

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
- IV. Ideal and real mixtures
- V. Thermodynamic description of colligative properties: boiling point elevation, freezing point depression, osmosis
- VI. Practical importance of colligative properties

I. Mixtures

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- **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

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- **Solution:** a homogeneous mixtures 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 solute at a given T and p

II. Partial molar quantities

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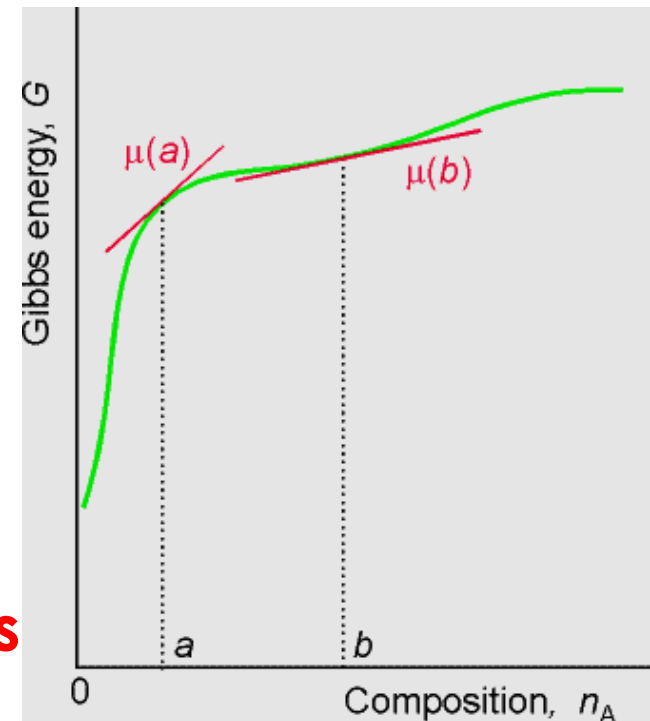
- Partial molar Gibbs free energy was discussed earlier (**chemical potential**)

- ▣ **Pure substance:** chemical potential is identical to the molar Gibbs energy: $\mu = G_m$

- ▣ **For a component in a mixture,** chemical potential is the **partial** molar Gibbs energy:

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'}$$

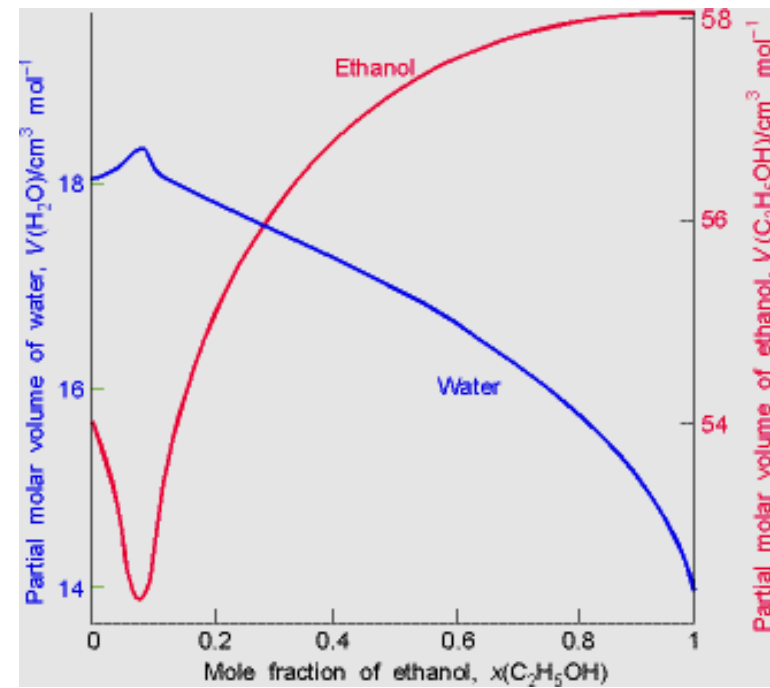
- ▣ The **chemical potential is always positive**



II. Partial molar quantities

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- 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: $V_j = \left(\frac{\partial V}{\partial n_j} \right)_{p,T,n'}$
- Particular example: **partial molar volume** in the **water-ethanol** system.



III. Thermodynamics of mixing

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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):

$$G_i = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^\theta + RT \ln \frac{p}{p^\theta} \right) + n_B \left(\mu_B^\theta + RT \ln \frac{p}{p^\theta} \right)$$

- After (f):

$$G_f = n_A \left(\mu_A^\theta + RT \ln \frac{p_A}{p^\theta} \right) + n_B \left(\mu_B^\theta + RT \ln \frac{p_B}{p^\theta} \right)$$

- 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

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- **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:

$$\Delta_{\text{mix}}S = -\left(\frac{\partial \Delta_{\text{mix}}G}{\partial T}\right)_{p,n'} = -nR \sum x_j \ln x_j > 0$$

- 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

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- **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

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- **In ideal mixtures**, the solvent (A) and the solute (B) both follow Raoult's law:
 - $p_A = x_A p_A^*$ and
 - $p_B = x_B p_B^*$.
- **Ideal dilute solutions**: the solvent follows Raoult's law, the solute follows Henry's law $p_B = x_B K_B$.

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.

