Chapter 13 Problems: Entropy and Applications

<u>1</u>. Eqs. 13.2.10° and 13.2.15° apply for all processes for an ideal gas. Show that the two expressions are equivalent.

Answer: Starting with Eq. 13.2.15°: $\Delta S = C_p \ln \dfrac{T_2}{T_1} - nR \ln \dfrac{P_2}{P_1}$

Using the ideal gas equation of state to find the pressure ratio:

$$\frac{P_2}{P_1} = \frac{nRT_2/V_2}{nRT_1/V_1} = \frac{T_2V_1}{T_1V_2}$$

Substituting this ratio into the original equation gives:

$$\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{T_2V_1}{T_1V_2}$$

$$= C_p \ln \frac{T_2}{T_1} - nR \ln \frac{T_2}{T_1} - nR \ln \frac{V_1}{V_2}$$

However, $C_p = C_v + nR$ for an ideal gas:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} - nR \ln \frac{T_2}{T_1} - nR \ln \frac{V_1}{V_2}$$

The middle two terms cancel. Flipping the volume ratio, $\ln(V_1/V_2) = -\ln(V_2/V_1)$, gives:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

<u>2</u>. Eq. 13.2.10° applies for all processes for an ideal gas, assuming a constant heat capacity. However, for an adiabatic reversible process, $\Delta S = 0$. Does Eq. 13.2.10° give $\Delta S = 0$ for an adiabatic reversible process?

Answer: For an adiabatic reversible process, $V_2T_2{}^c = V_1T_1{}^c$ where $c = C_v/nR$, for solving for the volume ratio:

$$\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^c = \left(\frac{T_1}{T_2}\right)^{C_v/nR}$$

Substitution into Eq. 13.2.10° gives:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_v \ln \frac{T_2}{T_1} + nR \ln \left(\frac{T_1}{T_2}\right)^{C_v/nR}$$

$$= C_v \ln \frac{T_2}{T_1} + nR \frac{C_v}{nR} \ln \left(\frac{T_1}{T_2}\right) = C_v \ln \frac{T_2}{T_1} - C_v \ln \left(\frac{T_2}{T_1}\right) = 0$$

3. Calculate the change in entropy for 1.00 mole of ideal gas that is expanded against a constant external pressure of 1.00 atm from an initial pressure of 10.0 atm to a final pressure of 1.00 atm. During this process the temperature also drops from 25.00 °C to 0.00 °C. The heat capacity is C_P = 7/2 nR.

Answer: Even though the expansion is irreversible, knowing the initial and final states allows us to construct an equivalent reversible process. Using Eq. 13.2.15° gives:

$$\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

You can think of this equation as the result of a reversible constant pressure process followed by a reversible isothermal process.

$$\Delta S = 7/2(1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{273.2 \text{ K}}{298.2 \text{ K}} - (1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{1.00 \text{ atm}}{10.0 \text{ atm}}$$
$$= \text{-2.548 J K}^{-1} + 19.14 \text{ J K}^{-1} = 16.6 \text{ J K}^{-1}$$

Notice that we can use any pressure units for the ratio, since the units cancel out.

4. For a closed system we know that $\Delta U = q + w$, $\Delta U = q_{rev} + w_{max}$, and that a reversible process does maximum work on expansion and minimum work on contraction. Use these statements to derive the Clausius inequality.

Answer: Since internal energy is a state function and independent of the path for a process:

$$\Delta U = q + w = q_{rev} + w_{max} \qquad\qquad 1$$

Rearranging this expression to group the work terms and the heat transfer terms gives:

$$q - q_{rev} = w_{max} - w \qquad\qquad 2$$

Consider the expansion first. In doing comparisons, we like to arrange equations so that we are comparing positive quantities. In an expansion, the internal energy of the system drops and w_{max} and w are negative. Multiplying the last equation by -1 allows us to compare positive values for the work terms:

$$q_{rev} - q = (-w_{max}) - (-w) > 0 \qquad\qquad 3$$

The inequality holds because a reversible process does maximum work on expansion. Adding q to both sides of the inequality gives:

$$q_{rev} > q \qquad\qquad 4$$

Dividing both sides of this equation by T and using the definition of the entropy, $\Delta S = q_{rev}/T$ gives the Clausius inequality:

$$\Delta S > \frac{q}{T} \qquad\qquad 5$$

Now consider contraction. The work terms for a contraction are positive and a reversible process does minimum work on contraction. Eq. 2 then becomes:

$$q - q_{rev} = w_{max} - w < 0 \qquad \text{or} \quad q - q_{rev} < 0 \qquad\qquad 6$$

Adding q_{rev} to both sides of this inequality gives Eq. 4 again. So the derivation works for both expansions and contractions.

   You may wonder why we didn't use this derivation in this chapter. First, this derivation requires a rigorous proof of the statement that "a reversible process does maximum work on expansion and minimum work on contraction." Secondly, the form of Eq. 13.1.8 and the concept of "lost work" plays an important role in the development of irreversible thermodynamics.

<u>5</u>. In the section on "*Temperature as an Integrating Factor*" we derived Eq. 13.2.28° using Eq. 13.2.10°. Repeat the derivation of the entropy change for path 2, Eq. 13.2.28°. However, this time start from the heat transfers directly, Eqs. 13.2.16° and 13.2.18°, find dS_1 and dS_2. Then do the integrals. Note when path specific information is eliminated.

Answer: For path 2, we need to calculate the entropy change for each step and then add. For the constant pressure first step from Eq. 13.2.16°:

$$dS_1 = \frac{đq_{rev,1}}{T} = \frac{C_v}{T}dT + \frac{P_1}{T}dV \qquad\qquad \text{(cst P, reversible, closed, ideal gas)} \quad 1$$

Notice that both T and V change along this path. We can use the ideal gas equation of state for the second term, $P_1/T = nR/V$:

$$\Delta S_1 = \int_T^{T_i} \frac{C_v}{T}dT + \int_{V_1}^{V_2} \frac{nR}{V}dV \qquad\qquad \text{(cst. P, closed, ideal gas)} \quad 2$$

Eq. 1 is path specific, but after substitution of $P_1/T = nR/V$, the second term only depends on the initial and final states! Integrating the last equation results in:

$$\Delta S_1 = C_v \ln \frac{T_i}{T} + nR \ln \frac{V_2}{V_1} \qquad\qquad \text{(cst. P \& } C_v\text{, closed, ideal gas)} \quad 3$$

For the second step, at constant volume, dividing Eq. 13.2.18° by T gives:

$$dS_2 = \frac{đq_{rev,2}}{T} = \frac{C_v}{T}dT \qquad\qquad \text{(cst V, reversible, closed)} \quad 4$$

Integrating from T_i to back to the original temperature, T, gives:

$$\Delta S_2 = C_v \ln \frac{T}{T_i} \qquad\qquad \text{(cst. V \& } C_v\text{, reversible, closed)} \quad 5$$

The total change in entropy is the sum of 3 and 5:

$$\Delta S = C_v \ln \frac{T_i}{T} + nR \ln \frac{V_2}{V_1} + C_v \ln \frac{T}{T_i} \qquad\qquad \text{(cst. } C_v\text{, closed, ideal gas)} \quad 6$$

However, the temperature dependent terms cancel to give:

$$\Delta S = nR \ln \frac{V_2}{V_1} \qquad\qquad \text{(closed, ideal gas)} \qquad 7$$

The intermediate temperature no longer appears in the equation, so the final result is path independent and only depends on the initial and final states.

