

Entropy Analyses of Four Familiar Processes

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In an entropy analysis, spontaneous change in a physico-chemical process is traced to an increase in the *total* entropy of the system and its interacting surroundings. Such analyses are direct applications of the entropy principle, the second law of thermodynamics. In this paper we show how four such presentations can be made.

For processes occurring in closed systems at constant temperature and constant pressure accompanied only by P - V work, the standard criterion of spontaneous change is expressed by the Gibbs free energy function as

$$\Delta G_{T,P} < 0$$

Because $\Delta G_T = \Delta H - T\Delta S$, it is customary to discuss the contributions of energy minimization (ΔH) and of entropy maximization ($T\Delta S$) to an overall negative value for $\Delta G_{T,P}$ and hence to determining the direction of spontaneous change of a chemical process. Thus, although a role for the entropy function is admitted, it is a role in which the entropy change has been reexpressed in energy units and in which the entropy change of the system is seen in competition with the energy change of the system. However, as we shall emphasize in this paper, the total entropy change is a more fundamental and more general index of spontaneous change than is ΔG .

Laws of Thermodynamics

The second law of thermodynamics governs spontaneous change and equilibrium in all processes. This principle can be expressed as

$$\Delta S_{\text{tot}} = \Delta S_{\sigma} + \Delta S_{\theta} \geq 0 \quad (1)$$

and

$$\Delta S_{\theta} = \Delta H_{\theta}/T \quad (2)$$

where ΔS_{tot} is the *total* entropy change accompanying the process, ΔS_{σ} is the entropy change in the chemical or "reactive" system, and ΔS_{θ} is the entropy change of the thermal reservoir.¹ As indicated in eq 2, ΔS_{θ} can always be calculated from the enthalpy change of the thermal reservoir.² ΔS_{tot} is often designated as ΔS_{univ} , the entropy change of the "universe". What we are calling a thermal reservoir is more often called a "heat bath" or the "thermal surroundings". Commonly in thermodynamics, no subscript is used for variables that describe *the* (reactive) system itself. However, for discussions where we wish to distinguish the subsystems that make up an overall system, it is useful to have such subscripts. Sometimes "sys" is used instead of " σ ", and "surr" is used instead of " θ ". Thus, an equivalent expression to eq 1 is

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

The inequality sign applies to spontaneous processes, and the equals sign applies to equilibrium or reversible processes. *Displaying ΔS_{tot} and its component ΔS_i 's is what we mean by an entropy analysis.*

¹ Bent, H. A. *The Second Law*; Oxford: New York, 1965.

² Equation 2 is equivalent to the familiar expression, $\Delta S = Q_{\text{rev}}/T$, applied to a thermal reservoir. Under constant pressure conditions $Q_{\text{rev}} = \Delta H_{\theta}$ for the thermal reservoir.

The first law of thermodynamics is a bookkeeping relationship for energies exchanged between the reactive system and various parts of the surroundings. Since this law contains only an equals sign, energy is conserved and energy changes per se have nothing to do with the direction of spontaneous change. Indeed, the reverse of a spontaneous process that satisfies the first law (energy conserved) and the second law ($\Delta S_{\text{tot}} > 0$) is equally first-law satisfactory even though $\Delta S_{\text{tot}} < 0$. Energy changes may be of consequence for spontaneity insofar as they are associated with entropy changes in the thermal reservoir. An energy change in the reactive system may be balanced, in part, by work other than P - V work for which there is no entropy consequence in the surroundings.) For processes occurring under constant pressure for both the reactive system and the thermal reservoir and no work other than P - V work, the first law is

$$\Delta U_{\text{tot}} = \Delta U_{\sigma} + P_{\sigma}\Delta V_{\sigma} + \Delta U_{\theta} + P_{\theta}\Delta V_{\theta} = 0$$

which reduces to

$$\Delta H_{\sigma} + \Delta H_{\theta} = 0 \quad (3)$$

Furthermore, if the thermal reservoir is so large that its temperature and that of the reactive system change little, we have, from eqs 1 and 3,

$$\Delta S_{\theta} = \frac{\Delta H_{\theta}}{T} = -\frac{\Delta H_{\sigma}}{T} \quad (4)$$

Working Equation for Entropy Analyses; Relationship to the Gibbs Free Energy Function

