Entropy and the Second Law of Thermodynamics

PROBLEMS AND SOLUTIONS

20–1. Show that

$$\oint dY = 0$$

if Y is a state function.

If Y is a state function, dY must be an exact differential. This means that $\int_1^2 dY = Y_2 - Y_1$ and $\int_2^1 dY = Y_1 - Y_2$. Then

$$\oint dY = \int_1^2 dY + \int_2^1 dY = Y_2 - Y_1 + (Y_1 - Y_2) = 0$$

20–2. Let $z = z(x, y)$ and $dz = xy dx + y^2 dy$. Although dz is not an exact differential (why not?), what combination of dz and x and/or y is an exact differential?

The quantity dz is not an exact differential because the coefficient of the dx term is not independent of y. An exact differential would be dz/y, because the coefficient of dx is independent of y and the coefficient of dy is independent of x in

$$\frac{dz}{y} = x dx + y dy$$

20–3. Use the criterion developed in MathChapter H to prove that δq_{rev} in Equation 20.1 is not an exact differential (see also Problem H–11).

We can write δq_{rev} as

$$\delta q_{\text{rev}} = C_V(T) dT + \frac{nRT}{V} dV \tag{20.1}$$

The cross-derivatives of an exact differential are equal, so we will find the cross derivatives of δq_{rev} to determine its nature. These are the coefficient of dT differentiated with respect to V and the coefficient of dV differentiated with respect to T, or

$$\frac{\partial C_V(T)}{\partial V} = 0 \quad \text{and} \quad \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V}$$

Because these two quantities are not equal, δq_{rev} is an inexact differential.

20–4. Use the criterion developed in MathChapter H to prove that $\delta q_{rev}/T$ in Equation 20.1 is an exact differential.

We use Equation 20.2 to express $\delta q_{rev}/T$ as

$$\frac{\delta q_{rev}}{T} = \frac{C_V(T)}{T}dT + \frac{nR}{V}dV$$

The cross-derivatives of an exact differential are equal, so we will find the cross derivatives of $\delta q_{rev}/T$ to determine its nature. These are the coefficient of dT differentiated with respect to V and the coefficient of dV differentiated with respect to T, or

$$\frac{\partial}{\partial V}\left(\frac{C_V(T)}{T}\right) = 0 \qquad \text{and} \qquad \frac{\partial}{\partial T}\left(\frac{nR}{V}\right) = 0$$

Because these two quantities are equal, $\delta q_{rev}/T$ is an exact differential.

20–5. In this problem, we will prove that Equation 20.5 is valid for an arbitrary system. To do this, consider an isolated system made up of two equilibrium subsystems, A and B, which are in thermal contact with each other; in other words, they can exchange energy as heat between themselves. Let subsystem A be an ideal gas and let subsystem B be arbitrary. Suppose now that an infinitesimal reversible process occurs in A accompanied by an exchange of energy as heat δq_{rev}(ideal). Simultaneously, another infinitesimal reversible process takes place in B accompanied by an exchange of energy as heat δq_{rev}(arbitrary). Because the composite system is isolated, the First Law requires that

$$\delta q_{rev}(\text{ideal}) = -\delta q_{rev}(\text{arbitrary})$$

Now use Equation 20.4 to prove that

$$\oint \frac{\delta q_{rev}(\text{arbitrary})}{T} = 0$$

Therefore, we can say that the definition given by Equation 20.4 holds for any system.

We use the First Law as suggested in the problem and substitute Equation 20.1 for δq_{rev}(ideal) to write

$$\delta q_{rev}(\text{arbitrary}) = -\delta q_{rev}(\text{ideal})$$

$$= -C_V(T)dT - \frac{nRT}{V}dV$$

$$\frac{\delta q_{rev}(\text{arbitrary})}{T} = \frac{-C_V}{T}dT - \frac{nR}{V}dV$$

$$= d\left[\int \frac{-C_V(T)}{T}dT - nR\int \frac{dV}{V} + \text{constant}\right]$$

Then δq_{rev}(arbitrary)$/T$ is the derivative of a state function. We know that the cyclic integral of a state function is equal to 0 (Problem 20–1). Therefore, we can write (as we did in Section 20–2 for ideal gases)

$$\oint \frac{\delta q_{rev}(\text{arbitrary})}{T} = 0$$

and Equation 20.4 holds for any system.

20–6. Calculate q_{rev} and ΔS for a reversible cooling of one mole of an ideal gas at a constant volume V_1 from P_1, V_1, T_1 to P_2, V_1, T_4 followed by a reversible expansion at constant pressure P_2 from P_2, V_1, T_4 to P_2, V_2, T_1 (the final state for all the processes shown in Figure 20.3). Compare your result for ΔS with those for paths A, B + C, and D + E in Figure 20.3.

Step 1. P_1, V_1, $T_1 \rightarrow P_2$, V_1, T_4
Because there is no change in the volume of the ideal gas, $\delta w = 0$, and we can write

$$dq_{rev,1} = dU = C_V(T)dT$$

$$q_{rev,1} = \int_{T_1}^{T_4} C_V(T)dT$$

$$\Delta S_1 = \int_{T_1}^{T_4} \frac{C_V(T)}{T}dT$$

Step 2. P_2, V_1, $T_4 \rightarrow P_2$, V_2, T_1
In this case, we write (by the First Law)

$$\delta q_{rev,2} = dU - \delta w = C_V(T)dT + PdV$$

$$q_{rev,2} = \int_{T_4}^{T_1} C_V(T)dT + \int_{V_1}^{V_2} P_2 dV$$

$$\Delta S_2 = \int_{T_4}^{T_1} \frac{C_V(T)}{T}dT + \int_{V_1}^{V_2} \frac{P_2}{T}dV$$

$$= \int_{T_4}^{T_1} \frac{C_V(T)}{T}dT + \int_{V_1}^{V_2} \frac{R}{V}dV$$

For the entire process, P_1, V_1, $T_1 \rightarrow P_2$, V_2, T_1, we have

$$q_{rev} = \int_{T_1}^{T_4} C_V(T)dT + \int_{T_4}^{T_1} C_V(T)dT + \int_{V_1}^{V_2} P_2 dV = P_2(V_2 - V_1)$$

$$\Delta S = \int_{T_1}^{T_4} \frac{C_V(T)}{T}dT + \int_{T_4}^{T_1} \frac{C_V(T)}{T}dT + \int_{V_1}^{V_2} \frac{R}{V}dV = R\ln\frac{V_2}{V_1}$$

The value of q_{rev} differs from those found for paths A, B + C, and D + E (Section 20–3), but the value of ΔS is the same (because entropy is a path-independent function).

20–7. Derive Equation 20.8 without referring to Chapter 19.

The temperature T_2 is the final temperature resulting from the reversible adiabatic expansion of one mole of an ideal gas. For a reversible expansion, $dw = -PdV = -nRTdV/V$, and for an adiabatic expansion $dU = dw$. Then, because $dU = C_V dT$,

$$\frac{C_V dT}{T} = \frac{-nRdV}{V}$$

$$\int_{T_1}^{T_2} \frac{C_V}{T}dT = -nR\int_{V_1}^{V_2} \frac{dV}{V}$$

$$\int_{T_1}^{T_2} \frac{C_V}{T}dT = -nR\ln\frac{V_2}{V_1}$$

which is Equation 20.8.

20–8. Calculate the value of ΔS if one mole of an ideal gas is expanded reversibly and isothermally from 10.0 dm³ to 20.0 dm³. Explain the sign of ΔS.

