

TWO-COMPONENT SYSTEMS: THERMODYNAMICS OF MIXTURES AND DILUTE SOLUTIONS

- i. The definition of mixture.
- ii. Partial molar quantities. Definition and determination of partial molar volume
- iii. Thermodynamics of mixing. Free energy and entropy of mixing. Excess functions
- iv. Ideal and real mixtures
- v. Thermodynamic description of colligative properties: boiling point elevation, freezing point depression, solubility, partition, osmosis
- vi. Practical importance of colligative properties

I. Mixtures

- **Mixture:** multicomponent, macroscopically homogeneous system with dispersion on the molecular level, usually of substances in the same phase
 - **unlimited miscibility:** two or more substances form mixtures in any ratio
 - **limited miscibility:** two or more substances form mixtures only in certain ranges of ratios
 - **ideal mixtures:** mixing is accompanied by a change in free energy as follows:

$$\Delta_{\text{mix}}G = nRT \sum_i x_i \ln x_i$$
 - **real mixture:** non-ideal mixture, the previous relation does not hold

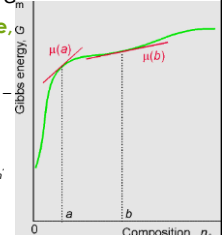
I. Mixtures

- **Solution:** a homogeneous mixture in which the concentration of one of the components (l or s) is much larger than those of the others
 - **solvent:** the component in the solution with the large concentration (A)
 - **solute:** the component(s) in the solution with moderate concentration(s) (B, C...)
 - **solubility:** the maximum concentration of a substance in a given solvent at a given T and p
- **Mixture:** multicomponent, molecularly non-dispersed, heterogeneous system (e.g. powder mixtures, colloids); the (large specific) surface of the components is important. (It is not discussed in classical thermodynamics.)

II. Partial molar quantities

- Partial molar free energy was discussed earlier (**chemical potential**)
 - **Pure substance:** the chemical potential is identical to the molar free energy: $\mu = G_m$
 - **For a component in a mixture:** the chemical potential is the **partial molar free energy** (i.e. the slope of the Gibbs free energy-composition (n_i) function at constant p, T and n_j'):

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n_i}$$
 - The **chemical potential** is always **positive**.

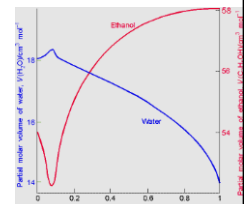


II. Partial molar quantities

- **Gibbs-Duhem equation:** $\sum_j n_j d\mu_j = 0$
 - **Implication:** a change in the chemical potential of one of the components is necessarily accompanied by changes in the chemical potentials of the other components as well.

II. Partial molar quantities

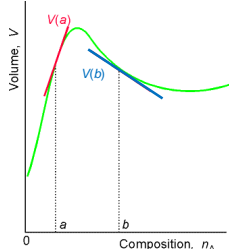
- A (more) visual partial molar quantity: the **partial molar volume**.
 - **Definition:** the change in volume one mol of a given substance contributes to the „infinitely large“ system (in terms of volume). (Similarity to the chemical potential.)
 - **Formula:** $v_j = \left(\frac{\partial V}{\partial n_j} \right)_{p,T,n_i}$
- Particular example: **partial molar volume** in the **water-ethanol** system.
- Notice in the figure that if one grows, then the other drops.



II. Partial molar quantities

partial molar volume for water and ethanol at 25 °C:

- Partial molar volumes depend on the composition.
- $dV = V_A dn_A + V_B dn_B$ and $0 = n_A dV_A + n_B dV_B$ (**Gibbs-Duhem equation**)
- $V = n_A V_A + n_B V_B$ (but volumes are not additive!)
 - Measurement: from the slope dV/dn
 - **Negative** partial molar volumes do exist (although molar volumes are always positive!).



III. Thermodynamics of mixing

First through the example of **gas mixtures**.

