CHAPTER

FUNDAMENTALS OF NONEQUILIBRIUM THERMODYNAMICS

3

3.1 INTRODUCTION

Physical systems identified by permanently stable and reversible behavior are rare. Unstable phenomena result from inherent fluctuations of the respective state variables. Near global equilibrium, the fluctuations do not disturb the equilibrium; the trend toward equilibrium is distinguished by asymptotically vanishing dissipative contributions. In contrast, nonequilibrium states can amplify the fluctuations, and any local disturbances can even move the whole system into an unstable or metastable state. This feature is an important indication of the qualitative difference between equilibrium and nonequilibrium states.

Kinetic and statistical models often require more detailed information than is available to describe nonequilibrium systems. Therefore, it may be advantageous to have a phenomenological approach with thermodynamic principles to describe natural processes. Such an approach is the formalism used in nonequilibrium thermodynamics to investigate physical, chemical, and biological systems with irreversible processes. In the formalism, the Gibbs equation is a key relation since it combines the first and second laws of thermodynamics. The Gibbs relation, combined with the general balance equations based on the local thermodynamic equilibrium, determines the rate of entropy production. Quantifying entropy production helps in analyzing the level of energy dissipation during a process, and in describing coupled phenomena.

The first attempts to develop nonequilibrium thermodynamics theory occurred after the first observations of some coupled phenomena of thermal diffusion and thermoelectric. Later, Onsager developed the basic equations of the theory, and Casimir, Meixner, and Prigogine refined and developed the theory further. This chapter outlines the principles of nonequilibrium thermodynamics for systems not far from global equilibrium. In this region, the transport and rate equations are expressed in linear forms, and the Onsager reciprocal relations are valid. Therefore, sometimes this region is called the *linear* or *Onsager region* and the formulations are based on *linear nonequilibrium thermodynamics* theory. In this region, instead of thermodynamic potentials and entropy, a new property called *entropy production* appears. The formulation of linear nonequilibrium thermodynamics has proven to be valid and useful for a wide range of transport and rate processes of physical, chemical, and biological systems.

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3.2 LOCAL THERMODYNAMIC EQUILIBRIUM

A local thermodynamic state is determined as elementary volumes at individual points for a nonequilibrium system. These volumes are small such that the substance in them can be treated as homogeneous and contain enough molecules for the phenomenological laws to be applicable. This local state shows *microscopic reversibility* that is the symmetry of all mechanical equations of motion of individual particles with respect to time. In the case of microscopic reversibility for a chemical system, when there are two alternative paths for a simple reversible reaction, and one of these paths is preferred for the backward reaction, the same path must also be preferred for the forward reaction. Onsager's derivation of the reciprocal rules assumes microscopic reversibility. The reversibility of molecular behavior gives rise to a kind of symmetry in which the transport processes are coupled to each other. Although a thermodynamic system may not be in equilibrium, the local states may be in *local thermodynamic equilibrium*; all intensive thermodynamic variables become functions of position and time. The local equilibrium temperature is defined in terms of the average molecular translational kinetic energy within the small local volume

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_{\mathrm{B}} T$$

where k_B is the Boltzmann constant and v is the velocity of molecules with mass m. Here the average kinetic energy is limited to the translational kinetic energy of the molecules, which are treated as point masses and the internal degrees of freedom such as molecular rotation and vibration are not accounted.

The definition of energy and entropy in nonequilibrium systems can be expressed in terms of energy and entropy densities $u(T,N_k)$ and $s(T,N_k)$, which are the functions of the temperature field $T(x)$ and the mole number density $N(x)$; these densities can be measured. The total entropy and energy of the system is obtained by the following integrations

$$S = \int_V \{s[T(x)], [N_k(x)]\}\, dV \tag{3.1}$$

$$U = \int_V \{u[T(x)], [N_k(x)]\}\, dV \tag{3.2}$$

From the internal energy density u and entropy density s, we obtain the local variables of

$$(\partial u/\partial s)_{V,N_k} = T(x),$$

$$-(\partial u/\partial V)_{s,N_k} = P,$$

and

$$(\partial s/\partial N_k)_u = -\mu(x)/T(x)$$

The densities in Eqs. (3.1) and (3.2) are dependent on the locally well-defined temperature. Also, the classical thermodynamic equations such as the Gibbs and the Gibbs–Duhem equations

$$dU = TdS - Pd\left(\frac{1}{\rho}\right) + \sum_{i=1}^{n} \mu_i dx_i$$

$$-SdT + \left(\frac{1}{\rho}\right)dP = \sum_{i=1}^{n} x_i d\mu_i$$

are valid in local equilibrium. For a large class of nonequilibrium systems, thermodynamic properties such as temperature, pressure, concentration, internal energy, and entropy are locally well-defined concepts. Exceptions to the local thermodynamic equilibrium assumption are discussed in chapters 12–15.

Prigogine expanded the molecular distribution function in an infinite series around the equilibrium molecular distribution function f_0

$$f = f_0 + f_1 + f_2 + \cdots$$

The equation above is valid not only for an equilibrium system, but also for a nonequilibrium system that is characterized by the equilibrium distribution function of $(f_0 + f_1)$ representing a nonequilibrium system sufficiently close to global equilibrium. Prigogine's analysis applies only to mixtures of monatomic gases and is dependent on the Chapman–Enskog model. The domain of validity of the local equilibrium is not known in general from a microscopic perspective. The range of validity of the local thermodynamic equilibrium is determined only through experiments. Experiments show that the postulate of local thermodynamic equilibrium is valid for a wide range of macroscopic systems of common gases and liquids, and for most transport processes if the gradients of intensive thermodynamic functions are small and their local values vary slowly in comparison with the local state of the system. For chemical reactions, the reactive collision rates are relatively smaller than overall collision rates. The change in an intensive parameter is comparable to the molecular mean free path, and energy dissipation rapidly damps large deviations from global equilibrium. The local equilibrium concept is not valid in highly rarefied gases where collisions are too infrequent. The extension of equilibrium thermodynamics to nonequilibrium systems based on the local equilibrium assumption is a well-accepted practice in nonequilibrium thermodynamics.

3.3 STATIONARY STATES

Intensive properties that specify the state of a substance are time independent in equilibrium systems and in nonequilibrium stationary states. Extensive properties specifying the state of a system with boundaries are also independent of time, and the boundaries are stationary in a coordinate system. Therefore, the stationary state of a substance at any point is related to the stationary state of the system.

In a stationary state the total entropy does not change with time, and we have

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0 \tag{3.3}$$

The term $d_e S/dt$ is the reversible entropy change in time because of an entropy flow between the system and its surroundings. On the other hand, $d_i S/dt$ represents the rate of entropy production inside the system.

For the total entropy to be constant, the entropy flowing out of the system must be equal to the entropy entering the system and the entropy generated within the system.

$$\frac{d_{\mathrm{i}}S}{dt} + \left(J_{s,\mathrm{in}} - J_{s,\mathrm{out}}\right) = 0 \tag{3.4}$$

Entropy change inside an elementary volume by irreversible phenomena is the local value of the sum of entropy increments. By the second law of thermodynamics, the entropy production $d_{\mathrm{i}}S$ is always positive for irreversible changes and zero for reversible changes. From Eqs. (3.3) and (3.4), the entropy exchange with the surrounding must be negative at stationary state

$$\frac{d_{\mathrm{e}}S}{dt} = -\frac{d_{\mathrm{i}}S}{dt} = \left(J_{\mathrm{s,in}} - J_{\mathrm{s,out}}\right) < 0$$

The stationary state is maintained through the decrease in entropy exchanged between the system and its surrounding. Therefore, the total entropy produced within the system must be discharged across the boundary at stationary state.

For a system at a stationary state, boundary conditions do not change with time. Consequently, a nonequilibrium stationary state is not possible for an isolated system for which $d_{\mathrm{e}}S/dt = 0$. In addition, a steady state cannot be maintained in an adiabatic system in which irreversible processes are occurring, since the entropy produced cannot be discharged, as an adiabatic system cannot exchange heat with its surroundings. In equilibrium, all the terms in Eq. (3.3) vanish because of the absence of both entropy flow across the system boundaries and entropy production due to irreversible processes, and we have $d_{\mathrm{e}}S/dt = d_{\mathrm{i}}S/dt = dS/dt = 0$.

3.4 BALANCE EQUATIONS AND ENTROPY PRODUCTION

Balance equations of extensive quantities describe a change in a system (except in rare gases and shock waves). These balance equations also contain intensive quantities specifying the local state of a continuous medium. Intensive parameters described by the macroscopic properties of the medium are based on the behavior of many particles.

It is necessary to consider the mechanics of a continuous medium to determine the thermodynamic state of a fluid. The properties of a fluid can be determined that are at rest relative to a reference frame or moving along with the fluid. Every nonequilibrium intensive parameter in a fluid changes in time and in space.

3.4.1 TOTAL DIFFERENTIAL

Consider the temperature as a function of time and space $T = T\,(t,x,y,z)$; the *total differential* of T is

$$dT = \frac{\partial T}{\partial t}dt + \frac{\partial T}{\partial x}dx + \frac{\partial T}{\partial y}dy + \frac{\partial T}{\partial z}dz$$

Dividing the total differential by the time differential, we obtain the *total time derivative* of T

$$\frac{dT}{dt} = \frac{\partial T}{\partial t} + \frac{\partial T}{\partial x}\frac{dx}{dt} + \frac{\partial T}{\partial y}\frac{dy}{dt} + \frac{\partial T}{\partial z}\frac{dz}{dt}$$

The partial time derivative of T, $\partial T/\partial t$, shows the time rate of change of temperature of a fluid at a fixed position at constant x, y, and z

$$\frac{dT}{dt} = \frac{\partial T}{\partial t}$$

If the derivative in the equation above vanishes, then the temperature field becomes stationary. The terms dx/dt, dy/dt, and dz/dt are the components of the velocity of the observer relative to the velocity of the fluid.

3.4.2 SUBSTANTIAL DERIVATIVE

If the velocity of the observer is the same as the mass average velocity of the fluid $\mathbf{v}$ with components v_x, v_y, and v_z, then the rate of temperature change is given by

$$\frac{DT}{Dt} = \frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y} + v_z\frac{\partial T}{\partial z}$$

or

$$\frac{DT}{Dt} = \frac{\partial T}{\partial t} + \mathbf{v}\cdot\nabla T \tag{3.5}$$

The special operator, DT/Dt is the *substantial time derivative*, and means the time rate of change if the observer moves with the substance.

A scalar or a vector function expressed in terms of $\partial/\partial t$ can be converted into the substantial form; for a scalar function $T = T(x, y, z, t)$, we have

$$\begin{aligned}\rho\frac{DT}{Dt} &= \frac{\partial(\rho T)}{\partial t} + \left(\frac{\partial(\rho v_x T)}{\partial x}\right) + \left(\frac{\partial(\rho v_y T)}{\partial y}\right) + \left(\frac{\partial(\rho v_z T)}{\partial z}\right)\\ &= \rho\left(\frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y} + v_z\frac{\partial T}{\partial z}\right) + T\left(\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z}\right)\end{aligned} \tag{3.6}$$

The second term in the second line of Eq. (3.6) is the equation of continuity and vanishes, so that in vector form Eq. (3.6) becomes

$$\rho\frac{DT}{Dt} = \frac{\partial(\rho T)}{\partial t} + (\nabla\cdot\rho\,\mathbf{v}T)$$

This equation is valid for every local quantity, which may be a scalar, an element of a vector, or an element of a tensor.

3.4.3 BALANCE EQUATIONS

An extensive quantity E for a fluid in volume V can be expressed in terms of the specific quantity e

$$E = \int_V \rho\, e dV$$

The partial time derivative of E pertaining to the entire body is equal to the total differential

$$\frac{\partial E}{\partial t} = \frac{dE}{dt} = \frac{d}{dt}\int_V \rho e dV = \int_V \frac{\partial(\rho e)}{\partial t} dV \tag{3.7}$$

In Eq. (3.7) the quantity ρe is determined per unit volume when the observer is at rest.

The amount of substance entering through an elementary surface area da per unit time is $\rho \mathbf{v}\cdot d\mathbf{a}$, where $d\mathbf{a}$ is a vector with magnitude da and pointing in a direction normal to the surface. Along with the substance flow there is a convection flow $\rho \mathbf{v} e$, and the amount transported per unit time is $-\int(\rho v e)\cdot d\mathbf{a}$. The conduction flow $\mathbf{J}_e$ is a vector with the same direction as the flow, and the amount transported per unit time by means of conduction without a flow of substance is $-\int \mathbf{J}_e \cdot d\mathbf{a}$. The so-called source term, the rate of energy production inside the elementary volume of substance at a given point is

$$\dot{E}_{\text{prod}} = \frac{dE}{dVdt}$$

Hence, for the entire volume at rest relative to the coordinate system, the balance equation per unit time Eq. (3.7) is expressed as

$$\frac{dE}{dt} = \int_V \frac{\partial(\rho e)}{\partial t} dV = -\int_A (\rho\, e\mathbf{v})\cdot d\mathbf{a} - \int_A \mathbf{J}_e \cdot d\mathbf{a} + \int_V \dot{E}_{\text{prod}} dV \tag{3.8}$$

Using the Gauss—Ostrogradsky theorem, the equation above can be written over the entire volume

$$\frac{dE}{dt} = \int_V \frac{\partial(\rho e)}{\partial t} dV = -\int_V [\nabla\cdot(\rho\, e\mathbf{v})] dV - \int_V (\nabla\cdot\mathbf{J}_e) dV + \int_V \dot{E}_{\text{prod}} dV \tag{3.9}$$

From the equation above, the local balance equation for a fixed observer becomes

$$\frac{\partial(\rho e)}{\partial t} = -\nabla\cdot(\rho e\mathbf{v}) - \nabla\cdot\mathbf{J}_{\text{e}} + \dot{E}_{\text{prod}} \tag{3.10}$$

The local balance equation for properties subject to a conservation law is called the *conservation equation,* which is given for e as follows

$$\frac{\partial(\rho e)}{\partial t} = -\nabla\cdot(\rho e\mathbf{v}) - \nabla\cdot\mathbf{J}_{\text{e}}$$

If the system is in a stationary state, the extensive property E does not change with time $dE/dt = 0$, and we have

$$\nabla\cdot(\mathbf{J}_e + \rho e\mathbf{v}) = 0 \tag{3.11}$$

The equation above shows that the net amount of E exchanged through the boundary must be zero, and the divergence of the sum of the conduction and convection flows governed by a *conservation law* is equal to zero in the stationary state. For the values $e = 1$, $\mathbf{J}_\mathrm{e} = 0$, and the source term $\dot{E}_\mathrm{prod} = 0$, Eq. (3.10) becomes

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) = -\rho(\nabla \cdot \mathbf{v}) - \mathbf{v} \cdot \nabla \rho \tag{3.12}$$

The local balance equations for an observer moving along with the fluid are expressed in substantial time derivative form. From Eq. (3.10), we can express the substantial time derivative of e by

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{J}_\mathrm{e} + \dot{E}_\mathrm{prod} \tag{3.13}$$

On the right side of this equation, the divergence of the convection flow of e, $-\nabla \cdot (\rho\, e\mathbf{v})$, vanishes since the observer (coordinate system) is moving along with the fluid. In terms of the conservation law, where the source term vanishes, Eq. (3.13) becomes

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{J}_e \tag{3.14}$$

Engineering systems mainly involve a single-phase multicomponent fluid mixture with fluid friction, heat transfer, mass transfer, and several chemical reactions. A local thermodynamic state of the fluid is specified by two intensive parameters, for example, velocity of the fluid and the chemical composition in terms of component mass fractions. For a unique description of the system, balance equations must be derived for mass, momentum, energy, and entropy. The balance equations, considered on a per-unit volume basis, can be written in terms of the partial time derivative with an observer at rest, and in terms of the substantial derivative with an observer moving along with the fluid. Later, the balance equations are used in the Gibbs relation to determine the rate of entropy production. The balance equations allow us to clearly identify the importance of the local thermodynamic equilibrium postulate in deriving the relationships for entropy production.

3.4.4 THE MASS BALANCE EQUATIONS

The mass flow of component i, $\rho_i \mathbf{v}_i$, is a vector showing the flow of a component relative to a motionless coordinate system. On the other hand, diffusion flow shows the transport of a component relative to a coordinate system moving at the reference velocity $\mathbf{v}$. The diffusion flow relative to the center-of-mass velocity $\mathbf{v}$ (or mass average velocity) is

$$\mathbf{j}_i = \rho_i(\mathbf{v}_i - \mathbf{v})$$

where $(\mathbf{v}_i - \mathbf{v})$ is the diffusion velocity. Mass average velocity is

$$\mathbf{v} = \sum_{i=1}^{n} w_i \mathbf{v}_i$$

Here w_i is the mass fraction of component i. We can express the molar diffusion flow $\mathbf{J}_{i,\mathrm{M}}$ based on the molar average velocity $\mathbf{v}_\mathrm{M}$

$$\mathbf{J}_{i,\mathrm{M}} = c_i(\mathbf{v}_i - \mathbf{v}_\mathrm{M}) \text{ with } \mathbf{v}_\mathrm{M} = \sum_{i=1}^{n} x_i \mathbf{v}_i$$

The sum of diffusion flows of all components is zero

$$\sum_{i=1}^{n} \mathbf{j}_i = \sum_{i=1}^{n} \mathbf{J}_{i,\mathrm{M}} = \sum_{i=1}^{n} \mathbf{J}_{i,V} = 0$$

Of the n diffusion flows, only $n-1$ of the flows are independent.

The mass balance equation for component i is like the general form given in Eq. (3.10) after setting $e = w_i$ and $\mathbf{J}_\mathbf{e} = \mathbf{j}_i$. The amount of component produced or consumed inside a unit volume per unit time is the result of chemical reactions. The mass balance equation is

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}) - \nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^{l} \nu_{ij} J_{\mathrm{r},j}$$

Here $J_{\mathrm{r},j}$ is the chemical reaction rate per unit volume for reaction j, ν_{ij} the specific stoichiometric coefficient of species i in the chemical reaction j, and M_i the molecular mass of component i.

From Eqs. (3.5) and (3.14), we can represent the mass balance in the substantial time derivative

$$\frac{D\rho_i}{Dt} = \frac{\partial \rho_i}{\partial t} + \mathbf{v} \cdot \nabla \rho_i = -\nabla \cdot (\rho_i \mathbf{v}) - \nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^{l} \nu_{ij} J_{\mathrm{r},j} + \mathbf{v} \cdot \nabla \rho_i \tag{3.15}$$

Using Eq. (3.12) and (3.15) becomes

$$\frac{D\rho_i}{Dt} = -\rho_i (\nabla \cdot \mathbf{v}) - \nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^{l} \nu_{ij} J_{\mathrm{r},j} \tag{3.16}$$

When an observer moves at the center-of-mass velocity of the fluid, the conservation equation from the substantial derivative of the density becomes

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = -\rho (\nabla \cdot \mathbf{v})$$

The conservation of mass with the specific volume $v = 1/\rho$ is

$$\frac{Dv}{Dt} = v (\nabla \cdot \mathbf{v}) \tag{3.17}$$

Using Eq. (3.16), the balance equation for the amount can also be written in terms of mass fraction w_i

$$\frac{\partial (\rho w_i)}{\partial t} = -\nabla \cdot (\rho\, w_i \mathbf{v}) - \nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^{l} \nu_{ij} J_{\mathrm{r},j} \tag{3.18}$$

With the substantial derivative, the equation above becomes

$$\rho \frac{D(w_i)}{Dt} = -\nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^{l} \nu_{ij} J_{\mathrm{r},j} \tag{3.19}$$

In the stationary state $dm/dt = 0$, and we have $\nabla \cdot (\rho \mathbf{v}) = 0$.