For an isothermal reaction of an ideal gas, $\delta w = -\delta q$, so $\delta q = PdV$. Then

$$\Delta S = \int \frac{\delta q_{rev}}{T} = \int \frac{P}{T} dV$$

Using T from the ideal gas equation gives

$$\Delta S = \int \frac{nR}{V} dV = nR \ln 2.00 = 5.76 \text{ J·K}^{-1}$$

The value of ΔS is positive because the gas is expanding.

20–9. Calculate the value of ΔS if one mole of an ideal gas is expanded reversibly and isothermally from 1.00 bar to 0.100 bar. Explain the sign of ΔS.

As in the previous problem, because the reaction is isothermal, $\delta q = PdV$. For an ideal gas,

$$dV = -\frac{nRT}{P^2} dP = -\frac{V}{P} dP$$

so we write ΔS as

$$\Delta S = \int \frac{P}{T} dV = \int -\frac{V}{T} dP = \int -\frac{nR}{P} dP = -nR \ln 0.1 = 19.1 \text{ J·K}^{-1}$$

The value of ΔS is positive because the gas expands.

20–10. Calculate the values of q_{rev} and ΔS along the path $D + E$ in Figure 20.3 for one mole of a gas whose equation of state is given in Example 20–2. Compare your result with that obtained in Example 20–2.

Path $D + E$ is the path described by $(P_1, V_1, T_1) \rightarrow (P_1, V_2, T_3) \rightarrow (P_2, V_2, T_1)$. For the first step,

$$\delta q_{rev} = dU - \delta w = C_V(T)dT - PdV$$

and for the second step (because the volume remains constant)

$$\delta q_{rev} = dU = C_V(T)dT$$

Then

$$\int \delta q_{rev,D+E} = \int_{T_1}^{T_3} C_V(T)dT - \int_{V_1}^{V_2} P_1 dV + \int_{T_3}^{T_1} C_V(T)dT$$
$$= -\int_{V_1}^{V_2} P_1 dV = -P_1(V_2 - V_1)$$

and

$$\Delta S_{rev,D+E} = -\int_{V_1}^{V_2} \frac{P_1}{T} dV$$

Substituting for T from the equation of state gives

$$\Delta S_{rev,D+E} = \int_{\overline{V}_1}^{\overline{V}_2} \frac{nP_1 Rd\overline{V}}{P_1(\overline{V} - b)} = nR \ln \left(\frac{\overline{V}_2 - b}{\overline{V}_1 - b} \right)$$

The quantity q_{rev} differs from those for the two paths in Example 20–2, but ΔS for all three paths is the same.

20–11. Show that ΔS_{D+E} is equal to ΔS_A and ΔS_{B+C} for the equation of state given in Example 20–2.

From Example 20–3,

$$\Delta S_A = \Delta S_{B+C} = nR \ln \frac{\overline{V}_2 - b}{\overline{V}_1 - b}$$

and the equation of state used is

$$P = \frac{RT}{\overline{V} - b}$$

In Example 20–1, we calculated ΔS_{D+E} for an ideal gas. Without using the ideal gas equation of state, however, we found in Example 20–1 that

$$\Delta S_D = \int_{T_1}^{T_3} \frac{C_V(T)}{T} dT + P_1 \int_{V_1}^{V_2} \frac{dV}{T}$$
$$\Delta S_E = \int_{T_3}^{T_1} \frac{C_V(T)}{T} dT$$

and

$$\Delta S_{D+E} = P_1 \int_{V_1}^{V_2} \frac{dV}{T}$$

We can substitute T from the equation of state to write

$$\Delta S_{D+E} = P_1 \int_{\overline{V}_1}^{\overline{V}_2} \frac{nRd\overline{V}}{P_1(\overline{V} - b)} = nR \int_{\overline{V}_1}^{\overline{V}_2} \frac{d\overline{V}}{\overline{V} - b} = nR \ln \frac{\overline{V}_2 - b}{\overline{V}_1 - b}$$

Therefore ΔS_{D+E} is equal to ΔS_A and ΔS_{B+C}.

20–12. Calculate the values of q_{rev} and ΔS along the path described in Problem 20–6 for one mole of a gas whose equation of state is given in Example 20–2. Compare your result with that obtained in Example 20–2.

For both steps, because the ideal gas equation was not used in calculating q_{rev}, q_{rev} is the same as it was in Problem 20–6:

$$q_{rev} = -P_2(V_2 - V_1)$$

Substituting the equation of state from Example 20–2 into the expression for ΔS from Problem 20–6 gives

$$\Delta S = \int_{\overline{V}_1}^{\overline{V}_2} \frac{nP_2}{T} d\overline{V} = \int_{\overline{V}_1}^{\overline{V}_2} \frac{nR}{\overline{V} - b} d\overline{V} = nR \ln \left(\frac{\overline{V}_2 - b}{\overline{V}_1 - b} \right)$$

This is (by no coincidence) the same value as that found for ΔS_A, ΔS_{B+C}, and ΔS_{D+E}.

20-13. Show that

$$\Delta S = C_P \ln \frac{T_2}{T_1}$$

for a constant-pressure process if C_P is independent of temperature. Calculate the change in entropy of 2.00 moles of $H_2O(l)$ ($\overline{C}_P = 75.2 \text{ J·K}^{-1}·\text{mol}^{-1}$) if it is heated from 10°C to 90°C.

Because ΔS is a state function, we can calculate it using a reversible process. For a constant-pressure reversible process (Equation 19.37), $\delta q_{rev} = dH = C_P dT$, and so

$$\Delta S = \frac{q_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_P}{T} dT = n\overline{C}_P \ln\left(\frac{T_2}{T_1}\right)$$

For 2.00 mol of H_2O,

$$\Delta S = (2.00 \text{ mol})(75.2 \text{ J·K}^{-1}·\text{mol}^{-1}) \ln \frac{363}{283} = 37.4 \text{ J·K}^{-1}$$

20-14. Show that

$$\Delta \overline{S} = \overline{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

if one mole of an ideal gas is taken from T_1, V_1 to T_2, V_2, assuming that $\overline{C}_V$ is independent of temperature. Calculate the value of $\Delta \overline{S}$ if one mole of $N_2(g)$ is expanded from 20.0 dm³ at 273 K to 300 dm³ at 400 K. Take $\overline{C}_P = 29.4 \text{ J·K}^{-1}·\text{mol}^{-1}$.

For the path $(T_1, V_1) \rightarrow (T_2, V_2)$, $\delta w = -PdV$ and $\delta q = dU - \delta w = C_V dT + PdV$. We can then write $\Delta \overline{S}$ as

$$\Delta \overline{S} = \frac{1}{n}\left(\int \frac{C_V}{T} dT + \int \frac{P}{T} dV\right)$$

$$= \int \frac{\overline{C}_V}{T} dT + \int \frac{R}{V} dV$$

$$= \overline{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Because $\overline{C}_P - \overline{C}_V = R$ for an ideal gas, we can write this as

$$\Delta \overline{S} = (\overline{C}_P - R) \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For N_2,

$$\Delta \overline{S} = (29.4 \text{ J·mol}^{-1}·\text{K}^{-1} - 8.314 \text{ J·K}^{-1}·\text{mol}^{-1}) \ln \frac{400}{273} + 8.314 \text{ J·K}^{-1}·\text{mol}^{-1} \ln \frac{300}{20.0}$$

$$= 30.6 \text{ J·K}^{-1}·\text{mol}^{-1}$$

20-15. In this problem, we will consider a two-compartment system like that in Figure 20.4, except that the two subsystems have the same temperature but different pressures and the wall that separates them is flexible rather than rigid. Show that in this case,

$$dS = \frac{dV_B}{T}(P_B - P_A)$$

Interpret this result with regard to the sign of dV_B when $P_B > P_A$ and when $P_B < P_A$.

