

## THE PHASE RULE

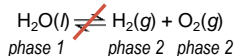
- I. Number of components, phases, degrees of freedom.
- II. The phase rule and its derivation.
- III. Application of the phase rule in **one-component** systems.
- IV. Phase changes and their detection methods.
- V. Application of the phase rule in **two-component** systems.
- VI. Reactive systems.
- VII. Application of the phase rule in **three-component** systems.

## I. Number of components, phases and degrees of freedom

- 2
- **Phase (P)**: a macroscopic part of a system which shows identical properties everywhere. It may be composed of several *components* (e.g.: NH<sub>3</sub> gas, water–hydrochloric acid, iron ore ...).
- **Component (C)**: the **minimal** number of **independent** types of substances (*elements, compounds, ions*) necessary to give the compositions of **all phases**.
  - In non-reactive system, the concept is simple, more demanding in reactive multiphase systems.
  - **Substance: every** chemical present.
- **Degree of freedom (F)**: the number of intensive physical properties whose values can be changed externally without changing the number of phases in the system.

## I. Number of components, phases and degrees of freedom

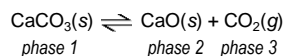
A system containing hydrogen, oxygen and water (example calculation for the number of components):



- Three substances (O<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O) and two phases (liquid and gas, **P = 2**) are present.
- At room temperature, O<sub>2</sub> and H<sub>2</sub> do not react, water does not decompose.
- Therefore, this is a three-component system (**C = 3**).

## I. Number of components, phases and degrees of freedom

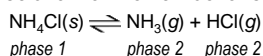
Heating of solid calcium carbonate (example calculation for the number of components):



- If the composition of *phase 3*, CO<sub>2</sub>(g), is known,
- and the composition of *phase 2*, CaO(s), is also known,
- then the combination of these two gives exactly the composition of *phase 1* through stoichiometry.
- Therefore, this system is characterized by
  - three phases (**P = 3**),
  - but two *components* (**C = 2**) although there are three *substances*.

## I. Number of components, phases and degrees of freedom

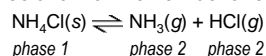
Thermal degradation of solid ammonium chloride (example calculation for the number of components):



- Three *substances* and two *phases* (solid and gas, **P = 2**) are present.
- Ammonia and hydrogen chloride gases are present in exactly the ratio set by the stoichiometry of the chemical equation (1:1),
- so the compositions of both phases can be given by the single substance NH<sub>4</sub>Cl (**C = 1**).

## I. Number of components, phases and degrees of freedom

Solid ammonium chloride + HCl(g) at high temperature (example calculation for the number of components):

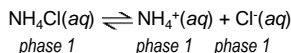


- Three *substances* and two *phases* (solid and gas, **P = 2**) are present.
- Ammonia and hydrogen chloride in the gas phase are NOT in the stoichiometric ratio (1:1) determined by the reaction equation,
- so for giving the composition of the two phases, it is necessary to specify two different kinds of substances, e.g. NH<sub>4</sub>Cl and HCl (**C = 2**).

## I. Number of components, phases and degrees of freedom

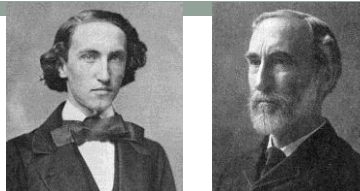
### Dilute ammonium chloride solution

(example calculation for the number of components):



- First "feeling"; **C = 2** (NH<sub>4</sub>Cl and H<sub>2</sub>O).
  - A total of 6 substances (NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NH<sub>3</sub>, H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> – but no NH<sub>4</sub>Cl!).
  - The connection between them are
    - 1 mass balance equation: [NH<sub>4</sub><sup>+</sup>] + [NH<sub>3</sub>] = [Cl<sup>-</sup>]
    - 1 charge balance equation: [NH<sub>4</sub><sup>+</sup>] + [H<sub>3</sub>O<sup>+</sup>] = [Cl<sup>-</sup>] + [OH<sup>-</sup>]
    - and 2 equilibrium constants: K<sub>w</sub> and K<sub>b</sub>(NH<sub>4</sub><sup>+</sup>)
    - **C = 6 – (1+1+2) = 2**

