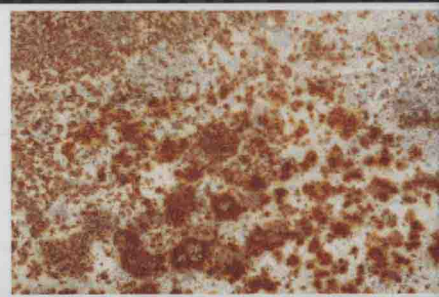
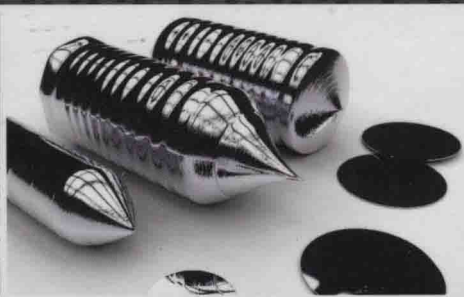
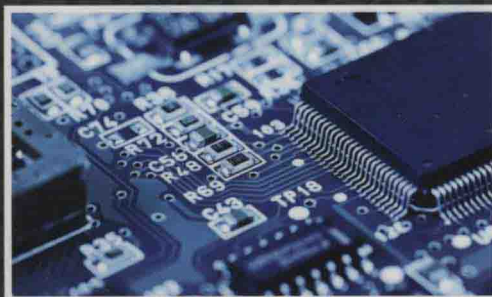


RYAN O'HAYRE

MATERIALS KINETICS FUNDAMENTALS



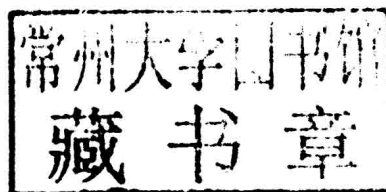
**PRINCIPLES, PROCESSES,
AND APPLICATIONS**

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MATERIALS KINETICS FUNDAMENTALS

Principles, Processes, and
Applications

RYAN O'HAYRE



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MATERIALS KINETICS FUNDAMENTALS

To Lisa, who knows you should try everything at least twice

PREFACE

We are used to thinking about our material world in static terms. Consider the glass of water on your desk, the blue-colored sheets on your bed, the wooden door to your bathroom—these are essentially unchanging and permanent objects, right? But come back tomorrow and the level of water in that glass might be just a little bit lower. Come back in two years and your blue sheets might be fading to grey. Come back in one hundred years and your wooden door may have crumbled to dust.

As these examples illustrate, while it is tempting to think of our material world in static terms, the truth is that tiny changes are constantly taking place. If we could examine that glass of water at the atomic scale, we would see the water molecules churning and vibrating at a fantastic rate, with billions of the most energetic molecules escaping from the liquid and evaporating into the air of the room every second! At the atomic scale, we would see that the blue-colored sheets on your bed are constantly bombarded by high-energy photons (light), causing irreversible damage to the blue dye molecules coating the cotton fibers. From the moment the tree was chopped down to make your wooden door, it began its slow but inevitable decay back to the atmospheric carbon dioxide and water from which it was made. When we purposely process or manufacture materials, the changes we affect on them can be even more stunning. Consider the miraculous conversion (in a kiln) of soft clay into a strong and resilient ceramic pot or the conversion of common beach sand (via many, many steps) to a high-purity single-crystal silicon wafer.

Some changes are fast while others are much slower. In cold and rainy Seattle, it might take three weeks for a glass of water to evaporate, while in the desert of Arizona, it might only take a day. If your blue sheets are exposed to intense direct sunlight, they might photo bleach in a matter of months rather than years. If you

burned that wooden door, you could convert it back into carbon dioxide and water in a few minutes instead of waiting 100 years for microbes to do the same work.

Understanding these changes is the domain of kinetics. At its core, kinetics deals with rates; in other words, kinetics tells us *how fast* something takes place—for example, how fast water can evaporate from a glass. In this textbook, you will uncover the secrets to understanding the kinetic processes described above as well as many others. This textbook is designed to provide you with an accessible and (hopefully) interesting introduction to the main concepts and principles underlying kinetic processes in materials systems. A key point here is that this textbook focuses on *materials* kinetics. While there are a large number of books on chemical kinetics, there are far fewer that focus on materials kinetics and fewer still that provide an accessible, introductory-level treatment of this subject. This textbook aims to equip you with that knowledge.

Following this mandate, the first part of this textbook, “Kinetic Principles,” is devoted to a basic treatment of fundamental and universally important kinetic concepts such as diffusion and reaction rate theory. Illustrated diagrams, examples, text boxes, and homework questions are all designed to impart a unified, *intuitive* understanding of these basic kinetic concepts. Armed with these tools, the second part of the textbook, “Applications of Materials Kinetics,” shows you how to apply them to qualitatively and quantitatively model common kinetic processes relevant to materials science and engineering. Since materials scientists and engineers are chiefly concerned with the solid state, the text focuses on gas–solid, liquid–solid, and solid–solid kinetic processes. A wide variety of exciting real-world examples are used to illustrate the application of kinetic principles to materials systems, including silicon processing and integrated circuit fabrication, gas transport through membranes, thin-film deposition, sintering, oxidation, carbon-14 dating, nucleation and growth, steel degassing, and kinetic aspects of energy conversion devices such as fuel cells and batteries.

