Chapter 22: Linear Non-equilibrium Thermodynamics

What is required for a chemical reaction to progress to a useful extent?

Flux-force relationships describe the approach of physical properties to equilibrium. Chemical kinetics describes the approach of chemical reactions to equilibrium. Classical thermodynamics is the study of equilibrium. Thermodynamics describes why the system evolves. A complete description of a reaction should combine an understanding of the thermodynamic driving forces for the chemical reaction with the rate of progress towards equilibrium. Can the central concepts of thermodynamics be applied to a system during the progression towards equilibrium? In particular, can the concept of entropy be developed as a useful tool for understanding the evolution of non-equilibrium systems? Many approaches have been developed for the study of non-equilibrium systems. For systems close to equilibrium, linear non-equilibrium thermodynamics provides a description of the temporal and spatial dependence of the approach to equilibrium. Linear non-equilibrium thermodynamics unifies flux-force relationships, chemical kinetics, and thermodynamics by introducing the concept of entropy production. Non-equilibrium theories are necessary for studying the behavior of the atmosphere, biogeochemical cycles, bio-energetics, chemical separations, battery technology, and nano-systems, among others. The main question is to determine if and how thermodynamics can be applied to non-equilibrium systems.

22.1 Fluxes Create Entropy: Entropy Production

The total change in entropy for an isolated system determines if a process is spontaneous. At constant temperature and pressure, the increase in entropy for an isolated system corresponds to a decrease in Gibbs energy. The change in Gibbs energy is the driving force for chemical change. The change in Gibbs energy for a chemical reaction at constant temperature and pressure is determined by the changes in chemical potentials for the reactants and products. Thermodynamics applies to systems at equilibrium. The application of a temporary internal constraint allows the system to be at equilibrium before a process is started. After release of the temporary constraint, the system approaches final equilibrium. The application of a temporary constraint allows the system to be at equilibrium before as well as after the process, even though the process is irreversible.

The key to uniting thermodynamics and kinetics for non-equilibrium systems is to postulate that entropy can be defined for non-equilibrium systems. The key to the success of this approach is that the local environment in various parts of the system is sufficiently close to equilibrium that a local temperature and entropy can be determined.[3] The temperature and entropy can then vary from place to place and from time to time and still be good descriptions of the system. This approach is called **linear non-equilibrium thermodynamics**. The definition of the entropy for a non-equilibrium process is a simple extension of the work we have already done.

Fluxes are Driven by Thermodynamic Forces: For a closed system in the absence of chemical reactions, the entropy change for the system is given by Eq. 13.1.8. However, the spontaneity of a process is determined by the total entropy change for an isolated system. Consider an isolated composite constructed from the system of interest and the surroundings. The change in the total entropy of the system and the entropy change of the surroundings are given by Eqs. 13.5.1 and 13.5.5:[1]

$$dS_{tot} = dS + dS_{surr} \qquad (13.5.5)$$

$$dS = \frac{\text{đ}q}{T} + \left(\frac{P - P_{ext}}{T}\right) dV \qquad (13.1.8) \qquad dS_{surr} = \frac{\text{đ}q_{surr}}{T_{surr}} = -\frac{\text{đ}q}{T_{surr}} \qquad (13.5.1)$$

Substituting Eqs. 13.1.8 and 13.5.1 into Eq. 13.5.5 gives the total change in entropy as:

$$dS_{tot} = \frac{\text{đ}q}{T} + \left(\frac{P - P_{ext}}{T}\right) dV - \frac{\text{đ}q}{T_{surr}}$$

$$dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) \text{đ}q + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) dV \qquad \text{(closed)} \qquad 22.1.1$$

We argued in Chapt. 13 that the second term, the lost work term, is always positive for a spontaneous process at constant temperature. We will now show that the heat transfer term is always positive for a spontaneous process at constant volume.

