

# Mixtures

## Lectures in Physical Chemistry 5



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## Mixing

**DEF** mixtures: macroscopically homogeneous, multicomponent systems

No chemical reactions during the mixing,  
but changes in the structure of the liquid are possible  
(e.g. changing hydrogen bonds)

**DEF** unlimited mixing: perfect mixing at all ratios

**DEF** limited mixing: mixing only between some limits of concentrations

**DEF** solubility: maximal concentration of a compound in a mixture

If in a mixture the concentration of one of the components  
is much higher than that of the others:

⇒ this component is called the solvent

⇒ component in small concentration is called the solute

⇒ the mixture is called the solution

## Concentration units

### DEF mass fraction:

mass of the component divided by the total mass of the mixture.

The sum of the mass fractions of all components is equal to one.

Mass percentage (% , m/m%) is equal to the mass fraction times 100

### DEF mole fraction ( $x$ ): number of moles of the component divided by the total number of moles of the mixture.

The sum of the mole fractions of all components is equal to one.

Mole percentage (mol%) is equal to the mole fraction times 100.

### DEF molarity ( $c$ , [mol dm<sup>-3</sup>]) number of moles in 1 dm<sup>3</sup> **solution**.

Volume increases with increasing temperature

⇒ molarity is a function of temperature

### DEF Raoult concentration or molality ( $m$ , [mol kg<sup>-1</sup>])

number of moles in 1 kg **solvent**.

Low concentration solution with water solvent

$\rho/g\text{ cm}^{-3} \approx \rho(\text{water})/g\text{ cm}^{-3} \approx 1 \Rightarrow m$  and  $c$  have similar values

## Change of extensive properties at mixing

Change of extensive property  $Y$   
due to mixing:

$$\Delta Y = Y - \sum_i n_i Y_{m,i}^*$$

$Y$   $Y$  of the mixture

$Y_{m,i}^*$  molar  $Y$  of pure component  $i$

$n_i$  amount of matter of the component

$\Delta Y$  change of  $Y$  due to mixing

$\Delta Y$  can be for example:

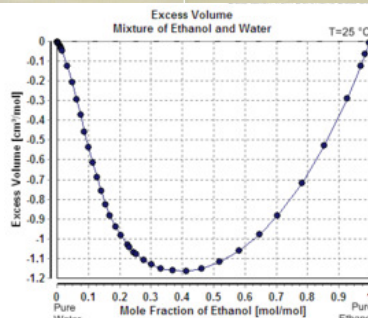
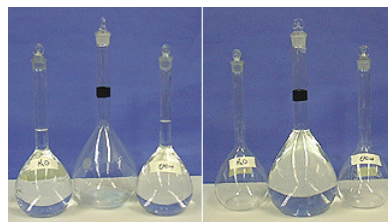
$\Delta H$  enthalpy of mixing

$\Delta V$  volume change of mixing

$\Delta S$  entropy of mixing

### ethanol–water volume change at mixing

$$\Delta V = V - (n_{\text{v\acute{e}z}} V_{m,\text{v\acute{e}z}}^* + n_{\text{etanol}} V_{m,\text{etanol}}^*)$$



## Gibbs free energy of mixing

At constant pressure and temperature, the formation of mixtures is accompanied with the decrease of Gibbs free energy.  
Of course, since mixing is a spontaneous process.

Gibbs free energy of mixing:

$$\Delta G = G - \sum_i n_i G_{m,i}^* < 0$$

$G$  Gibbs free energy of the mixture  
 $G_{m,i}^*$  the Gibbs free energy of component  $i$  in its pure form  
 $n_i$  amount of matter (number of moles) of component  $i$   
 $\Delta G$  Gibbs free energy of mixing

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## Ideal mixtures

**DEF** Ideal mixture: a mixture is ideal if at constant  $p, T$  the Gibbs free energy of mixing can be calculated by

$$\Delta G = nRT \sum_i x_i \ln x_i$$

$0 < x_i < 1 \Rightarrow \ln x_i$  negative  $\Rightarrow x_i \ln x_i$  negative  $\Rightarrow \Delta G$  negative  
 $\Rightarrow$  **G always decreases at mixing**

interpretation of ideal mixtures (this is not the definition!):

in ideal mixtures the interactions between the different kind of particles are identical to those of the same kind of particles.

Almost ideal mixtures are formed at the mixing of chemically similar compounds (e.g. mixtures of hydrocarbons of similar molecular weight).

