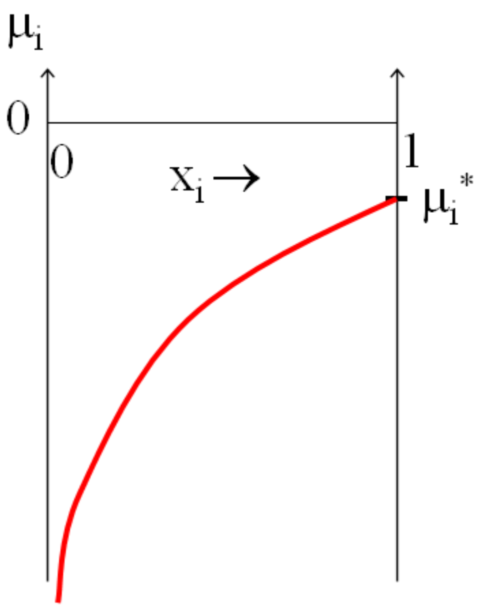


Fig. 3.14

Determination of the activity coefficient from liquid-vapor equilibrium data of a two component system:

According to ***Dalton's law*** *if the vapor is an ideal gas*

$$p_i = y_i \cdot p \tag{3.31}$$

We apply both Raoult's law for real mixtures and Dalton's law for the vapor phase. The partial vapor pressure of a component is independent of the mode of expression:

$$p_1 = \gamma_1 x_1 p_1^* = y_1 p \tag{3.32a}$$

$$p_2 = \gamma_2 x_2 p_2^* = y_2 p \tag{3.32b}$$

From these equations we have

$$\gamma_1 = \frac{y_1 p}{x_1 p_1^*} \qquad \gamma_2 = \frac{y_2 p}{x_2 p_2^*} \tag{3.33}$$

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, the activity coefficients can be calculated.

3.8 Entropy of mixing and Gibbs free energy of mixing

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

We study three important cases of mixing:

Mixing of ideal gases

Ideal mixture of liquids

Real mixtures

1. Mixing of ideal gases

Modell before mixing: the two gas components (1 and 2) are separated by wall, see Fig. 3.15a.

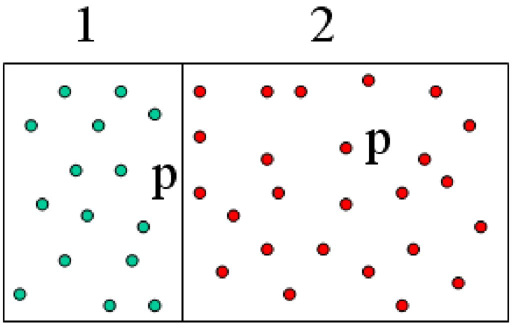


Fig. 3.15a

Then the wall is removed. Both gases fill the space (Fig. 3.15b). There is no interaction ($\Delta_{mix}H= 0$). The pressures of the components are reduced to $p_1$and p_2 partial pressures:

$$p_1= y_1p \text{ and } p_2 = y_2p \tag{3.34}$$

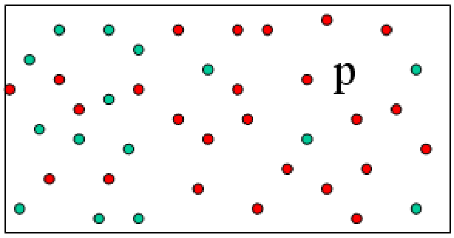


Fig. 3.15b

Pressure dependence of entropy (at constant temperature): *the entropy of mixing is the sum of the two entropy changes, see equation (1.71)*

$$\Delta S = -nR \ln \frac{p_2}{p_1} \tag{3.35}$$

therefore (p →y_1p, p →y_2p)

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

since $n_1 = n \cdot y_1$ and $n_2 = n \cdot y_2$

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

for one mol dividing by **n**:

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

Generalizing for more than two components:

$$\Delta_{mix} S(id) = -nR \sum y_i \ln y_i \tag{3.36c}$$

Since the mole fractions are smaller than 1 so each term is negative (lny<1).

Therefore ***the entropy of mixing is always positive***.

The Gibbs function of mixing is

$$\Delta_{mix}G = \Delta_{mix}H - T\,\Delta_{mix}S \tag{3.37}$$

Since the enthalpy term is zero for ideal mixtures, substituting (3.36a)

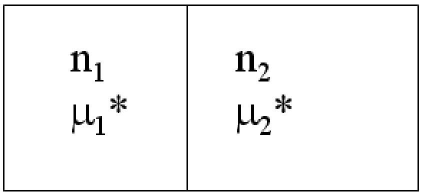
$$\Delta_{mix} G(id) = nRT \sum y_i \ln y_i \tag{3.38}$$

that is always negative.

2. Ideal mixture of liquids

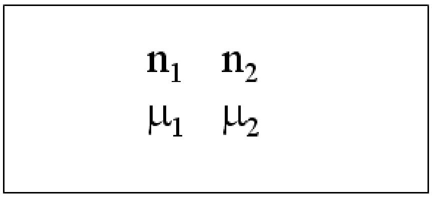
First we calculate the Gibbs function of mixing.

Before mixing:



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

After mixing:



$$\mu_1 = \mu_1^* + RT \ln x_1 \qquad \mu_2 = \mu_2^* + RT \ln x_2$$

Therefore

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

Detailed

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

The *Gibbs function of mixing* is

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

Considering

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

For two components

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

Generalizing for more than two components

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

Pay attention on the **similarity** of equations (3.38) and (3.39).Both refer to ideal mixtures.

Since $\Delta_{mix}G = \Delta_{mix}H - T\,\Delta_{mix}S$ and for ideal mixtures the enthalpy term is zero

$$\Delta_{mix}S(id)=-\frac{\Delta_{mix}G(id)}{T}$$

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

It is always positive since the disorder increases by mixing. This is reflected in the negative values of *lnx* multipliers.

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 introduces the changes of thermodynamic functions as functions of mole fraction at about room temperature for ideal mixtures. Since the change of the molar enthalpy of mixing is in this case zero, therefore the molar Gibbs function of mixing is in this case equal to the absolute value of $T\Delta_mS_m$.

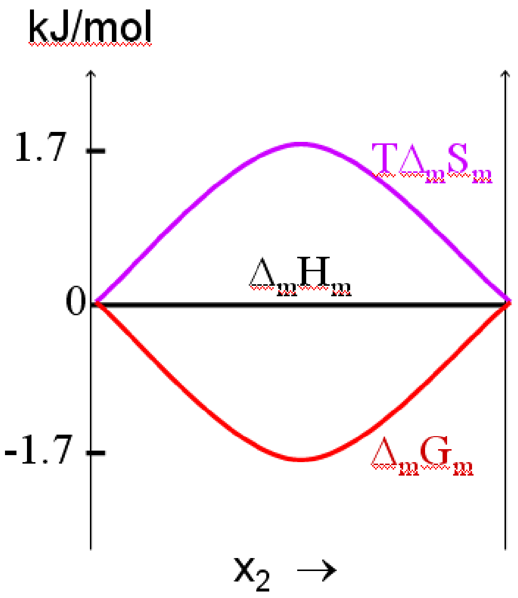


Fig. 3.16

3. Studying **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 first two ones. The subscripts ‘m’-s 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

Case 1: *negative deviation* of $\Delta_m H_m$ from the ideal behavior:

$T\Delta_m S_m > \Delta_m G_m$. 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 this figure with Fig. 3.4a).

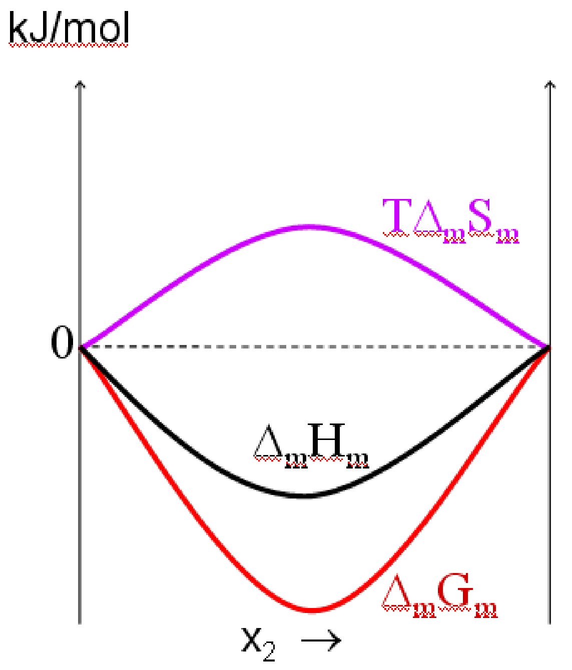


Fig. 3.17

Case 2. If both $\Delta_m H_m > 0$ and $T\Delta_m S_m > 0$, then two cases are possible.

Case 2a. $\Delta_m H_m > T\Delta_m S_m$, *therefore* $\Delta m G_m > 0$. Therefore the two *components are immisible* (see Fig. 3.18, compare with Fig. 3.4b).

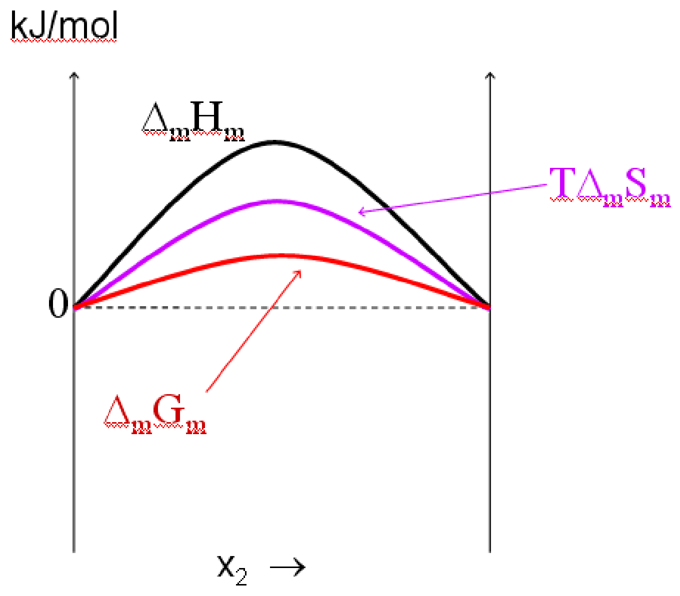


Fig. 3.18

Case 2b. $\Delta_m H_m < T\Delta_m S_m$, *therefore* $\Delta_m G_m < 0$. Therefore the *components are miscible* (see Fig. 3.19, compare it with Fig. 3.4a).

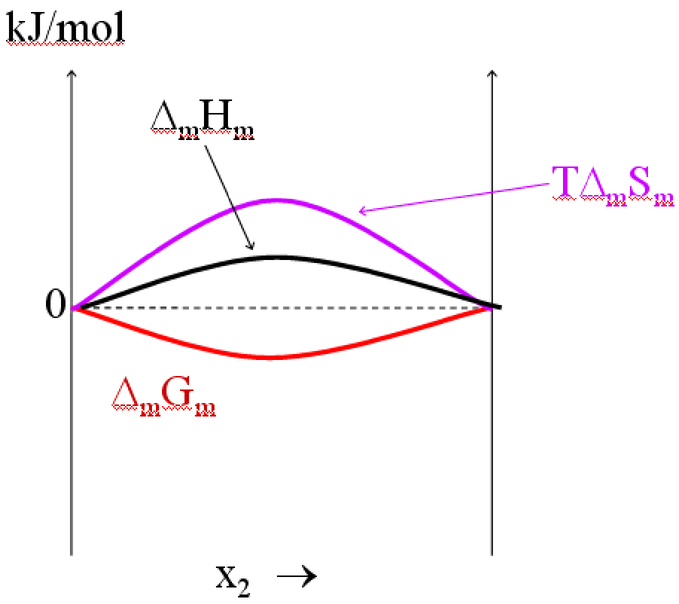


Fig. 3.19

3.9. Vapor pressure and boiling point diagrams of miscible liquids

According to the phase rule: F = C - P + 2 (2.58). 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 = constant: the diagram is called *vapor pressure diagram*;

or p = constant, in this case the diagram is called *boiling point diagram*.

Ideal solutions [See (3.18) and (3.19)]

We derive *Konovalov's first law*.

According to Raoult's law: $p_1 = x_1 \cdot p_1^*$ and $p_2 = x_2 \cdot p_2^*$

The total pressure is $p = p_1 + p_2$

Dividing the expressions of the two partial pressures by one another

$$\frac{p_1}{p_2} = \frac{y_1}{y_2} = \frac{x_1 \cdot p_1^*}{x_2 \cdot p_2^*}$$

Rearranging this equation, applying $x_1 + x_2 = 1$,

$$\frac{1-y_2}{y_2} = \frac{1-x_2}{x_2} \cdot \frac{p_1^*}{p_2^*}$$

assuming $p_1^* < p_2^*$, we have

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

Therefore $$y_2 > x_2 \qquad (3.41)$$

This is ***Konovalov's first law***, 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 is a *vapor pressure diagram, L: liquid curve, V: vapor curve.* The vapor pressure diagram is determined by

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

On the vapor pressure diagram the *mole fractions of both liquid and vapor phases are readable on the abscissa* through projecting from ordinate p on the L and V curves, respectively.

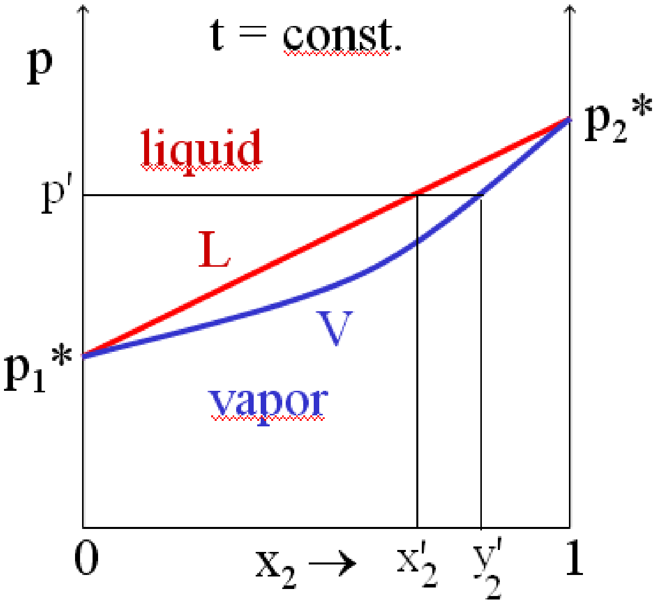


Fig. 3.20

Looking at Fig. 3.20 on the primed quantities, you can see Konovalov’s first law is valid.