3.4.5 THE MOMENTUM BALANCE EQUATIONS

Fluid motion may be described by applying Newton's second law to a particle. The momentum flow of a substance $\rho\mathbf{vv}$ is equal to the product of the mass flow $\rho\mathbf{v}$ and the barycentric velocity. Newton's second law of motion states that the change in the momentum of a body is equal to the resultant of all forces, mass force $\mathbf{F}$ and surface force $\boldsymbol{\sigma}$, acting on that body. If $\mathbf{F}_i$ is the force exerted per unit mass of component i, we have

$$\mathbf{F} = \frac{1}{\rho}\sum_{i=1}^{n}\rho_i\mathbf{F}_i = \sum_{i=1}^{n} w_i\mathbf{F}_i$$

The mass forces may be the gravitational force, the force due to the rotational motion of a system, and the Lorentz force that is proportional to the vector product of the molecular velocity of component i and the magnetic field strength. The normal stress tensor $\boldsymbol{\omega}$ produces a surface force.

The time derivative of the momentum density is the conservation of momentum

$$\frac{\partial}{\partial t}(\rho\mathbf{v}) = -\nabla\cdot\boldsymbol{\omega} + \rho\mathbf{F} \tag{3.20}$$

By considering the following relations (Bird et al., 2002)

$$\boldsymbol{\omega} = \rho\mathbf{vv} + P\boldsymbol{\delta} + \boldsymbol{\tau}$$

$$\nabla\cdot(P\boldsymbol{\delta}) = \nabla P$$

Eq. (3.20) becomes

$$\frac{\partial}{\partial t}(\rho\mathbf{v}) = -\nabla\cdot(\rho\,\mathbf{vv}) - \nabla P - \nabla\cdot\boldsymbol{\tau} + \rho\,\mathbf{F} \tag{3.21}$$

where $\boldsymbol{\delta}$ is the unit tensor. The terms on the right side represent the change of momentum due to the convection momentum flow $\nabla\cdot(\rho\mathbf{vv})$, the pressure force ∇P, the viscous force $\nabla\cdot\boldsymbol{\tau}$, and the mass force $\rho\mathbf{F}$, respectively. The momentum balance equation for a coordinate system moving along with the fluid is given by using the substantial derivative

$$\rho\frac{D\mathbf{v}}{Dt} = -\nabla P - \nabla\cdot\boldsymbol{\tau} + \rho\,\mathbf{F} \tag{3.22}$$

The left side of the equation above contains the center-of-mass acceleration $d\mathbf{v}/dt$. Using the Newtonian fluid expression for the stress with the constant density and viscosity, we have the Navier—Stokes equation

$$\rho\frac{D\mathbf{v}}{Dt} = -\nabla P + \mu\nabla^2\mathbf{v} + \rho\,\mathbf{F}$$

The state of mechanical equilibrium is characterized by vanishing acceleration $d\mathbf{v}/dt = 0$. Usually, mechanical equilibrium is established faster than thermodynamic equilibrium, for example, in the initial state when diffusion is considered. In the case of diffusion in a closed system, the acceleration is very small, and the corresponding pressure gradient is negligible; the viscous part of the stress tensor also vanishes $\boldsymbol{\tau} = 0$. The momentum balance, Eq. (3.20), is limited to the *momentum conservation equation*

$$\nabla P = \sum_{i=1}^{n} \rho_i \mathbf{F}_i = \rho\, \mathbf{F}$$

Hence, the pressure gradient is equal to the sum of the mass forces acting on the substance in a unit volume.

3.4.6 THE ENERGY BALANCE EQUATIONS

The time variation of the total energy e per unit volume is subject to a law of conservation, and given in terms of convection flow $\rho\, e\mathbf{v}$ and conduction flow $\mathbf{J}_\mathrm{e}$

$$\frac{\partial(\rho e)}{\partial t} = -\nabla\cdot(\rho\, e\mathbf{v}) - \nabla\cdot\mathbf{J}_\mathrm{e} \tag{3.23}$$

The total specific energy e of a substance is

$$e = u + \frac{1}{2}v^2 + e_\mathrm{p}$$

and consists of the specific internal energy u, the specific kinetic energy $1/2v^2$, and the specific potential energy e_p.

The conduction flow of the total energy $\mathbf{J}_\mathrm{e}$ consists of the conduction flow of the internal energy $\mathbf{J}_\mathrm{u}$ the potential energy flow $\sum_i e_{\mathrm{p}i}\mathbf{j}_i$ due to the diffusion of components, and the work of surface force $\boldsymbol{\omega}\cdot\mathbf{v}$ per unit surface area, and is expressed as follows

$$\mathbf{J}_\mathrm{e} = \mathbf{J}_\mathrm{u} + \sum_{i=1}^{n} e_{\mathrm{p}i}\mathbf{j}_i + \boldsymbol{\omega}\cdot\mathbf{v}$$

The divergence of the total energy flow becomes

$$\nabla\cdot\mathbf{J}_\mathrm{e} = \nabla\cdot\left(\mathbf{J}_\mathrm{u} + \sum_{i=1}^{n} e_{\mathrm{p}i}\mathbf{j}_i + \boldsymbol{\omega}\cdot\mathbf{v}\right) \tag{3.24}$$

By using the mass flow, $\mathbf{j}_i = \rho_i(\mathbf{v}_i - \mathbf{v})$, the time variation of the potential energy of a unit volume of the fluid is given by

$$\frac{\partial(\rho e_\mathrm{p})}{\partial t} = -\nabla\cdot\left(\rho\, e_\mathrm{p}\mathbf{v} + \sum_{i=1}^{n} e_{\mathrm{p}i}\mathbf{j}_i\right) - \rho\, \mathbf{F}\cdot\mathbf{v} - \sum_{i=1}^{n} \mathbf{j}_i\cdot\mathbf{F}_i + \sum_{i=1}^{n} e_{\mathrm{p}i}M_i \sum_{j=1}^{l} \nu_{ij}J_{\mathrm{r}j} \tag{3.25}$$

where the mass force $\mathbf{F}_i$ is associated with the derivative of the specific potential energy e_{pi} of component i by

$$\mathbf{F}_i = -\nabla e_{\mathrm{p}i}$$

with the properties of conservative mass forces

$$\frac{\partial e_{\mathrm{p}i}}{\partial t} = 0, \quad \frac{\partial \mathbf{F}_i}{\partial t} = 0$$

The last term on the right side of Eq. (3.25) is zero if the potential energy is conserved for the chemical reaction j

$$\sum_{i=1}^{n} e_{\mathrm{p}i} M_i \nu_{ij} = 0$$

The balance equation for the kinetic energy is obtained by scalar multiplication of the momentum balance, Eq. (3.22), and the mass average velocity. By using relations analogous to Eq. (3.12) $\mathbf{v}\cdot(-\nabla P) = -\nabla\cdot(P\mathbf{v}) + P(\nabla\cdot\mathbf{v})$ and $\mathbf{v}\cdot(-\nabla\cdot\boldsymbol{\tau}) = -\nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) + \boldsymbol{\tau}:(\nabla\mathbf{v})$, we obtain

$$\rho\frac{D\left(1/2 v^2\right)}{Dt} = -\nabla\cdot(P\mathbf{v}) - \nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) + P(\nabla\cdot\mathbf{v}) + \boldsymbol{\tau}:(\nabla\mathbf{v}) + \rho\mathbf{v}\cdot\mathbf{F} \tag{3.26}$$

The time variation of the kinetic energy per unit volume (for a motionless reference frame) is

$$\frac{\partial\left(1/2\,\rho v^2\right)}{\partial t} = -\nabla\cdot\left(1/2\,\rho v^2\mathbf{v}\right) - \nabla\cdot(P\mathbf{v}) - \nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) + P(\nabla\bullet\mathbf{v}) + \boldsymbol{\tau}:(\nabla\mathbf{v}) + \rho\mathbf{v}\cdot\mathbf{F} \tag{3.27}$$

In Eq. (3.27), the term $-\nabla\cdot\left(\frac{1}{2}\rho v^2\mathbf{v}\right)$ is the convection transport of kinetic energy, $-\nabla\cdot(P\mathbf{v})$ is the work of the pressure, $-\nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v})$ is the work of the viscous forces, and $\rho\mathbf{v}\cdot\mathbf{F}$ is the work of the mass forces. Part of the kinetic energy $P(\nabla\cdot\mathbf{v})$ is transformed reversibly into internal energy, and the part $\boldsymbol{\tau}:(\nabla\mathbf{v})$ is transformed irreversibly and dissipated (Bird et al., 2002).

We find the rate of change of the internal energy for an observer at rest by subtracting Eqs. (3.25) and (3.27) from the total energy conservation relation Eq. (3.23) and using Eq. (3.24)

$$\rho\frac{\partial u}{\partial t} = -\nabla\cdot(\rho u\mathbf{v}) - \nabla\cdot\mathbf{J_u} - P(\nabla\cdot\mathbf{v}) - \boldsymbol{\tau}:(\nabla\mathbf{v}) + \sum_{i=1}^{n}\mathbf{j}_i\cdot\mathbf{F}_i \tag{3.28}$$

The term $-\nabla\cdot(\rho u\mathbf{v})$ is the divergence of the convection internal energy flow, $-\nabla\cdot\mathbf{J}_u$ is the divergence of the conduction internal energy flow, $-P(\nabla\cdot\mathbf{v})$ is the reversible increment of internal energy due to volume work $-\boldsymbol{\tau}:(\nabla\mathbf{v})$ is the irreversible increment of internal energy due to viscous dissipation, and $\sum_{i=1}^{n}\mathbf{j}_i\cdot\mathbf{F}_i$ is the transport of potential energy by diffusion flows. We can represent Eq. (3.28) in terms of the substantial derivative

$$\rho\frac{Du}{Dt} = -\nabla\cdot\mathbf{J_u} - P(\nabla\cdot\mathbf{v}) - \boldsymbol{\tau}:(\nabla\mathbf{v}) + \sum_{i=1}^{n}\mathbf{j}_i\cdot\mathbf{F}_i \tag{3.29}$$

Comparing Eq. (3.29) with Eq. (3.26) the terms $P(\nabla\cdot\mathbf{v})$ and $\boldsymbol{\tau}:(\nabla\mathbf{v})$ appear with opposite sign in both equations. They represent the interconversion between the kinetic and the internal energy. The reversible conversion $P(\nabla\cdot\mathbf{v})$ can be positive if the fluid expands or negative in the converse. The irreversible conversion $-\boldsymbol{\tau}:(\nabla\mathbf{v})$ is proportional to the square of the velocity gradient and always positive since for a Newtonian fluid $\boldsymbol{\tau} = -\mu\nabla\mathbf{v}$.

The internal energy balance equation for the fluid is based on the momentum balance equation. The assumption of local thermodynamic equilibrium will enable us to introduce the thermodynamic relationships linking intensive quantities in the state of equilibrium and to derive the internal energy balance equation based on equilibrium partial quantities. By assuming that the diffusion is a slow phenomenon, $-\sum_{i}^{n}\mathbf{j}_i/\rho << \rho v^2$, the change of the total energy of all components per unit volume becomes

$$\frac{\partial}{\partial t}\left[\sum_{i=1}^{n}\rho_i\left(u_i+\frac{1}{2}v_i^2+e_{\mathrm{p}i}\right)\right]=\frac{\partial}{\partial t}\left[\rho\left(u+\frac{1}{2}v^2+e_{\mathrm{p}}\right)\right] \tag{3.30}$$

This form is based on the concept of local thermodynamic equilibrium. From Eq. (3.30), the convection flow of the total energy is

$$\sum_{i=1}^{n}\rho_i\left(u_i+\frac{1}{2}v_i^2+e_{\mathrm{p}i}\right)\mathbf{v}_i=\sum_{i=1}^{n}u_i\mathbf{J}_i+\rho\left(u+\frac{1}{2}v^2+\rho e_{\mathrm{p}}\right)\mathbf{v}+\sum_{i=1}^{n}e_{\mathrm{p}i}\mathbf{J}_i=\sum_{i=1}^{n}u_i\mathbf{J}_i+\rho e\mathbf{v}+\sum_{i=1}^{n}e_{\mathrm{p}i}\mathbf{J}_i \tag{3.31}$$

Eq. (3.31) contains the convection flow of the total energy and energy changes due to the diffusion flows. If $\mathbf{J}'_q$ is the pure heat conduction without a flow of internal energy due to diffusion of the substance, the total energy conservation given in Eq. (3.23) becomes

$$\frac{\partial(\rho e)}{\partial t}=-\nabla\cdot(\rho e\mathbf{v})-\nabla\cdot\left(\mathbf{J}'_q+\sum_{i=1}^{n}u_i\mathbf{j}_i+\sum_{i=1}^{n}e_{pi}\mathbf{j}_i-\boldsymbol{\omega}\cdot\mathbf{v}\right) \tag{3.32}$$

where $\boldsymbol{\omega}\cdot\mathbf{v}$ is the work of surface force per unit surface area and $\boldsymbol{\omega}$ is the normal stress tensor. We may relate the terms $\mathbf{J}_{\mathrm{u}}, \mathbf{J}'_{\mathrm{q}}$, and $\mathbf{j}_i$ by

$$\mathbf{J}_{\mathrm{u}}=\mathbf{J}'_{\mathrm{q}}+\sum_{i=1}^{n}u_i\mathbf{j}_i$$

The second term on the right represents the net flow of internal energy transported along with the diffusion of species i.

EXAMPLE 3.1 CONSERVATION OF ENERGY

Describe the change of energy in closed and open subsystems in a composite system.

Solution:

The change of energy dE has two parts; $d_{\mathrm{e}}E$ is the part exchanged with the surroundings, and $d_{\mathrm{i}}E$ is the part produced or consumed within the system

$$dE=d_{\mathrm{e}}E+d_{\mathrm{i}}E \tag{a}$$

a. *Closed subsystems*: For a closed subsystem with a chemical reaction characterized by the extent of reaction ε, the total differential of E with respect to the variables V,T, and ε is

$$dE=\left(\frac{dE}{\partial V}\right)_{T,\varepsilon}dV+\left(\frac{dE}{\partial T}\right)_{V,\varepsilon}dT+\left(\frac{dE}{\partial\varepsilon}\right)_{T,V}d\varepsilon \tag{b}$$

The energy flow from the surroundings is equal to the sum of the changes in heat and the mechanical work (pressure work)

$$dE=\delta q+PdV \tag{c}$$

Combination of Eqs. (b) and (c) yields

$$\delta q=q_v dV+C_v dT-\Delta H_{\mathrm{r}}d\varepsilon$$

With $C_v = \left(\frac{\partial E}{\partial T}\right)_{V,\varepsilon}$, $q_v - P = \left(\frac{\partial E}{\partial V}\right)_{T,\varepsilon}$, $-\Delta H_{\mathrm{r}} = \left(\frac{\partial E}{\partial \varepsilon}\right)_{V,T}$

where C_v is the heat capacity at constant volume and specified value of ε, q_v is the heat effect of pressure work (compression) at constant T, and ΔH_{r} is the heat of reaction.In terms of enthalpy, the energy conservation is

$$dH = \delta q + VdP$$

The total differential of enthalpy in terms of P,T, and ε leads to

$$dH = \left(\frac{dH}{\partial P}\right)_{T,\varepsilon} dP + \left(\frac{dH}{\partial T}\right)_{P,\varepsilon} dT + \left(\frac{dH}{\partial \varepsilon}\right)_{T,P} d\varepsilon$$

$$\delta q = H_i dP + C_p dT - \Delta H_{\mathrm{r}} d\varepsilon$$

with the following definitions: $C_p = \left(\frac{\partial H}{\partial T}\right)_{P,\varepsilon}$, $H_i + V = \left(\frac{\partial H}{\partial P}\right)_{T,\varepsilon}$, $-\Delta H_{\mathrm{r}} = \left(\frac{\partial H}{\partial \varepsilon}\right)_{T,P}$ where C_p is the heat capacity at constant pressure and ε, and H_i is the specific molar enthalpy of species i.

b. *Open subsystems*: Eq. (c) for an open subsystem must account for the exchange of matter with the environment, and is modified as follows

$$dE = \delta q' + PdV \ (\text{for} - dV)$$

Here $\delta q'$ accounts for the heat flow due to heat transfer as well as mass transfer. The enthalpy also is modified as follows

$$dH = \delta q' + VdP \ (\text{for} - dP)$$

Subsystem I and II may both exchange matter and energy, and we have

$$dH^{\mathrm{I}} = \delta^{\mathrm{I}} q' + V^{\mathrm{I}} dP^{\mathrm{I}},\ dH^{\mathrm{II}} = \delta^{\mathrm{II}} q' + V^{\mathrm{II}} dP^{\mathrm{II}}$$

where $\delta^{\mathrm{I}} q'$ is the total flow of energy by phase I for a time interval of dt. By assuming equal pressures $P = P^{\mathrm{I}} = P^{\mathrm{II}}$, we have the following change of the total enthalpy

$$dH = \delta^{\mathrm{I}} q' + \delta^{\mathrm{II}} q' + \left(V^{\mathrm{I}} + V^{\mathrm{II}}\right) dP$$

Comparing this equation with the first law of thermodynamics $dH = \delta q - VdP$ (for a closed system and for $-dP$), we obtain

$$\delta q = \delta^{\mathrm{I}} q' + \delta^{\mathrm{II}} q'$$

where $\delta^{\mathrm{I}} q'$ is the summation of ordinary heat flow from the surroundings $\delta_{\mathrm{e}}^{\mathrm{I}} q$ plus the energy flow $\delta_{\mathrm{i}}^{\mathrm{I}} q'$ from subsystem II

$$\delta^{\mathrm{I}} q' = \delta_{\mathrm{e}}^{\mathrm{I}} q + \delta_{\mathrm{i}}^{\mathrm{I}} q',\ \delta^{\mathrm{II}} q' = \delta_{\mathrm{e}}^{\mathrm{II}} q + \delta_{\mathrm{i}}^{\mathrm{II}} q' \tag{d}$$

The total heat flow from the surroundings is: $\delta q = \delta_{\mathrm{e}}^{\mathrm{I}} q + \delta_{\mathrm{e}}^{\mathrm{II}} q$ Therefore, from Eq. (d), we have

$$\delta_{\mathrm{i}}^{\mathrm{I}} q' + \delta_{\mathrm{i}}^{\mathrm{II}} q' = 0 \tag{e}$$

The equation above suggests that the energy flows exchanged between subsystem I and II are equal with opposite signs.

