

Chapter 1

Introduction to Materials Kinetics

1.1 Chapter Summary

The purpose of this chapter was to set the stage for learning about kinetics and to give a broad overview of the field of materials kinetics. The main points introduced in this chapter include:

- Thermodynamics predicts whether a process *should* happen, while kinetics predicts *how fast* it will happen. In the simplest terms, kinetics deals with rates. Additionally, kinetics describes how these rates are impacted by important system variables such as pressure, temperature, or concentration.
- When thermodynamics predicts that a process is favorable, this does not necessarily mean that it *will* happen. There are many thermodynamically favorable processes that do not occur because the kinetic barriers are too high. A “yes” from thermodynamics really means “maybe.”
- Many kinetic phenomena can be described by basic concepts that broadly fall into one of two domains: *reaction processes* and *transport processes*. Reaction kinetics describes the rates at which reactions occur while transport kinetics describes the rates at which matter (e.g., atoms or molecules), or charge, or energy is physically transported from one place to another.
- An overall kinetic process can often be broken down into a series of more detailed individual kinetic steps, some of which must occur in *series*, while others can take place in *parallel*. The overall rate for a process is determined by the interaction between all of these individual steps, and is often governed by one step which is much slower than the others—this is known as the rate limiting step.
- A homogeneous kinetic process is one which occurs in a single phase, while a heterogeneous kinetic process involves several (two or more) distinct regions or phases. Almost all solid-state kinetic processes are heterogeneous because almost all solid-state systems manifest heterogeneity. Therefore, the field of materials kinetics mainly confronts heterogeneous kinetic processes.
- Compared to the gas and liquid phase, transport of matter in the solid phase tends to be much slower and more difficult—thus atomic transport processes such as diffusion become much more important in determining kinetic behavior in solid-state systems.
- Kinetic processes can be classified according to the phases of mater involved. Using this scheme, there are six main classes of kinetic processes: gas–gas, gas–liquid, liquid–liquid, gas–solid, liquid–solid, and solid–solid. The field of materials kinetic is chiefly concerned with kinetic processes involving at least one solid phase.

1.2 Chapter Exercises

Review Questions

Problem 1.1. Define kinetics. Contrast kinetics vs. thermodynamics.

In the simplest terms, kinetics deals with rates. Additionally, kinetics describes how these rates are impacted by important system variables such as pressure, temperature, or concentration.

Thermodynamics predicts whether a process should happen, while kinetics predicts how fast it will happen.

Problem 1.2. The transformation of diamond to graphite is an example of a thermodynamically favorable, but kinetically frustrated process. A kinetically frustrated process is one that will not occur over a reasonable scientifically observable time-period. Come up with another example of a process that is thermodynamically favorable, but is kinetically frustrated.

There are many possible processes and systems that rely on kinetic limitations. A few important examples would be metallic glasses, extreme high-surface area systems like nanopowders, and low temperature solid-state diffusion.

Problem 1.3. (a) Give the definition of a homogeneous kinetic process (b) Give an example of a homogeneous kinetic process. Provide diagrams, text, and equations to fully support your example in sufficient detail.

(a) A homogeneous kinetic process is one that involves only one phase. (b) Most gas-gas and liquid-liquid interactions are considered to be homogeneous. However, most solid-solid processes, while technically single phase, are often heterogeneous. This is true whenever there are discrete boundaries between the participants, such as in grain growth and particle coarsening. In Figure 1.3 of the textbook, a) is considered homogeneous, however, c) and f) are not, since for c) the oil is insoluble in the water and for f) the precipitating CuAl_2 phase is distinct and different from the matrix aluminum solid phase.

Problem 1.4. (a) Give the definition of a heterogeneous kinetic process (b) Give an example of a heterogeneous kinetic process. Provide diagrams, text, and equations to fully support your example in sufficient detail.

(a) A heterogeneous kinetic process is one that involves more than one phase or more than one discrete solid phase or region. (b) Besides typical gas-liquid, gas-solid and liquid-solid processes, there are many heterogeneous processes that are either solid-solid or even gas/liquid-solid-solid. The metal oxidation detailed in Figure 1.1 of the textbook is a common three phase heterogeneous kinetic process. In Figure 1.3 of the textbook, b-f) are all heterogeneous processes.

Problem 1.5. Create a figure similar to Figure 1.3 but providing different (i.e., new) examples of each of the six main types of kinetic processes.

Below are some typical processes for each type.

Gas–Gas Stratospheric ozone formation Hydrogen–oxygen combustion	Gas–Liquid Hydrocarbon evaporation Raindrop formation Water carbonation	Liquid–Liquid Fresh and salt water mixing Acid and base reaction
Gas–Solid Ice sublimation Pulsed Laser Deposition (PLD) Gas adsorption	Liquid–Solid Solidification Precipitation	Solid–Solid Grain growth/Sintering Solid precipitation Phase transformation

Problem 1.6. Give an example of a kinetic process involving at least two *series* steps. Provide diagrams, text, and equations to fully support your example in sufficient detail.

There are many options for processes involving series steps. Reaction–diffusion processes (almost all gas–solid kinetic processes, such as condensation or corrosion) and solution–diffusion processes are archetypal.

Problem 1.7. Give an example of a kinetic process involving at least two *parallel* steps. Provide diagrams, text, and equations to fully support your example in sufficient detail.

Processes involving parallel steps are common, although they are more typical in chemical reactions than materials related phenomena. One example is diffusion through a membrane in parallel with a known leak. Others include any process where the decomposition or phase change of a material can have at least two possibilities, such as the parallel loss of solid ice due to melting and sublimation.

