

Transport: A Nonequilibrium Process

27.1 Transport: An Irreversible Process

So far, the focus of this book has been on systems at equilibrium, where they experience no net flux of heat, work, or matter. Classical thermodynamics treats these systems easily. As we pointed out earlier, the greatest value of thermodynamics is that the behavior of a system can be predicted, even when the mechanistic details are not known. Homogeneous systems, at constant temperature and pressure, such as the solutions of electrolytes and macromolecules described so far, are composed of molecules that individually experience a variety of forces, both orienting and randomizing. On an instantaneous time scale, this might lead to net movements of mass or energy; however, the time average of the forces leads to the steady-state condition of equilibrium. The activity of a component is the reflection of the time-average molecular forces acting in a system at equilibrium. There are cases in which the time average of a force or forces acting on a system results in the flow of material. When these events occur, transport phenomena result. Transport phenomena and the principles associated with nonequilibrium behavior are extremely important in biological systems because, as we have already suggested, true equilibrium states are achieved only in death. Steady-state systems, which have constant fluxes, are common. These systems are treated by nonequilibrium methods.

There are four phenomena associated with transport. These include diffusion, electrical conduction, heat flow (conduction) and fluid flow (convection). Each of these represents net movement in the direction of a gradient from a higher to a lower potential. The gradients are due to differences in chemical potential, electrical potential, temperature, or pressure, respectively. All of these phenomena are important in biological systems although our primary focus will be on diffusion and electrical

conduction. The general equation that applies to all forms of transport events is written:

$$J_x = -B \frac{\partial A}{\partial x} = -BF_A \quad (27.1)$$

This equation states that the flow of material in the x direction, J_x , is proportional by some constant B to the gradient of force of type A in the x direction. Similar equations could be written for each coordinate, x, y , or z .

Transport phenomena do not fall in the realm of classical thermodynamics. It is possible to analyze and study these nonequilibrium processes mechanistically, that is, to calculate the forces on each molecule and then relate the combined actions of each and every molecule to the properties of the system. This approach can provide a qualitative picture of the events that lead to transport. There are substantial problems with a strict mechanistic approach. The first problem lies in defining the actual forces that may be acting on a particular molecule. As we will see, the dimensions of molecules are important parameters in calculating transport properties mechanistically. In a system of macromolecules, this can be a significant difficulty. In many cases, biochemists and biophysicists do not even know all the components that go into making a system, much less their dimensions. Furthermore, the approximations for studying the forces on moving objects, such as Stokes's law, which is a mainstay of this approach, assume that the transport occurs in a medium that is a continuum. Such an assumption, especially in the case of aqueous media, ignores the forces that act between a component and its solvent and other components, leading to approximations that can be drastically at variance with reality. Ideally, a set of laws and equations parallel (or complementary) to those applied in the equilibrium studies already described can be found for cases where equilibrium is approached but not yet reached. Such a macroscopic set of empirically

(or phenomenologically) derived descriptions of properties (such as transport or kinetic rates) could complement the molecular-mechanistic approach. The study of nonequilibrium or irreversible thermodynamics provides this effective phenomenological approach. The subject of irreversible thermodynamics is a detailed and relatively complicated subject, and we will only touch on the general ideas and vocabulary here. Details can be found in the references listed at the end of the chapter.

27.2 Principles of Nonequilibrium Thermodynamics

We have stated that the principles of thermodynamics are universally valid. It was never stipulated that only systems at equilibrium could be treated. The reason that only equilibrium systems have been treated to this point has been one of definition and convenience. This occurred because some of the fundamental variables of state, namely, temperature, pressure, and entropy, were defined at equilibrium. They are more difficult to define during an irreversible or nonequilibrium process. Other variables of state do not suffer from this limitation and can be successfully used under any circumstances; these include volume, mass, energy, and amount of a component. Recognizing that variables like temperature and pressure are intensive, whereas volume, mass, and energy are extensive can help explain this difference. An intensive property was defined as one in whose evaluation a small sample was representative of the entire system. This has meaning only if a system is at equilibrium. Consider the example of two heat reservoirs of different temperature connected by a metal bar through which heat travels by thermal conduction. The flow of heat will be irreversible from the reservoir of greater temperature to the one of lower temperature. Choosing small samples at points along the bar will give different measurements for the temperature. Clearly, this does not fit the requirement for an intensive variable. Consequently, the method used to define the temperature parameter must be different in this system because it is not equilibrium. A similar argument could be made for pressure or entropy. Until the variables such as tem-

perature and pressure can be defined in an irreversible system, thermodynamic calculations will not be successful.

Through the use of a new postulate, *local equilibrium*, this problem can be overcome. The system is divided into small cells, small enough that effectively each point in the system is treated, but large enough so that each cell contains thousands of molecules. At a specific time, t , the cells are isolated from the system and allowed to come to equilibrium in time dt . Therefore, at time $t + dt$, measurements can be made that give an equilibrium temperature or pressure. The variable of state at time t is then considered to be equal to the measurable variable at time $t + dt$. The relationships derived by this postulate are then considered to be equivalent to the relationships derived from equilibrium states. It must be realized that this postulate has its limitations. The presumption is that the variables in the system are not changing too rapidly. If the time, dt , necessary for the cell to achieve local equilibrium, approximates the time during which a change for the whole system may be measured, then the postulate cannot be reasonably applied.

