

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 the 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 which 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, and so on, times the number of atoms which have enough energy to traverse the path.

1.1

Arrhenius Plot

Taking the logarithm of both sides of Equation 1.1:

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

So that plotting $\ln R$ vs $1/T$ gives a straight line with slope $-Q/k$, as illustrated in Figure 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.

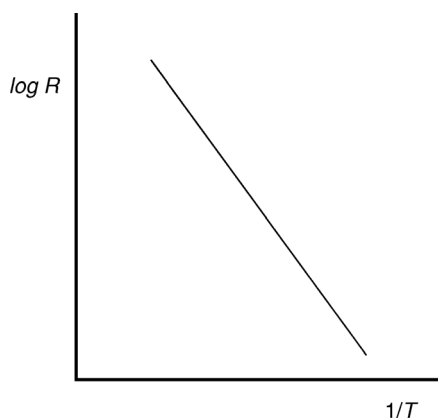


Figure 1.1 Arrhenius Plot.

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 Equation 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:

1.2.1

What is Temperature?

We all know what temperature is: it is something that we measure with a thermometer. The temperature scales which 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 molecules striking it. The pressure is due to the change of momentum of the atoms or molecules which 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 Figure 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:

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

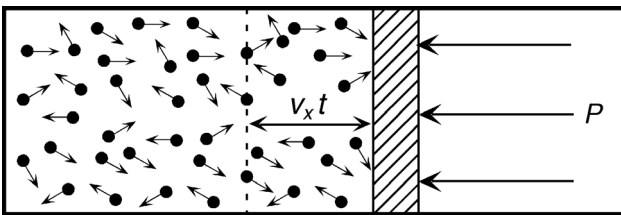


Figure 1.2 The change in momentum of the molecules striking a piston creates pressure on the piston.

where v_{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 Avogadro'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.

$$\begin{aligned} \text{Gas constant: } R &= 1.98 \text{ cal mol}^{-1} \text{ K}^{-1} \\ &= 0.00198 \text{ kcal mol}^{-1} \text{ K}^{-1} \\ &= 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 8.31 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Boltzmann's constant: } k &= 8.621 \times 10^{-5} \text{ eV atom}^{-1} \text{ K}^{-1} \\ &= 1.38 \times 10^{-16} \text{ erg atom}^{-1} \text{ K}^{-1} \\ &= 1.38 \times 10^{-23} \text{ J atom}^{-1} \text{ K}^{-1} \end{aligned}$$

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

$$\frac{R}{k} = \frac{8.31 \times 10^7}{1.38 \times 10^{-16}} = 6.023 \times 10^{23} \text{ molecules mol}^{-1} = \text{Avogadro's Number}$$

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 which 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 to 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 states:

$$PV = NRT \quad (1.10)$$

or

$$P = nkT \quad (1.11)$$

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

The change in pressure, dP , which will result from a change in atom density, dn , is

$$dP = kTdn \quad (1.12)$$

In a gravitational field, the number of atoms per unit volume decreases with height, and ndh is the number of atoms between heights h and $h + dh$.

The change in pressure between h and $h + dh$ due to the weight of the atoms in dh is:

$$dP = P_{h+dh} - P_h = -mgndh \quad (1.13)$$

Combining Equations 1.12 and 1.13 gives:

$$\frac{dn}{n} = -\frac{mg}{kT} dh \quad (1.14)$$

or:

$$n = n_0 \exp\left(-\frac{mgh}{kT}\right) \quad (1.15)$$

which is the variation of atom density with height in the atmosphere due to the earth's gravitational field.

mgh is the potential energy of an atom at height h . This analysis is similar for a generalized force field, and the distribution of the atoms in the force field has the same form:

$$n = n_0 \exp\left(-\frac{E_p}{kT}\right) \quad (1.16)$$

where E_p is the potential energy of the atoms in the force field.

The kinetic energy distribution of the atoms can be derived by examining the kinetic energy that an atom at height zero needs to reach a height h (ignoring scattering).