V. Colligative properties

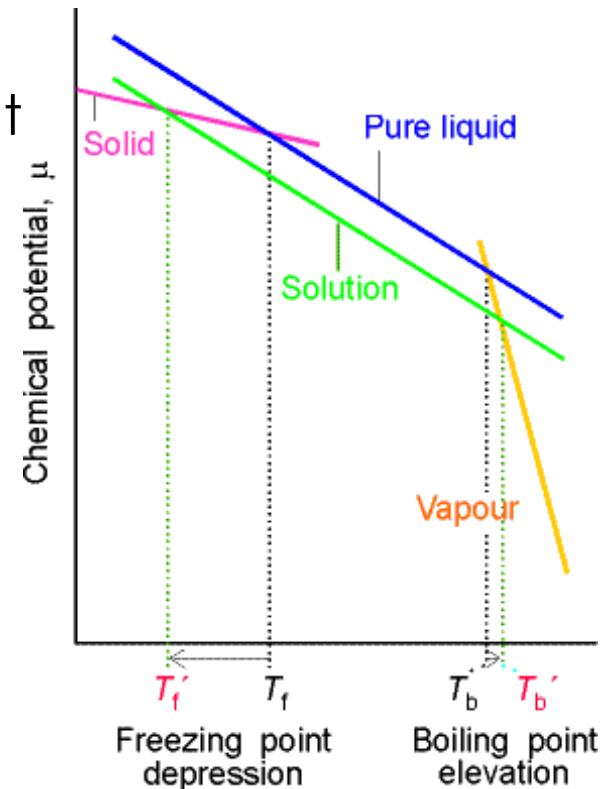
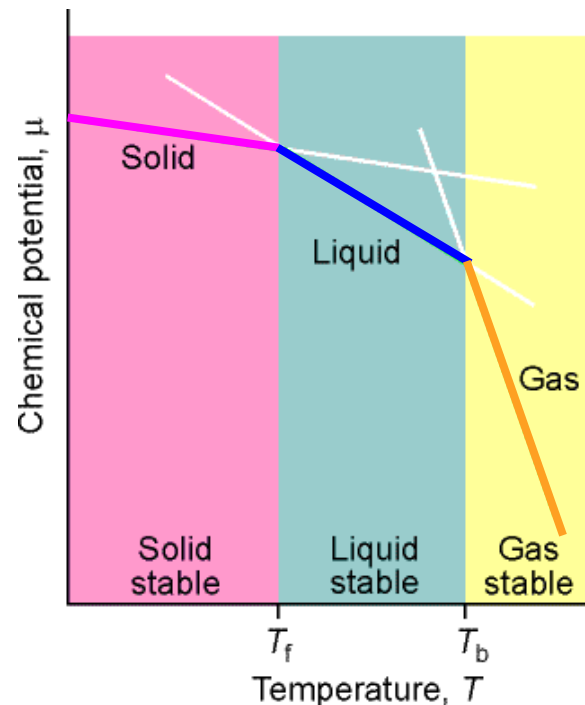
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- Some properties of dilute solutions are not proportional to the molar concentration of the solute, but to the amount of species (e.g. *ions*) present.
- The following properties are discussed:
 - a) **boiling point elevation**,
 - b) **freezing point depression**,
 - c) **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

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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:

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{vap}} H} \right) x_B$$

- 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.

V. Colligative properties

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a) boiling point elevation:

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

V. Colligative properties

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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:

$$\Delta T = \left(\frac{RT^*{}^2}{\Delta_{\text{fus}} H} \right) x_B$$

- 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.

V. Colligative properties

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b) freezing point depression:

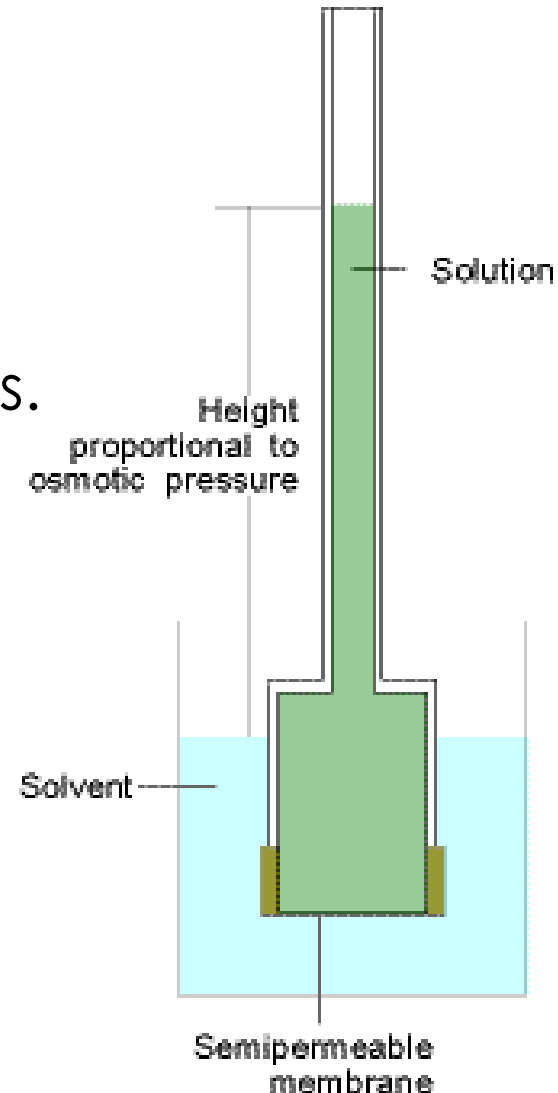
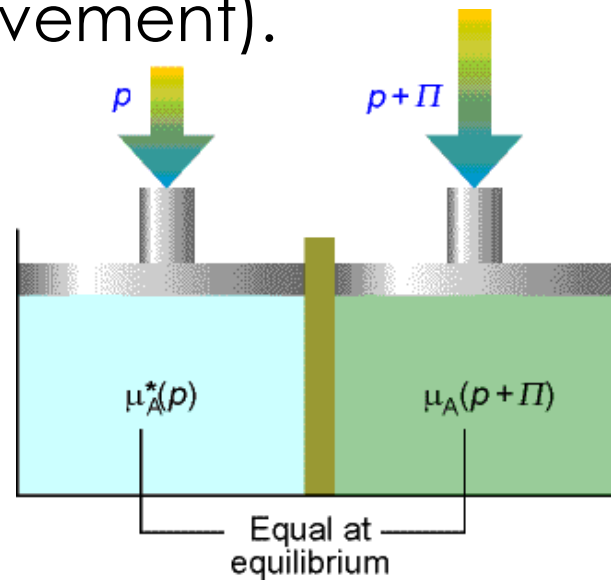
Solvent	Melting point (°C)	Molal freezing point depression constant (K · kg/mol)
<u>Water</u>	0.0	1.86
<u>Naphthalene</u>	80.2	6.80
<u>Chloroform</u>	-63.5	4.68
<u>Benzene</u>	5.5	5.12
<u>Camphor</u>	179	39.7
<u>Ethyl alcohol</u>	-114.6	1.99
<u>Cyclohexane</u>	6.4	20.2
<u>Carbon tetrachloride</u>	-22.8	29.8
<u>Acetic acid</u>	16,6	3.9
<u>Phosphorus</u>	44	39.9
<u>Potassium chloride</u>	772	25.3
<u>Iron</u>	1536	~80