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.

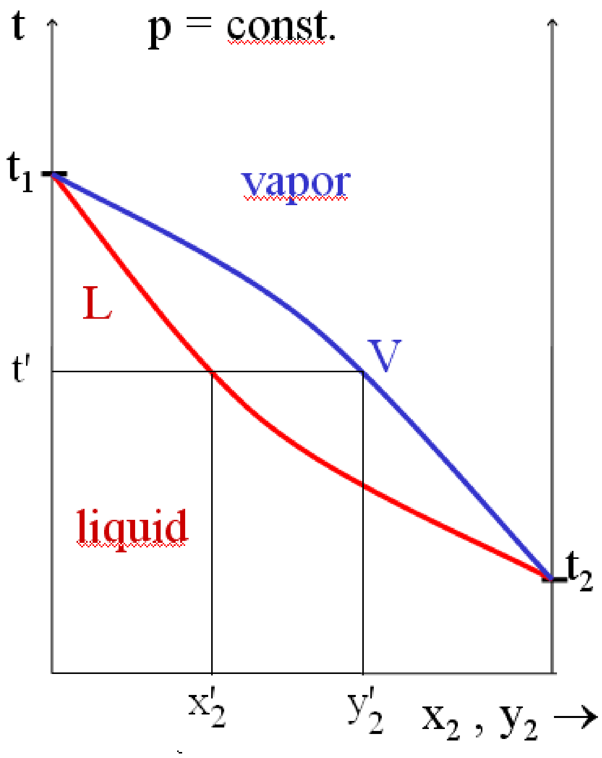


Fig. 3.21

The boiling point of the more volatile component is lower.

Fig. 3.21 introduces how it is possible to determine on the boiling point diagram isothermal (x,y) mole fraction pair. *V is the vapor curve (condensation curve*), *L is the liquid curve (boiling point curve).*

Compare the forms of the vapor pressure and the boiling point diagrams!

The level rule

We derive it for a two phase system (Fig. 3.22), superscript „l” means liquid phase, „v” vapor phase.

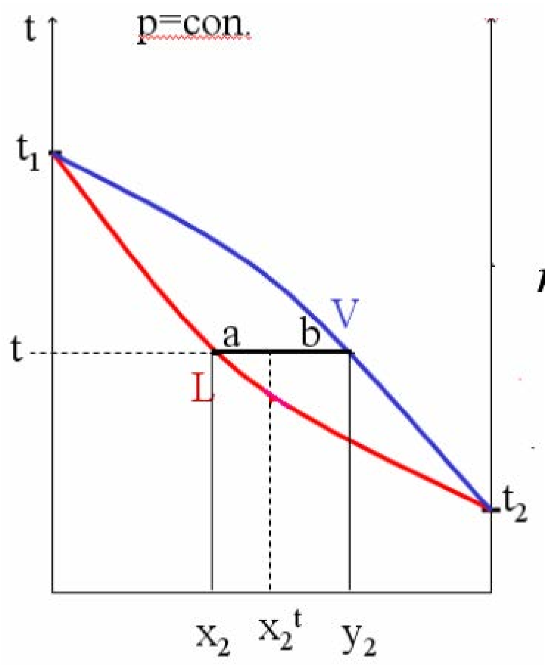


Fig. 3.22

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

$$n \cdot x_2^t = n^l \cdot x_2 + n^v \cdot y_2$$

Rearanging:

$$n^l x_2^t + n^v x_2^t = n^l x_2 + n^v y_2$$

and

$$n^l \left(x_2^t - x_2\right) = n^v \left(y_2 - x_2^t\right)$$

According the meaning of ***a*** and ***b***

$$\frac{n^v}{n_l} = \frac{a}{b} \tag{3.43}$$

Equation 3.43 is the *level rule*, this is an inverse ratio. Looking at Fig 3.22: to smaller “a” belong larger amount of the liquid phase on the double phase area between the curves L and V. A longer “b” means smaller amount of the vapor phase.

Real solution

Case 1: *Vapor pressure, positive deviation* from ideal (Fig. 3.23)

The total vapor pressure may have a maximum: the **azeotrope** where the vapor and the liquid composition is equal. Examples: water-dioxane and water-ethanol. At “1” both mole fractions of component “1” are 1.

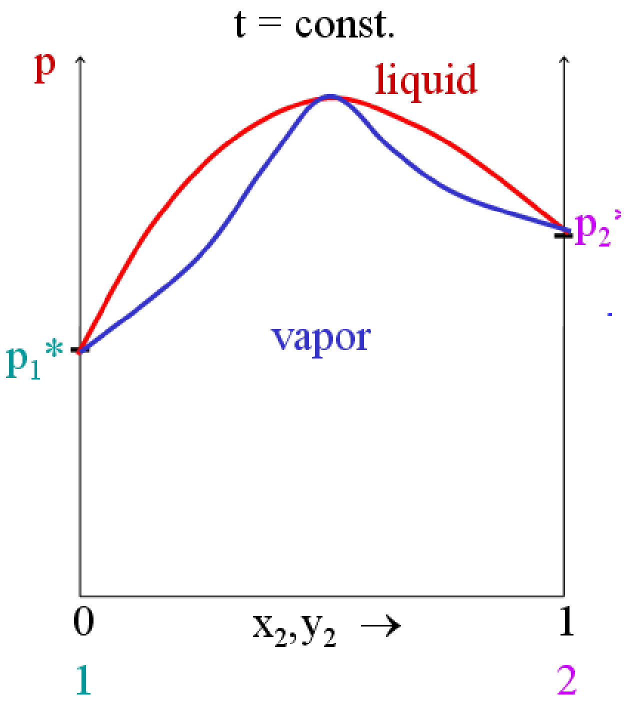


Fig. 3.23

Corresponding *boiling point - positive deviation* from ideal

The azeotrope on the boiling point diagram at positive deviation appears at minimum. See Fig. 3.24! L is boiling point curve, V is the condensation curve. Cooling the vapor and arriving the V curve the condensation begins. Left from the azeotrope point in the two phase area the relation is $x_1>y_1$, right from this point in the two phase region the relation is $x_2<y_2$.

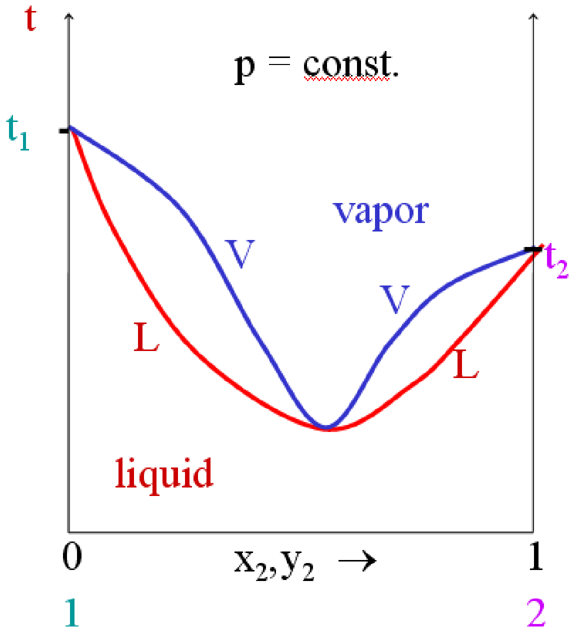


Fig. 3.24

Case 2 Vapor pressure, negative deviation

The total vapor pressure may have a minimum: *azeotrope with minimum.*

See the vapor pressure diagram on Fig. 3.25! Examples are: aceton-methanol, acetone-chloroform and water-nitric acid.

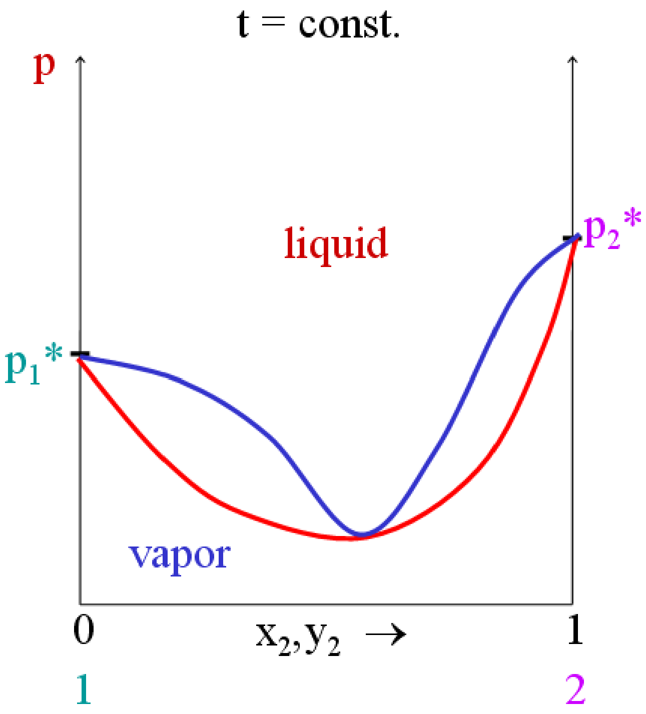


Fig. 3.25

The corresponding *boiling point diagram has a maximum*, i.e. it is a high boiling azeotrope (Fig. 3.26).

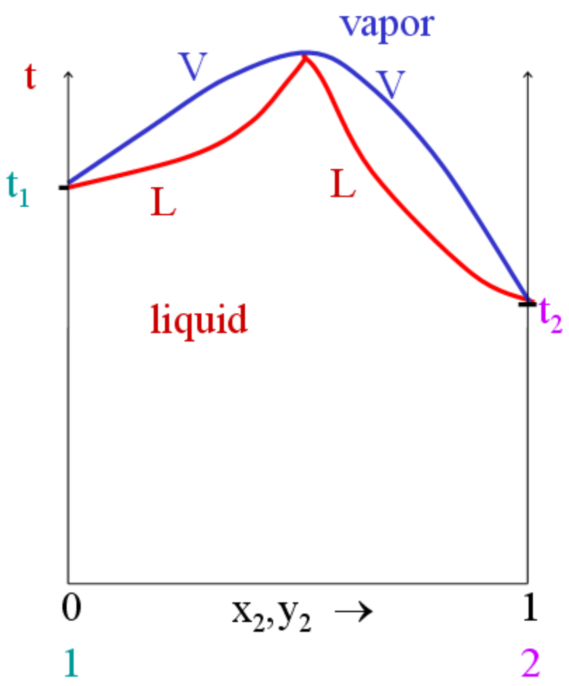


Fig. 3.26

3.10 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).

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{3.13}$$

Dividing by n:

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

At constant T, μ depends on composition only.

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial x_1}\right) dx_1 \qquad d\mu_2 = \left(\frac{\partial \mu_2}{\partial x 2}\right) dx_2$$

Since (3.13)

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

Two component system: $dx_1 = - dx_2$

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

$$\mu_1 = \mu_1^0 + RTln \frac{p_1}{p^0} \quad \text{and} \quad \mu_2 = \mu_2^0 + RTln \frac{p_2}{p^0}$$

Therefore

$$\frac{\partial \mu_1}{\partial x_1} = RT \frac{\partial lnp_1}{\partial x_1} \quad \text{and} \quad \frac{\partial \mu_2}{\partial x_2} = RT \frac{\partial lnp_2}{\partial x_2}$$

So $$x_1 \frac{\partial lnp_1}{\partial x_1} = x_2 \frac{\partial lnp_2}{\partial x_2}$$

Rearranged considering that dlnp=dp/p

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

Since $x_1=1-x_2$

$$- \frac{1 - x_2}{p_1} \frac{dp_1}{dx_1} = \frac{x_2}{p_2} \frac{dp_2}{dx_2}$$

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

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

According to (3.44) if the partial mole fraction increases, the partial pressure also increases:

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

Case A: $\frac{dp}{dx_2} = 0$, *the total vapor pressure has a maximum or minimum.*

$$1 - \frac{x_2}{1 - x_2}\frac{p_1}{p_2} = 0$$

Applying Dalton’s law: $p_1 = y_1 p = (1-y_2)p$ and $p_2 = y_2 p$

Based on (3.44)

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

rearranged

$$\frac{x_2}{1 - x_2}\frac{1 - y_2}{y_2} = 1$$

from this equation

$$\frac{1 - y_2}{y_2} = \frac{1 - x_2}{x_2}$$

and

$$\frac{1}{y_2} - 1 = \frac{1}{x_2} - 1$$

Consequently

$$\begin{aligned} y_2 &= x_2 \\ y_1 &= x_1 \end{aligned} \qquad (3.45)$$

This is ***Konovalov’s third law.*** *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.

Case B. $\frac{dp}{dx_2} > 0$. Extreme value does not exist.

$$1-\frac{x_2}{1-x_2}\frac{p_1}{p_2}>0$$

Applying Dalton’s law: $p_1 = y_1p =(1-y_2)p$ and $p_2 = y_2p$

We have

$$1-\frac{x_2}{1-x_2}\frac{(1-y_2)p}{y_2p}>0$$

Rearranging

$$1>\frac{x_2}{1-x_2}\frac{(1-y_2)p}{y_2p}$$

Therefore

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

and

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

Therefore

$$y_2 > x_2 \tag{3.46}$$

This is ***Konovalov’s second law.*** *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 of Konovalov’s second law on Figs. 3.23 and 3.25.

3.11 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.