Example: benzene (B) – toluene (T) mixture: the B-B intermolecular interactions are similar to those of the T-T and B-T interactions.

**Warning!** These interactions are significant, unlike in the mixtures of ideal gases!

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## $\Delta H = 0$ and $\Delta V = 0$ at the formation of ideal mixtures

temperature dependence of  $G$   
(Gibbs–Helmholtz equation) :

$$\left( \frac{\partial}{\partial T} \frac{\Delta G}{T} \right)_p = -\frac{\Delta H}{T^2}$$

$$-\frac{\Delta H}{T^2} = \left( \frac{\partial}{\partial T} \frac{\Delta G}{T} \right)_p = \left( \frac{\partial}{\partial T} nR \sum_i x_i \ln x_i \right)_p = 0 \quad \text{therefore always } \Delta H=0$$

pressure dependence of  $G$ :

$$\left( \frac{\partial \Delta G}{\partial p} \right)_T = \Delta V$$

$$\Delta V = \left( \frac{\partial \Delta G}{\partial p} \right)_T = \left( \frac{\partial}{\partial p} nRT \sum_i x_i \ln x_i \right)_T = 0 \quad \text{therefore always } \Delta V=0$$

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## Entropy of mixing

$\Delta G$  of mixing  
for ideal mixtures

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = 0$$

$$\Delta G = -T\Delta S \Rightarrow \Delta S = -\Delta G / T$$

$$\Delta G = nRT \sum_i x_i \ln x_i$$

Entropy of mixing for ideal mixtures:  $\Delta S = -nR \sum_i x_i \ln x_i$

$0 < x_i < 1 \Rightarrow \ln x_i$  negative  $\Rightarrow x_i \ln x_i$  negative  $\Rightarrow \Delta S$  always positive  
 $\Rightarrow$  **S always increases at mixing**

### Real mixtures:

- $\Delta V$  and  $\Delta H$  are not zero
- $\Delta G$  and  $\Delta S$  cannot be calculated with the equations above

### Famous real mixtures:

ethanol – water mixture:  $\Delta V$  and  $\Delta H$  are not zero

$\text{H}_2\text{SO}_4$  – water mixture:  $\Delta V$  and  $\Delta H$  are not zero (large heat production at mixing!)

## Partial molar volume

### Thought experiment 1:

Large barrel, filled with water; 1 mole of water is added. What is the change of volume?

volume of 1 mole water (= molar volume of water) = 18 cm<sup>3</sup>

The change of the volume of water is 18 cm<sup>3</sup>.

### Thought experiment 2:

Large barrel, filled with mixture of 50% ethanol – 50% water;

1 mole of water is added. What is the change of volume?

Within the mixture, the volume of 1 mole of water is less.

The change of the volume is 16.9 cm<sup>3</sup> (much less than 18 cm<sup>3</sup>)

Adding 1 mole of water, the composition remains almost identical.



**partial molar volume:** change of the volume, if 1 mole of one of the components is added to the mixture at constant temperature  $T$ , pressure  $p$ , and mixture composition.

- depends on the composition of the mixture
- does not depend on the quantity of the mixture (if the composition does not change)
- depends on which component is added
- it is equal to the molar volume, if component A is added to pure A (e.g., water is added to pure water)

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## Partial molar quantities

**DEF partial molar quantity:** change of an extensive quantity, if 1 mole of component  $i$  is added to the mixture at constant temperature  $T$ , pressure  $p$ , and mixture composition  $n_j$ .

partial molar quantity  $\Rightarrow \bar{Y}_i = \left( \frac{\partial Y}{\partial n_i} \right)_{p, T, n_j}$

$\leftarrow$  change of  $Y$  is investigated

$\leftarrow$  1 mole is added

$\leftarrow$  fixed:  $p$ ,  $T$  and composition

partial molar quantity belonging to the pure component = molar quantity

The partial molar quantities depend on the mixture composition and may be negative as well.

important feature: extensive quantity  $Y$  of a real mixture can be calculated from the partial molar quantities:

$$Y = \sum_i n_i \bar{Y}_i$$

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## Chemical potential

**DEF** chemical potential  $\mu_i$  of component  $i$  of a mixture is the partial molar Gibbs free energy:

$$\text{partial molar Gibbs free energy (chemical potential)} \Rightarrow \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n_j} \begin{array}{l} \leftarrow \text{change of } G \text{ is investigated} \\ \leftarrow 1 \text{ mole is added} \\ \leftarrow \text{fixed: } p, T \text{ and composition} \end{array}$$

