THE PHASE RULE

I. Number of components, number of phases, umber of 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. Application of the phase rule in **three-component** systems.

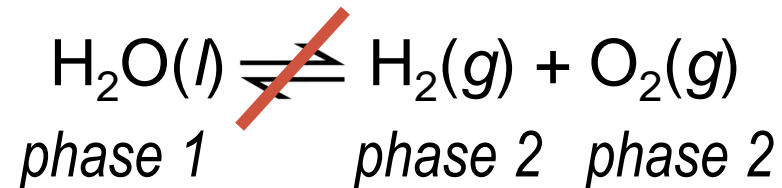# I. Number of components, phases and degrees of freedom.

- **<u>Phase</u> (*P*)**: a macroscopic part of a system which shows identical properties everywhere. It may be composed of several *components* (e.g.: NH_3 gas, water–hydrochloric acid, air, iron ore …).

- **<u>Component</u> (*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.

- **<u>Degree of freedom</u> (*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):

$$H_2O(l) \rlap{\diagup}{\rightleftharpoons} H_2(g) + O_2(g)$$

phase 1   *phase 2   phase 2*

- Three substances (O_2, H_2 and H_2O) and two phases (liquid and gas, **P = 2**) are present.

- At room temperature, O_2 and H_2 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):

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

phase 1   *phase 2*   *phase 3*
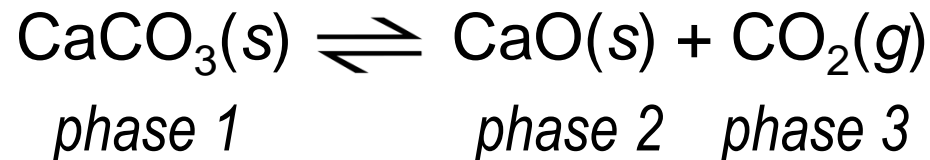
- If the composition of *phase 3*, $CO_2(g)$, is known,

- 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):

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$
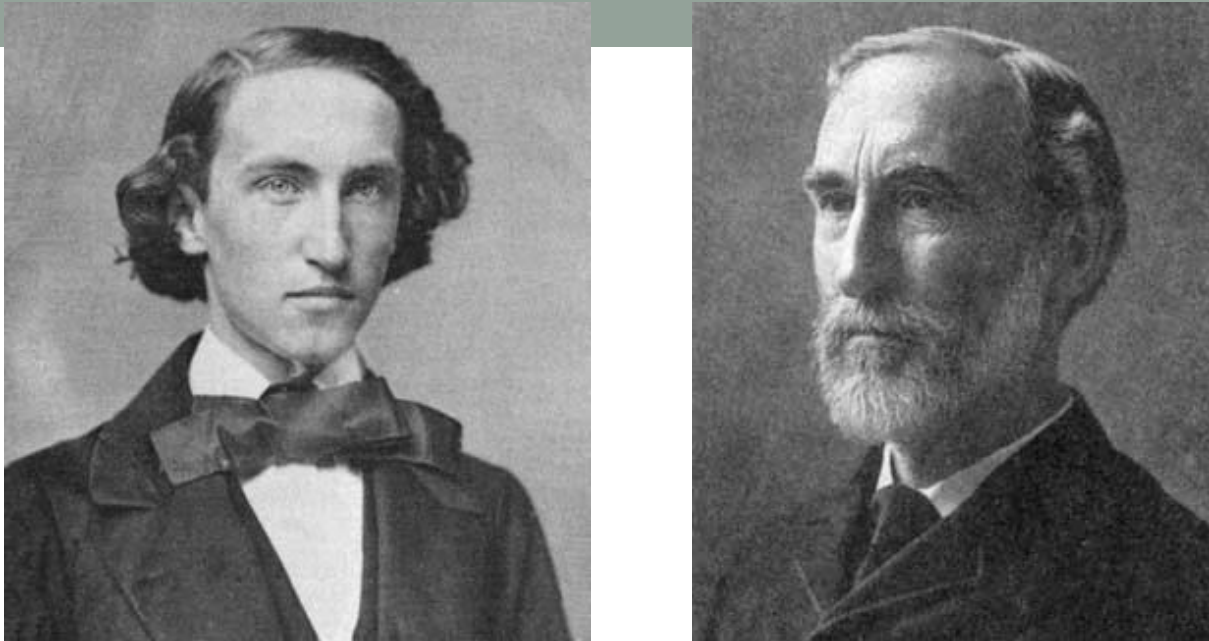
phase 1　　　*phase 2*　　*phase 2*
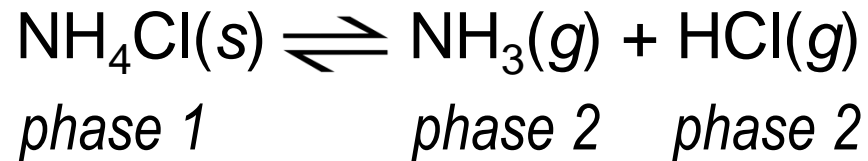
- Three *substances* and two *phases* (solid and gas, **P = 2**) are present.

- 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_4Cl (**C = 1**).