3.4.7 THE ENTROPY BALANCE EQUATIONS

The entropy balance is

$$\frac{\partial(\rho s)}{\partial t} = -\nabla \cdot (\rho s \mathbf{v}) - \nabla \cdot \mathbf{J}_{\mathrm{s}} + \sigma \tag{3.33}$$

The equation above shows that the rate of change of the entropy per unit volume of substance is due to the convection entropy flow $\rho s\mathbf{v}$, the conduction entropy flow $\mathbf{J}_{\mathrm{s}}$, and the entropy source strength σ.

The conduction entropy flow is

$$\mathbf{J}_s = \frac{\mathbf{J}''_q}{T} + \sum_{i=1}^{n} s_i \mathbf{j}_i \tag{3.34}$$

The conduction entropy flow consists of the heat flow $\mathbf{J}''_{\mathrm{q}}$ and the diffusion flow $\mathbf{j}_i$. The $\mathbf{J}''_{\mathrm{q}}$ is reduced heat flow that is the difference between the change in energy and the change in enthalpy due to matter flow. With the substantial derivative and using Eq. (3.34), we obtain the entropy balance equation based on local thermodynamic equilibrium

$$\rho\frac{Ds}{Dt} = -\nabla\cdot\left(\frac{\mathbf{J}''_{\mathrm{q}}}{T} + \sum_{i=1}^{n} s_i \mathbf{j}_i\right) + \sigma \tag{3.35}$$

3.5 ENTROPY PRODUCTION EQUATION

If the local thermodynamic equilibrium holds, the Gibbs relation in terms of specific properties is

$$Tds = du + Pdv - \sum_{i=1}^{n} \mu_i dw_i \tag{3.36}$$

The equation above can be applied to a fluid element moving with the mass average velocity $\mathbf{v}$. After replacing the differential operators with substantial time derivative operators, we have

$$\rho\frac{Ds}{Dt} = \frac{\rho}{T}\frac{Du}{Dt} + \frac{\rho P}{T}\frac{Dv}{Dt} - \frac{\rho}{T}\sum_{i=1}^{n}\mu_i\frac{Dw_i}{Dt} \tag{3.37}$$

The individual terms on the right side of Eq. (3.37) are substituted by Eq. (3.29)

$$\rho\frac{Du}{Dt} = -\nabla\cdot\mathbf{J}_{\mathbf{u}} - P(\nabla\cdot\mathbf{v}) - \boldsymbol{\tau}:(\nabla\mathbf{v}) + \sum_{i=1}^{n}\mathbf{j}_i\cdot\mathbf{F}_i$$

by Eq. (3.17)

$$\rho P\frac{Dv}{Dt} = P(\nabla\cdot\mathbf{v})$$

and by Eq. (3.19)

$$\rho\sum_{i=1}^{n}\mu_i\frac{D(w_i)}{dt} = -\sum_{i=1}^{n}\mu_i(\nabla\cdot\mathbf{j}_i) - \sum_{j=1}^{l}A_j J_{\mathrm{r}j}$$

where the affinity A of a chemical reaction j is $A_j = -\sum_{i=1}^{n} M_i\mu_i\nu_{ij}$. After the substitutions of the relations above, Eq. (3.37) becomes

$$\rho\frac{Ds}{Dt} = -\frac{\nabla\cdot\mathbf{J_u}}{T} - \frac{1}{T}\boldsymbol{\tau}\colon(\nabla\mathbf{v}) + \frac{1}{T}\sum_{i=1}^{n}\mathbf{j}_i\cdot\mathbf{F}_i + \frac{1}{T}\sum_{i=1}^{n}\mu_i(\nabla\cdot\mathbf{j}_i) + \frac{1}{T}\sum_{j=1}^{l}A_jJ_{\mathrm{r}j} \tag{3.38}$$

Using the following transformations

$$\frac{\nabla\cdot\mathbf{J}_u}{T} = \nabla\cdot\left(\frac{\mathbf{J}_u}{T}\right) + \frac{1}{T^2}\mathbf{J}_u\cdot\nabla T,$$

$$\frac{\mu_i}{T}(\nabla\cdot\mathbf{j}_i) = \nabla\cdot\left(\frac{\mu_i}{T}\mathbf{j}_i\right) - \mathbf{j}_i\cdot\nabla\left(\frac{\mu_i}{T}\right)$$

Eq. (3.38) reduces to

$$\rho\frac{Ds}{Dt} = -\nabla\cdot\left(\frac{\mathbf{J_u} - \sum_{i=1}^{n}\mu_i\mathbf{j}_i}{T}\right) - \frac{1}{T^2}\mathbf{J_u}\cdot\nabla T - \frac{1}{T}\sum_{i=1}^{n}\mathbf{j}_i\cdot\left[T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i\right] - \frac{1}{T}\boldsymbol{\tau}\colon(\nabla\mathbf{v}) + \frac{1}{T}\sum_{j=1}^{l}A_jJ_{\mathrm{r}j} \tag{3.39}$$

Comparison of the balance Eqs. (3.35) and (3.39) allows identifying the entropy flow and the entropy source strength contributions. It yields an expression for the conduction entropy flow

$$\mathbf{J}_{\mathrm{s}} = \frac{\mathbf{J}''_{\mathrm{q}}}{T} + \sum_{i=1}^{n}s_i\mathbf{j}_i = \frac{1}{T}\left(\mathbf{J}_{\mathrm{u}} - \sum_{i=1}^{n}\mu_i\mathbf{j}_i\right) \tag{3.40}$$

Using the relation between the chemical potential and enthalpy $\mu_i = h_i - Ts_i = u_i + Pv_i - Ts_i$ we can relate the second law heat flow $\mathbf{J}''_{\mathrm{q}}$, the conduction energy flow $\mathbf{J}_{\mathrm{u}}$, and the pure heat flow $\mathbf{J}'_{\mathrm{q}}$ as follows

$$\mathbf{J}''_{\mathrm{q}} = \mathbf{J}_{\mathrm{u}} - \sum_{i=1}^{n}h_i\mathbf{j}_i = \mathbf{J}'_{\mathrm{q}} - \sum_{i=1}^{n}Pv_i\mathbf{j}_i \tag{3.41}$$

Heat flow can be defined in various ways if diffusion occurs in multicomponent fluids. The concept of heat flow emerges from a macroscopic treatment of the energy balance or the entropy balance. The internal energy of a substance is related to the molecular kinetic energy and the potential energy of the intermolecular interactions. If a molecule travels without colliding with other molecules, the loss of kinetic energy is due to diffusion. If the kinetic energy loss is the result of molecular collisions, it is classified as heat conduction.

However, changes in the potential energy of intermolecular interactions are not uniquely separable. There is ambiguity in defining the heat flow for open systems. We may split U into a diffusive part and a conductive part in several ways and define various numbers of heat flows. In the molecular mechanism of energy transport, the energy of the system is associated with the kinetic energy of the molecules and with the potential energy of their interactions. The kinetic energy changes in an elemental volume are easily separated. If a molecule leaves the volume, the kinetic energy loss may be due to diffusion. If the kinetic energy loss occurs because a molecule at the surface of the volume transfers energy by collision to a molecule outside the volume, then this loss may be called heat flow. However, the potential energy of molecular interactions is the sum of the potential energies of interactions for each molecular pair. When some molecules leave the volume and other molecules collide at the surface with molecules outside the volume, they produce a complicated change in the potential energy. These changes cannot be uniquely separated into the contributions of pure diffusion and of molecular collisions.

From Eqs. (3.35), (3.39), and (3.40), the entropy source strength or the rate of local entropy production per unit volume σ is defined by

$$\sigma = \mathbf{J_u} \cdot \nabla\left(\frac{1}{T}\right) - \frac{1}{T}\sum_{i=1}^{n} \mathbf{j}_i \cdot \left[T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i\right] - \frac{1}{T}\boldsymbol{\tau} \colon (\nabla\mathbf{v}) + \frac{1}{T}\sum_{j=1}^{l} A_j J_{\mathrm{r}j} \geq 0 \tag{3.42}$$

and is always positive. The equation above shows that σ results from a sum of the products of conjugate flows and forces

$$\sigma = \sum_{k=1}^{n} J_k X_k \geq 0$$

Eq. (3.42) identifies the following independent flows and forces to be used in the phenomenological equations:

- Heat transfer: $X_q = \nabla\left(\frac{1}{T}\right)$
- Mass transfer: $X_i = \frac{\mathbf{F}_i}{T} - \nabla\left(\frac{\mu_i}{T}\right)$ with $\nabla\left(\frac{\mu_i}{T}\right) = \nabla\left(\frac{\mu_i}{T}\right)_T + h_i \nabla\left(\frac{1}{T}\right)$
- Viscous dissipation: $X_v = -\frac{1}{T}(\nabla\mathbf{v})$
- Chemical reaction: $\frac{A_j}{T} = -\sum_{i=1}^{n} \nu_{ij} \frac{M_i \mu_i}{T}$ $(j = 1,2, \ldots,l)$

Eq. (3.42), first derived by Jaumann in 1911, determines the local rate of entropy production by summing four distinctive contributions as a result of the products of flows and forces:

- Entropy production associated with heat transfer: $\sigma_{\mathrm{q}} = \mathbf{J}_{\mathrm{u}} X_{\mathrm{q}}$
- Entropy production due to mass transfer: $\sigma_{\mathrm{m}} = \sum_{i=1}^{n} \mathbf{j}_i X_i$
- Entropy production because of viscous dissipation of fluid: $\sigma_{\mathrm{V}} = \boldsymbol{\tau} : X_v$
- Entropy production arising from chemical reactions: $\sigma_{\mathrm{c}} = \sum_j^l J_{\mathrm{r}j} \frac{A_j}{T}$

Eq. (3.42) consists of three distinct sums of the products that are scalars with rank zero σ_0, vectors with rank one σ_1, and tensors with rank two σ_2

$$\sigma_0 = \boldsymbol{\tau}'' \colon \left(\frac{-(\nabla \cdot \mathbf{v})}{T}\right) + \sum_{j=1}^{l} \frac{A_j}{T} J_{\mathrm{r}j} \geq 0 \tag{3.43}$$

$$\sigma_1 = \mathbf{J}_{\mathrm{u}} \cdot \nabla\left(\frac{1}{T}\right) + \frac{1}{T}\sum_{i=1}^{n} \mathbf{j}_i \cdot \left[\mathbf{F}_i - T\nabla\left(\frac{\mu_i}{T}\right)\right] \geq 0 \tag{3.44}$$

$$\sigma_2 = \boldsymbol{\tau}' : \left(\frac{-(\nabla\mathbf{v})^S}{T}\right) \geq 0 \tag{3.45}$$

where $\boldsymbol{\tau} : (\nabla\mathbf{v}) = \boldsymbol{\tau}' : (\nabla\mathbf{v})^S + \boldsymbol{\tau}'' : (\nabla\cdot\mathbf{v})$. The tensor $\boldsymbol{\tau}''$ is one third of the trace of the viscous stress tensor $\boldsymbol{\tau} = \boldsymbol{\tau}' + \boldsymbol{\delta}\boldsymbol{\tau}''$. Similarly, we split the tensor $(\nabla\mathbf{v}) = (\nabla\mathbf{v})^S + \frac{1}{3}\boldsymbol{\delta}(\nabla\cdot\mathbf{v})$ as the sum of a symmetric part and antisymmetric part. By construction, the trace of the symmetric parts is zero and as usual, the double dot product of antisymmetric and symmetric tensor vanishes. According to Curie–Prigogine's principle, in isotropic medium, only coupling between phenomena of tensorial characters differing by an even number of ranks is possible. The $\boldsymbol{\tau}'' : (-(\nabla\cdot\mathbf{v})/T)$ contribution is related to the rate of change of specific volume and is due to the bulk viscosity.

3.5.1 RATE OF ENTROPY PRODUCTION

The time derivative of entropy production is called the *rate of entropy production*, and can be calculated from the laws of the conservation of mass, energy, and momentum, and the second law of thermodynamics expressed as equality. If the *local entropy production* σ is integrated over the volume, it is called the *volumetric rate of entropy production*

$$P = \frac{d_{\mathrm{i}}S}{dt} = \int_V \sigma dV = \int_V \sum_i J_i X_i dV$$

This integration enables one to determine the total entropy production. When phenomena at the interface between two phases are considered, the amount of entropy produced is taken per unit surface area.

Nonequilibrium thermodynamics estimates the rate of entropy production for a process. This estimation is based on the positive and definite entropy due to irreversible processes and of Gibbs relation

$$TdS = dU + PdV - \sum \mu_i dN_i$$

Entropy depends explicitly only on energy, volume, and concentrations because the Gibbs relation is a fundamental relation and is valid even outside thermostatic equilibrium.

The rate of entropy production can be split into three parts:

$$\sigma = \sigma_o + \sigma_1 + \sigma_2$$

where σ_{o} is the scalar, σ_1 is the vectorial, and σ_2 is the tensorial (rank two) parts as shown in Eqs. (3.43)–(3.45). The choice of thermodynamic forces and flows must ensure that in the equilibrium state when the thermodynamic forces vanish ($X_i = 0$), the entropy production must also be zero. In contrast to entropy, the rate of entropy production is not a state function since it depends on the path taken between the given states.

The loss of energy is directly proportional to the rate of entropy production because of irreversible processes in a system. The loss of energy may be estimated based on the temperature of the surroundings of the system T_o, and we have

$$\dot{E}_{\text{loss}} = mT_o\left(\frac{d_{\text{i}}S}{dt}\right) = (\text{kg})(\text{K})(\text{kJ/kg s K}) = \text{kW} \tag{3.46}$$

As the equation above indicates, the surrounding conditions represent a state where the process reaches equilibrium at which the thermodynamic driving forces vanish. The value of energy $\dot{E}_{\text{loss}}$ is the rate of energy dissipated to the surroundings.

3.5.2 DISSIPATION FUNCTION

From the rate of entropy production and the absolute temperature, we derive the *dissipation function* Ψ, which is also a positive quantity

$$\Psi = T\sigma = T\sum J_k X_k \geq 0$$

The increment of the dissipation function can be split into two contributions

$$d\Psi = d_{\text{X}}\Psi + d_{\text{J}}\Psi$$

where $d_{\text{X}}\Psi = T\sum_k J_k dX_k$ and $d_{\text{J}}\Psi = T\sum_k X_k dJ_k$. When the system is not far away from global equilibrium, and the linear phenomenological equations are valid, we have $d_{\text{X}}\Psi = d_{\text{J}}\Psi = d\Psi/2$, and a stationary state satisfies $d\Psi \leq 0$.

The dissipation function for l chemical reactions in terms of the affinity A and the velocity of the reaction J_{r} is

$$\Psi = T\sum_j^l J_{\text{r}j}(A_j/T) \geq 0$$

The change of entropy as a result of the irreversible phenomena inside a closed adiabatic system is always positive. This principle allows for the entropy to decrease at some place in the systems as long as a larger increase in the entropy at another place compensates the loss. The quantities σ and Ψ are scalars; they are the products of two scalars, the dot product of two vectors, or the double dot products of two tensors of rank two.

3.6 LINEAR NONEQUILIBRIUM THERMODYNAMIC POSTULATES

The linear nonequilibrium thermodynamics approach mainly is based on the following four postulates:

1. The quasiequilibrium postulate states that systems are not far from equilibrium; the gradients, or the thermodynamic forces are not too large. Within the system, local thermodynamic equilibrium holds.
2. All flows in the system are a linear function of all the forces involved; the proportionality constants in these equations are the phenomenological coefficients.

3. The matrix of phenomenological coefficients is symmetric provided that the conjugate flows and forces are identified by the entropy production equation or the dissipation function.
4. The Curie—Prigogine principle states that in an isotropic system, no coupling of flows and forces occurs if the tensorial order of the flows and forces differs by an odd number. However, in an anisotropic medium, such couplings are possible.

The field of linear nonequilibrium thermodynamics provides a new insight into the transport and rate processes, as well as the coupled processes in physical, chemical, electrochemical, and biological systems. Nonequilibrium thermodynamics identifies the conjugated flows and forces from the rate of entropy production or from the dissipation function and establishes the phenomenological equations with these forces and flows. Onsager's reciprocal relations relate the phenomenological coefficients pertaining to interactions or coupling between the processes. When the phenomenological equations relate the conjugate forces and flows linearly, the phenomenological coefficients obey the Onsager reciprocal relations. Therefore, the reciprocal rules reduce the number of unknown coefficients, which are related to the transport and rate coefficients.

There exist many "phenomenological laws"; for example, Fick's law relates to the flow of a substance and its concentration gradient, and the mass action law explores the reaction rate and chemical concentrations or affinities. Ohm's law and Fourier's law are also phenomenological laws. When two or more of these phenomena occur simultaneously in a system, they may couple and induce new effects, such as facilitated and active transport in biological systems. In active transport, a substrate can flow against the direction imposed by its thermodynamic force. Without the coupling, such "uphill" transport would be in violation of the second law of thermodynamics. Therefore, dissipation due to either diffusion or chemical reaction can be negative only if these two processes couple and produce a positive total entropy production.

The phenomenological coefficients are important in defining the coupled phenomena. For example, the coupled processes of heat and mass transport give rise to the Soret effect (which is the mass diffusion due to heat transfer), and the Dufour effect (which is the heat transport due to mass diffusion). We can identify the cross-coefficients of the coupling between the mass diffusion (vectorial process) and chemical reaction (scalar process) in an anisotropic membrane wall. Therefore, the linear nonequilibrium thermodynamics theory provides a unifying approach to describing various processes usually studied under separate disciplines.

The form of the expressions for the rate of entropy production does not uniquely determine the thermodynamic forces or generalized flows. For an open system, for example, we may define the energy flow in various ways. We may also define the diffusion in several alternative ways depending on the choice of reference average velocity. Thus, we may transform the flows and the forces in various ways. If such forces and flows, which are related by the phenomenological coefficients obeying the Onsager relations, are subjected to a linear transformation, then the dissipation function is not affected by that transformation.

An isotropic system cannot support a vector quantity associated with it. Therefore, the vectorial flows can only be related to the vector forces. The scalar reaction rates can be functions of the scalar forces and the trace of the dyadic, but not the vector forces. According to the *Curie—Prigogine principle*, vector and scalar quantities interact only in an anisotropic medium. This principle has important consequences in chemical reactions and transport processes taking place in living cells.

