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# Kinetic Processes

Crystal Growth, Diffusion, and Phase Transitions  
in Materials



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## Preface

This book is based on a course on Kinetic Processes which I taught for several years in the Materials Science Department at the University of Arizona. This is a required course for first year graduate students, although some of the material contained in the book would be suitable for a lower level course. The course initially derived from a series of lectures which I gave at Bell Labs, augmented by course notes from a similarly titled course at MIT. The content of the book has a highly personal flavor, emphasizing those areas to which I have made scientific contributions. I have concentrated on developing an understanding of kinetic processes, especially those involved in crystal growth, which is, perhaps, the simplest form of a first order transformation. The book assumes a basic understanding of thermodynamics, which underlies all kinetic processes and can be used to predict transformation kinetics for simple cases. The understanding of the complexities of crystal growth has developed significantly over the past several decades, but it is a wonderfully complex process, with still much to be learned. I have tried to present a coherent account of these processes, based on my view of the subject, which is available at present only in a dispersed form in the published literature, but it has not been assembled and coordinated as I have attempted to do here.

The book concentrates on atomic level processes and on how these processes translate into the microscopic and macroscopic descriptions of kinetic processes. It is aimed at a level appropriate for practitioners of materials processing. I have kept the mathematics at the minimum level necessary to expose the underlying physics. Many of my mathematically inclined friends will cringe at the simplified treatments which I present, but nevertheless, I suspect that non-mathematically inclined students will struggle with them. My colleagues in the crystal growth community, on the other hand, will cringe at my over-simplified descriptions of how single crystals and thin films, the basic materials for high-tech devices, are produced.

There are two streams of context in this book. One concentrates on basic kinetic processes, and the other on modern applications, where these kinetic processes are of critical importance. These two streams are interleaved. The book starts with an introduction to the basis of classical kinetics, the Boltzmann distribution. The following four chapters deal with diffusion processes in fluids, in amorphous materials, in simple crystals, and in semiconductors. This is followed by Chapter 6, on ion implantation, the important method for doping semiconductors, and includes a discus-

sion of Rutherford backscattering. The next chapter introduces the diffusion equation, and some standard solutions. Chapter 8 deals with Stefan problems which are moving boundary problems encountered in phase transformations. Chapter 9 contains a general description of the kinetic processes involved in phase transformations, and is followed by Chapter 10 which contains a brief description of the methods used for growing single crystals. This is not intended to teach anyone how to grow crystals: there are individual books on several of these methods. Chapter 11 describes segregation at a moving interface, and is followed by Chapter 12, on the interface instabilities which can result from this segregation. These instabilities are described by non-linear equations which have been studied extensively, but are far beyond the scope of this book. Chapter 13 outlines some aspects of chemical kinetic theory, and is followed Chapter 14 on the formal aspects of phase transformations. Chapter 15 treats the initial formation of a new phase by a nucleation process. The next few chapters are on atomic processes at surfaces. Chapter 16 outlines adsorption, surface nucleation and epitaxial growth. This treatment only scratches the surface of the knowledge which has been accumulated by surface scientists. Chapter 17 discusses methods for the deposition of thin films, and Chapter 18 is on plasmas, which are used for both deposition and etching. Chapter 19 discusses rapid thermal processing, which is used to control and fine tune thermal annealing. The next few chapters return to fundamental considerations. Chapter 20 discusses the kinetics of first order phase transformations, and the following chapter discusses the important role of the surface roughening transition in these processes. The final chapters are on kinetic processes in alloys. Chapter 22 is on equilibrium in alloys and on growth processes in alloys near equilibrium. It is followed by a discussion, in Chapter 23, of phase separation, also known as spinodal decomposition. Chapter 24 is on rapid phase transformations, where kinetic processes modify the usual equilibrium segregation; where the rate of motion of the interface is comparable the rate of diffusive motion of the atoms. Chapter 25 contains a brief account of coarsening, sintering and grain growth, which applies not only to alloys. Again, much more is known about these processes than could be included here. Chapter 26 presents a discussion of dendritic growth, including a simple mathematical model. This growth mode is an extreme version of interfacial instabilities as discussed in Chapter 12, and has been the focus of extensive mathematical modeling, including the development of the phase field method. Chapter 27 discusses the formation of a two phase solid from a single phase liquid. The final chapter, 28, discusses an important aspect of the formation of the grain structure in metal castings. It is by no means an introduction to the computer models of segregation and fluid flow which are used to design castings today.