Entropy plays an important role in our systems of interest and will be seen as a driving force in transport phenomena. How does the treatment of irreversible systems work in the case of entropy? Instead of employing the relationship $\Delta S = q_{rev}/T$, it is more convenient to determine ΔS from another relationship, for example:

$$\Delta S = C_p \ln \frac{T_2}{T_1} \quad (27.2)$$

Once the entropy of each cell is determined, the free energy for each cell can be determined:

$$dG = V dP - S dT + \sum \mu_i dn_i \quad (27.3)$$

We know that reversible processes take an infinite amount of time to complete but do not lead to the production of entropy. Irreversible processes, on the other hand, occur in a finite time and create entropy. The rate of a process therefore can be defined in terms of the rate of entropy production with respect to time, dS/dt . This means that, as a reaction or process proceeds in an isothermal system, there will be heat flow into and out of the surroundings and system. The differential change in entropy will be given by:

$$dS = d_rS + d_sS \quad (27.4)$$

where d_rS is the entropy change in the system, and d_sS is that in the surroundings. Further, dS will always be zero or greater.

Historically, the formulation of irreversible thermodynamics started when Thomson (Lord Kelvin) was investigating the relationship between the flow of electricity and heat flow in thermocouples. If two dissimilar metal wires are twisted together at one end and a voltmeter is used to complete the circuit between the two, a voltage can be demonstrated arising from the contact of the two phases. This is the *contact potential*. If both ends are connected, there will be two junctions in the circuit. If these two junctions are isothermal and an electric current is passed between them, heat will be absorbed from the surroundings at one junction, and an equal amount of heat will be released at the other junction. This heat flow is reversible in that when the direction of the current is changed, the direction of heat flow also changes. This reversible heat is called the *Peltier heat*. A second source of heat is also produced during this process due to the resistance of the metal to the flow of charge, and this heat is called the *Joule heat*. Joule heat is irreversible. If the two junctions are now placed at two different temperatures, an electromotive force will exist between them. The electromotive force between the two junctions is called the *Seebeck emf*. If a charge is allowed to move around the circuit because of the Seebeck emf, experiment will demonstrate that the Peltier heat appearing at the junctions is not sufficient to account for the work accomplished. Thomson therefore proposed a second reversible heat associated with the flow of current, the *Thomson heat*. The Thomson and the Peltier heats are reversible and are accompanied by two irreversible heats in this system, one due to Joule heating and one due to heat conduction. Thomson treated the thermocouple as if it were a reversible heat engine in which only the Thomson and Peltier heats circulated. He described a series of relationships that showed there was no entropy production, that is, that the two heats were equal and reversible. Thomson's theoretical treatment of this system was experimentally validated even though he ignored the two irreversible terms. Thomson himself recognized that the treatment was incomplete because the process described is an irreversible one; hence

the total entropy of the process must be positive. However, his analysis assumed that the entropy increase associated with the Joule heating and the heat conduction would be positive and constant and therefore tested the hypothesis that the Peltier and Thomson heats did not add to the entropy generation of the process, that is, that they were indeed reversible. His result demonstrated that in transport phenomena there are reversible and irreversible processes.

A unifying method for generally treating irreversible systems was given by Onsager in 1931. Onsager based his formulation on the *principle of microscopic reversibility*, which says that at equilibrium any process and its reverse process are taking place on average at the same rate. He further assumed that for a process near equilibrium, equations may be written for the transport process in which the fluxes are linearly proportional to the forces. The theory is valid only for deviations from equilibrium where this linear relationship exists. Processes like the one just described can be generally treated by considering that in a transport process there are a number of flows that occur simultaneously. For example, in the case of thermoelectricity, there is a flux of heat, J_1 , and one of current, J_2 . The two flux equations take the general form:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \quad (27.5)$$

The term X_x represents the force gradient, L_{ij} are the phenomenological coefficients, and L_{ii} are the direct coefficients. In this case, X_1 represents the temperature gradient and X_2 the electrical gradient. The forces represented by X_x are thermodynamic driving forces and have the form:

$$\frac{\partial S}{\partial X_x} = F_x \quad (27.6)$$

This type of analysis indicates that when more than one gradient is causing flux, there will be a coupling of the flows. The direct coefficients represent the fluxes due to the directly related gradient, that is, the flow of heat due to a thermal gradient. These always increase the entropy of the reservoirs. The cross terms, L_{ij} , are the coupled flows caused by the gradient that is not directly related, that is, the flux of heat caused by the flow of electricity. Onsager

showed that the phenomenological coefficients are equal:

$$L_{ij} = L_{ji} \quad (27.7)$$

This equality is called the *Onsager reciprocity relation*. The coupling between the flows indicates the interaction of one flow with another. The idea that some fluxes are independent while others occurring simultaneously are interacting and reversibly coupled is an important one in transport phenomena.

In mechanistic terms, transport can be thought of as the balance between the motion of a particle moving directly down a gradient of force and the scattering of the particle away from this direct path because of interactions between other forces or particles. Although the relationships of irreversible thermodynamics are probably the most accurate expression of the balance between direct and scatter-

ing forces, there are two mechanistic models frequently considered. One is the concept of the mean free path, and the other is based on relaxation time. In the next chapter we will focus on the concept of the mean free path and see how this approach can be used to examine diffusion in a solution.

Further Reading

- Haase R. (1969) *Thermodynamics of Irreversible Processes*. Dover Publications, Inc., New York.
 Waldram, J. R. (1985) *The Theory of Thermodynamics*. Cambridge University Press, Cambridge.

Problems

1. Explain in qualitative but succinct terms the following statement: "Entropy is the primary driving force in transport phenomena." What does this imply about the time scale of transport phenomena?