- Mixing is spontaneous, so G must decrease:
- **Free energy of mixing** ($\Delta_{\text{mix}}G$) for ideal gases:
 - Before (i): $G_i = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^0 + RT \ln \frac{p}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p}{p^0} \right)$
 - After (f): $G_f = n_A \left(\mu_A^0 + RT \ln \frac{p_A}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p_B}{p^0} \right)$
 - Difference: $G_f - G_i = \Delta_{\text{mix}}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$
 - As $n_j = nx_j$ and $x_j = \frac{p_j}{p}$: $\Delta_{\text{mix}}G = nRT \sum x_j \ln x_j < 0$

III. Thermodynamics of mixing

- **Entropy of mixing** ($\Delta_{\text{mix}}S$) for ideal gases:
 - As $(\partial G / \partial T)_{p,n} = -S$, derivation of $\Delta_{\text{mix}}G$ gives: $\Delta_{\text{mix}}S = - \left(\frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{p,p'} = -nR \sum x_j \ln x_j > 0$
 - The driving force of mixing is the increase in entropy: disorder increases during mixing.
- **Enthalpy of mixing** ($\Delta_{\text{mix}}H$) for ideal mixtures:
 - $\Delta_{\text{mix}}H = 0$ (p and T constant)
- **Volume change of mixing** for ideal mixtures:
 - $\Delta_{\text{mix}}V = 0$
- **Internal energy change of mixing** for ideal mixtures:
 - $\Delta_{\text{mix}}U = 0$ (p and T constant).

IV. Ideal and real mixtures

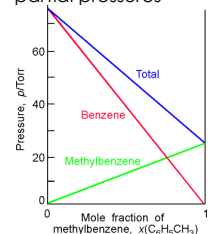
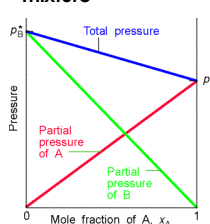
- **Ideal mixtures** are rare:
 - mixtures of ideal gases and
 - mixtures of chemically similar substances.
 - The A-A and B-B molecular interactions are very similar, so are the A-B interactions.
- **In real mixtures**, this is not true: the A-B interaction is significant, which has effects on the thermodynamic functions of mixing.
- The formulas obtained for ideal mixtures are transferred to real mixtures as well.

IV. Ideal and real mixtures

- In **ideal mixtures**, the **solvent** (A) and the **solute** (B) both follow **Raoult's law**:
 - $p_A = x_A p_A^*$ and
 - $p_B = x_B p_B^*$.
- In **real mixtures**, at **low concentrations**, the partial pressure of the **solute** (B) is proportional to its molar fraction in the liquid phase:
 - $p_B = x_B K_B$.
 - This is called **Henry's law** (valid mainly for dissolved gases) where the proportionality constant is Henry's constant (K_B) instead of p_A^* .
- **Ideal dilute solutions**: the **solvent follows Raoult's law**, the **solute follows Henry's law**.

IV. Ideal and real mixtures

- The total pressure and the partial pressures in an **ideal binary mixture**
- The mixture of two similar liquids (**benzene** and **toluene**): **total and partial pressures**



IV. Ideal and real mixtures

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- Real binary mixture: the validity of Raoult's and Henry's law and the ideal mixtures
- The validity of Raoult's and Henry's law for a chloroform – acetone mixture

IV. Ideal and real mixtures

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Thermodynamics of **Real mixtures and solutions**:

- To keep the formalism of the ideal mixtures – analogously to the fugacity of real gases – the activity a (and the γ activity coefficient) is introduced to replace the concentration.
- Separate discussion for
 - the activity of the solvent and
 - the activity of the solute(s).
- The references state is important: the definition of standard states.

IV. Ideal and real mixtures

Excess functions in real mixtures of liquids

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- The A–A and B–B, so the A–B interactions are significantly different. Depending on the magnitudes, liquids can be
 - miscible unlimitedly,
 - miscible limitedly or
 - non-miscible.
- The **excess function** is the difference between the measured real and ideal values, for example: $S^E = \Delta_{mix}S - \Delta_{mix}S^{ideal}$.
- (Regular mixture: $S^E = 0$ but $H^E \neq 0$.)

IV. Ideal and real mixtures

Excess functions in real mixtures of liquids

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- Experimental excess functions:**
 - H^E in the benzene – cyclohexane mixture (endothermic mixing):
 - V^E in the tetrachloro ethylene – cyclopentane mixture (both expansion and contraction occur)

V. Colligative properties

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- Some properties of dilute solutions are not proportional to the molar concentration of the solute, but to the amount of species (e.g. ions) present.
- The following properties are discussed:
 - boiling point elevation,
 - freezing point depression,
 - solubility,
 - partition,
 - osmosis.
- These phenomena were first **described experimentally** in a **quantitative way (formulas)**, then **interpreted in thermodynamics**.

