FUNDAMENTALS OF HEAT AND MASS TRANSFER

SECOND EDITION

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INTRODUCTION

From the study of thermodynamics, you have learned that energy can be transferred by interactions of a system with its surroundings. These interactions are called work and heat. However, thermodynamics deals with the end states of the process during which an interaction occurs and provides no information concerning the nature of the interaction or the time rate at which it occurs. The objective of this text is to extend thermodynamic analysis through study of the *modes* of heat transfer and through development of relations to calculate heat transfer *rates*. In this chapter we lay the foundation for much of the material treated in the text. We do so by raising several questions. *What is heat transfer*? *How is heat transferred*? *Why is it important to study it*? In answering these questions, we will begin to appreciate the physical mechanisms that underlie heat transfer processes and the relevance of these processes to our industrial and environmental problems.

1.1 WHAT AND HOW?

A simple, yet general, definition provides sufficient response to the question: What is heat transfer?

> *Heat transfer (or heat) is energy in transit due to a temperature difference.*

Whenever there exists a temperature difference in a medium or between media, heat transfer must occur.

As shown in Figure 1.1, we refer to different types of heat transfer processes as *modes*. When a temperature gradient exists in a stationary medium, which may be a solid or a fluid, we use the term *conduction* to refer to the heat transfer that will occur across the medium. In contrast, the term *convection* refers to heat transfer that will occur between a surface and a moving fluid when they are at different temperatures. The third mode of heat transfer is termed *thermal radiation*. All surfaces of finite temperature emit energy in the form of

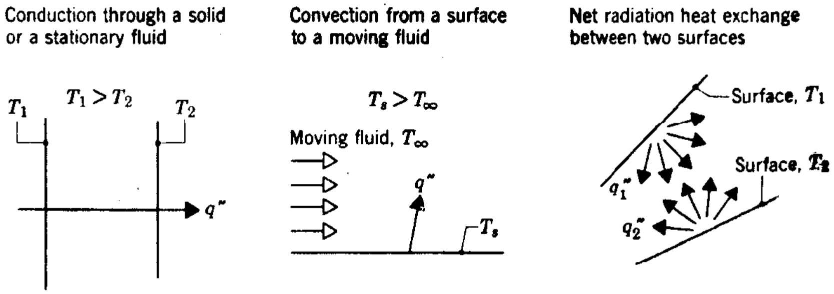

Figure 1.1 Conduction, convection, and radiation heat transfer modes.

electromagnetic waves. Hence, in the absence of an intervening medium, there is net heat transfer by radiation between two surfaces at different temperatures.

1.2 PHYSICAL ORIGINS AND RATE EQUATIONS

As engineers it is important that we understand the *physical mechanisms* that underlie the heat transfer modes and that we be able to use the rate equations that quantify the amount of energy being transferred per unit time.

1.2.1 Conduction

At mention of the word "conduction," we should immediately conjure up concepts of *atomic* and *molecular activity*, for it is processes at these levels that sustain this mode of heat transfer. Conduction may be viewed as the transfer of energy from the more energetic to the less energetic particles of a substance due to interactions between the particles.

The physical mechanism of conduction is most easily explained by considering a gas and using ideas familiar from your thermodynamics background. Consider a gas in which there exists a temperature gradient and assume that there is *no* bulk motion. The gas may occupy the space between two surfaces that are maintained at different temperatures, as shown in Figure 1.2. We associate the temperature at any point with the energy of the gas molecules in the vicinity of the point. This energy is related to the random translational motion, as well as to the internal rotational and vibrational motions, of the molecules. Moreover, higher temperatures are associated with higher molecular energies, and when neighboring molecules collide, as they are constantly doing, a transfer of energy from the more energetic to the less energetic molecules must occur. In the presence of a temperature gradient, energy transfer by conduction must then occur in the direction of decreasing temperature. This transfer is

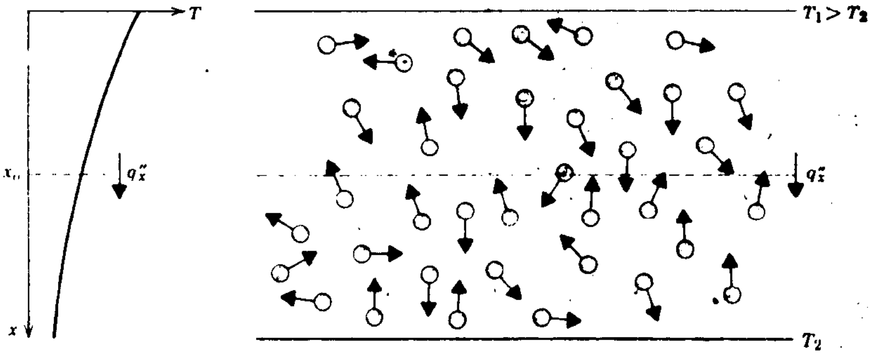

Figure 1.2 Association of conduction heat transfer with diffusion of energy due to molecular activity.

evident from Figure 1.2. The hypothetical plane at x_o is constantly being crossed by molecules from above and below due to their *random* motion. However, molecules from above are associated with a larger temperature than those from below, in which case there must be a *net* transfer of energy in the positive x direction. We may speak of the net transfer of energy by random molecular motion as a *diffusion* of energy.

