BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

DEPARTMENT OF PHYSICAL CHEMISTRY AND MATERIAL SCIENCE

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PHYSICAL CHEMISTRY 1.

Compendium and problem book

BUDAPEST, 2013

1. FUNDAMENTALS OF THERMODYNAMICS

PHYSICAL CHEMISTRY
studied the changes in chemicals systems applying physical methods.

SYSTEM is the part of the world which we have a special interest in.
Chemical system: ensemble of atoms and molecules.
They may be investigated form:

- *phenomenological* view, i.e., one regards the system as continuous material;
- *particle view*, the system is regarded as ensemble of discrete particles.

THERMODYNAMICS
Phenomenological method, it is the quantitative description of chemical and physical processes, through the study of the energy transitions during these processes.
Two types of energy changes are distinguished in these processes::

- *work* (W) , the system works (its energy decreases), or an external system works on it. (its energy increases);
- *heat (Q)* transport to the environment (it decreases) or receiving from it (it increases).

ENERGY
Working ability of the system.

WORK
Physical definition:

$$W = \int \mathbf{F}.d\mathbf{r} \qquad (1)$$

F: force, d**r**: displacement
Result: The result of the work maybe visible as change in position or form (expansion work, deformation work), or invisible internal change in the system energy (electric, magnetic, atomic, molecular). The *expansion work* has stressed importance in thermodynamics

$$W = -\int pdV \qquad (2)$$

p is the pressure (more precisely, the external pressure that can be substituted with the pressure of the system if the change is reversible), V is the volume. The system works if its volume increases, that means, its energy decreases.. The works, other than expansion works are called *useful (or other) works.*

HEAT
If the system receives (adsorbs) or emits energy, than this change in energy causes change in phase, in temperature, or produces chemical reaction.

SYSTEM
The investigated part of the world we are interested in. A system is *open*, if mass transfer is possible trough its boundaries. If neither energy nor mass transport is possible through the boundaries, the system is *isolated.* If mass transport is not but energy one is possible through the boundaries, the system is *closed.* If heat transport is possible trough the *walls* of the system, the system is d*iathermi*c, otherwise *adiabatic*. The wall is the physical boundary of the system.

system	mass transfer	heat transfer

open	+	
isolated	-	-
closed	-	+
diathermic		through walls: +
adiabatic		through walls: -

PROCESS

It should be a chemical reaction or a physical change in state of the system. If the process products heat (the energy of the system decreases) it is called exothermal, otherwise, if it adsorbs heat (the system energy increases), it is an endothermic process.

INTERNAL ENERGY

It is the sum of the kinetic and potential energy of all particles (atoms, molecules) of the system. The thermodynamics studies and describes their changes during the processes (with phenomenological tools):

$$\Delta U = W + Q \tag{3}$$

This is *the first low of thermodynamics*, expressing the law of the energy conservation. The internal energy, the total energy of the system can be expressed formally as the full work and heat investigated in to the system:

$$U = W + Q \tag{4}$$

PHYSICOCHEMICAL PROPERTIES

A physicochemical property is *extensive*, if its quantity depends on the extent of the system (like energy, mass or volume) and is additive, and it is *intensive*, if it does not depend on the extent of the system and is not additive (temperature, pressure, concentration)

STATE PARAMETER

These are the physical properties of the system (continuum) that are measurable direct and describe the physical state of the system: pressure, temperature, volume and composition.

STATE FUNCTION

A function, that describes the dependence of the physical quantities on the state parameters, (internal energy, enthalpy, entropy, see below). Its value depends during the process only on the initial and final states of the system and is independent of the path.

PATH FUNCTION

A function describing the dependence of the physical quantity on the state parameters but depends on the path of the process (work, heat).

EQUILIBRIUM

The *thermodynamic equilibrium* is a *state* of the system where macroscopic processes do not take place, the system parameters do not change in time. If the system is in a non-equilibrium state the system tends to come into an equilibrium state. Meta-stabile state: the system is not in a minimal energy state, energy is necessary for crossing an energy barrier ("frozen" system).

REVERSIBILITY

A *reversible* change is one that can be reversed by an infinitesimal 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.

EQUATION OF STATE

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

ENTHALPY

Subtracting the expansion work from the internal energy for processes proceeding at constant pressure the result is the sum of the heat and the useful work, the change in *enthalpy*. The enthalpy is a state function. Thermodynamics applies this function for the description of processes at constant pressure. The change of the enthalpy during a process is

$$\Delta H = \Delta U + p.\Delta V = Q_p \tag{5}$$

is equal to heat at transfer at constant pressure Q_p, if there is not work of or on the system. The definition of the enthalpy is

$$H = U + p.V \tag{6}$$

IDEAL GAS

It follows the equation of state

$$pV = nRT \tag{7}$$

R is the gas constant, 8.313 J mol^{-1} K^{-1}, T is the absolute temperature, n is the quantity of the gas in mols.

PROCESS TYPES (equations for ideal gas)

Isothermal: the temperature is constant.

$$\Delta U = 0 \text{ and } \Delta H = 0 \tag{8}$$

Isobaric: the pressure is constant

$$Q = \Delta H \quad W = -p.\Delta V \tag{9}$$

Isochor: the volume is constant

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

(10)

Adiabatic: there is not heat transfer across the system walls

$$Q = 0 \text{ i.e.} \tag{11}$$

$$W = \Delta U \tag{12}$$

Change in phase:

$$\Delta T = 0 \qquad \Delta p = 0 \tag{13}$$

$$Q = \Delta H \qquad W = -p.\Delta V \tag{14}$$

HEAT CAPACITY

It is the energy necessary for the unit change of the temperature of the material.

If it refers to unit mass, it is the *specific heat capacity* (C), for unit mol, it is called *molar heat capacity* (C_m). The value of heat capacity depends on the conditions of measurement. The change in temperature m ay be proceed at constant pressure (C_p, or C_{mp}, resp.) or at constant volume (C_V or C_{mV}, resp.).

Since both U and H are state functions, for *arbitrary* process

$$\Delta U = n \int C_{mV} dT \tag{15}$$

$$\Delta H = n \int C_{mp} dT \tag{16}$$

For *isochor* process

$$Q = \Delta U = n \int C_{mV} dT \tag{17}$$

For *isobaric* process

$$Q = \Delta H = n \int C_{mp} dT \tag{18}$$

For *adiabatic* process

$$Q = 0 \tag{19}$$

For ***ideal gas as working material*** *a*ccording to (7)

For *isothermal* process

$$\Delta U = \Delta H = 0 \tag{20}$$

$$W = -Q = n.R.T\, ln\left(\frac{p_2}{p_1}\right) = -n.R.T.ln\left(\frac{V_2}{V_1}\right) \tag{21}$$

For *isobaric process*

$$W = -n.R.(T_2 - T_1) \tag{22}$$

For *isochor* process

$$W = 0 \qquad Q = \Delta U = n \int C_{mV} dT \tag{23}$$

For *adiabatic process*

$$W = \Delta U = n.\int C_{mV} dT \qquad Q=0 \tag{24}$$

$$p.V^{\kappa} = \text{const.} \quad T.p^{\frac{1-\kappa}{\kappa}} = \text{const.} \quad TV^{\kappa-1} = \text{const.} \tag{25}$$

$$\text{with } \kappa = \frac{C_{mp}}{C_{mV}} \tag{26}$$

Theoretical values, although good approaches for ideal gases:

$$C_{mp} - C_{mV} = R \tag{27}$$

For one atomic ideal gas

$$C_{mV} = \frac{3}{2} R \tag{28}$$

For two atomic ideal gas:

$$C_{mV} = \frac{5}{2} R \tag{29}$$

One $\frac{1}{2}R$ of C_{mV} belongs to each degree of freedom of the molecule (ideal case). An N-atomic molecule has 3N degrees of freedom (3 coordinates for each atom). Three of them are rotations (rotation around the three perpendicular axes in space), for linear molecules only two; three of them are translations (movements in the three directions of space). All other degrees of freedom are vibrations of the molecule.

PROBLEMS
(You can use the expressions of Table 1)

Please, pay attention! The following marks are used:
"." or "*" for multiplication, "," for decimalization

E1. What is the work product, ΔH and ΔU, if 1 mol ideal gas is expanded in a piston to fivefold? During the expansion the temperature is constant, 25 °C.

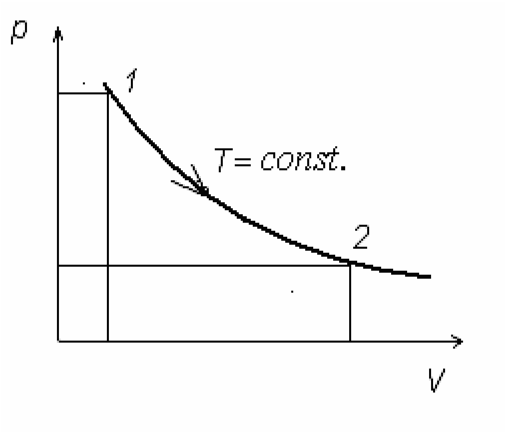
Ideal gas, isothermal, process, consequently ΔU=0, i.e. W=-Q. Ideal gas, so ΔH=0. The work is

$$W = -Q = -nRT.ln\left(\frac{V_2}{V_1}\right).$$

The number of mols, the temperature and the volume ratio is given, R=8,314 J $mol^{-1}K^{-1}$,

$$W = -Q = -1.8{,}314.298.ln(5) = -3987{,}5\,J$$

The flowchart of the process in p-V diagram is (the T=constant curve is a hyperbola since $p = \frac{nRT}{V}$)



E2. What is the work product if 5 mol ideal gas is heated from 0 °C to 500 °C at 10^5 Pa constant pressure?

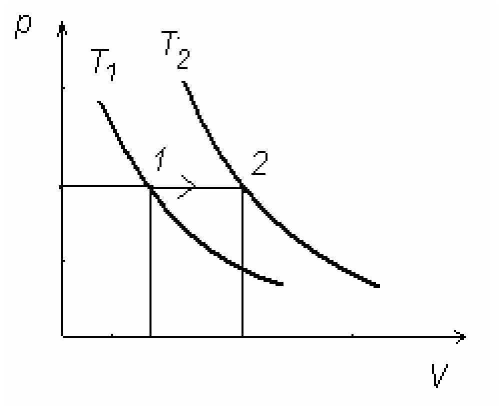
Ideal , isobaric process, i.e. Q=ΔH and

$$W = -n.R(T_2 - T_1)$$

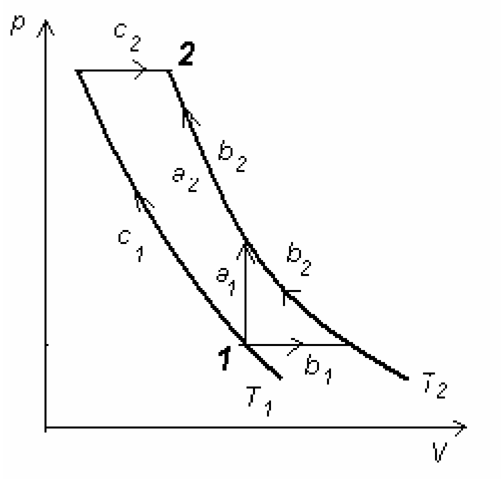
Therefore

$$W = -5.8{,}314(798 - 298) = -20785J$$

The flowchart of the process in p-V diagram is


p
T1
T2
1
2
V

E3. The temperature of 1 mol argon (ideal gas) is 25 °C and its pressure is 10^5 Pa. It will be heated to 100 °C and its pressure will be increased to 5.10^5 Pa. What is the work (W), the heat (Q), ΔH and ΔU as well, along the following three paths (see figure, a,b,c), if friction does not exist.



T_1=25+273=298K, T_2=100+273=373K.

a.)the system is heated at constant volume from 25 °C to 100 °C, then the pressure is increased in a cylindrical piston to 5.10^5 Pa at constant temperature..

a1. Isochor process, $W_{a1}=0$. $\Delta V_{a1}=0$.

One-atomic ideal gas, $C_{mV}=3/2$ R

$$Q = \Delta U = n\int C_{mV} dT \text{ , here } Q = \Delta U = n\int \frac{3}{2} R.dT = \frac{3}{2} n.R(T_2 - T_1)\text{, i.e.}$$

$$Q_{a1} = \Delta U_{a1} = \frac{3}{2} n.R(T_2 - T_1) = 1{,}5.1.8{,}314.(373 - 298) = 936J$$

$$\Delta H = n\int C_{mp} dT \qquad itt \qquad \Delta H_{a1} = n\int \frac{5}{2} RdT = \frac{5}{2} n.R(T_2 - T_1)\text{, i.e.}$$

$$\Delta H_{a1} = \frac{5}{2} n.R(T_2 - T_2) = \frac{5}{2}.1.8{,}314.(373 - 298) = 1559J$$

The new pressure is $p_2 = \frac{T_2}{T_1} p_1 = \frac{373}{298} 1.10^5 = 1{,}252.10^5$ Pa

a2. Isothermal process with pressure change of an ideal gas, i.e. ΔU=0, ΔH=0.

$$W = -Q = nRT.ln\left(\frac{p_3}{p_2}\right)\textbf{.} \text{ Therefore}$$

$$Q_{a2} = -1.8{,}314.373.\ln\left(\frac{5.10^5}{1{,}252.10^5}\right) = -4294J$$

W_{a2}=4294J

Summing up:
W_a=0+4294= 4294J
Q_a=936-4294= -3358J
ΔU_a=935+0= 936J

ΔH_a=1559+0= 1559J
W_a+Q_a=936J=ΔU_a

b.) The gas is heated in a cylindrical piston at constant pressure from 25 °C to100 °C, then its pressure is increased to 5.10^5 Pa at constant temperature.

b1. Isobaric process, $Q = \Delta H = n\int C_{mp}\,dT$, $W = -p.\Delta V$

$$Q_{b1} = n\int C_{mp}dT \quad \text{here} \quad Q_{b1} = n\int \frac{5}{2}R.dT = \frac{5}{2}n.R.(T_2 - T_1) \text{, i.e.}$$

$$Q_{b1} = \Delta H_{b1} = \frac{5}{2}.1.8{,}314(373-298) = 1559J$$

$$W_{b1} = -n.R(T_2 - T_1) = -1.10^5.8{,}314.(375-298) = -623J$$

$$\Delta U_{b1} = W_{b1} + Q_{b1} = -623 + 1559 = 936J$$

b2. Isothermal process, with pressure change, for ideal gas ΔU=0, ΔH=0.

$$W = -Q = nRT.ln\left(\frac{p_3}{p_2}\right).$$

$p_2=p_1$

$$Q_{b2} = -1.8{,}314.373.ln\left(\frac{5.10^5}{1.10^5}\right) = -4991J$$

W_{b2}=4991J
Summing up:
W_b=-623+4991= 4368J
Q_b=1559-4991= -3432J
ΔU_b=936+0= 936J
ΔH_b=1559+0= 1559J

c.) The work gas is compressed at 25 C° in a cylindrical piston to 5.10^5 Pa, then the temperature is increased from 25 C° to 100 C° at constant pressure..

c1. Isothermal process with pressure change, for the ideal gas ΔU=0, ΔH=0.

$$W = -Q = nRT.ln\left(\frac{p_2}{p_1}\right)$$

$$Q_{c1} = -1.8{,}314.298.ln\left(\frac{5.10^5}{1.10^5}\right) = -3987J$$

W_{c1}=3987J

c2. Isobaric process, $Q = \Delta H = n\int C_{mp}\,dT$, W= -p.ΔV

$$Q_{c2} = n\int C_{mp}dT \quad \text{here} \quad Q_{c2} = n\int \frac{5}{2}R.dT = \frac{5}{2}n.R.(T_2 - T_1) \text{, i.e.}$$

$$Q_{c2} = \Delta H_{c2} = \frac{5}{2}.1.8{,}314(373-298) = 1559J$$

$$W_{c2} = -n.R.(T_2 - T_1) = -1.8{,}314(373-298) = -623J$$

$$\Delta U_{c2} = W_{c2} + Q_{c2} = -623 + 1559 = 936J$$

Summing up,

W_c= 3987-623= 3364J
Q_c= -3987+1559= -2428J
ΔU_c=0+936= 936J
ΔH_c=0+1559= 1559J

Comparing the results for the three processes the values of U and H are the same, since they are state functions and their values are independent of the process path. In contrary to these W and Q are path functions, therefore their values depend oon the path between the initial and the final states.