### reminder:

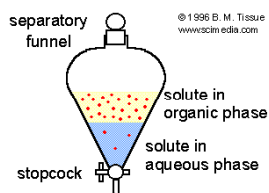
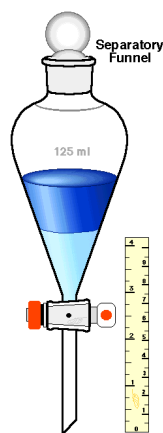
In a single component multiphase system (at constant  $T, p$ ), there is equilibrium among the phases if the molar Gibbs free energy of the species is identical in each phase.

### new law:

In a multicomponent multiphase system (at constant  $T, p$ ), there is equilibrium among the phases if the chemical potential (=partial molar Gibbs free energy) of each species is identical in each phase.

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## Separatory funnel



separatory funnel *or* sep funnel

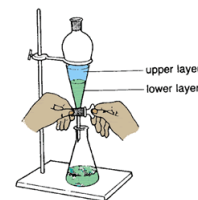
aqueous phase (usually the lower phase) with dissolved non-polar organics  
pure non-polar lipophilic organic solvent (usually the upper phase)

mixing and reaching the equilibrium  
down: low concentration in water  
upper: high concentration in the organic solvent

### IMPORTANT:

The condition of equilibrium is not equal concentrations in the two phases **but the equal chemical potential of the solute in the two phases!**

The concentrations can be very different!



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## Chemical potential in an ideal mixture

Chemical potential of species  $i$  in an ideal mixture:

$$\mu_i = G_{mi}^*(p, T) + RT \ln x_i$$

Consequence:

pure solvent:  $x_1 = 1 \Rightarrow \ln x_1 = 0 \Rightarrow \mu_1 = G_{m1}^*(p, T)$

in this case the chemical potential of the solvent is equal to its molar Gibbs free energy (as a partial molar quantity should behave)

If small amount of solute is dissolved in a solvent, e.g.

$x_2 = 0.01 \Rightarrow x_1 = 0.99 \Rightarrow \ln 0.99 = \text{small negative number}$

chemical potential of the solvent is slightly smaller, than its molar Gibbs free energy

( $x_1$  is the mole fraction of the solvent,  $x_2$  is the mole fraction of the solute)

more solute is dissolved

$x_2$  is larger  $\Rightarrow x_1$  is smaller

chemical potential of the solvent decreases as the mole fraction of the solvent decreases

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## Chemical potential in an ideal mixture 2

Derivation of the equation. You do not have to know it on the test/exam.

Change of  $G$  at mixing:

$$\Delta G = G - \sum_i n_i G_{mi}^* \quad (1)$$

(1) rearranged:

$$G = \sum_i n_i G_{mi}^* + \Delta G \quad (2)$$

definition of an ideal mixture:

$$\Delta G = nRT \sum_i x_i \ln x_i = RT \sum_i n_i \ln x_i \quad (3)$$

(3) inserted to (2):

$$G = \sum_i n_i G_{mi}^* + RT \sum_i n_i \ln x_i \quad (4)$$

(4) rearranged (merged summations):

$$G = \sum_i n_i (G_{mi}^* + RT \ln x_i) \quad (5)$$

definition of the chemical potential:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n_j} \quad (6)$$

Differentiating of  $G$  defined in eq. (5), according to eq. (6). The only remaining term is the multiplying factor of  $n_i$

$$\mu_i = G_{mi}^*(p, T) + RT \ln x_i$$

cf.  $d(ax + by + cz) / dy = b$

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## Chemical potential in a mixture ideal gases

Mixtures of ideal gases are surely ideal mixtures due to the lack of interactions.