The situation is much the same in liquids, although the molecules are more closely spaced and the molecular interactions are stronger and more frequent. Similarly, in a solid, conduction may be attributed to atomic activity in the form of lattice vibrations. The modern view is to ascribe the energy transfer to *lattice waves* induced by atomic motion. In a nonconductor, the energy transfer is exclusively via these lattice waves; in a conductor it is also due to the translational motion of the free electrons. We treat the important properties associated with conduction phenomena in Chapter 2 and in Appendix A.

Examples of conduction heat transfer are legion. The exposed end of a metal spoon suddenly immersed in a cup of hot coffee will eventually be warmed due to the conduction of energy through the spoon. On a winter day there is significant energy loss from a heated room to the outside air. This loss is principally due to conduction heat transfer through the wall that separates the room air from the outside air.

It is possible to quantify heat transfer processes in terms of appropriate *rate equations*. These equations may be used to compute the amount of energy being transferred per unit time. For heat conduction, the rate equation is known as *Fourier's law*. For the one-dimensional plane wall shown in Figure 1.3, having a temperature distribution $T(x)$, the rate equation is expressed as

$$q''_x = -k\frac{dT}{dx} \tag{1.1}$$

The *heat flux* q''_x (W/m^2) is the heat transfer rate in the x direction *per* unit area perpendicular to the direction of transfer, and it is proportional to the temperature gradient, dT/dx, in this direction. The proportionality constant k is a *transport* property known as the *thermal conductivity* (W/m · K) and is a characteristic of the wall material. The minus sign is a consequence of the fact that heat is transferred in the direction of decreasing temperature. Under the steady-state conditions shown in Figure 1.3, where the temperature distribution

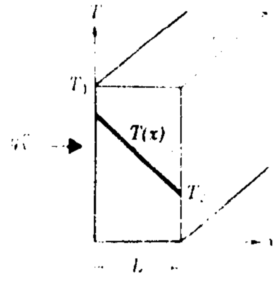

Figure 1.3 One-dimensional heat transfer by conduction (diffusion of energy).

Atomic fluorescence spectroscopy	GC/AFS	Many metallic and metalloid elements			Multi-element capability. Dispersive or nondispersive mode.	
(i) flame			0.1-10	3-4		35
(ii) furnace				3-4		39, 40
Inductively coupled plasma mass spectrometry	GC/ICPMS	Most metallic and nonmetallic elements		3	Not yet applied to inorganics or organometallics. Isotope ratio measurements.	36
Molecular emission cavity analysis	GC/MECA	S, P, As, Sb, B, Si, Ge, Sn, C, N. Possibly other elements.	2-100	1-2	Related to flame-photometric detector.	41, 42

Assumptions:

1. Steady-state conditions.
2. One-dimensional conduction through the wall.
3. Constant properties.

Analysis:

Since heat transfer through the wall is by conduction, the heat flux may be determined from Fourier's law. Using Equation 1.2

$$q''_x = k\frac{\Delta T}{L} = 1.7\ \text{W/m}\cdot\text{K} \times \frac{250\ \text{K}}{0.15\ \text{m}} = 2833\ \text{W/m}^2$$

The heat flux represents the rate of heat transfer through a section of unit area. The wall heat loss is then

$$q_x = (HW)q''_x = (0.5\ \text{m} \times 3.0\ \text{m})\ 2833\ \text{W/m}^2 = 4250\ \text{W} \qquad \triangleleft$$

Comments:

1. Note direction of heat flow.
2. Note distinction between heat flux and heat rate.

1.2.2 Convection

The convection heat transfer *mode* is comprised of *two mechanisms* In addition to energy transfer due to *random molecular motion* (diffusion), there is also energy being transferred by the *bulk*, or *macroscopic, motion* of the fluid. This fluid motion is associated with the fact that, at any instant, large numbers of molecules are moving collectively or as aggregates. Such motion, in the presence of a temperature gradient, will give rise to heat transfer. Because the molecules in the aggregate retain their random motion, the total heat transfer is then due to a superposition of energy transport by the random motion of the molecules and by the bulk motion of the fluid. It is customary to use the term *convection* when referring to this cumulative transport and the term *advection* when referring to transport due to bulk fluid motion.