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_J 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:

  - $\mu_{J,\alpha} = \mu_{J,\beta} = \ldots$ 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:

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

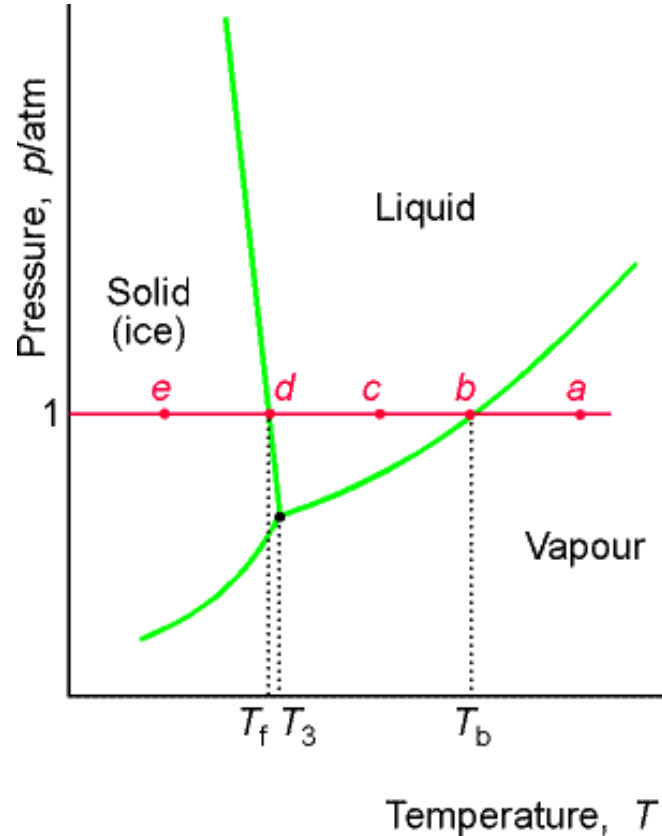# III. Application of the phase rule in **one-component** systems
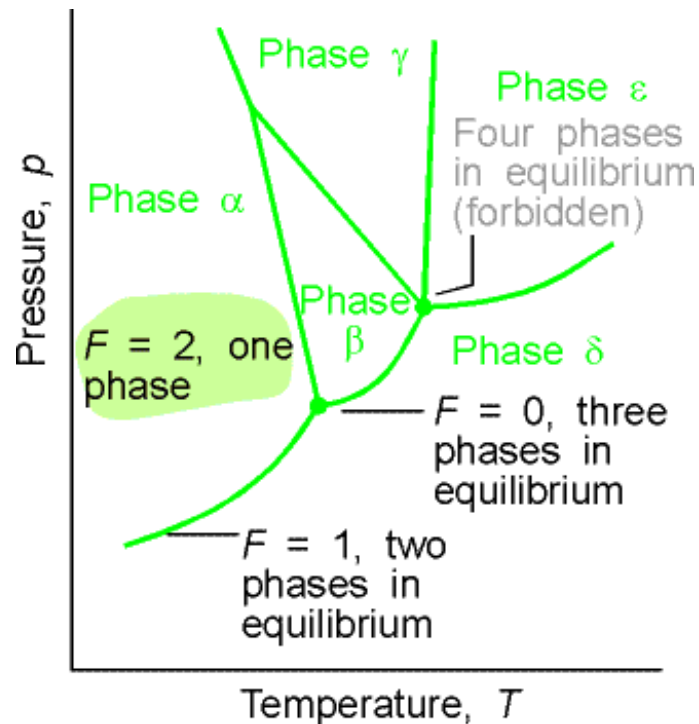
One-component systems ($C = 1$):

- in areas: $F = 1 - 1 + 2 = \mathbf{2}$
  - Both T and p are freely modifiable.
- on lines: $F = 1 - 2 + 2 = \mathbf{1}$
  - Either T or p is freely modifiable.
- in a triple point: $F = 1 - 3 + 2 = \mathbf{0}$
  - Characteristic constants.

- Four phases cannot be present in equilibrium!
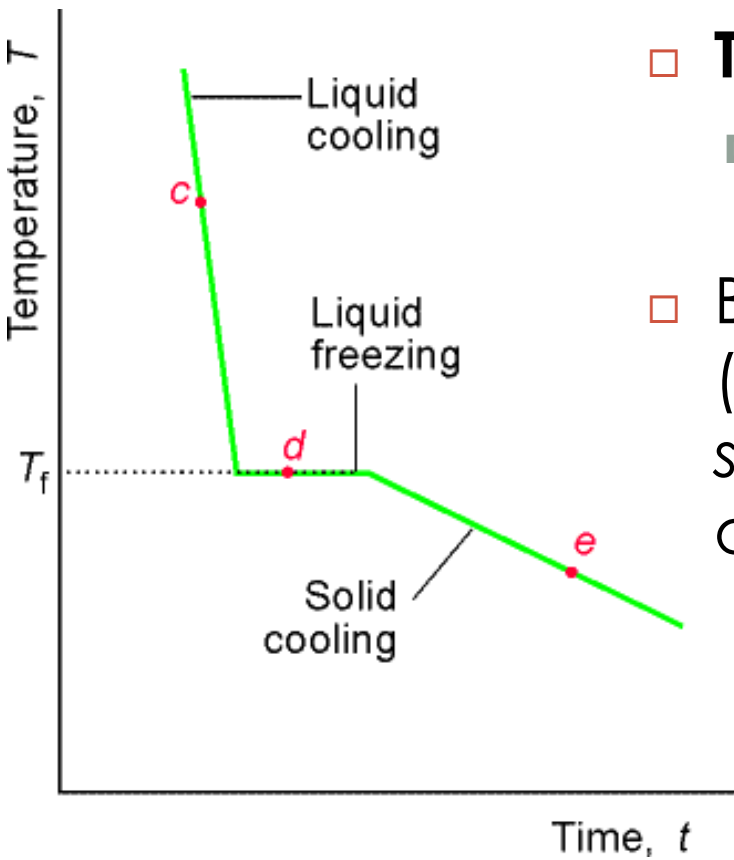
$$F = C - P + 2$$

IV. Phase changes and their detection

- Upon increasing T (p = constants):
  - Gas (*a*) → liquid (*c*) → solid (*e*) transition detectable.
  - In point *b* (T_b), boiling or condensation occurs.
  - In point *d* (T_f), melting or freezing occurs.