Combining eqs 1 and 4 gives us the working equation for many entropy analyses and reveals a relationship between $\Delta G_{T,P}$ and ΔS_{tot} . The first equation is

$$\Delta S_{\text{tot}} = \Delta S_{\sigma} - \frac{\Delta H_{\sigma}}{T} \geq 0 \quad (5)$$

This expression applies under conditions of constant temperature and pressure, which are the common conditions for chemical applications. In general, ΔS_{σ} and ΔH_{σ} for a chemical reaction or a phase change are weak functions of temperature. Moreover, the residual temperature dependences of ΔS_{σ} and of ΔH_{σ} tend to cancel in eq 5. Thus, values of ΔS_{σ} and ΔH_{σ} at one temperature, typically 298 K, may be used in eq 5 over a range of temperature, provided the phases of all reactants and of all products remain unchanged. Often in our examples, we will omit the " σ " subscript on ΔH_{σ} and ΔS_{σ} . Superscript " \circ " and super-bar will remind us of the reactive system identification of these quantities.

A rearrangement of eq 5 shows how the Gibbs free energy function is ΔS_{tot} in disguise under certain conditions. Thus,

$$T\Delta S_{\text{tot}} = T\Delta S_{\sigma} - \Delta H_{\sigma} \geq 0$$

and

$$T\Delta S_{\text{tot}} = -\Delta G_{T,P} \geq 0$$

or

$$-T\Delta S_{\text{tot}} = \Delta G_{T,P} \leq 0$$

Consequently, a quick answer to the question, "what is ΔS_{tot} for a chemical reaction?", is that

$$\Delta S_{\text{tot}} = -\frac{\Delta G_{T,P}}{T}$$

for a process occurring in a closed system at constant temperature and pressure with no work effect other than P - V work. It is also worth noting that ΔS_{tot} is closely related to that important index of chemical reactivity, the equilibrium constant. Since $\Delta G^\circ = -RT \ln K$,

$$\Delta S_{\text{tot}} = R \ln K$$

Another noteworthy aspect of eq 5 is that $-\Delta H_\sigma/T$ is ΔS_θ , the entropy change in the thermal reservoir. For an exothermic reaction (ΔH_σ negative) the entropy change in the thermal reservoir is a positive contribution to ΔS_{tot} . For a given value of ΔH_σ the magnitude of this positive entropy change in the thermal reservoir increases as T decreases. That is why exothermic reactions are favored at low temperatures, not because of energy minimization per se.

Spontaneous change is always a matter of entropy maximization if we take account of all the entropy changes, as is natural for direct applications of the second law, which is cast in "global" (or "universe") terms. In contrast, the Gibbs free energy function is a "local," reactive-system-oriented function that has a direct relationship to the global quantity ΔS_{tot} when only P - V work may be done. Because of this limitation in the application of the Gibbs function to reactive systems, it is unnecessary to put the " σ " subscript on ΔG .

Many systems, such as open chemical systems, galvanic or electrolytic cells, or the interaction of light with matter, have worklike terms in addition to P - V work. For these more complicated systems or for an osmotic system in which pressure is not constant, the change in the Gibbs free energy function *alone* is not a proper measure of spontaneity. ΔS_{tot} always is, however. For example, for an electrochemical system,

$$\Delta S_{\text{tot}} = -\frac{\Delta G}{T} - \frac{\Delta U_{\text{elec}}}{T} \geq 0$$

where ΔU_{elec} is the change in energy in the electrical subsystem. This expression can be rewritten as

$$T\Delta S_{\text{tot}} = -\Delta G - \Delta U_{\text{elec}} \geq 0$$

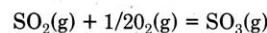
Thus, we see that the sum of ΔG and ΔU_{elec} must be considered as an alternative to ΔS_{tot} in this case. For any system $T\Delta S_{\text{tot}}$ reflects the high-quality, work-type energy that is degraded into low-quality, heat-type energy in a spontaneous process. Bent has called this "work wasted."³

Entropy Analyses

In the remainder of the paper we consider entropy analyses of four examples selected from processes of general interest in chemical science. A prototypical entropy analysis for the melting or freezing of water and, in particular, a consideration of how the spontaneous direction of this phase transition reverses at 0 °C can be found in the *The Second Law*.¹ An entropy analysis of a chemical reaction of ideal gases occurring under equilibrium conditions can be found in the same source. In addition, Rioux has presented a discussion of the entropy contributions for various colligative properties.⁴ We begin our series of examples with an entropy analysis of a chemical reaction under nonequilibrium conditions.