V. Colligative properties

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c) 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 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.**

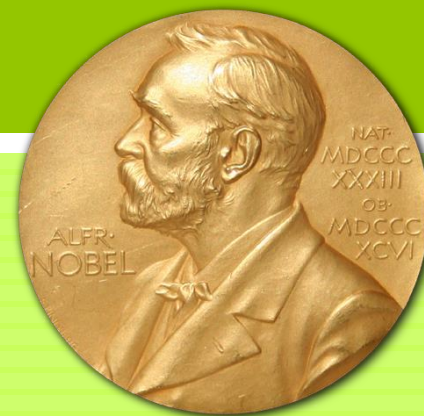


„He was a Dutch physical and organic chemist and **the first winner of the Nobel Prize in Chemistry**. He is best known for his discoveries in chemical kinetics, chemical equilibrium, osmotic pressure, and stereochemistry. His work in these subjects helped found the discipline of physical chemistry as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

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.

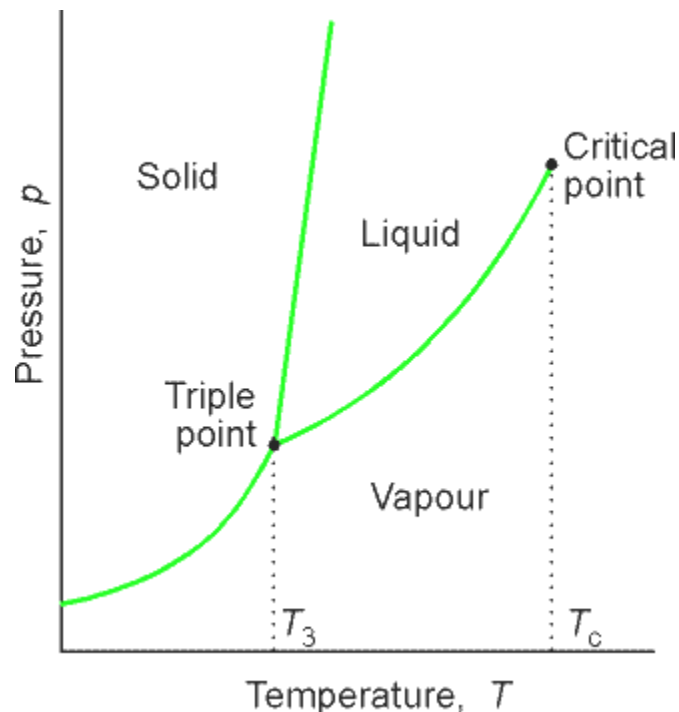
MIXTURES OF VOLATILE LIQUIDS

- I. Vapor pressure of liquid mixtures
- II. Vapor pressure–composition diagrams
- III. Temperature–composition diagrams. Distillation
- IV. Azeotropic mixtures
- V. 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 (fixed T)**: vapor pressure–composition diagram.
 - **Change T and x_j (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 Nernts–Berthelot partition, which is the essence of extraction.*)

II. Vapor pressure–composition diagrams

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2. **p – x 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).

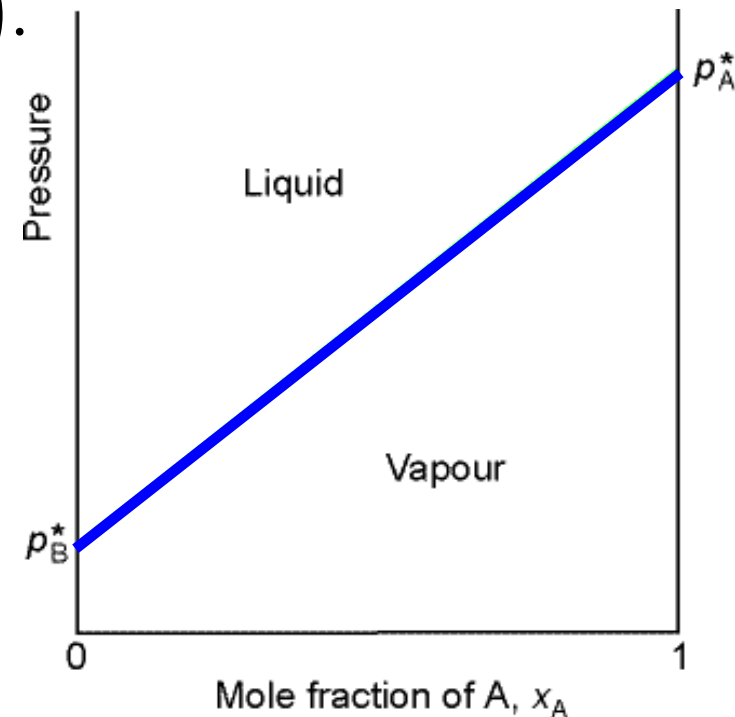
▣ Ideal mixtures:

- ▣ **Raoult's law** is valid:

- ▣ $p_A = x_A p_A^*$ and $p_B = x_B p_B^*$

- ▣ The total vapor pressure:

- ▣
$$p_{\text{tot}} = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^* = p_B^* + x_A (p_A^* - p_B^*)$$