We are especially interested in convection heat transfer, which occurs between a fluid in motion and a bounding surface when the two are at different temperatures. Consider fluid flow over the heated surface of Figure 1 4 A consequence of the fluid–surface interaction is the development of a region in the fluid through which the velocity varies from zero at the surface to a finite value u_∞ associated with the flow. This region of the fluid is known as the *hydrodynamic*, or *velocity, boundary layer*. Moreover, if the surface and flow as much as 20% of elemental iodine introduced into the column was strongly retained. A derivatization similar to that described above for chlorine may, therefore, be required.

Other elements, with the exception of Hg, may be too reactive or involatile for conventional GC. However, a variety of metallic elements (Na, K, Cs, Ba, Eu, Yb, Tm, Tl, Pb, Bi, Po, Am, Cf, Fm, Md, Lr, etc.) [54-58] can be chromatographed by thermochromatography (Section 12.1.2.3) at 600-1400 K in titanium, graphite, or quartz columns. Thermochromatography includes any GC technique that operates above the maximum temperature of conventional GC, ca. 400°C. Typically, this will involve the use of tube furnaces with packed or unpacked quartz or other tubing as the chromatographic column. Although this technique does not at present appear to be suitable for analytical element separations, it does allow the adsorption and volatilization behavior of metallic elements to be studied and has been useful for the characterization of heavy actinide elements.

12.1.2 Binary compounds of metallic and nonmetallic elements

The main groups to be considered here comprise monomeric hydrides, halides, and oxides sufficiently volatile to be determined by conventional GC or by thermochromatography. Gaseous species, e.g., CH_4, NH_3, H_2S, CO, CO_2, and SO_2 are not discussed.

12.1.2.1 Water

For the determination of water, GC is rapidly evolving as a very selective and sensitive method. It can replace, or complement, established methods, based on oven drying, Karl Fischer titrations, infrared absorption, and thermogravimetry [59,60].

For determining water in liquids and solids above ca. 0.1%, established procedures based on chromatographic separation on porous polymers and thermal conductivity detection are suitable, provided water is well separated from other components in the chromatogram. Sorbents described for this purpose are based on polystyrenes, including Porapaks Q, N, T, Super Q, Chromosorbs 101, 102, 104, Polysorb 1, GPX-103 [61-65]; methacrylate polymers and copolymers [66,67], and carbon molecular sieves, such as Carbosieve S and Carbopack C [61]. On many porous polymers tailing of the water peak occurs. This can be reduced by the addition of polar compounds, such as methanol, to the carrier gas [68]. Porous polymers coated with polar stationary phases have also been enlisted to decrease tailing and retention and to improve selectivity [69]. Recent applications of such columns are described for water determination in vitamin C [70], liquid ketones [66,71], crude mineral oil [64], pharmaceuticals [65], liquid petroleum [72], and high-purity hydrides [73]. Because of the limited sensitivity of this procedure, water concentrations below 0.1% require a preconcentration step [63], which increases analysis time.

Low concentration (<0.1%) of water in solids, liquids, and gases can be determined indirectly by reaction GC. In these methods water is converted to hydrogen, methane, acetylene, or other organic compounds [9]. Their advantage is that they permit the use of associated with a phase change between the liquid and vapor states of the fluid. Two special cases of interest in this text are *boiling* and *condensation*.

Regardless of the particular nature of the convection heat transfer mode, the appropriate rate equation is of the form

$$q'' = h(T_s - T_\infty) \tag{1.3}$$

where q'', the *convective heat flux* (W/m^2), is proportional to the difference between the surface and fluid temperatures, T_s and T_∞, respectively. This expression is known as *Newton's law of cooling*, and the proportionality constant h (W/m$^2 \cdot$ K) is referred to as the *convection heat transfer coefficient*, the *film conductance*, or the *film coefficient*. It encompasses all the effects that influence the convection mode. It depends on conditions in the boundary layer, which are influenced by surface geometry, the nature of the fluid motion, and a number of the fluid thermodynamic and transport properties. Moreover, any study of convection ultimately reduces to a study of the means by which h may be determined. Although consideration of these means is deferred to Chapter 6, it is important to note that convection heat transfer will frequently appear as a boundary condition in the solution of conduction problems (Chapters 2 to 5). In the solution of such problems we presume h to be known, using typical values given in Table 1.1. Note the range of values associated with the various convection processes.

1.2.3 Radiation

Thermal radiation is energy emitted by matter that is at a finite temperature. Although we focus primarily on radiation from solid surfaces, emission may also occur from liquids and gases. Regardless of the form of matter, the emission may be attributed to changes in the electron configurations of the constituent atoms or molecules. The energy of the radiation field is transported by electromagnetic waves (or alternatively, photons). While the transfer of energy by conduction or

Table 1.1 Typical values of the convection heat transfer coefficient

PROCESS	h (W/m$^2 \cdot$ K)
Free convection	5–25
Forced convection	
Gases	25–250
Liquids	50–20,000
Convection with phase change	
Boiling or condensation	2500–100,000