Consider a constant volume process. If the temperature of the system is colder than the surroundings, $T < T_{surr}$, then:[2]

$$\left(\frac{1}{T} - \frac{1}{T_{surr}}\right) > 0 \qquad \text{(cst. V)} \qquad 22.1.2$$

The system absorbs energy from the warmer surroundings, $\text{đ}q > 0$, so that the product of the two positive terms in Eq. 22.1.1 gives $dS_{tot} > 0$. If the system is hotter than the surroundings, $T > T_{surr}$, then:

$$\left(\frac{1}{T} - \frac{1}{T_{surr}}\right) < 0 \qquad \text{(cst. V)} \qquad 22.1.3$$

The system transfers thermal energy to the colder surroundings, $\text{đ}q < 0$, so that the product of the two negative terms again guarantees that $dS_{tot} > 0$. Eq. 22.1.1 can be summarized as that a temperature gradient is necessary for heat transfer and a pressure gradient is necessary for expansion work. Eq. 22.1.1 can be written more directly in terms of the temperature gradient by taking a common denominator in the first, heat transfer term to give:

$$dS_{tot} = \left(\frac{T_{surr} - T}{T\,T_{surr}}\right) \text{đ}q + \left(\frac{P - P_{ext}}{T}\right) dV \qquad \text{(closed)} \qquad 22.1.4$$

The temperature gradient is given by the temperature difference, $\Delta T = T - T_{surr}$, and the pressure gradient is given by the pressure difference, $\Delta P = P - P_{ext}$. Eq. 22.1.1 applies to initial and final equilibrium states. To apply Eq. 22.1.1 to a non-equilibrium process, we simply allow the entropy to vary with time:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) \frac{\text{đ}q}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) \frac{dV}{dt} \qquad \text{(near-equilibrium, closed)} \qquad 22.1.5$$

The time derivative of the total entropy is called the **entropy production**. A spontaneous, irreversible process produces entropy. The entropy production terms have the general form of flux-force relationships, $dS_{tot}/dt = \Sigma\, F_i\, J_i$, with F_i the thermodynamic force and J_i the corresponding flux. In Eq. 22.1.5:

$\left(\frac{1}{T} - \frac{1}{T_{surr}}\right)$ is the thermodynamic force for energy transfer in the form of heat

$\left(\frac{P}{T} - \frac{P_{ext}}{T}\right)$ is the thermodynamic force for energy transfer in the form of work

A simple example is the entropy production caused by thermal energy transfer at constant volume. The rate of heat flow is given by the thermal flux from Eqs. 7.2.13 and 7.2.18.

$$J_q = \frac{\text{đ}q}{dt} = -\frac{\mathcal{K}\mathcal{A}}{\delta}(T - T_{surr}) \qquad (7.2.13) \qquad \text{and} \qquad (T - T_{surr}) = (T_o - T_{surr})\, e^{-\frac{\mathcal{K}\mathcal{A}}{\delta C_P} t} \qquad (7.2.18)$$

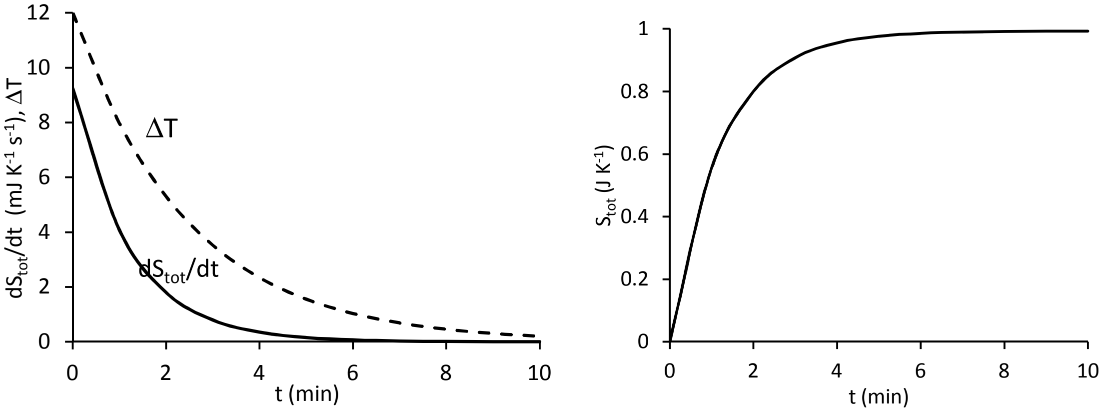
where $\mathcal{K}$ is the thermal conductivity and $\mathcal{A}$ is the contact area between the system and the surroundings. The rate of entropy production, at constant volume, is given by substituting Eqs. 7.2.13 into Eq. 22.1.5:

$$\frac{dS_{tot}}{dt} = \left(\frac{\mathcal{K}\mathcal{A}}{\delta}\right)\frac{(T - T_{surr})^2}{T\,T_{surr}} \cong \left(\frac{\mathcal{K}\mathcal{A}}{\delta\, T_{surr}^2}\right)(T - T_{surr})^2 \qquad \text{(near-equilibrium, cst. V)} \quad 22.1.6$$

For a system close to thermal equilibrium, $T \cong T_{surr}$ and assuming the system and surroundings are close to room temperature, $T \cong 300$ K, gives $TT_{surr} \cong T_{surr}^2$ as a good approximation in the denominator of Eq. 22.1.6. Substituting the integrated heat flux relationship, Eq. 7.2.18, into Eq. 22.1.6 gives:

$$\frac{dS_{tot}}{dt} = \left(\frac{\mathcal{K}\mathcal{A}}{\delta\, T_{surr}^2}\right)(T_o - T_{surr})^2\, e^{-\frac{2\mathcal{K}\mathcal{A}}{\delta C_P} t} \qquad \text{(near-equilibrium, cst. V)} \quad 22.1.7$$

This result combines the thermodynamic driving force and the energy flux, Figure 22.1.1.



(a). (b).

Figure 22.1.1: (a). Entropy production for cooling a 200 mL cup of coffee. The initial temperature is $T_o = 310$ K, the surroundings are at $T_{surr} = 298$ K, the thermal conductivity of borosilicate glass is $\mathcal{K} = 1.14\ \text{J s}^{-1}\ \text{K}^{-1}\ \text{m}^{-1}$, the cross sectional area of a coffee cup is $\mathcal{A} = 0.015\ \text{m}^2$ and the glass thickness is $\delta = 3$ mm. (b). The total entropy is maximized.

The entropy production is positive for a spontaneous process and the total entropy is maximized. The entropy production is zero at equilibrium. Correspondingly, for flowing systems near equilibrium, the entropy production is minimized for a system at steady-state.[1] Eq. 22.1.1 is even more insightful when extended to chemical reactions.

Chemical Potential Gradients Drive Chemical Reactions: For a closed system with chemical reactions, the entropy change caused by the reaction is given by adding the chemical work terms from Eqs. 15.1.2 and 15.3.9 into Eq. 13.5.5 to give:

$$dS_{tot} = \frac{\text{đ}q}{T} + \left(\frac{P - P_{ext}}{T}\right) dV - \frac{1}{T} \sum_{i=1}^{n_s} \nu_i \, \mu_i \, d\xi \qquad \text{(closed)} \qquad 22.1.8$$

For example, the simple reaction $A \rightleftarrows B$ gives:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) \frac{\text{đ}q}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) \frac{dV}{dt} - \frac{\mu_B - \mu_A}{T} \frac{d\xi}{dt} \qquad \text{(closed)} \qquad 22.1.9$$

The chemical potential gradient is $(\mu_B - \mu_A)$. If the chemical potential of the products is less than the reactants, a favorable chemical potential gradient drives the reaction in the forward direction. Assuming a first-order process in both directions, the reaction progresses according to $(1/V)\, d\xi/dt = k_f\,[A] - k_r\,[B]$. The chemical reaction produces entropy. If the reactants or products are ionic species and an electric potential gradient is present, the electrochemical potentials are used in place of the chemical potentials. The electrochemical potential gradient gives the thermodynamic impetus for the process and the chemical kinetics determine the rate of progress to equilibrium. The rate of entropy production depends on the chemical gradient and the reaction rate. Both the thermodynamic driving force and favorable kinetics are necessary for the reaction to progress.