## Josiah Willard Gibbs (1839 – 1903)



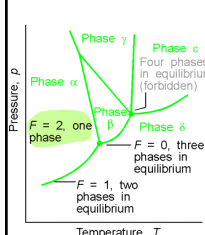
Commentators and biographers have remarked on the contrast between Gibbs's quiet, solitary life in turn of the century New England and the great international impact of his ideas. Though his work was almost entirely theoretical, the practical value of Gibbs's contributions became evident with the development of industrial chemistry during the first half of the 20th century. According to Robert A. Millikan, in pure science, Gibbs "did for statistical mechanics and for thermodynamics what Laplace did for celestial mechanics and Maxwell did for electrodynamics, namely, made his field a well-nigh finished theoretical structure."

## II. The phase rule and its derivation

- **Intensive properties:** *p*, *T* and *x<sub>j</sub>* mole fractions.
- Giving the composition of phases needs *C*–1 mole fractions.
- In *P* phases, *P*(*C*–1) mole fractions are needed, so there are *P*(*C*–1)+2 variables.
- In equilibrium, for each component *J*:
  - $\mu_{J,\alpha} = \mu_{J,\beta} = \dots$  in *P* phases, which means *P*–1 equations for each component.
  - For *C* components, there are *C*(*P*–1) equations.
- Each such equation decreases the number of freely modifiable intensive properties, originally *P*(*C*–1)+2.
- So the number of degrees of freedom:

$$F = [P(C - 1) + 2] - C(P - 1) = C - P + 2$$

## III. Application of the phase rule in one-component systems



### One-component systems (C = 1):

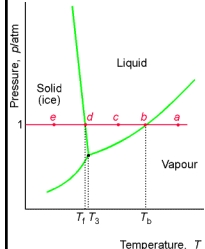
- in areas: **F = 1 – 1 + 2 = 2**
  - *T* and *p* are freely modifiable.
- on lines: **F = 1 – 2 + 2 = 1**
  - Either *T* or *p* is freely modifiable.
- in a triple point: **F = 1 – 3 + 2 = 0**
  - Characteristic constants.
- Four phases cannot be present in equilibrium!

$$F = C - P + 2$$

## III. Application of the phase rule in one-component systems

- **One-component system, one (equilibrium) phase:**
  - Infinitely many *p*–*T* pairs are possible → *F* = 2.
- **One-component system, two phases in equilibrium:**
  - The  $\mu$  is the same in the two ( $\alpha, \beta$ ) phases:  $\mu_\alpha(p, T) = \mu_\beta(p, T)$ .
  - One equation with two unknowns. There are many solutions, but *p* determines *T* (or *T* determines *p*). This is a degree of freedom: *F* = 1.
- **One-component system, three phases in equilibrium:**
  - The  $\mu$  is the same in the three ( $\alpha, \beta, \gamma$ ) phases, but  $\mu_\alpha(p, T) = \mu_\beta(p, T)$  and  $\mu_\beta(p, T) = \mu_\gamma(p, T)$  results  $\mu_\alpha(p, T) = \mu_\gamma(p, T)$ .
  - Two equations with two unknowns. The solution is only one single pair of *p* and *T*. → No freedom: *F* = 0.

## IV. Phase changes and their detection



- Upon increasing *T* (*p* = constants):
  - Gas (*a*) → liquid (*c*) → solid (*e*) transition detectable.
  - In point *b* (*T<sub>b</sub>*), boiling or condensation occurs.
  - In point *d* (*T<sub>f</sub>*), melting or freezing occurs.
- It is possible to monitor changes along a single vertical line (so that *T* = constant).

### IV. Phase changes and their detection

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- The  $g \rightarrow l$  or  $s \rightarrow l$  transition is easy to detect (and measured through the melting or freezing point).
- Thermal analysis:**
  - a favorable method to measure the enthalpy of phase transition.
- Based on the **cooling curve** (measured at constant pressure), an  $s_\alpha \rightarrow s_\beta$  phase transition (not usually observed easily) can also be studied.