II. Vapor pressure–composition diagrams

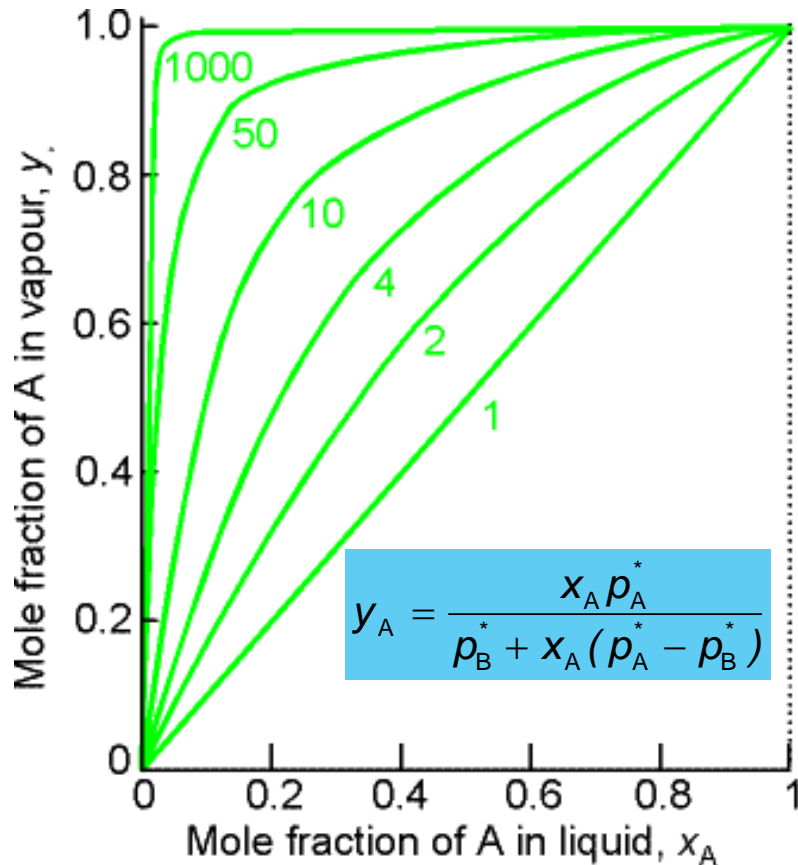
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- **The composition of the vapor above the mixture:**
- Common sense (and experience): the more volatile components is more abundant in the vapor phase.
 - ▣ gas-phase mole fractions from **Dalton's law**:
 - ▣ $y_A = p_A/p$ és $y_B = p_B/p$
 - ▣ From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

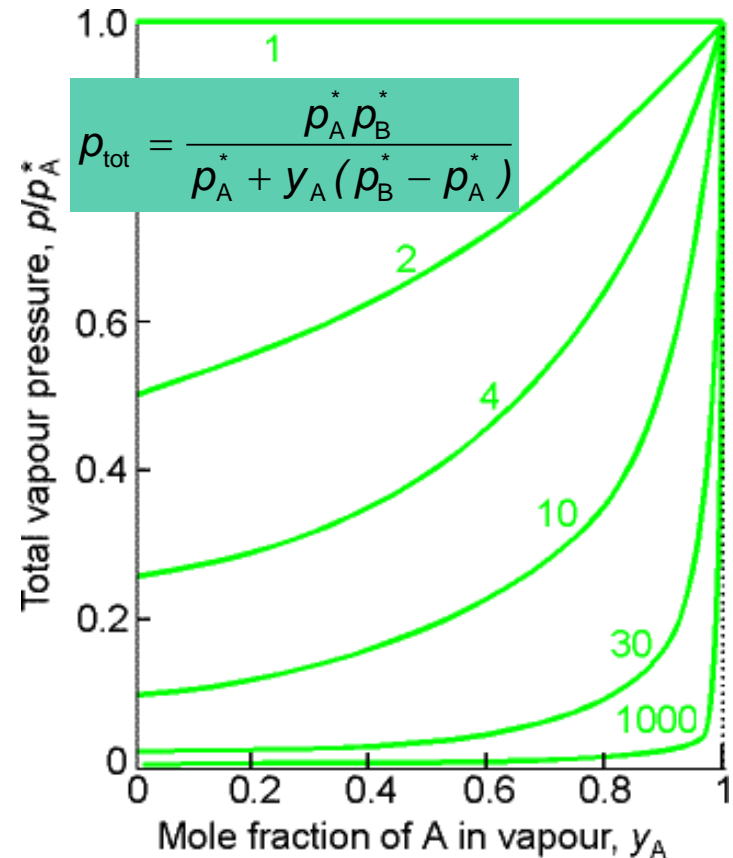
II. Vapor pressure–composition diagrams

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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:



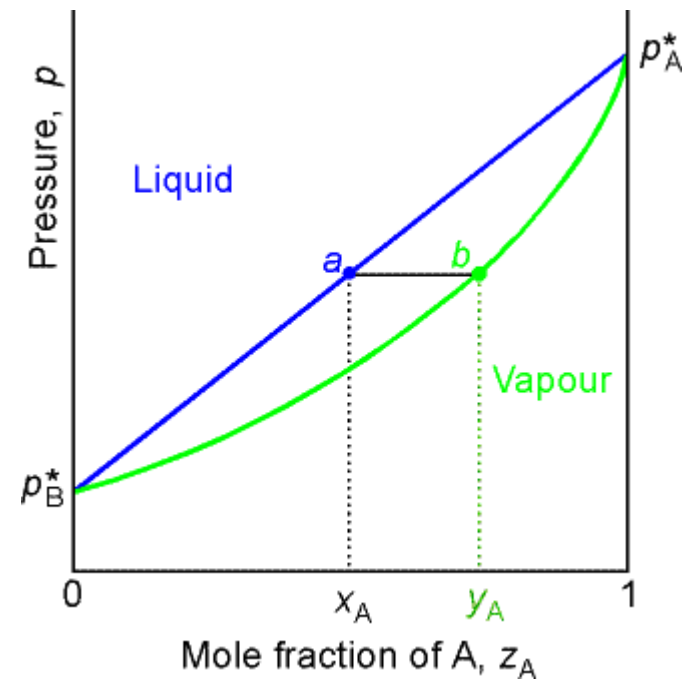
Dependence of the total vapor pressure on the mole fraction of component A in the vapor (y_A):