E4. The pressure of 5 mol nitrogen (ideal gas) is 10.10^5 Pa, its temperature is 227 °C. It is cooled to 27 °C, and adiabatic expanded to 3 .10^5 Pa.. What is the change of H, U, W and Q during the full process?

$$C_{mV} = \frac{5}{2}R \qquad C_{mp} = \frac{7}{2}R \qquad \kappa = 1{,}4$$

isochor

$$\Delta H = nC_{mp}(T_2 - T_1) = 5 * 3{,}5 * 8{,}314 * (300 - 500) = -29099J$$
$$\Delta U = nC_{mV}(T_2 - T_1) = 5 * 2{,}5 * 8{,}314 * (300 - 500) = -20785J$$
$$\Delta S = nC_{mV}\ln\left(\frac{T_2}{T_1}\right) = 5 * 2{,}5 * 8{,}314 * \ln\left(\frac{300}{500}\right) = -53{,}087553J/K$$

W=0

$Q = \Delta U = -20785J$

adiabatic

$$p_2 = p_1\frac{T_2}{T_1} = 10.10^5\frac{300}{500} = 6.10^5\,Pa$$
$$T_3 = T_2\left(\frac{p_2}{p_3}\right)^{\frac{1-\kappa}{\kappa}} = 300\left(\frac{6.10^5}{3.10^5}\right)^{\frac{-0,4}{1,4}} = 246{,}1K$$
$$\Delta H = nC_{mp}(T_3 - T_2) = 5 * 3{,}5 * 8{,}314 * (246{,}1 - 300) = -7842{,}2J$$
$$\Delta U = nC_{mV}(T_2 - T_1) = 5 * 2{,}5 * 8{,}314 * (246{,}1 - 300) = -5601{,}6J$$

$\Delta S = 0$

$W = \Delta U = -5601{,}6J$

$Q = 0$

For the full process:

$\Delta H = -29099 - 7842{,}2 = -36941{,}2 J$

$\Delta U = -20785 - 5601{,}6 = -26386{,}6 J$

$\Delta S = -53{,}09 + 0 = -53{,}09 J / K$

$W = 0 - 5601{,}6 = -5601{,}6 J$

$Q = -20785 + 0 = -20785 J$

FURTHER PROBLEMS

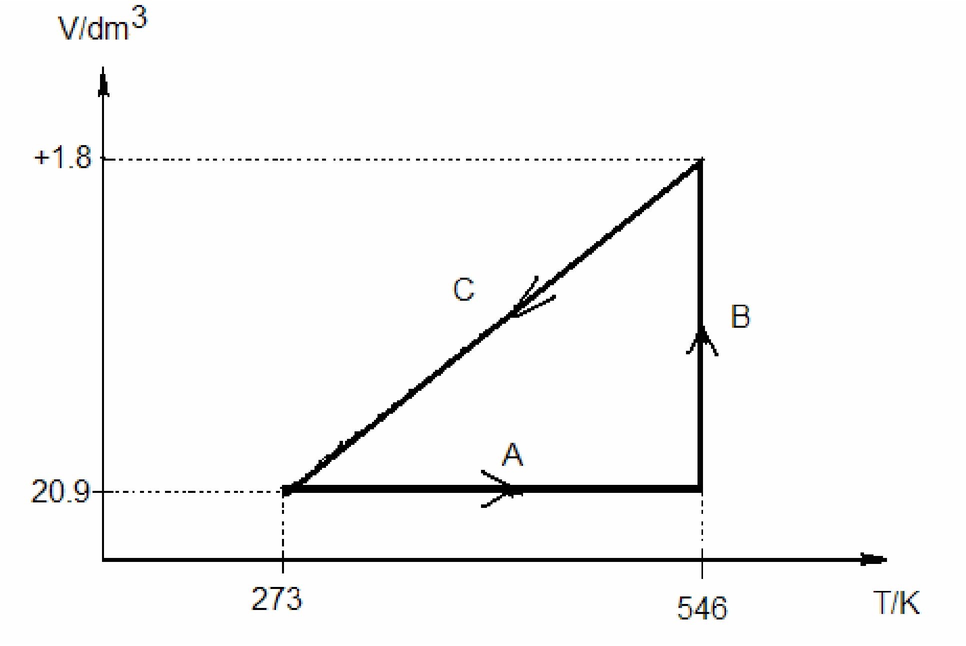
E5. The pressure of, 1 m^3 argon (ideal gas) is 10^6 Pa, its temperature is 298K. It is expanded adiabatic and reversible in a piston to 2 m^3. What are the p and T in the final state? What is the work and the change in the internal energy and the enthalpy?
(T = 188 K, p = 3,15.10^5 Pa; $W = \Delta U$ = -554 kJ, ΔH = -925 kJ)

E6. 1 dm^3 ideal gas is in a piston. Its pressure is 1,2.10^5 Pa, the temperature is 298 K. It is expanding to 10^5 Pa, the piston is fixed and the gas is heated to the final temperature. The observed pressure is 1,076.10^5 Pa. What is the C_p/C_V value of the gas?
(κ = 1,672).

E7. 1 mol ideal nitrogen gas is expanded on adiabatic reversible path from 373K to 273 K. What is the work if the initial pressure is 10^6 Pa, and 5.10^5 Pa, respectively?
(ΔU = -2059 J in both cases)

E8. What is the difference in internal energy of 10 mol hydrogen (ideal gas) at 20 kPa pressure and at 700 K (initial state) and its final state at 5 kPa and 500 K? It is possible to carry out the same process also in two steps, the first is adiabatic, the second one is isothermal. What are the changes in the internal energy during these two steps? C_{mp} = 28,66 J/(mol.K), regard it independent of temperature!
(ΔU = -40,692 kJ, ΔU_1 = -47,243 kJ, ΔU_2 = 6,551 kJ).

E9. 1 mol argon (ideal gas) is work gas of the cycle process presented in the figure. C_{mp} = 20,785 J/mol.K. Fill the table!



Process	Type	Q (kJ/mol)	W (kJ/mol)	ΔU (kJ/mol)	ΔS (kJ/mol)
A B C					
cycle					

[A.) isochor, Q = 3,405 kJ/mol, W = 0, ΔU = 3,405 kJ/mol, ΔS = 8,644 J/(mol.K),
B.) isothermal, Q = 3,147 kJ/mol, W = -3,147 kJ/mol, ΔU=0, ΔS = 5,763 J/(mol·K),
C.) isobaric, Q = -5,674 kJ/mol, W = 2,270 kJ/mol, ΔU = -3,405 kJ/mol, ΔS = -14,407 J/(mol.K)
Full cycle: Q = 0,878 kJ/mol, W = -0,877 kJ/mol, ΔU = 0, ΔS = 0.]

E10. 1 mol nitrogen (ideal gas) is compressed on a reversible adiabatic path from 0,02 m^3 to 0,01 m^3. The final temperature is 125 °C. Calculate the initial temperature! What was the work and the change of the internal energy? $\kappa = 1,40$.
(T = 301,6 K, $\Delta U = W$ = 2025,5 J)

2. THE SECOND LAW OF THERMODYAMICS

THE SECOND LAW

The processes have direction, they strive from the non-equilibrium state for the equilibrium state (spontaneous process). The return to the final state needs investing of work. The process is *irreversible*.
In other words, *it is impossible to carry out a process resulting only heat transfer from the environment and converting it quantitatively to work (Planck's theorem).*

ENTROPY

We look for a state function (extensive quantity) that describes, similarly to the expansion work, the heat appearing or disappearing during a reversible process. An intensive quantity is necessary to it. Multiplying this intensive quantity with the change of the state function, the result should be the reversible heat. The state function is the entropy (S), the intensive quantity is the temperature.

$$Q_{rev} = \int TdS \tag{30}$$

The definition of the entropy change is:

$$\Delta S = \int \frac{\delta Q_{rev}}{T} \tag{31}$$

In spontaneous processes

$$dS \geq \frac{\delta Q_{rev}}{T} \qquad (\delta Q \text{ is not a total differential, therefore } \delta \text{ is used instead of d}) \tag{32}$$

The entropy is the measure of the process irreversibility.

HELMHOTZ FREE ENERGY

Subtracting the reversible heat from the internal energy, the result is the expression of the isochor reversible work. The Helmhotz free energy is the generalization of this expression, a state function

$$A=U-TS \tag{33}$$

Its change during a process:

$$\Delta A = \Delta U - \Delta(TS) \tag{34}$$

as long as the change of the U function is simply calculable, the second member left needs even the absolute value of the entropy

$$\Delta(TS) = T_2S_2 - T_1S_1 \tag{35}$$

GIBBS FREE ENERGY

The expression of the isobaric reversible useful work is the result of the subtraction of the reversible heat from the enthalpy. The generalization of this function is again a state function, the Gibbs free energy

$$G=H-TS \tag{36}$$

Its change during a process

$$\Delta G = \Delta H - \Delta(TS) \tag{37}$$

Similarly to (35) for these calculations is the absolute value of the entropy necessary.

The general equation for e.g. enthalpy with consideration of the increasing temperature of a solid sample up to its vapour phase.

$$H_m^0(T) = \int_{298}^{T_m} C_{mp}^s dt + \Delta H_m^0(\text{fusion}) + \int_{T_m}^{T_b} C_{mp}^l dT + \Delta H_m^0(\text{evaporation}) + \int_{T_b}^{T} C_{mp}^g dT \tag{38}$$

How to use Table 2?

Definition of a dimensionless quantity:

$$X = T/1000\ \mathrm{K} \tag{39}$$

For the molar heat capacity:

$$C_m^0 = a + bX + cX^{-2} + dX^2 \quad (\mathrm{JK^{-1}\ mol^{-1}}) \tag{40}$$

The molar enthalpy is:

$$H_m^0 = 10^3\left[H(+) + aX + \frac{b}{2}X^2 - cX^{-1} + \frac{d}{3}X^3\right] \quad (\mathrm{Jmol^{-1}}) \tag{41}$$

The molar entropy is:

$$S_m^0 = S(+) + a\ln\left(\frac{T}{\mathrm{K}}\right) + bX - \frac{c}{2}X^{-2} + \frac{d}{2}X^2 \quad (\mathrm{JK^{-1}\ mol^{-1}}) \tag{42}$$

The molar Gibbs free energy is:

$$\mu_0 = 10^3\left[H(+) - S(+)X - aX\left(\ln\frac{T}{\mathrm{K}} - 1\right) - \frac{b}{2}X^2 - \frac{c}{2}X^{-1} - \frac{d}{6}X^3\right] \quad (\mathrm{Jmol^{-1}}) \tag{43}$$

EXERCISES

Please, pay attention! The following marks are used:
"." Or "*" for multiplication, "," for decimalization

F1. 2 mol oxygen ($O_{2,}$) is heated from 27°C to 727 °C at 10^5 Pa constant pressure. Calculate the changes of the enthalpy, the entropy, the Gibbs free energy and the molar heat capacity during the process! Use the data of Table 2. Compare the results to the corresponding data for ideal gas!.

Recalculation of temperatures from °C to K

T_1=27+273=300K, T_2=727+273=1000K

According to Table 2

$$H_m^0 = 10^3\left[H(+) + aX + \frac{b}{2}X^2 - \frac{c}{X} + \frac{d}{3}X^3\right] \quad Jmol^{-1} \qquad X = 10^{-3}T/K$$

$$S_m^0 = S(+) + a\,lnT + b.X - \frac{c}{2}\frac{1}{X^2} + \frac{d}{2}X^2 \quad Jmol^{-1}K^{-1}$$

$$C_m^0 = a + bX + c\frac{1}{X^2} + dX^2 \quad Jmol^{-1}K^{-1}$$

$$G = H - TS$$

$$\Delta G = \Delta H - \Delta(TS)$$

The data for oxygen (g) in Table 2 are as follows:

a= 29,1540 b= 6,4770 c= -0,1840 d= -1,0170 H(+)= -9,4890 S(+)= 36,1660

X(T_2)=1000/1000=1 X(T_1)=300/1000=0,3

$$\mathrm{H}_\mathrm{m}^0(1000) = 10^3\left[-9{,}4890 + 29{,}1450*1 + 0{,}5*6{,}4770*1^2 - \frac{-0{,}1840}{1} + \frac{-1{,}0170}{3}*1^3 = 22748{,}5 \ \ \mathrm{Jmol^{-1}}\right]$$

$$\mathrm{H}_\mathrm{m}^0(300) = 10^3\left[-9{,}4890 + 29{,}1450*0{,}3 + 0{,}5*6{,}4770*0{,}3^2 - \frac{-0{,}1840}{0{,}3} + \frac{-1{,}0170}{3}*0{,}3^3 = 152{,}8 \ \ \mathrm{Jmol^{-1}}\right]$$

$$\Delta\mathrm{H}^0 = \mathrm{n}[\mathrm{H}_\mathrm{m}^0(1000) - \mathrm{H}_\mathrm{m}^0(300)] = 2*(22748{,}5 - 152{,}8) = 45191 \ \ \mathrm{J} = 45{,}19 \ \ \mathrm{kJ}$$

$$\mathrm{S}_\mathrm{m}^0(1000) = 36{,}1660 + 29{,}1540 + ln(1000) + 6{,}4470*1 - \frac{-0{,}1840}{2*1^2} + \frac{-1{,}0170}{2}*1^2 = 244{,}5652 \ \ \mathrm{Jmol^{-1}K^{-1}}$$

$$\mathrm{S}_\mathrm{m}^0(300) = 36{,}1660 + 29{,}1540 + ln(300) + 6{,}4470*0{,}3 - \frac{-0{,}1840}{2*0{,}3^2} + \frac{-1{,}0170}{2}*0{,}3^2 = 210{,}1575 \ \ \mathrm{Jmol^{-1}K^{-1}}$$

$$\Delta S^0 = n\left[S_m^0(1000) - S_m^0(300)\right] = 2 * (244{,}5652 - 210{,}1575) = 68{,}154 \quad JK^{-1}$$

$$C_m^0(1000) = 29{,}1540 + 6{,}4770 * 1 + \frac{-0{,}1840}{1^2} + (-1.0170) * 1^2 = 34{,}4300 \quad Jmol^{-1}K^{-1}$$

$$C_m^0(300) = 29{,}1540 + 6{,}4770 * 0{,}3 + \frac{-0{,}1840}{0{,}3^2} + (-1.0170) * 0{,}3^2 = 28{,}9611 \quad Jmol^{-1}K^{-1}$$

$$G_m^0(1000) = 227845 - 1000 * 244{,}5652 = -221816{,}7 \quad Jmol^{-1}$$

$$G_m^0(300) = 152{,}8 - 300 * 210{,}1575 = -62894{,}5 \quad Jmol^{-1}$$

$$\Delta G^0 = n\left[G_m^0(1000) - G_m^0(300)\right] = 2 * \left[(-221816{,}7) - (-62894{,}5)\right] = -317845 \quad J = -317{,}85 \quad kJ$$