3.7 GRADIENT OF CHEMICAL POTENTIAL AT CONSTANT TEMPERATURE

Chemical potential is a function of T, N_i, and P, and the total differential of chemical potential is

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,P} dN_i + \left(\frac{\partial \mu_i}{\partial T}\right)_{N_i,P} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{N_i,T} dP \tag{3.47}$$

Using the Gibbs energy density G, the second partial term becomes the partial molar entropy of species i

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{N_i,P} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial N_i}\right)_{P,T} = \frac{\partial}{\partial N_i}\left(\frac{\partial G}{\partial T}\right)_{P,T} = -\left(\frac{\partial S}{\partial N_i}\right)_{P,T} = -S_i$$

If we consider a system under mechanical equilibrium, $dP = 0$, Eq. (3.47) then becomes

$$\nabla\mu_i = (\nabla\mu_i)_{P,T} - S_i\nabla T \text{ or } \nabla\mu_i + S_i\nabla T = (\nabla\mu_i)_{P,T} \tag{3.48}$$

3.8 SIMULTANEOUS HEAT AND MASS TRANSFER

Eq. (3.44) represents the entropy production for vectorial processes of heat and mass transfer. In Eq. (3.44), the conduction energy flow can be replaced by the heat flow $\mathbf{J}''_\mathrm{q}$ using Eq. (3.41) and the total potential $\mu*$ comprising the chemical potential and the potential energy per unit mass of component i $\mu_i* = \mu_i + e_\mathrm{pi}$ where $\nabla e_\mathrm{pi} = -\mathbf{F}_i$. Using Eq. (3.48), the isothermal gradient of the total potential is

$$\nabla_T\mu_i^* = \nabla\mu_i + S_i\nabla T + \nabla e_\mathrm{pi}$$

From the thermodynamic force for mass transfer, we have

$$T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i = \nabla\mu_i - \mu_i\frac{\nabla T}{T} + \nabla e_\mathrm{pi} = \nabla_T\mu_i^* - H_i\frac{\nabla T}{T}$$

where $\mu_i = H_i - TS_i$. Using the relation above, we can rearrange Eq. (3.44) as follows

$$\sigma_1 = \mathbf{J}''_\mathrm{q}\cdot\nabla\left(\frac{1}{T}\right) - \frac{1}{T}\sum_{i=1}^{n}\mathbf{j}_i\cdot\nabla_T\mu_i^* \geq 0 \tag{3.49}$$

Since only the $n-1$ diffusion flows are independent, we have

$$\sum_{i=1}^{n}\mathbf{j}_i\cdot\nabla_T\mu_i^* = \sum_{i=1}^{n-1}\mathbf{j}_i\cdot\nabla_T\left(\mu_i^* - \mu_n^*\right)$$

Introducing this equation into Eq. (3.49), we have

$$\sigma_1 = \mathbf{J}''_\mathrm{q}\cdot\nabla\left(\frac{1}{T}\right) - \frac{1}{T}\sum_{i=1}^{n-1}\mathbf{j}_i\cdot\nabla_T\left(\mu_i^* - \mu_n^*\right) \geq 0$$

Therefore, the thermodynamic driving force of mass flow becomes

$$X_i = \frac{1}{T}\nabla_T\left(\mu_i^* - \mu_n^*\right)$$

We relate the dissipation function to the rate of local entropy production using Eqs. (3.42)−(3.45)

$$\Psi = T\sigma = T(\sigma_0 + \sigma_1 + \sigma_2) = \Psi_0 + \Psi_1 + \Psi_2$$

If the dissipation function identifies the independent forces and flows, and using $T\nabla(1/T) = -\nabla(\ln T)$ then we have

$$\Psi_0 = -\boldsymbol{\tau}'' : (\nabla \cdot \mathbf{v}) + \sum_{j=1}^{l} A_j J_{\mathrm{r}j} \geq 0$$

$$\Psi_1 = -\mathbf{J}_{\mathrm{q}}'' \cdot \nabla \ln T - \sum_{i=1}^{n-1} \mathbf{j}_i \cdot \nabla_T \left(\mu_i^* - \mu_n^*\right) \geq 0 \tag{3.50}$$

$$\Psi_2 = -\boldsymbol{\tau}' : (\nabla \mathbf{v})^S \geq 0$$

Using the following transformation of the thermodynamic force for mass transfer

$$T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i = \nabla\mu_i - \frac{\mu_i}{T}\nabla T + \nabla e_{\mathrm{p}i} = \nabla\mu_i^* - \frac{\mu_i}{T}\nabla T$$

and

$$(\nabla\mu_i)_{P,T} = \nabla\mu_i + S_i \nabla T \text{ and } \mathbf{J}_{\mathrm{s}} = \frac{\mathbf{J}_{\mathrm{q}}''}{T} + \sum_{i=1}^{n} S_i \mathbf{j}_i$$

Therefore, Eq. (3.50) becomes

$$\Psi_1 = -\mathbf{J}_{\mathrm{s}} \cdot \nabla T - \sum_{i=1}^{n-1} \mathbf{j}_i \cdot \nabla\left(\mu_i^* - \mu_n^*\right) \geq 0$$

As shown by Prigogine, for diffusion in mechanical equilibrium, any other average velocity may replace the center-of-mass velocity, and the dissipation function does not change. When diffusion flows are considered relative to various velocities, the thermodynamic forces remain the same and only the values of the phenomenological coefficients change.

The formulation of linear nonequilibrium thermodynamics is based on the combination of the first and second laws of thermodynamics with the balance equations including the entropy balance. These equations allow additional effects and processes to be considered. The linear nonequilibrium thermodynamics approach is widely recognized as a useful phenomenological theory that describes the transport and rate processes without the need for the detailed coupling mechanisms of the coupled and complex processes.

3.9 PHENOMENOLOGICAL EQUATIONS

When systems are near global equilibrium, linear relations exist between flows J_i and thermodynamic driving forces X_k

$$J_i = L_{ik} X_k \tag{3.51}$$

where the parameters L_{ik} are called the *phenomenological coefficients*. For example, Fourier's law relates heat flow to the temperature gradient, while Fick's law provides a relation between mass diffusion and concentration gradient. The temperature and concentration gradients are the thermodynamic forces. The Fourier and Fick laws consider a single force and a single flow and are not capable of describing coupled heat and mass flows. Choice of a force X_i conjugate to a flow J_i requires that the product J_iX_i has the dimension of entropy production. The validity of Eq. (3.51) should be determined experimentally for a certain type of process; for example, linear relations hold for an electrical conductor that obeys Ohm's law. Fluctuations occurring in turbulent flow deviate relatively little from the local equilibrium state.

If a nonequilibrium system consists of several flows caused by various forces, Eq. (3.51) may be generalized in the linear region of the thermodynamic branch (Fig. 2.2 in Chap. 2), and we obtain

$$J_i = \sum_k L_{ik} X_k \tag{3.52}$$

These equations are called the *phenomenological equations*, which are capable of describing multiflow systems and the induced effects of the nonconjugate forces on a flow. Generally, any force X_i can produce any flow J_i when the cross-coefficients are nonzero. Eq. (3.52) assumes that the induced flows are also a linear function of nonconjugated forces. For example, ionic diffusion in an aqueous solution may be related to concentration, temperature, and the imposed electromotive force.

By introducing the linear phenomenological equations into the entropy production, $\sigma = \sum JX$, we have

$$\sigma = \sum_{i,k=1}^{n} L_{ik} X_i X_k \geq 0 \tag{3.53}$$

This equation shows that the entropy production is a quadratic form in all the forces. In continuous systems, the base of reference for diffusion flow affects the values of transport coefficients and the entropy due to diffusion. Prigogine proved the invariance of entropy for an arbitrary base of reference if the system is in mechanical equilibrium ($dv/dt = 0$) and the divergence of viscous tensors vanishes.

Eq. (3.53) leads to a quadratic form

$$\sigma = \left(\sum_{i=1}^{n} L_{ii} X_i^2 + \sum_{i,k=1}^{n} \frac{L_{ik} + L_{ki}}{2} X_i X_k \right) \geq 0 \ (\mathrm{i} \neq \mathrm{k}) \tag{3.54}$$

In matrix form, the equation above becomes,......

$$\sigma = \sum_{i,k=1}^{n} L_{ik} X_i X_k = [X_1 \ X_2 \ldots X_n] \begin{bmatrix} L_{11} L_{12} \ldots. L_{1n} \\ L_{21} L_{22} \ldots L_{2n} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ L_{n1} L_{n2} \ldots. L_{nn} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ \ldots. \\ X_n \end{bmatrix} \geq 0 \tag{3.55}$$

A necessary and sufficient condition for $\sigma \geq 0$ is that all its principal minors be nonnegative

$$\begin{vmatrix} L_{ii} & L_{ik} \\ L_{ki} & L_{kk} \end{vmatrix} = L_{ii} L_{kk} - L_{ik} L_{ki} \geq 0$$

If only a single force occurs, Eq. (3.55) becomes

$$\sigma = L_{ii} X_i^2 \geq 0$$

and then the phenomenological coefficients cannot be negative $L_{ii} \geq 0$. For a system at metastable equilibrium, we may have $\mathbf{J}_i = 0$, $\sigma = 0$ and $X_k \neq 0$. Otherwise, all forces and flows are independent, and the inequality sign holds in Eq. (3.55).

3.9.1 FLOWS

Mass flow, heat flow, and chemical reaction rate are some examples of the "flows" J_i. The flows may have vectorial or scalar characters. *Vectorial flows* are directed in space, such as mass, heat, and electric current. *Scalar flows* have no direction in space, such as those of chemical reactions. The other more complex flow is the viscous flow characterized by tensor properties. At equilibrium state, the thermodynamic forces become zero and hence the flows vanish

$$J_{i,\mathrm{eq}}(X_i = 0) = 0$$

As an example, the diffusion flow vector $\mathbf{J}_i$ for component i is the number of moles per unit area a per unit time t in a specified direction, and defined by

$$\mathbf{J}_i = \frac{1}{a}\frac{d\mathbf{N}_i}{dt}$$

Considering a small area da at any point x, y, z perpendicular to average velocity $\mathbf{v}_i$, in which $\mathbf{v}_i$ is constant, the volume occupied by the particles passing da in unit time will be $\mathbf{v}_i da$. If the concentration per unit volume is c_i then the total amount of the substance is: $\mathbf{N}_i = c_i \mathbf{v}_i da$. The local flow, which the amount of substance passing in a unit area per unit time, is $\mathbf{J}_i = c_i \mathbf{v}_i$. Generally, these three quantities $\mathbf{J}_i$, c_i and $\mathbf{v}_i$ are the functions of the time and space coordinates. If the area da is not perpendicular to the flow vector, we consider a unit vector $\mathbf{i}$, perpendicular to da, whose direction will specify the direction of the area

$$d\mathbf{a} = \mathbf{i}\, da$$

The scalar product $\mathbf{v}_i \cdot d\mathbf{a}$ gives the volume dV, which is multiplied by the local concentration c_i to find differential flow $\mathbf{J}_i \cdot d\mathbf{a}$ which is the amount of the substance passing an area at any angle with the velocity vector $\mathbf{v}_i$. For a volume enclosed by a surface area a, the total amount of species i leaving that volume is $\int_{\mathbf{a}} \mathbf{J}_i \cdot d\mathbf{a}$. The divergence of the flow $\mathbf{J}_i$ is

$$\nabla \cdot \mathbf{J}_i = \frac{\partial J_{i,x}}{\partial x} + \frac{\partial J_{i,y}}{\partial y} + \frac{\partial J_{i,z}}{\partial z}$$

Here $J_{i,x}$, $J_{i,y}$, and $J_{i,z}$ are the Cartesian coordinates of the vector $\mathbf{J}_i$. As the volume V and the product $\mathbf{J}_i \cdot d\mathbf{a}$ are scalars, the divergence is also a scalar quantity. A positive divergence means a source of component i, while a negative divergence indicates a sink, and at points of $\nabla \cdot \mathbf{J}_i = 0$, there is no accumulation and no removal of material. Transformation of the surface integral of a flow into a volume integral of a divergence using the Gauss–Ostrogradsky theorem is

$$\int_V \nabla \cdot \mathbf{J}_i dV = \int_a \mathbf{J}_i da$$

The divergence of the mass flow vector $\rho\mathbf{v}$ is used in the continuity equation

$$\frac{\partial\rho}{\partial t} = -(\nabla\cdot\rho\mathbf{v})$$

Similarly, the local equivalent of the law of conservation of mass for an individual component i is

$$\frac{\partial c_i}{\partial t} = -(\nabla\cdot\mathbf{J}_i)$$

The equation above cannot describe a flow process for a reacting component.

Another conserved property is the total energy, and in terms of local energy density e for each point in the system, we have

$$\frac{\partial e}{\partial t} = -(\nabla\cdot\mathbf{J}_\mathrm{e})$$

where $\mathbf{J}_e$ is the energy flow. The total entropy of a system is related to the local entropy density s_v

$$S = \int_V s_v dV \tag{3.56}$$

The total entropy changes with time as follows

$$\frac{dS}{dt} = \int_V \frac{\partial s_v}{\partial t} dV \tag{3.57}$$

The entropy flow $\mathbf{j}_s$, on the other hand, is the result of the exchange of entropy with the surroundings

$$\frac{d_\mathrm{e}S}{dt} = -\int_\mathbf{a} \mathbf{j}_s\cdot d\mathbf{a} = -\int_V (\nabla\cdot\mathbf{j}_\mathrm{s})\, dV \tag{3.58}$$

An irreversible process causes the entropy production σ in any local element of a system, and the rate of total entropy production is

$$\frac{d_iS}{dt} = \int_V \sigma dV \tag{3.59}$$

Therefore, the total change in entropy $\frac{dS}{dt} = \frac{d_\mathrm{e}S}{dt} + \frac{d_\mathrm{i}S}{dt}$ becomes

$$\int_V \frac{\partial s_v}{\partial t} dV = -\int_V (\nabla\cdot\mathbf{j}_\mathrm{s})dV + \int_V \sigma dV \tag{3.60}$$

Therefore, for any local change, an irreversible process in a continuous system is described as

$$\frac{\partial s_v}{\partial t} = -\nabla\cdot\mathbf{j}_S + \sigma \tag{3.61}$$

The equation above is the expression for a nonconservative change in local entropy density and allows the determination of the entropy production from the total change in entropy and the evaluation of the dependence of σ on flows and forces.

Stationary state flow processes resemble equilibria in their invariance with time; partial time differentials of density, concentration, or temperature will vanish, although flows continue to occur in the system, and entropy is being produced. If the property is conserved, the divergence of the corresponding flow must vanish, and hence the steady flow of a conserved quantity is constant and source-free. At equilibrium, all the steady state flows become zero.

At stationary state, the local entropy density must remain constant because of the condition $\partial s_\mathrm{v}/\partial t = 0$. However, the divergence of entropy flow does not vanish, and we obtain

$$\sigma = \nabla \cdot \mathbf{j}_\mathrm{s}$$

The equation above indicates that in a stationary state, the entropy produced at any point of a system must be removed by a flow of entropy at that point. In the state of equilibrium, all the flows including the flow of entropy production vanish, and we obtain the necessary condition for equilibrium as

$$\sigma = 0$$

3.9.2 THERMODYNAMIC FORCES

The thermodynamic "forces" X_i of the chemical potential gradient, temperature gradients, and the chemical affinity cause the flows. The affinity A is

$$A_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i, (\mathrm{j} \; = \; 1, 2, \ldots, l)$$

where ν_{ij} is the stoichiometric coefficient of the ith component in the jth reaction, n is the number of components in the reaction, and l is the number of reactions. For thermodynamic vectorial forces, such as a difference in chemical potential of component i, μ_i, proper spatial characteristics must be assigned for the description of local processes. For this purpose, we consider all points of equal μ_i as the potential surface. For the two neighboring equipotential surfaces with chemical potentials μ_i and $\mu_i + d\mu_i$, the change in μ_i with number of moles N is $\partial\mu_i/\partial N$, which is the measure of the local density of equipotential surfaces. At any point on the potential surface, we construct a perpendicular unit vector with the direction corresponding to the direction of maximal change in μ_i. With the unit vectors in the direction x, y, and z denoted by $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$, respectively, the gradient of the field in Cartesian coordinates is

$$\nabla\mu_i = \mathbf{i}\frac{\partial\mu_i}{\partial x} + \mathbf{j}\frac{\partial\mu_i}{\partial y} + \mathbf{k}\frac{\partial\mu_i}{\partial z}$$

A thermodynamic driving force occurs when a difference in potential exists, and its direction is the maximal decrease in μ_i. Consequently, at the point x, y, z, the local force $\mathbf{X}$ causing the flow of component i is expressed by

$$\mathbf{X}_i = -\nabla\mu_i$$

and for a single dimensional flow, it becomes

$$\mathbf{X}_i = -\mathbf{i}\frac{\partial\mu_i}{\partial x}$$

From the definition of the chemical potential, we have

$$-\frac{\partial \mu_i}{\partial \mathrm{x}} = \frac{\partial}{\partial x}\left(\frac{-\partial G}{\partial N_i}\right) = \frac{\partial}{\partial N_i}\left(\frac{-\partial G}{\partial x}\right) \tag{3.62}$$

where $-dG$ shows the free energy available to perform useful work, δW, and the differential of work with distance, $\delta W/dx$, is a force. Therefore, $\mathbf{X}_i$ is a force per mole of component i, causing a flow in the direction of the unit vector. The overall thermodynamic force that is the difference in chemical potential for the transport of the substance between regions 1 and 2 in discontinuous systems is the integral of Eq. (3.62)

$$\int_1^2 \mathbf{X}_i dx = -\mathbf{i}\int_1^2 \frac{\partial \mu_i}{\partial x} dx = \mathbf{i}\left(\mu_{i,1} - \mu_{i,2}\right) \cong -\Delta\mu_i$$

Here, $\Delta\mu_i$ is a difference in potential, while $\mathbf{X}_i$ is a conventional force used in classical mechanics. Electric potential ψ that causes a current at the point x, y, z lead to the definition of electric force $\mathbf{X}_e$

$$\mathbf{X}_e = -\nabla\psi$$

where $\mathbf{X}_e$ is the force per unit charge, or the local intensity of the electric field.

When we consider the difference in electric potential between two points instead of local electric forces, the quantity of electromotive force $\Delta\psi$ is defined in a single direction by

$$\Delta\psi = -\mathbf{i}\int_1^2 \frac{d\psi}{dx} dx = \mathbf{i}(\psi_1 - \psi_2)$$

Other types of forces of irreversible processes may be derived similarly.

In general, the flows and forces are complicated nonlinear functions of one another. However, we can expand the nonlinear dependence of the flows J_i and the forces X_i in a Taylor series about the equilibrium

$$-J_i = J_{i,\mathrm{eq}}(X_j = 0) + \sum_{j=1}^{n}\left(\frac{\partial J_i}{\partial X_j}\right)_{\mathrm{eq}} X_j + \frac{1}{2!}\sum_{j=1}^{n}\left(\frac{\partial^2 J_i}{\partial X_j^2}\right)_{\mathrm{eq}} X_j^2 + \ldots$$

$$-X_i = X_{i,\mathrm{eq}}(J_k = 0) + \sum_{k=1}^{n}\left(\frac{\partial X_i}{\partial J_k}\right)_{\mathrm{eq}} J_k + \frac{1}{2!}\sum_{k=1}^{n}\left(\frac{\partial^2 X_i}{\partial J_k^2}\right)_{\mathrm{eq}} J_k^2 + \ldots$$

If we disregard the higher order terms, these expansions become linear relations, and we have the general type of *linear phenomenological equations* for irreversible phenomena

$$J_i = \sum_{k=1}^{n} L_{ik} X_k$$

$$X_i = \sum_{k=1}^{n} K_{ik} J_k \ (\mathrm{i,k} = 1, 2, \ldots, \mathrm{n})$$

These equations show that any flow is caused by all the forces and any force is the result of all the flows present in the system. The coefficients L_{ik} and K_{ik} are called the *phenomenological coefficients*. The coefficients L_{ik} are the *conductance coefficients* and K_{ik} the *resistance coefficients*. The straight coefficients with the same indices relate the conjugated forces and flows. The cross-coefficients with $i \neq k$ represent the coupling phenomena.