- It is possible to monitor changes along a single vertical line (so that T = constant).

□ 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.

Liquid cooling

c

Liquid freezing

T_f

d

e

Solid cooling

Temperature, T

Time, t

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

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.

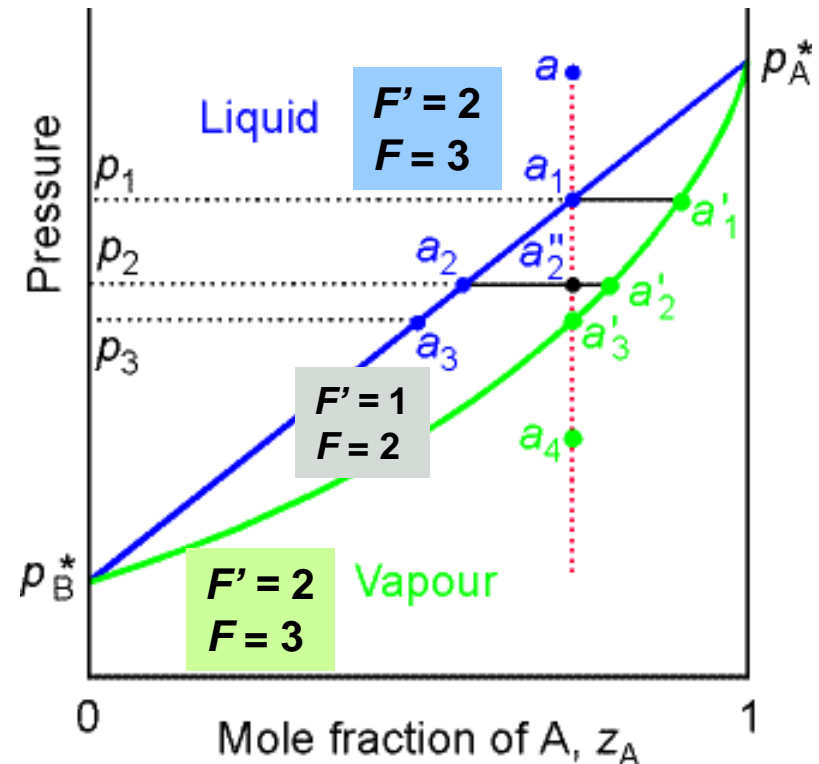 - Change T and x_J (keep p constant): temperature–composition diagram.
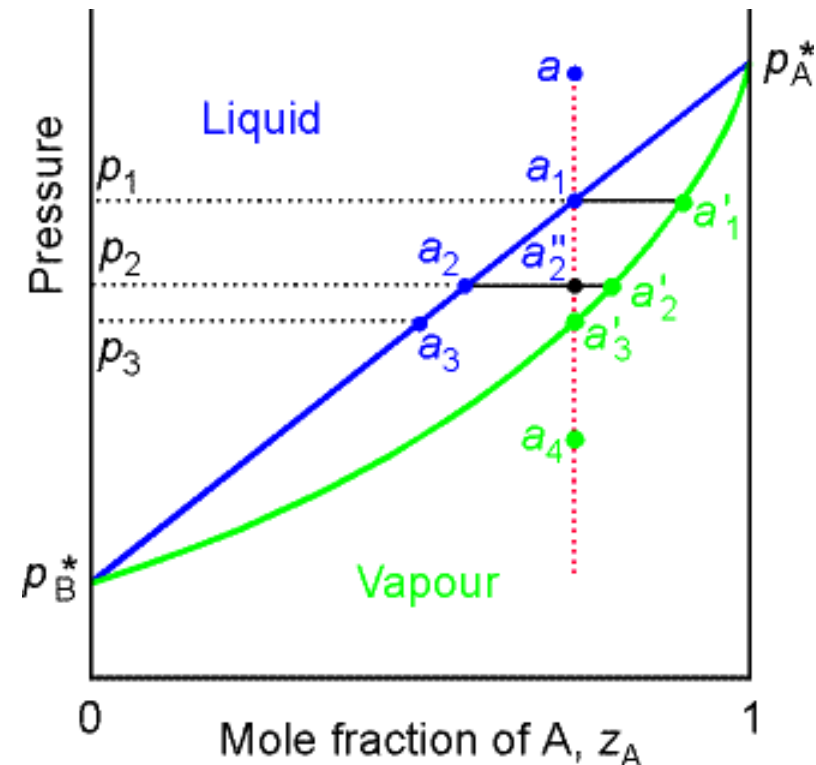
V. Application of the phase rule in **two-component** systems

- Interpretation of diagrams: combination
- The change of the state of the system in response to pressure decrease at composition a:

$$F' = 3 - P$$

- Vertical line: isopleth

- Pressure decrease:

  - high $p \Rightarrow$ only l,

  - intermediate $\Rightarrow$ l and g,

  - low $p \Rightarrow$ only g.