We can use the First Law to write δq for each compartment as

$$\delta q_A = dU_A - \delta w_A = dU_A + P_A dV_A$$
$$\delta q_B = dU_B - \delta w_B = dU_B + P_B dV_B$$

We can write the total entropy of the system as

$$dS = dS_A + dS_B = \frac{\delta q_A}{T_A} + \frac{\delta q_B}{T_B}$$

$$= \frac{dU_A}{T_A} + \frac{P_A}{T_A} dV_A + \frac{dU_B}{T_B} + \frac{P_B}{T_B} dV_B$$

Because the two-compartment system is isolated, $dV_A = -dV_B$ and $dU_A = -dU_B$. Also, $T_A = T_B$. The quantity dS above then becomes

$$dS = (P_B - P_A)\frac{dV_B}{T}$$

When $P_B > P_A$, compartment B will expand, so, because dS must be greater than zero, dV_B is positive. Likewise, when $P_B < P_A$, compartment A will expand, so (again, because dS must be greater than zero) dV_B is negative.

20-16. In this problem, we will illustrate the condition $dS_{prod} \geq 0$ with a concrete example. Consider the two-component system shown in Figure 20.8. Each compartment is in equilibrium with a heat reservoir at different temperatures T_1 and T_2, and the two compartments are separated by a rigid heat-conducting wall. The total change of energy as heat of compartment 1 is

$$dq_1 = d_e q_1 + d_i q_1$$

where $d_e q_1$ is the energy as heat exchanged with the reservoir and $d_i q_1$ is the energy as heat exchanged with compartment 2. Similarly,
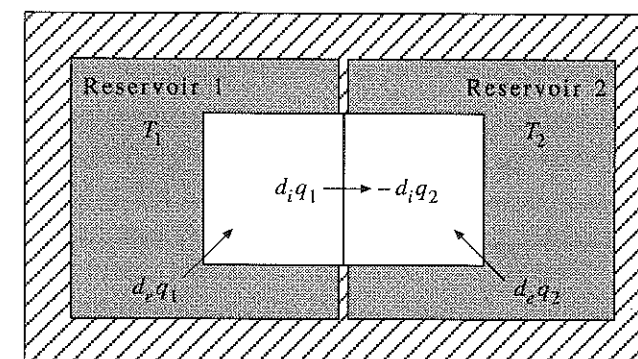
$$dq_2 = d_e q_2 + d_i q_2$$

FIGURE 20.8
A two-compartment system with each compartment in contact with an (essentially infinite) heat reservoir, one at temperature T_1 and the other at temperature T_2. The two compartments are separated by a rigid heat-conducting wall.

Clearly,

$$d_i q_1 = -d_i q_2$$

Show that the entropy change for the two-compartment system is given by

$$dS = \frac{d_e q_1}{T_1} + \frac{d_e q_2}{T_2} + d_i q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= dS_{\text{exchange}} + dS_{\text{prod}}$$

where

$$dS_{\text{exchange}} = \frac{d_e q_1}{T_1} + \frac{d_e q_2}{T_2}$$

is the entropy *exchanged* with the reservoirs (surroundings) and

$$dS_{\text{prod}} = d_i q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

is the entropy *produced* within the two-compartment system. Now show that the condition $dS_{\text{prod}} \geq 0$ implies that energy as heat flows spontaneously from a higher temperature to a lower temperature. The value of dS_{exchange}, however, has no restriction and can be positive, negative, or zero.

As stated in the text of the problem, we can write

$$d_i q_1 = -d_i q_2$$

The energy as heat exchanged between compartments 1 and 2 is involved in the entropy transferred between the two compartments. We can therefore express dS_{exchange} as

$$dS_{\text{exchange}} = \frac{d_e q_1}{T_1} + \frac{d_e q_2}{T_2}$$

Similarly, the energy as heat exchanged between the compartments and the reservoirs is involved in the entropy produced within the two-compartment system, so we can write dS_{prod} as

$$dS_{\text{prod}} = \frac{d_i q_1}{T_1} + \frac{d_i q_2}{T_2} = d_i q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

These are the only two means of changing the entropy of the system, so we can find dS_{tot} to be

$$dS_{\text{tot}} = dS_{\text{exchange}} + dS_{\text{prod}} = \frac{d_e q_1}{T_1} + \frac{d_e q_2}{T_2} + d_i q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Now take the condition $dS_{\text{prod}} \geq 0$. This is the same as saying that

$$d_i q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$

Arbitrarily, let $T_1 > T_2$. Then $1/T_1 - 1/T_2 < 0$, so $d_i q_1 < 0$ and heat is flowing from compartment 1 to compartment 2. If $T_2 > T_1$, by the same reasoning, $d_i q_1 > 0$ and heat is flowing from compartment 2 to compartment 1.

20–17. Show that

$$\Delta S \geq \frac{q}{T}$$

for an isothermal process. What does this equation say about the sign of ΔS? Can ΔS decrease in a reversible isothermal process? Calculate the entropy change when one mole of an ideal gas is compressed reversibly and isothermally from a volume of 100 dm^3 to 50.0 dm^3 at 300 K.

We defined ΔS as (Equation 20.22)

$$\Delta S \geq \int \frac{\delta q}{T}$$

For an isothermal process T is constant, so we can write this expression as

$$\Delta S \geq \frac{1}{T} \int \delta q$$

and integrate over δq to write

$$\Delta S \geq \frac{q}{T}$$

We know that q can be positive or negative, while T is always positive; therefore, ΔS can be positive or negative for an isothermal process. For one mole of an ideal gas compressed reversibly and isothermally, $dU = 0$, so $\delta q_{\text{rev}} = -\delta w = P dV$. Then

$$\delta q_{\text{rev}} = P dV = \frac{nRT}{V} dV$$

$$q_{\text{rev}} = nRT \ln \frac{V_2}{V_1}$$

and the change in entropy is given by

$$\Delta S = nR \ln \frac{V_2}{V_1} = (1 \text{ mol})(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln 0.5 = -5.76 \text{ J} \cdot \text{K}^{-1}$$

The quantity ΔS is equal to q/T, rather than greater than it, because this is a reversible process.

20–18. Vaporization at the normal boiling point (T_{vap}) of a substance (the boiling point at one atm) can be regarded as a reversible process because if the temperature is decreased infinitesimally below T_{vap}, all the vapor will condense to liquid, whereas if it is increased infinitesimally above T_{vap}, all the liquid will vaporize. Calculate the entropy change when two moles of water vaporize at 100.0°C. The value of $\Delta_{\text{vap}}\overline{H}$ is 40.65 kJ·mol^{-1}. Comment on the sign of $\Delta_{\text{vap}}S$.

At constant pressure and temperature, $q_{\text{rev}} = n\Delta \overline{H}_{\text{rev}}$ (Equation 19.37). We know from the previous problem that, for a reversible isothermal process,

$$\Delta S = \frac{q}{T} = \frac{(2 \text{ mol})(40.65 \text{ kJ} \cdot \text{mol}^{-1})}{373.15 \text{ K}} = 217.9 \text{ J} \cdot \text{K}^{-1}$$

As the water becomes more disordered, changing from liquid to gas, the entropy increases.

20–19. Melting at the normal melting point (T_{fus}) of a substance (the melting point at one atm) can be regarded as a reversible process because if the temperature is changed infinitesimally from exactly T_{fus}, then the substance will either melt or freeze. Calculate the change in entropy when two moles of water melt at 0°C. The value of $\Delta_{\text{fus}}\overline{H}$ is 6.01 kJ·mol^{-1}. Compare your answer with the one you obtained in Problem 20–18. Why is $\Delta_{\text{vap}}S$ much larger than $\Delta_{\text{fus}}S$?