Considering the oxygen gas ideal and the molar heat capacity independent of the temperature, then we

$$C_m^0 = \frac{7}{2}R = 3{,}5 * 8{,}314 = 29{,}099 \quad Jmol^{-1}K^{-1}$$

$$\Delta H^0 = nC_m^0(T_2 - T_1) = 2 * 29{,}099(1000 - 300) = 40738{,}6 \quad J = 40{,}74 \quad kJ$$

$$\Delta S^0 = n\int_{T_1}^{T} \frac{C_m^0}{T}dT = nC_m^0 \ln\frac{T_2}{T_1} = 2 * 29{,}099 * \ln\frac{1000}{300} = 70{,}07 \quad JK^{-1}$$

The Gibbs free energy calculations need the values of the absolute entropies from Table 2,

$$\Delta G^0 = \Delta H^0 - (T_2S_2 - T_1S_1) = 20370 - (1000 * 489{,}13 - 300 * 420{,}32) = -342665{,}6 \quad J = -342{,}67 \quad kJ$$

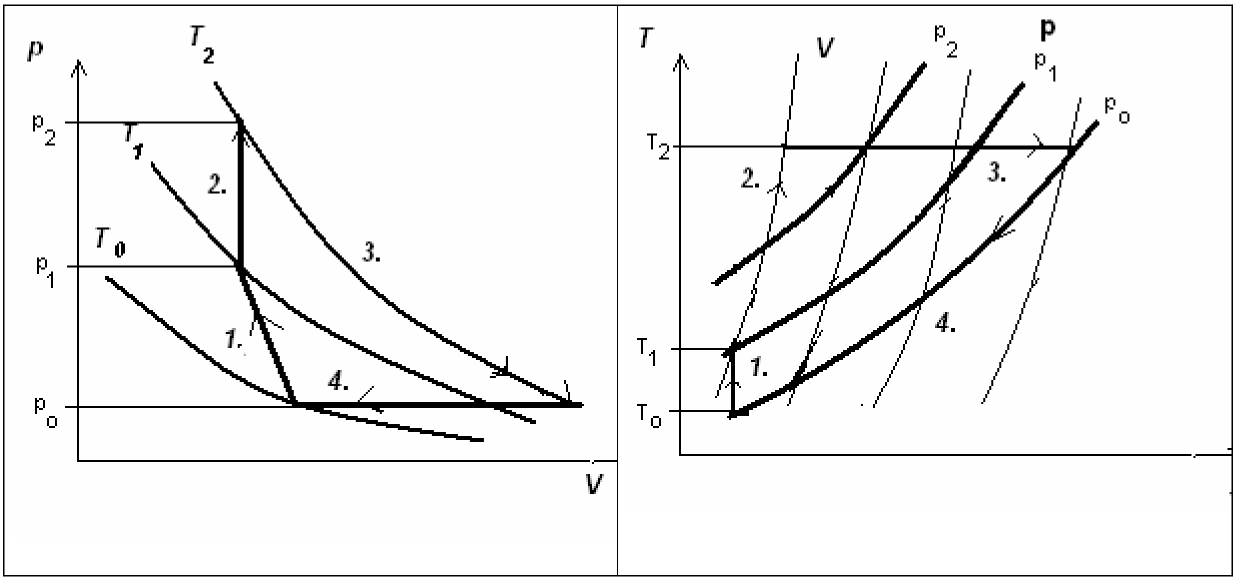
Summerizing:

	ΔH^0 / kJ	ΔS^0 / JK^{-1}	ΔG^0 / kJ	C_m^0 / $Jmol^{-1}K^{-1}$
Tabnle 2	45,19	68,15	-317,85	300K: 28,69; 100K: 34,43
Ideal gas	40,74	70,07	-342,67	29,10

F2. The following reversible cycle process is performed with 160 g oxygen (ideal gas):

1.) It is adiabatic and reversible compressed from 20 °C and 0,1 Mpa to 2 Mpa;
2.) then heated in isochor process to 500 °C;
3.) following, it is expanded to 0,1 Mpa in isothermal process;
4.) at last, it is heated to 20 °C in isobaric process. .

What are the values of W, Q, ΔU, ΔH, ΔS, ΔG, ΔA in the individual steps and in the full process? Consider the specific heat capacity independent of the temperature!



Initial data:

T_o=293,15 K $< T_1 <$ T_2=773,15 K
p_o=0,1 Mpa $< p_1 <$ p_2=2 Mpa

1.) *Adabatic and reversible process*: Q=0, therefore ΔS=0, and ΔU=W.

Change in internal energy: $\Delta U = n\int C_{mV} dT$ here $\Delta U = n\int \frac{5}{2} R dT = n\frac{5}{2}R(T_1 - T_0)$

(2 atomic ideal gas, $C_{mV} = \frac{5}{2}R$).

$T_0 = 20{,}0 + 273{,}15 = 293{,}15 K$ $n = \frac{160}{32} = 5 mol$

Calculation of the *T_1 temperature*:

$$T_1 = T_0 \left(\frac{p_0}{p_1} \right)^{\frac{1-\kappa}{\kappa}}$$

$$\left[pV^{\kappa} = const.; \quad TV^{\kappa-1} = const.; \quad Tp^{\frac{1-\kappa}{\kappa}} = const. \right]$$

2 atomic ideal gas: $\kappa = \frac{C_{mp}}{C_{mV}} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5}$ $\quad (C_{mp} - C_{mv} = R,\ \text{ideal gas})$

$$T_1 = T_0 \left(\frac{p_0}{p_1} \right)^{\frac{1-\frac{7}{5}}{\frac{7}{5}}} = 293{,}15 \left(\frac{0{,}1.10^6}{2.10^6} \right)^{-\frac{2}{7}} = 293{,}15.0{,}05^{-\frac{2}{7}} = 293{,}15 * 2{,}3535 = 689{,}94K$$

$$\Delta U = n\frac{5}{2}R(T_1 - T_0) = 5 * 2{,}5 * 8{,}314 * (689{,}94 - 293{,}15) = 41237J$$

Change in enthalpy: $\Delta H = n\int C_{mp}dT$ here $\Delta H = n\int \frac{7}{2}RdT = n\frac{7}{2}R(T_1 - T_0)$

$$\Delta H = n\frac{7}{2}R(T_1 - T_0) = 5 * 3{,}5 * 8{,}314 * (689{,}94 - 293{,}15) = 57731J$$

Change in Helmhotz free energy: $\Delta A = \Delta U - \Delta(T.S)$ here $\Delta A = \Delta U - nS_0(T_1 - T_0)$

Change in Gibbs free energy: $\Delta G = \Delta H - \Delta(T.S)$ here $\Delta G = \Delta H - nS_0(T_1 - T_0)$

The entropy(S) is for these calculations:

From Table 2, O_2: S_m^0 (298)=205,146 kJ. $Mol^{-1}K^{-1}$

Subscript *m* refers to molar quantity, the superscript zero refers to the standard pressure.

The following function is necessary for other temperatures:

$$S_m^0 = S(+) + a\ln T + b.X - \frac{c}{2}\frac{1}{X^2} + \frac{d}{2}X^2 \qquad (X=10^{-3}T/K) \qquad (38)$$

The result is in $Jmol^{-1}K^{-1}$ units, in case of applying the constants for oxygen from Table 2. .
For 293,15 K

$$S_{m,0}^0(293{,}15) = S_{m,1} = 36{,}116 + 29{,}154 * \ln 293{,}15 + 6{,}477.10^{-3} * .293{,}15 - \frac{-0{,}184}{2} * \frac{10^6}{293{,}15^2} + \frac{-1{,}017}{2} * \frac{293{,}15^2}{10^6} =$$

$$= 36{,}116 + 165{,}615 + 1{,}899 + 1{,}071 - 0{,}046 = 204{,}656 Jmol^{-1}K^{-1}$$

Since the pressure is not the standard (i.e. not 10^5 Pa), we assume the independence of entropy from the pressure:

$$\Delta A = \Delta U - nS_{m,0}^0(T_1 - T_0) = 41237 - 5 * 204{,}656 * (689{,}94 - 293{,}15) = -364790J$$

$$\Delta G = \Delta H - nS_{m,0}^0(T_1 - T_0) = 57723 - 5 * 204{,}656 * (689{,}94 - 293{,}15) = -348304J$$

2.) Isochor process, t_2=500 °C, W=0, Q=ΔU

T_2=500+273,15=773,15 K $\quad p_2 = p_1\frac{T_2}{T_1} = 2.10^6 * \frac{773,15}{689,94} = 2,2422.10^6\, Pa$

Change in internal energy: $\Delta U = n\int C_{mV}dT$ here $\Delta U = n\int \frac{5}{2}RdT = n\frac{5}{2}R(T_2 - T_1)$

$$\Delta U = n\frac{5}{2}R(T_2 - T_1) = 5 * 2,5 * 8,314 * (773,15 - 689,94) = 8647,6J$$

Change in enthalpy:: $\Delta H = n\int C_{mp}dT$ here $\Delta H = n\int \frac{7}{2}RdT = n\frac{7}{2}R(T_2 - T_1)$

$$\Delta H = n\frac{7}{2}R(T_2 - T_1) = 5 * 3,5 * 8,314 * (773,15 - 689,94) = 12106,6J$$

Change in Helmhotz free energy: $\Delta A = \Delta U - \Delta(T.S)$ here $\Delta A = \Delta U - n(S_{m,2}T_2 - S_{m,1}T_1)$

Change in Gibbs free energy: $\Delta G = \Delta H - \Delta(T.S)$ here $\Delta G = \Delta H - n(S_{m,2}T_2 - S_{m,1}T_1)$

Calculation of the entropy: the entropy of the initial state of the partial process 2 is equal to entropy of the initial state of the partial process 1, the temperature is 689,94 K,

S_1=S_0=5*204,656=1023,280 JK^{-1}

The change in entropy is

$$\Delta S = n.C_{mV}.ln\frac{T_2}{T_1} = n.\frac{5}{2}R.ln\frac{T_2}{T_1} = 5 * 2,5 * 8,314 * ln\frac{773,15}{689,94} = 103,925 * 0,113863 = 11,834JK^{-1}$$

Therefore

S_2=1023,280+11,834=1035,114 JK^{-1}

$$S_2T_2 - S_1T_1 = 1035,114 * 773,15 - 1023,280 * 689,94 = 800298,4 - 706001,8 = 94296,6J$$

Applying this result:

$\Delta A = \Delta U - \Delta(T.S)$ here $\Delta A = \Delta U - (S_2T_2 - S_1T_1)$

$$\Delta A = \Delta U - (S_2T_2 - S_1T_1) = 8647,6 - 94296,6 = -85649,6J$$

$\Delta G = \Delta H - \Delta(T.S)$ here $\Delta G = \Delta H - (S_2T_2 - S_1T_1)$

$$\Delta G = \Delta H - (S_2T_2 - S_1T_1) = 12106,6 - 94296,6 = -82190,0J$$

3.) *In the isothermal process the ideal gas is extended to* 0,1 Mpa, i.e. ΔU=0, ΔH=0, Q=-W, ΔG=ΔA. According to the data: p_3=p_0

The work: $W = nRT.\ln\frac{p_3}{p_2} = 5*8{,}314*773{,}15*\ln\frac{0{,}1.10^6}{2{,}242210^6} = -99956J$

Therefore the heat is: *Q*=99956*J*

One can choose between two methods for the entropy calculations:

$$\Delta S = \frac{Q}{T} = \frac{99956}{773{,}15} = 129{,}28JK^{-1} \qquad \Delta S = nR\,ln\frac{p_2}{p_3} = 5*8{,}314*ln\frac{2{,}2422.10^6}{0{,}1.10^6} = 129{,}28JK^{-1}$$

$$S_3 = S_2 + \Delta S = 1035{,}11 + 129{,}28 = 1164{,}39JK^{-1}$$

The change in Helmhotz free energy is
here $\Delta A = \Delta U - T.\Delta S = 0 - 773{,}15*129{,}28 = -99956J$

The change in Gibbs free energy here $\Delta G = \Delta H - T.\Delta S = 0 - 773{,}15*129{,}28 = -99956J$

4.) *The ideal gas is cooled to* 20 °C in this process, i.e. *Q=ΔH.* From the data: $T_4=T_0,\ p_4=p_0.$

Change in internal energy: $\Delta U = n\int C_{mV}dT$ here $\Delta U = n\int\frac{5}{2}RdT = n\frac{5}{2}R(T_4 - T_3)$

$$\Delta U = n\frac{5}{2}R(T_4 - T_3) = 5*2{,}5*8{,}314*(293{,}15 - 773{,}15) = -49884J$$

Change in enthalpy: $\Delta H = n\int C_{mp}dT$ here $\Delta H = n\int\frac{7}{2}RdT = n\frac{7}{2}R(T_4 - T_3)$

$$\Delta H = n\frac{7}{2}R(T_4 - T_3) = 5*3{,}5*8{,}314*(293{,}15 - 773{,}15) = -69838J$$

The heat: Q=ΔH=-69838J

The work: $W = -n.R(T_4 - T_3) = -5*8{,}314*(293{,}15 - 773{,}15) = 19953{,}6J$

The calculation of the entropy for calculations of changes in Helholtz and Gibbs free energys

$$\Delta S = n\int\frac{C_{mp}}{T}dT \qquad \text{here} \qquad \Delta S = n\int_{T_3}^{T_1}\frac{\frac{7}{2}R}{T}dT = n.\frac{7}{2}R\,ln\frac{T_4}{T_3}$$

$$\Delta S = 5*3{,}5*8{,}314*ln\frac{293{,}15}{773{,}15} = -141{,}099JK^{-1}$$

$S_4=S_3+\Delta S=$ 1164,39-141,10=1023,29 JK^{-1}

$$S_4T_4 - S_3T_3 = 1023{,}29*293{,}15 - 1164{,}39*773{,}15 = 299977{,}5 - 900248{,}1 = -600270{,}6J$$

Change of the Helmhotz free energy: $\Delta A = \Delta U - \Delta(T.S)$ here $\Delta A = \Delta U - (S_4T_4 - S_3T_3)$

$\Delta A = \Delta U - (S_4T_4 - S_3T_3) = -49884 + 600271 = 550387J$

Change of the Gibbs free energy: $\Delta G = \Delta H - \Delta(T.S)$ here $\Delta G = \Delta H - (S_4T_4 - S_3T_3)$

$\Delta G = \Delta H - (S_4T_4 - S_3T_3) = -69838 + 600271 = 530433J$

The sum of the full cycle:

step	W/J	Q/J	ΔU/J	ΔH/J	ΔS/JK^{-1}	ΔG/J	ΔA/J
1.	41237	0	41237	57731	0	-348304	-364790
2.	0	8648	8648	12107	11,83	-82190	-85650
3.	-99956	99956	0	0	129,28	-99956	-99956
4.	19954	-69838	-49884	-69838	-141,10	530433	550387
Σ	-38765	38766	1	0	0,01	-17	-9

U, H, S, G, A are state functions, therefore their values have to be zero for the full cycle. The present deviations are results of the uncertainties inn the calculations. Q and W are path functions, in a reversible process their absolute values have to be equal.