<u>6</u>. Given the total differential for the function z(x,y):

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

Show that dz is not an exact differential. The integrating factor for dz is (1/x). Define a new differential as df = dz/x. Show that df is exact. In other words, df is a state function.

Answer: Comparing the total differential dz to:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad\qquad 1$$

Gives: $\left(\dfrac{\partial z}{\partial x}\right)_y = \dfrac{y}{x}$ and $\left(\dfrac{\partial z}{\partial y}\right)_x = -1$ $\qquad\qquad 2$

The mixed partials are not equal:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \left(\frac{\partial\, y/x}{\partial y}\right)_x = \frac{1}{x} \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y = \left(\frac{\partial\, (-1)}{\partial x}\right)_y = 0 \qquad 3$$

So, dz is not an exact differential. However, multiplying both sides of Eq. 1 by the integrating factor (1/x) gives:

$$df = (1/x)\, dz = \frac{y}{x^2} dx - \frac{1}{x} dy \qquad\qquad 4$$

with $\left(\dfrac{\partial f}{\partial x}\right)_y = \dfrac{y}{x^2}$ and $\left(\dfrac{\partial f}{\partial y}\right)_x = -\dfrac{1}{x}$ $\qquad\qquad 5$

Now the mixed partials give:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial\, y/x^2}{\partial y}\right)_x = \frac{1}{x^2} \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial\, (-1/x)}{\partial x}\right)_y = \frac{1}{x^2} \qquad 6$$

Therefore df is an exact differential and f is a state function.

<u>7</u>. The lowest temperature heat capacity measurement for benzene is 3.79 K, where $C_p = 0.051463$ J K^{-1} mol^{-1}. The heat capacity data for crystalline and liquid benzene in Figure 13.4.1 can be fit to power series expansions. Because of the complex shape of the curve, this fitting is best done over three temperature ranges. The breaks between the ranges are arbitrary and are simply chosen to get a good fit to the overall curve. There are no solid-state phase transitions. The enthalpy of fusion for benzene is 10.59 kJ mol^{-1} at the normal melting point of 278.6 K. Calculate the absolute entropy of benzene at 298.2 K.

Table Problem 6: Approximate Heat Capacity for Solid and Liquid Benzene

solid	C_p (J K^{-1} mol^{-1})
3.79 – 20 K	$C_p = 0.10321\ T + 0.02431\ T^2$
20 – 84 K	$C_p = -16.5375 + 1.3854\ T - 0.00770\ T^2$
84 -278.6 K	$C_p = 38.2869 + 0.01075\ T + 1.097 \times 10^{-3}\ T^2$
liquid	
278.6 – 300 K	$C_p = 81.228 + 0.1794\ T$

Answer: For the cubic polynomial C_p curve fits, the integrals are given by:

$$\int_{T_1}^{T_2} \frac{C_p^{\ solid}}{T}\ dT = \int_{T_1}^{T_2} \frac{a + b\ T + c\ T^2}{T}\ dT = \int_{T_1}^{T_2} (a/T + b + c\ T)\ dT =$$

$$= a\ (\ln T\big|_{T_1}^{T_2} + b\ (T\big|_{T_1}^{T_2} + \frac{c}{2}\ (T^2\big|_{T_1}^{T_2} =$$

$$= a\ \ln \frac{T_2}{T_1} + b\ (T_2 - T_1) + \frac{c}{2}\ (T_2^2 - T_1^2)$$

The low temperature Debye extrapolation is covered in the text. The results of the integrals are given in the following table:

T_1 (K)	T_2 (K)	$a\ \ln(T_2/T_1)$ J K^{-1} mol^{-1}	$b\ (T_2\text{-}T_1)$ J K^{-1} mol^{-1}	$\frac{c}{2}(T_2^2\text{-}T_1^2)$ J K^{-1} mol^{-1}	$\frac{A}{3}(T_2^3\text{-}T_1^3)$ J K^{-1} mol^{-1}	total J K^{-1} mol^{-1}
0	3.79				0.0172	0.017
3.79	20	0	-1.673	4.687		3.01
20	84	-23.733	88.666	-25.626		39.31
84	278.6	45.904	2.092	38.703		86.70
278.6	298.2	5.501	3.502			9.00

The entropy of fusion is: $\Delta_{fus}S = \dfrac{\Delta_{fus}H}{T_{melt}} = \dfrac{10.59 \times 10^3 \text{J mol}^{-1}}{278.6\ \text{K}} = 38.01\ \text{J K}^{-1}\ \text{mol}^{-1}$

The total then is $S°_{298\ K} = 176.04$ J K^{-1} mol^{-1}
The literature value is 173.3 J K^{-1} mol^{-1}, which is close considering the approximations in the curve fitting. The coefficients from the curve fits don't have a particular interpretation. The curve fits are presented only as a way to make the integrals easier to do.