Fig. 3.27 presents a boiling point diagram, **the effect of partial miscibility in the liquid phase.**

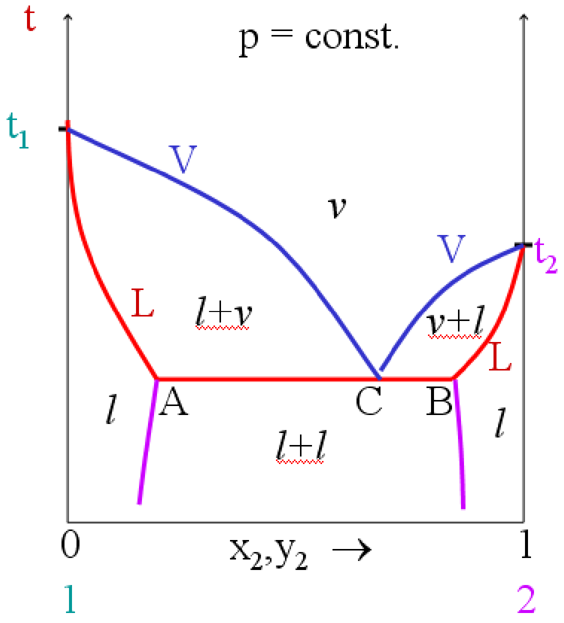


Fig. 3.27

Along the the ***A-C-B*** line equilibrium of three phases exists, thedegree of freedom: F=1 (see equation 2.58). **A:** component **1** is saturated with **2, B:** component **2** is saturated with **1**. **C** labels the boiling temperature of the two-phase region, **L** is the boiling point curve, **V** is the condensation curve. „***l***” is the liquid **B** rigth from the minimum of the **V** curve and it is labels the liquid **A** left from this minimum, both A and B are present at the two-liquid phase area („*l*+*l*”), „***v***” labels the vapor phase.

Example: butanol(1)-water(2).

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

$$p = \gamma_1^A x_1^A p_1^* + \gamma_2^B x_2^B p_2^* \tag{3.47}$$

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

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. The drops of one component are dispersed in the other component, like on Fig. 3.28. Example: the water-toluene mixture.

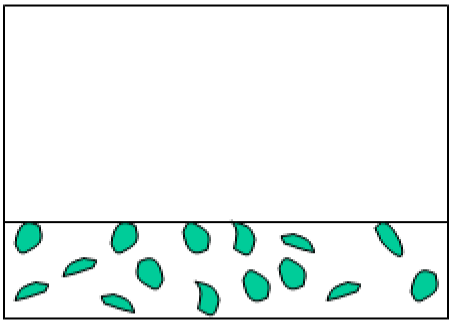


Fig. 3.28

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

$$p = p_1^* + p_2^*$$ (see 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.***

Fig. 3.29 is the boiling point diagram in case of *complete immiscibility in the liquid phase. The boiling temperature is independent of the composition of the mixture,* the L vaporozation curve is horizontal.

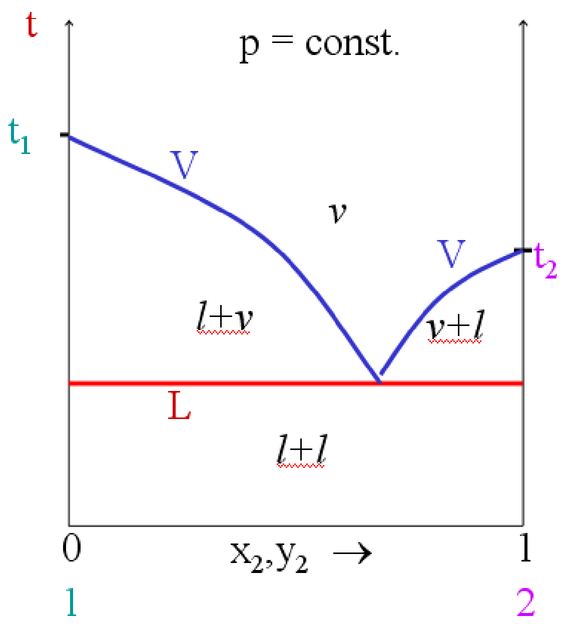


Fig. 3.29

Fig. 3.29 is the boiling point diagram in case of *complete immiscibility in the liquid phase. The boiling temperature is independent of the composition of the mixture*, the L vaporization curve is horizontal.

Theory of the s***team distillation:*** calculation of molar ratio of the components in the vapor phase. steam distillation is a method for distilling compounds which are heat-sensitive.

For steam distillation . *1: water, 2: organic material.*

According to *Dalton´s law*.: $p_1 = y_1 p$ and $p_2 = y_2 p$

Therefore

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

Applying n=m/M

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

And at last

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

This method is suitable also for *determination of molar mass.*

3.12 Solid - liquid equilibria: simple eutectic diagrams

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

Example: benzene and naphthalene.

Fig. 3.30 is a *solid-liquid phase diagram of miscible liquids.*

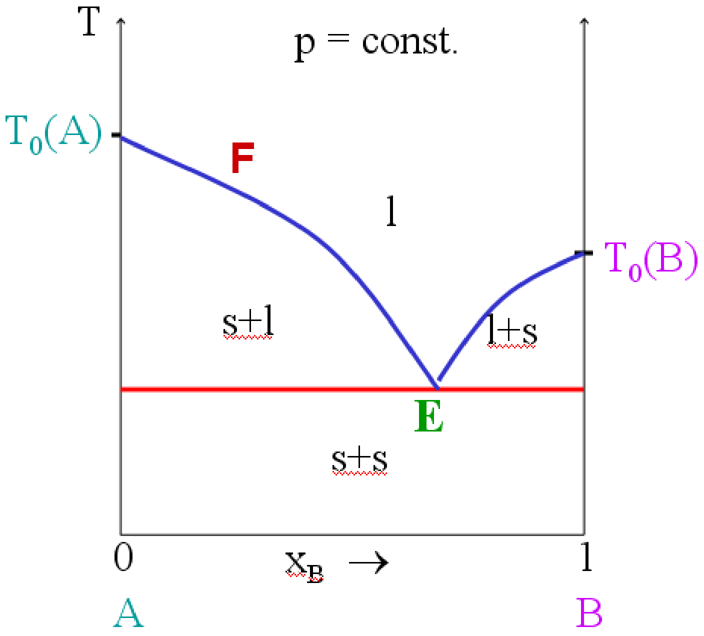


Fig. 3.30

F: freezing point curve, **E:** eutectic point, **T$_0$:** melting point, pure component.

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

Derivation of the freezing point curve (F)

Equilibrium:

$$\mu_A(s)=\mu_A(l) \tag{3.50}$$

Detailed:

$$\mu_A^*(s)=\mu_A^*(l)+RT\ln a_A \tag{3.51}$$

Since the starred chemical potentials are the molar Gibbs functions of the pure components,

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

Where **a**$_A$ is the activity of A in the saturated solution.

Since G = H - TS and dG =Vdp –SdT at constant pressure

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Differenciating G/T with respect to T we have (H=G+TS)

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

This equation is called ***Gibbs-Helmholtz equation.***

We apply now this equation to our earlier result:

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

Based on (3.52)

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

Rearranged we have the enthalpy of fusion (fus):

$$\frac{d\ln a_A}{dT} = \frac{\Delta H_{mA}(\,fus\,)}{RT^2}$$

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:

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

Observed the similarity to the Clausius-Clapeyron equation (2.30)!

It is now possible to express the temperature as a function of mole fraction:

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

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.*

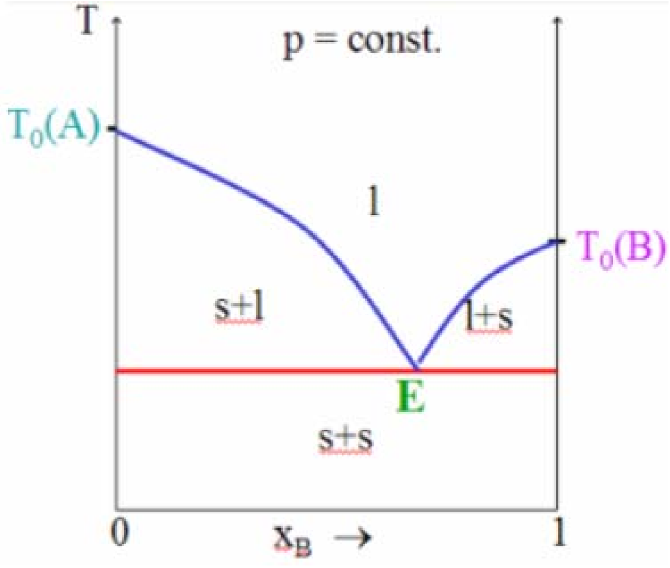


Fig. 3.31

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

3.13 Solid-liquid phase diagrams

One can find a great similarity to liquid-vapor equilibria. The main types of this kind phase diagrams are:

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

Now we studied the individual cases in detail.

1. Complete miscibility in solid state.

Case A) *There does not exist minimal temperature of melting*.

Look at Fig. 3.32 and compare it to Fig. 3.21 or Fig.3.22!

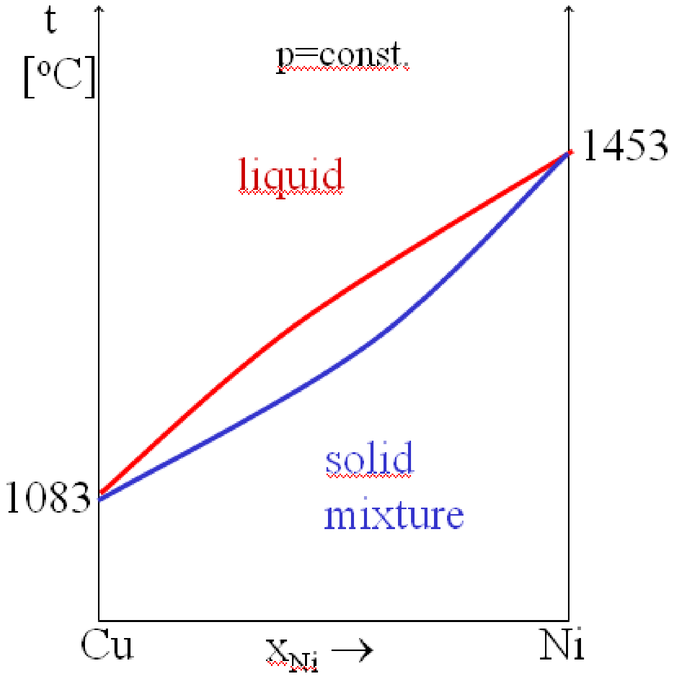


Fig. 3.32

Case B) *Minimal temperature of melting exist.* Look at Fig. 3.33 and compare it with Fig. 3.24!

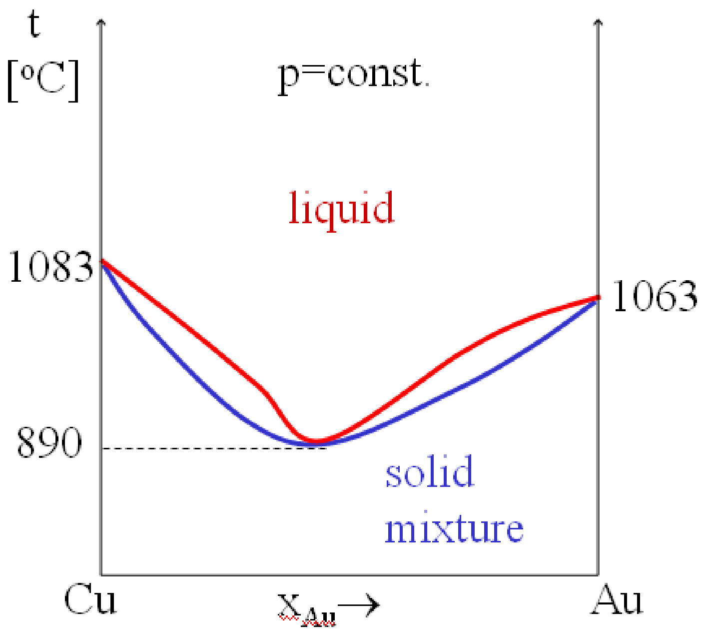


Fig. 3.33

2. Partial miscibility in solid state. Compare Fig.3.34 to Fig. 3.27!

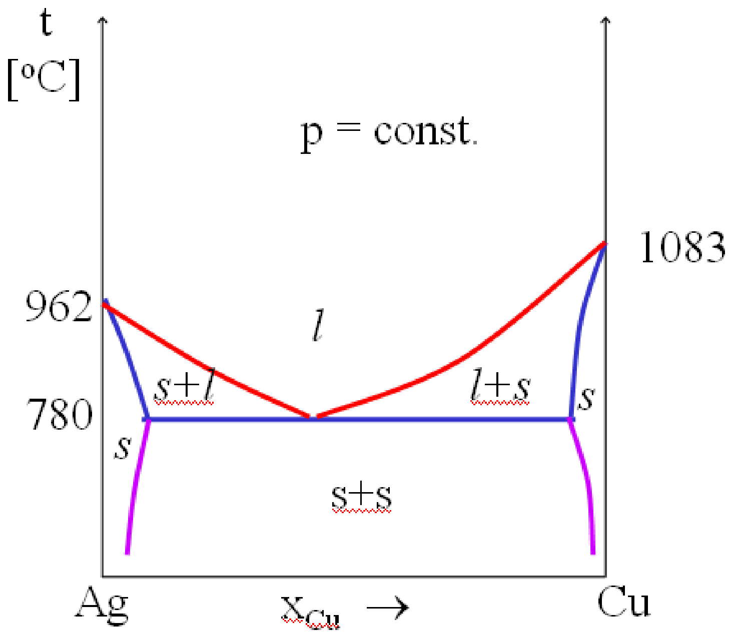


Fig. 3.34

Fig. 3.34 is complicate. One finds several different regions. Liquid state (*l*) is one phase, the solid one contains two. The two solid states (s) are small amount of copper is solved in silver (left hand side) and small amount of silver in copper (right hand side) both at lower temperatures. Similarly, at lower temperatures both solid phases exist at lower temperatures (s+s).

3. Complete immiscibility in solid state

See Fig. 3.35 and compare it with Fig. 3.29!

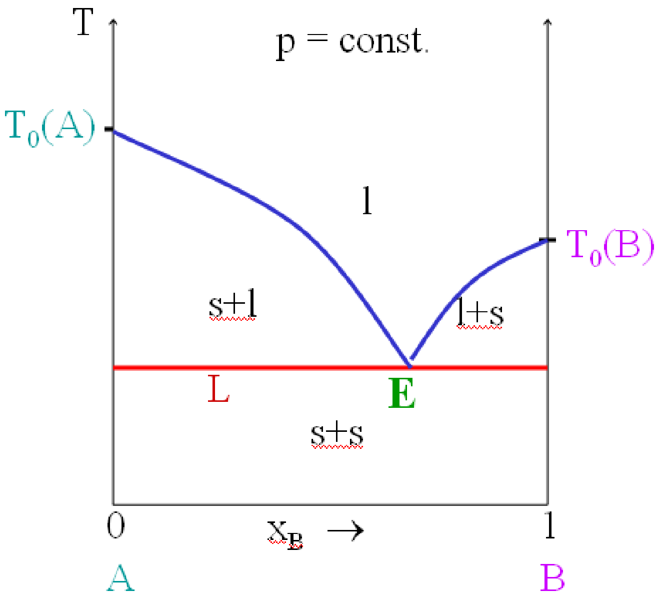


Fig. 3.35

The naphthalene-benzene system has such kind property.