At constant pressure, $q = n\Delta\overline{H}$ (Equation 19.37). For a reversible isothermal process, we can express ΔS as (Problem 20.17)

$$\Delta S = \frac{q}{T} = \frac{(2\text{ mol})(6.01\text{ kJ}\cdot\text{mol}^{-1})}{273.15\text{ K}} = 44.0\text{ J}\cdot\text{K}^{-1}$$

The quantity $\Delta_{fus}S$ is much less than $\Delta_{vap}S$ because the difference in disorder between a solid and a liquid is much less than that between a liquid and a gas.

20–20. Consider a simple example of Equation 20.23 in which there are only two states, 1 and 2. Show that $W(a_1, a_2)$ is a maximum when $a_1 = a_2$. *Hint*: Consider ln W, use Stirling's approximation, and treat a_1 and a_2 as continuous variables.

A simplified version of Equation 20.23, for two states only, is

$$W = \frac{(a_1 + a_2)!}{a_1! a_2!}$$

Let $a_1 = x$, with x being a continuous variable, and let $a_1 + a_2 = N$. Then we can express W in terms of N and x:

$$W = \frac{N!}{(N-x)! x!}$$
$$\ln W = \ln N! - \ln(N-x)! - \ln x!$$

Using Stirling's approximation for ln $N!$ (MathChapter J), we can find the first derivative of ln W with respect to x:

$$\ln W = \ln N! - \ln(N-x)! - \ln x!$$
$$= N \ln N - N - [(N-x)\ln(N-x) - (N-x)] - (x \ln x - x)$$
$$\frac{d(\ln W)}{dx} = 0 + \frac{N-x}{N-x} + \ln(N-x) - 1 - \ln x - \frac{x}{x} + 1$$
$$= \ln(N-x) - \ln x$$

We are looking for the value of x that produces the maximum value of W, which is where $dW/dx = 0$. Because

$$\frac{1}{W}\frac{dW}{dx} = \frac{d(\ln W)}{dx}$$

the desired value of x will also give $[d(\ln W)/dx] = 0$. Setting this derivative equal to zero, we find

$$0 = \ln(N - x_{max}) - \ln x_{max}$$
$$\ln x_{max} = \ln(N - x_{max})$$
$$2x_{max} = N$$

And clearly $x_{max} = N/2$. Thus, the maximum value of W occurs when $a_1 = a_2 = N/2$.

20–21. Extend Problem 20–20 to the case of three states. Do you see how to generalize it to any number of states?

For the case of three states, Equation 20.23 becomes

$$W = \frac{(a_1 + a_2 + a_3)!}{a_1! a_2! a_3!}$$

Let $a_1 = x$ and $a_2 = y$, where x and y are continuous variables, and let $a_1 + a_2 + a_3 = A$. Then

$$W = \frac{A!}{(A - x - y)! x! y!}$$
$$\ln W = \ln A! - \ln(A - x - y)! - \ln x! - \ln y!$$

We can use Stirling's approximation for ln $A!$ (MathChapter J) to write ln W and differentiate to find an expression for $d(\ln W)/dx$:

$$\ln W = A \ln A - A - [(A - x - y)\ln(A - x - y) - (A - x - y)] - (x \ln x - x) - (y \ln y - y)$$
$$\frac{d(\ln W)}{dx} = \ln(A - x - y) + 1 - 1 - \ln x - 1 + 1 = \ln(A - x - y) - \ln x$$

Similarly,

$$\frac{d(\ln W)}{dy} = \ln(A - x - y) - \ln y$$

As in the previous problem, the values of x and y which give the largest values of W occur where $d(\ln W)/dx = 0$ and $d(\ln W)/dy = 0$. Therefore,

$$0 = \ln(A - x_{max} - y) - \ln x_{max}$$
$$\ln x_{max} = \ln(A - x_{max} - y)$$
$$2x_{max} = A - y$$

Because we want the point at which both x and y are at their maxima, we substitute this value into the expression for $d(\ln W)/dy$ to find

$$0 = \ln(A - x_{max} - y_{max}) - \ln y_{max}$$
$$2y_{max} = \frac{A}{2} + \frac{y_{max}}{2}$$
$$y_{max} = \frac{A}{3}$$

Then (substituting back into the first equality) $x_{max} = A/3$. Thus, the maximum value of W occurs when $a_1 = a_2 = a_3 = A/3$. Problem J.10 generalizes this to any number of states.

20–22. Show that the system partition function can be written as a summation over levels by writing

$$Q(N, V, T) = \sum_E \Omega(N, V, E)e^{-E/k_bT}$$

Now consider the case of an isolated system, for which there is only one term in $Q(N, V, T)$. Now substitute this special case for Q into Equation 20.43 to derive the equation $S = k_B \ln \Omega$.

In Chapter 17, we defined the partition function $Q(N, V, T)$ as (Equation 17.14)

$$Q(N, V, T) = \sum_j e^{-E_j/k_bT}$$

Here a term representing an energy level of degeneracy Ω is written Ω times. We can write this, alternatively, as a sum over energy levels, where a term representing an energy level is written once and multiplied by its degeneracy Ω:

$$Q(N, V, T) = \sum_E \Omega(N, V, E)e^{-E/k_B T}$$

These two expressions are equivalent. For an isolated system, there will be only one term in $Q(N, V, T)$, so

$$Q = \Omega(N, V, E)e^{-E/k_B T}$$

$$\ln Q = \ln \Omega - \left(\frac{E}{k_B T}\right)$$

Applying Equation 20.43 allows us to write

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

$$= k_B T \left(\frac{E}{k_B T^2}\right) + k_B \ln \Omega - \frac{E}{T}$$

$$= k_B \ln \Omega$$

which is Boltzmann's equation.

20–23. In this problem, we will show that $\Omega = c(N)f(E)V^N$ for an ideal gas (Example 20–3). In Problem 18–42 we showed that the number of translational energy states between ε and $\varepsilon + \Delta\varepsilon$ for a particle in a box can be calculated by considering a sphere in n_x, n_y, n_z space,

$$n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2\varepsilon}{h^2} = R^2$$

Show that for an N-particle system, the analogous expression is

$$\sum_{j=1}^{N}(n_{xj}^2 + n_{yj}^2 + n_{zj}^2) = \frac{8ma^2 E}{h^2} = R^2$$

or, in more convenient notation

$$\sum_{j=1}^{3N} n_j^2 = \frac{8ma^2 E}{h^2} = R^2$$

Thus, instead of dealing with a three-dimensional sphere as we did in Problem 18–42, here we must deal with a $3N$-dimensional sphere. Whatever the formula for the volume of a $3N$-dimensional sphere is (it is known), we can at least say that it is proportional to R^{3N}. Show that this proportionality leads to the following expression for $\Phi(E)$, the number of states with energy $\leq E$,

$$\Phi(E) \propto \left(\frac{8ma^2 E}{h^2}\right)^{3N/2} = c(N)E^{3N/2}V^N$$

where $c(N)$ is a constant whose value depends upon N and $V = a^3$. Now, following the argument developed in Problem 18–42, show that the number of states between E and $E + \Delta E$ (which is essentially Ω) is given by

$$\Omega = c(N)f(E)V^N \Delta E$$

where $f(E) = E^{\frac{3N}{2}-1}$.