8. Calculate the absolute entropy of methylammonium chloride at 298.15 K. There are three crystalline forms. For the low temperature β-form, the heat capacity is 0.4209 J K^{-1} mol^{-1} at 12.04 K. The enthalpy of the equilibrium solid-state phase transition from the β to γ-form is 1.7790 kJ mol^{-1} at 220.4 K. The enthalpy of the equilibrium solid-state phase transition from the γ to α-form is 2.8183 kJ mol^{-1} at 264.5 K. All values are at standard state. The integrals of C_p/T for the three phases are:[1]

$$\int_{12.04\text{ K}}^{220.4\text{ K}} \frac{C_p^\beta}{T}\, dT = 93.412 \qquad \int_{220.4\text{ K}}^{264.5\text{ K}} \frac{C_p^\gamma}{T} = 15.439 \qquad \int_{264.5\text{ K}}^{298.15\text{ K}} \frac{C_p^\alpha}{T} = 10.690 \text{ J K}^{-1}\text{ mol}^{-1}$$

Answer: The plan is to add the C_p/T integrals and the entropy changes for the phase transitions. The integral from 0 K to 12.04 K is done using the Debye relationship for the heat capacity.
   The transition entropies for the solid-state phase transitions are:

$$\beta \to \gamma: \quad \Delta_{tr}S^\circ = \Delta_{tr}H^\circ/T_{tr} = 1.7790 \text{ kJ mol}^{-1}(1000 \text{ J}/1 \text{ kJ})/220.4 \text{ K} = 8.0717 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\gamma \to \alpha: \quad \Delta_{tr}S^\circ = \Delta_{tr}H^\circ/T_{tr} = 2.8183 \text{ kJ mol}^{-1}(1000 \text{ J}/1 \text{ kJ})/264.5 \text{ K} = 10.6552 \text{ J K}^{-1}\text{ mol}^{-1}$$

The Debye form for the heat capacity is Eq. 13.4.3 giving $C_p = AT_{low}^3 = 0.4209 \text{ J K}^{-1}\text{ mol}^{-1}$ at the lowest experimental temperature, T_{low}. The integral from 0 K is, Eq. 13.4.6:

$$\int_{0\text{ K}}^{T_{low}} \frac{C_p^\beta}{T}\, dT = \int_{0\text{ K}}^{T_{low}} AT^2\, dT = \frac{AT_{low}^3}{3} = \frac{0.4209 \text{ J K}^{-1}\text{ mol}^{-1}}{3} = 0.1403 \text{ J K}^{-1}\text{ mol}^{-1}$$

The absolute entropy, which is also called the Third Law entropy, is the sum:

$$\begin{array}{c} \scriptstyle (0 \to 12.04 \text{ K}) \;+\; (12.04 \to 220.4 \text{ K}) \;+\; \Delta_{tr}S^\circ(\beta\to\gamma) \;+\; (220.4 \to 264.5 \text{ K}) \;+\; \Delta_{tr}S^\circ(\gamma\to\alpha) \;+\; (264.5 \to 298.15 \text{ K}) \\ S_{298.15\text{ K}}^\circ = 0.1403 \;+\; 93.412 \qquad + 8.0717 + \qquad 15.439 \quad + 10.6552 + 10.690 \text{ J K}^{-1}\text{ mol}^{-1} \\ = 138.41 \text{ J K}^{-1}\text{ mol}^{-1} \end{array}$$

<u>9</u>. One mole of an ideal gas undergoes an isothermal reversible compression from an initial pressure of 1.00 bar to a final pressure of 10.00 bar. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: For an isothermal expansion of an ideal gas, $P_2V_2 = P_1V_1$ or $(V_2/V_1) = (P_1/P_2)$. For an isothermal expansion of an ideal gas $T = T_{surr}$ and Eq. 13.2.4° gives:

$$\Delta S = nR \ln(V_2/V_1) = nR \ln(P_1/P_2) = 1 \text{ mol } (8.314 \text{ J K}^{-1}\text{ mol}^{-1}) \ln (1.00/10.0) = -19.1 \text{ J K}^{-1}$$
$$\Delta S_{surr} = -\Delta S = 19.1 \text{ J K}^{-1}$$
$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

<u>10</u>. One mole of an ideal gas undergoes an isothermal expansion against a constant external pressure of 1.00 bar. In this process the system does 900.0 J or work from an initial volume of 1.00 L, that is w = -900.0 J. The temperature is 298.2 K. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: The work for an isothermal expansion against a constant external pressure of P_{ext} is:

$$w = -P_{ext}\, \Delta V = -P_{ext}\, (V_2 - V_1)$$

Solving for the final volume gives:

$$w = -900.0 \text{ J} = -1.00\text{x}10^5 \text{ Pa } (V_2 - 1.00 \text{ L})(1 \text{ m}^3/1000 \text{ L})$$

or $V_2 = 10.0$ L. The entropy change for the system is the same as a reversible expansion, since entropy is a state function and Eq. 13.2.4° again applies:

$$\Delta S = nR \ln(V_2/V_1) = 1 \text{ mol } (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln (10.0 \text{ L}/1.00 \text{ L}) = 19.1 \text{ J K}^{-1}$$

For the surroundings we use Eq. 13.5.2:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q}{T}$$

Since $\Delta U = 0$ for an isothermal process in an ideal gas, $q = -w = 900.$ J

$$\Delta S_{surr} = \frac{-q}{T} = \frac{-900. \text{ J}}{298.2 \text{ K}} = -3.02 \text{ J K}^{-1}$$

The entropy change of the surroundings is negative, because the surroundings transfer heat into the system to "pay" for the work done. Finally the total entropy is given by:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 19.1 \text{ J K}^{-1} - 3.02 \text{ J K}^{-1} = 16.1 \text{ J K}^{-1}$$

The expansion is spontaneous.

11. The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an adiabatic reversible expansion. The initial temperature is 298.2 K. The gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: Since this is an adiabatic reversible expansion, $q = q_{rev} = 0$:

$$\Delta S = \frac{q_{rev}}{T} = 0 \text{ and } \quad \Delta S_{surr} = \frac{-q}{T} = 0$$

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

We assume an isolated composite system consisting of the system and the surroundings. A reversible process is not spontaneous, so ΔS for the composite, isolated system is zero. If the system and surroundings are taken to be the universe, and if we assume that the universe is isolated, then $\Delta S_{tot} = \Delta S_{univ} = 0$.

12. The pressure of one mole of an ideal gas drops from 10.0 bar to 1.00 bar in an adiabatic expansion against a constant external pressure of 1.00 bar. The initial temperature is 298.2 K. Assume the gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: The temperature and pressure change for an adiabatic expansion so Eq. 13.2.15° must be used. However, the change in temperature must be calculated from $\Delta U = w$, Eq. x.x.x:

$$C_v (T_2 - T_1) = -P_{ext} (V_2 - V_1)$$

For a diatomic gas $C_v = 5/2$ nR. The volumes can be calculated using the ideal gas law:

$$5/2\ nR\ (T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

The nR is a common factor and cancels out. Substituting in the initial conditions and the final pressure gives:

$$5/2\ (T_2 - 298.2\ K) = -1.00\ bar\left(\frac{T_2}{1.00\ bar} - \frac{298.2\ K}{10.0\ bar}\right)$$

Simplifying:

$$5/2\ T_2 - 745.5\ K = -T_2 + 29.82\ K$$

Solving for T_2 gives 221.5 K. Using $C_p = C_v + nR = 7/2\ nR$, the entropy change is then:

$$\Delta S = C_p\ \ln\frac{T_2}{T_1} - nR\ \ln\frac{P_2}{P_1}$$

$$= (1\ mol)(8.314\ J\ mol^{-1}\ K^{-1})\left[7/2\ \ln(221.5\ K/298.2\ K) - \ln(1.00\ bar/10.0\ bar)\right]$$

$$= 10.5\ J\ K^{-1}$$

Since q = 0, then $\Delta S_{surr} = 0$ and $\Delta S_{tot} = \Delta S$. As expected, this expansion is spontaneous. Note that $\Delta U = w = C_v\ \Delta T = -1.59\ kJ$ and $\Delta H = C_p\ \Delta T = -2.23\ kJ$ for this example.