The diagram has a characteristic point. At the **eutectic point E** (composition) the melting and the freezing temperature is equal. The melting point is independent of the composition, the curve is a horizontal line.

4. Formation of compounds

Case *A), Congruent melting* (Fig. 3.36). The figure has a shape like two figures of type 3.35 are present in it. The reason is the formation of a compound in solid state, in this case at mole fraction 0.5. This compound behaves like a new component.

This type of melting is called *congruent melting.* See detailed Fig. 3.37.

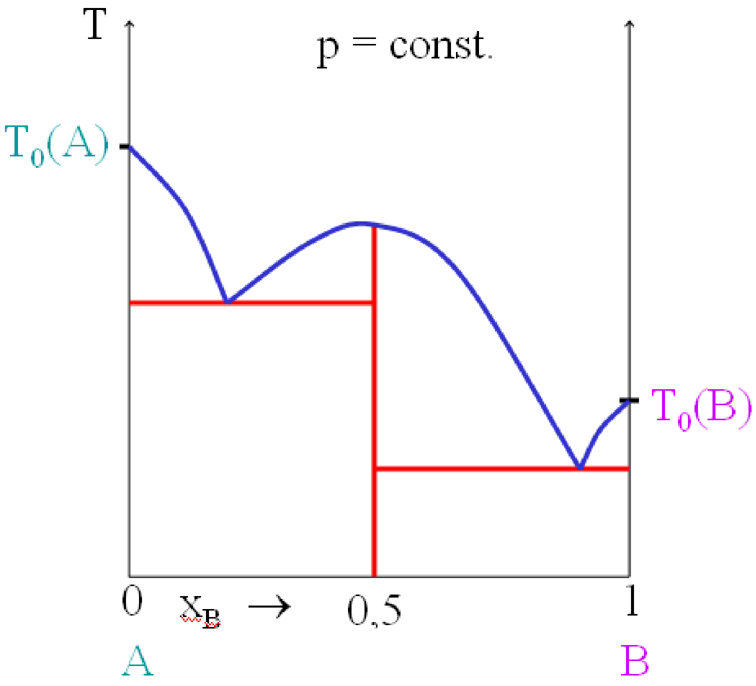


Fig. 3.36

Example is the phenol(A)-aniline (B)system, the compound C is formed in solid state (Fig. 3.37). The liquid state (melt) is homogeneous, one phase.

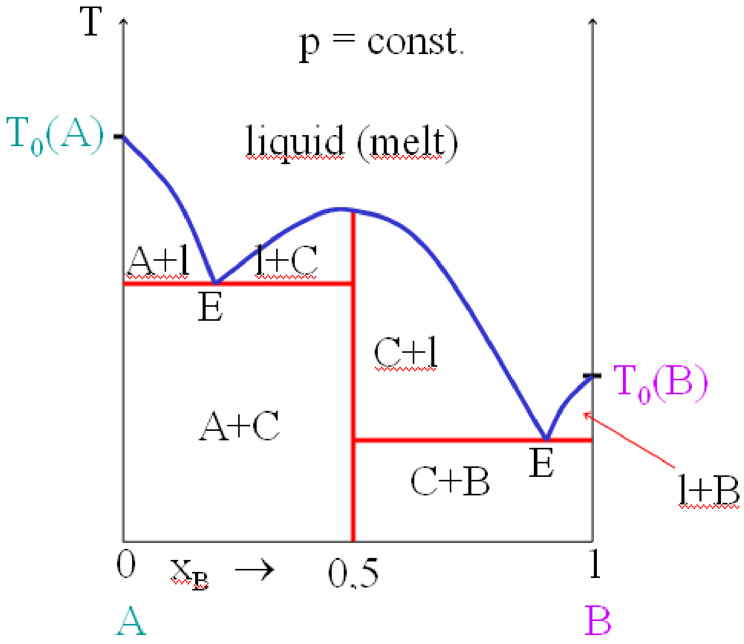


Fig. 3.37

Pay attention on the several regions! Always only two solid phases exist together, A+C or C+B.

Case B), *Incongruent melting*

During the melting a compound decomposes (Fig. 3.38).

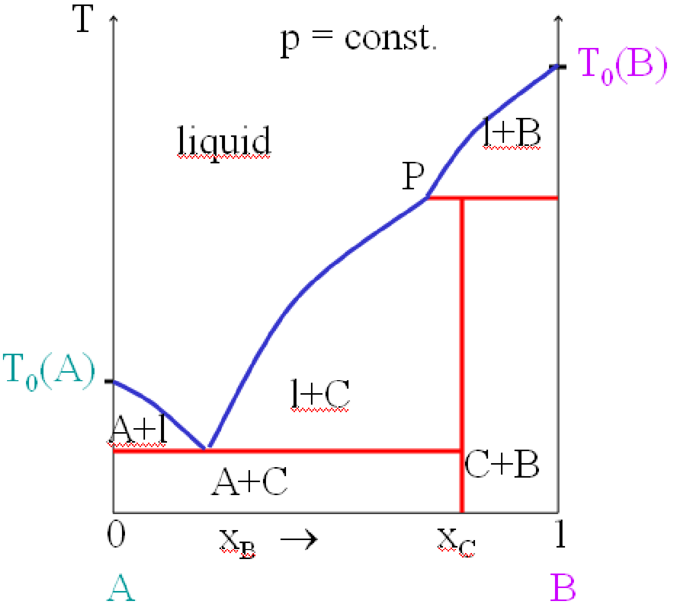


Fig. 3.38

In comparison to the congruent melting here the compound C formed and exists in solid state decomposes at the **peritectic point (P).** Over this temperature it does not exist neither in solid state.

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).

Example: *Na-K incongruent melting (Fig. 3.39)* Formation of a compound during the cooling (here:Na_2K). Cooling Na: formation: Na deposits,then fromation of Na2K (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.

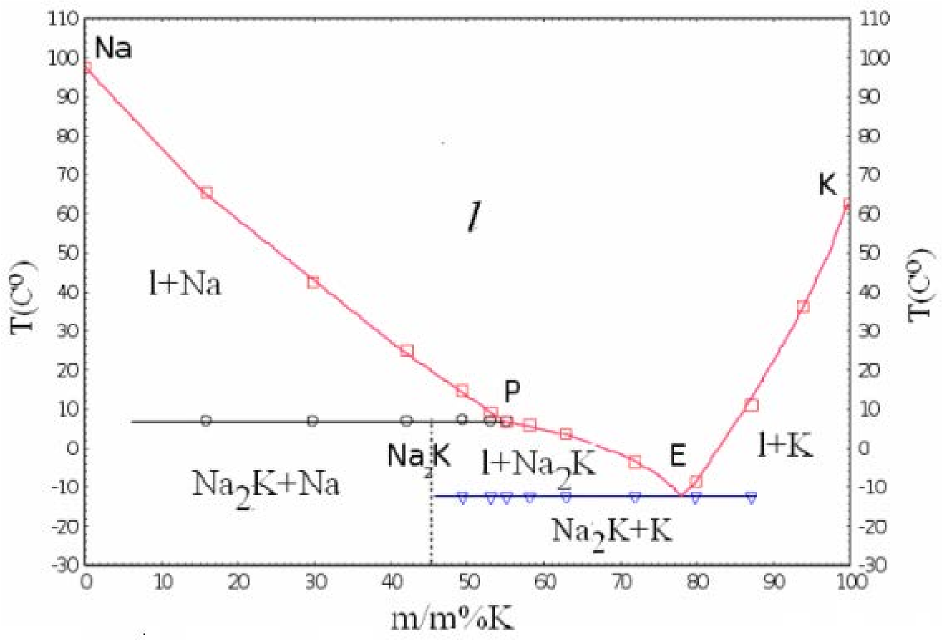

Na
K
l
l+Na
P
E
l+K
Na2K
l+Na2K
Na2K+Na
Na2K+K
T(C°)
m/m%K
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
0
10
20
30
40
50
60
70
80
90
100

Fig. 3.39

4. ADVANCED CHEMICAL THERMODYNAMICS

4.0 Colligative properties

Colligative means depending on quantity. The following phenomena are colligative:

Vapor pressure lowering: see subsection 4.1

Boiling point elevation: see subsection 4.1

Freezing point depression: see subsection 4.2

Osmotic pressure: see subsection 4.3

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

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). However, real mixtures show negative or positive deviations from it (Fig. 4.1).

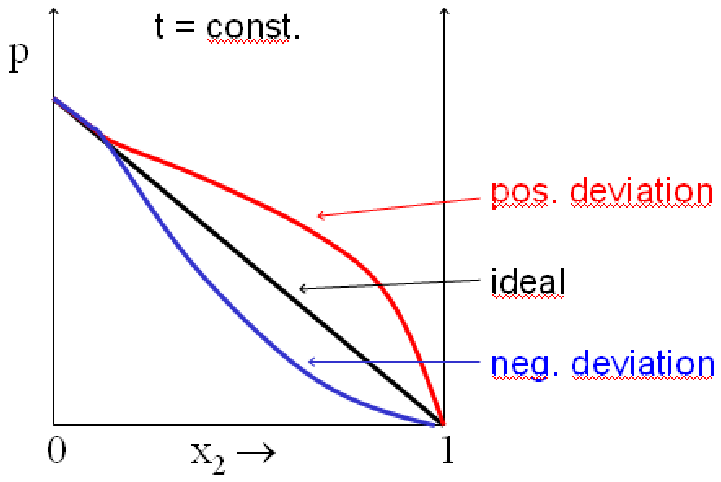


Fig. 4.1

We derive the **vapor pressure lowering** (if component 2 is non-volatile) expressing first the partial pressure of component 1:

$$p_1 = x_1 \cdot p_1^*$$

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

$$p_1 = p_1^* - x_2 \cdot p_1^*$$

Now we have the *relative vapor pressure lowering, see also (3.22)*

$$x_2 = \frac{p_1^* - p_1}{p_1^*} \tag{4.1}$$

Fig. 4.2 is the p-T diagram of the solvent (black) and the solution (red), see also Fig. 2.4, ΔT$_f$ denoteste freezing point lowering, ΔT$_b$ **boiling point elevation.**

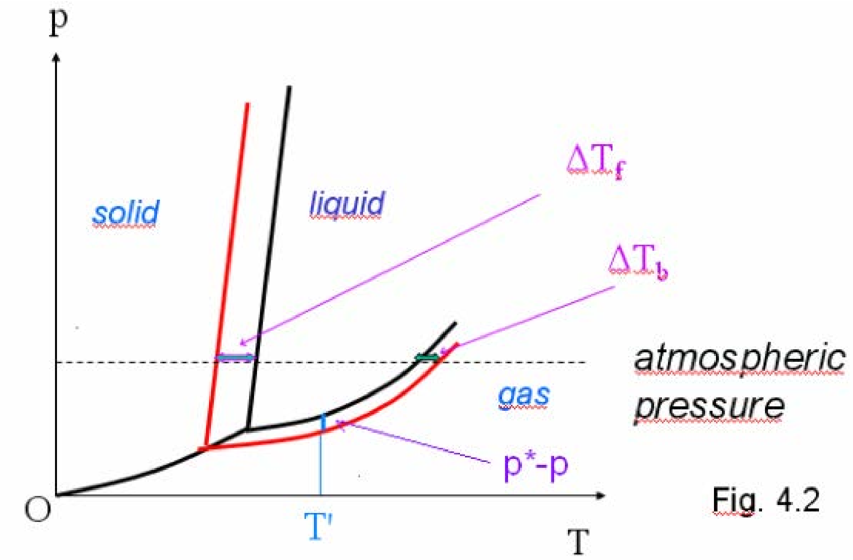


Fig. 4.2

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 vapor pressure lowering is observable.

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:

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

$$\mu_1^*(g) = \mu_1^*(l) + RT\,\mathbf{ln}\,x_1$$

See also equation (3.24)! The chemical potencials of the pure component are equal to the molar Gibbs functions (starred), in dilute solutions the activity coefficient of the solute is pratically one, the mole fraction is used.

So we can write

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

Since $G = H - TS$ and $dG = Vdp - SdT$,

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

also according to (2.21).

Now we derive the important **Gibbs-Hemholtz equation.** We differenciate G/T with respect to T, using the rule of fraction differenciation:

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

We apply (4.3) to our former equation (4.2) in form

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

Differenciating

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

Introducing the enthalpy like in (4.3)

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

The enthalpy difference is the heat of vaporization:

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

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:

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

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 ($x_2<<1$):

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

The terms containig higher power than 1 of x_2 are very small and negligible.

So

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

and

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

our result is at last

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

In dilute liquid solutions ***molality*** *(****m*** *= mol solute per kg solvent) or* ***concentration (molarity)*** *(****c*** *= mol solute per dm3 solution) are used (instead of mole fraction).*

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

Where m_2: molality of solute and M_1: molar mass of solvent. With this

$$\Delta T = \frac{RT_b^2 M_1}{\Delta H_{m1}(vap)} \cdot m_2 \tag{4.6}$$

Since the first multiplier on the right hand side depends on the parameters of the solvent only, it is regarded as constant, the *molal boiling point elevation:*

$$K_b = \frac{RT_b^2 M_1}{\Delta H_{m1}(vap)}$$

We can right

$$\Delta T = K_b \cdot m_2 \tag{4.7}$$

Examples (pay attention on the **molality** units!):

K_b(water) = 0.51 K·kg/mol

K_b(benzene) = 2.53 K·kg/mol

Applications: 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):

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

with 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)

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

Let $T_0 - T = \Delta T$ and $T \cdot T_0 \approx T_0^2$ we have from (4.9)

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

Rearranging (4.10) the *freezing point depression* is

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

Observe its similarity to (4.6)! Since $x_2 \approx m_2 \cdot M_1$, we have

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

The first multiplier on the right hand side contains solvent parameters only. This is the *molal freezing point depression*:

$$K_f = \frac{RT_0^2 M_1}{\Delta H_m(fus)}$$

So we can express the freezing point depression as

$$\Delta T = K_f \cdot m_2 \tag{4.13}$$

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

Pay attention on the very high K_f value of camphor. If the investigated compound is soluble in camphor, the determination of its molar weight is highly sensitive.

