

# Exercise for the Lecture on Materials Science

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## Exercise Sheet 6

Solution

### Exercise 1: Water

1. To determine the number of degrees of freedom, we use the Gibbs phase rule:

$$F = K + N - P$$

$F$ : Number of intensive variables (degrees of freedom)

$K$ : Number of components

$N$ : Number of independent state variables

$P$ : Number of coexisting phases in equilibrium

For the water system:

- $K = 1$  (one component:  $\text{H}_2\text{O}$ )
- $N = 2$  (variables: temperature  $T$  and pressure  $p$ )
- Simplified:  $F = 3 - P$

#### Point A

- Phase: Liquid water
- $P = 1$
- $F = 3 - 1 = 2$

#### Point B

- Phase: Water vapor
- $P = 1$
- $F = 3 - 1 = 2$

#### Point C

- Phase: Ice I
- $P = 1$
- $F = 3 - 1 = 2$

### Point D

- Phases: Ice III + Liquid
- $P = 2$
- $F = 3 - 2 = 1$

2. **Why can water remain liquid below 0 °C, even though this is below the freezing point? Explain the physical mechanism.**

**Solution:** Water can be supercooled because the formation of a stable crystalline nucleus is required for crystallization. Without existing nucleation sites, a nucleus must form spontaneously through thermal fluctuations. However, it must exceed a critical size to become stable, as smaller clusters dissolve due to surface energy. In pure water, homogeneous nucleation occurs only at significant undercooling.

3. **Calculate the critical radius of an ice nucleus at an undercooling of 10 K. Given:**  $\gamma = 0,033 \text{ J/m}^2$ ,  $\Delta H_f = 3,34 \cdot 10^8 \text{ J/m}^3$ ,  $T_m = 273,15 \text{ K}$ ,  $\Delta T = 10 \text{ K}$

**Solution:**

$$r^* = \frac{2\gamma \cdot T_m}{\Delta H_f \cdot \Delta T} = \frac{2 \cdot 0,033 \cdot 273,15}{3,34 \cdot 10^8 \cdot 10} = \frac{18,04}{3,34 \cdot 10^9} \approx 5,4 \cdot 10^{-9} \text{ m} = 5,4 \text{ nm}$$

**Answer:** The critical radius is approximately 5,4 nm.

4. **Explain the difference between homogeneous and heterogeneous nucleation during water freezing. Give typical examples from nature or technology.**

**Solution:**

- **Homogeneous nucleation:** Nuclei form uniformly within the liquid phase, without preferred sites. This requires significant undercooling due to the absence of favorable interfaces. Example: highly pure, supercooled water in lab conditions.
- **Heterogeneous nucleation:** Nucleation occurs at existing surfaces or impurities such as dust, cellulose, or bacteria. These reduce the activation energy, enabling nucleation at lower undercooling. Examples: freezing of cloud droplets on aerosols, ice on airplane wings, bacteria such as *Pseudomonas syringae*.

5. **How do dust particles or impurities influence the probability of ice nucleation in clouds?**

**Solution:** Impurities like dust, soot, or biological particles (e.g., pollen, bacteria) reduce the surface energy for nucleation. As a result, the activation barrier is lowered, and nucleation can occur at higher temperatures. These heterogeneous nucleation sites are crucial for ice formation in the atmosphere and are referred to as "ice nuclei." Without them, many clouds would remain liquid and produce little precipitation.

## Exercise 2: Spinodal decomposition in a binary alloy

### 1. Difference between spinodal and binodal decomposition:

- **Binodal decomposition:** occurs through nucleation and growth. The system is metastable; small fluctuations are suppressed, and a critical nucleus size must be exceeded.
- **Spinodal decomposition:** occurs spontaneously through continuously growing concentration fluctuations. The system is unstable, and any small fluctuation leads to phase separation.

### 2. Condition for spinodal instability:

Spinodal decomposition occurs when the free enthalpy curve has negative curvature with respect to composition:

$$\frac{\partial^2 G}{\partial c^2} < 0$$

Differentiating  $G(c)$ :

$$\frac{\partial^2 G}{\partial c^2} = \frac{\partial^2}{\partial c^2} [\Omega c(1-c) + RT(c \ln c + (1-c) \ln(1-c))]$$

Separately:

$$\frac{\partial^2}{\partial c^2} [\Omega c(1-c)] = -2\Omega$$

$$\frac{\partial^2}{\partial c^2} [RT(c \ln c + (1-c) \ln(1-c))] = RT \left[ \frac{1}{c(1-c)} \right]$$

Combined:

$$\frac{\partial^2 G}{\partial c^2} = -2\Omega + \frac{RT}{c(1-c)}$$

Spinodal instability occurs when:

$$\frac{RT}{c(1-c)} < 2\Omega$$

### 3. Composition range for spinodal decomposition:

Given:

$$T = 300 \text{ K}, \quad \Omega = 2,5 \cdot 10^3 \text{ J/mol}, \quad R = 8,314 \text{ J/mol K}$$

Calculation:

$$\frac{RT}{2\Omega} = \frac{8,314 \cdot 300}{2 \cdot 2500} = \frac{2494,2}{5000} \approx 0,499$$

Hence:

$$\frac{1}{c(1-c)} < \frac{1}{0,499} \Rightarrow c(1-c) > 0,499 \Rightarrow c \in (0,293, 0,707)$$

**Answer:** The condition for spinodal instability is:

$$c(1 - c) > 0.499 \Rightarrow c \in (0.293, 0.707)$$

**Only within this concentration range is the system spinodally unstable.** Outside this range (e.g., at  $c = 0.2$  or  $c = 0.8$ ), we have:

$$\frac{\partial^2 G}{\partial c^2} > 0$$

This means the system is metastable or even stable in those regions. In these cases, no spontaneous phase separation occurs through growing concentration fluctuations.