13. The pressure inside an inflated balloon filled with 1.00 mol of helium is 112.0 kPa. Assume the gas expands from the opening in the balloon in an adiabatic expansion. In other words, assume the gas expands quickly and we measure the final temperature of the gas before any thermal energy can be transferred from the surroundings. The initial temperature is 298.2 K. The atmospheric pressure is 101.3 kPa. Calculate the entropy change of the system and the surroundings and the entropy change of the universe.

Answer: To help visualize this expansion, as the helium leaves the balloon, think of the gas expanding inside a soap bubble. The surface of the soap bubble pushes back the atmosphere and work is done against the constant external ambient pressure.
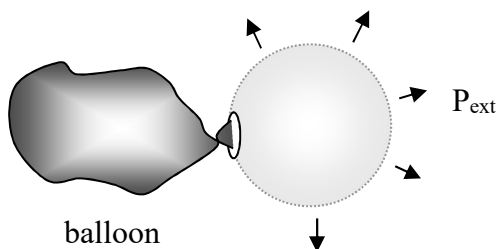
balloon

The temperature and pressure change for an adiabatic expansion so Eq. 13.2.15° must be used. However, the change in temperature must be calculated from $\Delta U = w$, Eqs. 9.8.23-9.8.24:

$$C_v\ (T_2 - T_1) = -P_{ext}\ (V_2 - V_1)$$

For a monatomic gas $C_v = 3/2\ nR$. The volumes can be calculated using the ideal gas law:

$$3/2\ nR\ (T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

The nR is a common factor and cancels out. The gas expands until the pressure of the helium is equal to the ambient pressure $P_2 = P_{ext}$. Substituting in the initial conditions and the final pressure gives:

$$3/2 \ (T_2 - 298.2 \ K) = -101.3 \ kPa \left(\frac{T_2}{101.3 \ kPa} - \frac{298.2 \ K}{112.0 \ kPa} \right)$$

Simplifying:

$$3/2 \ T_2 - 447.3 \ K = -T_2 + 269.7 \ K$$
$$5/2 \ T_2 = 717.0 \ K$$

Solving for T_2 gives 286.8 K. Using $C_p = C_v + nR = 5/2 \ nR$, the entropy change is then:

$$\Delta S = C_p \ \ln \frac{T_2}{T_1} - nR \ \ln \frac{P_2}{P_1}$$
$$= (1 \ mol)(8.314 \ J \ mol^{-1} \ K^{-1})[5/2 \ \ln(286.8 \ K/298.2 \ K) - \ln(101.3 \ kPa/112.0 \ kPa)]$$
$$= (1 \ mol)(8.314 \ J \ mol^{-1} \ K^{-1})[-0.09745 + 0.1004]$$
$$= (1 \ mol)(8.314 \ J \ mol^{-1} \ K^{-1})[0.00295]$$
$$= 0.0245 \ J \ K^{-1}$$

The $\ln(101.3/112.0)$ term has only three significant figures; then normal significant figure rules give only one significant figure in the final result. Since $q = 0$, then $\Delta S_{surr} = 0$ and $\Delta S_{tot} = \Delta S$. As expected, this expansion is spontaneous. Note that $\Delta U = w = C_v \ \Delta T = -142.$ J and $\Delta H = C_p \ \Delta T = -237.$ J for this example.

14. One mole of an ideal gas at 298.2 K triples its volume in an isothermal irreversible expansion against $P_{ext} = 0$. Calculate the changes in entropy of the system, the surroundings, and the total entropy change.

Answer: The entropy change for the system is the same as a reversible expansion, since entropy is a state function and Eq. 13.2.4° again applies:

$$\Delta S = nR \ \ln(V_2/V_1) = 1 \ mol \ (8.314 \ J \ K^{-1} \ mol^{-1}) \ \ln \ (3.00) = 9.13 \ J \ K^{-1}$$

For the surroundings we use Eq. 13.5.2:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q}{T}$$

The work for an isothermal expansion against an external pressure of zero, $P_{ext} = 0$, is:

$$w = -P_{ext} \ \Delta V = 0$$

Since $\Delta U = 0$ for an isothermal process in an ideal gas, $q = -w = 0$

$$\Delta S_{surr} = 0$$

Finally the total entropy is given by:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 9.13 \ J \ K^{-1}$$

The expansion is spontaneous.

15. Calculate the molar entropy change for the phase transition of water to water vapor at room temperature, 298.15K, and one atmosphere pressure. The difference in heat capacity on vaporization is -41.9 J K⁻¹ mol⁻¹. The standard enthalpy of vaporization of water <u>at 373.15 K</u> is 40.7 kJ mol⁻¹.

Answer: When the pressure is at 1 atm, we can only use Eq. 13.3.2 at the normal boiling point, because only at that temperature is the system in equilibrium:

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b} = \frac{40.7 \times 10^3 \text{J mol}^{-1}}{373.15 \text{ K}} = 109.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

To find the entropy change at room temperature, use Eq. 13.3.7:

$$\Delta_{tr}S_{T2} = \Delta_{tr}S_{T1} + \Delta_{tr}C_p \ln \frac{T_2}{T_1}$$

$$= 109.1 \text{ J K}^{-1} \text{ mol}^{-1} + (-41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{298.15 \text{ K}}{373.15 \text{ K}}$$

$$= 109.1 + 9.36 \text{ J K}^{-1} \text{ mol}^{-1} = 118.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

16. Consider the reaction:
    pyruvic acid → acetaldehyde + CO_2 (g)

(which is catalyzed by the enzyme pyruvate decarboxylase.) Calculate $\Delta_r S°$ for this reaction for the system and the surroundings at 298.2 K. The values in the table below are at 298.2 K.