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.*** The reason: *the chemical potential of the solvent is greater in the more dilute solution.*

We discuss the case: *the „more dilute" solution may be a pure solvent,* the component 1.

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)****.*

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

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

or

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

The equation (4.14) is similar to the ideal gas law (1.27).

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

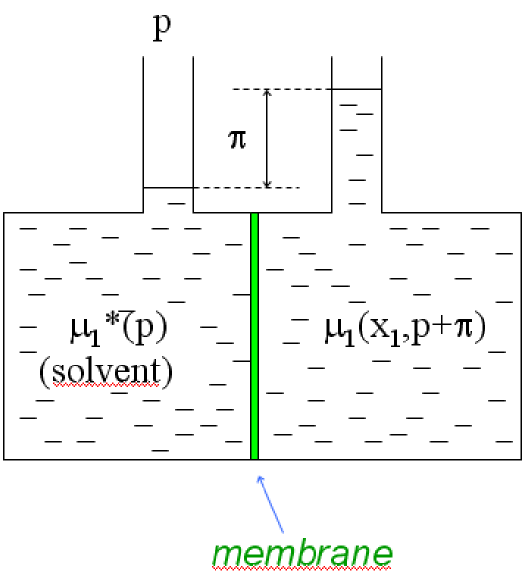


Fig. 4.3

Now we interpret Fig. 4.3. The condition for equilibrium is

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

The right hand side of (4.16) 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

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

Discussing this equation, the left hand side and the first term on the right and side is equal. The pressure dependence of μ_1 is negligible since

$\left(\frac{\partial G}{\partial p}\right)_T = V$ therefore the corresponding partial molar quantity is $\left(\frac{\partial \mu_1}{\partial p}\right)_T = V_1$ (see 2.19b).

The patial molar volume of the solent is paractically independent of the pressure. So the integral is only $V_1\pi$. We have now

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

Rearranged

$$\Delta\mu_1 = -\pi V_1 \left(x_1\right) \qquad (4.18)$$

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: $\Delta\mu_1(x_1) = RT\ln x_1$ (see 3.24).

For dilute solution as already mentioned $-\ln x_1 = -\ln(1-x_2) \approx x_2$, and we can write

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

Rearraging

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

Since $n_1 >> n_2$ and $V_1^* \cdot n_1 \approx V_1$

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

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

or

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

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**.*

The heat of mixing *(Q_s)*is equal to the enthalpy of mixing *(ΔH_{mix}):*

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

Dividing theat of mixing by the number of moles ($n=n_1+n_2$) we have the *molar heat of mixing:*

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

The *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 does not exist change of state. In **real solutions** Q_{ms} (also in case of change in phase, like the 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), Fig. 4.4.

In this case $Q_{ms}>0$. Endothermic process, see section 3.1:

in an *isothermal process* we must add heat*;*

in an *adiabatic process* the mixture cooles down.

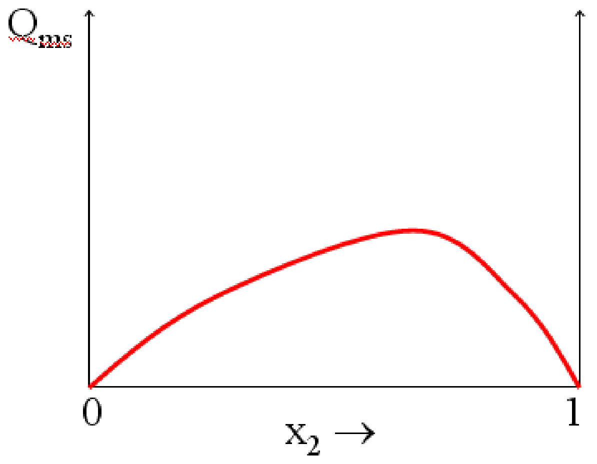


Fig. 4.4

Real solution with negative deviation (the attractive forces between unlike molecules are greater than those between the like molecules), Fig. 4.5.

In this case $Q_{ms} < 0$. *Exothermic process, see section 3.1.*

in an *isothermal process* we must distract heat;

in an *adiabatic process* the mixture warmes up.

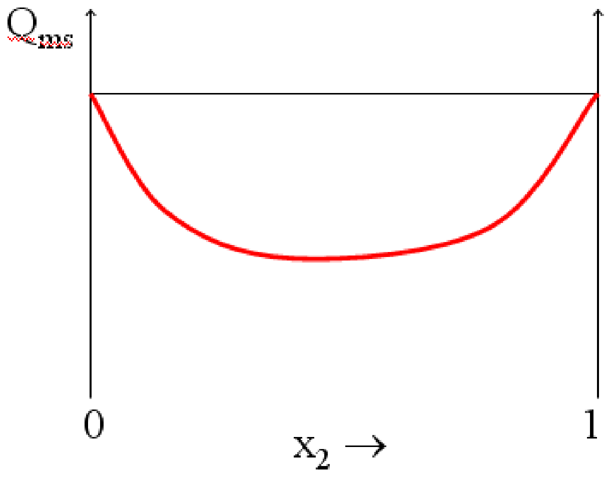


Fig. 4.5

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:*

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

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):

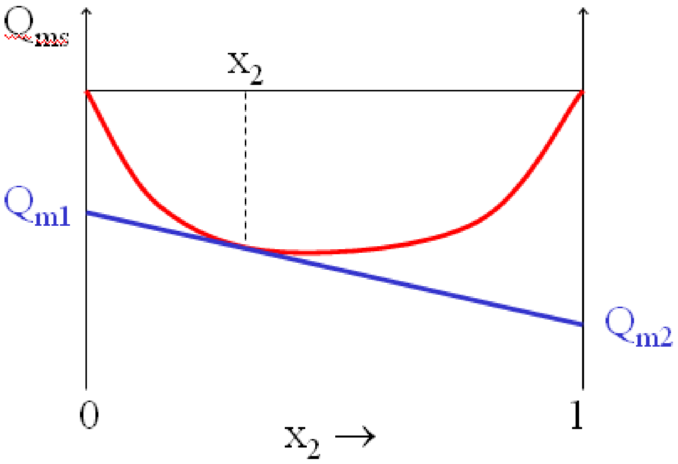


Fig. 4.6

Explanation to Fig. 4.6.

$$Q_s = H - (n_1 H^*_{m1} + n_2 H^*_{m2}) \qquad \textit{[Like (3.2)]}$$

Differentiating with respect to the amount:

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

According to the definition of of the differential heat of solution (4.22)

$$Q_{m1} = H_{m1} - H^*_{m1} \tag{4.23}$$

That means, 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 the solutions and temperatures. These diagrams can be used for the calculation of the heat effects. 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!

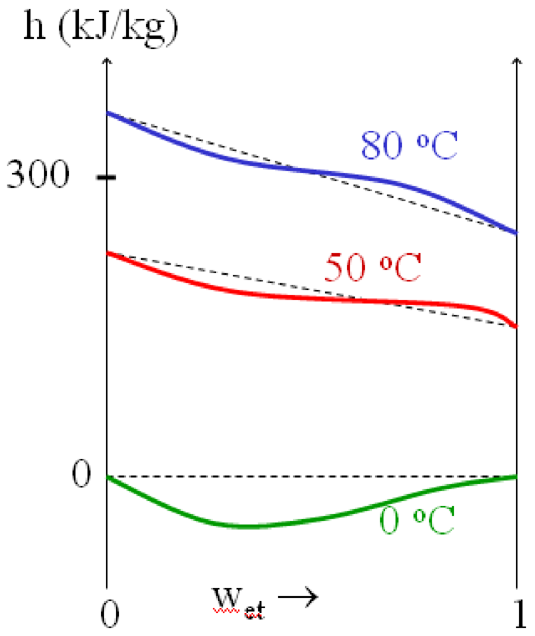


Fig. 4.7

Fig. 4.8 introduces the isothermal mole fraction depence of heat of solution of the dioxane-water system.

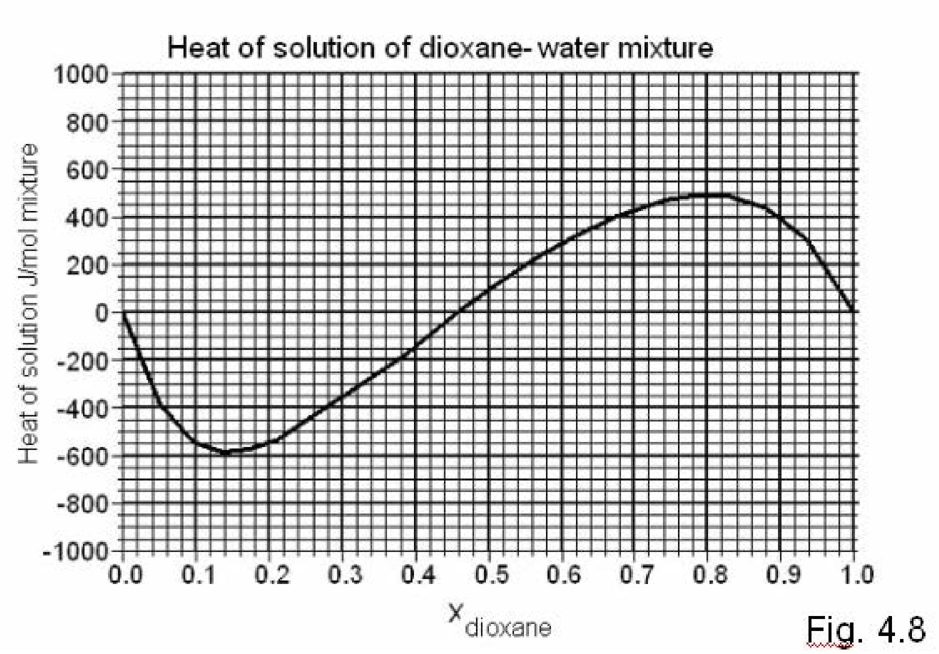


Fig. 4.8

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

$$Q_s = (m_1+m_2)h - (m_1h_1+m_2h_2) \tag{4.24}$$

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).

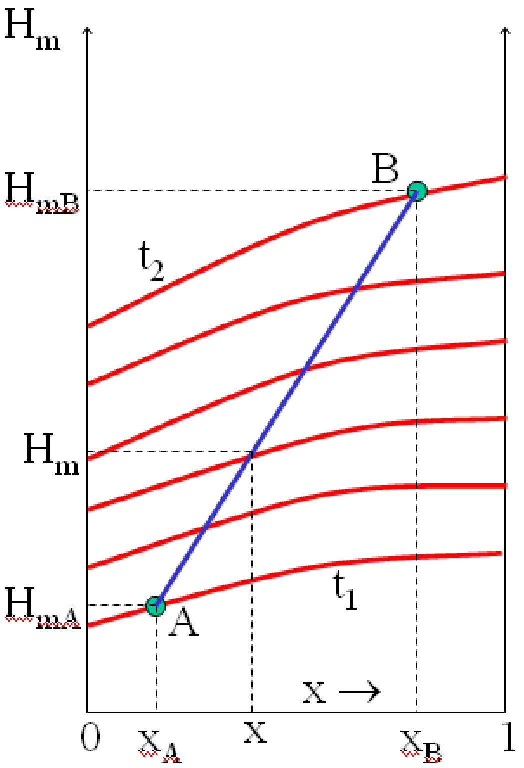


Fig. 4.9

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:

$$(n-n_B)x_A+n_Bx_B = nx \quad \text{and} \quad (n-n_B)H_{mA}+n_BH_{mB} = nH_m$$

Rearranging these equations:

$$n_B(x_B - x_A) = n(x - x_A) \text{ and } n_B(H_{mB}-H_{mA}) = n(H_m-H_{mA})$$

Dividing these equations by one another

$$\frac{H_{mB}-H_{mA}}{x_B-x_A} = \frac{H_m-H_{mA}}{x-x_A} \tag{4.25}$$

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 equation, like

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

4.5 Henry's law

In a very dilute solution every dissolved molecule is surrounded by solvent molecules (Fig. 4.10):

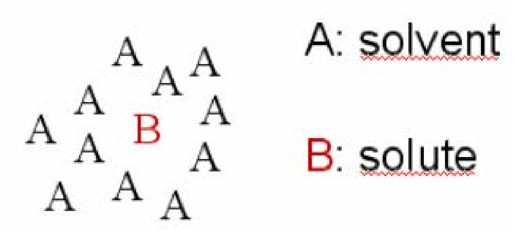


Fig. 4.10

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. Look at Fig 4.11 and observe deviations from the ideal behavior!

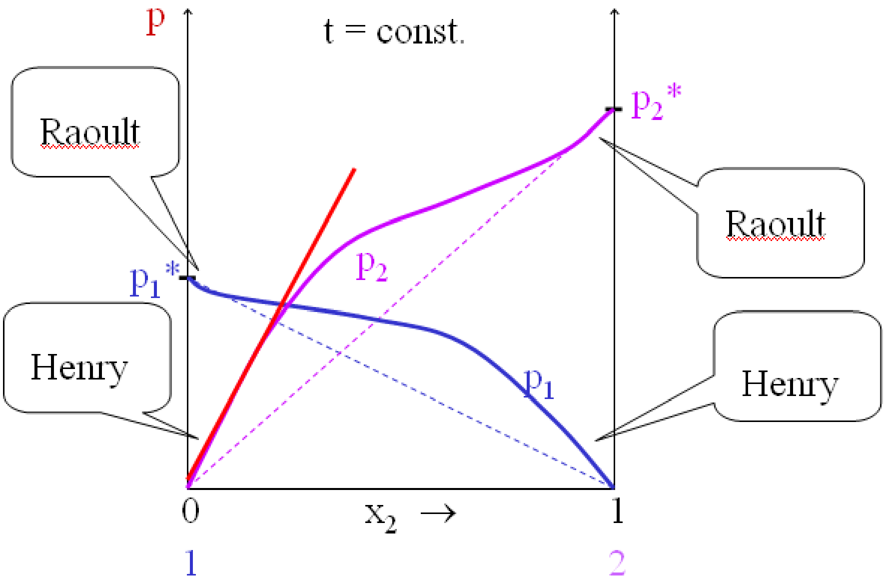


Fig. 4.11

Here component 2 is the solute on the left hand side of Fig. 4.11:

$$p_2 = k_H \cdot x_2 \tag{4.27}$$

k_H is the ***Henry constant.***

In the same range the Raoult´s law applies to the solvent (component 1):

$$p_1 = p_1^* \cdot x_1 \qquad \text{[like (3.18)]}$$

The two equations are similar. There is a difference in the constants. p_1* has an exact physical meaning (the vapor pressure of pure substance) while k_H does not have any exact meaning.