F3. The temperature of 3 mol nitrogen gas (ideal gas) is 327 °C, its pressure is 0,2 Mpa. It is cooled at constant volume until its pressure decreased to 150 kPa, then it is expanded on isothermal path to 75 kPa. The next (last) step is to bring the gas back into the final state. Friction loss is negligible. The work of the full cycle is 2371 J. What is the change in the individual steps in W, Q an U? Prove that the last process is adiabatic! The cycle is reversible. Use the data of Table 2!

Results

(Only for controlling of the solutions)

PROCESS	W /kJ	Q /kJ	ΔU /kJ
1.	0	-10,15	-10,15
2.	-7,780	7,780	0
3.	10,15	0	10,15

Guide to the solution

1. *Isochor process*:

   $Q_1 = \Delta U_1$

   $W_1 = 0$

   $\Delta U = \Delta H - V\Delta p$ (see Table 1, general equations)

$$V_0 = V_1 = \frac{nRT_0}{p_0}$$

Equation for the molar enthalpy in Table 2A

$$H_m^0 = 10^3\left[H(+) + aX + \frac{b}{2}X^2 - \frac{c}{X} + \frac{d}{3}X^3\right] \quad Jmol^{-1} \qquad X = 10^{-3}T/K$$

(superscript zero: standard pressure)).

T must be substituted in □elvin. Data for nitrogen gas:

H(+)=-9,982 a=30,428 b=2,544 c=-0,238 d=0,000

Equation for the molar entropy:

$$S_m^0 = S(+) + a.\ln T + bX - \frac{c}{2X^2} + \frac{d}{2}X^2 \qquad Jmol^{-1}K^{-1}$$

Here $S(+)$=16,203.

2. *Isothermal process*

According to table 1 (general equations)

$$\Delta U = \Delta H - \Delta(pV)$$
$$Q = T\Delta S$$
$$W = \Delta U - Q = \Delta H - \Delta(pV) - T\Delta S$$

Since the work gas iz ideal, the isothermal change in entropy is calculable as

$$\Delta S = n.R.\ln\frac{p_1}{p_2} \quad .$$

3. *Is this process adiabatic, indeed?*

Since the total work of the cycle is given, this is with negative sign the heat of the process. If the sum of the heats of the first two steps is equal to this value, then for the third step is $Q_3=0$ apart from small numerical errors). So the adiabatic property of the third process is proved. Then the necessary relations are:

$$\Delta U = \Delta H - \Delta(pV)$$
$$Q = 0$$
$$W = \Delta U = \Delta H - \Delta(pV)$$

F4. Calculate the changes of the thermodynamic functions of 1 kmol N_2 (ideal gas) during the process increasing its temperatrure form 27 °C to 327 °C and it pressure form 0,1 Mpa to 1 Mpa! Use the data of Table 2!
(ΔU = 6578 kJ, ΔH = 9072 kJ, ΔS = 1,71 kJ/.K, ΔG =-49495 kJ, ΔA = -51989 kJ)

Calculate the thermodynamic functions of a pure substance!

F5. 1 mol liquid benzene is evaporated at its boiling point and heated the vapour at 0,1 Mpa to 427 °C. What is change in enthalpy, entropy and Gibbs free energy, if the entropy of the liquid benzene is 194,6 $J.mol^{-1}.K^{-1}$ at its boiling point, 80 °C , and the heat of vaporization is at this temperature 31,8 $kJ.mol^{-1}$.

N= 1 mol. The data of Table 2 refer 0,1 Mpa ("o" subscript)

Enthalpy

$$\Delta H = n\lambda_{353} + n\int_{353}^{700} C_{mp} dT = n\lambda_{353} + n\left(H_m^0(700{,}15) - H_m^0(353{,}15)\right)$$

Considering $X_2=10^{-3}*T_2$ és $X_1=10^{-3}*T_1$ and

$$H_m^0(T) = 10^3\left[H(+) + a.X + \frac{b}{2}X^2 - \frac{c}{X} + \frac{d}{3}X^3\right]$$

Since the state is the same and we are in the same temperature region of the table:

$$\Delta H_m^0 = 10^3\left[a.(X_2 - X_1) + \frac{b}{2}(X_2^2 - X_1^2) - c.(\frac{1}{X_2} - \frac{1}{X_1}) + \frac{d}{3}(X_2^3 - X_1^3)\right]$$

for benzene vapour at 700 K

$$H_m^0(700) = 10^3\left[\begin{array}{l} 52{,}32 + 44{,}141 * 0{,}700 + \frac{245{,}312}{2} * 0{,}700^2 - \\ -\frac{-2{,}632}{0{,}700} + \frac{-75{,}525}{3} * 0{,}700^3 \end{array}\right] =$$

$$= 10^3[52{,}32 + 30{,}899 + 60{,}101 + 3{,}760 - 8{,}635] = 1{,}38445.10^5\,Jmol^{-1}$$

for benzene vapour at 353 K

$$H_m^0(353) = 10^3\left[\begin{array}{l} 52{,}32 + 44{,}141 * 0{,}353 + \frac{245{,}312}{2} * 0{,}353^2 - \\ -\frac{-2{,}632}{0{,}353} + \frac{-75{,}525}{3} * 0{,}353^3 \end{array}\right] =$$

$$= 10^3[52{,}32 + 15{,}582 + 15{,}284 + 7{,}456 - 1{,}107] = 0{,}89535.10^5\,Jmol^{-1}$$

$$\Delta H = 1 * 31{,}8.10^3 + 1 * \left(1{,}38445.10^5 - 0{,}89535.10^5\right) = 8{,}07210.10^4\,J$$

Entropy

$$\Delta S = n.\frac{\lambda_{353}}{T} + n\int_{353}^{700}\frac{C^0_{mp}}{T} = n\frac{\lambda_{353}}{T} + n\left[S^0_m(700) - S^0_m(353)\right]$$

$$S^0_m(T) = S(+) + a.\ln T + b.X - \frac{c}{2X^2} + \frac{d}{2}X^2$$

Since the state is the same and we are in the same temperature region of the table:

$$\Delta S^0_m = a * \ln\frac{T_2}{T_1} + b * (T_2 - T_1) - \frac{c}{2}\left(\frac{1}{X_2^2} - \frac{1}{X_1^2}\right) + \frac{d}{s}\left(X_2^2 - X_1^2\right)$$

The absolute entropy values are necessary for the calculation of ΔG,

For benzene vapour at 700 K

$$S^0_m(700) = -62{,}602 + 44{,}141 * \ln 700 + 245{,}312 * 0{,}700 -$$
$$-\frac{(-2{,}632)}{2} * \frac{1}{0{,}700^2} + \frac{-75{,}525}{2} * 0{,}700^2 =$$
$$= \left[-62{,}602 + 289{,}171 + 171{,}718 + 2{,}686 - 18{,}504\right] = 382{,}469\,\mathrm{Jmol^{-1}K^{-1}}$$

for benzene vapour at 353 K

$$S^0_m(353) = -62{,}602 + 44{,}141 * \ln 353 + 245{,}312 * 0{,}353 -$$
$$-\frac{(-2{,}632)}{2} * \frac{1}{0{,}353^2} + \frac{-75{,}525}{2} * 0{,}353^2 =$$
$$= \left[-62{,}602 + 258{,}952 + 86{,}595 + 10{,}561 - 4{,}706\right] = 288{,}800\,\mathrm{Jmol^{-1}K^{-1}}$$

$$\Delta S = 1 * \frac{31{,}8.10^3}{353} + 1 * (382{,}469 - 288{,}800) = 90{,}085 + 93{,}669 = 183{,}754\,\mathrm{JK^{-1}}$$

Gibbs free energy

$$\Delta G = \Delta H - (T_2S_2 - T_1S_1)$$

for liquid benzene

$S_1 = S_l(353) = 1*194{,}6 = 194{,}6$ J.K^{-1}

for benzene vapour

$S_2 = S_v(700) = S_l(353) + \Delta S = 194{,}6 + 183{,}8 = 378{,}4$ J.K^{-1}

$$\Delta G = 80754 - (700 * 378{,}4 - 353 * 194{,}6) = 80754 - 264880 + 68694 = -115432\,\mathrm{J} =$$
$$= -115{,}432\,\mathrm{kJ}$$

F6. Liquid methanol is heated form 30 °C to 128 °C. In between at 338 K its state changes.

What is the entropy product? What is the heat of boiling?

	A	b	c	d	H(+)	S(+)
$CH_3OH(g)$	4,310	128,725	0,452	-44,099	-206,369	181,421
$CH_3OH(l)$	81,588				-263,776	-338,248

	Temperature (K)	H^0_m (J/mol)
$CH_3OH(g)$	401	-196366,17
$CH_3OH(g)$	338	-199464,09
$CH_3OH(l)$	338	-236199,26
$CH_3OH(l)$	303	-239054,84

$\Delta H^0_m = 42688{,}67 \quad J/mol \qquad \lambda = 36735{,}17 \quad J/mol$

F7. What is the molar heat of vaporation of n-pentane at its boiling point?

Data from Table 2 for the vapour

n-C5H12(g) 309,000 124,675 136,900 -3,238 -25,623 -200,328 -419,709

Temperature 309,000 K (35,850 °C)
ΔH^0_m = -145040,776644 J/mol
ΔS^0_m = 353,130422 J/K/mol
ΔG^0_m = -254158,077024 J/mol
ΔC^0_m = 130,618084 J/K/mol

Data from Table 2 for the liquid

n-C5H12(l) 309,000 165,686 0,000 0,000 0,000 -223,328 -684,154

Temperature 309,000 K (35,850 °C)

ΔH^0_m = -172131,026000 J/mol
ΔS^0_m = 265,780383 J/K/mol
ΔG^0_m = -254257,164286 J/mol
ΔC^0_m = 165,686000 J/K/mol

ΔH_m= 27,090 kJ/mol

3. PHASE EQUILIBRIA OF PURE SUBSTANCES

Change of the Gibbs free energy:

In general:

$$dG = dH - TdS - SdT \tag{43}$$

Substituting dH-t (Equ. 5):

$$dG = dU + pdV + Vdp - Tds - SdT \tag{44}$$

Resolving dU: ($dU = TdS - pdV$)

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT = Vdp - SdT \tag{45}$$

Since the Gibbs free energy depends on the quantity of the substance (45) must be completed with a new member:

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \sum_{i,j\neq i}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i \tag{46}$$

CHEMICAL POTENTIAL

The molar Gibbs free energy of pure compounds is called chemical potential.

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = G_m \tag{47}$$

Under other thermodynamic conditions:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{V,S} = \left(\frac{\partial H}{\partial n}\right)_{p,S} = \left(\frac{\partial A}{\partial n}\right)_{V,T} \tag{48}$$

PARTIAL CHEMICAL POTENTIAL

The chemical potential of the component „i' in a multi-component system is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j\ j\neq i} \tag{49}$$

Change of the chemical potential in pure substance (one-component system)

$$d\mu = V_m dp - S_m dT \tag{50}$$

In case of equlibrium (the example is here the vapour-liquid equilibrium):

$$\mu_g = \mu_l \tag{51}$$

and

$$d\mu_g = d\mu_l \tag{52}$$

Relations (51) and (52) are valid for any (gas-liquid, gas-solid, liquid-solid and solid-solid) phase equlibria. From relation (52)

$$-S_{m,g}dT + V_{m,g}dp = -S_{m,l}dT + V_{m,l}dp \tag{53}$$

and in this way

$$\left(V_{m,g} - V_{m,l}\right)dp = \left(S_{m,g} - S_{m.l}\right)dT \tag{54}$$

Since in equilibrium (37) $\Delta H_m = T.\Delta S_m$ ($\Delta G_m = 0$)

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T.\Delta V_m} \quad \text{(Clapeyron equation)} \tag{55}$$

Temperature dependence of the vapour pressure

If the vapour can be considered as ideal gas and the molar volume of the liquid state is negligible to that of the vapour, then one can use the approach $\Delta V_m \approx V_{m,g}$. According to approach the ideal gas law is applicable in this case and may substituted in (55). Moreover, the change of the molar enthalpy may substituted with the heat of vaporization (λ). With these, (55) has the form

$$\frac{dp}{dT} = \frac{\Delta H_m}{T\dfrac{RT}{p}} = \frac{\lambda p}{RT^2} \tag{56}$$

and

$$\frac{dp}{dT} = p\frac{\lambda}{RT^2}$$

With a short formulation

$$\frac{d\ln\{p\}}{dT} = \frac{\lambda}{RT^2} \qquad \{p\} = \frac{p(Pa)}{1\,Pa} \tag{57}$$

Integrating under λ=constant condition (with this λ is regarded as mean heat of vaporization is

$$\int d\ln\{p\} = \int \frac{\lambda}{RT^2}\,dT \tag{58}$$

and now we have

$$\ln\{p\} = -\frac{\lambda}{RT} + B \quad \text{(the Clausius-Clapeyron equation)} \tag{59}$$

This is a good approach for the estimation of the vapour pressure. Here $\{p\} = \frac{p(\mathrm{Pa})}{1\mathrm{Pa}}$ is a dimensionless quantity and B is constant. Integrating similarly like in (58) the result is a similarly well applicable equation, after all for the estimation of the change in vapour pressure in a close region or for interpolation:

$$ln\frac{p_2}{p_1} = \frac{\lambda}{R}\frac{T_2 - T_1}{T_1.T_2} \tag{60}$$

EXERCISES

G1. Calculate the heat of vaporization of benzene at its boiling point applying the following data: boling point at 101,3 kPa is 80,10 °C. The change of the boling pont is describable about 10^5Pa using the equation

$$\frac{dt}{dp} = \frac{dT}{dp} = 0,320 K.kPa^{-1}$$

The density of the liquid is at 80,10 °C: 814,4 kg.m^{-3}, the density of the vapour is at the same temperature 2,741 kg.m^{-3}.
Using relation (55):

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

$$\Delta v = \frac{1}{\rho_g} - \frac{1}{\rho_l} = \frac{1}{2,741} - \frac{1}{814,4} = 0,36483 - 0,0012279 = 0,3636 m^3 kg^{-1}$$

$$\Delta V_m = 0,3636 m^3 kg^{-1} \times \frac{78 g.mol^{-1}}{1000 g.kg^{-1}} = 0,02836 m^3 mol^{-1}$$

$$\Delta h = T.\Delta v.\frac{dp}{dT} = 353,25 K \times 0,3636 m^3 kg^{-1} \times \frac{1}{0,320 K.kPa^{-1}} = 401,4 kJ.kg^{-1}$$

$$\lambda = \Delta \mathrm{H_m} = 353,25\mathrm{K} \times 0,02836 \mathrm{m^3 mol^{-1}} \times \frac{1}{0,320 \mathrm{K.kPa^{-1}}} = 31,32 \mathrm{J.mol^{-1}}$$

G2 . The vapour pressure dependence of ethylpropionate is as function of the temperature

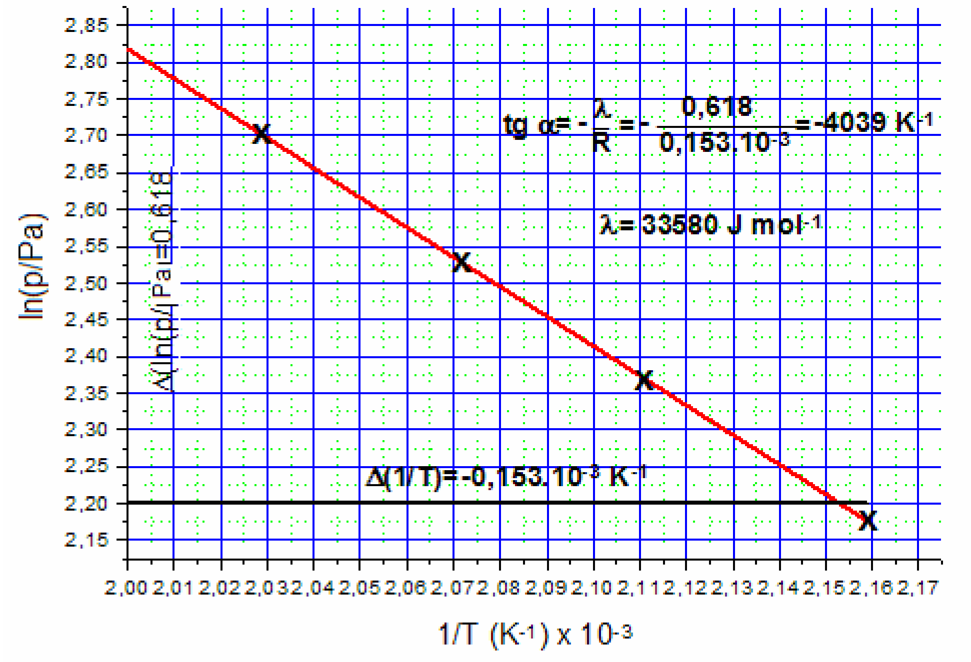
t /°C	190	200	210	220
p /kPa	882,5	1058	1261	1493

1. Compile diagram $ln\left(\frac{p}{p^0}\right) - \frac{1}{T}$ using the data of this table. Drawing the “best” line crossing the data points, the mean heat of vaporization can calculated from its slope. (see equation 59).

