5 Entropy and the Second and Third Laws of Thermodynamics

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual.*

Conceptual Problems

Q5.1 Under what conditions is $\Delta S < 0$ for a spontaneous process?

For a spontaneous process, $\Delta S + \Delta S_{surroundings} > 0$. A process is spontaneous if $\Delta S < 0$ only if $\Delta S_{surroundings} > 0$ and $\left| \Delta S_{surroundings} \right| > \left| \Delta S \right|$.

Q5.2 Why are ΔS_{fusion} and $\Delta S_{vaporization}$ always positive?

This is the case because ΔH_{fusion} and $\Delta H_{vaporization}$ are always positive. In each of these transitions, attractive forces must be overcome. In both of these process, the disorder in the system increases.

Q5.3 An ideal gas in thermal contact with the surroundings is cooled in an irreversible process at constant pressure. Are ΔS, $\Delta S_{surroundings}$, and ΔS_{total} positive, negative, or zero? Explain your reasoning.

For a constant pressure process, $\Delta S = nC_{P,m} \ln \dfrac{T_f}{T_i}$ and if $\Delta T < 0, \Delta S < 0$. For a process that actually occurs, $\Delta S_{total} > 0$. Therefore, $\Delta S_{surroundings} > 0$.

Q5.4 The amplitude of a pendulum consisting of a mass on a long wire is initially adjusted to have a very small value. The amplitude is found to decrease slowly with time. Is this process reversible? Would the process be reversible if the amplitude did not decrease with time?

No, because dissipative forces (in this case friction) are acting on the system. If the amplitude did not decrease, no dispersive forces act on the system and the oscillation is reversible in the limit of very small amplitudes. If the amplitude did not decrease with time, no dissipative forces act on the system, and because the amplitude is very small, the process is reversible.

Q5.5 A process involving an ideal gas is carried out in which the temperature changes at constant volume. For a fixed value of ΔT, the mass of the gas is doubled. The process is repeated with the same initial mass and ΔT is doubled. For which of these processes is ΔS greater? Why?

ΔS is greater if the mass is doubled, because ΔS increases linearly with the amount of material. By contrast, S only increases as the logarithm of the temperature. This increase is much slower than a linear increase.

Q5.6 You are told that $\Delta S = 0$ for a process in which the system is coupled to its surroundings. Can you conclude that the process is reversible? Justify your answer.

No. The criterion for reversibility is $\Delta S + \Delta S_{surroundings} = 0$. To decide if this criterion is satisfied, $\Delta S_{surroundings}$ must be known.

Q5.7   Under what conditions does the equality $\Delta S = \Delta H/T$ hold?

Because $dS = \dfrac{\not{d}q_{reversible}}{T}$, the equality holds if $\not{d}q_{reversible} = dH$. This is the case for a reversible process at constant pressure.

Q5.8   Is the following statement true of false? If it is false, rephrase it so that it is true. The entropy of a system cannot incease in an adiabatic process.

False. The entropy of a system cannot incease in a reversible adiabatic process.

Q5.9   Which of the following processes is spontaneous?

a.   The reversible isothermal expansion of an ideal gas.

b.   The vaporization of superheated water at 102°C and 1 bar.

c.   The constant pressure melting of ice at its normal freezing point by the addition of an infinitesimal quantity of heat.

d.   The adiabatic expansion of a gas into a vacuum.

(a)   is not spontaneous because the system and surroundings are in equilibrium during a reversible process.

(b)   is spontaneous because the equilibrium phase under the stated conditions is a gas.

(c)   is not spontaneous because the process is reversible if the amount is infinitesimal.

(d)   is spontaneous because at equilibrium, the density of a gas is uniform throughout its container.

Q5.10   One joule of work is done on a system, raising its temperature by one degree centigrade. Can this increase in temperature be harnessed to do one joule of work? Explain.

No, because it would violate the second law of thermodynamics. Heat cannot be converted to work with 100% efficiency.

Q5.11   Your roommate decides to cool the kitchen by opening the refrigerator. Will this strategy work? Explain your reasoning.

It will not work if the refrigerator is totally inside the room because cooling the room would require that the refrigerator takes up more energy than it releases. Because the efficiency of the refrigerator is less than 100%, the net effect will be to heat the room. However, if the refrigerator is mounted in a window or door so that the heat is not released into the room, it is possible to cool the room in this way.

Q5.12   An ideal gas undergoes an adiabatic expansion into a vacuum. Are ΔS, $\Delta S_{surroundings}$, and ΔS_{total} positive, negative, or zero? Explain your reasoning.