### IV. Phase changes and their detection

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- Diamond anvil cell:**
  - Based on a simple lever principle.
  - Extremely large pressures (Mbar) can be reached (relevant for e.g. the core of the Earth).
  - Detection of phase transition: the **infrared spectrum of a ruby grain** mixed to the sample is monitored.

### V. Application of the phase rule in two-component systems

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#### Liquid-liquid phase diagrams

$C = 2$ , so  $F = 2 - P + 2 = 4 - P$   $F' = 3 - P$

- Keep one of the degrees of freedom constant ( $p$  or  $T$ ):
  - Change  $p$  and  $x_j$  (keep  $T$  constant): (vapor) pressure – composition diagram.
  - Change  $T$  and  $x_j$  (keep  $p$  constant): temperature – composition diagram.

### V. Application of the phase rule in two-component systems

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- Interpretation of diagrams: combination
- The change of the state of the system in response to pressure decrease at composition  $z_A$ :
  - high  $p \Rightarrow$  only  $l$ ,
  - intermediate  $\Rightarrow l$  and  $g$ ,
  - low  $p \Rightarrow$  only  $g$ .

$z_A$ : the generic mole fraction of substance A in the system

### V. Application of the phase rule in two-component systems

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- Temperature – composition ( $T-z$ ) diagrams, distillation
  - decrease in pressure,
  - increase in temperature while the other intensive property is kept constant.
- A is more volatile than B.
  - Single-step:** the equilibrium liquid at  $T$  is established, the vapor is rich in A, it is condensed.
  - Multistep:** the vapor is getting gradually richer in A, increasingly pure condensate is obtained (fractional distillation).

### V. Application of the phase rule in two-component systems

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From last week's lecture:

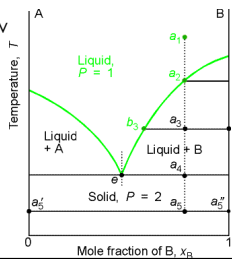
<p><b>V. Liquids with limited miscibility: phase separation.</b></p> <p>The range of limited miscibility usually depends on the temperature. There are three possibilities:</p> <p><b>Version 1:</b></p> <ul style="list-style-type: none"> <li>at high <math>T</math>, two phases (<math>P = 2</math>)</li> <li>at low <math>T</math>, one phase (<math>P = 1</math>)</li> <li>e.g. hexane, trichloroethylene</li> <li>lever rule: <math>n_L x_L + n_V x_V = n</math></li> <li><math>T_c</math>: upper critical temperature</li> </ul>	<p><b>V. Liquids with limited miscibility: phase separation.</b></p> <p>The range of limited miscibility usually depends on the temperature. There are three possibilities:</p> <p><b>Version 2:</b></p> <ul style="list-style-type: none"> <li>at high <math>T</math>, two phases (<math>P = 2</math>)</li> <li>at low <math>T</math>, only one phase (<math>P = 1</math>)</li> <li>e.g. water-miscible organic liquids</li> <li>lever rule: <math>n_L x_L + n_V x_V = n</math></li> <li><math>T_c</math>: lower critical temperature</li> </ul>	<p><b>IV. Azeotropic mixtures</b></p> <p>If a mixture of composition <math>z_A</math> is distilled, the composition of the remaining liquid can only change until it reaches <math>z_A^*</math>.</p> <p>If a mixture of composition <math>z_A</math> is distilled, the comp. of the vapor can only change until it reaches <math>z_A^*</math>.</p>
<p><b>V. Liquids with limited miscibility: phase separation.</b></p> <p>The range of limited miscibility usually depends on the temperature. There are three possibilities:</p> <p><b>Version 3:</b></p> <ul style="list-style-type: none"> <li>at high <math>T</math>, one phase (<math>P = 1</math>)</li> <li>at low <math>T</math>, one phase (<math>P = 1</math>)</li> <li>at intermediate <math>T</math>, two phases (<math>P = 2</math>)</li> <li>e.g. water-miscible system</li> <li>lever rule: <math>n_L x_L + n_V x_V = n</math></li> <li><math>T_c</math>: upper critical temperature</li> <li><math>T_c</math>: lower critical temperature</li> </ul>	<p><b>V. Liquids with limited miscibility: distillation.</b></p> <p>The distillation of such mixtures is also versatile:</p> <ul style="list-style-type: none"> <li>Distillation: <b>mixing before boiling</b></li> <li><math>T_{boil} &lt; T_c</math></li> <li><math>x_L</math> is lower than <math>x_V</math></li> <li><math>x_L</math> approaches 0, <math>x_V</math> approaches 1</li> <li>the condensate is <b>richer</b> in A than the mixture</li> <li>upon further cooling, separation into A/B occurs</li> <li>During distillation, the composition of the un-distilled liquid changes.</li> </ul>	<p><b>V. Liquids with limited miscibility: distillation.</b></p> <p>The distillation of such mixtures is also versatile:</p> <ul style="list-style-type: none"> <li>Distillation: <b>boiling before mixing</b></li> <li><math>T_{boil} &gt; T_c</math></li> <li><math>x_L</math> turns into <math>x_V</math></li> <li><math>x_V</math> turns into <math>x_L</math></li> <li>the condensate is <b>poorer</b> in A than the mixture</li> <li>the vapour is <b>poorer</b> in A than the mixture</li> <li>and above the same composition, no separation occurs upon distillation.</li> </ul>