V. Colligative properties

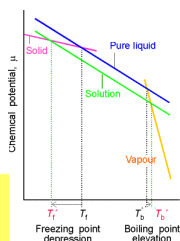
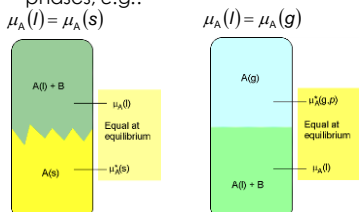
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- Common characteristics of colligative properties:
 - the solute is non-volatile, and
 - does not dissolve in the solid solvent

- The solute decreases the μ chemical potential of the **solvent**.

V. Colligative properties

- To understand colligative properties, we are looking for the T where the chemical potential of the solvent (A) is the same in the different phases, e.g.:



V. Colligative properties

a) boiling point elevation:

- The $\mu_A^*(l)$ chemical potential of the pure solvent decreases to $\mu_A^*(l) + RT \ln x_A$. This is equal to the $\mu_A^*(g)$ chemical potential of the vapor at the new boiling point.
- So, using the following: $\mu_A^*(g) - \mu_A^*(l) = \Delta_{\text{vap}}G$, $\Delta_{\text{vap}}G = \Delta_{\text{vap}}H - T\Delta_{\text{vap}}S$ and $x_A + x_B = 1$, the result is:
$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{vap}}H} \right) x_B$$
- The original experimental formula: $\Delta T = K_b m_B$, where K_b is the molal boiling point elevation constant, m_B is the molality.
- An early method to determine molar masses. Today it is not significant.

V. Colligative properties

a) boiling point elevation:

Solvent	Boiling point (°C)	Molal boiling point elevation constant (K · kg/mol)
Water	100.0	0.51
Phenol	181.7	3.04
Acetic acid	118.1	3.07
Benzene	80.2	2.53
Carbon disulfide	46.2	2.37
Carbon tetrachloride	76.5	4.95
Naphthalene	218.0	5.80
Diethyl ether	35.4	2.10
Tin(IV) chloride	114.1	9.45

V. Colligative properties

b) freezing point depression:

- The $\mu_A^*(l)$ chemical potential of the pure solvent decreases to $\mu_A^*(l) + RT \ln x_A$. This is equal to the $\mu_A^*(s)$ chemical potential of the pure solid solvent at the freezing point.
- So, in some steps:
$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{fus}}H} \right) x_B$$
- The original experimental formula: $\Delta T = K_f m_B$, where K_f is the molal freezing point depression constant, m_B is the molality.
- Still quite significant phenomenon (cooling mixtures, salting of icy roads, detection of counterfeit milk).

V. Colligative properties

b) freezing point depression:

Solvent	Melting point (°C)	Molal freezing point depression constant (K · kg/mol)
Water	0.0	1.86
Naphthalene	80.2	6.80
Chloroform	-63.5	4.68
Benzene	5.5	5.12
Camphor	179	39.7
Ethyl alcohol	-114.6	1.99
Cyclohexane	6.4	20.2
Carbon tetrachloride	-22.8	29.8
Acetic acid	16.6	3.9
Phosphorus	44	39.9
Potassium chloride	772	25.3
Iron	1536	-80

V. Colligative properties

c) Solubility:

- The phenomenon: a number of solids have maximum solubility in some solvents (saturated solutions can be prepared). This maximum concentration depends on T (solubility can increase or decrease with increasing temperature).
- There are pairs of materials which are „soluble“ in each other in any ratios (e.g. water and NaOH).