1. Chemical Reaction

For the reaction



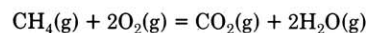
the standard enthalpy change at 298 K is $\Delta \bar{H}^\circ_{298} = -98.9$ kJ/mol rxn, and standard entropy change is $\Delta \bar{S}^\circ_{298} = -94.1$ J/K-mol rxn. From eqs 1 and 5 we have

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_\sigma + \Delta S_\theta = \Delta S_\sigma - \frac{\Delta H_\sigma}{T} = \Delta \bar{S}^\circ_{298} - \frac{\Delta \bar{H}^\circ_{298}}{298 \text{ K}} \\ &= -94.1 + 331.9 = 237.8 \text{ J/K-mol rxn} \end{aligned}$$

At 298 K, ΔS_{tot} is substantially greater than zero due to the large entropy increase in the thermal reservoir, which offsets the entropy decrease in the reactive system. Thus, SO_3 is the more stable oxide at low temperatures. At high temperatures, however, such as those in a flame of burning sulfur, the entropy change in the thermal reservoir, which depends inversely on the absolute temperature, is decreased to the point where $|\Delta S_\theta| < |\Delta S_\sigma|$. Consequently, $\Delta S_{\text{tot}} < 0$ for the reaction as written. Thus, the reaction in reverse is favored. SO_2 is more stable than SO_3 under these conditions. This entropy analysis of the relative stabilities of SO_2 and SO_3 is consistent with the chemistry of acid rain and the manufacture of sulfuric acid. In both cases, SO_2 , the primary product of sulfur burning, is converted to SO_3 at lower temperatures under catalytic conditions. In each temperature regime the formation of some of the favored product is accompanied by an increase in the total entropy.

2. Heat Engine

We examine an overall heat engine system in which the thermal energy is supplied to the high-temperature reservoir by a fuel-burning reaction such as



For this reaction $\Delta \bar{H}^\circ_{298} = -802.3$ kJ/mol rxn, and $\Delta \bar{S}^\circ_{298} = -5.1$ J/K-mol rxn. Figure 1 is a diagram of the essentials of the heat engine and the associated energy-supplying chemi-

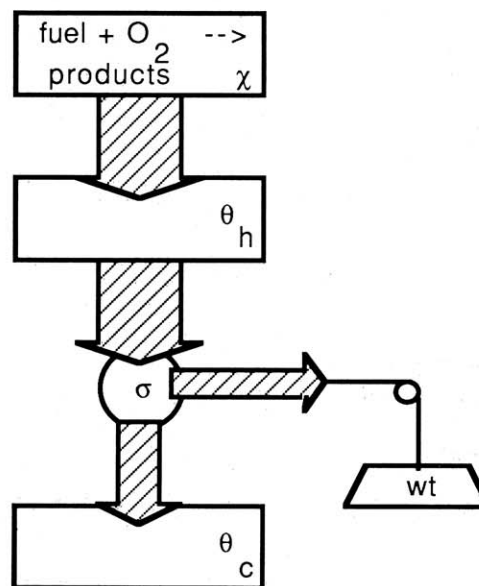


Figure 1. Essentials of a heat engine. A chemical reaction system (χ) supplies energy to the high temperature thermal reservoir (θ_h). Part of the thermal energy that flows into the energy converter (σ) goes to the low temperature thermal reservoir (θ_c), and the rest becomes mechanical energy, as represented by the weight in the gravitational field. Widths of the arrows signify the magnitudes of the energy flows.

³ Bent, H. A. ACS Audio Course, *Chemical Thermodynamics*; American Chemical Society: Washington, 1981.

⁴ Rioux, F. J. *Chem. Educ.* **1973**, *50*, 490-492.

cal reaction. The engine itself consists of several subsystems: a high-temperature (T_h) thermal reservoir, a low-temperature (T_c) thermal reservoir, a mechanical energy subsystem (wt, represented by a mass in the gravitational field), and an energy coupling device, which can be called a reactive system (σ). The arrows point in the directions of energy flows, and the widths of the arrows indicate the magnitudes of the energy flows. Changes associated with the chemical reaction are designated with the subscript "x".