## V. Application of the phase rule in two-component systems

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### Liquid-solid phase diagrams

- Two immiscible metals (e.g. Sb and Bi).
- The phase diagram is similar to the previous one, but now *l* and *s* occur in it.
- Upon cooling:
  - initially ( $a_1$ ):  $C = 2, P = 1$
  - at  $a_2$  *l* and B(*s*), so  $P = 2$
  - at  $a_3$ :  $P = 2$ , lever rule
  - from  $a_4$ :  $P = 2$ , pure A and B

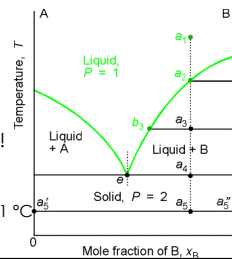


## V. Application of the phase rule in two-component systems

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Eutectics („easily melting“): at composition *e*

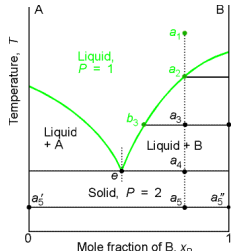
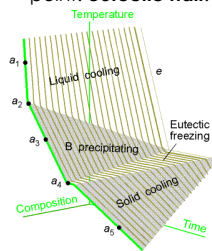
- the composition of *l* and *s* is the same  $F' = 3 - P$
- lowest  $T_{fus}$
- only composition with a definite freezing point
- neither A nor B form
- $F = 0$  if  $C = 2$  and  $P = 3$
- huge practical importance!
  - 67w% Sn + 33w% Pb: 183 °C (tin solder)
  - 23w% NaCl + 77w% water: -21 °C



## V. Application of the phase rule in two-component systems

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- Thermal analysis: cooling curves** measured.
- At eutectic compositions, there is only one break point: **eutectic halt!**

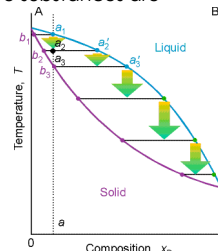


## V. Application of the phase rule in two-component systems

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Preparation of **ultrapure substances, controlled amounts of impurities:**

- In some technologies, highly pure substances are needed or the presence of exactly known amounts of „impurities“ (dopants), e.g. semiconductor industry.
- These can be prepared by **fractional crystallization**, but this is slow and expensive.

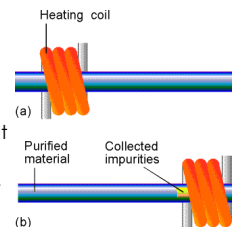


## V. Application of the phase rule in two-component systems

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Preparation of **ultrapure substances, controlled amounts of impurities:**

- In some technologies, highly pure substances are needed or the presence of exactly known amounts of „impurities“ (dopants), e.g. semiconductor industry.
- Purification by zone melting:** the impurity dissolves in the melt better than in the liquid.
- A melt zone travels through the rod-shaped sample – lots of times.