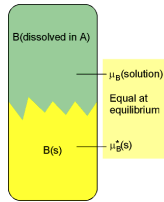
V. Colligative properties

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c) Solubility:

- **Not a colligative property**, but the thermodynamic description is the same:
 - for solute B, the chemical potential is $\mu_B = \mu_B^*(l) + RT \ln x_B$
 - and the $\mu_B^*(s)$ chemical potential of the undissolved solid is the same.
- Now, we are looking for x_B :

$$\ln x_B = -\frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$



V. Colligative properties

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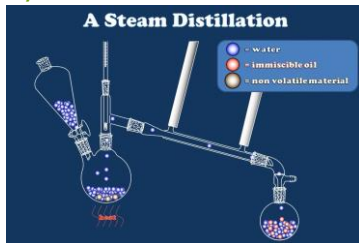
c) Solubility:

- solubility of **gases in liquids**:
 - effect of p : **Henry's law**
 - effect of T : $\Delta H < 0$, so dissolved gases (e.g. O_2 , CO_2) can be removed by boiling from water or other solvents
- solubility of **gases in melts**:
 - effect of T : $\Delta H > 0$, so better solubility at higher T !!!, cooling causes the formation of inclusions (*metalworking*)
- solubility of **liquids in liquids**:
 - **unlimited miscibility** (separation: distillation)
 - **limited miscibility** (multiple phases)
 - **essentially immiscible**: „partition” is important in practice; steam distillation.

V. Colligative properties

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c) Solubility:



<https://www.youtube.com/watch?v=opcULC0jjsY>

steam distillation

V. Colligative properties

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c) Solubility:

- If $p(T)$ reaches the atmospheric pressure, the two immiscible liquids begin to boil.
- This occurs at a lower temperature than for component B only.
- The „boiling point depression” is independent of the amount of water added!

$$p(T) = p_A^*(T) + p_B^*(T)$$



steam distillation

V. Colligative properties

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a) Nernst–Berthelot partition:

- (third) substance C dissolves in two practically immiscible liquids (A and B).
- If there is a significant difference in the solubilities, the phenomenon can be used for practical purposes.
- The μ of the third substance (C) is the same in the two liquids: $\mu_C^*(1) + RT \ln x_C(1) = \mu_C^*(2) + RT \ln x_C(2)$
- partition coefficient = $x_C(1) / x_C(2)$.
- **Practical use**: „extraction”; *multistep extraction is used in a number of industrial processes.*

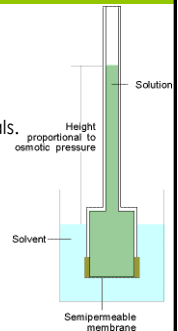
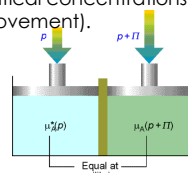


V. Colligative properties

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e) Osmosis:

- **Phenomenon**: a semipermeable membrane separates two solutions, pressure difference develops.
- **Reason**: different chemical potentials.
- **Trend**: identical concentrations (solvent movement).



V. Colligative properties

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e) Osmosis:

- Backpressure
 - can either be the extra hydrostatic pressure of the liquid column (in this case, dilution occurs)
 - or exercise with force (no dilution happens, simpler system, more accurate measurement). [With high pressure, even a reverse osmosis can be achieved.]
- **To illustrate:** Grapes swell in distilled water and "dry out" in concentrated NaCl (or sugar) solution.
 - Water diffuses to the more concentrated phase, thereby balancing the concentration difference and the chemical potential difference.



- **For non-ideal solutions of macromolecules:**

$$\Pi = [B]RT (1 + B[B] + \dots)$$

- In practice, calibration curves are used.

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e) Osmosis thermodynamics:

- In equilibrium, μ is equal across the membrane:

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi)$$

- Different concentration of the solute:

$$\mu_A(x_A, p + \Pi) = \mu_A^*(p + \Pi) + RT \ln x_A$$

- Effect of pressure: $\mu_A^*(p + \Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp$

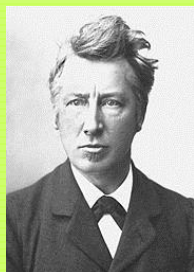
- From the three equations:

$$-RT \ln x_A = \int_p^{p+\Pi} V_m dp$$

- In dilute solutions, the **van't Hoff equation** is obtained:

$$\Pi V = n_B RT \text{ or (as } n_B/V = [B]) \Pi = [B]RT$$

- **This equation is valid for ideal, dilute solutions.**



„He was a Dutch physical and organic chemist and the **first winner of the Nobel Prize in Chemistry**. He is best known for his discoveries in chemical kinetics, chemical equilibrium, osmotic pressure, and stereochemistry. His work in these subjects helped found the discipline of physical chemistry as it is today.“

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Jacobus Henricus van 't Hoff, Jr.