(The slope can be calculated with using the method of least squares).

$10^3/T$ (K^{-1})	2,1591	2,1135	2,0698	2,0278
ln (p/kPa)	2,177	2,359	2,534	2,703

From the figure tg α=–4039, so $K = -\frac{\lambda}{R}$, and λ=33580 J mol^{-1}



2. Calculate the vapour pressure at 205 °C!

The vapour pressure at 205 °C:

Interpolation between 200 és 210 °C (60)

T_1=473,15 K T_2=483,15 K

$$\lambda = R\frac{T_1T_2}{T_2 - T_1} ln\frac{p_2}{p_1} = 8{,}314 \times \frac{473{,}15 \times 483{,}15}{483{,}15 - 473{,}15} \times ln\frac{1261}{1058} = 1{,}9006.10^5 \times 0{,}1755 = 33360 J.mol^{-1}$$

T_3=478,15K

$$ln\left(\frac{p_3}{p^0}\right) = ln\left(\frac{p_1}{p^0}\right) + \frac{\lambda}{R} \times \frac{T_3 - T_1}{T_1 \times T_3} =$$

$$= ln 10{,}58 + \frac{33360}{8{,}314} \times \frac{478{,}15 - 473{,}15}{473{,}15 \times 478{,}15} = 2{,}359 + 4012{,}5 \times 2{,}2101.10^{-5} = 2{,}447$$

$$p_3 = 11{,}561.10^5 Pa$$

3. What is the boiling point if the pressure is 1 MPa ?Use the Clausius-Clapeyron approximation!

The heat of vaporation at 1 MPa-on:

This pressure value should be between 190 °C and 200 °C (look at the diagram!). Again, interpolation is necessary.

T_1=463,15 K
T_2=473,15 K

$$\lambda = R\frac{T_1T_2}{T_2-T_1}ln\frac{p_2}{p_1} = 8,314\times\frac{463,15\times473,15}{473,15-463,15}\times ln\frac{1058}{882,5} = 1,8219.10^5\times0,1814 = 33050J.mol^{-1}$$

$$\frac{1}{T_3} = \frac{1}{T_1} - \frac{R}{\lambda}ln\frac{p_3}{p_1} = \frac{1}{463,15} - \frac{8,314}{33050}ln\frac{10^6}{8,825.10^5} = 2,1591.10^{-3} - 2,51558.10^{-4}\times0,124996 =$$

$$= 2,12766.10^{-3}K^{-1}$$

$$T_3 = 470,0K \sim 196,85^oC$$

What is the value of„B”?

$$B = ln\frac{p_1}{p^0} + \frac{\lambda}{RT_1} = ln8,825 + \frac{33050}{8,314\times463,15} = 2,178 + 8,583 = 10,761$$

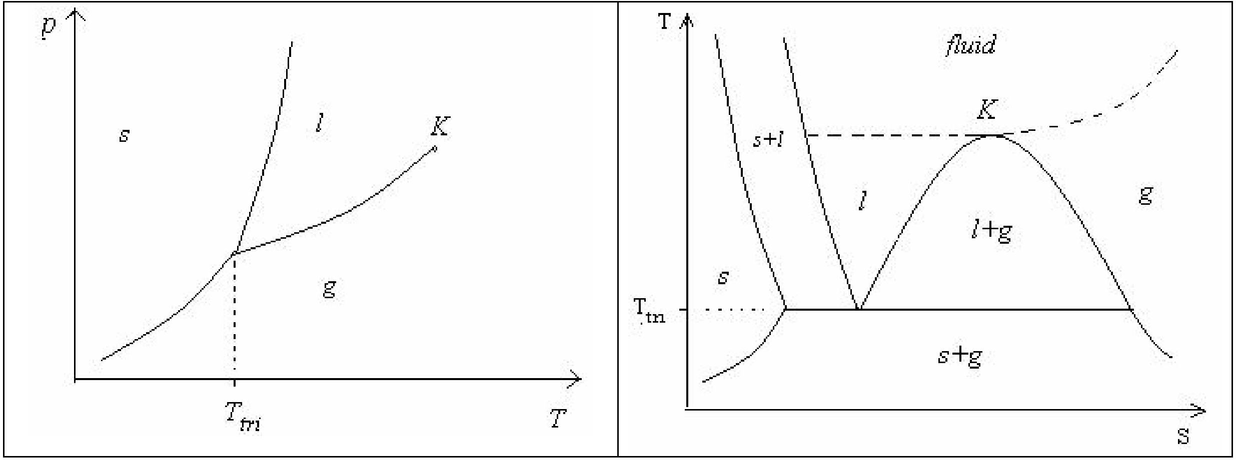
G3. The temperature dependence of the vapour pressure of the liquid iodine is (log means ^{10}lg)

$$\log\{p\} = 25,588 - 5,092\times\log(T/K) - \frac{3222}{T}$$

The same equation for the solid iodine has the form:

$$\log\{p\} = 18,380 - 2,013\times\log(T/K) - \frac{3512}{T}$$

What is the temperature of the triple point? What is the vapour pressure and the heat of fusion at this temperature?



At the triple point the vapour pressure of the sold and the liquid is equal.

$$p_s = p_l$$

$$25,588 - 5,092\times log(T/K) - \frac{3222}{T} = 18,230 - 2,013\times log(T/K) - \frac{3512}{T}$$

i.e.

$$7{,}208-3{,}079\times log\left(T/K\right)+\frac{290}{T}=0$$

The solution of this equation is, using iteration

T_{tri}=385,1 K ~ 112 °C

The vapour pressure of the liquid is

$$\log\left(\frac{p_{tri}}{p^0}\right)=18{,}380-2{,}013\times\log(385{,}1)-\frac{3512}{385{,}1}=18{,}380-5{,}2048-9{,}1197=4{,}0555$$

$$p_{tri}=11363Pa$$

The calculation of the heats of sublimation and vaporization::

$$\lambda_{s,l}=\lambda_{s,g}-\lambda_{l,g}$$

Calculation of the heat of sublimation:

$$\frac{\mathrm{dp}}{\mathrm{dT}}=\mathrm{p}\frac{\lambda}{\mathrm{RT}^2}\quad\rightarrow\quad\lambda=\frac{\mathrm{R.T}^2}{\mathrm{p}}\times\frac{\mathrm{dp}}{\mathrm{dT}}=\mathrm{R.T}^2\frac{\mathrm{d\ln}}{\mathrm{dT}}$$

$$ln\left(\frac{p}{p^0}\right)=ln(10)\times18{,}380-2{,}013\times ln\left(T/K\right)-ln(10)\times\frac{3512}{T}=$$

$$42{,}322-2{,}013\times ln\left(T/K\right)-\frac{8087}{T}$$

Differentiating:

$$\frac{\mathrm{d\ln\{p\}}}{\mathrm{dT}}=-\frac{2{,}013}{\mathrm{T}}+\frac{8087}{\mathrm{T}^2}=-5{,}2272.10^{-3}+5{,}4531.10^{-2}=0{,}049303\mathrm{K}^{-1}$$

$$\lambda_{\mathrm{s,g}}=\mathrm{R.T}^2\frac{\mathrm{d\ln\{p\}}}{\mathrm{dT}}=8{,}314\times385{,}1^2\times0{,}0493034=60790{,}2\mathrm{J.mol}^{-1}$$

The calculation of the heat of vaporization is possible on a similar way:

$$\ln\{\mathrm{p}\}=\ln(10)\times25{,}588-5{,}092\times\ln\left(\frac{\mathrm{T}}{\mathrm{T}^0}\right)-\ln(10)\times\frac{3222}{\mathrm{T}}=58{,}919-5{,}092\times\ln\left(\frac{\mathrm{T}}{\mathrm{T}^0}\right)-\frac{7419}{\mathrm{T}}$$

$$\frac{\mathrm{d\ln\{p\}}}{\mathrm{dT}}=-\frac{5{,}092}{\mathrm{T}}+\frac{7419}{\mathrm{T}^2}=-1{,}3225.10^{-2}+5{,}0026.10^{-2}=0{,}0368013\mathrm{K}^{-1}$$

$$\lambda_{\mathrm{l,g}}=\mathrm{R.T}^2\frac{\mathrm{d\ln\{p\}}}{\mathrm{dT}}=8{,}314\times385{,}1^2\times0{,}0368013=45375{,}4\mathrm{J.mol}^{-1}$$

And now at the end we have the heat of fusion

$$\lambda_{s,l} = 60790{,}2 - 45375{,}4 = 15414{,}8 J.mol^{-1}$$

G4. The melting point of the acetic acid changes with the temperature up to 2.10^8 Pa according to the equation:

$$t = 16{,}66 + 0{,}231.10^{-6}\,p - 2{,}25.10^{-16}\,p^2 \left[{}^\circ C\right] \quad p\left[Pa\right]$$

a.) Calculate the heat of fusion of acetic acid at standard pressure! Its specific volume increases at the melting point with 0,156 dm^3kg^{-1}?

b.) What is its melting point at 100 MPa? At this pressure the specific volume increases 0,115 dm^3kg^{-1}.

(a: $\Delta H_{m,1} = 195{,}93 \times 0{,}060 = 11{,}74 kJ.mol^{-1}$; b: $\Delta v_2 = 1{,}15.10^{-4}\ m^3kg^{-1}$;

$\Delta h_2 = \dfrac{310{,}66 \times 1{,}15.10^{-4}}{1{,}86.10^{-7}} = 192{,}07 kJ.kg^{-1}$; $\Delta H_{m,2} = 192{,}07 \times 0{,}060 = 11{,}52 kJ.mol^{-1}$).

G5. What changes the molar Gibbs free energy of methanol, if the liquid is in equilibrium with its vapour at 25 °C, and this system is heated to 50 °C under preserving the equilibrium state? The vapour phase is regarded as ideal gas. The equilibrium vapour pressure of methanol is 16,44 kPa at 25 °C, and 54,31 kPa at 50 °C. At 0,1 MPa $C_{mp,l}$ = 81,59 J/(mol.K), $C_{mp,g} = 4{,}310 + 128{,}725.10^{-3}T + 0{,}452.10^{6}T^{-2} - 44{,}099.10^{-6}T^{2}$ J/(mol.K), $S_{m,298(l)}$ = 126,61 J/(mol.K), $S_{m,298(g)}$ = 239,70 J/(mol.K).
(ΔG = -3205,1 J/mol)

G6. **D**ata for the vapor pressure of CH3Br:

t/°C	-69,974	-44,326	-30,062	-8,140
p/mbar	17,31	100,45	223,19	630,00

What is the vapour pressur at +4,2 °C? Use the Clausius-Clapeyron approach! (p = 110 kPa, the extrapolation result is not accurate, the measured result is 105,5 kPa)

G7. The vapor pressure of the liquid iodine:

$\log (p/Pa) = 25{,}588 - 5{,}092 \log T - 3222/T$

The vapor pressure of the solid ioodine is:

$\log(p/Pa) = 18{,}380 - 2{,}013 \log T - 3512/T$

What is the triple point temperature? What is the vapor pressure and the heat fusion at the triple point, Mekkora a hármaspont hõmérséklete?
Help: $p_{solid}=p_{liquid}$ at the triple point.
(T = 385,1 K; p = 11,37 kPa; λ=15,4 kJ/mol)

G8. The vapor pressure of ethylpropionate depend on the temperature as

t/°C	190	200	210	220
p/kPa	882,5	1058	1261	1493

Calculate the vapour pressure at 205 °C, and the boiling point at 1 MPa. Use the Clausius-Clapeyron approximation.

(p = 1,16 MPa, t=196,8 °C)

G9. The vapor pressure of ethanol increases near 50 °C 1380 Pa/K. What is the molar heat of vaporization if the density of the saturated vapour is at 50 °C is 0,506 g/dm^3, that of the liquid 760 g/dm^3 ? Help: remember on the connection of vapor density and the molar voluime!

(ΔH_m = 40,5 kJ/mol)

G10. Calculate the constants of the $\ln(p/\mathrm{kPa}) = -\lambda'/(RT) + B$ equation for acetonitryl from the experimental data

t/°C	89,66	94,52	99,89	104,30
p/kPa	129,4	149,0	173,8	196,4

(λ' = 32,4$_5$ kJ/mol, B = 15,625)

Vapor-liquid equilibria in multicomponent systems

1. Ideal mixture in liquid- and vapor phase, gas mixture behaves as ideal gas

Partial pressure

Raoult's law expresses the behaviour of the ideal liquid mixture. The partial pressure p_i of the component *i* is proportional to its mole fraction x_i. The proportionality factor is the vapor pressure of the pure component at the given temperature (p_i^*):

$$p_i = x_i p_i^* \tag{61}$$

The full pressure (p) of the mixture is

$$p = \sum_i p_i = \sum_i x_i p_i^* \tag{62}$$

The temperature dependence of the partial pressures for ideal mixtures can be calculated using equations (59) and (61), respectively. In ideal case equ. 62 is applicable.

Mole fraction in gas phase: According Dalton's law

$$y_i = \frac{p_i}{p} \tag{63}$$

Mass balance: n_l moles in the liquid phase and n_g in the gas phase,

$$n=n_l+n_g \tag{64}$$

b refers to the full system, n_i the molar mass of component i in the full system:

$$n_l = \frac{n_i - n.y_i}{x_i - y_i} \tag{65}$$

$$n_g = \frac{n_i - n.x_i}{y_i - x_i} \tag{66}$$

In case of two components:

$$\frac{n_g}{n_l} = \frac{x_b - x}{y - x_b} \tag{67}$$

x_b is the mole fraction in the full system. Please, note

$$\frac{n_{1,l}}{n_{2,l}} = \frac{x_1}{x_2} \qquad (68)$$

2. Real liquid mixture, ideal vapor

Activity: generalization of Raoult's law:

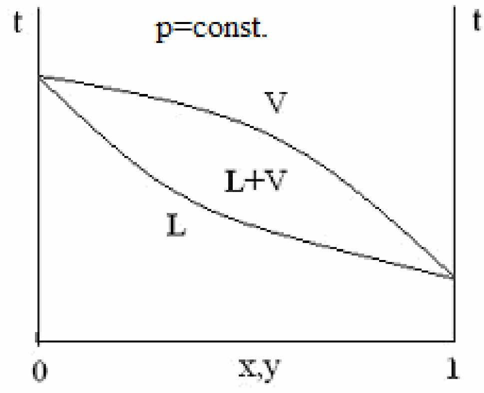
$$p_i = a_i p_i^* = \gamma_i x_i p_i^* \qquad (69)$$

The mole fraction is replaced by ***a*** *(rational) axtivity,* the mole fraction is corrected by the γ (*rational) activity coefficient*. The deviation from the ideal behaviour may be positive ($\gamma>1$) or negatíve ($\gamma<1$), but in a two component system either both components show positive deviation or both have negative one.