The general equation for ideal mixtures:  $\mu_i = G_{mi}^*(p, T) + RT \ln x_i$  (1)

For gases, the molar Gibbs free energy is usually defined at pressure  $p^\theta = 10^5$  Pa:  $G_{mi}^*(p^\theta, T)$

For gases, the composition is usually defined by partial pressures  $p_i$

Therefore, the following equation is better applicable for the calculation of chemical potential in gas mixtures:

$$\mu_i = G_{mi}^*(p^\theta, T) + RT \ln \frac{p_i}{p^\theta}$$

**Derivation** (you do not have to know it on the test/exam):

$x_i = p_i/p$  is inserted to equation (1):

$$\mu_i = G_{mi}^*(p, T) + RT \ln \frac{p_i}{p} = G_{mi}^*(p, T) + RT \ln p_i - RT \ln p \quad (2)$$

pressure dependence of  $G$  for ideal gases (see Lecture 3, page 22) :

$$G_{mi}^*(p, T) = G_{mi}^*(p^\theta, T) + RT \ln \frac{p}{p^\theta} = G_{mi}^*(p^\theta, T) + RT \ln p - RT \ln p^\theta \quad (3)$$

inserting (3) to eq. (2) (term for total pressure  $p$  is eliminated!):

$$\mu_i = G_{mi}^*(p^\theta, T) + RT \ln p_i - RT \ln p^\theta = G_{mi}^*(p^\theta, T) + RT \ln \frac{p_i}{p^\theta} \quad 15$$

## Real mixtures: activity and fugacity

These equations are very nice looking, but applicable for ideal mixtures only:

$$\mu_i = G_{mi}^*(p, T) + RT \ln x_i \quad \text{for gases: } \mu_i = G_{mi}^*(p^\theta, T) + RT \ln \frac{p_i}{p^\theta}$$

**Idea:** we keep these equations (because we like them very much), and start using  $a_i$  „effective mole fraction“ instead of the real mole fraction  $x_i$   
 $f_i$  „effective partial pressure“ instead of the real partial pressure  $p_i$

**Calculation of the chemical potential in real mixtures:**

$$\mu_i = G_{mi}^*(p, T) + RT \ln a_i \quad \text{for gases: } \mu_i = G_{mi}^*(p^\theta, T) + RT \ln \frac{f_i}{p^\theta}$$

$a_i$  : activity („effective mole fraction in real mixtures“); unit: -  
 $f_i$  : fugacity („effective partial pressure in real mixtures“); unit: Pa

If the real mixture is nearly ideal mixture, then the activity / fugacity is almost identical to the mole fraction / partial pressure.

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## Colligative properties

Colligative properties depend only on the quantity of the solute, not on its quality

Colligative properties:

- elevation of boiling point
- depression of freezing point
- osmotic pressure

„elevation of boiling point” and „depression of freezing point” have common origin

The common background of the three colligative properties is that the **chemical potential of the solvent** depends only on the amount of the dissolved matter and is independent of its quality.

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## Reason of the shifts of boiling and freezing points

**ice/water/water vapour/aquatic solution system:**

the molar Gibbs free energy  $G_m$  (or the corresponding chemical potential) as a function of temperature  $T$

we have learned that (see Lecture 3, p. 20):

$$dG_m = V_m dp - S_m dT$$

at constant pressure  $dp = 0$

$$dG_m / dT = -S_m$$

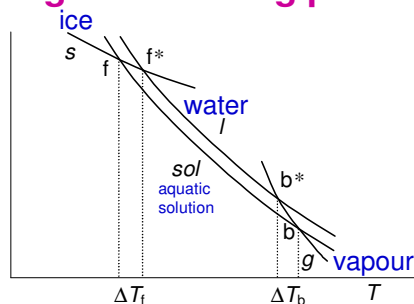
if  $T$  increases, then  $G_m$  (and  $\mu_m$ ) decreases, since  $S_m$  is always positive

ice:	$S_m$ small	$G_m(T)$ function small negative slope
liquid water:	$S_m$ medium	$G_m(T)$ function medium negative slope
water vapour:	$S_m$ large	$G_m(T)$ function large negative slope

The chemical potential of ice and vapour remains identical, those of water decreases if something is dissolved in the liquid water (the curve is shifted downwards):

$$\mu_i = G_{mi}^*(p, T) + RT \ln x_i$$

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## Elevation of boiling point

At a given pressure, the boiling point of the solution is always higher than the boiling point of the pure solvent.

Using the previous figure, from the shift of the crossing of the lines, we may obtain for the elevation of boiling point:

$$\Delta T = \left( \frac{RT^{*2}}{\Delta H_{\text{vap}}} \right) x_2$$

$T^*$  boiling point of the solvent,  $\Delta H_{\text{vap}}$  evaporation enthalpy of the solvent  
 $x_2$  mole fraction of the solute      nothing refers to the quality of the solute!