Chemical potential gradients are conveniently illustrated using Frost diagrams, Chapt. 21.4. For many energy applications and for biological systems the Frost diagram for carbon is central, Figure 22.1.2. Acetaldehyde, CH_2O, and glucose, $(CH_2O)_6$, have the same empirical formula. Cell potentials and chemical potentials for acetaldehyde are representative of glucose and glucose polymers, on a per carbon atom basis. Similarly, formic acid, HCOOH, and methanol, CH_3OH, are representative of organic acids and alcohols, respectively, on a per carbon atom basis. Reaction progress in the direction of decreasing chemical potential is necessary for a spontaneous process. The larger the decrease, the larger is the chemical potential gradient. Photosynthesis converts CO_2 to carbohydrates and carbohydrates are converted over geological time to hydrocarbons. The extreme stability of CO_2 helps to produce favorable chemical potential gradients for the combustion of hydrocarbons and carbohydrates. Conversely, the production of carbohydrates is energy intensive because of the extreme stability of CO_2. In addition, the sequestration of CO_2 in any other form than liquid or supercritical CO_2 is also energy intensive. The chemical potential gradients from carbohydrates to CO_2 drive the vast majority of biological and industrial processes.

Notice that the entropy production is defined in terms of heat transfers, $\text{đ}q$, volume changes, dV, and changes in the moles of all species. The changes in moles of each reactant and product are determined using the extent of the chemical reaction, $dn_i = \nu_i d\xi$. These changes are well defined for non-equilibrium systems. The entropy production does not require the determination of any thermodynamic state functions that are only defined for equilibrium systems.

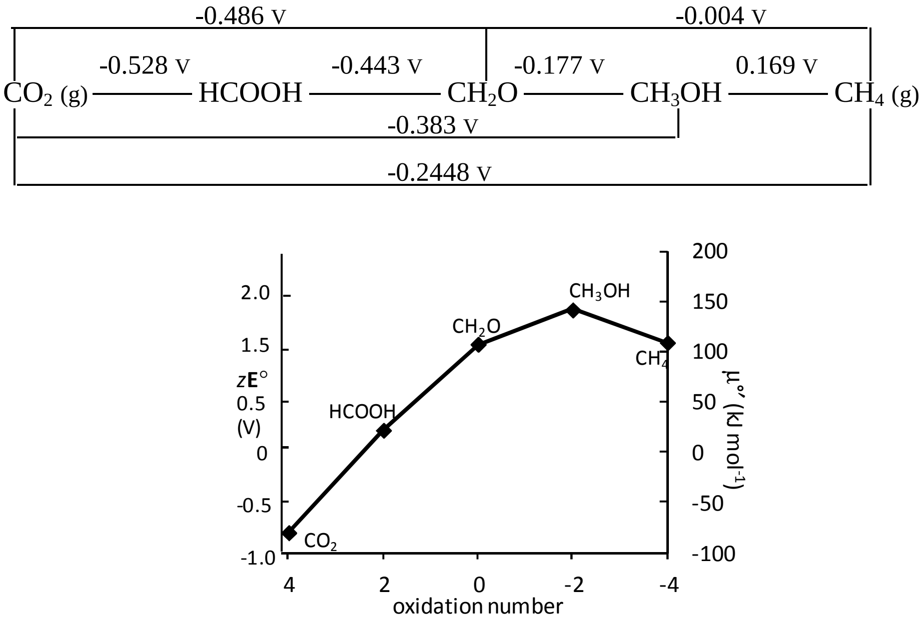


Figure 22.1.2: Latimer and Frost diagrams for carbon in aqueous solution at pH 7. See Problems 21.40 and 21.41 for the construction of this diagram. The energy axes are referenced to elemental carbon, graphite.