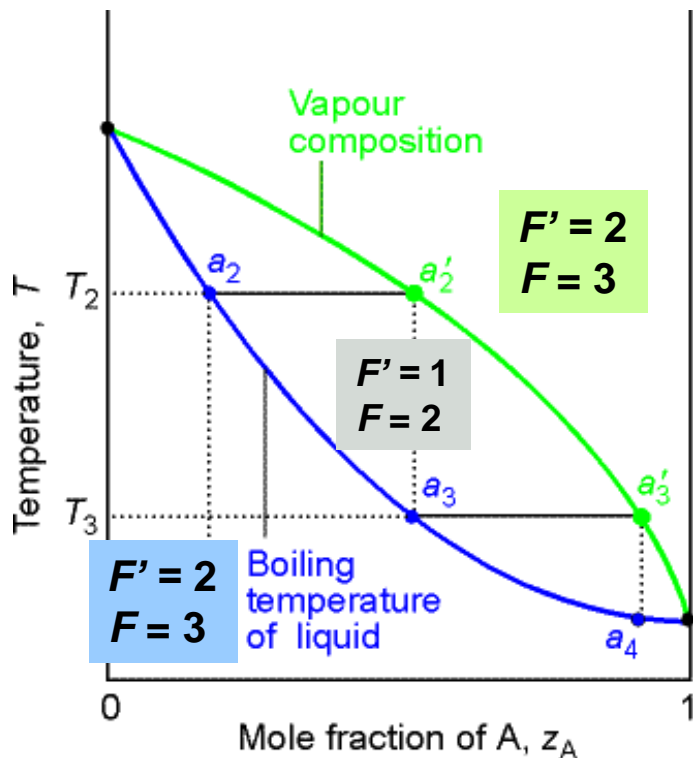z_A: the generic mole fraction of substance A in the system

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

□ Temperature–composition (T–z) diagrams, distillation

$$F' = 3 - P$$

- increase in temperature while the other intensive property is kept constant.

□ A is more volatile than B.

- **Single-step**: the equilibrium valid 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).

Liquid-solid phase diagrams

- Two immiscible metals.

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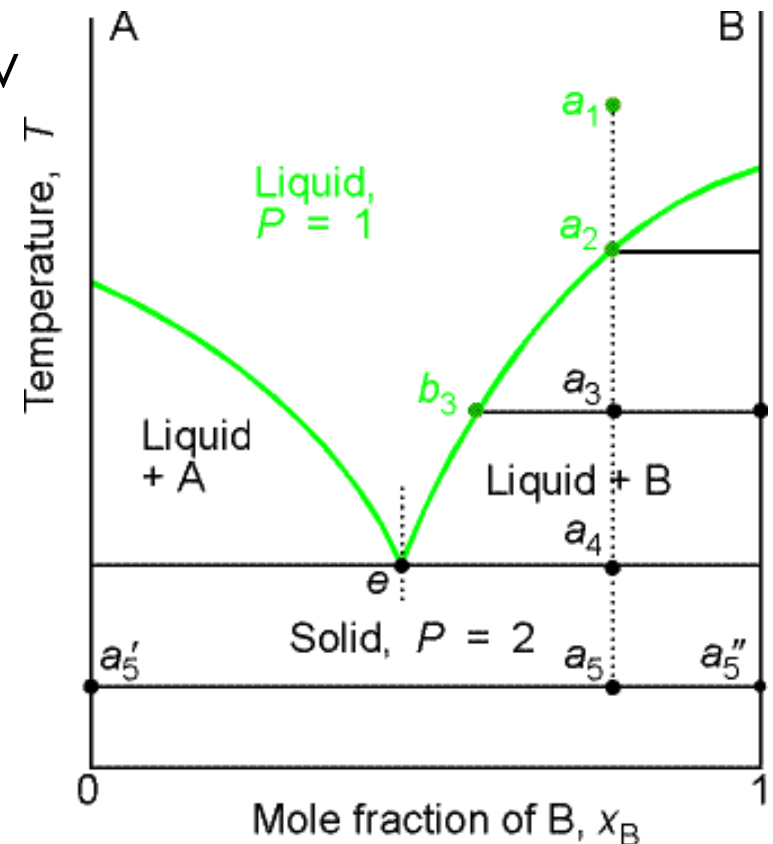
V. Application of the phase rule in **two-component** systems

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

- □ the composition of *l* and *s* is the same

$$F' = 3 - P$$

- □ lowest T_{fus}

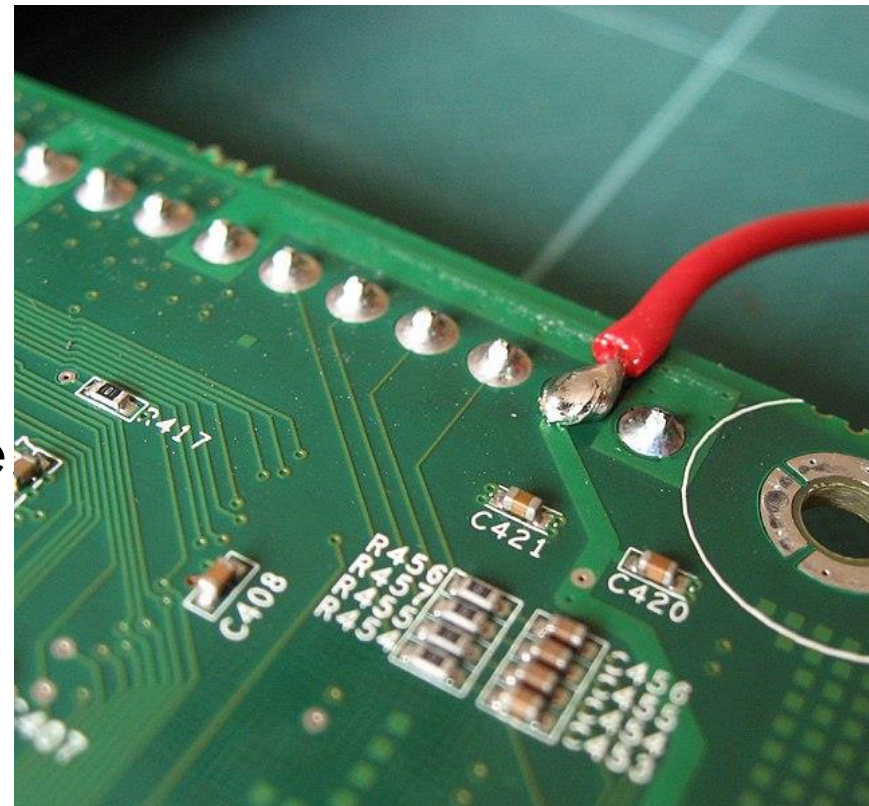- □ only composition with a definite freezing point