For an N-particle system, we wish to consider all the N particles in one $3N$-dimensional space, instead of the N particles in N individual three-dimensional spaces. The equation from Problem 18–42 then becomes

$$\sum_{j=1}^{3N} n_j^2 = \frac{8ma^2 E}{h^2} = R^2$$

As in Problem 18–42, $\Phi(E) \propto$ the volume of the sphere, so

$$\Phi(E) \propto R^{3N} = \left(\frac{8ma^2 E}{h^2}\right)^{3N/2}$$

Letting $c(N)$ be a proportionality constant allows us to write

$$\Phi(E) = c(N)E^{3N/2}V^N$$

Now, as in Problem 18–42, $\Omega = \Phi(E + \Delta E) - \Phi(E)$, so

$$\Omega = c(N)(E + \Delta E)^{3N/2}V^N - c(N)E^{3N/2}V^N$$

$$= c(N)V^N \left[(E + \Delta E)^{3N/2} - E^{3N/2}\right]$$

$$= c(N)V^N E^{3N/2}\left[\left(1 + \frac{\Delta E}{E}\right)^{3N/2} - 1\right]$$

$$= c(N)V^N E^{3N/2}\left\{1 + \frac{3N}{2}\frac{\Delta E}{E} + O\left[\left(\frac{\Delta E}{E}\right)^2\right] - 1\right\}$$

$$= \frac{3N}{2}c(N)V^N E^{3N/2}\frac{\Delta E}{E} + O\left[\left(\frac{\Delta E}{E}\right)^2\right]$$

$$= c(N)V^N E^{\frac{3N}{2}-1}\Delta E = c(N)f(E)V^N \Delta E$$

where we have incorporated the factor of $3N/2$ into $c(N)$ and defined $f(E) = E^{\frac{3N}{2}-1}$.

20–24. Show that if a process involves only an isothermal transfer of energy as heat (*pure heat transfer*), then

$$dS_{sys} = \frac{dq}{T} \qquad \text{(pure heat transfer)}$$

The process involves only an isothermal transfer of energy as heat, so $\delta w = 0$ and $dU = \delta q$. Therefore,

$$dS_{sys} = \frac{\delta q}{T} = \frac{dU}{T} = \frac{dq}{T}$$

where we can write dq instead of δq because $\delta q = dU$, and U is a state function.

20–25. Calculate the change in entropy of the system and of the surroundings and the total change in entropy if one mole of an ideal gas is expanded isothermally and reversibly from a pressure of 10.0 bar to 2.00 bar at 300 K.

Because this is an isothermal reversible expansion, $\delta q = -\delta w = P dV$. We then use the ideal gas equation to write

$$\Delta S_{sys} = \int \frac{\delta q_{rev}}{T} = \int \frac{P}{T} dV = \int \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

For an isothermal expansion of an ideal gas, $P_1 V_1 = P_2 V_2$. We can then write the change of entropy of the gas as

$$\Delta S_{sys} = (1 \text{ mol})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \ln 5.00 = +13.4 \text{ J} \cdot \text{K}^{-1}$$

For a reversible expansion, $\Delta S_{tot} = 0$, so $\Delta S_{surr} = -\Delta S_{sys} = -13.4 \text{ J} \cdot \text{K}^{-1}$.

20–26. Redo Problem 20–25 for an expansion into a vacuum, with an initial pressure of 10.0 bar and a final pressure of 2.00 bar.

As in Problem 20–25, $\Delta S_{sys} = 13.4 \text{ J} \cdot \text{K}^{-1}$. However, because this is an irreversible expansion into a vacuum, $\Delta S_{surr} = 0$, so $\Delta S_{tot} = 13.4 \text{ J} \cdot \text{K}^{-1}$.

20–27. The molar heat capacity of 1-butene can be expressed as

$$\overline{C}_P(T)/R = 0.05641 + (0.04635 \text{ K}^{-1})T - (2.392 \times 10^{-5} \text{ K}^{-2})T^2 + (4.80 \times 10^{-9} \text{ K}^{-3})T^3$$

over the temperature range 300 K $< T <$ 1500 K. Calculate the change in entropy when one mole of 1-butene is heated from 300 K to 1000 K at constant pressure.

At constant pressure, $\delta q = dH = n\overline{C}_P dT$. Then Equation 20.22 becomes (assuming a reversible process)

$$\Delta S = n \int_{300}^{1000} \frac{\overline{C}_P}{T} dT$$

$$= (1 \text{ mol}) R \int_{300}^{1000} \left[0.05641 T^{-1} + (0.04635 \text{ K}^{-1}) - (2.392 \times 10^{-5} \text{ K}^{-2})T \right.$$
$$\left. + (4.80 \times 10^{-9} \text{ K}^{-3})T^2 \right] dT$$

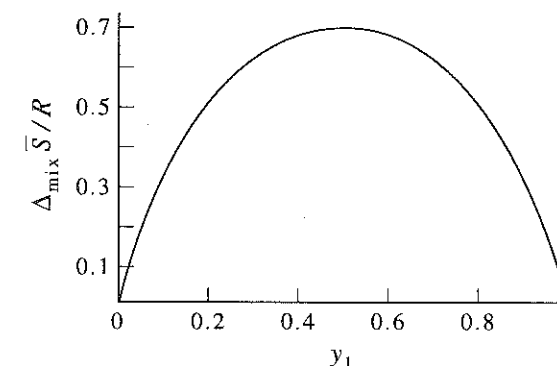$$= 192.78 \text{ J} \cdot \text{K}^{-1}$$

20–28. Plot $\Delta_{mix}\overline{S}$ against y_1 for the mixing of two ideal gases. At what value of y_1 is $\Delta_{mix}\overline{S}$ a maximum? Can you give a physical interpretation of this result?

We can use Equation 20.30 for two gases:

$$\Delta_{mix}\overline{S} = -R \left(y_1 \ln y_1 - y_2 \ln y_2 \right)$$

Because $y_1 + y_2 = 1$, we can write this as

$$\Delta_{mix}\overline{S}/R = -y_1 \ln y_1 - (1 - y_1) \ln(1 - y_1)$$

The quantity $\Delta_{mix}\overline{S}$ is a maximum when $y_1 = 0.5$. This means that the gases are most disordered when there are equal amounts of both present in a container.

20–29. Calculate the entropy of mixing if two moles of $N_2(g)$ are mixed with one mole $O_2(g)$ at the same temperature and pressure. Assume ideal behavior.

The mole fractions y are 2/3 for $N_2(g)$ and 1/3 for $O_2(g)$. Therefore,

$$\Delta_{mix}\overline{S} = -R y_1 \ln y_1 - R y_2 \ln y_2$$
$$= -\frac{2R}{3} \ln \frac{2}{3} - \frac{R}{3} \ln \frac{1}{3} = 5.29 \text{ J} \cdot \text{K}^{-1}$$

20–30. Show that $\Delta_{mix}\overline{S} = R \ln 2$ if equal volumes of any two ideal gases under the same conditions are mixed.

Because there are equal volumes of ideal gases under the same conditions, $y_1 = y_2 = 0.5$ (Problem 20–28). Now Equation 20.30 gives

$$\Delta_{mix}\overline{S} = -R y_1 \ln y_1 - R y_2 \ln y_2$$
$$= -\frac{R}{2} \ln \frac{1}{2} - \frac{R}{2} \ln \frac{1}{2}$$
$$= -R \ln \frac{1}{2} = R \ln 2$$

20–31. Derive the equation $dU = TdS - PdV$. Show that

$$d\overline{S} = \overline{C}_V \frac{dT}{T} + R \frac{d\overline{V}}{\overline{V}}$$

for one mole of an ideal gas. Assuming that $\overline{C}_V$ is independent of temperature, show that

$$\Delta \overline{S} = \overline{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{\overline{V}_2}{\overline{V}_1}$$

for the change from $T_1, \overline{V}_1$ to $T_2, \overline{V}_2$. Note that this equation is a combination of Equations 20.28 and 20.31.