1852 – 1911

VI. Practical importance of colligative properties

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- **Freezing point depression:**
 - cooling mixtures,
 - use of salts on the roads in the winter,
 - detection of milk forging
- **Boiling point elevation:**
 - seldom used today for molar mass determination
- **Partition:**
 - extraction in laboratories and in the industry
- **Solubility:**
 - dissolution,
 - T-dependence of solubility

VI. Practical importance of colligative properties

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□ Osmosis:

- Especially important in cell biology. In human cells, the osmotic pressure is about 8 bar, which corresponds to a 0.9 % (m/m) sodium chloride solution (physiological salt solution). This is often used in injections.
- Thirst after eating salty foods.
- Hemodialysis.
- Osmometry is still significant method in the clinical practice for determining (average) molar masses.
- In plants, osmotic pressure can be as large as 20 bar.
- Industrial applications:
 - preparation of sweet water (reverse osmosis),
 - sugar industry.

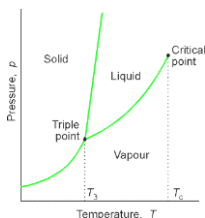
MIXTURES OF VOLATILE LIQUIDS

- i. Vapor pressure of liquid mixtures
- ii. Vapor pressure–composition diagrams
- iii. Temperature–composition diagrams. Distillation
- iv. Azeotropic mixtures
- v. Vapor pressure above immiscible liquids. Steam distillation
- vi. Significance of distillation

I. Vapor pressure of liquid mixtures

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1. One component: all phases and equilibria can be given on a single T vs. p phase diagram



I. Vapor pressure of liquid mixtures

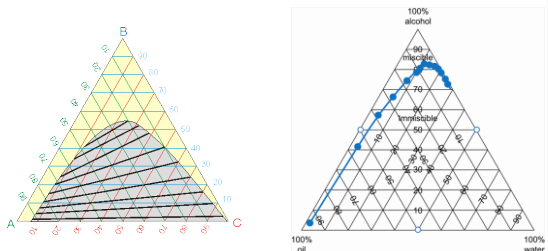
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2. Two component liquid mixtures are versatile:
 - Unlimited miscibility: the composition of the vapor above the mixture depend on the composition of the mixture (x_j), T and p .
 - **Change p and x_j (at fixed T)**: vapor pressure–composition diagram.
 - **Change T and x_j (at fixed p)**: temperature–compositions diagram.
 - Only limited miscibility: the number of phases also has to be shown.
 - **Immiscible components**. (These are good pairs of solvent for Nernst-Berthelot partition, which is the essence of extraction.)

I. Vapor pressure of liquid mixtures

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3. For three-component mixtures, only a composition diagram („triangle diagram”) can be constructed for a given p and T .

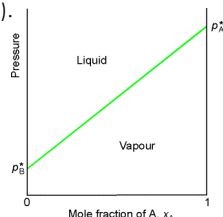


II. Vapor pressure–composition diagrams

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2. **p - x_j diagrams**: the dependence of the equilibrium vapor pressure above the mixtures on the composition.

- x : composition of the mixture (l),
- y : composition of the vapor (g).
- Ideal mixtures:
 - **Raoult's law** is valid:
 - $p_A = x_A p_A^*$ and $p_B = x_B p_B^*$



- The total vapor pressure:
 - $p_{tot} = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^* = p_B^* + x_A (p_A^* - p_B^*)$

II. Vapor pressure–composition diagrams

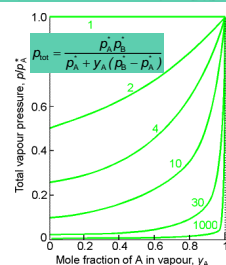
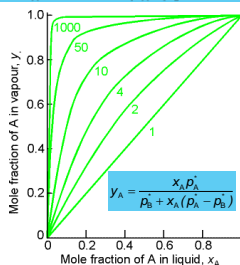
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- **The composition of the vapor above the mixture**:
- Common sense (and experience): the more volatile components is more abundant in the vapor phase.
 - gas-phase mole fractions from **Dalton's law**:
 - $y_A = p_A/p$ és $y_B = p_B/p$
 - From liquid phase mole fractions:
 - $y_A = \frac{x_A p_A^*}{p_B + x_A (p_A^* - p_B^*)}$ and $y_B = 1 - y_A$
 - Dependence of the total vapor pressure on the composition of the gas phase:
 - $p_{tot} = \frac{p_A p_B}{p_A + y_A (p_B - p_A)}$