- □ neither A nor B form

- □ $F = 0$ if $C = 2$ and $P = 3$

- □ huge practical importance
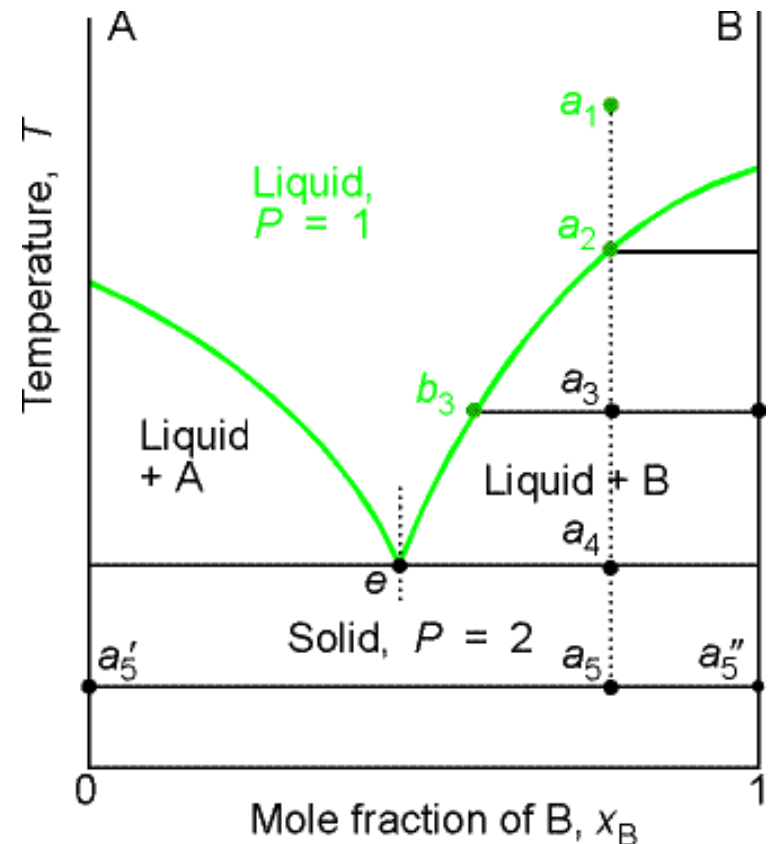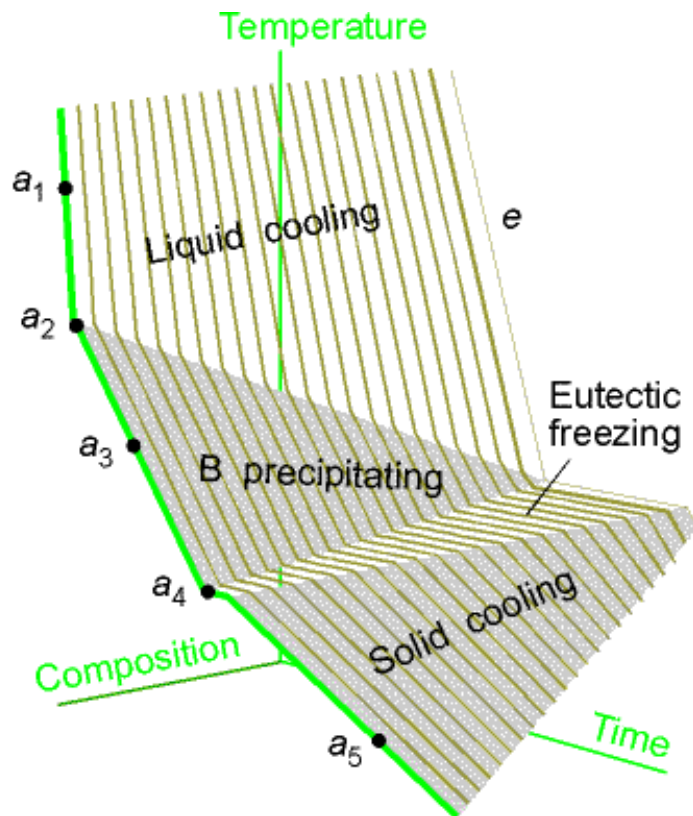 - ▫ 67s% Sn + 33s% Pb: 183 °C (tin solder)
  - ▫ 23s% NaCl + 77s% water: -21 °C