3.10 ONSAGER'S RELATIONS

Onsager's reciprocal relations state that, provided a proper choice is made for the flows and forces, the matrix of phenomenological coefficients is symmetrical. These relations are proved to be an implication of the property of "microscopic reversibility," which is the symmetry of all mechanical equations of motion of individual particles with respect to time t. The Onsager reciprocal relations are the results of the global gauge symmetries of the Lagrangian, which is related to the entropy of the system considered. This means that the results in general are valid for an arbitrary process.

The cross-phenomenological conductance and resistance coefficients are defined as

$$L_{ik} = \left(\frac{\partial J_i}{\partial X_k}\right)_{X_j} = \left(\frac{J_i}{X_k}\right)_{X_j=0} \quad (i \neq k)$$

$$K_{ik} = \left(\frac{\partial X_i}{\partial J_k}\right)_{J_i} = \left(\frac{X_i}{J_k}\right)_{J_i=0} \quad (i \neq k)$$

The phenomenological coefficients are not a function of the thermodynamic forces and flows; on the other hand, they can be functions of the parameters of the local state as well as the nature of a substance. The values of L_{ik} and K_{ik} must satisfy the following conditions

$$L_{ii} > 0 \quad (i = 1, 2, \ldots, n)$$

$$L_{ii} L_{kk} > \frac{1}{4}(L_{ik} + L_{ki})^2 \quad (i \neq k;\ i, k = 1, 2, \ldots, n)$$

or

$$K_{ii} > 0 \quad (i = 1, 2, \ldots, n)$$

$$K_{ii} K_{kk} > \frac{1}{4}(K_{ik} + K_{ki})^2 \quad (i \neq k;\ i, k = 1, 2, \ldots, n)$$

The matrix of phenomenological coefficients L_{ki} and K_{ki} are related by $\mathbf{K} = \mathbf{L}^{-1}$ where $\mathbf{L}^{-1}$ is the inverse of the matrix **L**. In a general matrix form in terms of the conductance L_{ij} and resistance K_{ij} coefficients becomes

$$\sigma = \mathbf{X}^{\mathrm{T}} \mathbf{L} \mathbf{X} = \mathbf{J}^{\mathrm{T}} \mathbf{K} \mathbf{J}$$

The equation above suggests that the local rate of entropy production is a quadratic form in all forces and in all flows.

3.11 TRANSFORMATION OF FORCES AND FLOWS

The Onsager reciprocal relations remain valid when homogeneous relationships relate the flows to each other. This enables to select the most suited description of flows and independent forces, if they enable to write the rate of entropy production or the dissipation function as a sum of the products of conjugate flows and forces.

3.11.1 TWO-FLOW SYSTEMS

For a two-flow system, we have the phenomenological equations in terms of the flows

$$J_1 = L_{11}X_1 + L_{12}X_2$$

$$J_2 = L_{21}X_1 + L_{22}X_2$$

From these relations, we can derive the independent forces

$$X_1 = \frac{L_{22}}{|L|}J_1 - \frac{L_{12}}{|L|}J_2$$

$$X_2 = -\frac{L_{21}}{|L|}J_1 + \frac{L_{11}}{|L|}J_2$$

We can also write the phenomenological equations in terms of the forces

$$X_1 = K_{11}J_1 + K_{12}J_2$$

$$X_2 = K_{21}J_1 + K_{22}J_2$$

The following relations link the phenomenological coefficients of L_{ik} to K_{ik}

$$K_{11} = \frac{L_{22}}{|\mathbf{L}|};\ K_{12} = -\frac{L_{12}}{|\mathbf{L}|};\ K_{21} = -\frac{L_{21}}{|\mathbf{L}|};\ \mathrm{K}_{22} = \frac{L_{11}}{|\mathbf{L}|} \tag{3.63}$$

where $|\mathbf{L}|$ is the determinant of the matrix: $|\mathbf{L}| = L_{11}L_{22} - (L_{12})^2$ with Onsager's relations.

EXAMPLE 3.2 RELATIONSHIPS BETWEEN THE CONDUCTANCE AND RESISTANCE PHENOMENOLOGICAL COEFFICIENTS

For a three-flow system, derive the relationships between the conductance and resistance phenomenological coefficients.

Solution:
Consider the linear phenomenological equations relating forces to flows with resistance coefficients.

$$X_1 = K_{11}J_1 + K_{12}J_2 + K_{13}J_3$$

$$X_2 = K_{21}J_1 + K_{22}J_2 + K_{23}J_3$$

$$X_3 = K_{31}J_1 + K_{32}J_2 + K_{33}J_3$$

After applying the Onsager relations to the linear matrix solutions, we have

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3$$

$$-J_1 = \frac{\left(K_{23}^2 - K_{22}K_{33}\right)}{D}X_1 + \frac{\left(K_{12}K_{33} - K_{23}K_{13}\right)}{D}X_2 + \frac{\left(K_{13}K_{22} - K_{23}K_{12}\right)}{D}X_3$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3$$

$$-J_2 = \frac{(K_{12}K_{33} - K_{13}K_{23})}{D}X_1 + \frac{(K_{13}^2 - K_{11}K_{33})}{D}X_2 + \frac{(K_{11}K_{23} - K_{12}K_{13})}{D}X_3$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3$$

$$-J_3 = \frac{(K_{13}K_{22} - K_{12}K_{23})}{D}X_1 + \frac{(K_{11}K_{23} - K_{12}K_{13})}{D}X_2 + \frac{(K_{12}^2 - K_{11}K_{22})}{D}X_3$$

Where

$$D = -K_{13}^2K_{22} + 2K_{12}K_{13}K_{23} - K_{12}^2K_{33} - K_{11}K_{23}^2 + K_{11}K_{22}K_{33}$$

EXAMPLE 3.3 TRANSFORMATION OF PHENOMENOLOGICAL EQUATIONS: DEPENDENT FLOWS

Transform the thermodynamic forces and flows when the forces are independent, while the flows are linearly dependent in a two-flow system, $0 = yJ_1 + J_2$.

Solution:
The local entropy production is: $\sigma = J_1X_1 + J_2X_2$
Using the linear relation between the flows, $0 = yJ_1 + J_2$, the local entropy production becomes

$$\sigma = J_1X_1 - yJ_1X_2 = J_1(X_1 - yX_2) \tag{a}$$

The linear phenomenological equations are

$$J_1 = L_{11}X_1 + L_{12}X_2 \tag{b}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{c}$$

However, from Eq. (a), which is a novel linear relation, the modified phenomenological equation for J_1 is

$$J_1 = L'_{11}X'_1 \tag{d}$$

where $X'_1 = X_1 - yX_2$
Then, the second flow is: $J_2 = -yJ_1 = -yL'_{11}(X_1 - yX_2)$

Using the linear relation between the flows in Eq. (b), we have

$$-yJ_1 = -yL_{11}X_1 - yL_{12}X_2 \tag{e}$$

Subtracting Eq. (c) from Eq. (e) gives zero and we get two conditions

$$yL_{11} + L_{21} = 0 \rightarrow L_{21} = -yL_{11} \tag{f}$$

$$yL_{12} + L_{22} = 0 \rightarrow L_{12} = -L_{22}/y \tag{g}$$

Substituting Eq. (g) into Eq. (b), we find: $J_1 = L_{11}X_1 - \frac{L_{22}}{y}X_2$
Comparing the equation above with Eq. (d) and Eq. (b), we have $L'_{11} = \frac{L_{22}}{y^2}$
From Eq. (f) and (g), we have

$$L_{12} = -\frac{L_{22}}{y} = -\frac{y^2L'_{11}}{y} = -yL'_{11} = L_{21}$$

The equation above shows that Onsager's reciprocal relations are satisfied in the phenomenological equations (Wisniewski et al., 1976).

EXAMPLE 3.4 TRANSFORMATION OF PHENOMENOLOGICAL EQUATIONS: DEPENDENT FORCES

Transform the thermodynamic forces and flows when the flows are independent, while the thermodynamic forces are linearly dependent in a two-flow system, $0 = yX_1 + X_2$.

Solution:

The local entropy production is: $\sigma = J_1X_1 + J_2X_2$
Using the linear relation between the thermodynamic forces, $0 = yX_1 + X_2$, the local entropy production becomes

$$\sigma = J_1X_1 - yJ_2X_1 = X_1(J_1 - yJ_2) \tag{a}$$

The linear phenomenological equations in terms of the resistance coefficients are

$$X_1 = K_{11}J_1 + K_{12}J_2 \tag{b}$$

$$X_2 = K_{21}J_1 + K_{22}J_2 \tag{c}$$

However, from Eq. (a), the modified phenomenological equation for the force X_1 is

$$X_1 = K'J' = K'(J_1 - yJ_2) \tag{d}$$

Then, the second thermodynamic force is

$$X_2 = -yK'(J_1 - yJ_2) \tag{e}$$

Using the linear relation between the forces in Eqs. (b) and (c), we have

$$yX_1 = yK_{11}J_1 + yK_{12}J_2 \tag{f}$$

$$-yX_1 = K_{21}J_1 + K_{22}J_2 \tag{g}$$

Adding Eq. (g) from Eq. (f), we get

$$yK_{11} + K_{21} = 0 \rightarrow -\frac{K_{21}}{y} = K_{11} \tag{h}$$

$$yK_{12} + K_{22} = 0 \rightarrow K_{12} = -\frac{K_{22}}{y} \tag{i}$$

Substituting Eq. (i) in Eq. (b), we find

$$X_1 = K_{11}J_1 - \frac{K_{22}}{y}J_2 \tag{k}$$

Comparing Eq. (k) with Eq. (d), we have

$$X_1 = K'J_1 - yK'J_2 = K_{11}J_1 - \frac{K_{22}}{y}J_2$$

$$K_{11} = \frac{K_{22}}{y^2} \text{ and } K_{12} = K_{21}$$

These results show that Onsager's relations are satisfied in Eqs. (b) and (c) since the dependency of the forces to the flows are linear (Wisniewski et al., 1976).

EXAMPLE 3.5 TRANSFORMATION OF PHENOMENOLOGICAL EQUATIONS: DEPENDENT FLOWS AND FORCES

Transform the phenomenological equations when the flows and forces are linearly dependent:

$$0 = zJ_1 + J_2 \text{ and } 0 = yX_1 + X_2$$

Solution:

The local entropy production is: $\sigma = J_1X_1 + J_2X_2 = J_1X_1 + (-zJ_1)(-yX_1) = J_1X_1(1 + zy)$

The linear phenomenological equations are

$$J_1 = L_{11}X_1 + L_{12}X_2 = L'X' \tag{a}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{b}$$

where X' is defined by

$$X' = (1+zy)X_1 = (1+zy)\left(-\frac{X_2}{y}\right) = -\left(\frac{1}{y}+z\right)X_2 \tag{c}$$

The phenomenological coefficient is

$$L' = L'_{11} \tag{d}$$

Using the linear flows and forces in Eqs. (a)–(c), we have

$$J_1 = L'(1+zy)X_1 \tag{e}$$

$$J_2 = -zL'(1+zy)X_1 \tag{f}$$

From Eqs. (a) and (b), we obtain

$$J_1 = (L_{11} - yL_{12})X_1 \tag{g}$$

$$J_2 = (L_{21} - yL_{22})X_1 \tag{h}$$

Comparing Eqs. (e) and (f) with Eqs. (g) and (h), we find

$$(L_{11} - yL_{12})X_1 = L'(1+zy)X_1 \rightarrow (1+zy)L' = L_{11} - yL_{12} \tag{i}$$

$$(L_{21} - yL_{22})X_1 = -L'z(1+zy)X_1 \rightarrow -(1+zy)L'z = L_{21} - yL_{22} \tag{k}$$

In a two-flow system, there are 2° of freedom in choosing the phenomenological coefficients. With the linear relations of flows and forces, there is 1° of freedom that is $L_{12} = L_{21,}$ and L_{22} is proportional to L'

$$\mathrm{L}_{22} = wL'$$

With the equation above, the relations in Eqs. (i) and (k) become

$$\begin{aligned}
L_{21} - yL_{22} &= -L'z(1+zy)\\
L_{21} - y(wL') &= -L'z(1+zy)\\
L_{21} &= -L'\left(z+z^2y\right) + ywL'\\
L_{12} = L_{21} &= -L'\left(z+z^2y-yw\right)
\end{aligned}$$

and

$$\begin{aligned}
L_{11} - yL_{12} &= L'(1+zy)\\
L_{11} &= L'(1+zy) - yL'\left(z+z^2y-yw\right)\\
L_{11} &= L'\left(1-z^2y^2+y^2w\right)
\end{aligned}$$

Since the local entropy production is positive if $L_{ii} > 0$, $L' = L'_{11} > 0$, and $L_{11}L_{22} - L_{12}^2 > 0$, the conditions $L' = L'_{11} > 0$ and $L_{ii} > 0$ restrict w to positive values, and we have

$$1 - z^2y^2 + y^2w > 0 \rightarrow y^2w > z^2y^2 - 1$$

$$w > \frac{z^2y^2}{y^2} - \frac{1}{y^2} \rightarrow w > z^2 - \frac{1}{y^2}$$

The inequality above leads to $w > z^2 > 0$.

3.12 CHEMICAL REACTIONS

For an elementary step reaction, we may relate the flow J_r and the affinity A to the forward J_{rf} and backward J_{rb} reaction rates as follows

$$J_r = J_{rf} - J_{rb}$$

$$A = RT \ln \frac{J_{\mathrm{rf}}}{J_{\mathrm{rb}}}$$

If we solve the equations above together, we obtain the reaction (velocity) flow

$$J_{\mathrm{r}} = J_{\mathrm{rf}}\left(1 - e^{-A/RT}\right) \tag{3.64}$$

Close to the thermodynamic equilibrium, where $A/RT << 1$, we can expand Eq. (3.64) as

$$J_{\mathrm{r}} = J_{\mathrm{rf,eq}} \frac{A}{RT} \tag{3.65}$$

On the other hand, we have the following linear phenomenological equation for chemical reaction i

$$J_{\mathrm{r}i} = \sum_{j=1}^{l} L_{ij} \frac{A_j}{T}$$

We can compare these linear phenomenological equations with Eq. (3.65) to obtain the phenomenological coefficients

$$L_{ij} = \frac{J_{\mathrm{rf,eq},ij}}{R}$$

At equilibrium, we have $J_{\mathrm{rf,eq}} = J_{\mathrm{rb,eq}}$.

For an overall reaction with l number of intermediate reactions, the linear phenomenological law is valid, if every elementary reaction satisfies the condition $A/RT << 1$, and the intermediate reactions are fast and hence a steady state is reached.

For a closed system, if the change of mole numbers dN_k is due to irreversible chemical reactions, the entropy production is

$$d_{\mathrm{i}}S = -\frac{1}{T}\sum \mu_k dN_k \geq 0$$

The rate of entropy production P is

$$P = \frac{d_{\mathrm{i}}S}{dt} = -\frac{1}{T}\sum \mu_k \frac{dN_k}{dt} \geq 0$$

where μ_k is the chemical potential that can be related to measurable quantities, such as P, T, and N_o. In terms of the affinity A, equation above becomes

$$\frac{d_{\mathrm{i}}S}{dt} = \sum \left(\frac{\tilde{A}_k}{T}\right) \frac{d\varepsilon_k}{dt} \geq 0$$

For a reaction B → 2D, the affinity is $A = \mu_B - 2\mu_D$, ε is the extent of the reaction and $d\varepsilon/dt$ is the velocity of the reaction. At thermodynamic equilibrium, the affinity $\tilde{A}$ and the velocity of the reaction vanish.

The rate of entropy production due to electrochemical reactions is

$$\frac{d_{\mathrm{i}}S}{dt} = \frac{\tilde{A}}{T} \frac{d\varepsilon}{dt} \geq 0$$

where $\tilde{A}$ is the electrochemical affinity defined by

$$\tilde{A}_i = A_i + z_i F(\psi_1 - \psi_2) = \tilde{\mu}_1 - \tilde{\mu}_2$$

Here z_i is the electrovalence of ionic species i, F is the Faraday number, which is the electrical charge associated with 1 g-ion of a species with an electrovalence of 1, and ψ_1 is the electrical potential at position 1. The term $\tilde{\mu}_i$ is the electrochemical potential of species i, and defined by

$$\tilde{\mu}_i = \mu_i + z_i F\psi$$

The level of electrical current is related to the extent of the electrochemical reaction by

$$I = z_i F \frac{d\varepsilon}{dt} = z_i F J_\mathrm{r}$$

3.13 HEAT CONDUCTION

The entropy production for a heat conduction process is

$$\sigma = \mathbf{J}_\mathrm{q} \cdot \nabla\left(\frac{1}{T}\right) = -\mathbf{J}_\mathrm{q} \cdot \frac{\nabla T}{T^2} \tag{3.66}$$

where $\mathbf{J}_\mathrm{q}$ is the heat flow (or generalized flow) and $\nabla(1/T)$ is the thermodynamic force X_q. Eq. (3.66) identifies the forces and flows. The phenomenological equation and the Fourier equation for the heat conduction is

$$\mathbf{J}_\mathrm{q} = L_\mathrm{qq}\mathbf{X}_\mathrm{q} = -k\nabla T$$

Therefore, we have

$$-\mathbf{J}_\mathrm{q} = \frac{L_\mathrm{qq}}{T^2}\nabla T = k\nabla T$$

and

$$L_\mathrm{qq} = kT^2$$

If the dissipation function $\Psi = T\sigma$ is used to identify the thermodynamic forces, then the phenomenological coefficient is

$$L'_\mathrm{qq} = kT$$

EXAMPLE 3.6 ENTROPY PRODUCTION IN HEAT CONDUCTION

Consider one-dimensional heat conduction in an isotropic solid rod. The surface of the rod is insulated and the cross-sectional area is constant (Fig. 3.1). Describe the entropy production and the dissipation function for the heat conduction in an isotropic rod.