In order to reach a height h , an atom must have an upwards kinetic energy equal to, or greater than, the potential energy at height h . It must have an upwards velocity greater than u , given by:

$$\frac{1}{2}mu^2 \geq mgh \quad (1.17)$$

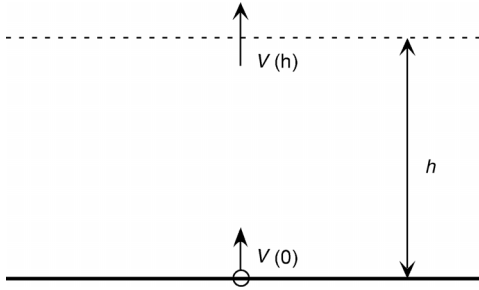


Figure 1.3 An atom with enough kinetic energy at height 0 can reach height h .

With a velocity less than u , the atom will not get to height h . In Figure 1.3, the number of atoms passing through the plane at h is the number moving upwards at height zero with velocity greater than u , so

$$n_{v>0}(h) = n_{v>u}(0) \quad (1.18)$$

Assuming that the temperature is the same at zero and at h , the distribution of velocities will be the same, and the only difference will be the density of atoms, so:

$$\frac{n_{v>u}(0)}{n_{v>0}(0)} = \exp\left(-\frac{mgh}{kT}\right) = \exp\left(-\frac{mu^2}{2kT}\right) \quad (1.19)$$

or

$$n_{v>u} = n_0 \exp\left(-\frac{E_k}{kT}\right) \quad (1.20)$$

where E_k is the kinetic energy of the atom. This is the Boltzmann distribution of velocities. It says that the fraction of atoms with velocity (or kinetic energy) greater than some value is given by a Boltzmann factor with the average kinetic energy of the atoms in the denominator of the exponent.

Recalling that kT is the average kinetic energy of the atoms, the exponent is just the ratio of two kinetic energies. The Boltzmann factor describes the spread in the distribution of energies of the atoms. Given an average kinetic energy kT per atom, the Boltzmann factor tells how many of the atoms have an energy greater than a specific value.

In general, if there is a potential energy barrier of height Q , the Boltzmann factor says that a fraction of the atoms given by $\exp(-Q/kT)$ will have enough kinetic energy to get over the barrier. This is independent of how the potential varies along the path. The atom just has to have enough kinetic energy at the start to surpass the barrier. So, in general, if there is a potential barrier along a path, the atoms which are going in the right direction take a run at it, and those atoms which are going fast enough will make it over the barrier. And the fraction of the atoms which will make it over the barrier is given by the Boltzmann factor.

The original derivation of Boltzmann was concerned with atomic collisions between gas atoms, and the distribution of velocities and the spread in energy which the collisions produce. That is a very complex problem, but the result is remarkably simple. We have derived it crudely from Newton's laws and our practical definition of temperature which is based on the ideal gas law.

1.4 Kinetic Theory of Gases

From statistics based on Newton's laws, Boltzmann derived that the probability $P(v)$ that an atom of mass m will have a velocity v at a temperature T is given by:

$$P(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \quad (1.21)$$

where k is Boltzmann's constant. This distribution is illustrated in Figure 1.4.

The average velocity is given by:

$$\bar{v} = \int_0^{\infty} vP(v) dv = \sqrt{\frac{8kT}{\pi m}} \quad (1.22)$$

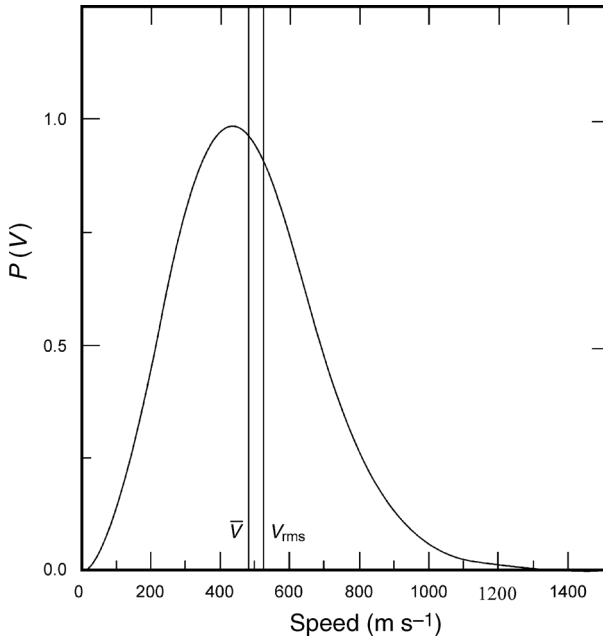


Figure 1.4 Typical velocity distribution, $P(v)$, of atoms in a gas at room temperature.

On average, the velocity of an atom in any one direction is $\bar{v}_x = \bar{v}_y = \bar{v}_z = \sqrt{\frac{2kT}{\pi m}}$. The root mean square velocity is slightly larger than the average velocity, and is given by $v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$. kT is a measure of the average *kinetic* energy of the atoms in the gas. This is also true in liquids and solids. At room temperature, \bar{v}_x is about 480 m s^{-1} , or about 1060 mph.

1.5 Collisions

Two atoms of diameter d will collide if their centers pass within d of each other. We can imagine a cylinder with a diameter $2d$, twice the diameter of an atom. The length of the cylinder, l , is such that the volume of the cylinder is the average volume per atom in the gas, $1/n$, where n is the number of atoms per unit volume in the gas. We then have: $\pi d^2 l = 1/n$. When an atom traverses a distance l , it is likely to collide with another atom. The average distance between collisions is thus given approximately by l , which is equal to $1/\pi d^2 n$. A rigorous treatment for the average distance between collisions in a gas, which is known as the mean free path, λ , gives:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \quad (1.23)$$

which is smaller by $\sqrt{2}$ than our crude estimate. For an ideal gas, $n = P/kT$, where P is the pressure, so that the mean free path can be written:

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P} \quad (1.24)$$

The diffusion coefficient (which will be discussed in more detail in the next chapter) is given by:

$$D = \frac{\bar{v}\lambda}{3} \quad (1.25)$$

The viscosity of a gas is given by:

$$\eta = \frac{mn\bar{v}\lambda}{3} \quad (1.26)$$

A surprising result is obtained by inserting the value of the mean free path Equation 1.23, into Equation 1.26 for the viscosity: the viscosity is independent of the pressure on the gas at a given temperature.

The thermal conductivity of a gas is given by the specific heat times the diffusion coefficient:

$$K = \frac{C_V \bar{v} \lambda}{3} \quad (1.27)$$

where C_V is the specific heat of the gas at constant volume. The flux of atoms through unit area in unit time is given by:

$$J = \frac{n\bar{v}_x}{2} = n\sqrt{\frac{kT}{2\pi m}} = \frac{P}{\sqrt{2\pi mkT}} \quad (1.28)$$

which is an expression we will use later for the flux of gas atoms to a surface. For one atmosphere pressure of nitrogen gas at room temperature, the flux is about 6×10^{23} atoms $\text{cm}^{-2} \text{s}^{-1}$.

Further Reading

The definition of temperature and the derivation of the Boltzmann function are taken from:

Feynman, R.P., Leighton, R.B., and Sands, M. (1963) Ch. 40, in *The Feynman Lectures on Physics*, vol. 1, Addison-Wesley Publ. Co., Reading MA.

Huang, K. (1963) *Statistical Mechanics*, John Wiley & Sons, Inc., New York, NY.

Lupis, C.H.P. (1983) *Chemical Thermodynamics of Materials*, North-Holland, New York, NY.

Problems

- 1.1. The specific heat of a monatomic gas is $3 Nk$. What are the thermal conductivities of helium and argon at room temperature?
- 1.2. How many atoms of argon at a pressure of one atmosphere are incident on a square centimeter of surface at room temperature in one microsecond?