For the overall heat engine system, which includes two thermal reservoirs and two reactive systems, eq 1 has to be elaborated.

Thus,

$$\Delta S_{\text{tot}} = \Delta S_x + \Delta S_{\theta h} + \Delta S_{\theta c} + \Delta S_\sigma$$

from which ΔS_{wt} has been omitted since this term is always zero. During each cycle of the heat engine the entropy and the energy of the coupling mechanism are restored to initial values. Thus, $\Delta S_\sigma = 0$ and $\Delta H_\sigma = 0$. Also, $\Delta S_{\theta h} = 0$, because the increase in entropy in the thermal reservoir due to energy released from the chemical reaction is balanced by the decrease in entropy due to energy transferred into the energy coupler. The expression for ΔS_{tot} reduces to

$$\Delta S_{\text{tot}} = \Delta S_x + \Delta S_{\theta c}$$

or

$$\Delta S_{\text{tot}} = \Delta S_x + \frac{\Delta H_{\theta c}}{T_c} \quad (6)$$

with the use of eq. 2. The overall first-law expression is

$$\Delta U_{\text{tot}} = \Delta H_x + \Delta H_{\theta h} + \Delta H_\sigma + \Delta H_{\theta c} + \Delta U_{\text{wt}} = 0$$

where ΔU_{wt} is the energy change of the weight in the gravitational field. This first law expression reduces to

$$\Delta H_x + \Delta H_{\theta c} + \Delta U_{\text{wt}} = 0 \quad (7)$$

since $\Delta H_{\theta h} = \Delta H_\sigma = 0$. When the expression for $\Delta H_{\theta c}$ from eq 7 is substituted into eq 6, we have⁵

$$\Delta S_{\text{tot}} = \Delta S_x - \frac{\Delta H_x}{T_c} - \frac{\Delta U_{\text{wt}}}{T_c} \quad (8)$$

If the heat engine *itself* operates at the reversible limit, this equation may be rewritten as

$$\Delta S_{\text{tot}} = \Delta S_x - \frac{\Delta H_x}{T_h}$$

Under these conditions all the entropy production is due to the fuel-burning reaction.

When the methane-burning reaction is used to make steam at 100 °C, as in a classic steam engine,

$$\Delta S_{\text{tot}} = \Delta S^\circ_{298} - \frac{\Delta \bar{H}^\circ_{298}}{373 \text{ K}} = -5 + 2151 = 2146 \text{ J/K}\cdot\text{mol rxn}$$

Entropy production is huge. Consequently, the use of methane fuel in this way is enormously wasteful of the potential of the chemical reaction energy even when the heat engine mechanism itself runs at the reversible limit. If $T_c = 300 \text{ K}$, at best only 20% of the enthalpy of reaction is converted into useful mechanical energy.⁶ Consider a T_h of 800 K, as can be achieved in a modern steam turbine. Then,

$$\Delta S_{\text{tot}} = -5 \text{ J/K}\cdot\text{mol rxn} - \frac{(-802.3 \text{ kJ/mol rxn})}{800 \text{ K}} = 998 \text{ J/K}\cdot\text{mol rxn}$$

an entropy production that is much smaller than at 298 K. Because of the larger difference between T_h and T_c , a larger fraction (47%) of ΔH_x is converted into useful mechanical energy. Raising the temperature T_h even higher, as in a possible magnetohydrodynamic system, would further re-

duce the wasteful entropy production and increase the conversion of ΔH_x into mechanical energy.

Consideration of a modified form of eq 8 shows that ΔS_{tot} reflects the "work wasted" or amount of potentially useful energy that is degraded into thermal energy. Thus,

$$T_c \Delta S_{\text{tot}} = T_c \Delta S_x - \Delta H_x - \Delta U_{\text{wt}}$$

The useful energy available from the fuel-burning reaction is $-\Delta H_x + T_c \Delta S_x$, which equals $-\Delta G_x$. This amount of energy less the amount transformed into weight-lifted energy, ΔU_{wt} , is the amount of useful energy that is wasted.