Table for Problem 2:

substance	$\Delta_f H°$ (kJ mol⁻¹)	$S°$(J K⁻¹ mol⁻¹)
acetaldehyde	-192.30	160.2
CO_2	-393.51	213.74
pyruvic acid	-584.5	179.5

Answer: The data are:

pyruvic acid → acetaldehyde + CO_2 (g)
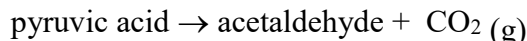
$\Delta_f H°$	-584.5	-192.30	-393.51	kJ mol⁻¹
$S°$	179.5	160.2	213.74	J K⁻¹ mol⁻¹

$\Delta_r H° = $ [products] − [reactants]
   $= [1\text{mol}(-192.30 \text{ kJ mol}^{-1}) + 1 \text{ mol}(-393.51 \text{ kJ mol}^{-1})] - [1 \text{ mol}(-584.5 \text{ kJ mol}^{-1})]$
   = -1.3 kJ

$\Delta_r S° = $ [products] − [reactants]
   $= [1\text{mol}(160.2 \text{ J K}^{-1} \text{ mol}^{-1}) + 1 \text{ mol}(213.74 \text{ J K}^{-1} \text{ mol}^{-1})] - [1 \text{ mol}(179.5 \text{ J K}^{-1} \text{ mol}^{-1})]$
   = 194.4 J K⁻¹

which is dominated by the increase in number of moles of gas. The change in entropy for the surroundings is:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-\Delta_r H}{T} = \frac{1.3 \text{ kJ } (1000 \text{ J } / 1\text{kJ})}{298.2} = 4.36 \text{ J K}^{-1}$$

which is spontaneous.

<u>17</u>. The chemical reaction that corresponds to the enthalpy of formation of urea, $(NH_2)_2CO$, is:

   C (graph) + 2 H$_2$ (g, 1 bar) + N$_2$ (g, 1bar) → (NH$_2$)$_2$CO (s) $\Delta_f H° = -333.1$ kJ mol^{-1}

Calculate the reaction entropy for the formation reaction, at standard state and at 298.15 K.

Answer: The formation reaction is the production of one mole of substance from the constituent elements in their standard states:

   C (graph) + 2 H$_2$ (g, 1 bar) + N$_2$ (g, 1bar) → (NH$_2$)$_2$CO (s) $\Delta_f H° = -333.1$ kJ mol^{-1}
   S°   5.740 130.574   191.50   104.6   J K^{-1} mol^{-1}

Remember that the enthalpy is an extensive function, so the stoichiometric coefficients are important. The reaction enthalpy change is given by Eq. 13.6.1 at standard state:

   $\Delta_r S° = [\Sigma \text{products}] - [\Sigma \text{reactants}] = \Sigma \nu_i \, S°$
   $\Delta_r S° = [104.6] - [5.740 + 2(130.574) + 191.50]$ J K^{-1} mol^{-1} = -353.7₉ J K^{-1} mol^{-1}

<u>18</u>. (a). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide:

   (NH$_2$)$_2$CO (s) + H$_2$O (l) → 2 NH$_3$ (g, 1 bar) + CO$_2$ (g, 1bar)

Using the data in the appendix, calculate the reaction enthalpy, at standard state and at 298.15 K.
(b). Consider the reaction as an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Calculate the change in entropy for the surroundings and the total entropy change at 298.15 K. (See Chapter 8 Problem 2b).

Answer: The plan is to note that the entropy change of the surroundings is determined from the reaction enthalpy, since at constant pressure, q$_{reaction}$ = q$_p$ = Δ_rH.
   The enthalpies of formation and absolute entropies, from Tables 8.4.1 and 8.4.2, are:

	(NH$_2$)$_2$CO (s)	+ H$_2$O (l)	→ 2 NH$_3$ (g, 1 bar)	+ CO$_2$ (g, 1bar)	units
$\Delta_f H°$	-333.1	-285.830	-46.11	-393.509	kJ mol^{-1}
S°	104.6	69.92	192.34	213.74	J K^{-1} mol^{-1}
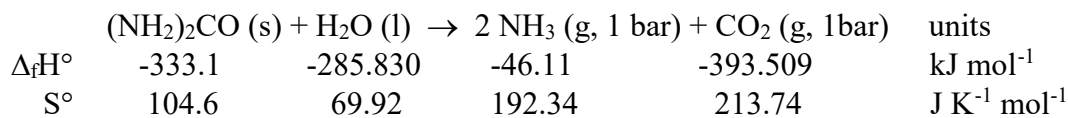
Remember that enthalpy and entropy are extensive functions, so the stoichiometric coefficients are important. The reaction enthalpy and entropy changes are given by Eqs. 8.4.9 and 13.6.1 at standard state:

   $\Delta_r H° = [\Sigma \text{products}] - [\Sigma \text{reactants}] = \Sigma \nu_i \, \Delta_f H°$
   $\Delta_r S° = [\Sigma \text{products}] - [\Sigma \text{reactants}] = \Sigma \nu_i \, S°$

(a). The reaction entropy is:

$$\Delta_r S° = [2(192.34) + 213.74] - [104.6 + 69.92] \text{ J K}^{-1} \text{ mol}^{-1} = 423.9 \text{ J K}^{-1} \text{ mol}^{-1}$$
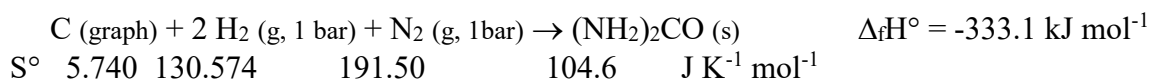
The reaction entropy is strongly favorable because three moles of gas are produced.
(b). The reaction enthalpy is (see Chapter 8 Problem 2b):

$$\Delta_r H° = [2(-46.11) + (-393.509)] - [(-333.1) + (-285.83)] \text{ kJ mol}^{-1} = 133.2 \text{ kJ mol}^{-1}$$

The entropy change of the surroundings is given by Eq. 13.5.4:

$$\Delta_r S_{surr} = -\Delta_r H°/T = -(133.2 \text{ kJ mol}^{-1})(1000 \text{ J/1 kJ})/298.15 \text{ K} = -446.7_5 \text{ J K}^{-1} \text{ mol}^{-1}$$

The total entropy change is:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 423.9 \text{ J K}^{-1} \text{ mol}^{-1} + (-446.7_5 \text{ J K}^{-1} \text{ mol}^{-1}) = -22.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction is not spontaneous at 298.15 K. Of course, enzyme catalysis won't change the spontaneity.