II. Vapor pressure–composition diagrams

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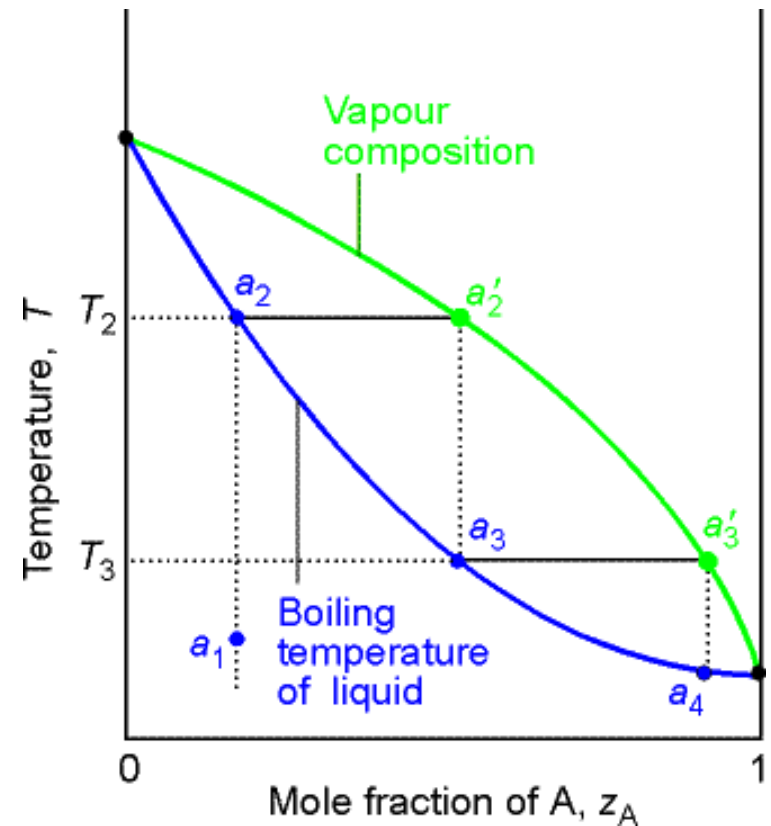
- Interpretation of diagrams, **their combination**
 - ▣ For distillation, the liquid and gas phase compositions are both significant.
 - ▣ z_A : generic mole fraction of substance A.
- The total vapor pressure of the ideal mixture as a function of the liquid-phase and vapor-phase mole fractions of substance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



III. Temperature–composition diagrams. Distillation

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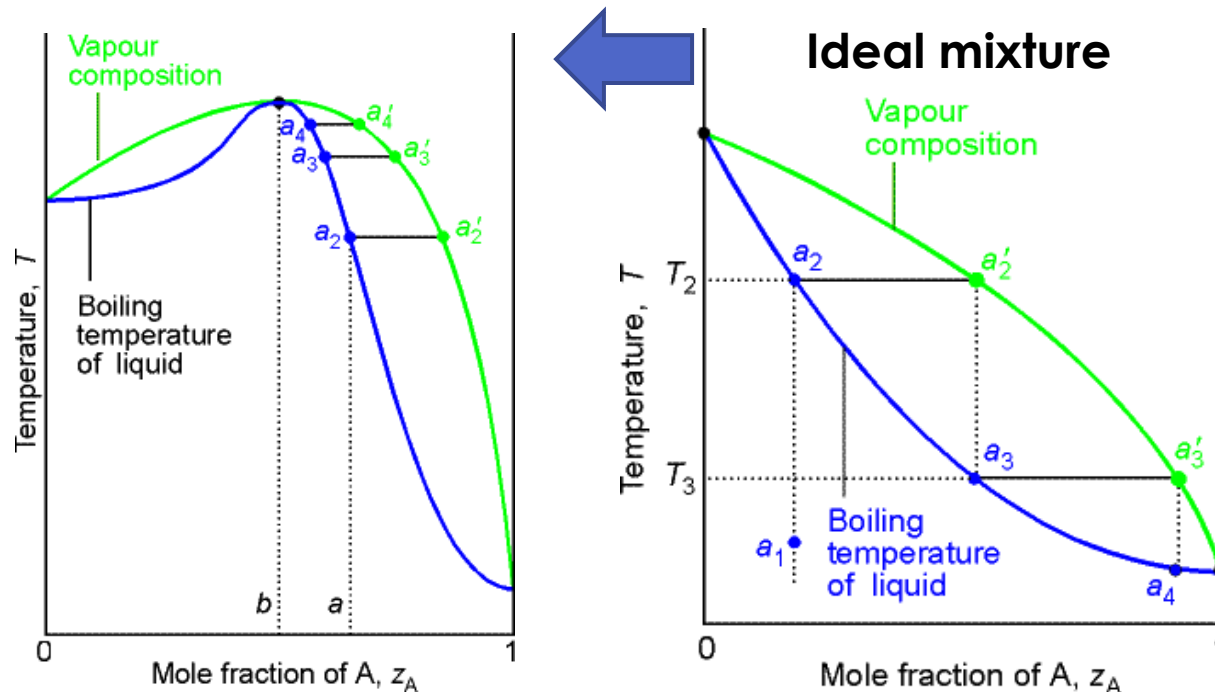
- To interpret distillation, temperature–composition diagrams are needed.
 - ▣ Two phases between the two lines,
 - ▣ only vapor above,
 - ▣ only liquid below.