From the definition of entropy, $\delta q_{rev} = TdS$, and by definition $\delta w_{rev} = -PdV$. The first law then gives $dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$. We divide through by T to obtain

$$dS = \frac{dU}{T} - \frac{P}{T}dV$$

Using the relation $dU = n\overline{C}_V dT$ and the ideal gas law, we find

$$dS = n\overline{C}_V \frac{dT}{T} - nR\frac{dV}{V}$$

or

$$d\overline{S} = \overline{C}_V \frac{dT}{T} - R\frac{d\overline{V}}{\overline{V}}$$

If $\overline{C}_V$ is temperature-independent, integrating gives

$$\int d\overline{S} = \overline{C}_V \int \frac{dT}{T} + R \int \frac{d\overline{V}}{\overline{V}}$$

$$\Delta\overline{S} = \overline{C}_V \ln\frac{T_2}{T_1} + R\ln\frac{\overline{V}_2}{\overline{V}_1}$$

20–32. Derive the equation $dH = TdS + VdP$. Show that

$$\Delta\overline{S} = \overline{C}_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

for the change of one mole of an ideal gas from T_1, P_1 to T_2, P_2, assuming that $\overline{C}_P$ is independent of temperature.

We derived the equation $dU = TdS - PdV$ in Problem 20–31. Now add $d(PV)$ to both sides of this equation to obtain

$$dU + d(PV) = dH = TdS + VdP$$

Now divide both sides by T to write

$$dS = \frac{dH}{T} - \frac{V}{T}dP$$

and use the relation $dH = n\overline{C}_P dT$ and the ideal gas law to obtain

$$dS = \frac{n\overline{C}_P}{T}dT - \frac{nR}{P}dP$$

or

$$d\overline{S} = \frac{\overline{C}_P}{T}dT - \frac{R}{P}dP$$

Assuming that $\overline{C}_P$ is temperature-independent, integrating gives

$$\Delta\overline{S} = \overline{C}_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

20–33. Calculate the change in entropy if one mole of $SO_2(g)$ at 300 K and 1.00 bar is heated to 1000 K and its pressure is decreased to 0.010 bar. Take the molar heat capacity of $SO_2(g)$ to be

$$\overline{C}_P(T)/R = 7.871 - \frac{1454.6\ \text{K}}{T} + \frac{160\,351\ \text{K}^2}{T^2}$$

We can use the result of the previous problem,

$$dS = \frac{n\overline{C}_P dT}{T} - \frac{nRdP}{P}$$

Then

$$\int dS = nR\int \frac{\overline{C}_P}{T}dT - nR\int \frac{dP}{P}$$

$$= (1.00\ \text{mol})(8.314\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})\left[\int_{300\ \text{K}}^{1000\ \text{K}} \left(\frac{7.871}{T} - \frac{1454.6\ \text{K}}{T^2} + \frac{160\,351\ \text{K}^2}{T^3}\right)dT - \ln\frac{0.010}{1.00}\right]$$

$$\Delta S = 95.6\ \text{J}\cdot\text{K}^{-1}$$

20–34. In the derivation of Equation 20.32, argue that $\Delta S_c > 0$ and $\Delta S_h < 0$. Now show that

$$\Delta S = \Delta S_c + \Delta S_h > 0$$

by showing that

$$\Delta S_c - |\Delta S_h| > 0$$

The two quantities $\Delta S_c > 0$ and $\Delta S_h < 0$ because the colder piece will become hotter and the hotter piece will become colder. Using the expressions for ΔS_c and ΔS_h in Section 20–6,

$$\Delta S_c = C_V \ln\frac{T_h + T_c}{2T_c} > 0 \qquad \text{and} \qquad \Delta S_h = C_V \ln\frac{T_h + T_c}{2T_h} < 0$$

Now, because $\Delta S_h < 0$, $|\Delta S_h| = -\Delta S_h$, and

$$|\Delta S_h| = C_V \ln\frac{2T_h}{T_h + T_c} > 0$$

The total change in entropy is given by

$$\Delta S = \Delta S_c + \Delta S_h = \Delta S_c - |\Delta S_h|$$

$$= C_V \ln\frac{(T_h + T_c)^2}{4T_h T_c} > 0$$

where we proved that $(T_h + T_c)^2 > 4T_h T_c$ in Section 20–6.

20–35. We can use the equation $S = k_B \ln W$ to derive Equation 20.28. First, argue that the probability that an ideal-gas molecule is found in a subvolume V_s of some larger volume V is V_s/V. Because the molecules of an ideal gas are independent, the probability that N ideal-gas molecules are found

in V_s is $(V_s/V)^N$. Now show that the change in entropy when the volume of one mole of an ideal gas changes isothermally from V_1 to V_2 is

$$\Delta S = R \ln \frac{V_2}{V_1}$$

The probability that the molecule is in subvolume V_s is V_s/V, because the numerator represents the situations where the molecule is in V_s and the denominator represents all positions available to the molecule. Now we can write (using Boltzmann's equation)

$$S = k_B \ln W = k_B \ln \left(\frac{V_s}{V}\right)^N = R \ln \frac{V_s}{V}$$

Now take $V_s = V_1$ and an arbitrary V_2 and V. The change in entropy when an ideal gas goes from V_1 to V_2 isothermally is then

$$\Delta S = R \left(\ln \frac{V_2}{V} - \ln \frac{V_1}{V} \right) = R \ln \frac{V_2}{V_1}$$

20–36. The relation $n_j \propto e^{-\varepsilon_j/k_B T}$ can be derived by starting with $S = k_B \ln W$. Consider a gas with n_0 molecules in the ground state and n_j in the jth state. Now add an energy $\varepsilon_j - \varepsilon_0$ to this system so that a molecule is promoted from the ground state to the jth state. If the volume of the gas is kept constant, then no work is done, so $dU = dq$,

$$dS = \frac{dq}{T} = \frac{dU}{T} = \frac{\varepsilon_j - \varepsilon_0}{T}$$

Now, assuming that n_0 and n_j are large, show that

$$dS = k_B \ln \left\{ \frac{N!}{(n_0-1)!n_1!\cdots(n_j+1)!\cdots} \right\} - k_B \ln \left\{ \frac{N!}{n_0!n_1!\cdots n_j!\cdots} \right\}$$

$$= k_B \ln \left\{ \frac{n_j!}{(n_j+1)!} \frac{n_0!}{(n_0-1)!} \right\} = k \ln \frac{n_0}{n_j}$$

Equating the two expressions for dS, show that

$$\frac{n_j}{n_0} = e^{-(\varepsilon_j-\varepsilon_0)/k_B T}$$

From the problem,

$$dS = \frac{\varepsilon_j - \varepsilon_0}{T}$$

Recall that (Equation 20.24) $S = k_B \ln W$. For the initial state,

$$S_{\text{initial}} = k_B \ln W = k_B \ln \left[\frac{N!}{n_0!n_1!\cdots n_j!\cdots} \right]$$

and for the final state

$$S_{\text{final}} = k_B \ln W = k_B \ln \left[\frac{N!}{(n_0-1)!n_1!\cdots(n_j+1)!\cdots} \right]$$