Most of what I know about this subject I have learned from my colleagues over the years. I would like to take this opportunity express the enjoyment I have experienced working with them, especially John Hunt and George Gilmer, without whose contributions this book would be a lot thinner. Colleagues at Bell Labs, including Harry Leamy, Kim Kimerling, John Weeks, Rudy Voorhoeve, Ho-Sou Chen, Bill Pfann, Richard Wagner, Bob Batterman, Jim Patel, John Hegarty, Kurt Nassau, Chuck Kurkjian, Ben Greene, Ray Wolfe, Ken Benson, Dennis Maher, David Joy, Helen Farrell, George Peterson, Walter Brown, Charlie Miller, Reggie Farrow, ... , (the list is endless) have all

been involved in my education. I began my interest in this area under the tutelage of Bruce Chalmers, and I owe much to fellow students Bill Tiller, Dick Davis, Don Uhlmann, Jacques Hauser, Bob Fliescher, and Jim Livingston, as well as to discussions with leaders in the field, David Turnbull and Charles Frank. My other great source of inspiration has been my colleagues in the field of crystal growth, Bob Sekerka, Bob Laudise, Franz Rosenberger, John Wilkes, Alex Chernov, Dave Brandle, Vince Fratello, Joe Wenkus, Don Hurlle, Brian Mullen, ... (another endless list). I would also like to acknowledge the direct and indirect contributions of my graduate students at the University of Arizona, Kirk Beatty, Don Hilliard, Katherine Gudgel, Mollie Minke, and Dan Bentz.

I would like to express my appreciation of the extensive and important contributions in the areas of crystal growth, phase transformations and materials processing, including some of my efforts, which have been made possible by the sponsorship of NASA.

I would like to thank Russell Linney for a critical reading of the manuscript, and Harry Sarkas, Franz Rosenberger, and Joe Simmons, as well as many of those mentioned above, for encouragement on this project.

This book would not have been possible without the continued support and understanding of a very special person, Gina Kritchevsky.

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## Chapter 1

### Introduction

The aim of this book is to provide an understanding of the basic processes, at the atomic or molecular level, which are responsible for kinetic processes at the microscopic and macroscopic levels.

Many of the rate processes dealt with in this book are classical rate processes described by Boltzmann statistics. That is, the rate at which a process occurs is given by an expression of the form:

$$R = R_0 \exp(-Q/kT) \quad (1.1)$$

The exponential term is known as Boltzmann factor,  $k$  is Boltzmann's constant and  $Q$  is called the activation energy. The Boltzmann factor gives the fraction of atoms or molecules in the system that have an energy greater than  $Q$  at the temperature  $T$ . So the rate at which the process occurs depends on a prefactor,  $R_0$ , which depends on geometric details of the path, the atom density, etc., times the number of atoms that have enough energy to traverse the path.

#### 1.1

##### Arrhenius Plot

Taking the logarithm of both sides of Eq. 1.1:

$$\ln R = \ln R_0 - Q/kT \quad (1.2)$$

Plotting  $\ln R$  vs  $1/T$  gives a straight line with slope  $-Q/k$ , as illustrated in Fig. 1.1. This kind of plot is known as an Arrhenius plot.

If the rate process has a single activation energy,  $Q$ , over the range of the measurement, this suggests strongly that the mechanism controlling the rate is the same over that range. If the slope changes, or if the curve is discontinuous, the mechanism controlling the rate has changed.

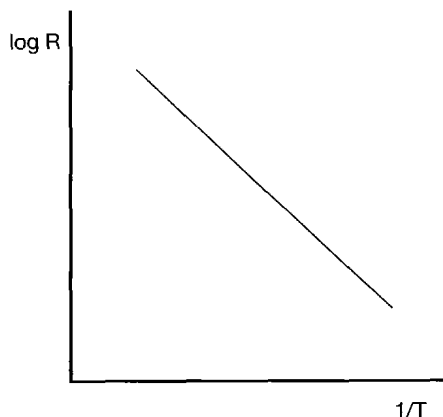


Figure 1.1 Arrhenius plot.

## 1.2

### The Relationship between Kinetics and Thermodynamics

There is a simple relationship between the rate equation above and thermodynamics, which can be written:

$$G = -kT \ln R = Q - kT \ln R_0 \quad (1.3)$$

This implies that the rate at which atoms leave a state depends on their properties in that state. Comparing Eq. 1.3 with  $G = H - TS$ , it is evident that  $Q$  is related to the enthalpy, and the entropy,  $S$ , is  $k \ln R_0$ . If two states or phases are in equilibrium, their free energies are equal, which is equivalent to the statement that rates of transition back and forth between the two states are the same.

The relationship between thermodynamics and kinetics will be a recurring theme in this book. The thermodynamics formalism was developed during the last century based on the understanding of steam engines. If it were being developed today by materials scientists, it would be done in terms of rate equations, which are formally equivalent, but much more amenable to physical interpretation.