3. Dissolution of a Solid in an Ideal Solvent

For the example of dissolving a solid in an ideal solvent we consider two cases. One is a finite change in which a solution forms between n_A moles of A, the liquid solvent, and n_B moles of B, the solid solute. The other case is the incremental change that occurs when a differential amount of the solid, dn_B , dissolves in a solution of mole fraction X_B . For simplicity we restrict the discussion to an ideal solution in which $\Delta H_{\text{mix}} = 0$ and $\Delta S_{\text{mix}} = -R \sum n_i \ln X_i$ for the liquid form of B dissolving in liquid A.

a. Finite Change

We can break down the dissolution process into two steps: the melting of pure solute B followed by the mixing of liquid solute B and solvent A. The melting step is accompanied by a net entropy decrease. The mixing step is accompanied by an entropy increase, which may be sufficient to offset the entropy decrease of the first step. For the melting step

$$n_B \text{B(c)} = n_B \text{B(l)}$$

we have

$$\Delta S_{\text{tot(melt)}} = \underbrace{-n_B \frac{\Delta \bar{H}^\circ_{\text{melt}}}{T}}_{(-)} + \underbrace{n_B \Delta \bar{S}^\circ_{\text{melt}}}_{(+)} < 0$$

where typical signs and magnitudes (repetition of sign) for the whole terms are indicated above the terms. For the mixing step

$$n_A \text{A(l)} + n_B \text{B(l)} = n_A \text{A}, n_B \text{B(sol)}$$

we have

$$\Delta S_{\text{tot(mix)}} = -R n_A \ln X_A - R n_B \ln X_B > 0$$

The overall entropy change is

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_{\text{tot(melt)}} + \Delta S_{\text{tot(mix)}} \\ &= n_B \left(-\frac{\Delta \bar{H}^\circ_{\text{melt}}}{T} + \Delta \bar{S}^\circ_{\text{melt}} \right) - R n_A \ln X_A - R n_B \ln X_B \quad (9) \end{aligned}$$

Figure 2 is a graph of $\Delta S_{\text{tot}}/n_A$ versus n_B/n_A . The maximum in the curve represents solubility equilibrium at a given

⁵ Equation 8 cannot be set equal to zero in order to define the limits on efficiency of energy conversion in terms of the standard measure, $\Delta U_{\text{wt}}/(-\Delta H_x)$. The overall process is not reversible. The fuel-burning chemical reaction takes place quite irreversibly even though the heat engine itself operates near the reversible limit. For the heat engine (HE) *itself* operating reversibly,

$$\begin{aligned} \Delta S_{\text{tot(HE)}} &= \frac{\Delta S_{\theta h(\text{HE})}}{T_h} + \frac{\Delta S_{\theta c}}{T_c} = \frac{\Delta H_{\theta h(\text{HE})}}{T_h} + \frac{\Delta H_{\theta c}}{T_c} = \frac{\Delta H_x}{T_h} \\ &\quad - \frac{\Delta U_{\text{wt}}}{T_c} - \frac{\Delta H_x}{T_c} = 0 \end{aligned}$$

⁶ Computed from the well-known expression for the efficiency of a heat engine, $\text{eff} = (T_h - T_c)/T_h$. This expression can be derived by an entropy analysis.¹

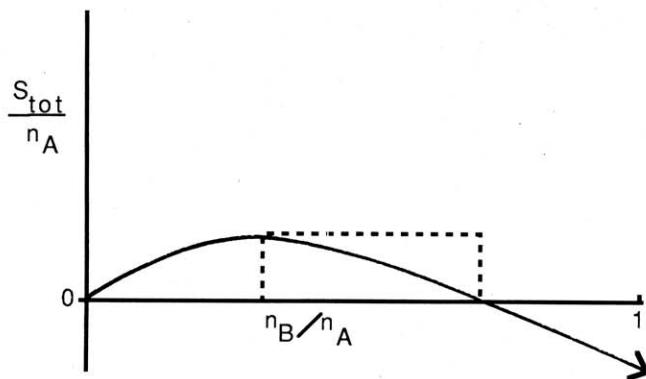
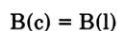


Figure 2. Dependence of the total entropy change per mole of solvent A on the moles of solute B per mole of solvent. As n_B/n_A goes to infinity, $\Delta S_{\text{tot}}/n_A$ goes to minus infinity.