Summing up, 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 examples of the solubilty of some gases on Fig. 4.12!

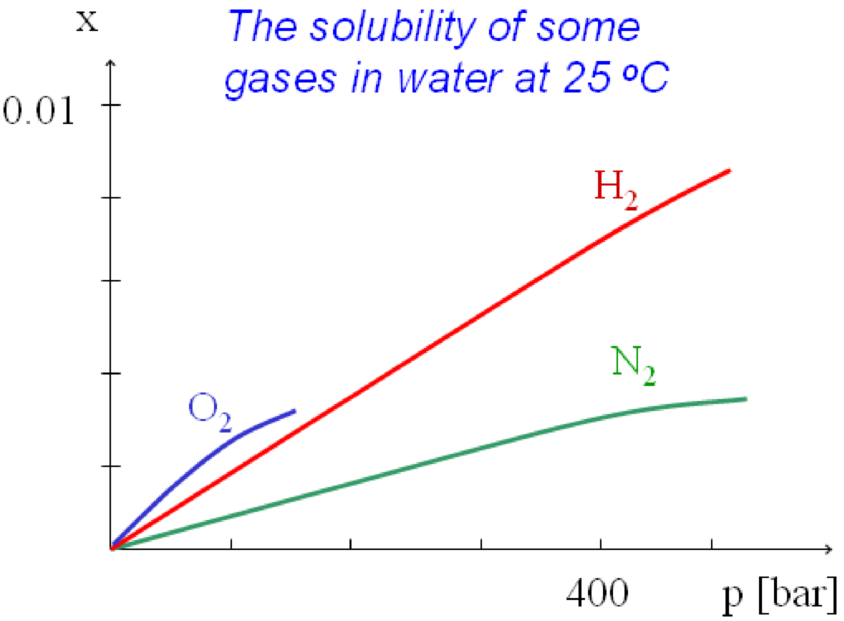


Fig. 4.12

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. See its applications below.

Solution of a gas *is a change of state: gas → liquid. It is usually an exothermic process.* The increasing temperature decreases the solubility.

***Increase of temperature**: the equilibrium is shifted towards the endothermic direction → desorption. The endothermic process works against the desorption, decreasing the temperature.*

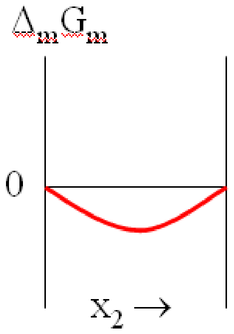
*The **solubility of gases** usually decreases with increasing the temperature.*

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 mean necessary the solubility (see Fig. 4.13d diagram, next figure).

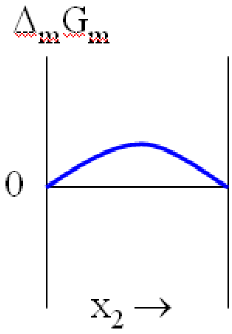
There exists another requirement: *the second derivative of the Gibbs free energy of mixing with respect to composition must be positive.*

Some examples of the dependence of molar Gibbs free energy as a function of mole fraction are presented in Fig. 4.13.



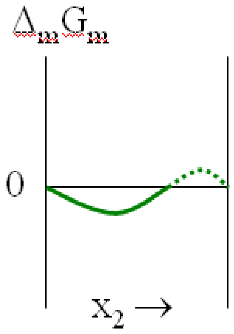
Complete miscibility

Fig. 4.13a



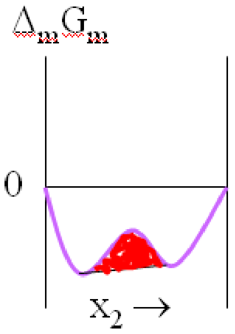
Complete immiscibility

Fig. 4.13b



Limited miscibility

Fig. 4.13c



Limited miscibility

Fig. 4.13d

Summing up, ***the conditions for stability are***

$$\Delta_{mix}G_m < 0 \tag{4.28}$$

and

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

Limited miscibility: see diagram 4.13d. Its critical part is in red. Follow the countour of this part from left to right! First thedirection of the tangent (the first derivative) is positive but ite absolute value decreases, then it is zero and have negative signwith increasing absolute value. The change of the forst derivative characterizes the second one. The second derivative increases, therefore in this mole fraction region the mixture is not stable (4.29), although according to (4.28) the mixibility is possible.

Look at Fig. 4.14! At the marked points the first derivative changes it sign from negative to positive, according to the requirements of (4.29).

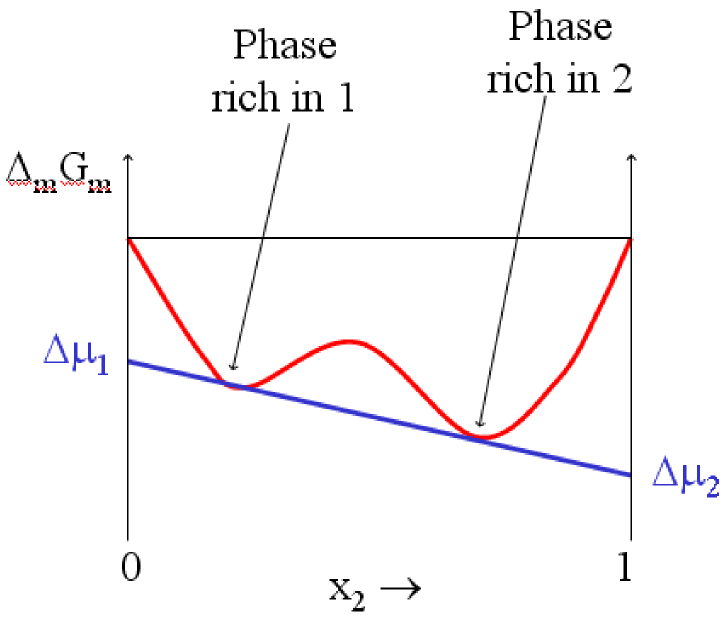


Fig. 4.14

Remember! The chemical potential is the partial molar Gibbs function.

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: $\Delta\mu_1$ 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 $\Delta\mu_2$.

Fig. 4.14: The common tangent of the two curves produces $\Delta\mu_1$ and $\Delta\mu$2 (method of intercepts, Fig. 3.7).

4.8 Liquid - liquid phase equilibria

The mutual solubility depends on temperature. In most cases the solubility increases with increasing temperature (thermal motion of molecules increases).

We can discribe the miscibility of liquids using the *thermodynamic definition:*

$$\Delta_{mix}G_m=\Delta_{mix}H_m-T\Delta_{mix}S_m<0$$

See subsection 3.8 and the definition of the definition of the Gibbs free energy of mixing (3.37).

We can understand the possibility of mixing at *molcular level*. The components of molecules can interact with some another. These may be associates between own ((like) of friend (unlike) molecules. There exist equilibria between the individual molecules and the associates. The strengths of theswe associates can determine the miscibility.

In some cases the miscibility of liquid components is limited. Three types exist:

Upper critical temperature of miscibility (Fig. 4.15),

Lower critical temperature of miscibility (Fig. 4.16),

Mixtures with both lower and upper critical temperatures of mixibitily (Fig. 4.17)

The backgrounds of the different behavior of the mixtures are the chemical properties of molecules and the interactions between the similar ("like") and different ("unlike") molecules, i.e. the equilibria (molecular description). Of course, also the entropy of mixing play role (thermodynamic description).

Upper (u) critical temperature (t_{uc}) of miscibility (Fig. 4.15)

In this case a weak complex is building between the molecules of one of the components at low temperature. So the interaction between the "like" molecules hinders the mixing. At higher temperatures this weak complex dissociates (the equilibrium shifts to the direction of the single molecules). So the mole fraction region of miscibility extends with temperature and at t_{uc} the miscibility will be complete. In case of our example, the n-hexane – nitrobenzene mixture, the nitrobenzene – nitrobenzene complex is building. Pay attention on the low t_{uc} temperature.

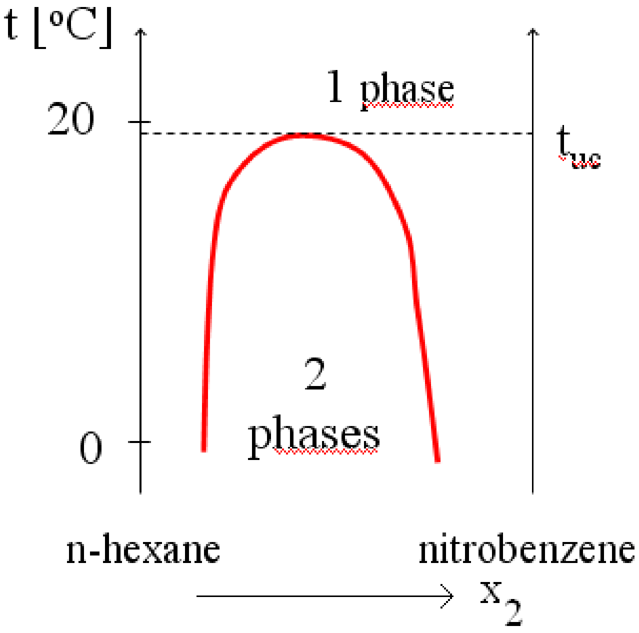


Fig. 4.15

Upper (l) critical temperature (t_{lc}) of miscibility (Fig. 4.16).

In this case the interaction between the molecules of the two components ("unlike" molecules) is stronger at lower temperatures than that between the "like" molecules. However, with increasing temperature the equilibria between the “unlike” molecules shifts to the individual molecules and the equilibria between the “like” molecules shift to their selfassociations, the two phases form stepwise from one phase. One can follow the shifts of the equilibria with the narrowing of mole fraction region of one phase. In our example, the trimethylamine – water system the trimethylamine molecules cannot associate with one another since the trimethyl group is too large. At higher temperatures the water-water association dominates over the trimethylamine - water one.

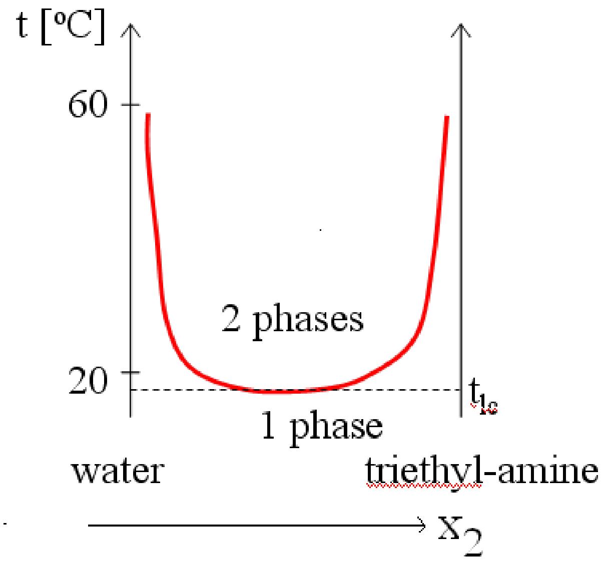


Fig. 4.16

Both lower and upper critical temperatures of mixibitily (Fig. 4.17)

This is a very special case. Namely, the equilibria formed at lower temperature shift to indicidual molecules and at higher temperature stepwise new equlibia forms and system consist again from one phase. Such kind systems are rare, the nicotine – water system is a well-known example.

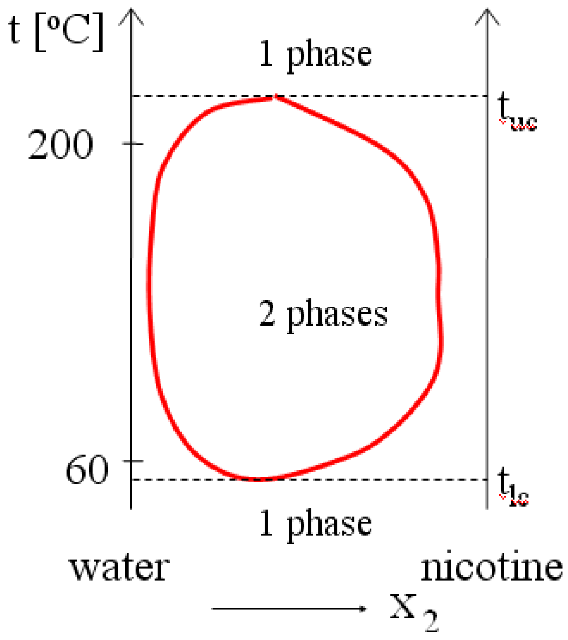


Fig. 4.17

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).

$$\mu_i^B = \mu_i^A \tag{4.30}$$

The chemical potential can be expressed as

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad \text{[see (3.25)]}$$

The activity can be expressed in terms of concentration:

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

In this case the standard chemical potential depends on the solvent, too:

$$\mu_i^{0B} + RT \ln a_i^B = \mu_i^{0A} + RT \ln a_i^A \tag{4.32}$$

Rearraging

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

The quantities on the right hand side depend on temperature only (i.e. they do not depend on composition). We can denote it by a constant

$$ln\frac{a_i^B}{a_i^A}=C$$

Therefore

$$\frac{a_i^B}{a_i^A}=K \tag{4.33}$$

The constant

is also constant. ***K*** is the *distribution constant* (depends on T only).

In case of *dilute solutions* (Henry range, see subsection 4.5) we can use concentrations instead of activities.

$$\frac{c_i^B}{c_i^A}=K_c \tag{4.34}$$

K_c is the *distribution constant in terms of concentration.*

Extraction: the processes based on distribution.

Calculation of the efficiency of extraction in a lab

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). The component for extraction is solved in volume V in concentration c_0, the solution is called mother liquor. The component concentration is after the first extraction step in volume V’ c'_1. The remaining concentration in V is c_1.

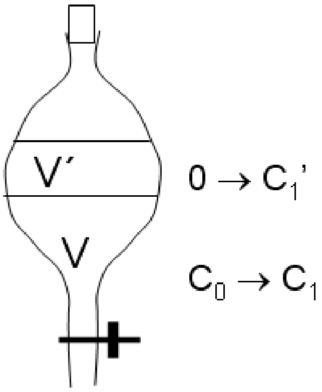


Fig. 4.18 .