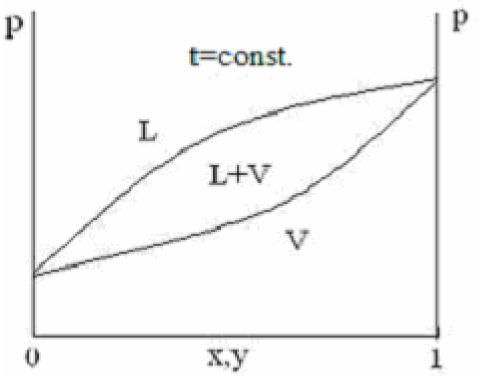
Azeotrop mixture. Sometimes the full pressure of the mixture has an extremum (at the same time also its boiling point) at a composition. At this mole fraction the compositon of the liquid and gas phases are the same. The azeotrop extremum may be maximum (maximal vapour pressure, minimal boiling point) or minimum (minimal vapour pressure, maximal boiling point)

Boiling point diagram (temperature – composition) and vapor pressure (vapor presssre –composition) diagram.

These are the usual diagrams for two component systems.
V: vapour curve; L: liquid curve



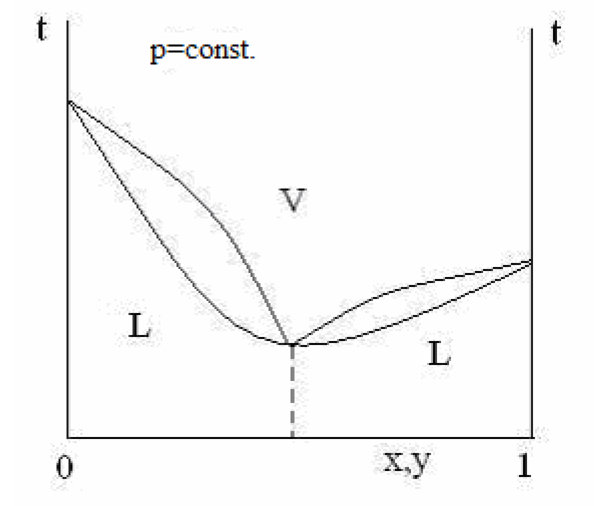
boiling point diagram

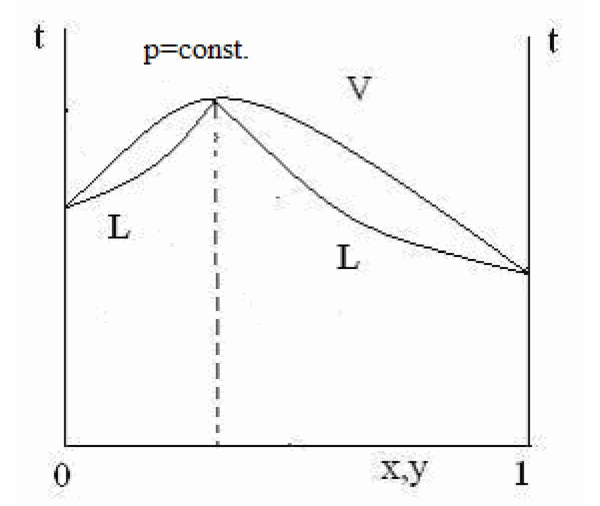


vapor pressure diagram

Azeotrop two component liquid mixtures: the ethanol-water mixture show positive deviation, its minimal boiling point is at 96 % (m/m) ethanol content. The hydrochloric acid – water mixture has maximal boiling point at 8 % (m/m) water content.

Vapor pressure diagrams of azeotrope mixture with vapour pessure maximum and minimum:


t
p=const.
t
V
L
L
0
x,y
1


t
p=const.
t
V
L
L
0
x,y
1

PROBLEMS

H1. At 140 °C the vapour pressure of chlorobenzene is 125,24 kPa, that of bromobenzene (2) 66,10 kPa. Assuming, the tho compounds build ideal mixture, calculate the composition of the mixture boiling at 100 kPa pressure at 140 °C. What is the composition of the vapour at this temperature? (y_1=0,177).

H2. 100 mole benzene-toluene mixture are in a closed piston, the benzene mole fraction is 0.65. The system is heated to 70 °C, the pressure is set to 53,3 kPa. How many material is evaporated? At 70 °C the vapour pressures of pure toluene (2) is 27,5 kPa, that of benzene (1): 72,0 kPa (ideal mixture).

$$x_1 = \frac{p - p_2^*}{p_1^* - p_2^*} = \frac{53{,}3 - 27{,}5}{72{,}0 - 27{,}5} = 0{,}580 \qquad x_2 = 0{,}420$$

$$p_1 = x_1 p_1^* = 0{,}580 \times 72{,}0 = 41{,}76\text{kPa}$$
$$p_2 = x_2 p_2^* = 0{,}420 \times 27{,}5 = 11{,}55\text{kPa}$$
$$y_1 = \frac{p_1}{p} = \frac{41{,}76}{53{,}3} = 0{,}783 \qquad y_2 = 0{,}217$$

Mivel $\frac{n_g}{n_l} = \frac{x_b - x}{y - x_b}$

$$n_l = \frac{y_1 - x_{1,b}}{x_{1,b} - x_1} n_g = \frac{0{,}783 - 0{,}65}{0{,}65 - 0{,}580} n_g = 1{,}90 n_g$$
$$n = n_l + n_g = 1{,}90 n_g + n_g = 2{,}90 n_g = 100\,mol$$
$$n_g = \frac{100}{2{,}90} = 34{,}5\,mol$$

H3. How many benzene must be added to 100 g toluene, so that in a 10 L vessel at 70 °C the vapour pressure of the mixture will be 60 kPa ? At 70 °C the vapor pressure of toluene (2) is: 27,5 kPa, that of benzene (1) 72,0 kPa (ideal mixture). The liquid volume is negligible.

$$p = x_1 p_1^* + (1 - x_1) p_2^*$$
$$x_1 = \frac{p - p_2^*}{p_1^* - p_2^*} = \frac{60 - 27{,}5}{72{,}0 - 27{,}5} = 0{,}730$$
$$x_2 = 0{,}270$$

$$p_1 = x_1 p_1^* = 0{,}730 \times 72{,}0 = 52{,}6\text{kPa}$$
$$p_2 = x_2 p_2^* = 0{,}270 \times 27{,}5 = 7{,}4\text{kPa}$$

$$n_{1,g} = \frac{p_1 V}{RT} = \frac{52,6.10^3 \times 1.10^{-2}}{8,314 \times 343,15} = 0,1844 mol \sim 14,383 g$$

$$n_{2,g} = \frac{p_2 V}{RT} = \frac{7,4.10^3 \times 1.10^{-2}}{8,314 \times 343,15} = 0,02594 mol \sim 2,386 g$$

$$n_g = 0,1844 + 0,02594 = 0,2103 mol \sim 16,769 g$$

$$y_1 = \frac{p_1}{p} = \frac{52,6}{60} = 0,877$$

$$y_2 = \frac{p_2}{p} = \frac{7,4}{60} = 0,123$$

$$n_{2,b} = \frac{m}{M} = \frac{100}{92} = 1,0870 mol \quad toluol$$

$$n_{2,l} = 1,0870 - 0,0259 = 1,0611 mol$$

$$\frac{x_1}{x_2} = \frac{n_{1,l}}{n_{2,l}}$$

$$n_{1,l} = n_{2,l}\frac{x_1}{x_2} = 1,0611 \times \frac{0,730}{0,270} = 2,8689 mol$$

$$n_{1,b} = n_{1,l} + n_{1,g} = 2,8689 + 0,1844 = 3,0533 mol \sim 238,16 g$$

H4. The vapour pressures of carbon disulfide (1) and ethanol (2) at 20 °C are $p_1^* = 39,52\text{kPa}$, and $p_2^* = 5,84\text{kPa}$, respectively. At the same temperature the mixture of composition $x_1=0,40$ begins to boil at the same temperature on 41,33 Pa. Distillating from this mixture a small amount, the vapour composition is $y_1=0,887$. Calculate the rational activity coefficients in the liquid mixture!

$$y_1 = 0,887$$

$$a_1 p_1^* = y_1 p$$

$$a_1 = y_1 \frac{p}{p_1^*} = 0,887 \times \frac{41,33}{39,52} = 0,9276$$

$$\gamma_1 = \frac{a_1}{x_1} = \frac{0,9276}{0,40} = 2,32$$

$y_2=0,113$

$$a_2 p_2^* = y_2 p$$

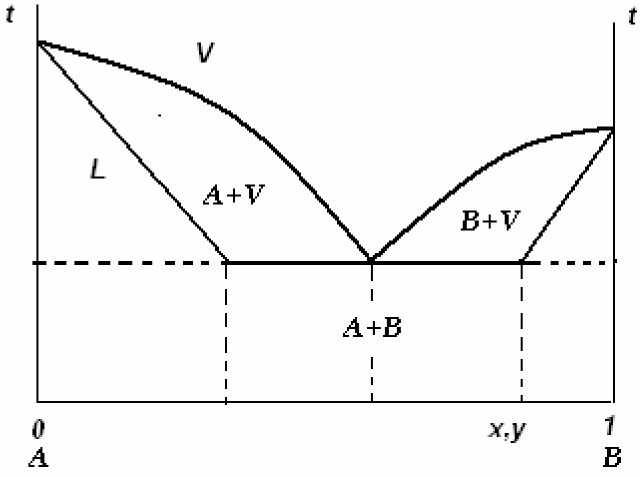
$$a_2 = y_2 \frac{p}{p_2^*} = 0,113 \times \frac{41,33}{5,84} = 0,7997$$

$$\gamma_2 = \frac{a_2}{x_2} = \frac{0,7997}{0,60} = 1,33$$

H5. Acetone (1) and choroform (2) form azeotrop mixture with boiling point 64,7 °C at 101,3 kPa pressure. The vapor pressure of acetone is at this temperature 134,6 kPa, the same of chloroform is 113,0 kPa. Calculate the rational activity coefficients of the two components in liquid phase at the azeotrop composition! Consider the vapor as ideal gas! (0,753; 0,896).

Two component (binary) liquid-gas equilibria with limited miscibility in liquid phase.

The L curve is horizontal line in a wide region of the two-phase liquid. The boiling point and the vapor composition is in this region independent of the liquid composition.



H6. The two phase mixture of 9 moles water (W) and 3 moles organic compound (OC) miscible limited with water is boiling at standard pressure at 87 °C. The mole fraction of water in the OC phase saturated with water is 0,20, while the mole fraction of OC in the W phase saturated with OC is 0,15. The partial pressure of the water in the equilibrium vapour phase is 53,7 kPa. Which phase does run out at first, and how many moles remain then in the liquid from the components? The system is closed, assuming that we increase slowly the volume of a piston, saving the equilibrium pressure.

The mole fraction of water is 0,75, in the W phase 0,85, in the vapor

$$y_W = \frac{53,7}{100} = 0,537$$

Since during the evaporation always less water goes over into the vapor phase in a lower ratio than it corresponds to its brutto compositon, the mole fraction of water increases in the liquid pahs, and 0,85 the organic phase disappears. Only two phases remain. Its mass is calculable with mass balance. If the initial number of all moles n=12, in gas phase n_v, in the liquid n_l, the mass balances is

$$(n_v + n_l) \times 0,75 = 0,537 n_v + 0,85 n_l$$

According to the lever rule: $(0,75 - 0,537) n_v = (0,85 - 0,75) n_l$

$$\frac{n_v}{n_l} = \frac{0,85 - 0,75}{0,75 - 0,537} = 0,469$$

$n = n_v + n_l = 1{,}469 n_l \qquad n = 12 mol$

$n_v = \frac{0{,}469 n_l}{1{,}469 n_l} n = 3{,}83 mol$

$n_l = 12 - 3{,}83 = 8{,}17 mol$

The result is the same if in the lever rule n_v is substituted for $(n - n_l)$. In the remaining W liquid phase

$n_{W,l} = 0{,}85 \times 8{,}17 = 6{,}94$ mol

for the organic compound $n_{OC,l}$=0,15×8,17=1,23 mol

Two component liquid-vapor equlibrium with non miscible liquid phases

In this case the vapor pressure is the sum of the vapor pressures of the two pure components:

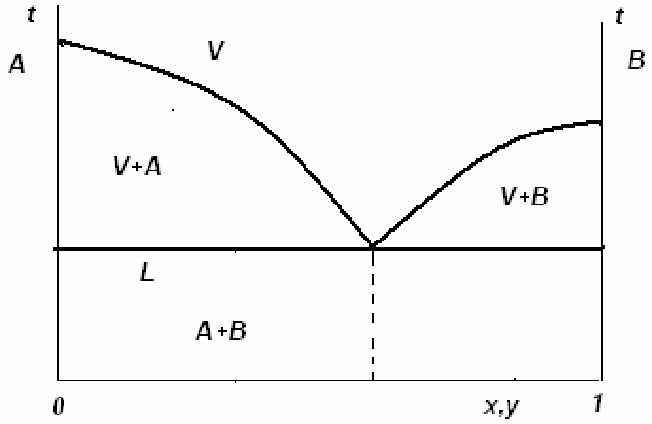
$$p = p_1^* + p_2^* \qquad (70)$$

The L curve is a horizontal line, i.e. the boiling point is independent of the composition of the mixture. The total vapour pressure is greater than any of the pure vapour pressures, the boiling point is always less the same of any pure component. This is the basic idea of the steam distillation.

The vapor (V) curve shows us the temperature where a component begins to condensate at a given composition of vapour. If a component has the mole fraction y in vapor, according to the Claysius-Clapeyron equation

$\ln(1-y) = \lambda/R(1/T - /T_o)$, λ is the heat of vaporization, T_o is its boiling point.