ACKNOWLEDGMENTS

First and foremost, I would like to thank nearly a decades-worth of students at the Colorado School of Mines for pushing me to make the subject of materials kinetics as interesting and accessible as possible. Without their inspiration, this textbook would not have been written. In particular, I thank the 2014 Metallurgical and Materials Engineering Junior Class at CSM for their extensive critiques, comments, and enthusiasm while test piloting a draft version of this book. If there are fewer errors or run-on sentences in this textbook than you might otherwise expect, it is due, in large part, to their careful scrutiny. I also thank current and former colleagues, including Fritz Prinz at Stanford University for getting me started on the whole textbook writing thing, Dennis Readey for first sparking my love of materials kinetics, Bob Kee for trading textbook-writing war stories, and Corinne Packard for numerous discussions on how to best approach various topics in materials kinetics.

I would also like to thank Dr. Michael Sanders for his inspired artistic rendering of the many diagrams and illustrations that decorate this textbook. I dare say that it is rare indeed to find an individual who combines a Ph.D. in Materials Science with over a decades-worth of experience as a professional graphics artist. The clear and insightful illustrations in this textbook are the result of Michael's fortuitous and impressive expertise in both areas.

I would also like to thank the Grandey Fund for Energy-Related Pedagogy at the Colorado School of Mines, whose generous support, in part, made this textbook possible.

On a personal note, I am forever thankful for the encouragement, confidence, support, and love of Lisa, Kendra, Arthur, Morgan, and little Anna as well as friends, family, and colleagues around the world.

LEARNING OBJECTIVES

This textbook is not intended to be a comprehensive treatise on the kinetics of materials. Instead, it is intended to be an accessible and (hopefully) interesting introduction to the main concepts and principles that underpin kinetic processes in materials systems. The following list details some of the basic concepts and skills that you will acquire by studying this textbook. For students taking a university course in materials kinetics using this textbook, this list of learning objectives can perhaps be a helpful place to begin exam preparations.

After studying this textbook, you should be able to:

1. Define kinetics and explain the difference between kinetics and thermodynamics.
2. Give examples of both homogeneous and heterogeneous kinetic processes.
3. Convert quantities from one set of units to another quickly and accurately. For example, you should be able to define flux and be able to correctly convert between various units for flux [e.g., $\text{mol}/(\text{cm}^2 \cdot \text{s})$ vs. $\text{A}/(\text{cm}^2 \cdot \text{s})$ vs. $\text{L}/(\text{cm}^2 \cdot \text{s})$ vs. $\text{g}/(\text{cm}^2 \cdot \text{s})$ vs. $\text{atoms}/(\text{cm}^2 \cdot \text{s})$].
4. Define mobility and write the general phenomenological equation for transport. Give examples of how this generalized equation can be applied to electrical/thermal conduction, diffusion, and convection, respectively.
5. Explain (in terms an intelligent high-school student could understand) the atomistic mechanisms of reactions. Define reaction order and give examples of first- and second-order reactions. Develop the general activated rate equation (Arrhenius relationship) that describes how reaction rate varies with temperature.

6. Apply kinetic reaction rate models to predict the progress of simple first- and second-order reactions (gas–gas reactions, radioactive decay).
7. Apply kinetic reaction rate equations to predict how reaction rates change with temperature, pressure, and concentration.
8. Compare and contrast gas, liquid, and solid-state diffusion processes. Predict and model (quantitatively) diffusion processes in all three phases of matter. Provide reasonable ballpark estimates for the approximate rates of diffusion in all three phases of matter.
9. Explain (in terms an intelligent high-school student could understand) the atomistic mechanisms of diffusion in gas and solid phases.
10. Discuss how diffusion in the gas phase depends on pressure and temperature.
11. Develop the general activated rate equation (Arrhenius relationship) that describes how solid-state diffusivity varies with temperature.
12. Give examples of kinetic processes that are reaction rate limited and processes that are diffusion limited. Write equations to quantitatively model simple coupled reaction/diffusion systems such as the passive oxidation of silicon.
13. Explain the difference between equilibrium, steady-state, and time-dependent (non-steady-state) processes. Provide concrete examples of each.
14. Explain the atomic mechanisms of solid-state nucleation and growth. Define the critical nucleation size and the critical nucleation barrier and sketch surface-mediated growth sites such as steps, kinks, and holes.
15. Discuss the kinetic and thermodynamic factors governing liquid–solid and solid–solid phase transformations. Explain and predict nucleation, growth, and time–temperature–transformation (TTT) processes in solid-state systems both qualitatively (through diagrams) and quantitatively (through equations).
16. Describe various types of solidification processes and apply information from phase diagrams to predict the type of microstructures that can arise from common isomorphous, eutectic, and peritectic solidification events.
17. Define surface energy and explain why surfaces have greater energy than the bulk. Provide examples of kinetic processes that are driven by surface energy considerations.
18. Describe (qualitatively) and mathematically model (quantitatively) morphological evolution processes in solid-state materials such as coarsening, grain growth, and sintering.

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