Material balance for the component to be extracted:

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

The distribution constant is

$$K_c = \frac{c_1'}{c_1}$$

Based on the last equations

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

The constant

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

is called ***extraction coefficient***. With this

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

Repeating the extraction with the same amount of solvent*:*

and similarly

$$c_1 V = c_2 V + c_2' V'$$

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

After two steps

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

After *N* repetitions

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

4.10 Three component phase diagrams

For three component liquid systems (one phase) according to the phase rule (subsection 2.11)***: F = C – P + 2 = 5 – P,*** F maybe four. If p and T are kept constant, two degrees of freedom still remain: two mole fractions ($x_C = 1 - x_A - x_B$).

Triangular coordinates are used for phase diagrams of three component systems: an equilateral triangle is suitable for representing the whole mole fraction range. Each composition corresponds to one point. Look at Fig. 4.19! *Pay attention on the order of the components and the directions of the mole fractions!*

Fig. 4.19 is a simple example, how to find a point on this kind diagrams. Let $x_A = 0.2$ and $x_B = 0.5$!

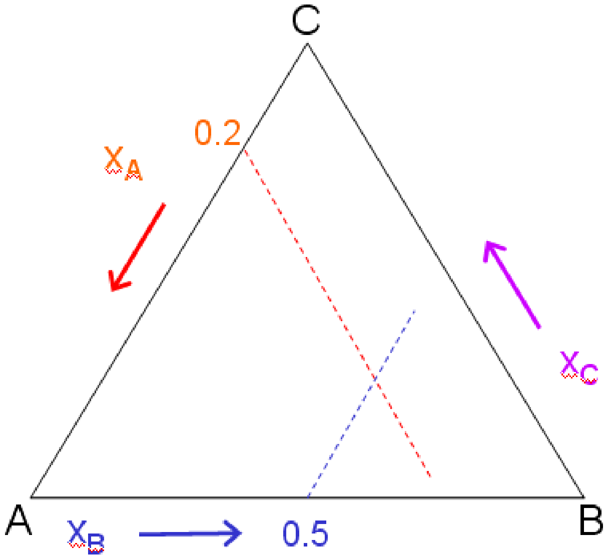


Fig. 4.19

How to use this diagram? We draw a parallel line with the line opposite the apex of the substance (orange line for x_A, blue for x_B). Their crossing point corresponds to the given composition. The value of x_C is given by a horizontal line through the crossing point.

Reading the composition on the triangle diagram

That means to find the composition of the mixture at a given P point of the triangle diagram. See Fig. 4.20!

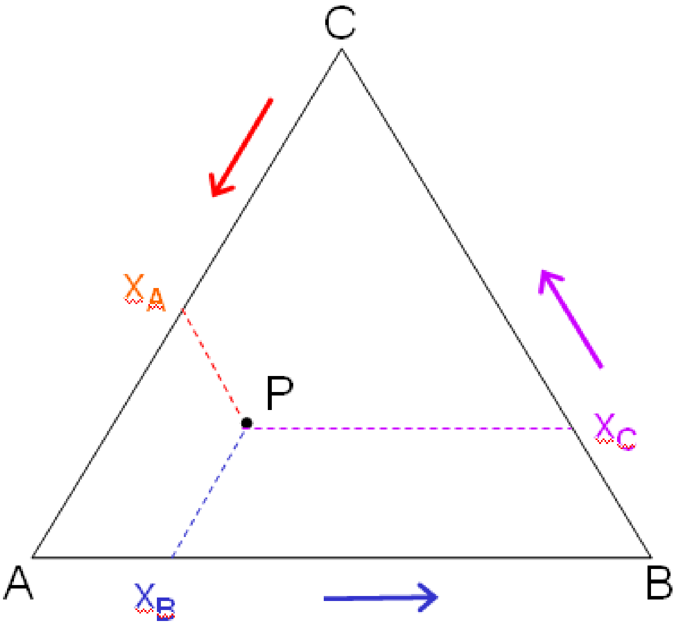


Fig. 4.20

For solving the task draw parallel lines with the lines opposite the apexes of the corresponding substances. The points where the broken lines cross the axes, gives the mole fractions.

A and B components are only partially miscible but both are completely miscible with C (Fig. 4.21)

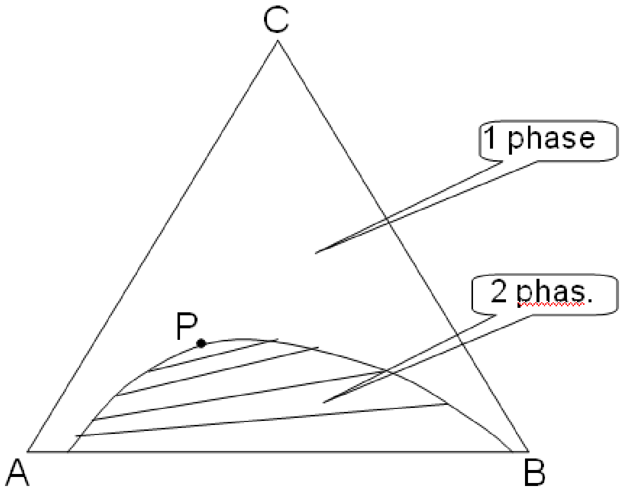


Fig. 4.21

The point P on Fig. 4.21 is the isothermal critical point of miscibility. curve on this diagram is the boundary of the two-phase reregion. The series of lines show the composition of the two phases there exist equilibrium. Along these curves both phases are present. Their ratio can calculated with the *level rule* (see subsection 3.9 and equation 3.43).

Miscibility in three component sytems

1. A and B are only partially miscible but both are completely miscible with C. The point P on Fig. 4.21 is the isothermal critical point of miscibility. The curve on this diagram is the boundary of the two-phase reregion. The series of lines show the composition of the two phases there exist equilibrium. Along these curves both phases are present. Their ratio can calculated with the *level rule* (see subsection 3.9 and equation 3.43).

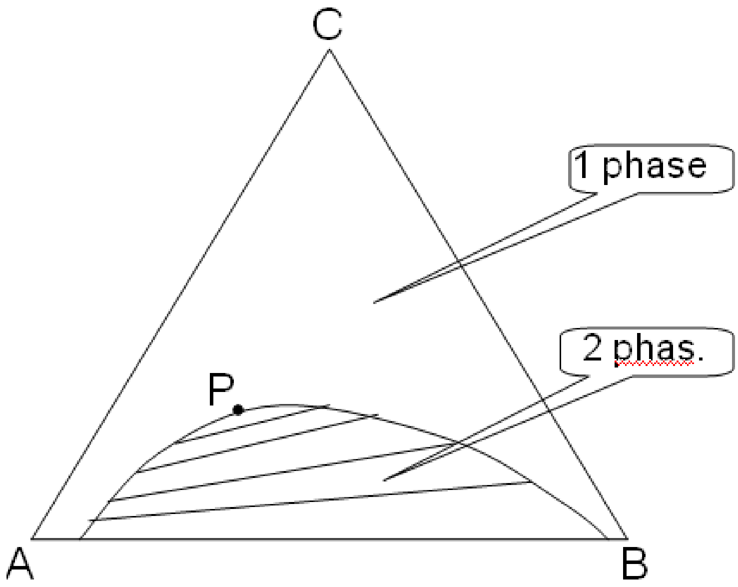


Fig. 4.21

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

Case a, see Fig. 4.22!

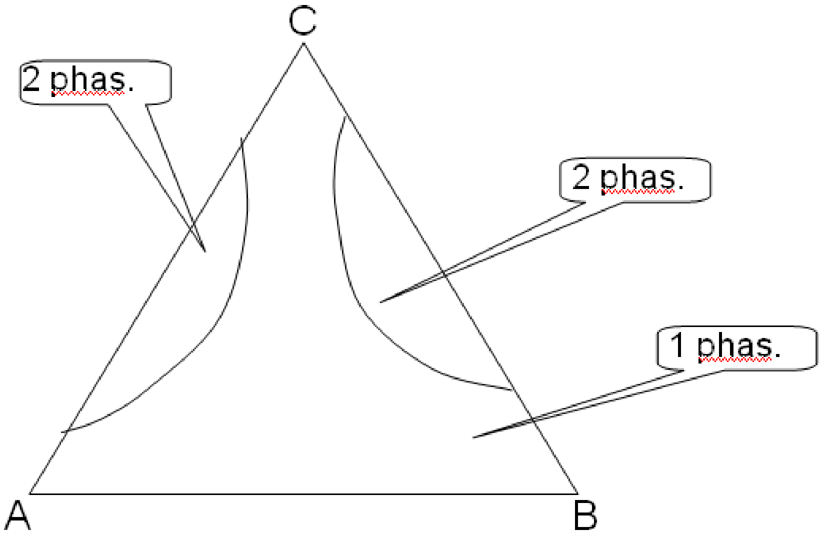


Fig. 4.22

Case b, see Fig. 4.23!

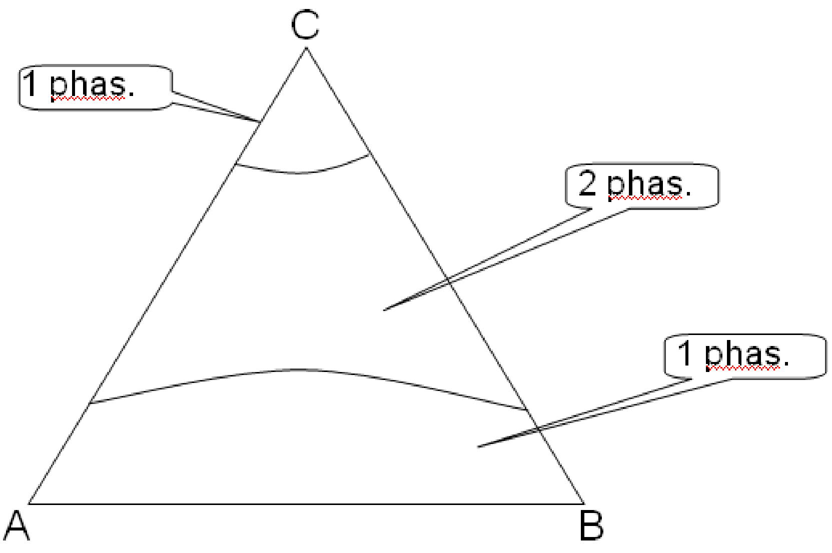


Fig. 4.23

Compare the relative positions of the one-phase abd two-phase areas on Figs. 4.22 and 4.23!

3. *All the three components are partially miscible with one of them*

Case a, see Fig. 4.24!

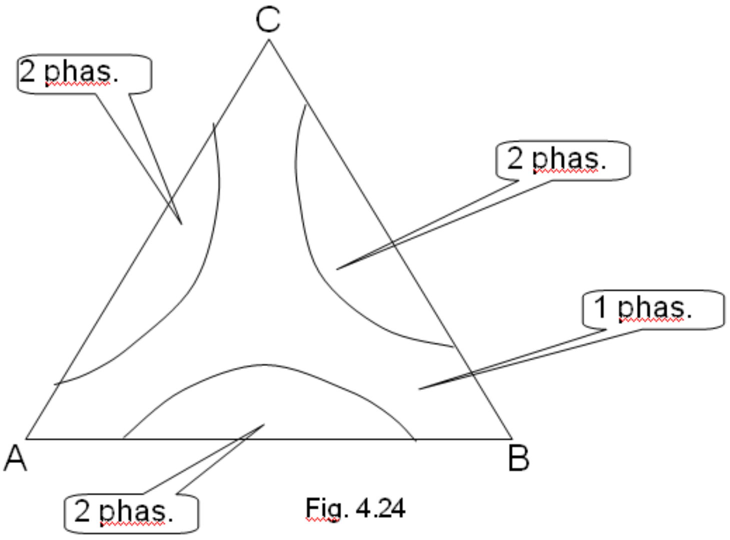


Fig. 4.24

Case b, see Fig. 4.25, where even three-phase regions exist!

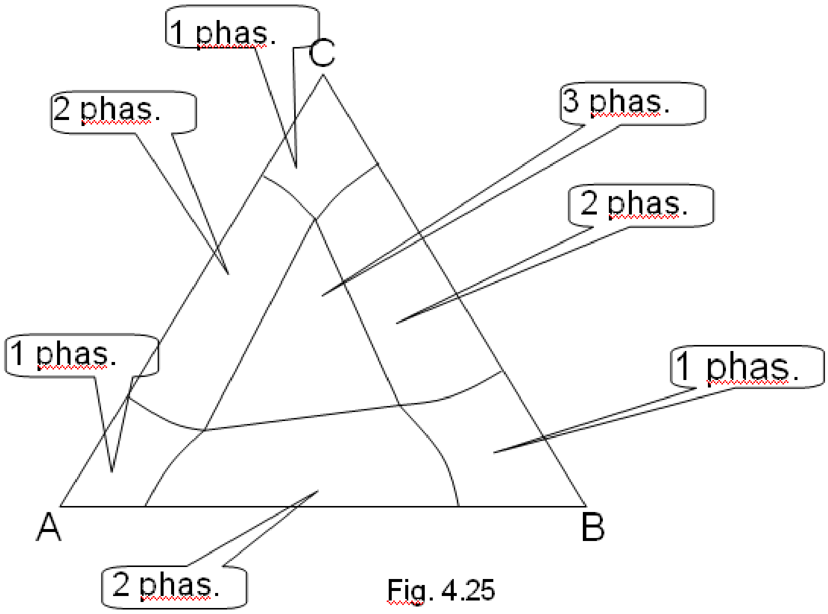


Fig. 4.25

4.11 Activities and standard states

Expression for the chemical potential is

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad \text{(like 3.25)}$$

Left hand side the first term is the standard activity, the second one is the dimensionless ***activity.***

1.) Ideal gases the activity is $a_i = \dfrac{p_i}{p^0}$ (partial pressure per standard pressure)

Standard state: standard pressure and ideal behavior.

2.) Real gases (see subsection 3.7). The activity for ideal gases is defined with ***f***ugacity (see equations 3.27 and 3.28):

$$a_i = \frac{f_i}{p^0} \tag{4.39}$$

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.

$$f_i = \varphi_i \cdot y_i \cdot p$$

Lewis – Randall rule: (4.40)

This is Dalton’s law (3.31) extended through the multiplier *fugacity constant* (φ).