Solution:

The entropy change of the rod element is

$$dS = \frac{q + \delta q}{T + dT} - \frac{q}{T} \approx \frac{Tq + T\delta q - qT - qdT}{T^2} = \frac{\delta q}{T} - \frac{qdT}{T^2} \tag{a}$$

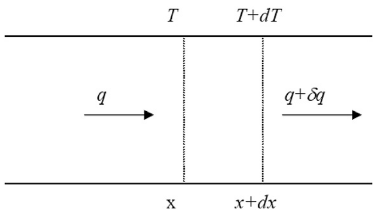


FIGURE 3.1

Heat conduction in an isotropic rod.

where δq is the actual uptake of heat and dT is the actual increase in temperature. Comparing $dS = d_e S + d_i S$with Eq. (a), we find the entropy production term

$$d_i S = -\frac{qdT}{T^2} > 0$$

The rate of entropy production is: $P = \frac{d_i S}{dt} = -\frac{qdT}{T^2 dt} = -\frac{\dot{q}dT}{T^2} > 0$
Here, $\dot{q}$ represents the heat flow rate. The rate of entropy production per unit volume is the entropy source strength

$$\sigma = -\frac{qdT}{aT^2 dtdx} = -\left(\frac{J_q}{T^2}\right)\left(\frac{dT}{dx}\right) > 0$$

where a is the area, $\boldsymbol{J_q}$ is the heat flow $J_q = \frac{q}{adt}$, and $X_q = -\frac{1}{T^2}\frac{dT}{dx}$ is the thermodynamic force due to the finite temperature difference $\nabla(1/T)$.
Three-dimensional heat conduction in an isotropic solid is

$$\sigma = \mathbf{J}_q \cdot \nabla\left(\frac{1}{T}\right) = -\frac{\mathbf{J}_q}{T} \cdot \nabla \ln T$$

In the equation above, $\mathbf{J}_q$ is the heat flow, $\nabla(1/T)$ is the inverse temperature gradient representing the thermodynamic force for heat conduction, and $\mathbf{J}_q/T = \mathbf{J}_s$ is the entropy flow.

3.14 MASS DIFFUSION

The local entropy production for diffusion of several substances per unit volume is

$$\sigma = -\sum_i \mathbf{J}_i \cdot \nabla\left(\frac{\mu_i}{T}\right) \tag{3.67}$$

Based on the entropy production, linear phenomenological equations for an isothermal flow of substance i become

$$\mathbf{J}_i = -\sum_k \frac{L_{ik}}{T} \nabla \mu_k$$

It is clear from the Gibbs–Duhem equation that not all the forces $\frac{1}{T}\nabla(\mu_k)$ are independent. For example, for a two-substance system at constant pressure and temperature, we have

$$0 = c_1 \nabla \mu_1 + c_2 \nabla \mu_2$$

The condition for no volume flow corresponding to no change in volume due to diffusion is

$$0 = \mathbf{J}_1 V_1 + \mathbf{J}_2 V_2$$

where V_i is the partial molar volume for substance i. Therefore, for a two-substance system Eq. (3.67) becomes

$$\sigma = -\frac{1}{T}\left(\mathbf{J}_1 - \frac{c_1}{c_2}\mathbf{J}_2\right)_T \cdot \nabla\mu_1 \rightarrow \sigma = -\frac{1}{T}\left(1 + \frac{V_1 c_1}{V_2 c_2}\right)_T \mathbf{J}_1 \cdot \nabla\mu_1$$

where $\nabla\mu_1 = (\partial\mu_1/\partial c_1)\nabla c_1$. Then, the linear phenomenological equation is

$$\mathbf{J}_1 = -\frac{L_{11}}{T}\left(1 + \frac{V_1 c_1}{V_2 c_2}\right)\nabla\mu_1$$

Comparing this equation with Fick's law $\mathbf{J}_1 = -D_1 \nabla C_1$, we have

$$\mathbf{J}_1 = -\frac{L_{11}}{T}\left(1 + \frac{V_1 c_1}{V_2 c_2}\right)\left(\frac{\partial\mu_1}{\partial c_1}\right)\nabla c_1 = -D_1 \nabla c_1$$

Therefore, the diffusion coefficient is related to the phenomenological coefficient by

$$D_1 = \frac{L_{11}}{T}\left(1 + \frac{V_1 c_1}{V_2 c_2}\right)\left(\frac{\partial\mu_1}{\partial c_1}\right)$$

For diffusion flow of substance 1 in a dilute solution, we have

$$D_1 = \frac{L_{11} R}{x_1}$$

since $\mu_1 = \mu^{\mathrm{o}}(P, T) + RT \ln(c_1/c) = \mu^{\mathrm{o}}(P, T) + RT \ln(x_1)$, where c is the concentration of the solution.

When a mass diffusion occurs in a closed system from higher chemical potential μ_2 to lower potential μ_1, we have the entropy production expressed by

$$d_{\mathrm{i}}S = -\left(\frac{\mu_2 - \mu_1}{T}\right)d\varepsilon \geq 0$$

where $d\varepsilon = -dN_1 = dN_2$. Here the flow of mass from one region to another is accounted for by the extent of reaction $d\varepsilon$, although no real chemical reaction takes place. The rate of entropy production is

$$P = \frac{d_{\mathrm{i}}S}{dt} = -\left(\frac{\mu_2 - \mu_1}{T}\right)\frac{d\varepsilon}{dt} \geq 0$$

3.15 ENTROPY PRODUCTION IN AN ELECTRICAL CIRCUIT

In electrical circuits, electrical energy is converted into heat irreversibly in resistors and capacitors, and entropy is produced. When there is an electrical field, the change of energy is

$$dU = TdS - pdV + \sum_i \mu_i dN_i + \sum_i F z_i \psi_i dN_i$$

where F is the Faraday constant, and z_i is the ion number. The product Fz_idN_i represents the amount of charge transferred. When we transfer the charge dI from a potential ψ_1 to a potential ψ_2, then the rate of entropy production is

$$\frac{d_iS}{dt} = -\frac{\psi_2 - \psi_1}{T}\sum_i Fz_i\frac{dN_i}{dt} = -\frac{\psi_2 - \psi_1}{T}\frac{dI}{dt} \tag{3.68}$$

In the equation above, the difference $(\psi_2 - \psi_1)$ is the voltage across the element, while dI/dt is the electric current.
For a resistor, using the Ohm law $V = (\psi_2 - \psi_1) = IR$, where R is the resistance, the rate of entropy production is

$$\frac{d_\mathrm{i}S}{dt} = \frac{VI}{T} = \frac{RI^2}{T} > 0 \tag{3.69}$$

In the equation above, RI^2 is the Ohmic heat rate produced by a current through an element, such as a resistor.

For a capacitor with capacitance C, the rate of entropy production is

$$\frac{d_\mathrm{i}S}{dt} = \frac{V_\mathrm{C}I}{T} = \frac{V_\mathrm{C}}{T}\frac{dI}{dt} = -\frac{C}{T}V_\mathrm{C}\frac{dV_\mathrm{C}}{dt} \tag{3.70}$$

where $dV_C = -\frac{dI}{C}$ is the voltage decrease when we transfer charge of dI. We can modify Eq. (3.70) as follows

$$\frac{d_\mathrm{i}S}{dt} = -\frac{1}{T}\frac{d}{dt}\left(\frac{CV_\mathrm{C}^2}{2}\right) = -\frac{1}{T}\frac{d}{dt}\left(\frac{I^2}{2C}\right)$$

where the terms $\left(CV_\mathrm{C}^2/2\right) = \left(I^2/(2C)\right)$ represent the electrostatic energy stored in a capacitor. Only for an ideal capacitor, there is no entropy production and no energy dissipation.

For an inductance, the rate of entropy production is

$$\frac{d_\mathrm{i}S}{dt} = -\frac{1}{T}\frac{d}{dt}\left(\frac{LI^2}{2}\right) = -\frac{LI}{T}\frac{dI}{dt} = \frac{VI}{T} \geq 0$$

where the energy stored in an inductance (in the magnetic field) is $LI^2/2$. The voltage is $V = -LdI/dt$.

The phenomenological equations for resistance, capacitance, and inductance are as follows

$$I = L_\mathrm{R}\frac{V}{T}, \quad I = L_\mathrm{C}\frac{V}{T}, \quad \text{and } I = -L_\mathrm{L}\frac{V}{T}$$

where L_R, L_C, and L_L are the phenomenological coefficients, which may be related to resistance. Using Ohm's law, we have

$$\frac{1}{R} = \frac{L_\mathrm{R}}{T}, \; R = \frac{T}{L_C}, \; \text{and } R = \frac{T}{L_\mathrm{L}}$$

EXAMPLE 3.7 ENERGY DISSIPATION IN A DIFFUSER

In heating and ventilation systems, diffusers that are diverging nozzles reduce the discharge velocity to enhance its mixing into the surroundings. Steam enters a diffuser at 30 psia and 300°F, and exits as a saturated vapor at 300°F. The steam enters at a velocity of 1467 ft/s, and leaves at 75 ft/s. The nozzle has an exit area of 0.5 ft^2. Determine the rate of energy dissipation when the environmental temperature is $T_o = 500$ R.

Solution:

Assume that there are no work interactions, the potential energy effects are negligible, and the nozzle operates at steady state.

State 1: Superheated steam: $P_1 = 30$ psia, $T_1 = 760$ R, $H_1 = 1189.0$ Btu/lb, $S_1 = 1.7334$ Btu/(lb R)

State 2: Saturated vapor: $T_1 = 760$ R, $H_2 = 1179.0$ Btu/lb, $S_2 = 1.6351$ Btu/(lb R), $V_2 = 6.466$ ft^3/lb.

The energy balance for a nozzle at steady state conditions yields: $\Delta\left(H + \frac{1}{2}v^2\right)\dot{m}_s = \dot{q}$

By estimating the steam flow rate, we can determine the heat loss from the nozzle:

$$\dot{m} = \frac{1}{V_2}A_2 v_2 = \frac{1}{6.466(\text{ft}^3/\text{lb})}\left(0.5\text{ft}^2\right)(75\text{ft/s}) = 5.8\ \text{lb/s}$$

Therefore, the heat loss is: $\dot{q}_{\text{out}} = \dot{m}\left(H_2 - H_1 + \frac{v_2^2 - v_1^2}{2}\right)$

$$\dot{q}_{\text{out}} = 5.8\left(1179.7 - 1189.0 + \frac{75^2 - 1467^2}{2}\left(\frac{1\ \text{Btu/lb}}{25037\ \text{ft}^2/\text{s}^2}\right)\right) = -302.55\ \text{Btu/s}$$

The entropy balance contains the nozzle and its surroundings, and we have

$$\dot{S}_{\text{prod}} = \sum(\dot{m}S)_{\text{out}} - \sum(\dot{m}S)_{\text{in}} - \sum\frac{\dot{q}_i}{T_i}$$

$$\dot{S}_{\text{prod}} = 5.8(1.6351 - 1.7334) - \frac{-302.55}{500} = 0.03501\ \text{Btu/(s R)}$$

The energy dissipated is

$$\dot{E}_{\text{loss}} = T_o\dot{S}_{\text{prod}} = 500(0.03501) = \mathbf{17.50\ Btu/s}$$

EXAMPLE 3.8 ENERGY DISSIPATION IN A COMPRESSOR

Air enters a compressor at 15 psia and 80°F, and exits at 45 psia and 300°F. The inlet air velocity is low, but increases to 250 ft/s at the outlet of the compressor. The power input to the compressor is 250 hp. The compressor is cooled at a rate of 30 Btu/s. Determine the rate of energy dissipation when the surroundings are at 540 R.

Solution:

Assume that the potential energy effects are negligible, and steady flow occurs in the compressor.

The properties of air can be obtained from Table E4 in Appendix E:

State 1: $P_1 = 15$ psia, $T_1 = 540$ R, $H_1 = 129.06$ Btu/lb, $S_1 = 0.60{,}078$ Btu/(lb R)

State 2: $P_2 = 45$ psia, $T_2 = 760$ R, $H_2 = 182.08$ Btu/lb, $S_2 = 0.68{,}312$ Btu/(lb R)

Using the energy balance, we can estimate the mass flow rate:

$$\dot{W}_{\text{in}} + \dot{q}_{\text{out}} = \dot{m}\left(H_2 - H_1 + \frac{v_2^2 - v_1^2}{2}\right)$$

$$(250\text{hp})\left(\frac{0.7068\text{Btu/s}}{1\text{hp}}\right) - 30\text{Btu/s} = \dot{m}\left(182.08 - 129.06 + \frac{250^2}{2}\left(\frac{1\ \text{Btu/lb}}{25037\ \text{ft}^2/\text{s}^2}\right)\right)$$

$$\dot{m} = 2.7\ \text{lb/s}$$

The entropy balance: $\dot{S}_{\text{prod}} = \sum(\dot{m}S)_{\text{out}} - \sum(\dot{m}S)_{\text{in}} - \sum\frac{\dot{q}_i}{T_i}$

By considering the variable heat capacity, we have

$$\Delta\dot{S} = \dot{m}\left(S_2 - S_1 - R\ln\frac{P_2}{P_1}\right)$$

$$\Delta\dot{S} = 2.7\ \text{lb/s}\left(0.6831 - 0.60078 - (0.06855\text{Btu/lb})\ln\left(\frac{45}{15}\right)\right) = 0.019\ \text{Btu/(s R)}$$

$$\dot{S}_{\text{prod}} = \Delta\dot{S} - \frac{\dot{q}_{\text{out}}}{T_o} = 0.019 - \frac{-30}{540} = 0.0745\ \text{Btu/(s R)}$$

The energy dissipated: $\dot{E}_{\text{loss}} = T_o\dot{S}_{\text{prod}} = 540(0.0745) = \mathbf{40.23\ Btu/s}$

EXAMPLE 3.9 ENERGY DISSIPATION IN AN ADIABATIC MIXER

In a mixer, we mix hot water (stream 1) at 1 atm and 90°C adiabatically with cold water (stream 2) at 15°C. The hot water flow rate is 60 kg/h. If the warm water (stream 3) leaves the mixer at 30°C, determine the rate of energy dissipation if the surroundings are at 300 K.

Solution:

Assume that the kinetic and potential energy effects are negligible, and this is a steady process.
The properties of water from the steam tables in Appendix D, Tables D1 and D2:
Stream 1: Hot water: $T_1 = 90°\text{C}$, $H_1 = 376.9$ kJ/kg, $S_1 = 1.1925$ kJ/(kg K)
Stream 2: Cold water: $T_2 = 15°\text{C}$, $H_2 = 62.94$ kJ/kg, $S_2 = 0.2243$ kJ/(kg K)
Stream 3: Warm water: $T_3 = 30°\text{C}$, $H_3 = 125.7$ kJ/kg, $S_3 = 0.4365$ kJ/(kg K)
The mass, energy, and entropy balances for the adiabatic mixer are.
Mass balance: $\dot{m}_{\text{out}} = \dot{m}_{\text{in}}$
Energy balance: $\dot{E}_{\text{out}} = \dot{E}_{\text{in}} \rightarrow \dot{m}_1H_1 + \dot{m}_2H_2 = \dot{m}_3H_3$
Entropy balance: $\dot{S}_{\text{prod}} = \sum(\dot{m}S)_{\text{out}} - \sum(\dot{m}S)_{\text{in}} \rightarrow \dot{S}_{\text{prod}} = \dot{m}_3S_3 - (\dot{m}_1S_1 + \dot{m}_2S_2)$
Combining the mass and energy balances, we estimate the flow rate of the cold water

$$\dot{m}_1H_1 + \dot{m}_2H_2 = (\dot{m}_1 + \dot{m}_2)H_3$$

$$\dot{m}_2 = \dot{m}_1\left(\frac{H_3 - H_1}{H_2 - H_3}\right) = 60\text{kg/h}\left(\frac{125.7 - 376.9}{62.94 - 125.7}\right) = 240.153\text{kg/h}$$

The mass flow rate of the warm water is: $\dot{m}_3 = \dot{m}_1 + \dot{m}_2 = 60.0 + 240.153 = 300.153$ kg/h
The rate of entropy production for this adiabatic mixing process:

$$\dot{S}_{\text{prod}} = \dot{m}_3S_3 - (\dot{m}_1S_1 + \dot{m}_2S_2)$$

$$\dot{S}_{\text{prod}} = 300.153(0.4365) - 60.0(1.1925) - 240.153(0.2243) = 5.6\ \text{kJ/(h K)}$$

The energy dissipated because of mixing: $\dot{E}_{\text{loss}} = T_o\dot{S}_{\text{prod}} = 300(5.6) = 1680.0\text{kJ/h} = 0.466\text{kW}$

EXAMPLE 3.10 ENERGY DISSIPATION IN A MIXER

In a mixer, we mix a saturated steam (stream 1) at 110°C with a superheated steam (stream 2) at 1000 kPa and 300°C. The saturated steam enters the mixer at a flow rate 1.5 kg/s. The product mixture (stream 3) from the mixer is at 350 kPa and 240°C. The mixer loses heat at a rate 2 kW. Determine the rate of energy dissipation if the surroundings are at 300 K.

Solution:

Assume that the kinetic and potential energy effects are negligible, this is a steady process, and there are no work interactions.
The properties of steam from the steam tables in Appendix D, Tables D1 and D2:
Stream 1:Saturated steam: $T_1 = 110°\text{C}$, $H_1 = 2691.3$ kJ/kg, $S_1 = 7.2388$ kJ/(kg K)
Stream 2: Superheated steam: $P_2 = 1000$ kPa, $T_2 = 300°\text{C}$, $H_2 = 3052.1$ kJ/kg, $S_2 = 7.1251$ kJ/(kg K)

Stream 3: Superheated steam: $P_3 = 350$ kPa, $T_3 = 240°\text{C}$, $H_3 = 2945.7$ kJ/kg, $S_3 = 7.4045$ kJ/(kg K)
The mass, energy, and entropy balances for the mixer at steady state are when $W_s = 0$:

$$\text{Mass balance}: \ \dot{m}_{\text{out}} = \dot{m}_{\text{in}} \rightarrow \dot{m}_1 + \dot{m}_2 = \dot{m}_3$$

$$\text{Energy balance}: \ \sum_i (H\dot{m})_{i,\text{out}} - \sum_i (H\dot{m})_{i,\text{in}} = \dot{q} + \dot{W}_s \rightarrow \dot{m}_3 H_3 - (\dot{m}_1 H_1 + \dot{m}_2 H_2) = \dot{q}_{\text{out}}$$

$$\text{Entropy balance}: \ \dot{S}_{\text{prod}} = \dot{m}_3 S_3 - (\dot{m}_1 S_1 + \dot{m}_2 S_2) - \frac{\dot{q}_{\text{out}}}{T_o}$$

Combining the mass and energy balances we estimate the flow rate of the super heated steam

$$\dot{q}_{\text{out}} = (\dot{m}_1 + \dot{m}_2) H_3 - (\dot{m}_1 H_1 + \dot{m}_2 H_2)$$

$$\dot{m}_2 = \frac{\dot{q}_{\text{out}} - \dot{m}_1 (H_3 - H_1)}{H_3 - H_2} = \frac{-2\text{ kW} - 1.5\text{ kg/s}(2945.7 - 2691.3)\text{kJ/kg}}{(2945.7 - 3052.1)} = 3.56\text{ kg/s}$$

The mass flow rate of the warm water is: $\dot{m}_3 = \dot{m}_1 + \dot{m}_2 = 1.5 + 3.56 = 5.06$ kg/h.
The rate of entropy production is

$$\dot{S}_{\text{prod}} = \dot{m}_3 S_3 - (\dot{m}_1 S_1 + \dot{m}_2 S_2) - \frac{\dot{q}_{\text{out}}}{T_o}$$

$$\dot{S}_{\text{prod}} = 5.105\text{ kg/s}(7.4045) - 1.5\text{ kg/s}(7.2388) - 3.605\text{ kg/s}(7.1251) - \frac{-2\text{ kJ/s}}{300} = 1.26\text{ kJ/(s K)}$$

The energy dissipated because of mixing: $\dot{E}_{\text{loss}} = T_o \dot{S}_{\text{prod}} = 300(1.26) = \mathbf{378.0 kW}$

EXAMPLE 3.11 ENERGY DISSIPATION IN A TURBINE

A superheated steam (stream 1) expands in a turbine from 5000 kPa to 325°C to 150 kPa and 200°C. The steam flow rate is 10.5 kg/s. If the turbine generates 1.1 MW of power, determine the rate of energy dissipation if the surroundings are at 300 K.