Components A and B:



H7. The following data are given for the water (W) – chlorobenzene (C) mixture:

t / °C	p_V^* /kPa	p_K^* /kPa	p /kPa

90	70,09	27,78	97,87
92	75,59	29,78	105,37
94	81,45	31,90	113,35
96	87,67	34,14	121,81

a./ What is boiling point of the at 105 kPa? Based on the data calculate the full pressure!
At first glance the boiling point is below 92 °C (the vapor pressure is there 105,37 kPa).
The heats of evaporation are since

$$\lambda = R \times \ln\frac{p_2}{p_1} \times \frac{T_1 T_2}{T_2 - T_1}$$

$$\lambda_W = 8{,}314 \times \ln\frac{75{,}59}{70{,}09} \times \frac{363{,}15 \times 365{,}15}{365{,}15 - 363{,}15} = 3{,}772.10^4 \,\mathrm{J/mol}$$

$$\lambda_C = 8{,}314 \times \ln\frac{29{,}78}{27{,}78} \times \frac{363{,}15 \times 365{,}15}{365{,}15 - 363{,}15} = 3{,}832.10^4 \,\mathrm{J/mol}$$

Correction to 105 kPa (very small deviation):

$$\Delta p = \Delta p_W + \Delta p_K = \left(\frac{\lambda_W}{RT^2} p_W + \frac{\lambda_C}{RT^2} p_C\right)\Delta T \qquad (p_W = p_W^* \qquad p_C = p_K^*)$$

$$\Delta T = \frac{RT^2 \Delta p}{p_W \lambda_W + p_C \lambda_C} = \frac{8{,}314 \times 365{,}5^2 \times (-370)}{3{,}772.10^4 \times 75{,}69.10^3 + 3{,}832.10^4 \times 9{,}78.10^3} = 0{,}1026\,\mathrm{K}$$

The correction is only 0,1 K, so the poiling point is 91,9 °C.

b./ How many steam is necessary for the steam distillation of 1 kg chlorobenzene at 105 kPa pressure ?
Partial pressures at 105 kPa:

$$\Delta p_W^* = \frac{3{,}772.10^4 \times 75{,}59.10^3}{8{,}314 \times 365{,}15^2} \times 0{,}1 = 257\,\mathrm{Pa}$$

$$\Delta p_C^* = \frac{3{,}832.10^4 \times 29{,}78.10^3}{8{,}314 \times 365{,}15^2} \times 0{,}1 = 102{,}9\,\mathrm{Pa}$$

at the boiling point 365,05 K (91,9 °C)

$$p_C^* = 29{,}78.10^3 - 102{,}9 = 29{,}68\,\mathrm{kPa}$$

$$p_W^* = 75{,}59.10^3 - 257 = 75{,}33\,\mathrm{kPa}$$

M_C=112,45 g/mol.

$$\alpha = \frac{p_W}{p_C} = \frac{75{,}33}{29{,}68} = 2{,}5377$$

$$n_C = \frac{1000}{112{,}45} = 8{,}893\,\mathrm{mol}$$

$$n_W = \alpha n_C = 2{,}5377 \times 8{,}893 = 22{,}57\,\mathrm{mol} = 18 \times 22{,}57 = 406{,}2\,\mathrm{g}$$

c./ At what temperature begins to boil the system of n_W=4 mole and n_C= 6 mole at 105 kPa pressure? Since the boiling point is independent of the composition, 91,9 °C. The system is closed!

d./What is the composition of the vapor phase?
It depends only on the temperature, therefore

$$y_W = \frac{p^*_W}{p} = \frac{75,32}{105} = 0,719 \qquad y_C=0,283$$

e./ Which phase does disappear at first during the boiling?
One have to add to 1 mole chlorobenzene α=2,5377 mole water, i.e here is necessar 6 × 2,5377= 15,23 mole water but only 6 moles are in the mixture. There fore the W phase disappears at first.

f./ At which temperature does evaporate the last drop? The system is closed!
That means, the composition does not change during the boiling. One have to look for the temperature where y_W=0,4.

Applying the calculated heat of evaporation for chlorobenzene and from the vapour pressure at 96 °C:

$$\ln p^*_{C,2} = \ln p^*_{C,1} + \frac{\lambda}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln(34,14) + \frac{3,832.10^4}{8,314}\left(\frac{1}{369,15} - \frac{1}{T_2}\right)$$

Calculating for more temperatures

t /°C	T /K	p^*_K /kPa	y_K	y_V
110	383,15	53,876	0,513	0,487
120	393,15	73,928	0,704	0,296
115	388,15	62,906	0,599	0,401≈0,4

The last drop evaporates at 115 °C.

g./ What is the composition of the gas phase at 106 °C and how many moles does it contain? Closed system!

We apply the equation used in point f.! Now T_2=379,15 K.

t /°C	T /K	p^*_C /kPa	y_C	y_W
106	379,15	47,816	0,455	0,545

Since all the water evaporates, $n_{W,l}=0$, $n_{VW,v}=4$ mol.

$$\frac{n_{C,v}}{n_{W,v}} = \frac{y_C}{y_W} \qquad p_W = p - p^*_C$$

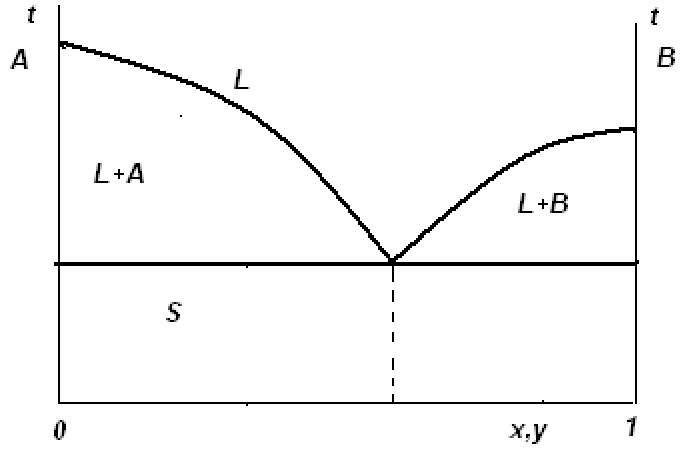
Since there is not water in the liquid phase, its vapor in not in equilibrium with its liquid, so its partial pressure is the difference between vapour pressure and that of the chlorobenzene.

$$n_{C,v} = \frac{y_C}{y_W} n_{W,v} = \frac{0,452}{0,548} \times 4 = 3,34 \text{mol}$$

$$n_{C,l} = 6 - 3,34 = 2,66 \text{mol}$$

Liquid-solid equilibrium

Here we use the freezing point diagrams. It should be have theoretically the same form like the boiling point diagrams of the two component vapour-liquid diagrams. The ideal mixing is in the solid state rare, the systems with limited miscibility or not miscible in solid state are more common. The last ones have minimal freezing points, called eutectic points. The mixture of eutectic composition behaves in freezing like a pure component (but only in freezing!), similarly to a mixture with minimal boiling point. The diagram



If the liquid phase is an ideal mixture, the freezing point depression can be calculated in good approach as

$$\ln(1-x)=\frac{\Delta H^0}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)=\frac{\Delta H^0}{R}\frac{T-T_0}{T_0T} \qquad (71)$$

x is the mole fraction of the solute, ΔH^0 is the heat of fusion of the solvent, T_0 is the freezing point of the solvent, T is that of the solution. If x is small,.

$$x=\frac{\Delta H^0}{RT_0^2}\Delta T \qquad (72)$$

is a good approach.

The concentration of the solvent is often molality (m) given. The molality is the amount of the solute in moles, in 1 kg solvent. So the freezing point depression is

$$\Delta T=\Delta T_m m \qquad (73)$$

where ΔT_m is the characteristic freezing point depression of the solvent in molality.

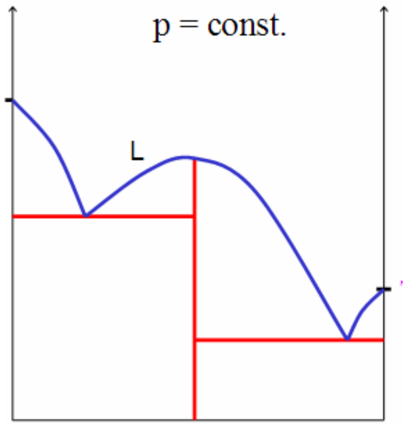
$$\Delta T_m=\frac{RT_0^2}{\Delta H^0}\frac{M}{1000}=\frac{RT_0^2}{q_{sl}} \qquad (74)$$

M the amount of the solvent in moles, q_{sl} is the heat of fusion of 1 kg solvent..

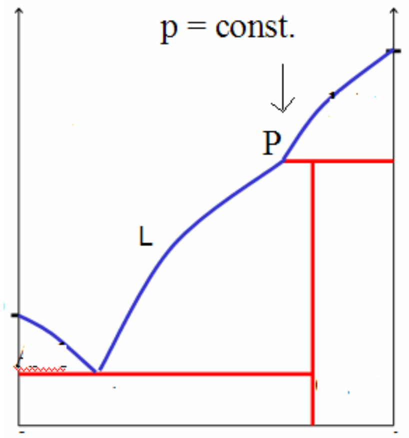
The left and right part of the L curve cut one another. The undercooling is often the case, in this case the curve continues below the eutectic point. If a small crystal (seed) of one component is thrown in the undercooled solution the solid phase begins to crystallize and the temperature heats to the eutectic one. Glasses are regarded as undercooled lquids.

Special freezing point diagrams.

Congruent melting: a compound (adduct) is formed in the solid phase from the two compounds. E.g. Ga+As is in equilibrium with GaAs. The freezing (L) curve has a maximum.



Incongruent melting: during the cooling a compound is formed from the liquid mixture, it begins to appear at the peritectic (P) point, a break on L curve, from K and Na Na_2K i9s formed. The diagram:



PROBLEMS

I1. Naphtalene (N) **and** p-dichlorobenzene (P) form ideal eutecticum. Naphtalene m.p. 80,2 °C, heat of fusion 19,0 kJ/mol, p-dichlorobenene m.p. 53,2 °C, heat of fusion 18,26 kJ/mol. Calculate the freezing point of the mixture with 55 % (n/n) p-dichlorobenzene content!

Look for the eutectic point (composition and temperature)! According to Eq. (71)

$$\ln(1-x)=\frac{\Delta H^0}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)=\frac{\Delta H^0}{R}\frac{T-T_0}{T_0T} \qquad (1)$$

Substitute for (1-x) the mole fraction of the solvent (ideal eutecticum) for both components. Expressing the temperature of the eutecticum in $1/T_0$, the two equations should be equal, therefore:

$$\frac{1}{T_P}-\frac{R\ln x_P}{\Delta H_N^0}=\frac{1}{T_N}-\frac{R\ln x_N}{\Delta H_P^0}$$

Considering that $x_N=1-x_P$,

After alteration

$$x_P^{\frac{\Delta H_P^0}{\Delta H_N^0}}=\exp\left(\frac{\Delta H_p^0}{R}\times\frac{T_N-T_P}{T_N T_P}\right)\times(1-x_P),$$

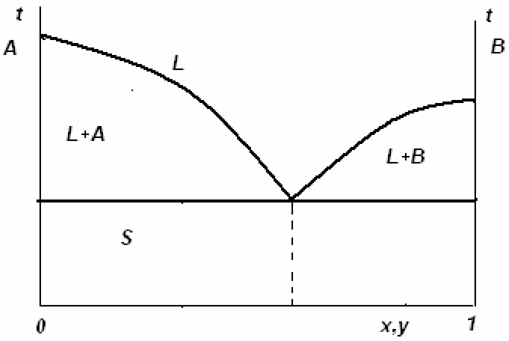
Subsituting $x_P=0,55$, the inequality is $0,5629 < 0,7526$;
substituting e.g. $x_P=0,70$, the inequality is $0,7098 > 0,5017$. Therefore the eutectic point is between these values. $x_P=0,55$ is on the naphthalene side of the eutectic point. Therefore naphthalene is the solvent. We have to increase x_p from 0,55 for have the equality.

Expressing 1/T from Eq. (1) and substituting:

$$\frac{1}{T}=\frac{1}{T_N}-\frac{R\,ln(1-x_P)}{\Delta H_N^0}=\frac{1}{353,35}-\frac{8,314\times ln(1-0,55)}{19000}=3,1797\,K^{-1}$$

T=314,5K=41,6°C

I2. O-nitrotoluene (O, m.p. –4,45 °C) and p-nitrotoluene (P, m.p 51,4 °C) form ideal eutecticum (E) , with melting point –15,2 °C, and 30,5 % (m/m) p-nitro-toluene content. How meny pure P compound can be yielded from 1 kg O-P mixture (M), having as melting point 12 °C, during heating to the temperature of the eutecticum?



We are at the side of P, this is the solvent. Namely, the melt has 12 °C m.p., this is over the m.p. of M is over m.p. of O but below the m.p. of P. Therefore during heating the heating curve can cross the L curve only on the P side. Since the molar masses of the two components is equal, the mass% is equal to the mol% .

Calculation at the P side

$$\Delta H_P^0 = R.ln\left(1-x_{E,O}\right)\frac{T_P T_E}{T_E - T_P} = 8{,}314 \times ln(1-0{,}695)\frac{324{,}55\times 257{,}95}{257{,}95-324{,}55} = 12410 Jmol^{-1}$$

$$\ln\left(1-x_{M,O}\right) = \frac{\Delta H_P^0}{R}\left(\frac{T_M - T_P}{T_P T_M}\right) = \frac{12410}{8{,}314}\times\frac{285{,}15-324{,}55}{324{,}55\times 285{,}15} = -0{,}6355$$

$x_{M,P} = 1 - x_{M,O} = 0{,}5297 \qquad x_{M,O} = 0{,}4703$

Eutecticum and P will precipite.

1000 g mixture contains 470,3 g O. All this amount is in the euteticum. Since its mole fraction in M is 0,695 (1-0,305), the mass of the eutecticum is $\frac{470{,}3}{0{,}695}$ = 676,7 g. The remaining mass of the mixture appears as solid P ,i.e. we have separately the remaining 1000-676,7=323,3 g. pure P.

I3. Meta(M)- and p-nitroaniline (P) form ideal eutecticum (E), with x_M=0,614, t_E=90 °C. parameters. 1 kg melt is cooled from 150 °C in an experiment, the components are m- és p-nitro-anilines, the composition is unknown. The crystallization began at 100 °C. The cooling is continued until the temperature arrives that of the eutecticum. Two type of crystals are found

a./ 374 ± 5 g ,
b./ 100 ± 5g
Questions: A./ Wat was the composition of the mixture?
B./ What was the composition of the resulted crystals?