Entropy Production is Localized in the System: The total entropy of the system and surroundings, S_{tot}, always increases for a spontaneous process. If the process is reversible, the total entropy change is zero; the entropy change of the system is exactly compensated by the entropy change of the surroundings. All transfers of heat to the surroundings are reversible. For a reversible process in the system, the entropy changes cancel because both system and surroundings heat transfers are reversible. For an irreversible process, the increase in entropy of the system is not completely compensated by the change in entropy of the surroundings. The entropy change of the surroundings is reversible, so the source of the irreversibility must be in the system. As a consequence, the total entropy increase is localized in the system. The rate of change of total entropy in Eq. 22.1.9 is usually written as d_iS/dt to emphasize this point, where d_iS is the irreversible component of the entropy change for the system.

Consider Example 13.7.2 for an irreversible isothermal expansion. When the volume doubles against one bar external pressure for one mole of ideal gas at 298 K, the entropy change of the system is 5.76 J K^{-1} and the entropy change of the surroundings is $dS_{surr} = – dq/T = -0.335$ J K^{-1}. Part of the entropy change of the system is compensated by the entropy change of the surroundings, but not all. If the process is instead reversible, the entropy change of the system remains the same, but the entropy change of the surroundings becomes $dS_{surr} = -dq_{rev}/T = – dS$. The entropy change of the system is completely compensated by the entropy change of the surroundings. Even though the entropy change for the surroundings is different between the irreversible and reversible process, the irreversibility is localized in the system. Monitoring the reversible entropy change of the surroundings tells us what is happening in the system.

22.2 Entropy Production for Chemical Reactions is a Flux-Force Relationship

Assume a closed system is held at constant temperature and pressure by contact with the surroundings; for a spontaneous process Eq. 22.1.8 reduces to:

$$\frac{d_iS}{dt} = -\frac{1}{T}\sum_{i=1}^{n_s} \nu_i\, \mu_i \frac{d\xi}{dt} > 0 \qquad \text{(closed, cst. T\&P)} \quad 22.2.1$$

For the general chemical reaction aA + bB → cC + dD the sum is explicitly:

$$\frac{d_iS}{dt} = -\frac{1}{T}(c\mu_C + d\mu_D - a\mu_A - b\mu_B)\frac{d\xi}{dt} > 0 \qquad \text{(closed, cst. T\&P)} \quad 22.2.2$$

The chemical potential term is the thermodynamic force, which is the chemical potential gradient for the reaction. At equilibrium, the chemical potential term gives the reaction Gibbs energy, $\Delta_rG = (c\mu_c + d\mu_D - a\mu_A - b\mu_B)$, Eq. 20.1.5. The flux is $d\xi/dt$. For the reaction to progress as written, $d\xi$ must be greater than zero, $d\xi > 0$. The chemical potential gradient must then be negative for the reaction to be spontaneous in the forward direction. We assume local equilibrium so that the chemical potentials are well defined quantities. The chemical potentials are functions of the partial pressures, concentrations, or activities of each reactant and product using Eqs. 16.6.20° or 19.1.11. The chemical potential gradient can then be expressed in a parallel fashion as Eq. 20.1.15°:

$$(c\mu_C + d\mu_D - a\mu_A - b\mu_B) = RT \ln\frac{Q}{K} \qquad \text{with} \qquad Q = \left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right) \quad 22.2.3$$

The rate of the overall reaction can also be expressed as a function of the activities using detailed balance:

$$\frac{1}{V}\frac{d\xi}{dt} = \frac{1}{V}\frac{d(\xi - \xi_{eq})}{dt} = k_f\, a_A^a\, a_B^b - k_r\, a_C^c\, a_D^d \qquad \text{with } K = k_f/k_r \quad 22.2.4$$