temperature. We see that $\Delta S_{\text{tot}}/n_A$ for the finite process is positive not only for increasingly concentrated solutions leading up to the maximum value of $\Delta S_{\text{tot}}/n_A$ but even for compositions beyond. However, the states shown in the dashed-line box cannot be reached directly by mixing solid B and liquid A. Beyond the maximum, $\Delta S_{\text{tot}}/n_A$ due to incremental additions of B would be negative. For the finite mixing process, as n_B/n_A approaches infinity, $\Delta S_{\text{tot}}/n_A$ goes to minus infinity due to the negative value of $\Delta S_{\text{tot(melt)}}$ that characterizes the (hypothetical) melting of an infinite amount of pure B at the temperature of interest. In Figure 2 the curve has been arbitrarily cut off at $n_B/n_A = 1$, the melting term contributes $-\Delta\bar{H}^{\circ}_{\text{melt}}/T + \Delta\bar{S}^{\circ}_{\text{melt}}$ and the mixing term contributes $2R \ln 2$ for what is typically a negative total. As n_B/n_A decreases, the positive entropy contribution of mixing the two liquids outweighs the negative entropy of melting. As the zero value of n_B/n_A is approached, the entropy of mixing and the entropy of melting approach zero because the amount of liquid B being mixed with a mole of A approaches zero.

b. Differential Change

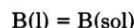
To find directly the equilibrium state of a saturated solution of solute B in solvent A, we employ the differential change in ΔS_{tot} as an increment of solute B dissolves in a solution of fixed amount of A. Alternatively, this process can be viewed as the dissolution of one mole of solid B in such a large quantity of solution that the concentration of the solution is unchanged. "Chemical" equations for this two-step differential analysis differ from those used in Part a for the finite change. The equations for the differential analysis are



for which

$$\Delta\bar{S}_{\text{tot(melt)}} = -\frac{\Delta\bar{H}^{\circ}_{\text{melt}}}{T} + \Delta\bar{S}^{\circ}_{\text{melt}}$$

and



for which

$$\Delta\bar{S}_{\text{tot(mix)}} = -R \ln X_B \quad (10)$$

We have used the super-bar designation on the $\Delta\bar{S}_{\text{tot}}$ terms in this context in order to stress that they are equivalent to differential quantities and would be if multiplied by dn_A . (Logically, we should have used the super-bar symbolism for $\Delta\bar{S}_{\text{tot}}$ for the chemical reactions in Examples 1 and 2 as we did for $\Delta\bar{S}^{\circ}$ and $\Delta\bar{H}^{\circ}$.)⁷ The overall expression for the entropy change is

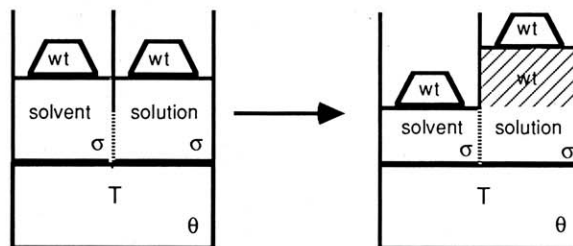


Figure 3. Osmosis. The transfer of solvent through a semipermeable membrane into a solution phase upon which an added pressure acts. Typically, the additional pressure is due to a column of solution phase, as shown in cross-hatching.

$$\begin{aligned} \Delta\bar{S}_{\text{tot}} &= \Delta\bar{S}_{\text{tot(melt)}} + \Delta\bar{S}_{\text{tot(mix)}} \\ &= \frac{-\Delta\bar{H}^{\circ}_{\text{melt}}}{T} + \Delta\bar{S}^{\circ}_{\text{melt}} - R \ln X_B \end{aligned}$$

We emphasize that the solvent is not in these equations for the differential change. The state of the solvent is unchanged when a differential amount of solute B melts and dissolves in the solution.