- **Thermal analysis**: **cooling curves** measured.
- At eutectic compositions, there is only one break point: **eutectic halt**!
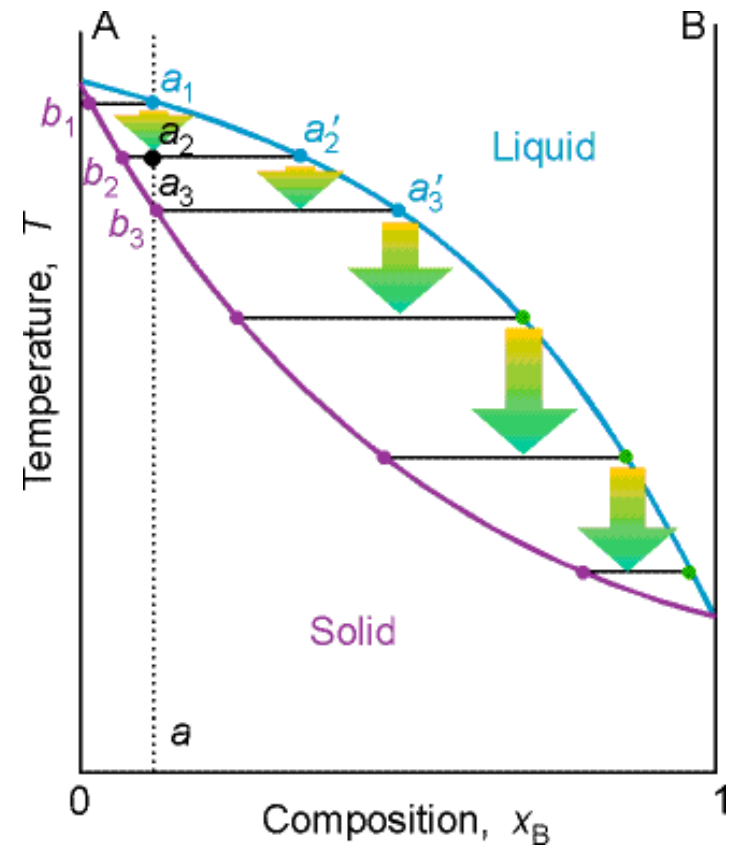
V. Application of the phase rule in **two-component** systems

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.

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.

Heating coil

(a)

Purified material   Collected impurities

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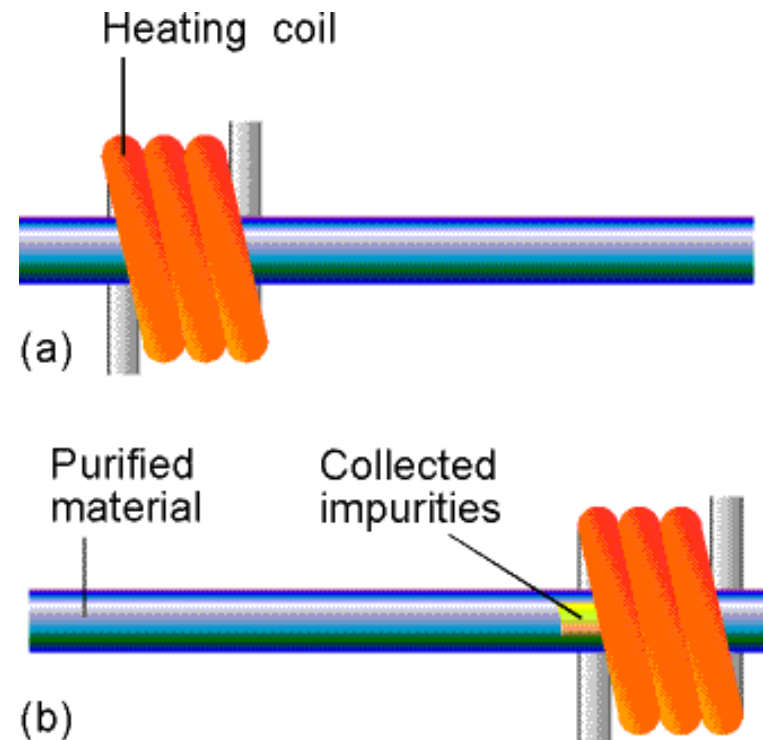
- The phase rule: $F = 3 - P + 2 = 5 - P$, so the number of degrees of freedom may be up to 4.
- If p and T re constant, the mole fractions of two components can still be modified.
  - **Triangle phase diagrams**: no p or T axis, all 3 axes are for composition.
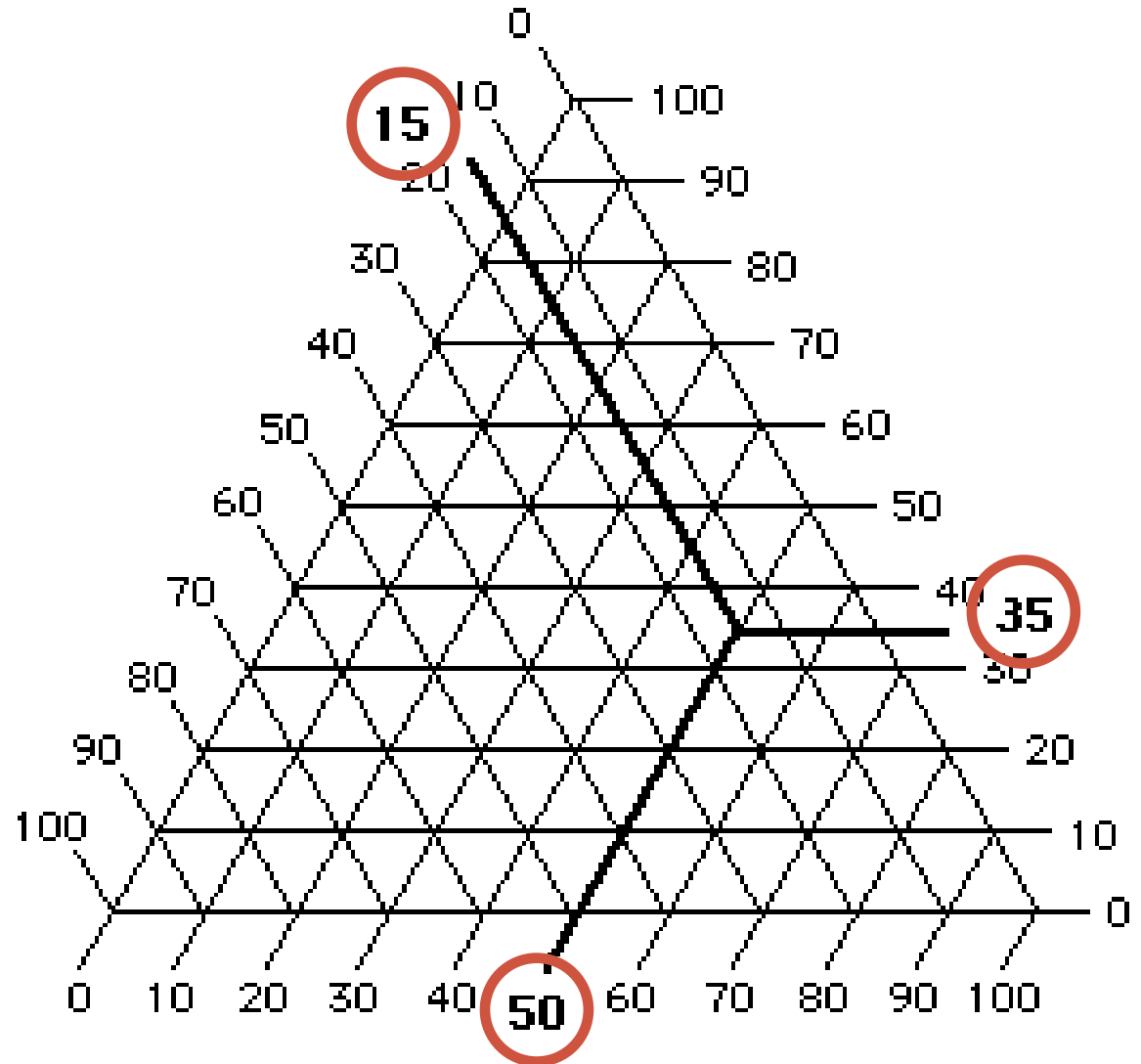 - Experimental information is essential.
  - Valid only at the given p and T.