This equation also applies to any step in a mechanism. The activities are given in terms of the extent by Eq. 3.1.4: $a_i = a_{io} + \nu_i\xi$, where a_{io} is the initial activity for species i. We denote the forward reaction rate as $\upsilon_f = k_f\, a_A^a\, a_B^b$ and the reverse reaction rate as $\upsilon_r = k_r\, a_C^c\, a_D^d$ giving the overall reaction rate as:

$$\frac{1}{V}\frac{d\xi}{dt} = \frac{1}{V}\frac{d(\xi - \xi_{eq})}{dt} = \upsilon_f - \upsilon_r \quad 22.2.5$$

Using the equilibrium constant, $K = k_f/k_r$, υ_f, and υ_r in Eq. 22.2.3 gives:

$$(c\mu_c + d\mu_D - a\mu_A - b\mu_B) = RT \ln\left(\frac{k_r\, a_C^c\, a_D^d}{k_f\, a_A^a\, a_B^b}\right) = -RT \ln \upsilon_f/\upsilon_r \quad 22.2.6$$

Substituting Eqs. 22.2.5 and 22.2.6 into Eq. 22.2.2 gives for a spontaneous process:

$$\frac{d_iS}{dt} = VR\,(\upsilon_f - \upsilon_r) \ln \upsilon_f/\upsilon_r > 0 \qquad \text{(closed, cst. T\&P)} \quad 22.2.7$$

At the beginning of the reaction the reverse rate is small, which makes the entropy production large and positive. At equilibrium, the forward and reverse reaction rates are equal and the entropy production is zero. This equation for the entropy production highlights the amazing similarity of Eqs. 22.2.7 and 12.4.24°, which has the general form ($p_i \ln p_i$).

The extent of the reaction, assuming the reaction is close to equilibrium, is given by Eq. 3.6.11, where the relaxation time is a combination of the forward and reverse rate constants for the specific stoichiometry of the reaction. Substituting Eqs. 22.2.6 and 3.6.11 into Eq. 22.2.2 gives:

$$\frac{d_iS}{dt} = VR\,\frac{(\xi - \xi_{eq})}{\tau}\ln\left(\frac{k_f\,(a_{ao} - a\xi)^a\,(a_{bo} - b\xi)^b}{k_r\,(a_{Co} - c\xi)^c\,(a_{Do} - d\xi)^d}\right) \qquad \text{(closed, cst.T\&P)} \qquad 22.2.8$$

For example, for the mechanistic step $A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C + D$:

$$1/\tau = k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq}) \qquad \text{(Chapt.3 Problem 30)} \quad 22.2.9$$

and neglecting activity coefficients, the entropy production is, Figure 22.2.1:

$$\frac{d_iS}{dt} = VR\,\frac{(\xi - \xi_{eq})}{\tau}\ln\left[\frac{k_f\,([A]_o - \xi)\,([B]_o - \xi)}{k_r\,([C]_o - \xi)\,([D]_o - \xi)}\right] \qquad \text{with} \quad (\xi - \xi_{eq}) = (\xi_o - \xi_{eq})e^{-t/\tau}$$

$$\text{(closed, cst.T\&P)} \qquad 22.2.10$$

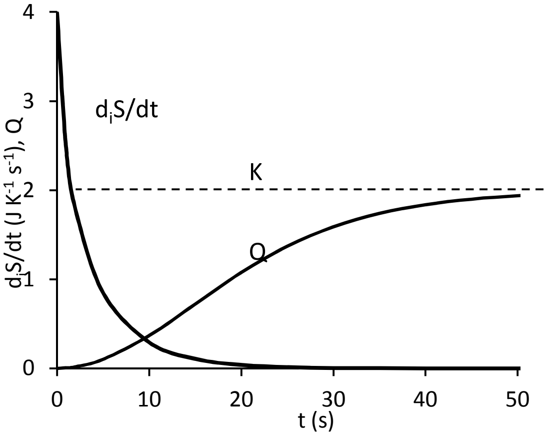


Figure 22.2.1: Entropy production for the reaction $A + B \rightleftarrows C + D$ with $k_f = 0.10\ L\ mol^{-1}s^{-1}$ and $k_r = 0.05\ L\ mol^{-1}s^{-1}$ giving $K = k_f/k_r = 2$ and $\tau = 10$ s. Entropy production at equilibrium is zero.