IV. Azeotropic mixtures

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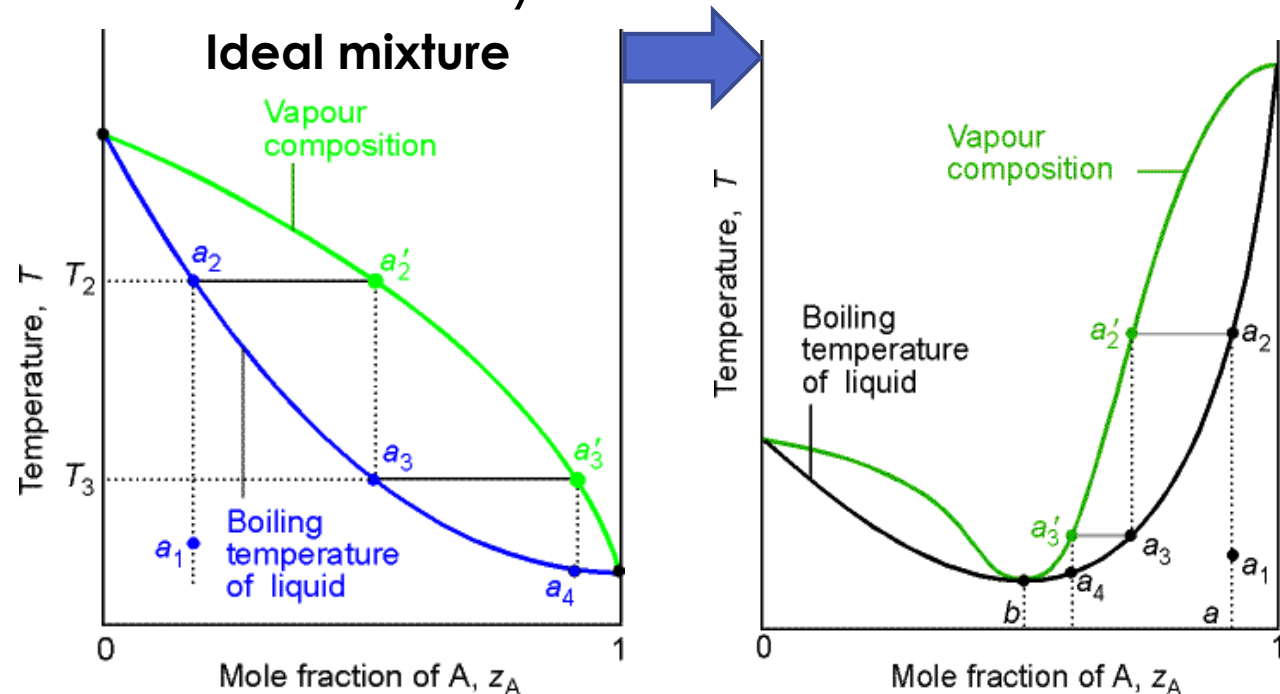
- On the line of phase boundary, a **maximum** may occur if the interactions between the components lower the vapor pressure below the ideal value.
- G^E (excess free energy) is **negative** (so *mixing is more favorable than the ideal case*).



IV. Azeotropic mixtures

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- 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*).

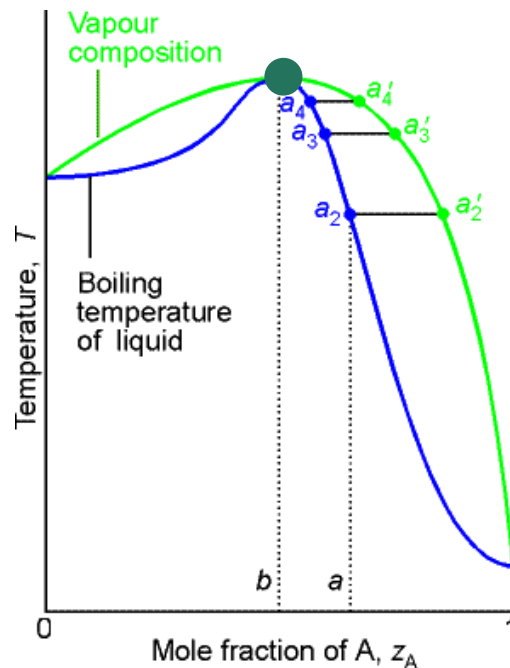


IV. Azeotropic mixtures

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High-boiling azeotropes (e.g. chloroform–acetone, nitric acid–water)

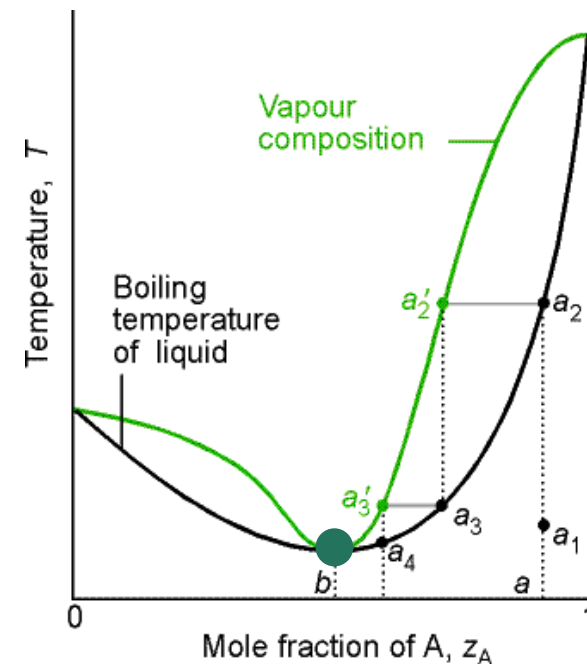
If a mixture of composition a is distilled, the composition of the remaining liquid can only change until b is reached.



$T_{\text{azeotrope}}$

Low-boiling azeotropes (e.g. dioxane–water, ethanol–water)