Standard state:

p → 1 bar; $y_i \to 1$; $\varphi_i \to 1$; $f_i \to 1$ bar.

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

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

Compare to (3.27)!

3.) *Solutions1:* *the component is regarded as solvent.*

Raoult´s law is applied.

The chemical potential is like

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

Standard state defines the pure liquid at p^0 pressure with

$x_i \to 1;\ {}^x\gamma_i \to 1;\ a_i \to x_i$

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.

Case A: *concentration, c (mol/dm³) is applied.*

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

Here

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

${}^{c}\gamma_i$ is the *activity coefficient applied to concentration,* c^0 is the *unit concentration* (1 mol/dm^3). The *infinite dilution* means in this case:

$c_i \rightarrow 0$, ${}^{c}\gamma_i \rightarrow 1$ and $a_i \rightarrow c_i$.

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

The standard state is a state where the activity is 1, i.e. $c_i \rightarrow 1$ *mol/dm*^{3}*,* ${}^{c}\gamma_i \rightarrow 1$ *and* $a_i \rightarrow c_i/c^0$*. This is a hypotetical (fictive) state: unit concentration beside infinite diluted solution.*

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

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

where ${}^{m}\gamma_i$ is the activity coefficient applied to molality, m^0*is the 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 (Fir. 4.26).

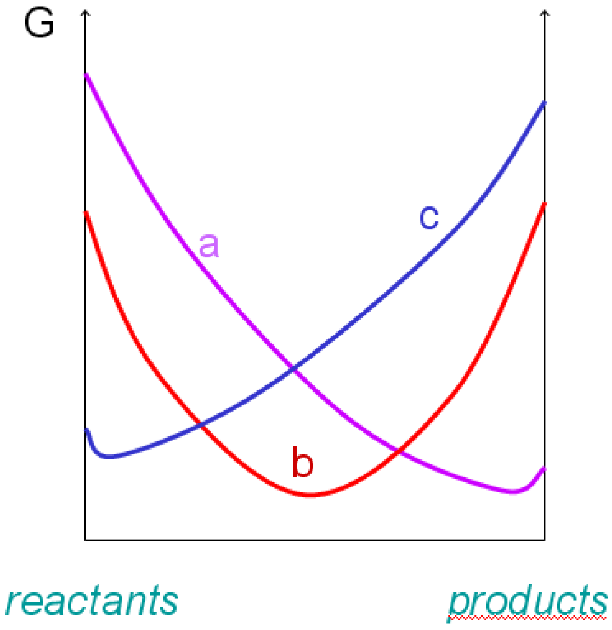


Fig. 4.26.

We can *conclude* from this figure:

Curve a: the equilibrium lies close to pure products. The reaction *„goes to completion”;*

Curve b: the equilibrium corresponds to case where *reactants and products present in similar proportions;*

Curve c: the equilibrium lies close to pure reactants. The reaction *„does not go”.*

Quantitative discussion

A: reactant, B: product

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

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

Three cases exist depending on composition:

Case 1: The reaction can go from left to right when G decreases:

$$\Sigma\nu_A\mu_A > \Sigma\nu_B\mu_B \tag{4.46}$$

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

Case 2: The reaction can go from right to left:

$$\Sigma\nu_A\mu_A < \Sigma\nu_B\mu_B \tag{4.47}$$

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

Case 3: The reaction stops at an equilibrium composition:

$$\Sigma\nu_A\mu_A = \Sigma\nu_B\mu_B \tag{4.48}$$

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

Rearraging (4.48), at equilibrium

$$\Sigma\nu_B\mu_B - \Sigma\nu_A\mu_A = 0 \tag{4.49}$$

Reaction Gibbs function is

$$\Delta_r\mu = \Delta_r G = 0 \tag{4.50}$$

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

Since

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

Subsituting (4.49) for the chamical potential

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

Rearranging

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

Applying the properties of the logarithm function

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

As result

$$\Delta_r\mu^0 = \Delta_r G^0 = -RT\ln K \tag{4.52}$$

The equilibrium constant is now

$$K = \frac{\Pi\, a_B^{\nu_B}}{\Pi\, a_A^{\nu_A}} \tag{4.53}$$

For example for

$$N_2 + 3H_2 = 2NH_3$$

the equilibrium constant is

$$K = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$$

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 the equilibrium constant (4.53).

For ***ideal gases*** $a_i = \frac{p_i}{p^0}$

Therefore

$$K = \frac{\Pi\left(\frac{p_B}{p^0}\right)^{\nu_B}}{\Pi\left(\frac{p_A}{p^0}\right)^{\nu_A}} \tag{4.54a}$$

From this

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

and so

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

where $\Delta\nu$ is the change in number of molecules and

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

Example for calculation of $\Delta\nu$

The reaction: $SO_2 + ½\, O_2 = SO_3$

$$\Delta\nu = 1 - 0.5 - 1 = -0.5$$

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

For ***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

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

Extending (4.55) for real gases:

$$K = K_\varphi \cdot K_p \cdot \left(p^0\right)^{-\Delta\nu}$$

(4.60)

K depends only on T, K_φ and K_p depend on p but their product deos not depend.

K is the „true" equlibrium constant.

Example: the pressure effect of the multipliers in (4.60) in the equlibrium constant of the gas reaction $1/2\ N_2 + 3/2\ H_2 = NH3$ at 450 ^{0}C (see table).

p(bar)	K_φ	$K_p \cdot 10^3$ $(\text{bar})^{-1}$	$K \cdot 10^3$
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

Strong effect of fugacity coefficient is observed at higher pressures only. Observe the decreasing of K_φ with pressure!

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.*

We 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 considering Dalton's law ($p_i = y_i \cdot p$):

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

where

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

and

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

The reaction quotient expressed in gas mole fractions:

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

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

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

In equilibrium gas reactions: increasing the pressure, the equilibrium shifts towards the direction where the number of molecules decreases, according to the *Le Chatelier's principle:* a system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect (subsection 4.6).

Reactions where the volume decreases at constant pressure ($\Delta\nu < 0$) are to be performed at high pressure. For example for performing the reaction $N_2 + 3H_2 = 2NH_3$ ($\Delta\nu = -2$) 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.

The 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.* The Gibbs function of the heterogeneos reaction is in this case

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

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

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

where

$$\mu_i^0(g) = G_{mi}^0(g)$$

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:

$$dG = Vdp - SdT \qquad \text{(see 2.19a)}$$

and

$$\left(\frac{\partial G_m}{\partial p}\right)_T = V_m \qquad \text{(see 2.19b)}$$

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

Example: C(graphite):

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

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:

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

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

We apply (4.54a) and at last

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

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:

$C(s) + CO2\,(g) = 2\,CO\,(g) \quad \Delta\nu=0$

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

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:

$$H_2(g) + I_2\,(s,g) = 2\,HI(g)$$

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

a) We regard the reaction as homogeneous gas reaction:

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

Since the vapor pressure of iodine (p_{I_2}) is constant, it can merged into K. It remains constant as long as solid iodine is present in the system.

b) We regard the reaction as heterogeneous. Therefore the iodine as solid component is left out from the equilibrium constant. K' differs from K!

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

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

Three cases will be discussed.

1. *The components are present in high concentrations*

(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:

$$a_i = {}^x\gamma_i \cdot x_i \tag{4.66a}$$

$$K = \frac{\Pi a_B^{\nu_B}}{\Pi a_A^{\nu_A}} \tag{4.66b}$$

$$K = K_\gamma \cdot K_x \tag{4.66c}$$

$$K_\gamma = \frac{\Pi^x \gamma_B^{\nu_B}}{\Pi^x \gamma_A^{\nu_A}} \tag{4.66d}$$

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:

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

Dichloro acetic acid + *pentene* = *ester*

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

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

$$R\,COOH + R'OH = RCOOR' + H_2O$$

$$K_x = \frac{x_{ester} \cdot x_{water}}{x_{acid} \cdot x_{alcohol}} \tag{4.67}$$

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:

$$\Delta_r \mu^0 = -RT \ln K$$

$$\mu_i = \mu_i^0 + RT \ln \frac{{}^c\gamma_i c_i}{c^0} \tag{4.68}$$

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

or

$$K = K_\gamma \cdot K_c \cdot \left(c^0\right)^{-\Delta\nu} \tag{4.69}$$

where

$$K_c = \frac{\Pi c_B^{\nu_B}}{\Pi c_A^{\nu_A}} \tag{4.70}$$

If ***molalities*** are used:

$$\mu_i = \mu_i^0 + RT\,ln\frac{{}^m\gamma_i m_i}{m^0} \tag{4.71}$$

and

$$K = K_\gamma \cdot K_m \cdot \left(m^0\right)^{-\Delta\nu} \tag{4.72}$$

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 $\mathbf{K_c}$ can be frequently used as equilibrium constant (it is assumed that the activity coefficients are independent of concentration, so $\mathbf{K_\gamma}$ is taken constant).

Dissociation equilibrium

$$KA = K^+ + A^- \tag{4.73}$$

Concentrations**:** $c_0(1-\alpha)$ $c_0 \cdot \alpha$ $c_0 \cdot \alpha$

K^+: cation, A^-: anion, c_0 : initial concentration, α : degree of dissociation, $0 \le \alpha \le 1$.

Applying (4.74) and the expressions for the concentrations of the components in the equilibrium

$$K_c = \frac{\alpha^2 c_0}{1-\alpha} \tag{4.74}$$

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).

Below we introduce some important applications.

1. *Autoprotolytic equilibrium of water*

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

The equilibrium constant is

$$K_w = a(H_3O^+)\cdot a(OH^-) \tag{4.75}$$

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.

The negative decimal logarithm of the activity of H_3O^+ is marked with (and called) pH and is used for the expression of the acidity:

$$pH = -lg\ a(H3O^+) \tag{4.76}$$

At 25 ^{0}C: $K_w \approx 10^{-14}$. If the activities of H_3O^+ and OH^- are equal, 10^{-7} mol/dm^3 at 25 ^{0}C, the solution is neutral, pH=7. Acidic solutions have pH values below 7,
basic solutions higher than 7.

2. *Ionization equilibrium of acids*

$$HA+H_2O = H_3O^+ + A^- \tag{4.77}$$

The *ionization constant* is

$$K_a = \frac{a(H_3O^+)\cdot a(A^-)}{a(HA)} \tag{4.78}$$

Its negative decimal logarithm is used:

$$pK_a = -\,lgK_a \tag{4.79}$$

pKa 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.

3. *Ionization equilibrium of bases*

Ionization of bases:

$$B+H_2O = BH^+ + OH^- \tag{4.80}$$

The dissociation constant is

$$K_b = \frac{a(BH^+)\cdot a(OH^-)}{a(B)} \tag{4.81}$$

The negative decimal logarithm is used:

$$pK_b = -\,lgK_b \tag{4.82}$$

K_a is also frequently used for bases, stronger basis - higher pK_a, it is for CH_3NH_2 10.64, for NH_4OH 9.23. The corresponding equilibrium is

$$BH^+ + H_2O = B + H_3O^+ \tag{4.83}$$

The dissociation constant

$$K_a = \frac{a(H_3O^+)\cdot a(B)}{a(BH^+)} \tag{4.84}$$

The product of the two constants:

$$K_a \cdot K_b = K_w \tag{4.85}$$

So *for bases* at 25 ^{0}C

$$pK_a = 14 - pK_b$$

Therefore their pKa values are higher then 7 (see the mentioned examples).

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:

$$\Delta_r G^0 = -RT \ln K \qquad \text{(see 4.52)}$$

$$\ln K = -\frac{1}{R} \cdot \frac{\Delta_r G^0}{T}$$

Deriving lnK with respect to temperature

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

Using the derivation of ratios

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

The result is the Gibbs-Helmholtz equation (see equation 3.52 and before).

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

van´t Hoff equation for the temperature dependence of the equlibrium constant. (d-s can be used instead of the sign of partial derivation because K depends on T only):

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2} \qquad (4.86)$$

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. With increasing temperaure the right hand side decreases. So dlnK/dT and so also lnK decreases with increasing temperature. Since K is the denominator on the left hand side, *K increases with increasing temperature* (see Fig. 4.27).

In case of *exothermic reactions* ($\Delta_r H^0 < 0$) K decreases (but lnK increases!) with increasing temperature (see Fig. 4.27).

We can undestand these results with *Le Chatelier's principle* (see also subsection 4.6): 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:

$$\ln K = -\frac{\Delta_r H^0}{RT} + const. \qquad (4.87)$$

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.

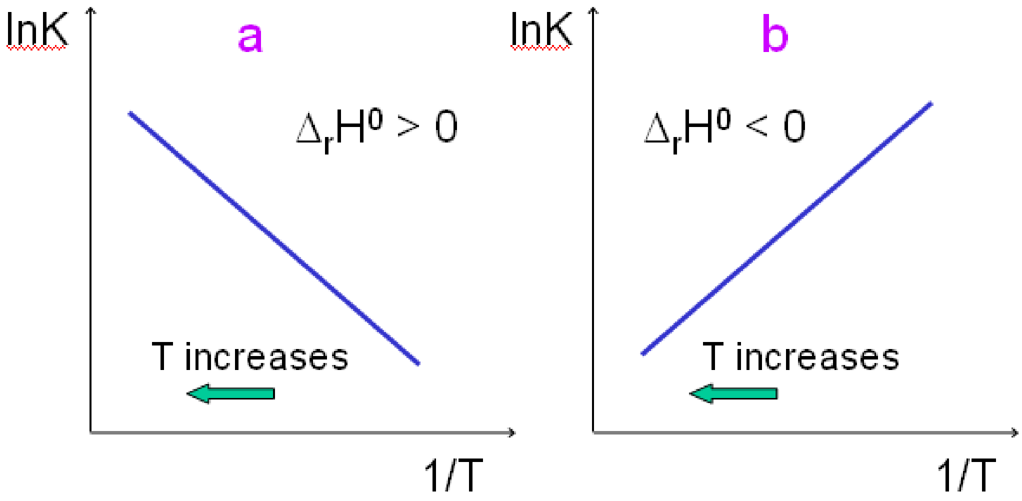

lnK
a
$\Delta_r H^0 > 0$
T increases
1/T
lnK
b
$\Delta_r H^0 < 0$
T increases
1/T

Fig. 4.27