<u>19</u>. The aging of marine aerosols produces $NaHSO_4$ cloud condensation nuclei, CCN. The distribution of CCN determines the formation and reflectivity of clouds, which play an important role in determining the albedo of the atmosphere (see Chapter 8 Problem 3). (a). Using the data in the appendix, calculate the entropy change for the system and for the surroundings for the following reactions separately and in sum, under standard conditions and at 298.15 K.

$$H_2S \text{ (g, 1bar)} + 2 O_2 \text{ (g, 1bar)} \rightarrow SO_3 \text{ (g, 1bar)} + H_2O \text{ (g, 1bar)}$$
$$SO_3 \text{ (g, 1 bar)} + H_2O \text{ (l)} \rightarrow H_2SO_4 \text{ (l)}$$
$$NaCl \text{ (s)} + H_2SO_4 \text{ (l)} \rightarrow HCl \text{ (g, 1bar)} + Na^+ \text{ (ao)} + HSO_4^- \text{ (ao)}$$

(b). Combine the three reactions to show the overall process. Use the combined reaction to calculate the overall reaction enthalpy. Compare with the result in part (a).

Answer: The plan is to use Hess's Law for each reaction and then the three reactions in sequence. Note that both gaseous and liquid water are involved in the reactions. Use the absolute entropy for pure liquid H_2SO_4. The reaction enthalpies are given in Chapter 8 Problem 3.

(a). The absolute entropies, from Table 8.4.1, combine to give the reaction entropies:

	H_2S (g, 1bar) +	2 O_2 (g, 1bar) →	SO_3 (g, 1bar) +	H_2O (g, 1bar)	units	1
S°:	205.8	205.029	256.76	188.715	J K^{-1}mol^{-1}	

	SO_3 (g, 1 bar) +	H_2O (l) →	H_2SO_4 (l)			2
S°:	256.76	69.92	156.904		J K^{-1}mol^{-1}	

	$NaCl$ (s) +	H_2SO_4 (l) →	HCl (g, 1bar) +	Na^+ (ao) +	HSO_4^- (ao)	3
S°:	72.4	156.904	186.799	59.0	131.8	J K^{-1} mol^{-1}

Each reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_r S° = [\Sigma products] - [\Sigma reactants] = \sum v_i\, S°$$

For reaction 1:

$\Delta_r S° = [188.715 + 256.76] - [205.8 + 2(205.029)]\ J\ K^{-1}mol^{-1} = -170.3_8\ J\ K^{-1}\ mol^{-1}$

$\Delta_r S_{surr} = -\Delta_r H°/T = -(-616.91\ kJ\ mol^{-1})(1000\ J/1\ kJ)/298.15\ K = 2069.1_3\ J\ K^{-1}\ mol^{-1}$

For reaction 2:

$\Delta_r S° = [156.904] - [256.76 + 69.92]\ J\ K^{-1}\ mol^{-1} = -169.77_6\ J\ K^{-1}\ mol^{-1}$

$\Delta_r S_{surr} = -\Delta_r H°/T = -(-132.44\ J\ K^{-1}\ mol^{-1})(1000\ J/1\ kJ)/298.15\ K = 444.13_1\ J\ K^{-1}\ mol^{-1}$

For reaction 3:

$\Delta_r S° = [131.8 + 59.0 + 186.799] - [72.4 + 156.904]\ J\ K^{-1}\ mol^{-1} = 148.3_0\ J\ K^{-1}\ mol^{-1}$

$\Delta_r S_{surr} = -\Delta_r H°/T = -(5.23\ J\ K^{-1}\ mol^{-1})(1000\ J/1\ kJ)/298.15\ K = -17.5_4\ J\ K^{-1}\ mol^{-1}$

The overall sequence gives:

$\Delta_r S° = (-170.3_8) + (-169.77_6) + 148.3_0\ J\ K^{-1}mol^{-1} = -191.8_6\ J\ K^{-1}mol^{-1}$

$\Delta_r S_{surr} = 2069.1_3 + 444.13_1 + (-17.5_4)\ J\ K^{-1}\ mol^{-1} = 2495.7_2\ J\ K^{-1}\ mol^{-1}$

 (b). We can check the results by working directly with the overall reaction. The sum of the three steps gives:

$H_2S\ (g) + 2O_2\ (g) + NaCl\ (s) + H_2O\ (l) \rightarrow HCl\ (g) + Na^+(ao) + HSO_4^-\ (ao) + H_2O\ (g)$

S°: 205.8   205.029   72.4   69.92   186.799   59.0   131.8   188.715 $J\ K^{-1}\ mol^{-1}$

$\Delta_r S° = [186.799 + 59.0 + 131.8 + 188.715] - [205.8 + 2(205.029) + 72.4 + 69.92]\ J\ K^{-1}\ mol^{-1}$
$\quad = -191.8_6\ J\ K^{-1}\ mol^{-1}$

The combined reaction enthalpy is $\Delta_r H° = -744.12\ kJ\ mol^{-1}$, giving the entropy change of the surroundings:

$\Delta_r S_{surr} = -\Delta_r H°/T = -(-744.12\ kJ\ mol^{-1})(1000\ J/1\ kJ)/298.15\ K = 2495.7_9\ J\ K^{-1}\ mol^{-1}$

The step-wise and combined reactions give the same result, to within round-off error. The combined reaction entropy is unfavorable. The overall reaction is enthalpy driven, since the entropy change of the surroundings is the dominant factor.

20. Use normal mode analysis to decide whether propane or 2-methylpropane has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

Answer: The results of a normal mode analysis using Spartan at the AM1 level is given in the table below. You didn't need to get the thermodynamic analysis, but it is included for comparison.

Table: Normal Mode Analysis for Several Hydrocarbons

Compound	translation	rotation	vibration	total	literature	$\tilde{\nu} < 500$ cm-1
methane	143.3	42.8	0.4	186.6	186.26	
acetylene	149.4	45.4	2.7	197.5	200.94	
ethylene	150.3	66.4	2.4	219.1	219.56	
ethane	151.2	68.1	10.9	230.3	229.60	204
cyclopropane	155.4	75.8	4.8	236.0	237.55	
propane	156.0	89.0	32.8	277.7	269.91	79, 190, 414(b)
2-methylpropane	159.4	93.5	44.4	297.3	294.64	149, 191x2, *398*x2, *478*
butane	159.4	96.7	45.4	301.4	310.23	103, 196, 206, *302*, *473*
cyclohexane	164.0	95.2	36.8	296.0	298.19	214x2, 331, *467*x2
benzene	163.1	86.7	19.1	268.9	269.31	*371*x2

Notice that 2-methylpropane has six low frequency normal modes, while propane has three. The lower the frequency of the normal mode the bigger the contribution to the entropy and heat capacity. From the table above, propane has the smallest frequency normal mode. However, the overall result for 2-methylpropane is a larger vibrational contribution to the entropy.