**Conclusion:** Spinodal decomposition does *not* occur at all concentrations, but only within the range

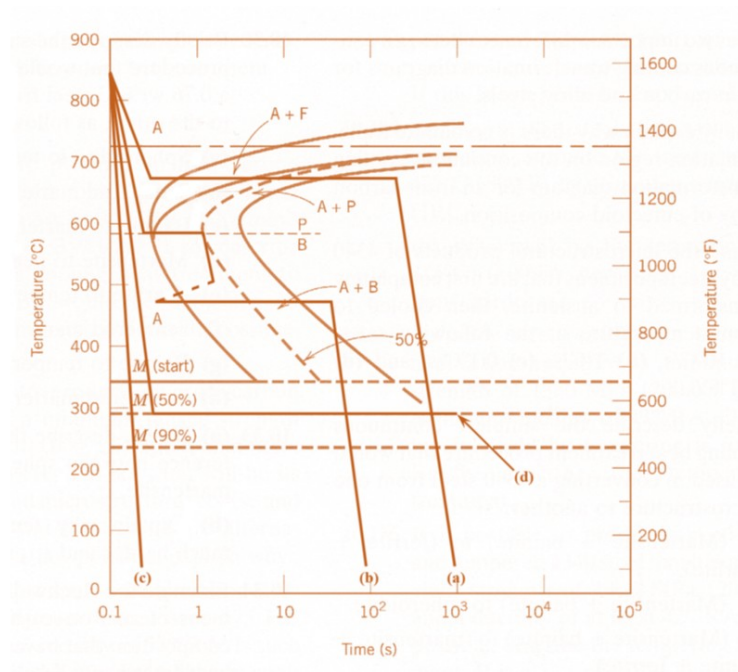
$$c \in (0.293, 0.707)$$

#### 4. Morphology and examples:

Spinodal decomposition typically results in a fine, periodic, sponge-like or labyrinthine microstructure with characteristic wavelength.

**Examples:** Polymer blends, glass phase separation, Cu-Ni-Mn alloys (e.g., spinodal hardening).

### Exercise 3: Time-Temperature-Transformation Diagram



## Exercise 4: MgO–Al<sub>2</sub>O<sub>3</sub> System

### (a) Al<sub>2</sub>O<sub>3</sub>-rich side: 82 mol% Al<sub>2</sub>O<sub>3</sub>

**Vacancy type:** Mg<sup>2+</sup> vacancies

**Explanation:**

Excess Al<sup>3+</sup> ions substitute Mg<sup>2+</sup>. To maintain charge neutrality, for every two Mg<sup>2+</sup> replaced, one Mg<sup>2+</sup> vacancy must be created.

**Approach:**

Assume  $N$  stoichiometric units of MgAl<sub>2</sub>O<sub>4</sub>.

⇒  $N$  Mg<sup>2+</sup>,  $2N$  Al<sup>3+</sup>

Add  $2x$  Al<sup>3+</sup>, remove  $3x$  Mg<sup>2+</sup>

Then:

$$\text{mol\%}(\text{Al}_2\text{O}_3) = \frac{(2N + 2x)/2}{(2N + 2x)/2 + N - 3x}$$

Inserting 0.82 and solving:

$$\frac{N + x}{2N - 2x} = 0,82 \quad \Rightarrow \quad x = \frac{0,64}{2,64}N \approx 0,242N$$

**Fraction of Mg<sup>2+</sup> vacancies:**

$$\frac{x}{\text{total cation sites}} = \frac{0,242N}{3N} = \boxed{8,1\%}$$

### (b) MgO-rich side: 39 mol% Al<sub>2</sub>O<sub>3</sub>

**Vacancy type:** O<sup>2-</sup> vacancies

**Explanation:**

Excess Mg<sup>2+</sup> substitutes Al<sup>3+</sup>. For every two Al<sup>3+</sup> replaced, one O<sup>2-</sup> vacancy is created to maintain charge neutrality.

**Approach:**

Assume  $N$  stoichiometric units.

⇒  $N$  Mg<sup>2+</sup>,  $2N$  Al<sup>3+</sup>

Add  $2y$  Mg<sup>2+</sup>, remove  $2y$  Al<sup>3+</sup>

Then:

$$\text{mol\%}(\text{Al}_2\text{O}_3) = \frac{(2N - 2y)/2}{(2N - 2y)/2 + N + 2y} = \frac{N - y}{2N + y}$$

Inserting 0.39 and solving:

$$\frac{N - y}{2N + y} = 0,39 \quad \Rightarrow \quad y = \frac{0,22}{1,39}N \approx 0,158N$$

**Fraction of O<sup>2-</sup> vacancies:**

$$\frac{y}{4N} = \frac{0,158N}{4N} = \boxed{4,0\%}$$