Another way to obtain the differential expression and impose the equilibrium conditions is to differentiate eq 9. Thus,^{8,9}

$$\Delta\bar{S}_{\text{tot}} = \left(\frac{\partial \Delta S_{\text{tot}}}{\partial n_B} \right)_{T,P,n_A} = \frac{-\Delta\bar{H}^{\circ}_{\text{melt}}}{T} + \Delta\bar{S}^{\circ}_{\text{melt}} - R \ln X_B$$

For equilibrium

$$\frac{-\Delta\bar{H}^{\circ}_{\text{melt}}}{T} + \Delta\bar{S}^{\circ}_{\text{melt}} - R \ln X_B = 0 \quad (11)$$

a result that is the same as above and that corresponds to the maximum in the curve of $\Delta\bar{S}_{\text{tot}}/n_A$ versus n_B/n_A as shown in Figure 2. This result for equilibrium is also the same as that obtained from the thermodynamics of general material equilibrium in which

$$-RT \ln K_X = \Delta\bar{G}^{\circ}_{\text{melt}} = \Delta\bar{H}^{\circ}_{\text{melt}} - T\Delta\bar{S}^{\circ}_{\text{melt}}$$

wherein $K_X = X_B$.

4. Osmosis

As a fourth example of an entropy analysis, we consider osmosis.¹⁰ In osmosis, pure solvent passes through a semipermeable membrane into a solution phase until equilibrium is obtained through the imposition of an excess pressure, the osmotic pressure, on the solution phase. Often this excess pressure is due to a column of the solution phase that has risen in the gravitational field. Figure 3 shows the essentials of the process of osmosis for a finite transfer of solvent into the solution phase and a rise of part of the solution phase in the gravitational field.

To do an entropy analysis of osmosis we must investigate how the transfer of solvent into the higher pressure region of

⁷ Craig, N. C. *J. Chem. Educ.* **1987**, *64*, 668.

⁸ $\Delta\bar{H}^{\circ} \equiv (\partial H/\partial \xi)_{T,P}$ and $\Delta\bar{S}^{\circ} \equiv (\partial S/\partial \xi)_{T,P}$ where ξ is the degree-of-advancement variable for a chemical reaction.

⁹ With the aid of $(\partial X_A/\partial n_B)_{n_A} = -X_A^2/n_A$ and $(\partial X_B/\partial n_B)_{n_A} = X_B X_B/n_B$.

¹⁰ My interest in the entropy analysis of osmosis arose in the summer of 1983 at the Camille and Henry Dreyfus/Woodrow Wilson Summer Institute for High School Chemistry Teachers. Walking under the tall trees on the Princeton University campus, I was stimulated to think about osmosis and to add an entropy analysis of this process to the other examples I had shown the participants.

the solution phase is accompanied by an entropy change. Thus, a consideration beyond that used in analyzing the solubility problem is needed. For added generality we shall also illustrate the use of nonideal solution theory. For the finite change process specifically illustrated in Figure 3 we shall be content with a qualitative discussion.

At constant temperature, the energy for lifting liquid in the gravitational field comes from the thermal reservoir. This energy decrease in the thermal reservoir is accompanied by an entropy decrease. We designate this entropy change as $\Delta S_{\theta(wt)}$ in order to distinguish it from another component of ΔS_{θ} due to an exchange of energy with the reactive system. The transfer of solvent into the solution phase is accompanied by an entropy increase in the reactive system, ΔS_{σ} , due to the dilution process. Because this transfer is accompanied by a ΔH_{σ} energy term for the nonideal solution, a second contribution to ΔS_{θ} is

$$\Delta S_{\theta(\sigma)} = \frac{-\Delta H_{\sigma}}{T}$$

The total entropy change is

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_{\sigma} + \Delta S_{\theta(\sigma)} + \Delta S_{\theta(wt)} \\ &\quad (++) \quad (\pm) \quad (-) \\ &= \Delta S_{\sigma} - \frac{\Delta H_{\sigma}}{T} + \Delta S_{\theta(wt)} > 0 \end{aligned} \quad (12)$$

Typical signs for the terms are indicated above the terms. The large, positive entropy change due to dilution of the solvent is the essential positive entropy contribution for this finite change process.

Osmosis proceeding toward equilibrium is an example of a process for which ΔG_T alone is not a proper index of spontaneity. The reason for this failure is that pressure does not remain constant during the process of transfer of solvent from its pure phase at P to the solution phase at $P + \Delta P$. Equation 12 can be reexpressed in terms of ΔG_T to give

$$\Delta S_{\text{tot}} = \frac{-\Delta G}{T} + \Delta S_{\theta(wt)} > 0$$

or

$$T\Delta S_{\text{tot}} = -\Delta G + T\Delta S_{\theta(wt)} > 0$$

Thus, the sum of $-\Delta G + T\Delta S_{\theta(wt)}$ serves as an alternative index of spontaneity for osmotic processes.