II. Vapor pressure–composition diagrams

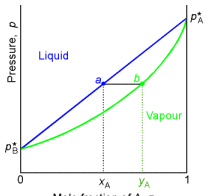
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The mole fraction of substance A in the vapor (y_A) as a function of liquid-phase x_A at different p_A^*/p_B^* values: Dependence of the total vapor pressure on the mole fraction of component A in the vapor (y_A):



II. Vapor pressure-composition diagrams

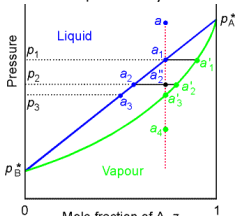
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- Interpretation of diagrams, **their combination**
 - For distillation, the liquid and gas phase compositions are both significant.
 - z_A : generic mole fraction of substance A.
- The total vapor pressure of the ideal mixture as a function of the liquid-phase and vapor-phase mole fractions of substance A:
 
 - Two phases between the two lines,
 - only liquid above,
 - only vapor below.

II. Vapor pressure-composition diagrams

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- Change in the state of the system upon pressure decrease at a given composition:
 - Red dotted line: **isopleth** (the same composition).
- Pressure reduction:**
 - only liquid (l) at high p,
 - l and g together in between,
 - only gas (g) at low p.
- At low pressure (and lower T) liquids evaporate more intensely (vacuum distillation).

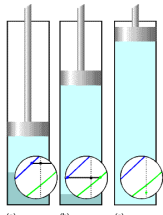


II. Vapor pressure-composition diagrams

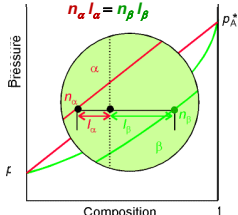
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- Lever rule:** a method to determine the ratio of liquid and gas quantities at a given pressure.

Interpretation:



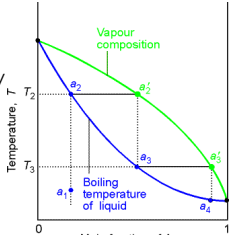
Equation:

$$n_A l_A = n_B l_B$$


III. Temperature-composition diagrams. Distillation

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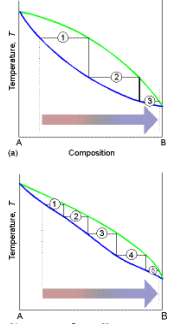
- To interpret distillation, temperature-composition diagrams are needed.
 - Two phases between the two lines,
 - only vapor above,
 - only liquid below.
- Distillation can be facilitated by
 - reducing the pressure (vacuum distillation) or
 - increasing the temperature
 - (while the other property is kept constant.)



III. Temperature-composition diagrams. Distillation

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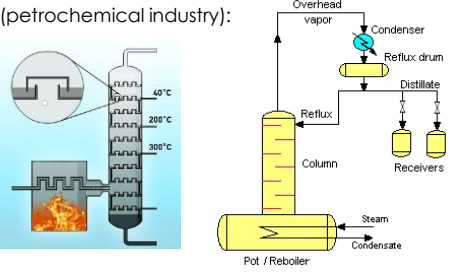
- Illustration of the theoretical plate number:
 - The theoretical plate number is the number of distillation steps necessary to separate the two-component mixture.



III. Temperature-composition diagrams. Distillation

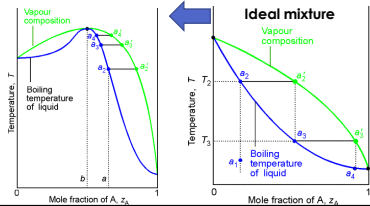
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- Implementation of the distillation with fractionation columns (petrochemical industry):



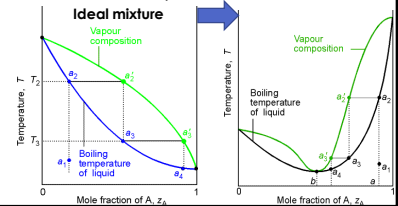
IV. Azeotropic mixtures

- On the line of phase boundary, a **maximum** may occur if the interactions between the components lower the vapor pressure below the ideal value.
- G^E (excess free energy) is **negative** (so mixing is more favorable than the ideal case).