The normal modes for propane, using MOPAC are a little different:

```
142.40391    187.97537    412.50857
```

The normal modes for 2-methylpropane, using MOPAC are:

```
144.44885    182.36068    199.92640    395.61601    398.93565    477.33557
```

The thermodynamic analysis is at the bottom of the output for Spartan, GAMESS, Gaussian, and MOPAC. The thermodynamic analysis for propane from MOPAC, with the THERMO keyword, at 300 K is:

```
          CALCULATED THERMODYNAMIC PROPERTIES
                         *
  TEMP. (K)    PARTITION FUNCTION    H.O.F.     ENTHALPY    HEAT CAPACITY   ENTROPY
                                    KCAL/MOL    CAL/MOLE     CAL/K/MOL     CAL/K/MOL

  300   VIB.        4.226                      1173.47287     8.68840       6.77570
        ROT.     .200E+05                       894.267       2.981        22.664
        INT.     .846E+05                      2067.740      11.669        29.439
        TRA.     .286E+27                      1490.445       4.968        37.291
        TOT.                       -24.224     3558.1849     16.6374       66.7306
```

The thermodynamic analysis for 2-methylpropane from MOPAC at 300 K is:

```
        CALCULATED THERMODYNAMIC PROPERTIES
                       *
  TEMP. (K)    PARTITION FUNCTION    H.O.F.     ENTHALPY    HEAT CAPACITY   ENTROPY
                                    KCAL/MOL    CAL/MOLE     CAL/K/MOL     CAL/K/MOL

  300   VIB.        9.160                      1911.82988    13.87179      10.77417
        ROT.     .517E+05                       894.267       2.981        24.547
        INT.     .473E+06                      2806.097      16.853        35.321
        TRA.     .433E+27                      1490.445       4.968        38.114
        TOT.                       -29.325     4296.5419     21.8208       73.4355
```

The vibrational frequencies for torsional modes are very sensitive to the level of the calculation. You will see large differences, especially for the lowest frequency normal modes, from program to program. However, the number of low frequency normal modes will be reproducible. There is

another problem with this approach. The normal mode analysis assumes that the vibrations are purely harmonic oscillators. We will see in the vibrational spectroscopy chapter that torsions are strongly anharmonic. Normal mode analysis does a poor job, quantitatively, in predicting the frequencies of these vibrations. For now, just counting low frequency normal modes will help you to visualize the vibrational contribution to the entropy. We will argue later about how to get good quantitative predictions.

21. Use normal mode analysis to decide whether cyclohexane or benzene has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

Answer: Since cyclohexane has more atoms, we would predict that cyclohexane would have the higher absolute entropy. The larger number of atoms predicts a greater moment of inertia for the molecule and thus a greater rotational contribution to the entropy. Also, remember that the number of normal modes for a non-linear molecule is 3N-6. So the number of vibrational normal modes for cyclohexane is greater, which would also predict a higher entropy.
   Please consult the table for the last problem for the results of the normal modes analysis. Cyclohexane has five vibrations with low wavenumbers, while benzene has only two. Therefore, cyclohexane will have a higher contribution from vibrations than benzene. The three lowest frequency vibrations for cyclohexane are hindered ring torsions. The low frequency vibrations for benzene are out-of-plane C-H bending vibrations.

22. Give an example for each of the following types of processes. Choose your examples from ideal gas expansions or compressions or phase transitions of pure substances. Specify the difference in the variable, P or T, that is responsible for the spontaneous or non-spontaneous direction of the process:
     (a). a spontaneous adiabatic and isothermal process,
     (b). a spontaneous isothermal process with a decrease in entropy for the system,
     (c). a non-spontaneous isothermal process with an increase in entropy for the system,
     (d). a spontaneous adiabatic process that decreases the temperature of the system.

Answers: (a). a spontaneous adiabatic and isothermal process: an irreversible expansion of an ideal gas against a vacuum. (Ideal mixing of gases is an additional example that will be covered in the next chapter.) The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow 0$ with $P_{ext} = 0$.

(b). a spontaneous isothermal process with a decrease in entropy for the system: an irreversible compression of an ideal gas with an external pressure greater than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{high}$ with $P_o < P_{ext}$. Another example is the liquefaction of 1 mol of a gas or freezing of 1 mol of a liquid at a temperature below the equilibrium phase transition temperature, at the chosen ambient pressure. A specific example is the freezing of water at -5°C at 1 bar ambient pressure. The independent variable is

the number of moles of gas or liquid, respectively: $dn_g = -1$ mol or $dn_{liq} = -1$ mol. The variable controlling the spontaneous direction is the temperature, $T < T_b^*$ or T_f^* with $T = T_{surr}$.

(c). a non-spontaneous isothermal process with an increase in entropy for the system: the isothermal expansion of an ideal gas against an external pressure greater than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{low}$ with $P_o < P_{ext}$ giving a non-spontaneous process. Another example is the melting of 1 mol of a solid at a temperature below the equilibrium phase transition temperature, at the chosen ambient pressure. The variable controlling the spontaneous direction is the temperature, $T < T_f^*$ with $T = T_{surr}$.

(d). a spontaneous adiabatic process that decreases the temperature of the system: an irreversible adiabatic expansion of an ideal gas against an external pressure less than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{low}$ with $P_o > P_{ext}$. For an adiabatic process for a phase transition, consider a phase transition in a thermos bottle. Melting decreases the temperature of the system for an adiabatic process. Then for a spontaneous adiabatic process that decreases the temperature of the system, the melting of 1 mol of a solid at a temperature above the equilibrium phase transition temperature is a good example. The variable controlling the spontaneous direction is the temperature, $T_o \rightarrow T_{low}$ with $T_o > T_f^*$.

23. The Clausius inequality relates the entropy changes of the system and surroundings. Consider an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Use the Clausius inequality, Eq. 13.1.9, to show that $dS > -dS_{surr}$ for a spontaneous process.

Answer: Consider the system and surroundings as an isolated composite. The Clausius inequality, Eq. 13.1.9, gives $dS > đq/T$. For a spontaneous isothermal process, $T = T_{surr}$ giving $dS_{surr} = -đq/T$. Substitution of this result for the surroundings into the right-side of the Clausius inequality gives, for a spontaneous isothermal process: $dS > -dS_{surr}$.

24. Determine if the following statements are true of false. If the statement is false, describe the changes that are required to make the statement true, if possible. Assume that the system and surroundings are an isolated composite. (Hint: three of the following statements are true.)

(a). The heat transfer for the system is equal in magnitude and opposite in sign to the heat transfer for the surroundings ($đq = -đq_{surr}$).

(b). The entropy change of the system is equal in magnitude and opposite in sign to the entropy change of the surroundings ($dS = -dS_{surr}$).