Then

$$dS = S_{\text{final}} - S_{\text{initial}}$$

$$= k_B \ln \left[\frac{N!}{(n_0-1)!n_1!\cdots(n_j+1)!\cdots} \right] - k_B \ln \left[\frac{N!}{n_0!n_1!\cdots n_j!\cdots} \right]$$

$$= k_B \ln \left[\frac{n_j!}{(n_j+1)!} \frac{n_0!}{(n_0-1)!} \right] = k_B \ln \frac{n_0}{n_j+1}$$

$$= k_B \ln \frac{n_0}{n_j}$$

where the last equality holds because $n_j \gg 1$. Equating the two expressions for dS, we find that

$$k_B \ln \frac{n_0}{n_j} = \frac{\varepsilon_j - \varepsilon_0}{T}$$

$$\ln \frac{n_j}{n_0} = -\frac{\varepsilon_j - \varepsilon_0}{k_B T}$$

$$\frac{n_j}{n_0} = e^{-(\varepsilon_j-\varepsilon_0)/k_B T}$$

20–37. We can use Equation 20.24 to calculate the probability of observing fluctuations from the equilibrium state. Show that

$$\frac{W}{W_{\text{eq}}} = e^{-\Delta S/k_B}$$

where W represents the nonequilibrium state and ΔS is the entropy difference between the two states. We can interpret the ratio W/W_{eq} as the probability of observing the nonequilibrium state. Given that the entropy of one mole of oxygen is $205.0\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at $25°\text{C}$ and one bar, calculate the probability of observing a decrease in entropy that is one millionth of a percent of this amount.

We can use Equation 20.24 to write

$$S_{\text{eq}} = k_B \ln W_{\text{eq}} \qquad \text{and} \qquad S = k_B \ln W$$

Then ΔS is

$$\Delta S = S - S_{\text{eq}} = k_B (\ln W - \ln W_{\text{eq}})$$

$$= k_B \ln \frac{W}{W_{\text{eq}}}$$

$$-\frac{\Delta S}{k_B} = \ln \frac{W}{W_{\text{eq}}}$$

$$e^{-\Delta S/k_B} = \frac{W}{W_{\text{eq}}}$$

The probability of observing a ΔS which is one millionth of one percent of $205\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is

$$\exp\left[-\frac{(1\ \text{mol})(1.00 \times 10^{-8})(205.0\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})}{1.381 \times 10^{-23}\ \text{J}\cdot\text{K}^{-1}} \right] = \exp[-1.485 \times 10^{17}] \approx 0$$

20–38. Consider one mole of an ideal gas confined to a volume V. Calculate the probability that all the N_A molecules of this ideal gas will be found to occupy one half of this volume, leaving the other half empty.

From Problem 20–35, we can write the probability as

$$\left(\frac{\frac{1}{2}V}{V}\right)^{N_A} = \left(\frac{1}{2}\right)^{N_A} \approx 0$$

20–39. Show that S_{system} given by Equation 20.40 is a maximum when all the p_j are equal. Remember that $\sum p_j = 1$, so that

$$\sum_j p_j \ln p_j = p_1 \ln p_1 + p_2 \ln p_2 + \cdots + p_{n-1} \ln p_{n-1}$$
$$+ (1 - p_1 - p_2 - \cdots - p_{n-1}) \ln(1 - p_1 - p_2 - \cdots - p_{n-1})$$

See also Problem J–10.

Begin with Equation 20.40,

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

Substituting the expression given for $\sum_j p_j \ln p_j$, we find

$$S_{system} = -k_B \left[p_1 \ln p_1 + p_2 \ln p_2 + \cdots + p_{n-1} \ln p_{n-1} \right.$$
$$\left. + (1 - p_1 - p_2 - \cdots - p_{n-1}) \ln(1 - p_1 - p_2 - \cdots - p_{n-1}) \right]$$
$$\frac{\partial S_{system}}{\partial p_j} = \ln p_j + 1 - \ln(1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1}) - 1$$
$$0 = \ln p_j - \ln(1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1})$$
$$p_j = 1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1}$$

Because p_j can be any of p_1 to p_{n-1}, and the above equality holds for all p_j, all the p_j must be equal.

20–40. Use Equation 20.45 to calculate the molar entropy of krypton at 298.2 K and one bar, and compare your result with the experimental value of 164.1 J·K^{-1}·mol^{-1}.

This problem is like Example 20–6. We use Equation 20.45,

$$\overline{S} = \frac{5}{2}R + R \ln \left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A} \right]$$

Assuming ideal behavior, at 298.2 K and one bar

$$\frac{N_A}{\overline{V}} = \frac{N_A P}{RT}$$
$$= \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})}{(0.08314 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.2 \text{ K})}$$
$$= 2.429 \times 10^{22} \text{ dm}^{-3} = 2.429 \times 10^{25} \text{ m}^{-3}$$

and

$$\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(0.08380 \text{ kg}\cdot\text{mol}^{-1})(1.3806 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(298.2 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2}\right]^{3/2}$$
$$= (8.199 \times 10^{21} \text{ m}^{-2})^{3/2} = 7.424 \times 10^{32} \text{ m}^{-3}$$

Then

$$\overline{S} = \frac{5}{2}R + 17.235R$$
$$= 164.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

This value is the same as the experimental value.

20–41. Use Equation 18.39 and the data in Table 18.2 to calculate the entropy of nitrogen at 298.2 K and one bar. Compare your result with the experimental value of 191.6 J·K^{-1}·mol^{-1}.

Recall from Chapter 18 that

$$Q = \frac{q^N}{N!}$$

Substituting into Equation 20.43 gives

$$S = Nk_B \ln q - k_B \ln N! + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$
$$= Nk_B \ln q - Nk_B \ln N + Nk_B + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$
$$= Nk_B + Nk_B \ln \frac{q}{N} + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V \tag{1}$$

For a diatomic ideal gas,

$$q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} g_{e1} e^{D_e/k_B T} \tag{18.39}$$

Then

$$\ln \frac{q}{N} = \ln \left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A} \right] + \ln \frac{T}{\sigma \Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T})$$
$$- \frac{\Theta_{vib}}{2T} + \ln g_{e1} + \frac{D_e}{k_B T}$$

and

$$\left(\frac{\partial \ln q}{\partial T}\right) = \frac{3}{2T} + \frac{1}{T} + \frac{\Theta_{vib}}{2T^2} + \frac{(\Theta_{vib}/T^2)e^{-\Theta_{vib}/T}}{1 - e^{-\Theta_{vib}/T}} - \frac{D_e}{k_B T^2}$$

Substituting into Equation 1 above, we find that

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln \left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A} \right] + \ln \frac{T}{\sigma \Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T})$$
$$+ \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

For N_2, $\Theta_{vib} = 3374$ K, $\Theta_{rot} = 2.88$ K, $\sigma = 2$, and $g_{e1} = 1$. The various factors are as follows:

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(4.653 \times 10^{-26} \text{ kg})(1.381 \times 10^{-23} \text{ J·K}^{-1})(298.2 \text{ K})}{(6.626 \times 10^{34} \text{ J·s})^2}\right]^{3/2}$$

$$= 1.435 \times 10^{32} \text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ dm}^3\text{·bar·mol}^{-1}\text{·K}^{-1})(298.2 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})}$$

$$= 4.117 \times 10^{-23} \text{ dm}^3 = 4.117 \times 10^{-26} \text{ m}^3$$

$$\ln\frac{T}{\sigma\Theta_{rot}} = \ln\frac{298.2 \text{ K}}{2(2.88 \text{ K})} = 3.947$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -1.22 \times 10^{-5}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = \frac{11.31}{e^{11.31} - 1} = 1.380 \times 10^{-4}$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 15.59 + 3.947 + 1.22 \times 10^{-5} + 1.380 \times 10^{-4}$$

$$= 23.04$$

This is $191.6 \text{ J·K}^{-1}\text{·mol}^{-1}$, which is also the experimental value.