Some people prefer the usage of molality (Raoult concentration):

$$\Delta T = K_b m_2 \qquad K_b = \frac{RT^{*2} M_1}{\Delta H_{\text{vap}}}$$

$m_2$  molality of the solute,  $M_1$  molar mass of the solvent,  
 $K_b$  ebullioscopic constant

*ebullioscopic constant*  $K_b$  is usually not calculated by the equation above, but measured in a laboratory. It is in water solvent  $K_b = 0.51 \text{ K kg mol}^{-1}$

⇒ dissolving 1 mole solute in 1 kg water elevates boiling point by 0.51 K 19

## Depression of freezing point

At a given pressure, the freezing point of the solution is always lower than the freezing point of the pure solvent.

Using the previous figure, from the shift of the crossing of the lines, we may obtain for the depression of freezing point:

$$\Delta T = \left( \frac{RT^{*2}}{\Delta H_{\text{fus}}} \right) x_2$$

$T^*$  freezing point of the solvent,  $\Delta H_{\text{fus}}$  enthalpy of fusion of the solvent  
 $x_2$  mole fraction of the solute      nothing refers to the quality of the solute!

Some people prefer the usage of molality (Raoult concentration):

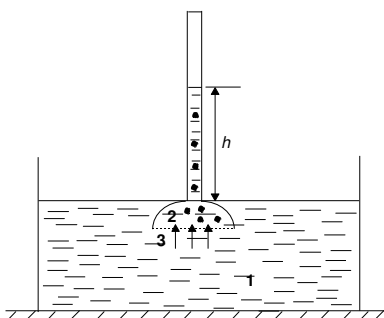
$$\Delta T = K_f m_2 \qquad K_f = \frac{RT^{*2} M_1}{\Delta H_{\text{fus}}}$$

$m_2$  molality of the solute,  $M_1$  molar mass of the solvent,  
 $K_f$  cryoscopic constant

*cryoscopic constant*  $K_f$  is usually not calculated by the equation above, but measured in a laboratory. It is in water solvent  $K_f = 1.86 \text{ K kg mol}^{-1}$

⇒ dissolving 1 mole solute in 1 kg water lowers freezing point by 1.86 K 20

## Osmosis



1 pure solvent  
2 solvent + solute  
3 semipermeable membrane

The solution and the pure solvent is separated by a semipermeable membrane. The membrane is permeable to the molecules of the solvent only. Solvent is flowing through the membrane till high pressure appears inside the membrane.

**DEF** osmotic pressure is the difference of pressures in equilibrium.  
In the arrangement above, the osmotic pressure is the hydrostatic pressure of the liquid column having height  $h$

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## van't Hoff equation for the osmotic pressure

$$\Pi V = n_2 RT \quad \text{or} \quad \Pi = c_2 RT$$

$\Pi$  osmotic pressure,  $R$  gas constant,  $T$  temperature,  $V$  volume of the solution  
 $n_2$  amount of dissolved compound,  $c_2$  concentration of dissolved compound

**derivation of the van't Hoff equation** (you have to know the main ideas!):

Basis approach:  
chemical potential of water  $\mu_1$  increases with increasing pressure  
chemical potential of water  $\mu_1$  decreases with increasing conc. of the solute  
the effects balance each other in **osmotic equilibrium**

$\mu_1$  inside membrane =  $\mu_1$  outside the membrane

$$\mu_1^*(p) + \int_p^{p+\Pi} V_m dp + RT \ln x_1 = \mu_1^*(p)$$

$$\int_p^{p+\Pi} V_m dp = -RT \ln x_1 \Rightarrow \Pi V_m = x_2 RT \Rightarrow \Pi \frac{V}{n} = \frac{n_2}{n} RT$$

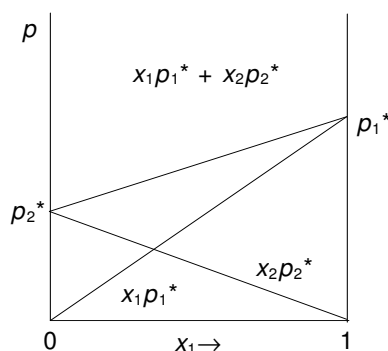
(1) the approximate result of the integration is  $\Pi V$   
(2) if  $x_2 \ll 1$ , then  $\ln x_1 = \ln(1-x_2) \approx -x_2$

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## Raoult's Law

Raoult's Law: In the vapour phase above ideal mixtures, partial pressure  $p_i$  of component  $i$  is decreased proportionally to its mole fraction  $x_i$  in the liquid, compared to equilibrium vapour pressure  $p_i^*$  of the pure component.