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



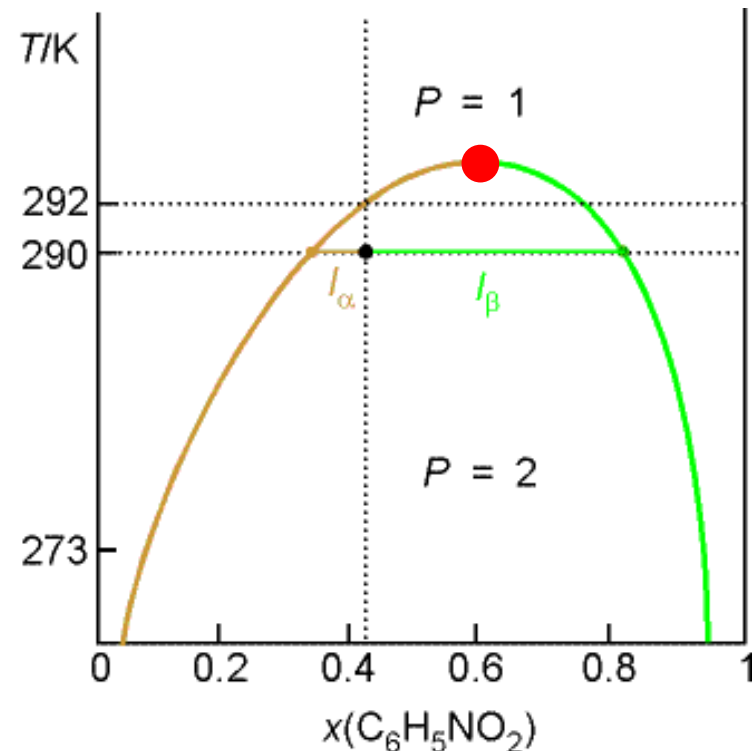
V. Liquids with limited miscibility: phase separation.

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- 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*
- ▣ T_{uc} : **upper critical temperature**



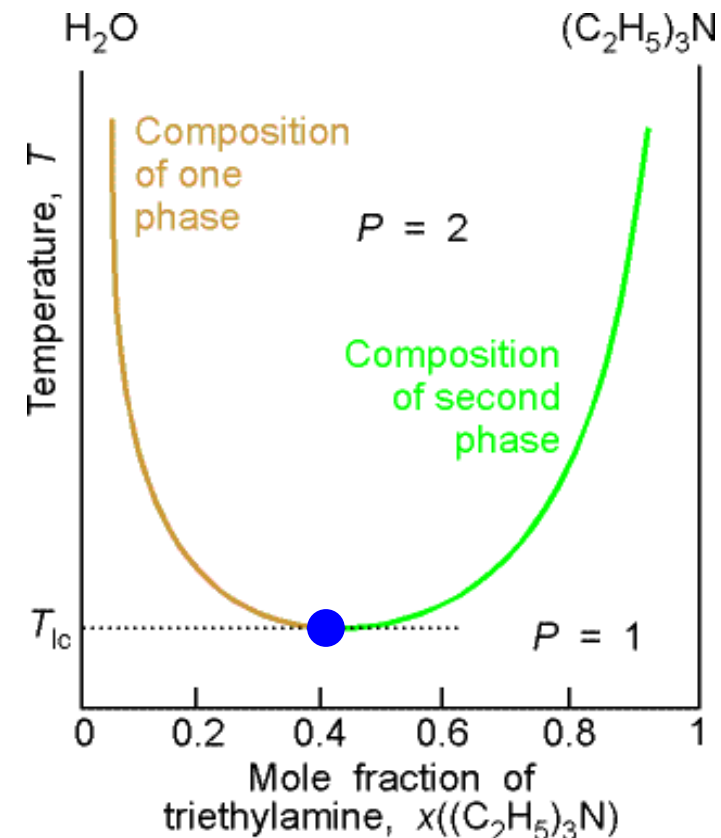
V. Liquids with limited miscibility: phase separation.

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- 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–triethylamine
- ▣ T_{lc} : **lower critical temperature**



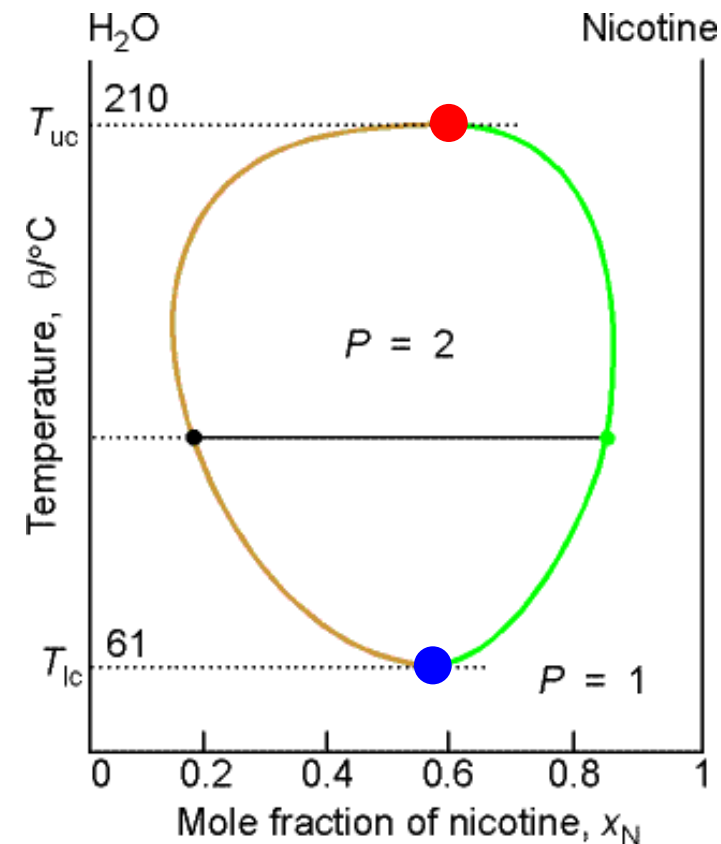
V. Liquids with limited miscibility: phase separation.