(c). For a spontaneous process, the magnitude of the entropy change of the system is never greater than the magnitude of the entropy change of the surroundings.

(d). Heat transfer to a system at low temperature gives a larger change in the entropy of the system than the transfer of the same amount of heat at high temperature.

(e). Spontaneous processes always result in dispersal of energy to the surroundings.

(f). The entropy of every system is zero at absolute zero.

(g). For a given heat transfer, the entropy change of the surroundings is independent of the details of the process for the system.

(h). One mole of xenon gas at 1 bar and 298.2 K is mixed with another mole of xenon gas at 1 bar and 298.2 K. The total entropy change of the combined systems is positive for the process.

Answers: (a). True: heat and work are transfers of energy and so necessarily for the transfer, đq = – đq$_{surr}$ and đw = – đw$_{surr}$.

(b). False: The entropy change for a spontaneous process is always positive for an isolated composite of the system and surroundings, by the Second Law, $dS + dS_{surr} > 0$. Only for a reversible process is $dS = – dS_{surr}$, since then đq = đq$_{rev}$.

(c). False: For a spontaneous endothermic process in a closed system, the entropy change of the system is positive and the entropy change of the surroundings is negative. By the Second Law for an isolated composite of the system and the surroundings, $dS + dS_{surr} > 0$. To give an increase in total entropy for an endothermic process, the magnitude of the entropy change of the system must be greater than the magnitude of the entropy change of the surroundings.

   However, to be more precise, we should use the Clausius inequality. Consider an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. The Clausius inequality, Eq. 13.1.9, is $dS > đq/T$. For a spontaneous isothermal process, $T = T_{surr}$ giving $dS_{surr} = – đq/T$. Substitution of the last result into the Clausius inequality gives for a spontaneous isothermal process: $dS > –dS_{surr}$. For an endothermic process, dS_{surr} is negative. The magnitude of dS_{surr} is then $|dS_{surr}| = –dS_{surr}$. To satisfy the Second Law, if the entropy change of the surroundings is negative then the entropy change of the system must be positive, and then $|dS| = dS$. The Clausius inequality then gives for a spontaneous endothermic process $|dS| > |dS_{surr}|$; the magnitude of the entropy change of the system must be greater than the magnitude of the entropy change of the surroundings.

(d). True: refer to Figure 13.1.1.

(e). False: By the Second Law, for an isolated composite of the system and the surroundings, $dS + dS_{surr} > 0$. However, the change in entropy of the surroundings can be negative, as for an endothermic process, or zero, as for an adiabatic process. The total entropy change can be dominated by the entropy change of the system, which allows an unfavorable entropy change of the surroundings. A spontaneous process may or may not give an increase of the entropy of the surroundings. A spontaneous process may or may not result in energy dispersal to the surroundings.

(f). False: the entropy of all pure, perfect crystalline substances is zero at absolute zero. Residual entropy can be locked into a system before cooling to absolute zero. Such a system is metastable, being trapped into a non-zero entropy state by a kinetic barrier.

(g). True: For a given heat transfer, đq, the entropy change of the surroundings is given by $dS_{surr} = – đq/T_{surr}$, irrespective of whether the process is reversible or irreversible.

(h). False: the entropy change is zero, because the xenon atoms in the two systems are indistinguishable. Consider the two systems as an isolated composite. The process is diagrammed as follows:

Xe	Xe
1 bar	1 bar
298.2 K	298.2 K

$\rightarrow$

Xe
1 bar
298.2 K
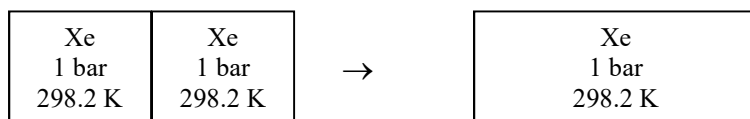
The instant that the barrier is removed, the combined system is at equilibrium. There are no gradients, so no process occurs.

<u>25</u>. Heat capacities are often approximated by a power series: $C_p = a + b\,T + c\,T^{-2}$, for a, b, and c constants. Find the change in enthalpy and entropy of a substance for a constant pressure process with a temperature change from T_1 to T_2.

Answer: The plan is to integrate the partial derivative relationships $(\partial H/\partial T)_P = C_p$ and $(\partial S/\partial T)_P = C_p/T$. For a constant heat capacity, $\Delta H = C_p(T_2 - T_1)$ and $\Delta S = C_p \ln(T_2/T_1)$.
   The enthalpy integral is:

$$\Delta H = \int_{T_1}^{T_2} C_p\, dT = \int_{T_1}^{T_2} (\,a + b\,T + c\,T^{-2}) \,dT$$
$$= \int_{T_1}^{T_2} a\, dT + \int_{T_1}^{T_2} bT\, dT + \int_{T_1}^{T_2} cT^{-2}\, dT$$
$$= a\,[\,T\,|_{T_1}^{T_2} + \frac{b}{2}\,[\,T^2\,|_{T_1}^{T_2} - c\,[\,T^{-1}\,|_{T_1}^{T_2}$$
$$= a\,(T_2 - T_1) + \frac{b}{2}\,(T_2^2 - T_1^2) + c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Compare this result with Chapter 7 Problem 29, which uses a different heat capacity power series expansion. The leading term, in both cases, agrees with the expression that assumes a constant heat capacity, $\Delta H = C_p(T_2 - T_1)$.
   The entropy integral is:

$$\Delta S = \int_{T_1}^{T_2} C_p/T\, dT = \int_{T_1}^{T_2} \left(\frac{a}{T} + b + c\,\frac{1}{T^3}\right) dT$$
$$= \int_{T_1}^{T_2} \frac{a}{T}\, dT + \int_{T_1}^{T_2} b\, dT + \int_{T_1}^{T_2} cT^{-3}\, dT$$
$$= a\,[\,\ln(T)|_{T_1}^{T_2} + b\,[\,T\,|_{T_1}^{T_2} - \frac{c}{2}\,[\,T^{-2}\,|_{T_1}^{T_2}$$
$$= a\,\ln\!\left(\frac{T_2}{T_1}\right) + b\,(T_2 - T_1) - \frac{c}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)$$

Compare this result with Eq. 13.2.34, which uses a different heat capacity power series expansion. An example from the NIST WebBook online database that uses a term in T^{-2} is carbon dioxide (g) (http://webbook.nist.gov).

<u>26</u>. Calculate the residual entropy at 0 K for NO, assuming random NO and ON orientations.

Answer: Given the two ways of orienting NO is the same as for CO and N_2O, the residual entropy is approximated as $S_o = R \ln w = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(2) = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$.