The system runs "downhill" on the chemical potential gradient and approaches equilibrium exponentially with a time constant τ. At equilibrium $\upsilon_f = \upsilon_r$, $Q = K$, and the entropy production is zero.

22.3 Summary – Looking Ahead

For systems close to equilibrium, the temperature, pressure, and chemical potential may be defined locally and vary as a function of time. The production of entropy is localized in the system and is a function of the heat transfer, the volume change, and the change in moles of all species. The entropy production is defined for irreversible processes in terms of readily measurable quantities and is not a function of thermodynamic state functions such as dU, dH, or dG. The result is called linear non-equilibrium thermodynamics. The chemical potential plays a general role in linear non-equilibrium systems. The chemical potential is defined through $dU = \text{đ}q + \text{đ}w + \Sigma\, \mu_i dn_i$ and is assumed to apply to irreversible as well as equilibrium systems. The entropy production for a spontaneous process is always positive. The entropy production is determined through the products of the thermodynamic forces and fluxes. The thermodynamic force for heat transfer is the temperature gradient. The thermodynamic force for PV work is the pressure gradient, and the thermodynamic force for matter transfer is the chemical potential gradient. A spontaneous process will not occur without a favorable gradient and flux. Chemical reactions provide the matter flux in closed systems. Entropy is maximized in a spontaneous process and entropy production is minimized.

The development of Eqs. 22.2.7 and 22.2.8 provide a unified thermodynamic and kinetic description of the behavior of the system. Entropy production provides a spontaneity criterion that is generally predictive for non-equilibrium systems. The focus on entropy production incorporates the interactions of the system with its surroundings. The interrelationship of the system and surroundings must be understood to predict the behavior of chemical processes. Pedigogically, the combination of thermodynamic and kinetic principles is a useful summary and review of the material we have covered so far.

We have barely scratched the surface on the theory of irreversible processes. The techniques developed in this chapter become more powerful when considering fluxes of many types, including electrical current and mass diffusion as well as heat flux, PV-work, and chemical reactions. The theory of systems near and far from equilibrium is an important current research area. Energy production, biogeoenvironmental chemistry, nanotechnology, and theoretical biology are important and very active application areas for non-equilibrium theory development.[3]

Non-equilibrium theories require important experimental parameters, including rate constants, equilibrium constants, and transport coefficients. To make further progress in understanding complex systems, theories that can calculate these parameters from first principles are necessary. Rate constants, equilibrium constants, and transport coefficients can only be determined using a molecular perspective. Our next concern is to develop the theory of the molecular world.

Summary

1. For systems close to equilibrium, the temperature, pressure, and chemical potential may be defined locally and vary as a function of time.
2. The production of entropy is localized in the system, d_iS.
3. The entropy production for a closed system with chemical reactions is:

$$d_iS = \frac{\text{đ}q}{T} + \left(\frac{P - P_{ext}}{T}\right) dV - \frac{1}{T}\sum_{i=1}^{n_s} \nu_i\, \mu_i\, d\xi$$

4. Entropy production is defined for irreversible processes in terms of readily measurable quantities and is not a function of thermodynamic state functions such as dU, dH, or dG.
5. The entropy production for a spontaneous process is always positive.
6. The entropy production for a flowing system is minimized in the steady state.