Solution:
Assume that the kinetic and potential energy effects are negligible, this is a steady process.
The properties of steam from the steam tables in Appendix D, Tables D1 and D2:
Stream 1: Superheated steam: $P_1 = 5000$ kPa, $T_1 = 325°\text{C}$, $H_1 = 3001.8$ kJ/kg, $S_1 = 6.3408$ kJ/(kg K)
Stream 2: Superheated steam: $P_2 = 150$ kPa, $T_2 = 200°\text{C}$, $H_2 = 2872.9$ kJ/kg, $S_2 = 7.6439$ kJ/(kg K)
$W_s = -1100$ kW, $\dot{m}_s = 10.5$ kg/s.
The mass, energy, and entropy balances are:

$$\text{Mass balance}: \ \dot{m}_{\text{out}} = \dot{m}_{\text{in}} = \dot{m}_s$$

$$\text{Energy balance} \sum_i (H\dot{m})_{i,\text{out}} - \sum_i (H\dot{m})_{i,\text{in}} = \dot{q} + \dot{W}_s$$

$$\text{Entropy balance}: \ \dot{S}_{\text{prod}} = \dot{m}_{\text{s}} (S_2 - S_1) - \frac{\dot{q}_{\text{out}}}{T_o}$$

We estimate the heat loss from the energy balance

$$\dot{q}_{\text{out}} = -\dot{W}_{\text{out}} + \dot{m}_s (H_2 - H_1) = 1100\text{ kJ/s} + 10.5\text{ kg/s}(2872.9 - 3001.8) = -253.45\text{ kJ/s}$$

And the entropy production from the entropy balance is

$$\dot{S}_{\text{prod}} = \dot{m}_{\text{s}} (S_2 - S_1) - \frac{\dot{q}_{\text{out}}}{T_o} = 10.5\text{ kg/s}(7.6439 - 6.3408) - \frac{-253.45}{300} = 14.53\text{ kW/K}$$

The amount of energy dissipated becomes:

$$\dot{E}_{\text{loss}} = T_o \dot{S}_{\text{prod}} = 300(14.53) = \mathbf{4359.0\text{ kW}}$$

EXAMPLE 3.12 GIBBS ENERGY AND DISTANCE FROM GLOBAL EQUILIBRIUM

Discuss the effect of the distance from global equilibrium for a chemical reaction system: R = P.

Solution:

For the chemical reaction considered, with the concentrations of [P] and [R], we have

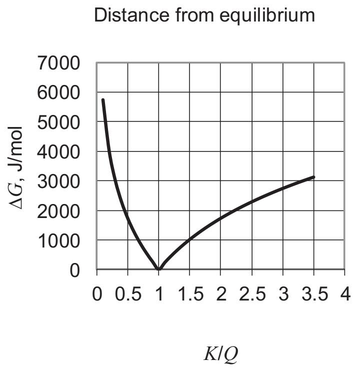
$$K = \frac{[P]_{\text{eq}}}{[R]_{\text{eq}}} \quad \text{(at chemical equilibrium)}$$

$$Q = \frac{[P]}{[R]} \quad \text{(at nonequilibrium)}$$

The displacement from equilibrium may be defined by: $\beta = \frac{Q}{K}$

The Gibbs free energy change is: $\Delta G = -RT \ln\left(\frac{1}{\beta}\right)$

As Fig. 3.2 displays, the absolute values of ΔG increase as the values of β move further from unity. For example, when $\beta = Q/K = 10$, then $\Delta G = 5743.1$ J/mol. The value of ΔG is at a minimum at $\beta = 1$ or $K = Q$, corresponding to the chemical equilibrium. If the values of $\beta < 1$, then $\Delta G < 0$, and such reactions occur spontaneously when necessary mechanisms exist.



$\lvert\Delta G\rvert$ (J/mol)	K/Q
5743.108	0.1
1728.848	0.5
0	1
1011.311	1.5
1728.848	2
2285.412	2.5
2740.159	3

$T = 300$ K
$R = 8.314$ J/(mol K)
$\lvert\Delta G\rvert = RT \ln(K/Q)$

FIGURE 3.2

Distance from global equilibrium in a chemical reaction system: R = P.

3.16 VALIDITY OF LINEAR PHENOMENOLOGICAL EQUATIONS

If a system is not far from global equilibrium, linear phenomenological equations represent the transport and rate processes involving small thermodynamic driving forces. Consider a simple transport process of heat conduction. The rate of entropy production is

$$\sigma = J_{\text{q}}\left(-\frac{1}{T^2}\frac{dT}{dx}\right) > 0$$

The corresponding linear relation between the heat flow and the thermodynamic force is

$$J_{\text{q}} = -\frac{L_{\text{qq}}}{T^2}\left(\frac{dT}{dx}\right) \tag{3.71}$$

The equation above is identical to Fourier's law of heat conduction, $k = L_{qq}/T^2$. The validity of Eq. (3.71) is the same as the validity of Fourier's law, and the equation is valid when the relative variation of temperature is small within the mean free path distance λ in the case of gases

$$\frac{\lambda}{T}\frac{\partial T}{\partial x} << 1$$

Since this condition is satisfied for most systems, the linear phenomenological equations are satisfactory approximations for transport processes.

For an elementary chemical reaction, the local entropy production and the linear phenomenological equation are

$$\sigma = \frac{A}{T}J_{\mathrm{r}} > 0,\ J_{\mathrm{r}} = L_{\mathrm{rr}}\frac{A}{T}$$

Considering a homogeneous chemical reaction S = P, the corresponding affinity is

$$A = \mu_{\mathrm{S}} - \mu_{\mathrm{P}}$$

For a mixture of perfect gases, the chemical potential is $\mu = \mu^o + RT \ln c$. We can relate the chemical potentials to the chemical equilibrium constant and the affinity by

$$RT \ln K(T) = -\sum_i \nu_i \mu_i^o(T)$$

$$A = -\sum_i \nu_i \mu_i^o - RT\sum_i \nu_i \ln c_i = RT \ln \frac{K(T)}{(c_{\mathrm{P}}/c_{\mathrm{S}})}$$

From the kinetic expression, we have

$$J_{\mathrm{r}} = J_{\mathrm{rf}} - J_{\mathrm{rb}} = k_{\mathrm{f}}c_{\mathrm{S}} - k_{\mathrm{b}}c_{\mathrm{P}} = k_{\mathrm{f}}c_{\mathrm{S}}\left(1 - \frac{1}{K}\frac{c_{\mathrm{P}}}{c_{\mathrm{S}}}\right)$$

where the indices *f* and *b* refer to forward and backward reactions.

$$J_{\mathrm{r}} = J_{\mathrm{rf}}\left[1 - \exp\left(-\frac{A}{RT}\right)\right] \tag{3.72}$$

The equation above is a general and nonlinear relation between reaction flow and affinity. However, when the reaction is close to equilibrium, we have

$$\left|\frac{A}{RT}\right| << 1 \tag{3.73}$$

When this condition is satisfied, we can expand the exponential Eq. (3.73) and it becomes

$$J_{\mathrm{r}} = \frac{J_{\mathrm{rf,eq}}}{R}\frac{A}{T} \tag{3.74}$$

Comparing Eq. (3.73) with Eq. (3.74), we have

$$L_{\mathrm{rr}} = \frac{J_{\mathrm{rf,eq}}}{R}$$

Since the condition in Eq. (3.73) is highly restrictive, the linear laws for chemical reactions are not always satisfactory.

3.17 CURIE—PRIGOGINE PRINCIPLE

According to the *Curie—Prigogine principle*, vector and scalar quantities interact only in an anisotropic medium. This principle as originally stated by Curie in 1908 is "quantities whose tensorial characters differ by an odd number of ranks cannot interact in an isotropic medium." Consider a flow $\mathbf{J}_i$ with tensorial rank m. The value of m is zero for a scalar, unity for a vector, and two for a dyadic. If a conjugate force X_j also has the same tensorial rank m, than the coefficient L_{ij} is a scalar, and is consistent with the isotropic character of the system. The coefficients L_{ij} are determined by the isotropic medium; they need not vanish, and hence the flow $\mathbf{J}_i$ and the force X_j can interact or couple. If a force X_j has a tensorial rank different from m by an even integer k, then L_{ij} has a tensor at rank k. In this case, $L_{ij}\,X_j$ is a tensor product. Since a tensor coefficient L_{ij} of even rank is also consistent with the isotropic character of the fluid system, the L_{ij} is not zero, and hence $\mathbf{J}_i$ and X_j can interact. However, for a force X_j whose tensorial rank differs from m by an odd integer k^*, L_{ij} has a tensorial rank of k^*. A tensor coefficient L_{ij} of odd rank implies an anisotropic character for the system. Consequently, such a coefficient vanishes for an isotropic system, and $\mathbf{J}_i$ and X_j do not interact. For example, if k^* is unity, then L_{ij} would be a vector.

3.18 TIME VARIATION OF ENTROPY PRODUCTION

The rate of entropy production inside a given system of volume V is

$$P = \int_V \sigma dV = \int_V \sum_{i=1}^{n} J_i X_i dV$$

The equation above shows the volumetric rate of entropy production. Both the flows and the forces may change with time, while they remain constant at the system boundaries at stationary state only. The time variation of P is

$$\frac{dP}{dt} = \int_V \left(\sum_i^n J_i \frac{dX_i}{dt} \right) dV + \int_V \sum_i^n \left(X_i \frac{dJ_i}{dt} \right) dV = \frac{d_X P}{dt} + \frac{d_J P}{dt} \tag{3.75}$$

The first term in Eq. (3.75) represents the variation of the rate of entropy production in terms of the variation of thermodynamic force

$$\frac{d_X P}{dt} = \int_V \frac{\partial_X \sigma}{\partial t} dV = \int_V \sum_i^n J_i \frac{dX_i}{dt} dV \leq 0$$

The second term in Eq. (3.75) represents the time variation of the flow

$$\frac{d_J P}{dt} = \int_V \frac{\partial_J \sigma}{dt} dV = \int_V \sum_i^n X_i \frac{dJ_i}{dt} dV \tag{3.76}$$

There is no definite sign for Eq. (3.76) in general. However, when the generalized flows are expressed by linear phenomenological equations with constant coefficients obeying to the Onsager relations

$$J_i = \sum_{k=1}^{n} L_{ik} X_k$$

then Eq. (3.76) and the Onsager relations ($L_{ik} = L_{ki}$) yield

$$\frac{d_{\mathrm{J}}P}{dt} = \int_V \sum_i^n \left(X_i \frac{dJ_i}{dt} \right) dV = \int_V \sum_{i,k=1}^{n} (L_{ik} X_i) \frac{\partial X_k}{\partial t} dV = \int_V \sum_{k=1}^{n} \left(J_k \frac{\partial X_k}{\partial t} \right) dV = \frac{d_{\mathrm{X}}P}{dt} = \frac{1}{2}\frac{dP}{dt} \le 0 \tag{3.77}$$

Therefore, from Eqs. (3.75) and (3.77), we have

$$\frac{dP}{dt} = 2\frac{d_{\mathrm{X}}P}{dt} = 2\frac{d_{\mathrm{J}}P}{dt} \le 0$$

At stationary state, the boundary conditions are time independent, and the rate of entropy production for linear phenomenological laws is at a minimum, leading to minimum energy dissipation. From Eq. (3.77), we have

$$\frac{\partial_{\mathrm{X}}\sigma}{\partial t} = \frac{\partial_{\mathrm{J}}\sigma}{dt} \le 0$$

EXAMPLE 3.13 ENTROPY PRODUCTION AND THE CHANGE OF THE RATE OF ENTROPY PRODUCTION WITH TIME IN HEAT CONDUCTION

For heat conduction in an isotropic medium (Fig. 3.1), derive a relationship for the rate of entropy production, the dissipation function, and the rate of entropy production change with time.

Solution:
The entropy source strength σ is: $\sigma = \mathbf{J}_{\mathrm{q}} \cdot \nabla\left(\frac{1}{T}\right) = -\frac{\mathbf{J}_{\mathrm{q}}}{T} \cdot \nabla \ln T$
Hence, the phenomenological equation for heat conduction is: $\mathbf{J}_{\mathrm{q}} = L_{\mathrm{qq}} \nabla\left(\frac{1}{T}\right)$ and we have $L_{\mathrm{qq}} = kT^2$
The rate of entropy production is obtained from the local value of entropy production σ

$$P = \int_V \sigma dV = \int_V \mathbf{J}_{\mathrm{q}} \cdot \nabla\left(\frac{1}{T}\right) dV = L_{\mathrm{qq}} \int_V \left[\nabla\left(\frac{1}{T}\right)\right]^2 dV \ge 0$$

The dissipation function for a reference temperature of T_o is

$$\Psi = T_o \int_V \sigma dV = T_o \int_V \mathbf{J}_q \cdot \nabla\left(\frac{1}{T}\right) dV = T_o k T^2 \int_V \left[\nabla\left(\frac{1}{T}\right)\right]^2 dV \ge 0$$

The time variation of the rate of entropy production with respect to the variation of the thermodynamic force ($d_x P$) is

$$\frac{d_{\mathrm{X}}P}{dt} = \int_V \mathbf{J}_q \cdot \frac{\partial}{\partial t}\left[\nabla\left(\frac{1}{T}\right)\right] dV = \int_A \left[\frac{\partial}{dt}\left(\frac{1}{T}\right)\right] \mathbf{J}_q \bullet dA - \int_V \left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right] (\nabla \cdot \mathbf{J}_q) dV \tag{a}$$

where the surface integral is zero, as the temperature does not change with time.
The divergence of the heat flow is obtained using the first law of thermodynamics

$$dU = \delta q - pdV$$

For a solid $dV = 0$, and we have $dU = C_v dT$, so therefore

$$-\nabla \cdot \mathbf{J}_q = \rho \frac{\delta q}{dt} = \rho \frac{\partial U}{dt} = \rho C_v \frac{\partial T}{dt} \tag{b}$$

Combining Eqs. (a) and (b) and assuming constant phenomenological coefficient for small temperature gradients and for $C_v > 0$, we get

$$\frac{dP}{dt} = 2\frac{d_X P}{dt} = -2\int_V \frac{\rho C_v}{T^2}\left(\frac{\partial T}{\partial t}\right)^2 dV \leq 0$$

This shows that the rate of entropy production decreases with time because of heat flow in an isotropic solid, and a minimum is reached in an equilibrium state.

3.19 MINIMUM ENTROPY PRODUCTION

The entropy production rate is

$$P = \int_V \sigma dV = \int_V \sum_{i=1}^{n} J_i X_i dV = \int_V \sum_{i,k=1}^{n} L_{ik} X_k X_i dV$$

The value of P will be extremal if its variation is equal to zero

$$\delta P = \delta \int_V \sum_{i,k=1}^{n} L_{ik} X_k X_i dV = 0 \tag{3.78}$$

The variation considered in the equation above may be subject to various constraints. For example, the flows J_i may vary when the forces X_i remain constant. It is also possible that the thermodynamic force may change while the flow remains the same, or they both may change.

For a set of linear phenomenological equations, consider the following potentials

$$\psi = \frac{1}{2}\sum_{i,k}^{n} L_{ik} X_k X_i \geq 0, \ \phi = \frac{1}{2}\sum_{i,k}^{n} K_{ik} J_i J_k \geq 0 \quad (\mathrm{i, k} = 1, 2, \ldots, \mathrm{n})$$

These potentials have the following properties

$$\frac{\partial \psi}{\partial X_i} = \frac{1}{2}\sum_{k}^{n} L_{ik} X_k = J_i, \ \frac{\partial \phi}{\partial J_i} = \frac{1}{2}\sum_{k}^{n} K_{ik} J_k = X_i \tag{3.79}$$

and

$$\begin{aligned} \frac{\partial^2 \psi}{\partial X_i \partial X_k} &= \frac{\partial J_i}{\partial X_k} = L_{ik} = L_{ki} = \frac{\partial J_k}{\partial X_i} = \frac{\partial^2 \psi}{\partial X_k \partial X_i} \\ \frac{\partial^2 \phi}{\partial J_i \partial J_k} &= \frac{\partial X_i}{\partial J_k} = K_{ik} = K_{ki} = \frac{\partial X_k}{\partial J_i} = \frac{\partial^2 \phi}{\partial J_k \partial J_i} \end{aligned} \tag{3.80}$$

Eqs. (3.77) and (3.78) indicate that the first derivatives of the potentials represent linear phenomenological equations, while the second derivatives are the Onsager reciprocal relations.

For an elementary volume, minimum entropy productions under various constraints are

$$\begin{aligned}
&\delta X_i = 0, \quad \delta J_i \neq 0, \quad \delta(\sigma - \phi)_{X_i} = 0\\
&\delta X_i \neq 0, \quad \delta J_i = 0, \quad \delta(\sigma - \psi)_{J_i} = 0\\
&\delta X_i \neq 0, \quad \delta J_i \neq 0, \quad \delta[\sigma - (\psi + \phi)] = 0
\end{aligned}$$

For the whole system under consideration, we have

$$\begin{aligned}
&\delta X_i = 0, \quad \delta J_i \neq 0, \quad \delta \int_V (\sigma - \phi)_{X_i} dV = 0\\
&\delta X_i \neq 0, \quad \delta J_i = 0, \quad \delta \int_V (\sigma - \psi)_{J_i} dV = 0\\
&\delta X_i \neq 0, \quad \delta J_i \neq 0, \quad \delta \int_V [\sigma - (\psi + \phi)] dV = 0
\end{aligned} \tag{3.81}$$

The principle of minimum entropy production in nonequilibrium thermodynamics is restricted to linear phenomenological equations obeying the Onsager relations. In equilibrium thermodynamics, systems tend to maximize the entropy or minimize the free energy.

In a general manner, if a system has n independent forces ($X_1, X_2, \ldots, X_n$), and j of them are held constant ($X_1, X_2, \ldots, X_j =$ constant), then the flows with $J_{j+1}, J_{j+2}, \ldots, J_n$ disappear at the stationary state with minimum entropy represented by

$$\frac{\partial}{\partial X_k}\left(\frac{d_i S}{dt}\right) = 0 \quad (k = j+1, \ldots, n) \tag{3.82}$$

Since ($d_iS/dt > 0$), the extremum in Eq. (3.82) is a minimum. Such a state is called a stationary state of jth order.

EXAMPLE 3.14 MINIMUM ENTROPY PRODUCTION IN A TWO-FLOW SYSTEM

Determine the conditions for minimum entropy production for a two-flow system.