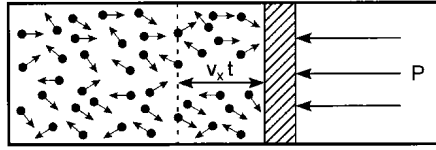
The origin of the Boltzmann factor will be outlined below, but first, we will attempt to answer the question:

#### What is temperature?

We all know what temperature is: it is something that we measure with a thermometer. The temperature scales that we use are defined based on fixed temperatures, such as the melting point of ice and the boiling point of water. We use the thermal expansion of some material to interpolate between these fixed points. But what is the physical meaning of temperature? What is being measured with this empirical system?

The simplest thermometer to understand is based on an ideal gas, where we can relate the temperature to the pressure of a gas in a container of fixed volume. The pressure on a wall or a piston derives from the force exerted on it by atoms or mo-

**Figure 1.2** The change in momentum of the molecules striking a piston creates pressure on the piston.



lecules striking it. The pressure is due to the change of momentum of the atoms or molecules that hit the piston. The force,  $F$ , on the piston is the change in momentum per second of the atoms or molecules striking it.

So we can write:

$F = (\text{change in momentum per molecule}) \times (\text{number of molecules per second striking the piston})$

If  $v_x$  is the component of the velocity of a molecule in the  $x$  direction, then the change in momentum when the molecule makes an elastic collision (an elastic collision is one in which the molecule does not lose any energy) with the piston is  $2mv_x$ , since the momentum of the incident molecule is reversed during the collision.

As illustrated in Fig. 1.2, only the molecules within a distance  $v_x t$  of the wall will strike it during time  $t$ , so the number of molecules hitting the wall per second is given by the number of molecules per unit volume,  $n$ , times the area of the piston,  $A$ , times  $v_x/2$ , since half of the molecules are going the other way. The force on the piston is thus:

$$F = (2mv_x) \left( \frac{1}{2} nv_x A \right) \quad (1.4)$$

And the pressure on the piston is:

$$P = \frac{F}{A} = nmv_x^2 \quad (1.5)$$

Writing  $n = N/V$ , and using the ideal gas law, we can write:

$$PV = Nm v_x^2 = NkT \quad (1.6)$$

This indicates that the thermal energy of an atom,  $kT$ , is just the kinetic energy of the atom. A more refined analysis relating the pressure to the motion of atoms in three dimensions gives:

$$kT = \frac{1}{3} m v_{\text{rms}}^2 = \frac{1}{2} m \bar{v}^2 \quad (1.7)$$

where  $v_{\text{rms}}$  is the root mean square average velocity of the atoms, and  $\bar{v}$  is the most probable velocity.

A familiar form of the ideal gas law uses the gas constant  $R$ , rather than Boltzmann's constant,  $k$ . The two are related by  $R = N_0 k$ , where  $N_0$  is Avagadro's number, which is the number of molecules in a mol.  $RT$  is the average thermal energy of a mol of atoms,  $kT$  is the average thermal energy of one atom.



Gas constant:  $R = 1.98 \text{ cal/mol.deg}$   
 $= 0.00198 \text{ kcal/mol.deg}$   
 $= 8.31 \text{ J/mol.deg}$   
 $= 8.31 \times 10^7 \text{ ergs/mol.deg}$

Boltzmann's constant:  $k = 8.621 \times 10^{-5} \text{ eV/atom.deg.}$   
 $= 1.38 \times 10^{-16} \text{ ergs/atom.deg.}$   
 $= 1.38 \times 10^{-23} \text{ J/atom.deg.}$

$1\text{eV/atom} = 23\text{kcal/mol}$

$$\frac{R}{k} = \frac{8.31 \times 10^7}{1.38 \times 10^{-16}} = 6.023 \times 10^{23} \text{ molecules/mol} = \text{Avagadro's number}$$

The important point from the above discussion is that the temperature is a measure of the average **kinetic** energy of the molecules. Not the total energy, which includes potential energy and rotational energy, just the kinetic energy. Temperature is a measure of how fast the atoms or molecules are moving, on average.

### 1.3

#### The Boltzmann Distribution

Where does  $N = N_0 \exp(-E/kT)$  come from?

We saw above that  $kT$  is a measure of the average kinetic energy of the atoms or molecules in an assembly. The Boltzmann function gives the fraction of atoms that have enough energy to surmount an energy barrier of height  $E$ , in an assembly of atoms with an average energy  $kT$ .

Let us look at an atom in a potential field. Gravity is a simple one.

The force of gravity on an atom is:

$$F = mg \tag{1.8}$$

The associated gravitational potential is:

$$\int_0^h F dx = mgh \tag{1.9}$$

which is the energy required lift an atom from height 0 to height  $h$  in gravity.  $mgh$  is the potential energy of an atom at height  $h$ .

For  $N$  atoms in a volume  $V$  at temperature  $T$ , the ideal gas law says:

$$PV = NRT \tag{1.10}$$

or

$$P = nkT \tag{1.11}$$

where  $n = N/V$ , the number of atoms per unit volume.