Calculation Questions

Problem 1.8. The SI value of the gas constant, R , is $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$. Convert R to the following units and show all your work in each case:

(a) $\text{cal}/(\text{mol} \cdot \text{K})$

$$8.314 \text{ J}/(\text{mol} \cdot \text{K}) \cdot \frac{1 \text{ cal}}{4.184 \text{ J}} = 1.987 \text{ cal}/(\text{mol} \cdot \text{K})$$

(b) $\text{L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$

$$\begin{aligned} \text{J} &= \text{N} \cdot \text{m} = \frac{\text{N}}{\text{m}^2} \cdot \text{m}^3 = \text{Pa} \cdot \text{m}^3 \\ 8.314 \text{ J}/(\text{mol} \cdot \text{K}) &\cdot \frac{1 \text{ atm}}{101325 \text{ Pa}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} = 0.08205 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}) \end{aligned}$$

(c) $\text{cm}^3 \cdot \text{atm}/(\text{mol} \cdot \text{K})$

$$0.08205 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}) \cdot \frac{1000 \text{ cm}^3}{1 \text{ L}} = 82.05 \text{ cm}^3 \cdot \text{atm}/(\text{mol} \cdot \text{K})$$

Problem 1.9. In Chapter 4, we will develop a formula based on the kinetic theory of gases to predict the self-diffusivity of a single-species ideal gas as:

$$D_{\text{gas}} = \sqrt{\frac{1}{6M}} \frac{(RT)^{3/2}}{\pi d^2 P N_A} \quad (1.1)$$

A simplified version of this formula, using non-SI units, is often given as:

$$D_{\text{gas}} = 1.61 \times 10^{-3} \sqrt{\frac{1}{M}} \frac{(T)^{3/2}}{d^2 P} \quad (1.2)$$

where T is in kelvin, P is in atm, d is in Å, and M is in g/mol. Derive how the pre-factor of 1.61×10^{-3} is obtained. Clearly show all your work.

It is important to remember that usually all non-SI units should be converted to SI units, however for this example those conversions will be “rolled into” the pre-factor. As in the previous problem, the key to this solution is understanding the flexible nature of SI units and a simple mathematical trick.

$$J = \text{N} \cdot \text{m} = \frac{\text{kg} \cdot \text{m}}{\text{s}^2} \cdot \text{m} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

$$\begin{aligned} D_{\text{gas}} &= \sqrt{\frac{1}{6M}} \frac{(RT)^{3/2}}{\pi d^2 P N_A} = \sqrt{\frac{1}{6}} \frac{R^{3/2}}{\pi N_A} \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} = \sqrt{\frac{1}{6}} \frac{R^{1/2} \cdot R}{\pi N_A} \cdot \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} \\ &= \frac{(8.314 \text{ kg} \cdot \text{m}^2/(\text{mol} \cdot \text{K} \cdot \text{s}^2))^{1/2} \cdot 8.314 \text{ Pa} \cdot \text{m}^3/(\text{mol} \cdot \text{K})}{6^{1/2} \cdot \pi \cdot 6.022 \times 10^{23}/\text{mol}} \cdot \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} \\ &= 5.1731 \times 10^{-24} \frac{\text{kg}^{1/2} \cdot \text{Pa} \cdot \text{m}^4}{\text{mol}^{1/2} \cdot \text{K}^{3/2}} \cdot \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} \\ &= 5.1731 \times 10^{-24} \frac{\text{kg}^{1/2} \cdot \text{Pa} \cdot \text{m}^4}{\text{mol}^{1/2} \cdot \text{K}^{3/2}} \cdot \frac{10^4 \text{ cm}^2}{1 \text{ m}^2} \cdot \frac{10^{20} \text{ Å}^2}{1 \text{ m}^2} \\ &\quad \cdot \frac{1 \text{ atm}}{101325 \text{ Pa}} \cdot \frac{\sqrt{1000} \text{ g}^{1/2}}{1 \text{ kg}^{1/2}} \cdot \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} \\ &= 1.61 \times 10^{-3} \text{ g}^{1/2} \cdot \text{cm}^2 \cdot \text{Å}^2 \cdot \text{atm}/(\text{mol}^{1/2} \cdot \text{K}^{3/2}) \sqrt{\frac{1}{M}} \frac{T^{3/2}}{d^2 P} \end{aligned}$$

Problem 1.10. If the energy required to move a unit electron charge across a potential difference of one volt is defined as an “electron volt,” denoted “eV,” calculate:

(a) An eV in joules

$$J = \frac{C}{V}$$
$$1 \text{ eV} = \frac{1.602 \times 10^{-19} \text{ C}}{1 \text{ V}} = 1.602 \times 10^{-19} \text{ J}$$

(b) The energy in joules to move one mole of electrons across a potential of one volt

$$1.602 \times 10^{-19} \text{ J} \cdot 6.022 \times 10^{23} \text{ e}^- / \text{mol} = 96.47 \text{ kJ/mol}$$

(c) The same as in (b) but in units of kilocalories/mole

$$96.47 \text{ kJ/mol} \cdot \frac{1 \text{ cal}}{4.187 \text{ J}} = 23.06 \text{ kcal/mol}$$

(d) Convert from the value of R (in J/(mol · K)) to the value of k (in eV/K)

$$8.314 \text{ J}/(\text{mol} \cdot \text{K}) \cdot \frac{1}{96.47 \text{ kJ/mol}} = 8.618 \times 10^{-5} \text{ eV/K}$$

(e) If thermal energy is given as kT, calculate the thermal energy in eV at 300 K and 1000 °C.

$$8.618 \times 10^{-5} \text{ eV/K} \cdot 300 \text{ K} = 2.59 \times 10^{-2} \text{ eV}$$
$$8.618 \times 10^{-5} \text{ eV/K} \cdot 1273 \text{ K} = 1.097 \times 10^{-1} \text{ eV}$$