20–42. Use Equation 18.57 and the data in Table 18.4 to calculate the entropy of $CO_2(g)$ at 298.2 K and one bar. Compare your result with the experimental value of $213.8 \text{ J·K}^{-1}\text{·mol}^{-1}$.

For a linear polyatomic ideal gas having three atoms,

$$q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{T}{\sigma\Theta_{rot}} \left(\prod_{j=1}^4 \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{vib,j}/T}}\right) g_{e1} e^{D_e/k_B T} \quad (18.57)$$

Then

$$\ln\frac{q}{N} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \sum_{j=1}^4 \ln(1 - e^{-\Theta_{vib,j}/T})$$

$$- \sum_{j=1}^4 \frac{\Theta_{vib,j}}{2T} + \ln g_{e1} + \frac{D_e}{k_B T}$$

and

$$\left(\frac{\partial \ln q}{\partial T}\right) = \frac{3}{2T} + \frac{1}{T} + \sum_{j=1}^4 \frac{\Theta_{vib,j}}{2T^2} + \sum_{j=1}^4 \frac{(\Theta_{vib,j}/T^2)e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} - \frac{D_e}{k_B T^2}$$

Substituting into Equation 1 from Problem 20–41, we find

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \sum_{j=1}^4 \ln(1 - e^{-\Theta_{vib,j}/T})$$

$$+ \sum_{j=1}^4 \left[\frac{(\Theta_{vib,j}/T)e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}}\right] + \ln g_{e1}$$

For CO_2, $\Theta_{vib,1} = 3360$ K, $\Theta_{vib,2} = \Theta_{vib,3} = 954$ K, $\Theta_{vib,4} = 1890$ K, $\Theta_{rot} = 0.561$ K, $\sigma = 2$, and $g_{e1} = 1$. The various factors are as follows:

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(7.308 \times 10^{-26} \text{ kg})(1.381 \times 10^{-23} \text{ J·K}^{-1})(298.2 \text{ K})}{(6.626 \times 10^{34} \text{ J·s})^2}\right]^{3/2}$$

$$= 2.825 \times 10^{32} \text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ dm}^3\text{·bar·mol}^{-1}\text{·K}^{-1})(298.2 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})}$$

$$= 4.117 \times 10^{-23} \text{ dm}^3 = 4.117 \times 10^{-26} \text{ m}^3$$

$$\ln\frac{T}{\sigma\Theta_{rot}} = \ln\left[\frac{298.2 \text{ K}}{2(0.561 \text{ K})}\right] = 5.583$$

$$\sum_{j=1}^4 \ln(1 - e^{-\Theta_{vib,j}/T}) = -0.08508$$

$$\sum_{j=1}^4 \frac{\Theta_{vib,j}}{T}\left(\frac{e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}}\right) = 0.2835$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 16.269 + 5.583 + 0.08508 + 0.2835$$

$$= 25.72$$

This is $213.8 \text{ J·K}^{-1}\text{·mol}^{-1}$, which is also the experimental value.

20–43. Use Equation 18.60 and the data in Table 18.4 to calculate the entropy of $NH_3(g)$ at 298.2 K and one bar. Compare your result with the experimental value of $192.8 \text{ J·K}^{-1}\text{·mol}^{-1}$.

For a nonlinear polyatomic ideal gas having four atoms,

$$q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right)^{1/2}\left(\prod_{j=1}^6 \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{vib,j}/T}}\right) g_{e1} e^{D_e/k_B T} \quad (18.60)$$

Then

$$\ln\frac{q}{N} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{\pi^{1/2}}{\sigma} + \frac{1}{2}\ln\left(\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right)$$

$$- \sum_{j=1}^6 \ln(1 - e^{-\Theta_{vib,j}/T}) - \sum_{j=1}^6 \frac{\Theta_{vib,j}}{2T} + \ln g_{e1} + \frac{D_e}{k_B T}$$

and

$$\left(\frac{\partial \ln q}{\partial T}\right) = \frac{3}{2T} + \frac{3}{2T} + \sum_{j=1}^6 \frac{\Theta_{vib,j}}{2T^2} + \sum_{j=1}^6 \frac{(\Theta_{vib,j}/T^2)e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} - \frac{D_e}{k_B T^2}$$

Substituting into Equation 1 from Problem 20–41, we find

$$\frac{\overline{S}}{R} = 4 + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{\pi^{1/2}}{\sigma} + \frac{1}{2}\ln\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}$$

$$-\sum_{j=1}^{6}\ln(1-e^{-\Theta_{vib,j}/T})+\sum_{j=1}^{6}\left[\frac{(\Theta_{vib,j}/T)e^{-\Theta_{vib,j}/T}}{1-e^{-\Theta_{vib,j}/T}}\right]+\ln g_{e1}$$

For NH_3, $\Theta_{vib,1}=4800$ K, $\Theta_{vib,2}=1360$ K, $\Theta_{vib,3}=\Theta_{vib,4}=4880$ K, $\Theta_{vib,5}=\Theta_{vib,6}=2330$ K, $\Theta_{rot,A}=\Theta_{rot,B}=13.6$ K, $\Theta_{rot,C}=8.92$ K, $\sigma=3$, and $g_{e1}=1$. The various factors are as follows:

$$\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}=\left[\frac{2\pi(2.828\times10^{-26}\text{ kg})(1.381\times10^{-23}\text{ J·K}^{-1})(298.2\text{ K})}{(6.626\times10^{34}\text{ J·s})^2}\right]^{3/2}$$
$$=6.801\times10^{31}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A}=\frac{RT}{N_AP}=\frac{(0.08314\text{ dm}^3\cdot\text{bar·mol}^{-1}\cdot\text{K}^{-1})(298.2\text{ K})}{(6.022\times10^{23}\text{ mol}^{-1})(1\text{ bar})}$$
$$=4.117\times10^{-23}\text{ dm}^3=4.117\times10^{-26}\text{ m}^3$$

$$\frac{1}{2}\ln\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}=4.842$$

$$\sum_{j=1}^{6}\ln(1-e^{-\Theta_{vib,j}/T})=-0.01132$$

$$\sum_{j=1}^{6}\frac{\Theta_{vib,j}}{T}\left(\frac{e^{-\Theta_{vib,j}/T}}{1-e^{-\Theta_{vib,j}/T}}\right)=0.05451$$

The standard molar entropy is then

$$\frac{\overline{S}}{R}=4+14.845-0.5262+4.842+0.01132+0.05451$$
$$=23.23$$

This is 193.1 $J\cdot K^{-1}\cdot mol^{-1}$. The slight disagreement with the experimental value is due to our use of the rigid rotator-harmonic oscillator model.

20–44. Derive Equation 20.35.

The maximum efficiency is defined as

$$\text{maxmimum efficiency}=\frac{-w}{q_{rev,h}}=\frac{q_{rev,h}+q_{rev,c}}{q_{rev,h}}=1+\frac{q_{rev,c}}{q_{rev,h}}$$

Because the process is cyclic and reversible, $\Delta S_{engine}=0$, and so (as in Equation 20.34)

$$q_{rev,c}=-q_{rev,h}\frac{T_c}{T_h}$$

The efficiency becomes

$$\text{maximum efficiency}=1-\frac{T_c}{T_h}=\frac{T_h-T_c}{T_h}\qquad(20.35)$$

20–45. The boiling point of water at a pressure of 25 atm is 223°C. Compare the theoretical efficiencies of a steam engine operating between 20°C and the boiling point of water at 1 atm and at 25 atm.

At one atmosphere, using Equation 20.35 gives an efficiency of

$$\text{efficiency}=1-\frac{293}{373}=21\%$$

At 25 atm, the same engine will give an efficiency of

$$\text{efficiency}=1-\frac{293}{496}=41\%$$