IV. Azeotropic mixtures

- On the line of phase boundary, a **minimum** may occur if the mixture is de-stabilized relative to the ideal case.
- G^E (excess free energy) is **positive** (so mixing is less favorable than the ideal case).



IV. Azeotropic mixtures

High-boiling azeotropes (e.g. chloroform-acetone, nitric acid-water) **Low-boiling azeotropes** (e.g. dioxane-water, ethanol-water)

If a mixture of composition **a** is distilled, the composition of the remaining liquid can only change until **b** is reached.

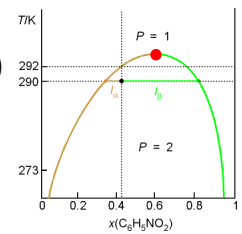


V. Liquids with limited miscibility: phase separation.

- The range of limited miscibility usually depends on the temperature. There are three possibilities:

Version 1:

- high T : only one phase ($P = 1$)
- low T : two phases ($P = 2$)
- e.g. hexane-nitrobenzene
- Lever rule: $n_a l_a = n_b l_b$
- T_{uc} : upper critical temperature

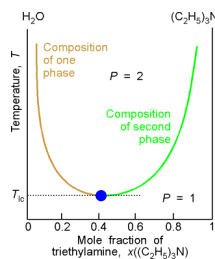


V. Liquids with limited miscibility: phase separation.

- The range of limited miscibility usually depends on the temperature. There are three possibilities:

Version 2:

- high T : two phases ($P = 2$)
- low T : only one phase ($P = 1$)
- e.g. water-triethyl amine
- Lever rule: $n_a l_a = n_b l_b$
- T_{lc} : lower critical temperature

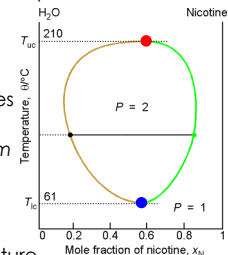


V. Liquids with limited miscibility: phase separation.

- The range of limited miscibility usually depends on the temperature. There are three possibilities:

Version 3:

- high T : one phase ($P = 1$)
- low T : one phase ($P = 1$)
- intermediate T : two phases ($P = 2$)
- e.g. water-nicotine system
- Lever rule: $n_a l_a = n_b l_b$
- T_{uc} : upper critical temperature
- T_{lc} : lower critical temperature



V. Liquids with limited miscibility: distillation.

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- The distillation of such mixtures is also versatile.
 - Distillation – **mixing before boiling**
 - T_{uc} is lower than $T_{azeotrope}$
 - $a_1(l)$ evaporates as $b_1(g)$
 - this condenses as $b_2(l)$ monophasic mixture,
 - upon further cooling, separation into $b_3(l)$ occurs.
 - During distillation, the composition of the un-distilled liquid changes.

V. Liquids with limited miscibility: distillation.

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- The distillation of such mixtures is also versatile.
 - Distillation – **boiling before mixing**
 - no T_{uc}
 - $a_1(l)$ turns into $b_1(g)$,
 - this condenses into biphasic $b_3(l)$: b_3' and b_3''
 - the $e(l)$ liquid is azeotropic, l and g have the same composition, no separation occurs upon distillation.

V. Immiscible liquids: steam distillation.

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- The total vapor pressure is the sum of the two individual vapor pressures:

$$p_{tot} = p_A^* + p_B^*$$
- If $p_{tot} = 1$ atm, the mixture boils. This T is lower than the boiling point of either liquids: this is the principle behind steam distillation.
- Useful separation method for heat-sensitive materials.

V. Immiscible liquids: steam distillation.

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VI. Significance of distillation

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- The most common separation method.
 - petroleum refining, petrochemical industry (production of gasoline, diesel, lubricants ...),
 - production and purification of laboratory and industrial solvents,
 - separation of industrial solvent mixtures,
 - production of high-alcohol content spirits.