Solution:

If the linear phenomenological equations hold for a two-flow coupled system

$$J_1 = L_{11}X_1 + L_{12}X_2, J_2 = L_{21}X_1 + L_{22}X_2$$

we can express the entropy production by the conductance coefficients L_{ij}

$$\sigma = J_1X_1 + J_2X_2 = L_{11}X_1^2 + L_{22}X_2^2 + (L_{12} + L_{21})X_1X_2$$

The equation yields a parabolic-like change of dissipation with respect to forces X_1 and X_2, as seen in Fig. 3.3. The system tends to minimize the entropy and eventually reaches zero entropy production if there are no restrictions on the forces. On the other hand, if we externally fix the value of one of the forces, for example, $X_2 = X_{20}$, then the system will tend toward the stationary state characterized by the minimum entropy production at $X_2 = X_{20}$. The system will move along the parabola of Fig. 3.3 and stop at point σ_0. At the minimum, the derivative of σ with respect to X_2 is zero

$$\frac{d\sigma}{dX_2} = 2L_{22}X_2 + (L_{12} + L_{21})X_1 = 0 \tag{a}$$

If the Onsager relations are valid, $L_{12} = L_{21}$, and then Eq. (a) becomes

$$0 = 2(L_{22}X_2 + L_{12}X_1) = 2J_2 = 0$$

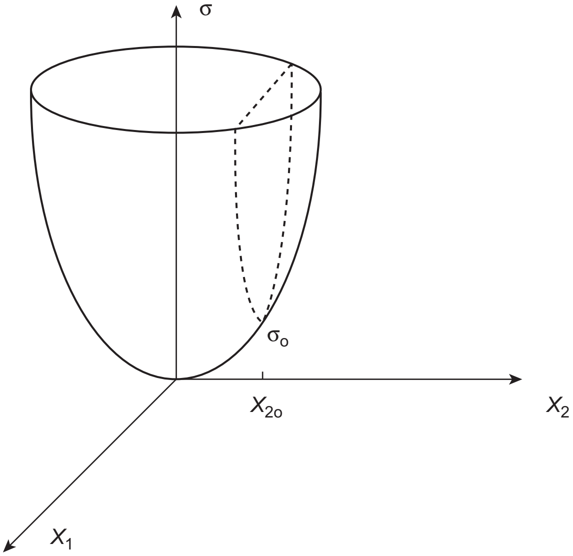


FIGURE 3.3

Representation of entropy production in terms of the forces in a two-flow system.

since J_2 is the flow given by the phenomenological equations. Therefore, a stationary point with respect to mass flow characterizes the state of minimum entropy production, and minimum energy dissipation (Kondepudi and Prigogine, 2015).

EXAMPLE 3.15 MINIMUM ENTROPY PRODUCTION IN AN ELEMENTARY CHEMICAL REACTION SYSTEM

Consider a monomolecular reaction, for example, the following isomerization reaction:

$$\mathrm{R} \overset{1}{\leftrightarrow} \mathrm{X} \overset{2}{\leftrightarrow} \mathrm{B}$$

In this open reaction system, the chemical potentials of reactant R and product B are maintained at a fixed value by an inflow of reactant R and an outflow of product B. The concentration of intermediate X is maintained at a nonequilibrium value, while the temperature is kept constant by the reaction exchanging heat with the environment. Determine the condition for minimum entropy production.

Solution:
The entropy production per unit volume is

$$\sigma = \frac{A_1}{T} J_{\mathrm{r1}} + \frac{A_2}{T} J_{\mathrm{r2}} \geq 0 \tag{a}$$

Where A_1 and A_2 are the affinities for reactions 1 and 2. The linear reaction flows with vanishing cross-coefficients are

$$J_{\mathrm{r1}} = L_{11}\frac{A_1}{T}, \quad J_{\mathrm{r2}} = L_{22}\frac{A_2}{T} \tag{b}$$

As the chemical potentials μ_R and μ_B are fixed by the flow conditions, we have a constant total affinity A

$$A = (\mu_{\mathrm{R}} - \mu_{\mathrm{X}}) + (\mu_{\mathrm{X}} - \mu_{\mathrm{B}}) = \mu_{\mathrm{R}} - \mu_{\mathrm{B}} = A_1 + A_2 \tag{c}$$

At the stationary state, we have $J_{\mathrm{r1}} = J_{\mathrm{r2}}$
After inserting Eq. (c) into Eqs. (a) and (b), we get

$$\sigma = \frac{A_1}{T} J_{\mathrm{r1}} + \frac{(A - A_1)}{T} J_{\mathrm{r2}} \geq 0 \tag{d}$$

$$J_{r1} = L_{11}\frac{A_1}{T},\ J_{r2} = L_{22}\frac{A - A_1}{T} \tag{e}$$

After combining Eqs. (d) and (e), we get

$$\sigma(A_1) = L_{11}\frac{A_1^2}{T^2} + L_{22}\frac{(A - A_1)^2}{T^2}$$

The entropy production is at a minimum with respect to the affinity of reaction 1

$$\frac{\partial \sigma(A_1)}{\partial A_1} = L_{11}\frac{2A_1}{T^2} - L_{22}\frac{2(A - A_1)}{T^2} = 0$$

Therefore, we have

$$L_{11}\frac{A_1}{T} - L_{22}\frac{A_2}{T} = J_{\mathrm{r1}} - J_{\mathrm{r2}} = 0$$

The equation above proves that with the linear reaction flows, the entropy production is minimized at nonequilibrium stationary state where the reaction velocities are equal to each other $J_{r1} = J_{r2}$.

EXAMPLE 3.16 MINIMUM ENERGY DISSIPATION IN HEAT CONDUCTION

Use the minimum entropy production principle to derive the relation for nonstationary heat conduction in an isotropic solid rod.

Solution:
For an isotropic rod, we have

$$\rho\frac{\partial s}{\partial t} = -\nabla\cdot\mathbf{J}_{\mathrm{s}} + \sigma\ (\text{entropy balance})$$

$$\rho\frac{\partial s}{\partial t} = \frac{\rho}{T}\frac{\partial u}{\partial t} = \rho C_v\frac{1}{T}\frac{\partial T}{\partial t}$$

where $\mathbf{J}_{\mathrm{s}} = \frac{\mathbf{J}_{\mathrm{q}}}{T}$. From Eq. (3.78), we have

$$\delta X_i \neq 0,\quad \delta J_i = 0,\quad \delta\int_V (\sigma - \psi)_{J_i} dV = 0$$

where

$$\psi = \frac{L_{\mathrm{qq}}}{2}\left(\nabla\left(\frac{1}{T}\right)\right)^2$$

With the Gauss–Ostrogradsky theorem, we have

$$\delta\int_V \left(\rho\frac{\partial s}{\partial t} - \psi\right)_{J_i} dV + \delta\int_a \mathbf{J}_{\mathrm{s}}\cdot d\mathbf{a} = 0 \tag{a}$$

For the isotropic rod with constant temperatures at the boundaries, Eq. (a) yields

$$\delta\int_V \left(\frac{\rho C_v}{T}\frac{\partial T}{\partial t} - \frac{L_{qq}}{2}\left[\nabla\left(\frac{1}{T}\right)\right]^2\right) dV = 0 \tag{b}$$

By using the absolute inverse temperature as the variable subject to change, Eq. (b) becomes

$$\int_V \left(\left(\frac{\rho C_v}{T}\frac{\partial T}{\partial t} + \nabla\cdot\left[L_{\mathrm{qq}}\nabla\left(\frac{1}{T}\right)\right]\right)\delta\left(\frac{1}{T}\right)\right) dV = 0$$

This variational equation based on Eq. (3.78) is equivalent to a differential heat conduction equation in the following form

$$\rho C_v \frac{\partial T}{\partial t} = -\nabla \cdot \left[L_{\mathrm{qq}} \nabla \left(\frac{1}{T} \right) \right] = \nabla \cdot \left(\frac{L_{\mathrm{qq}}}{T^2} \nabla T \right)$$

The Lagrangian of the variational problem is

$$\mathbb{L}_{\mathrm{q}} = \frac{\rho C_v}{T} \frac{\partial T}{\partial t} - \frac{L_{\mathrm{qq}}}{2} \left(\nabla \left(\frac{1}{T} \right) \right)^2$$

A Euler-Lagrange equation for the variational problem of $\delta \int_V \mathbb{L}_{\mathrm{q}} dV$ may be obtained by considering the differential heat conduction equation, and we have

$$\frac{\partial \mathbb{L}_{\mathrm{q}}}{\partial (1/T)} - \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \frac{\partial \mathbb{L}_{\mathrm{q}}}{\partial \left[\dfrac{\partial (1/T)}{\partial x_i} \right]} = 0$$

EXAMPLE 3.17 MINIMUM ENTROPY PRODUCTION IN ELECTRICAL CIRCUITS

Determine the conditions that minimize the entropy generation in electrical circuits with n elements connected in series. Assume that the voltage drop across the circuit is kept constant.

Solution:

The entropy production is: $\frac{d_i S}{dt} = \frac{V}{T} I$
where V is the voltage across the element, $(\psi_2 - \psi_1)$, and I is the current passing through the element. The phenomenological law is

$$I_j = L_{jj} \frac{V_j}{T} \tag{a}$$

Since the voltage drop across the circuit is kept constant, we have

$$V = \sum_{j}^{n} V_j \tag{b}$$

The total entropy production for the n circuit elements is

$$P = \frac{d_i S}{dt} = \frac{V_1}{T} I_1 + \frac{V_2}{T} I_2 + \ldots + \frac{V_n}{T} I_n \tag{c}$$

After combining Eqs. (a)–(c), we get

$$P = \frac{d_i S}{dt} = L_{11} \frac{V_1^2}{T^2} + L_{22} \frac{V_2^2}{T^2} + \ldots + L_{nn} \frac{\left[\sum_{j}^{n-1} (V - V_j) \right]^2}{T^2}$$

To minimize the rate of entropy production, we use $\partial P / \partial V_j$ with $n-1$ independent values of V_j, which leads to

$$I_1 = I_2 = \ldots = I_n$$

Therefore, in a circuit element, the entropy production is minimized if the current through the n elements is the same. In an electrical circuit, the relaxation to the stationary state is very fast, and nonuniform values of I are not observed.

PROBLEMS

3.1 Air enters a nozzle at 400 K and 60 m/s and leaves the nozzle at a velocity of 250 m/s. The air inlet and exit pressures are 300 and 100 kPa, respectively. If the nozzle loses 2.2 kJ/kg, determine the total entropy change if the surroundings are at 290 K.

3.2 Carbon dioxide enters a nozzle at 300 K and 10 m/s and leaves the nozzle at a velocity of 200 m/s. The inlet and exit pressures are 400 and 100 kPa, respectively. If the nozzle loses 3.0 kJ/kg, determine the total entropy change if the surroundings are at 290 K.

3.3 Air enters a diffuser at 280 K, 90 kPa, and 200 m/s and leaves the nozzle at a velocity of 80 m/s. The air exit temperature is 295 K. The air flow rate is 2.5 kg/s. Determine the total entropy change if the surroundings are at 290 K and the diffuser is adiabatic.

3.4 Steam enters a nozzle at 250 psia, 750°F, and 30 ft/s and leaves the nozzle at a velocity of 650 ft/s. The mass flow rate is 10 lbm/s. The steam leaves the nozzle at 180 psia. If the nozzle is adiabatic, determine the total entropy change if the surroundings are at 490 R.

3.5 Steam enters a nozzle at 20 psia, 700°F, and 10 ft/s and leaves the nozzle at a velocity of 500 ft/s. The mass flow rate is 8 lbm/s. The steam leaves the nozzle at 180 psia. The heat loss from the nozzle is 1.6 Btu/lbm. Determine the total entropy change if the surroundings are at 490 R.

3.6 A steam enters a nozzle (diffuser) at 500 kPa and 220°C, and exits at 400 kPa and 175°C. The steam enters at a velocity of 200 m/s, and leaves at 50 m/s. The nozzle has an exit area of 0.2 m^2. Determine the rate of energy dissipation when the environmental temperature is $T_o = 300$ K.

3.7 A steam enters a nozzle at 4000 kPa and 425°C with a velocity of 50 m/s. It exits at 286.18 m/s. The nozzle is adiabatic and has an inlet area of 0.005 m^2. Determine the rate of energy dissipation if the surroundings are at $T_o = 300$ K.

3.8 A steam enters a nozzle at 3200 kPa and 300°C with a velocity of 20 m/s. It exits at 274.95 m/s. The nozzle is adiabatic and has an inlet area of 0.01 m^2. Determine the rate of energy dissipation if the surroundings are at $T_o = 300$ K.

3.9

- **a.** At steady state, a 4-kW compressor is compressing air from 100 kPa to 300 K to 500 kPa and 450 K. The airflow rate is 0.02 kg/s. Estimate the rate of entropy change.
- **b.** If the compression takes place isothermally by remowing heat to the surroundings, estimate the rate of entropy change of air if the surroundings are at 290 K.

3.10

- **a.** At steady state, a 10-kW compressor is compressing air from 100 kPa to 300 K to 1500 kPa and 400 K. The airflow rate is 0.3 kg/s. Estimate the rate of entropy change.
- **b.** If the compression takes place isothermally by remowing heat to the surroundings, estimate the rate of entropy change of air if the surroundings are at 290 K.

3.11 Derive the following isentropic relation for ideal gases with constant specific heats.

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

where γ is the ratio of heat capacities at constant pressure to heat capacity at constant volume.

3.12 Refrigerant tetrafluoroethane (HFC-134a) enters the coils of the evaporator of a refrigerator as a saturated vapor liquid mixture at 240 kPa. The refrigerant absorbs 100 kJ of heat from the interior of the refrigerator maintained at 273.15 K, and leaves as saturated vapor at 240 kPa. Estimate the total entropy change.

3.13 Refrigerant tetrafluoroethane (HFC-134a) enters the coils of the evaporator of a refrigerator as a saturated vapor liquid mixture at 200 kPa. The refrigerant absorbs 85 kJ of heat from the interior of the refrigerator maintained at 280.15 K and leaves as saturated vapor at 250 kPa. Estimate the total entropy change.

3.14 Methane gas is compressed from an initial state at 100 kPa, 280 K and 10 m^3 to 600 kPa and 400 K. The compression process is polytropic (PV^{α} = constant). The average heat capacity of methane is $C_{p,\mathrm{av}} = 40.57$ J/(mol K). Estimate the total entropy change if the surroundings are at 300 K.

3.15 Hydrogen gas is compressed from an initial state at 100 kPa, 300 K and 5 m^3 to 300 kPa and 370 K. The compression process is polytropic (PV^{α} = constant). The average heat capacity of hydrogen is $C_{p,\mathrm{av}} = 29.1$ J/(mol K). Estimate the total entropy change if the surroundings are at 290 K.

3.16 A compressor receives air at 15 psia and 80°F. The air exits at 40 psia and 300°F. At the inlet the air velocity is low but increases to 250 ft/s at the outlet of the compressor. The power input to the compressor is 350 hP. The compressor is cooled at a rate of 200 Btu/s. Determine the rate of energy dissipation when the surroundings are at 540 R.

3.17 In a mixer, we mix a hot water at 1 atm and 80°C adiabatically with a cold-water stream at 25°C. The flow rate of the cold water is 20 kg/h. If the product leaves the mixer at 50°C, determine the rate of energy dissipation if the surroundings are at 295 K.

3.18 In a mixer, we mix a hot water at 1 atm and 86°C adiabatically with cold-water stream at 25°C. The hot water flow rate is 60 kg/h. If the warm water leaves the mixer at 35°C, determine the rate of energy dissipation if the surroundings are at 300 K.

3.19 In a mixer, we mix liquid water at 1 atm and 25°C with a superheated steam at 325 kPa and 200°C. The liquid water enters the mixer at a flow rate of 70 kg/h. The product mixture from the mixer is at 1 atm and 55°C. The mixer loses heat at a rate of 3000 kJ/h. Determine the rate of energy dissipation if the surroundings are at 300 K.

3.20 In a mixer, we mix liquid water at 1 atm and 20°C with a superheated steam at 1350 kPa and 300°C. The liquid water enters the mixer at a flow rate 70 kg/h. The product mixture from the mixer is at 1 atm and 55°C. The mixer loses heat at a rate of 1000 kJ/h. Determine the rate of energy dissipation if the surroundings are at 290 K.

3.21 Steam expands in a turbine from 6600 kPa to 350°C to a saturated vapor at 1 atm. The steam flow rate is 9.55 kg/s. If the turbine generates a power of 1.2 MW, determine the rate of energy dissipation if the surroundings are at 298.15 K.

3.22 Steam expands in a turbine from 8000 kPa to 400°C to a saturated vapor at 1 atm. The steam flow rate is 12.8 kg/s. If the turbine generates a power of 1.5 MW, determine the rate of energy dissipation if the surroundings are at 298.15 K.

3.23 Derive the relationships between the conductance type of phenomenological coefficients L_{ik} and the resistance type of phenomenological coefficients K_{ij} in a three-flow system.

3.24 Consider a monomolecular reaction in Example 3.9, and determine the condition for minimum entropy production when the rate of entropy production is expressed in terms of the concentration. In this open reaction system, the chemical potentials of reactant R and the product B are maintained at a fixed value by an inflow of reactant R and an outflow of product B. The concentration of intermediate X is maintained at a nonequilibrium value, while the temperature is kept constant by exchanging the heat of reaction with the environment. Determine the condition for minimum entropy production.

3.25 Consider the following sequence of reactions: $\mathrm{R} \overset{1}{\leftrightarrow} \mathrm{X}_1 \overset{2}{\leftrightarrow} \mathrm{X}_2 \overset{3}{\leftrightarrow} \ldots\ldots \overset{n-1}{\leftrightarrow} \mathrm{X}_{n-1} \overset{n}{\leftrightarrow} \mathrm{P}$. Identify the states at which the entropy production will be minimal.

3.26 Consider the following synthesis reaction

$$H_2 + Br_2 = 2HBr$$

This results from the following intermediate reactions

$$Br_2 \overset{1}{\leftrightarrow} 2Br$$

$$H_2 + Br \overset{2}{\leftrightarrow} HBr + H$$

$$H + Br_2 \overset{3}{\leftrightarrow} HBr + Br$$

The affinity of the net reaction is maintained at a constant value by the flows of H_2 and Br_2. One of the reactions is unconstrained. Show that the stationary state leads to minimal entropy production.

3.27 Consider one-dimensional heat conduction in a rod with a length of L. Obtain the function that minimizes the entropy production.

3.28 Consider an elementary reaction of $A = B$ and calculate the change of Gibbs free energy when $\beta = Q/K$ changes from 0.1 to 10.

3.29 For a three-component diffusion system derive the relations between the diffusion coefficients and the phenomenological coefficients under isothermal conditions.

3.30 Transform the thermodynamic forces and flows when the forces are independent, while the flows are linearly dependent in a two-flow system: $0 = J_1 + yJ_2$.

3.31 Transform the thermodynamic forces and flows when the flows are independent, while the thermodynamic forces are linearly dependent in a two-flow system: $0 = X_1 + yX_2$.

3.32 Transform the phenomenological equations when the flows and forces are linearly dependent, and the forces are linearly dependent: $0 = J_1 + zJ_2$ and $0 = X_1 + yX_2$.

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