Compound	Freezing point /°C	Heat of fusion / kJ.mol^{-1}
m-nitro-anilin	114,0	23,69
p-nitro-anilin	147,3	21,08

1.

$$\ln(1-x_M)=\frac{\Delta H_P^0}{R}\times\frac{T-T_P}{T_PT}=\frac{21080}{8,314}\times\frac{373,15-423,15}{423,15\times 373,15}=-0,8029$$

x_P=1-x_M=0,4480 x_M=0,5520

We are at the P side of E. The composition of the original mixture

m_M=1000×0,5520=552,0 g m_P=1000-552,0=448,0 g

Using the lever rule for the original mixture

$$m_E=\frac{1,0-m_P}{1,0-m_{E,P}}=\frac{1,0-0,448}{1,0-0,386}\times 1000=899,0\text{g}$$

$$m_P=\frac{m_P-m_{E,P}}{1,0-m_{E,P}}=\frac{0,448-0,386}{1,0-0,386}\times 1000=101,0\text{g}$$ crystal are yielded

2.

$$\ln(1-x_P)=\frac{\Delta H_M^0}{R}\times\frac{T-T_M}{T_MT}=\frac{23690}{8,314}\times\frac{373,15-387,15}{387,15\times 373,15}=-0,2761$$

$x_M=1-x_P=0,7587$ $x_P=0,2413$

We are at the M side of the E. The composition of the original mixture:

m_M=1000×0,7587=758,7 g m_P=1000-758,7=241,3 g

Calculation of the mass of the produced crystals:

$$m_E=\frac{m_P-0,0}{1,0-m_{E,M}}=\frac{0,2413-0,0}{1,0-0,614}\times 1000=625,1g$$

and

$$m_M=\frac{m_{E,P}-m_P}{m_{E,P}-0,0}=\frac{0.386-0,2413}{0,386-0,0}\times 1000=374,9g$$

CHEMICAL EQUILIBRIUM

Activities

$a_i = \frac{p_i}{p^0}$ ideal gas, p^0= standard pressure, a_i dimensionless (75)

$a_i = \frac{f_i}{p^0}$ real gas a_i= activity, f_i=fugacity (76)

$a_i = x_i$ ideal mixture (77)

$a_i = {}^x\gamma_i x_i$ real mixture ${}^x\gamma_i$ = activity coefficient (78)

$a_i = \frac{{}^c\gamma_i c_i}{c^0}$ mixture, chemical concentration (79)

c^0 = unit chemical concentration, mole solute / dm^3 mixture

$a_i = \frac{{}^m\gamma_i m_i}{m^0}$ (molality) m^0=unit molality, 1 mol solute /kg solvent (80)

The equilibrium constant

$\sum_A \nu_A M_A = \sum_B \nu_B M_B$ ν=stoichiometric coefficient (81)

$$K = K_a = \frac{\prod_B a_B^{\nu_B}}{\prod_A a_A^{\nu_A}} = \frac{\prod_B \left(\frac{{}^c\gamma_B c_B}{c^0}\right)^{\nu_B}}{\prod_A \left(\frac{{}^c\gamma_A c_A}{c^0}\right)^{\nu_B}} = K_\gamma K_c \left(c^0\right)^{-\Delta\nu} \quad (82)$$

$$K_\gamma = \frac{\prod_B \left({}^c\gamma_B\right)^{\nu_B}}{\prod_A \left({}^c\gamma_A\right)^{\nu_A}} \qquad K_c = \frac{\prod_B \left(c_B\right)^{\nu_B}}{\prod_A \left(c_A\right)^{\nu_A}} \qquad \Delta\nu = \sum_B \nu_B - \sum_A \nu_A \quad (83)$$

K_y is dimensionless but depends on pressure (excluding Δν=0), it is practical to use at constant pressure; K_p has dimension, it is practical to use at constant volume.

PROBLEMS

J1. Calculate the equilibrium constant of the reaction $C_3H_8 = CH_4 + C_2H_4$ at 960 K using data of Table 2.

$$\mu_T^0 = a(-x.y) - b\left(\frac{x^2}{2}\right) - c\left(\frac{1}{2x}\right) - d\left(\frac{x^3}{6}\right) + H(+) - S(+)x \qquad kJ/mole$$

$$x = \frac{T[K]}{1000} \quad y=\ln(T[K])-1 \quad \Delta_r\mu_T^0 = \sum_B \nu_B \mu_{T,B}^0 - \sum_A \nu_A \mu_{T,A}^0 \qquad \Delta_r\mu_T^0 = -RT\ln K$$

It is practical to collect the data in table since they are better applicable and this accelerates the calculations. The stoichiometric coefficients of the molecules in the reaction equation are placed in the left first column, products with positive, reactants with negative sign.

The other columns contain the constants of the molecules from Table 2.

How to calculate?

1. Calculate the x and y constants according to the above equations.

2. Fill the table with the stoichiometric coefficients and the data from Table 2.

3. Summing of the molecular constants a, b, c, d, H(+) and S(+) by columns multiplying the data with the corresponding stoichiometric coefficient of the molecules. Write the results in the Sum line.

4. Calculate the coefficients of the a, b, c, d, H(+) and S(+) quantities according to the above equation for the standard chemical potentials, and write the results int he Multiplier line.

5. Multiply the data in Sum line with those in the Multiplier line. Write the products in the Product line.

6. The sum of the data in Product line is the standard chemical potential of the reaction in kJ/mole. Multiply it with 1000 for get it J/mole for the calculation of the equilibrium constant.

7. Calculate the equilibrium constant using the above equation.

Number of: mol. .types 3

Temperature: 960 K x= 0,960 y= 5,8669

Molecule	ν	a	b	c	d	H(+)	S(+)
CH_4	1	11,933	77,647	0,142	-18,414	-81,242	96,731
C_2H_4	1	39,292	57,128	-1,297	0	33,863	-28,868
C_3H_8	-1	19,008	224,48	-0,582	-66,467	-120,855	94,474
Sum		32,217	-89,705	-0,573	48,053	73,476	-26,611
Multiplier		-5,6323	-0,4608	-0,5208	-0,1475	1	-0,96
Product		-181,454	41,3361	0,2984	-7,0857	73,476	25,5466

$\Delta_r\mu_T^0$	-47,883 kJ/mole	*1000 to J/mole
ln(K)	5,9993	
K	403,15	

J2. Calculate the equilibrium constant of the reaction $2H_2O=2H_2+O_2$ at 1500 K using the dta in Table 2! $(3{,}27.10^{-12)}$

J3. Calculate the equilibrium constant of the reaction $2KHCO_3(s)=K_2CO_3(s)+CO_2+H_2O$ at 389,5 K using the data of Table 2!

$$\mu_T^0 = a(-x.y) - b\left(\frac{x^2}{2}\right) - c\left(\frac{1}{2x}\right) - d\left(\frac{x^3}{6}\right) + H(+) - S(+)x \qquad kJ/mol$$

$$x = \frac{T[K]}{1000} \quad y = \ln(T[K]) - 1$$

Number of molec. types: 4

Temperature: 389.5 K x= 0.3895 y= 4.9649

Constants from Table 2

Molecule	ν	a	b	c	d	H(+)	S(+)
$K_2CO_{3(s)}$	1	97.947	92.090	-0.978	0.000	-1187.626	-435.556
CO_2	1	51.128	4.368	-1.469	0.000	-413.886	-87.078
$H_2O(g)$	1	34.376	7.841	-0.423	0.000	-253.871	-11.750
$KHCO_{3(s)}$	-2	47.698	143.093	0.000	0.000	-985.420	-198.925
Sum		88.055	-181.887	-2.870	0.000	115.457	-136.534
Multiplyer		-1.934	-0.076	-1.284	-0.010	1.000	-0.390
Product		-170.282	13.797	3.684	0.000	115.457	53.180

$\Delta_r\mu^o_T$=	15.8362 kJ/mole	Multiply with 1000!
ln(K)=	-4.8903	
K =	$7{,}51926.10^{-3}$	$(7{,}52.10^{-3})$

Disszociation and the ratio of conversation (dissociation)

Example: $PCl_5=PCl_3+Cl_2$; t=250 °C

K=1,13 (dissociaton constant) $K = K_\gamma K_y\left(\frac{p}{p^0}\right)^{\Delta\nu}$ We assume ideal mixture of ideal gases, therefore $K_\gamma=1$, and Dalton's law is valid.

J4. The ratio of the components in the initial mixture is $PCl_5:Cl_2=1:2$

a./ What is the ratio of dissociation at 200 kPa constant pressure?

Since the pressure is constant, p_0=200 kPa, the application of K_y is practical.

$$K = \left(\frac{p_0}{p^0}\right)^{\Delta\nu} K_y$$

$$\sum_A \nu_A M_A = \sum_B \nu_B M_B$$

$$K_y = \frac{\prod_B y_B^{\nu_B}}{\prod_A y_A^{\nu_A}}$$

$$\Delta\nu = +1 \quad p^0 = 100\text{kPa}$$

Starting with pure PCl_5:

	PCl_5	PCl_3	Cl_2	Σ
Initial molar ratio	1	0	0	1
Equilibrium molar ratio	$1-\alpha$	α	α	$1+\alpha$
Equlibrium mole fraction	$\frac{1-\alpha}{1+\alpha}$	$\frac{\alpha}{1+\alpha}$	$\frac{\alpha}{1+\alpha}$	1

$$K_y = \frac{y_{PCl_3} \cdot y_{Cl_2}}{y_{PCl_5}} = \frac{\frac{\alpha}{1+\alpha} \times \frac{\alpha}{1+\alpha}}{\frac{1-\alpha}{1+\alpha}} = \frac{\alpha^2}{(1-\alpha)(1+\alpha)} = \frac{\alpha^2}{1-\alpha^2}$$

$$K = \left(\frac{p}{p^0}\right)^{\Delta\nu} \frac{\alpha^2}{1-\alpha^2} = \frac{2\times10^5}{1\times10^5}\frac{\alpha^2}{1-\alpha^2} = 1{,}13$$

$$2\alpha^2 = 1{,}13 - 1{,}13\alpha^2$$

$$\alpha^2 = \frac{1{,}13}{3{,}13}$$

$$\alpha = 0{,}601$$

The initial molar ratio is PCl_5:Cl_2=1:2

	PCl_5	PCl_3	Cl_2	Σ
Initial molar ratio	1	0	2	3
Equlibrium molar ratio	$1-\alpha$	α	$2+\alpha$	$3+\alpha$
Equilibrium mole fraction	$\frac{1-\alpha}{3+\alpha}$	$\frac{\alpha}{3+\alpha}$	$\frac{\alpha}{3+\alpha}$	**1**

$$K_y = \frac{\frac{\alpha}{3+\alpha} \times \frac{2+\alpha}{3+\alpha}}{\frac{1-\alpha}{3+\alpha}} = \frac{\alpha(2+\alpha)}{(1-\alpha)(3+\alpha)} = \frac{2\alpha+\alpha^2}{3-2\alpha-\alpha^2}$$

$$K = \left(\frac{p_0}{p^0}\right)^{+1} \frac{2\alpha+\alpha^2}{3-2\alpha-\alpha^2} = \frac{2\times10^5}{1\times10^5}\frac{2\alpha+\alpha^2}{3-2\alpha-\alpha^2} = 1{,}13$$

$$4\alpha + 2\alpha^2 = 3{,}39 - 2{,}26\alpha - 1{,}13\alpha^2$$
$$3{,}13\alpha^2 + 6{,}26\alpha - 3{,}39 = 0$$
$$\alpha = \frac{-6{,}26 \pm 9{,}035}{6{,}26} = -1 \pm 1{,}443$$

$\alpha_1 = 0{,}443 \qquad \alpha_2 = -2{,}443$ (meaningless result)

b./ What is the ratio of dissociation at constant volume and 200 kPa initial pressure?

The volume is constant, it is practical to calculate with K_p; p_0=200 kPa.

$$K = (p^0)^{-\Delta\nu} K_p$$
$$\sum_A \nu_A M_A = \sum_B \nu_B M_B$$
$$K_p = \frac{\prod_B p_B^{\nu_B}}{\prod_A p_A^{\nu_A}}$$

Starting with pure PCl$_5$:

	PCl_5	PCl_3	Cl_2	Σ
Initial molar ratio	1	0	0	1
Equilibrium molar ratio	1-α	α	α	1+α
Equilibrium pressure	$p_0(1-\alpha)$	$p_0\alpha$	$p_0\alpha$	$p_0(1+\alpha)$

$$K_p = \frac{p_0\alpha \times p_0\alpha}{p_0(1-\alpha)} = p_0\frac{\alpha^2}{(1-\alpha)}$$

$$K = (p^0)^{-\Delta\nu} p_0 \frac{\alpha^2}{1-\alpha} = \frac{2\times10^5}{1\times10^5}\frac{\alpha^2}{1-\alpha} = 1{,}13$$

$$2\alpha^2 = 1{,}13 - 1{,}13\alpha$$
$$2\alpha^2 + 1{,}13\alpha - 1{,}13 = 0$$
$$\alpha = \frac{-1{,}13 \pm 3{,}212}{4}$$

$\alpha_1 = 0{,}520 \qquad \alpha_2 = -1{,}086$ (meaningless result)

Starting with PCl$_5$:Cl$_2$=1:2:

	PCl_5	PCl_3	Cl_2	Σ
Initial molar ratio	1	0	2	3
Initial pressure	$\frac{1}{3}p_0$	0	$\frac{1}{3}.2p_0$	p_0
Equilibrium molar ratio	1-α	α	2+α	3+α
Equilibrium pressure	$\frac{1}{3}p_0(1-\alpha)$	$\frac{1}{3}p_0\alpha$	$\frac{1}{3}p_0(2+\alpha)$	$\frac{1}{3}p_0(3+\alpha)$

$$K_p = \frac{\frac{1}{3}p_0\alpha \times \frac{1}{3}p_0(2+\alpha)}{\frac{1}{3}p_0(1-\alpha)} = \frac{1}{3}p_0\frac{\alpha(2+\alpha)}{(1-\alpha)}$$

$$K = \left(p^0\right)^{-\Delta\nu}\frac{1}{3}p_0\frac{\alpha(2+\alpha)}{1-\alpha} = \frac{\frac{1}{3}2\times10^5}{1\times10^5}\frac{\alpha(2+\alpha)}{1-\alpha} = 1{,}13$$

$$4\alpha + 2\alpha^2 = 3{,}39 - 3{,}39\alpha$$

$$2\alpha^2 + 7{,}39\alpha - 3{,}39 = 0$$

$$\alpha = \frac{-7{,}39 \pm 9{,}041}{4}$$

$\alpha_1 = 0{,}412$ $\alpha_2 = -4{,}108$ (meaningless result)

J5. What is the full pressure in the equilibrium gas mixture, if ***PCl_3* *és a* *Cl_2*** *are equimolar?*

a./ The partial pressure of PCl_5 is 0,1 MPa

Let regard the volume constant, it is practical to use K_p. The initial pressure is p_0.

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

$$\sum_A \nu_A M_A = \sum_B \nu_B M_B$$

$$K_p = \frac{\prod_B p_B^{\nu_B}}{\prod_A p_A^{\nu_A}}$$

	PCl_5	PCl_3	Cl_2	Σ
Initial molar ratio	1	0	0	1
Equilibrium molar ratio	1-α	α	α	1+α
Equilibrium pressure	$p_0(1-\alpha)$	$p_0\alpha$	$p_0\alpha$	$p_0(1+\alpha)$

$$\Delta\nu = 1$$

$$K_p = \frac{p_0\alpha \times p_0\alpha}{p_0(1-\alpha)}$$

$$K = \left(p^0\right)^{-1} p_0 \frac{\alpha^2}{1-\alpha}$$

For PCl$_5$:

$$p_{PCl_5} = (1-\alpha)p_0 = 10^5\,\text{Pa} \quad p_0 = \frac{10^5}{1-\alpha}$$

$$K = \left(p^0\right)^{-1} p_0 \frac{\alpha^2}{1-\alpha} = \frac{1}{10^5}\frac{10^5}{1-\alpha}\frac{\alpha^2}{(1-\alpha)^2} = 1{,}13$$

$$\frac{\alpha}{1-\alpha} = 1{,}0630$$

$$\alpha = 0{,}515$$

$$p_0 = 2{,}063 \times 10^5\,\text{Pa}$$

$$p = p_0(1+\alpha) = 2{,}063 \times 10^5 \times 1{,}515 = 312{,}5\,\text{kPa}$$

b./Yet inert gas with ***0,1MPa pressure is added.***

$$p_2 = p + p_k = 412{,}5\,\text{kPa}$$

K does not change, neither the partial pressures change at constant volume.

Further remarks:

1. K depends only on temperature.
2. The same chmical reaction may describe in several equivalent forms, e.g.. az like $N_2 + 3H_2 = 2NH_3$ or $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$.

The dividing with 2 means the equilibrium constant of the second equation is the square root of the first.

3. The values of the stoichiometric coefficients must be considered in the description of the equilibrium state: Let $2SO_2 + O_2 = 2SO_3$. Let mix at constant pressure SO_2 and O_2 (in presence of catalyst) in 3:1 ratio. If part α of oxygen is converted then in the equilibrium the participation of SO_2 is $3-2\alpha$, that of SO_3 is 2α, and from oxygen $1-\alpha$.