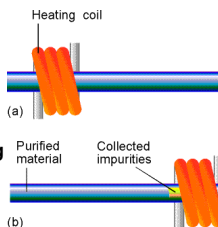


## V. Application of the phase rule in two-component systems

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Preparation of **ultrapure substances, controlled amounts of impurities:**

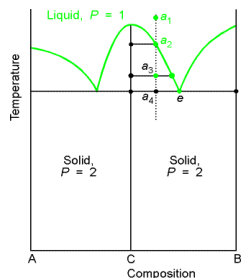
- In some technologies, highly pure substances are needed or the presence of exactly known amounts of „impurities“ (dopants), e.g. semiconductor industry.
- Controlled introduction of impurity by zone melting: doping** (artificial, controlled and uniform introduction („sweeping“) of an „impurity“).



## VI. Reactive systems

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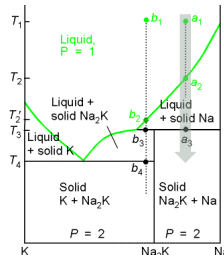
- In **reactive systems**, the components react and form a new substance:
- $A + B \rightarrow C$  (so  $C = 2$ )
- [A and C] and [B and C] both form eutectics.
  - (e.g.  $Ga + As = GaAs$ ).
- The phase diagrams of two – [A,C] and [B,C] – binary eutectic systems next to each other.



## VI. Reactive systems

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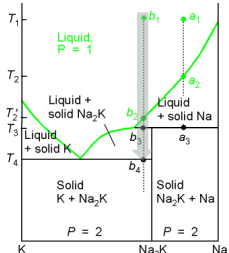
- In **reactive systems**, the components react and form a new substance:
- $A + B \rightarrow C$  (so  $C = 2$ )
- Incongruent melting:** compound C (e.g.  $Na_2K$ ) decomposes in the liquid state (at high T).
- Cooling along the  $a_1$  isopleth:
  - from  $a_2$  Na(s) and K-rich l
  - from  $a_3$  only Na(s) and  $Na_2K$ (s)



## VI. Reactive systems

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- In **reactive systems**, the components react and form a new substance:
- $A + B \rightarrow C$  (so  $C = 2$ )
- Incongruent melting:** compound C (e.g.  $Na_2K$ ) decomposes in the liquid state (at high T).
- Cooling along the  $b_1$  isopleth:
  - at  $b_2$  deposition of Na(s)
  - from  $b_3$  formation of  $Na_2K$ (s)
  - at  $b_4$  eutectics (2 phases): K(s) and  $Na_2K$ (s)



## VII. Application of the phase rule in three-component systems

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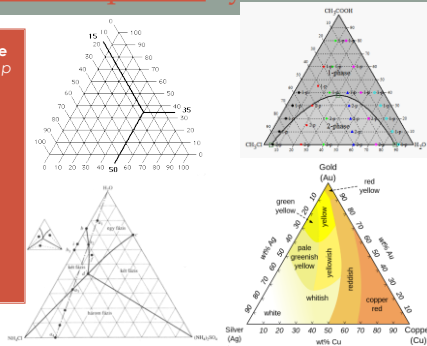
- The phase rule:  $F = 3 - P + 2 = 5 - P$ , so the number of degrees of freedom may be up to 4.
- If  $p$  and  $T$  re constant, the mole fractions of two components can still be modified.
  - Triangle phase diagrams:** no  $p$  or  $T$  axis, all 3 axes are for composition.
  - Experimental information is essential.
  - Valid only at the given  $p$  and  $T$ .

## VII. Application of the phase rule in three-component systems

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Triangle phase diagrams: no  $p$  or  $T$  axis, all 3 axes are for composition. Experimental information is essential.

Only valid at the given  $p$  and  $T$ .



## VII. Application of the phase rule in three-component systems

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- Bailing out/salt induced precipitation:** three-phase partition between a solution and two solid phases.
- Several different versions:
  - removal of a (useful) salt from a solution by adding another, less useful one,
  - precipitation of hydrophilic colloids by adding a salt (the salt removes the protective water layer),
  - precipitation of dissolved organic matter from aqueous solution by adding a salt (a decrease in the activity of water).