$$p_i = x_i p_i^*$$

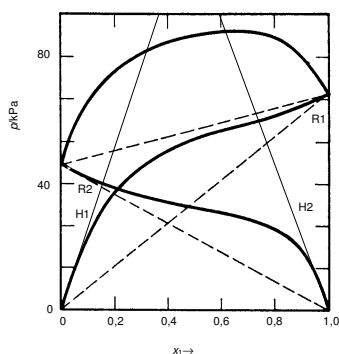


This means that the situation is the simplest possible: from the vapour pressure of pure liquid (1) to the vapour pressure of pure liquid (2) the transition is linear according to the mole fraction of species (1)

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## Henry's Law

Henry's Law: in real mixtures in the vapour phase partial pressure  $p_i$  of a minor compound is proportional to its mole fraction  $x_i$  in the liquid phase.



$$p_i = x_i K_i$$

$K_i$  is called the Henry's Law constant [Pa] refers to species  $i$  in a given mixture

The main application of Henry's Law is the solution of gases in liquids:

(e.g.  $O_2$  in water,

$N_2$  in the blood of a diver:

see „decompression sickness” (DCS))

Carbon disulfide ( $CS_2$ ) (1)–acetone (2) mixture: vapour pressure vs. composition

lower thick curves: partial pressures

upper thick curve: total pressure

R1, R2 (dashed lines): lines corresponding to Raoult's Law (not applicable here!)

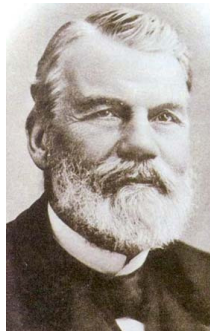
H1, H2 (thin lines): lines corresponding to Henry's Law

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## van't Hoff – Raoult – Henry



Jacobus Henricus van 't Hoff  
(1852 –1911)  
Holland physicist and chemist  
first Nobel prize in chemistry, 1901



François-Marie Raoult  
(1830 - 1901)  
French chemist

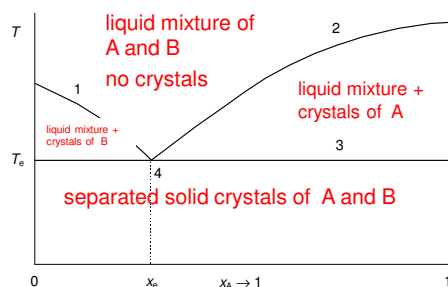


William Henry  
(1774 –1836)  
English chemist

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## Eutectics

Two or several compounds form an eutectic mixture, if the mixing is (almost) perfect in the liquid phase and the solid crystals are separated.



Starting from high temperature and an arbitrary composition, the composition of the liquid phase will always move to composition „4”.

curves 1 and 2: freezing point of the mixture with given composition  
(below this temperature crystals of either A or B appear)

line 3 no liquid phase below this temperature

point 4 eutectic point, which determines the  
eutectic temperature  
eutectic composition

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## Famous eutectics

### NaCl–water mixture:

eutectic composition: 23 % NaCl, 77% H<sub>2</sub>O

eutectic temperature at atmospheric pressure:  $-21\text{ }^{\circ}\text{C}$ .

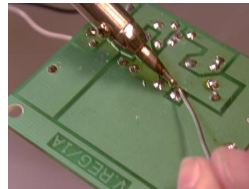


### solder:

Eutectic composition: 67 % Sn, 33% Pb

eutectic temperature

at atmospheric pressure:  $183\text{ }^{\circ}\text{C}$ .



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## Features of eutectics

In any A–B liquid mixture, the eutectic mixture has the lowest freezing point.

Salting of an icy road is not effective,

if the temperature is lower than the water–NaCl eutectic temperature ( $-21\text{ }^{\circ}\text{C}$ ).

Adding salt to water–ice equilibrium mixture in an adiabatic container, ice is melted (endothermic process)  $\Rightarrow$  temperature decreases. This way, the lowest attainable temperature is the eutectic temperature ( $-21\text{ }^{\circ}\text{C}$ ).

Already the alchemists could make below  $-10\text{ }^{\circ}\text{C}$  temperatures by mixing ice with salt (NaCl) or saltpeter (KNO<sub>3</sub>).

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**THE END**

**of topic  
mixtures**



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