VI. Application of the phase rule in **three-component** systems

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*.

VI. Application of the phase rule in **three-component** systems

Triangle phase diagrams: no *p* or *T* axis, all 3 axes are for composition.

Experimental information is essential.
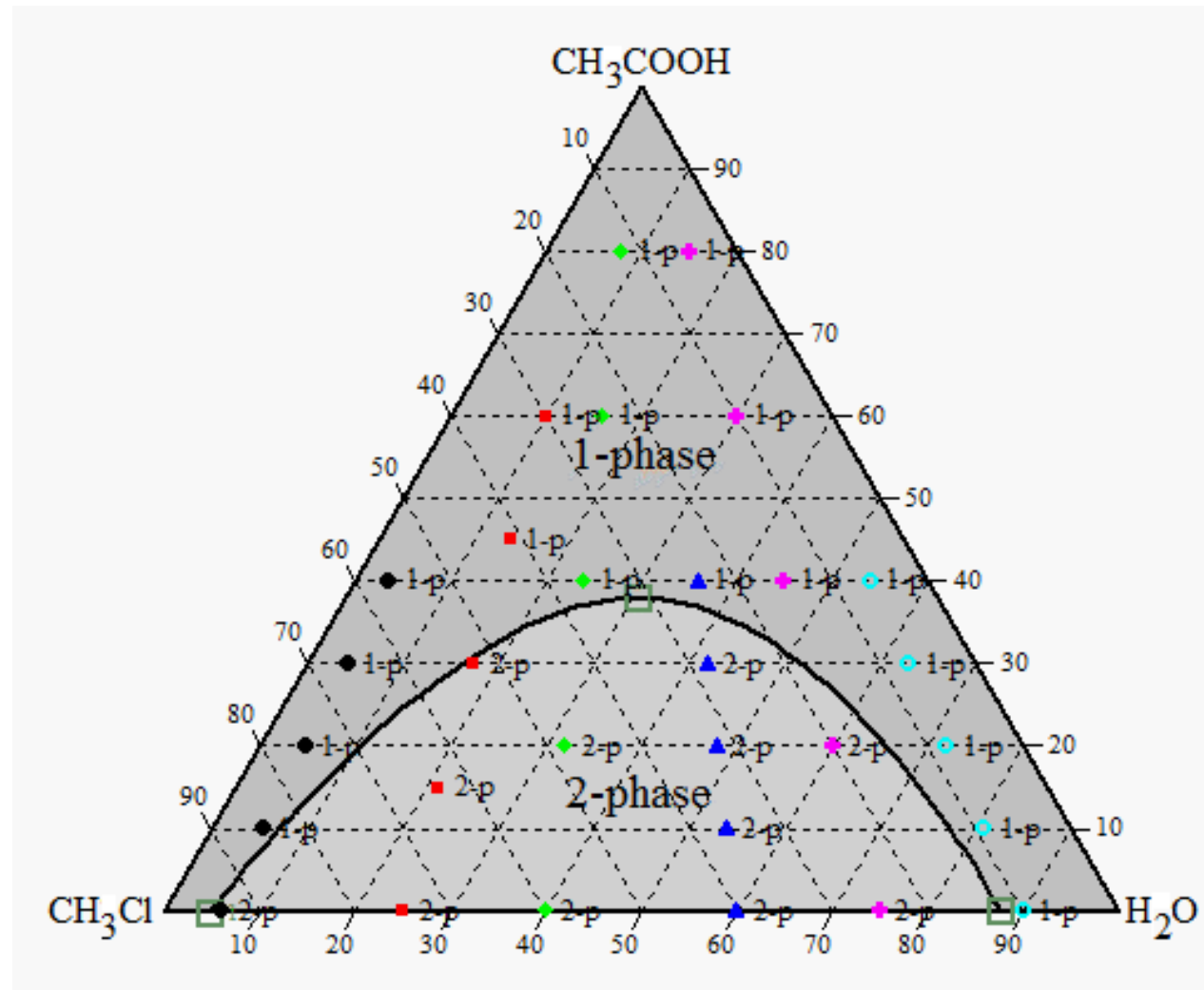
Only valid at the given *p* and *T*.