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- 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
- ▣ T_{uc} : **upper critical** temperature
- ▣ T_{lc} : **lower critical** temperature



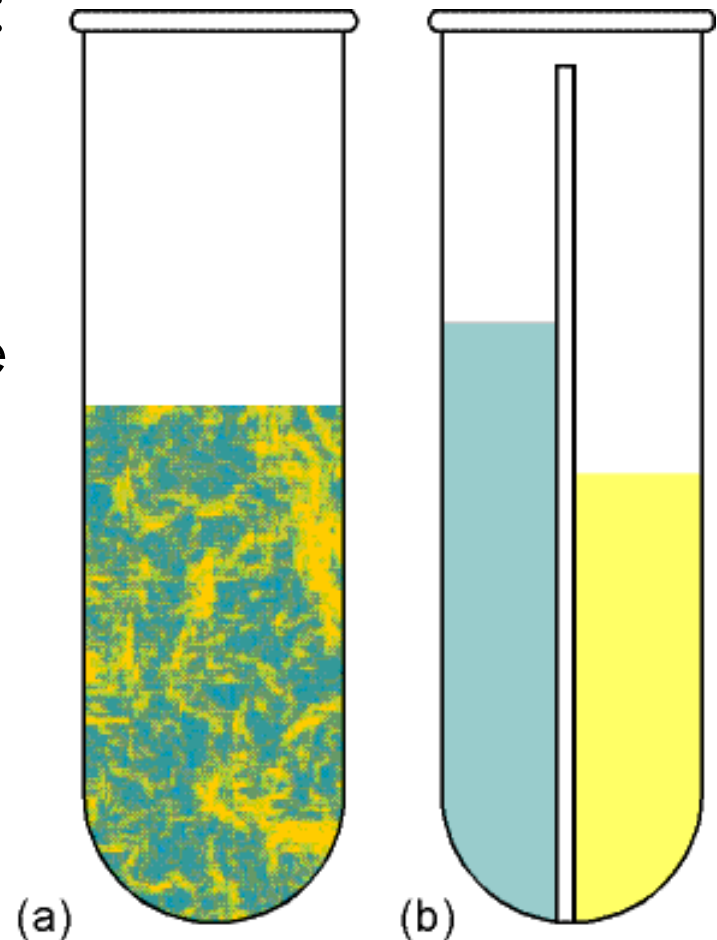
V. Immiscible liquids: steam distillation.

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

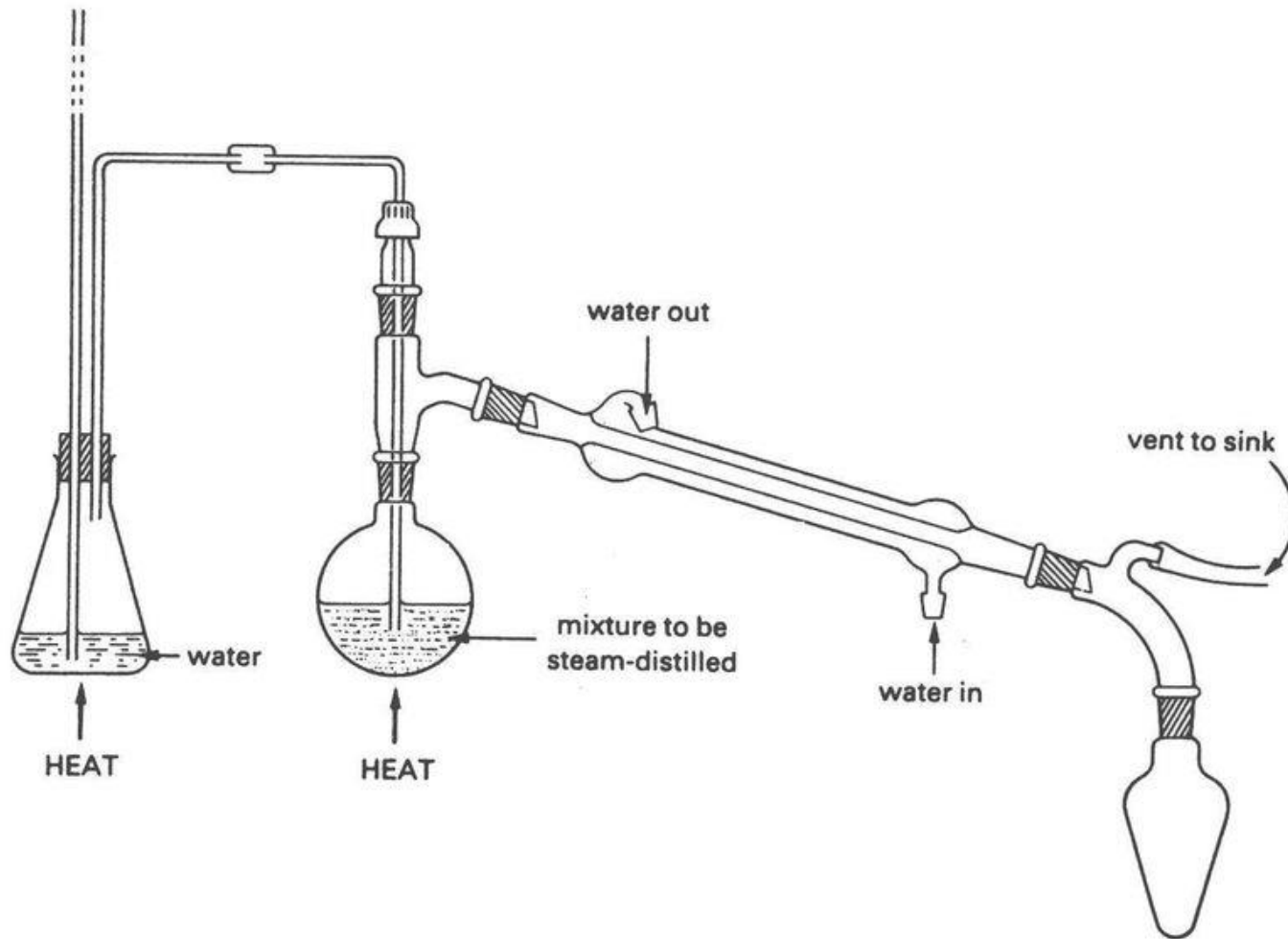
$$p_{\text{tot}} = p_A^* + p_B^*$$

- If $p_{\text{tot}} = 1 \text{ atm}$, 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 e.g.),
 - ▣ production and purification of laboratory and industrial solvents,
 - ▣ separation of industrial solvent mixtures,
 - ▣ production of high-alcohol content spirits.

VI. Significance of distillation

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Vacuum distillation



Rotary evaporation



VI. Significance of distillation

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Chemical industry



VI. Significance of distillation

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spirit distillation