We turn now to an entropy analysis of the differential process for the osmotic effect with particular emphasis on the condition for equilibrium. The change in Figure 3 must be an incremental one to be appropriate to the present analysis. An increment of the solvent moves from the pure solvent phase into the solution phase, where this increment must lift the weight that causes the added pressure. At equilibrium this added pressure is the osmotic pressure, Π . The added weight, which contributes to the pressure, can be viewed as due to a part of the solution that has risen in the gravitational field, as the figure suggests. Alternatively, the added weight is just that. The terms that contribute to the incremental change in the total entropy are of the same origin as those considered in the analysis of the finite change,

$$\Delta \bar{S}_{\text{tot}} = \Delta \bar{S}_{\sigma} + \Delta \bar{S}_{\theta(\sigma)} + \Delta \bar{S}_{\theta(wt)} \quad (13)$$

The super-bar designations emphasize that eq 13 applies to a differential change. The difference in mechanical energy needed to reduce the volume of solvent at pressure P and increase the volume of solution at pressure $P + \Pi$ comes from the thermal reservoir.⁴ The expression for this mechan-

ical energy (work) is $\Pi \bar{V}_A$, where \bar{V}_A is the partial molar volume of the solvent in the solution phase.¹¹ Thus, from a selective application of the first law, we have

$$\Pi \bar{V}_A + \Delta \bar{H}_{\theta(wt)} = 0$$

For $\Delta \bar{S}_{\theta(wt)}$ we have

$$\Delta \bar{S}_{\theta(wt)} = \frac{\Delta \bar{H}_{\theta(wt)}}{T} = -\frac{\Pi \bar{V}_A}{T} \quad (14)$$

Together the two σ terms in eq 13 are equal to $-R \ln a_A$. Thus,

$$\Delta \bar{S}_{\sigma} + \Delta \bar{S}_{\theta(\sigma)} = -R \ln a_A \quad (15)$$

where a_A is the activity of the solvent in the solution phase. Equation 15 for the transfer of pure liquid material into a nonideal solution is equivalent to eq 10 for an ideal solution. Only the solvent contributes to eqs 13 and 14 for the differential change, dn_A , occurring at constant n_B . When eqs 14 and 15 are substituted into eq 13, we have for osmotic equilibrium

$$\Delta \bar{S}_{\text{tot}} = -R \ln a_A - \frac{\Pi \bar{V}_A}{T} = 0 \quad (16)$$

Thus, the familiar expression for osmotic equilibrium,

$$RT \ln a_A = -\Pi \bar{V}_A$$

is seen to be closely related to the entropy changes that accompany an incremental transfer of the solvent component into the solution phase when an excess osmotic pressure Π acts on the solution phase.

If we recast eq 16 in energy units, we have

$$T\Delta \bar{S}_{\text{tot}} = -RT \ln a_A - \Pi \bar{V}_A = 0$$

or

$$T\Delta \bar{S}_{\text{tot}} = -\Delta \bar{G} - \Pi \bar{V}_A = 0$$

Once again, for this non-constant-pressure process, we see that ΔG alone is not a proper criterion of equilibrium (or spontaneous change).

Conclusion

By means of examples we have seen how entropy analyses can be applied to rather different but familiar physicochemical processes. Entropy analyses display the various entropy contributions to the overall entropy change, ΔS_{tot} . Such analyses are direct applications of the second law of thermodynamics and thereby provide a deeper understanding of a spontaneous process or of the equilibrium state than do standard treatments with the Gibbs function or the chemical potential. In addition, entropy analyses go beyond the limitations of the $\Delta G_{T,P}$ criterion for spontaneous change. Though apparently an energy criterion, $\Delta G_{T,P}$ succeeds because of its relationship to the entropy criterion, ΔS_{tot} , under certain conditions. For other conditions, heat engines and osmosis, for example, ΔG_T alone is not a proper index of spontaneity. ΔS_{tot} always is.

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¹¹ A term equal to $P(\bar{V}_A^* - \bar{V}_A)$ has been neglected, where \bar{V}_A^* is the molar volume of pure solvent.