VI. Application of the phase rule in **three-component** systems

Triangle phase diagrams: no p or T axis, all 3 axes are for composition.

Experimental information is essential.
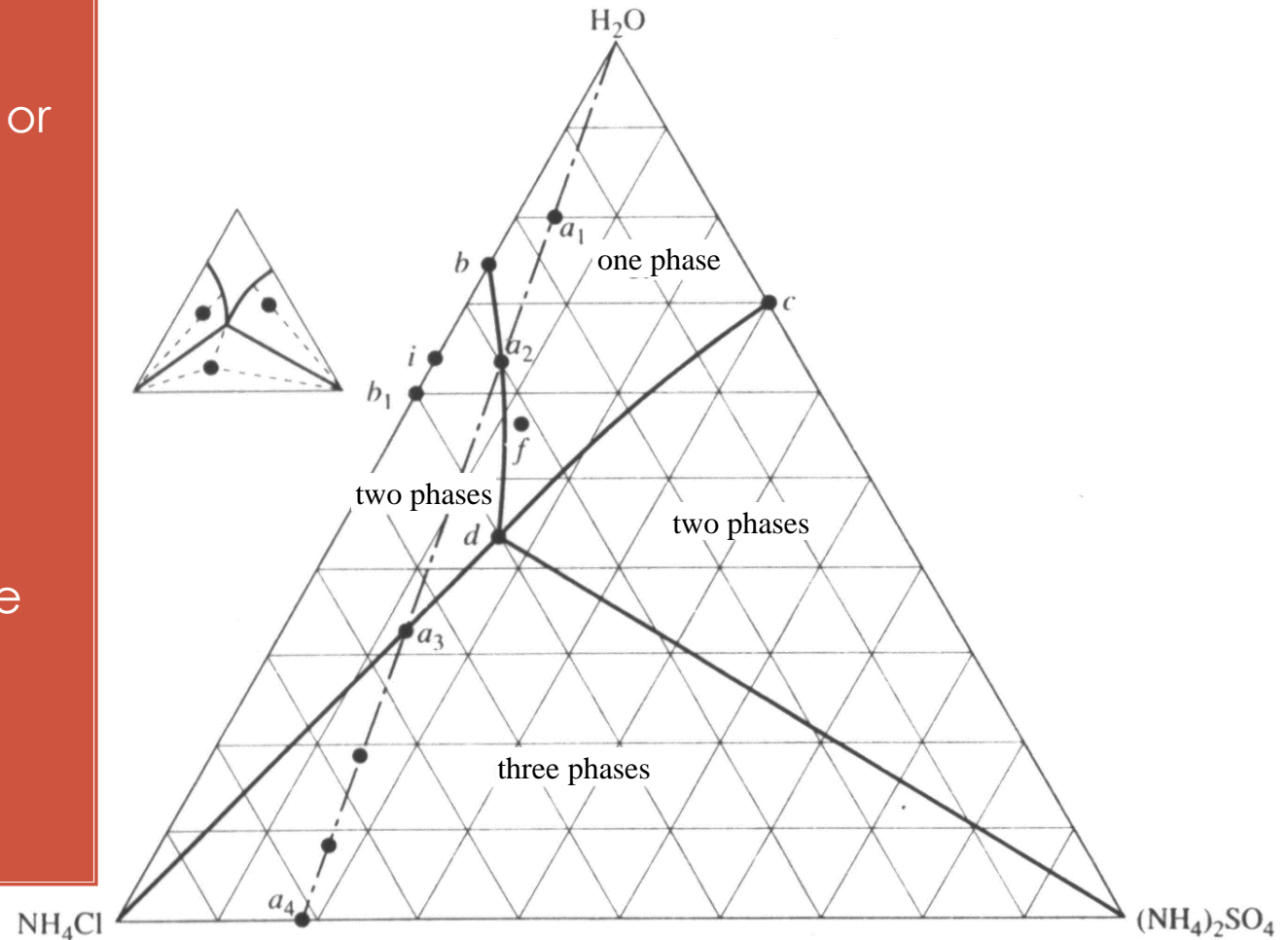
Only valid at the given p and T.

VI. Application of the phase rule in **three-component** systems

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.