

# Exercise for the Lecture on Materials Science

Prof. Peter Müller-Buschbaum, Lea Westphal, Ziyang Zhang, Doan Duy Ky Le

## Exercise Sheet 2

### Solution

#### Exercise 1 – Point Defects

a) The fraction of vacancies is given by the equation:

$$\frac{N_V}{N} = \exp\left(-\frac{Q_v}{kT}\right)$$

with:

$$Q_v = 0.55 \text{ eV}, k = 8.62 \times 10^{-5} \text{ eV/K}, T = 600 \text{ K}$$

Inserting the values:

$$\frac{N_V}{N} = \exp\left(-\frac{0.55}{8.62 \times 10^{-5} \cdot 600}\right) = \exp(-10.63) = 2.41 \times 10^{-5}$$

**Result:** Vacancy fraction =  $2.41 \times 10^{-5}$

b) Number of lattice sites  $N$ :

$$N = N_A \cdot \frac{\rho_{Al}}{A_{Al}} = 6.022 \times 10^{23} \cdot \frac{2.62}{26.98} = 5.85 \times 10^{22} \text{ atoms/cm}^3 = 5.85 \times 10^{28} \text{ atoms/m}^3$$

Then:

$$\frac{N_V}{N} = \exp\left(-\frac{Q_v}{kT}\right) \Rightarrow Q_v = -kT \ln\left(\frac{N_V}{N}\right)$$

with:

$$\ln\left(\frac{7.57 \times 10^{23} \frac{1}{\text{m}^3}}{5.85 \times 10^{28} \frac{1}{\text{m}^3}}\right) = \ln(1.29 \times 10^{-5}) = -11.26$$

and:

$$Q_v = -(8.62 \times 10^{-5} \text{ eV/K} \cdot 773 \text{ K}) \cdot (-11.26) = 0.75 \text{ eV/atom}$$

c) Assessment of the structure:

1. **True:** Blue in red-rich and red in blue-rich areas
2. **False:** Both phases have the same vacancy fraction
3. **False:** No interstitial atoms are visible. These are substitutional atoms.
4. **True:** Only one phase boundary is shown
5. **False:** Only one grain boundary (horizontal) is visible in the red-rich phase

## Exercise 2: Solid Solutions

### 1. Substitutional Solid Solution:

For two metals to form a complete substitutional solid solution, the **Hume-Rothery Rules** must be met:

(a) **Atomic radius:**

$$\left| \frac{r_1 - r_2}{r_1} \right| \leq 15\%$$

→ The atomic radius difference should not exceed **15%**

(b) **Crystal structure:**

→ Both metals should have the **same crystal structure** (e.g., fcc, bcc, hcp)

(c) **Electronegativity:**

→ Similar electronegativity to avoid strong bonding tendencies (e.g., inter-metallics)

(d) **Valence:**

→ Same valence preferred

→ Metals with higher valence dissolve more readily in those with lower valence

**Satisfied for:** Ni, Pd, Pt; additionally Fe and Co at high T

### 2. Interstitial Solid Solution:

Stable interstitial solid solutions require:

(a) **Atomic size:**

The radius of the interstitial atom must be **less than 59%** of the host atom

(b) **Electronegativity:**

Host and interstitial atom should have **similar electronegativity**

(c) **Valence:**

Ideally the **same valence**

Greater valence differences → lower solubility

**Satisfied for:** C, H, O

Table 1: Differences to Copper: Atomic Radius, Electronegativity, Crystal Structure, Valence

Element	$\Delta R$	$\Delta \chi$	Crystal Structure	$\Delta \text{Valence to Cu (+1)}$
Cu	0	0.00	fcc	0
C	-0.0568	+0.65	–	+3
H	-0.0818	+0.30	–	0
O	-0.0678	+0.54	–	+1
Ag	+0.0167	0.00	fcc	0
Al	+0.0153	-0.40	fcc	+2
Co	-0.0025	-0.10	hcp $\rightarrow$ fcc ( $T \uparrow$ )	+1
Cr	-0.0029	-0.30	bcc	+1
Fe	-0.0037	-0.10	bcc $\rightarrow$ fcc ( $T \uparrow$ )	+1
Ni	-0.0032	-0.10	fcc	+1
Pd	+0.0098	+0.30	fcc	0
Pt	+0.0109	+0.30	fcc	+1
Zn	+0.0054	-0.30	hcp	+1

**Note:** For Hume-Rothery rules, the valence relevant to alloying with copper (i.e., the number of conduction electrons) is what matters.

### Exercise 3: Steady-State Diffusion

Given:

$$D = 6.0 \times 10^{-11} \text{ m}^2/\text{s}, \quad J = 1.2 \times 10^{-7} \text{ kg}/\text{m}^2\text{s}, \quad C_s = 4.0 \text{ kg}/\text{m}^3, \quad C_x = 2.0 \text{ kg}/\text{m}^3$$

Fick's First Law:

$$J = -D \cdot \frac{C_s - C_x}{x}$$

Solving for  $x$ :

$$x = D \cdot \frac{C_s - C_x}{J}$$

Insert values:

$$x = 6.0 \times 10^{-11} \cdot \frac{4.0 - 2.0}{1.2 \times 10^{-7}} = 6.0 \times 10^{-11} \cdot \frac{2.0}{1.2 \times 10^{-7}} = 1.0 \times 10^{-3} \text{ m} = 1.0 \text{ mm}$$

**Result:** Depth  $x = 1.0 \text{ mm}$

## Exercise 4: Non-Steady-State Diffusion

### a) Time to reach target concentration at 2 mm depth

Given:

- $C_s = 1.30\%$ ,  $C_0 = 0.20\%$ ,  $C_x = 0.45\%$
- $x = 2.0\text{ mm} = 2.0 \cdot 10^{-3}\text{ m}$
- $D_0 = 2.3 \cdot 10^{-5}\text{ m}^2/\text{s}$ ,  $Q = 148,000\text{ J/mol}$
- $T = 1273\text{ K}$ ,  $R = 8.314\text{ J/mol}\cdot\text{K}$

The solution of Fick's Second Law for a semi-infinite solid:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Insert:

$$\frac{0.45 - 0.20}{1.30 - 0.20} = 0.227 \Rightarrow \operatorname{erf}(z) = 0.773$$

Interpolated from error function table:

$$\operatorname{erf}(0.850) = 0.7707, \quad \operatorname{erf}(0.900) = 0.7970$$

$$z = 0.850 + \frac{0.773 - 0.7707}{0.7970 - 0.7707} \cdot (0.900 - 0.850) \approx 0.854$$

Calculate  $D$ :

$$D = D_0 \cdot \exp\left(-\frac{Q}{RT}\right) = 2.3 \cdot 10^{-5} \cdot \exp\left(-\frac{148000}{8.314 \cdot 1273}\right) \approx 1.93 \cdot 10^{-5}\text{ m}^2/\text{s}$$

Calculate  $t$ :

$$t = \left(\frac{x}{2z\sqrt{D}}\right)^2 = \left(\frac{2.0 \cdot 10^{-3}}{2 \cdot 0.854 \cdot \sqrt{1.93 \cdot 10^{-5}}}\right)^2 \approx 7.1 \cdot 10^4\text{ s} = \boxed{19.72\text{ h}}$$

### b) Time to reach 5 mm depth (scaling rule)

Since temperature  $T$  is constant:

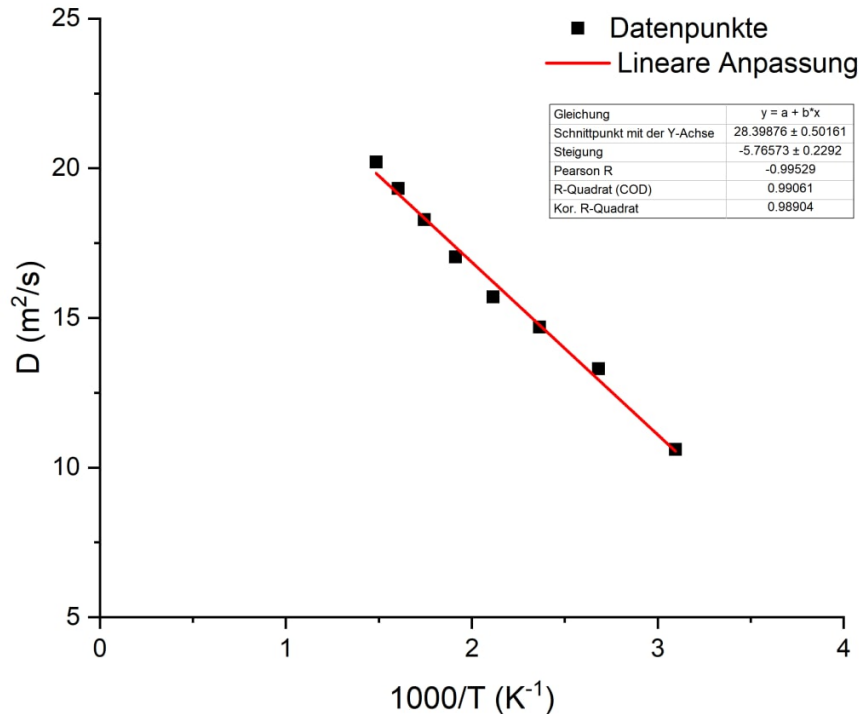
$$\frac{x^2}{t} = \text{const.} \Rightarrow \frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Given:

$$x_1 = 2.5\text{ mm}, \quad t_1 = 10\text{ h}, \quad x_2 = 5.0\text{ mm}$$

$$t_2 = t_1 \cdot \left(\frac{x_2}{x_1}\right)^2 = 10\text{ h} \cdot \left(\frac{5.0}{2.5}\right)^2 = 10 \cdot 4 = \boxed{40\text{ h}}$$

## Exercise 5: Activation Energy



- The temperature dependence of diffusion follows the *Arrhenius equation*:

$$D(T) = D_0 \cdot \exp\left(-\frac{Q}{RT}\right)$$

- For graphical evaluation, the equation is linearized:

$$\ln(D) = \ln(D_0) - \frac{Q}{R} \cdot \frac{1}{T}$$

- This corresponds to a linear function:

$$y = m \cdot x + t, \quad \text{where } y = \ln(D), \quad x = \frac{1000}{T}$$

- Using  $\frac{1000}{T}$  is a convention:
  - More readable scaling on the x-axis
  - Useful in typical ranges (300–1500K)
  - Widely used in technical and scientific literature
- From the plot, the slope is  $m = -5.7657$

- Relation to activation energy:

$$m = -\frac{Q_D}{2.3 \cdot R}$$

→ Solving for  $Q_D$ :

$$Q_D = -m \cdot 2.3 \cdot R \cdot 1000$$

- Inserting values:

$$Q_D = 5.7657 \cdot 2.3 \cdot 8.314 \cdot 1000 \approx \boxed{110 \text{ kJ/mol}}$$