7. The entropy production is determined through the products of the thermodynamic forces and fluxes. The thermodynamic force for heat transfer is the temperature gradient. The thermodynamic force for PV work is the pressure gradient, and the thermodynamic force for matter transfer is the chemical potential gradient.
8. A spontaneous process will not occur without a favorable thermodynamic gradient and flux.
9. The entropy production for a closed system, held at constant temperature and pressure by contact with the surroundings, is:

$$\frac{d_iS}{dt} = -\frac{1}{T}\sum_{i=1}^{n_s} \nu_i\,\mu_i\,\frac{d\xi}{dt}$$

10. For a single mechanistic step or the overall reaction of the form aA + bB $\rightarrow$ cC + dD, the forward rate of the reaction as $\upsilon_f = k_f\, a_A^a\, a_B^b$ and the reverse reaction rate as $\upsilon_r = k_r\, a_C^c\, a_D^d$ giving the entropy production for a closed system at constant T and P as:

$$\frac{d_iS}{dt} = VR\,(\upsilon_f - \upsilon_r)\ln \upsilon_f/\upsilon_r > 0$$

11. For reactions of the form aA + bB $\rightarrow$ cC + dD, which are sufficiently close to equilibrium that chemical relaxation kinetics is applicable, the entropy production for a closed system at constant T and P is given as:

$$\frac{d_iS}{dt} = VR\,\frac{(\xi - \xi_{eq})}{\tau}\ln\left(\frac{k_f\,(a_{ao} - a\xi)^a\,(a_{bo} - b\xi)^b}{k_r\,(a_{Co} - c\xi)^c\,(a_{Do} - d\xi)^d}\right)$$

12. For a mechanistic step or overall stoichiometry $A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C + D$, the relaxation time is:

$$1/\tau = k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})$$

and neglecting activity coefficients, the entropy production for the corresponding closed system at constant T and P is:

$$\frac{d_iS}{dt} = VR\,\frac{(\xi - \xi_{eq})}{\tau}\ln\left(\frac{k_f\,([A]_o - \xi)\,([B]_o - \xi)}{k_r\,([C]_o - \xi)\,([D]_o - \xi)}\right) \qquad \text{with} \quad (\xi - \xi_{eq}) = (\xi_o - \xi_{eq})e^{-t/\tau}$$

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Problems

1. For a closed system and PV work only, describe why the second, lost-work term in Eq. 22.1.5 always gives the change in entropy production as greater than zero for an isothermal process (established by contact of the system with the surroundings acting as a constant temperature bath).

2. Reproduce Figure 22.1.1. Use the parameters in the caption and assume that the heat capacity of coffee is that of pure water. Assume a density of 1.00 g mL^{-1}.

3. Reproduce Figure 22.2.1. Use the parameters in the caption and $[A]_o = [B]_o = 0.98$ M, $[C]_o = [D]_o = 0.02$ M. Make your plot for $\xi_o = 0.02$ mol.

4. Calculate the entropy production for the mechanism:

$$A + B \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} C$$

with $k_2 = 0.10$ L $mol^{-1}s^{-1}$, $k_{-1} = 0.05$ L $mol^{-1}s^{-1}$, $[A]_o = [B]_o = 0.98$ M, $[C]_o = 0.02$. Assume $\xi_o = 0.02$ mol. Plot the results similarly to Figure 22.2.1.

5. With reference to Table 13.7.1, evaluate the entropy production for isothermal reversible, isothermal irreversible, adiabatic reversible, adiabatic irreversible, and a constant pressure expansion of an ideal gas. For the irreversible expansions, assume a constant external pressure, P_{ext}. Assume a closed system with no chemical reactions. In each case, specify the forces and fluxes that are zero in each case.

6. Find the entropy production for the photochemical reaction: $A \xrightarrow{j_B} B$, assuming an optically thin solution with quantum yield Φ_B. Eqs. 5.1.17 and 5.1.19 give the appropriate kinetic relationships. Assume the reaction is at constant temperature and pressure, through contact with the surroundings. Neglect the heat flow to the solution through thermal transfer from the light source (the rate of thermal transfer is proportional to $1 – \Phi_B$, but for this problem assume đq = 0).