Because $\Delta T = 0$ for the expansion of an ideal gas into a vacuum, $\Delta S = nR\,\ln\dfrac{V_f}{V_i} > 0$. Because $\Delta S_{surroundings}$ is calculated using the actual heat flow into the surroundings, $\Delta S_{surroundings} = 0$ for an adiabatic process. $\Delta S_{total} = \Delta S + \Delta S_{surroundings} > 0$.

Q5.13   When a saturated solution of a salt is cooled, a precipitate crystallizes out. Is the entropy of the crystalline precipitate greater or less than the dissolved solute? Explain why this process is spontaneous.

Forming the crystalline precipitate is a process for which $\Delta S < 0$. However, $\Delta S_{surroundings}$ is opposite in sign and greater in magnitude so that $\Delta S + \Delta S_{surroundings} > 0$, making the process spontaneous.

Q5.14   A system undergoes a change from one state to another along two different pathways, one of which is reversible and the other of which is irreversible. What can you say about the relative magnitudes of $q_{reversible}$ and $q_{irreversible}$?

Because S is a state function, ΔS is the same for a reversible and an irreversible path between the same initial and final states. However, as discussed in Section 5.6, $\not{d}q_{reversible} - \not{d}q = TdS - \not{d}q \geq 0$.

Q5.15 An ideal gas in a piston and cylinder assembly with adiabatic walls undergoes an expansion against a constant external pressure. Are ΔS, $\Delta S_{surroundings}$, and ΔS_{total} positive, negative, or zero? Explain your reasoning.

Because the process is adiabatic, $\Delta S_{surroundings} = 0$. Because the process actually occurs, $\Delta S_{total} > 0$. Because $\Delta S = \Delta S_{total} - \Delta S_{surroundings}$, $\Delta S > 0$.

Q5.16 Is the equation

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV = C_V \ln\frac{T_f}{T_i} + \frac{\beta}{\kappa}(V_f - V_i)$$

valid for an ideal gas?

No. Because β and κ are not independent of V for an ideal gas, they can't be taken out of the integral.

Q5.17 Why is the efficiency of a Carnot heat engine the upper bound to the efficiency of an internal combustion engine?

This is the case because the maximum work that can be done on the surroundings in the expansion of a gas is in a reversible process.

Q5.18 Two vessels of equal volume, pressure, and temperature both containing Ar are connected by a valve. What is the change in entropy when the valve is opened, allowing mixing of the two volumes? Is ΔS the same if one of the volumes contained Ar, and the other contained Ne?

If the same gas is on either side of the valve, $\Delta S = 0$ because the individual atoms or molecules of the gas are indistinguishable. However, if the two gases are different, $\Delta S > 0$ because of the mixing of the gases.

Q5.19 Without using equations, explain why ΔS for a liquid or solid is dominated by the temperature dependence of S as both P and T change.

It is useful to think of $S = S(V,T)$. Because V changes very little with P for a liquid or solid, entropy changes are dominated by changes in T rather than P for liquids and solids.

Q5.20 Solid methanol in thermal contact with the surroundings is reversibly melted at the normal melting point at a pressure of 1 atm. Are ΔS, $\Delta S_{surroundings}$, and ΔS_{total} positive, negative, or zero? Explain your reasoning.

$\Delta S = \dfrac{\Delta H_{fusion}}{T_m} > 0$; Because the process is reversible, $\Delta S_{total} = 0$. $\Delta S_{surroundings} = -\Delta S = -\dfrac{\Delta H_{fusion}}{T_m} < 0$.

Q5.21 Can incandescent lighting be regarded as an example of cogeneration during the heating season? In a season where air conditioning is required?

It can be regarded as an example of cogeneration during the heating season because the waste heat from light production is used to heat the building. It is not an example of cogeneration if air conditioning is used because the waste heat reduces the effect of the air conditioning.

Numerical Problems

P5.1 Consider the formation of glucose from carbon dioxide and water, that is, the reaction of the photosynthetic process:
$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$.

The following table of information will be useful in working this problem:

$T = 298$ K	$CO_2(g)$	$H_2O(l)$	$C_6H_{12}O_6(s)$	$O_2(g)$
ΔH_f° (kJ mol^{-1})	−393.5	−285.8	−1273.1	0.0
S° (J mol^{-1}K^{-1})	213.8	70.0	209.2	205.2
$C^\circ_{P,m}$ (J mol^{-1}K^{-1})	37.1	75.3	219.2	29.4

Calculate the entropy and enthalpy changes for this chemical system at $T = 298\,\text{K}$ and $T = 310\,\text{K}$. Calculate also the entropy change of the surroundings and the universe at both temperatures, assuming that the system and surroundings are at the same temperature.

At 298.15 K

$$\Delta S_R^\circ = 209.2\,\text{J K}^{-1}\,\text{mol}^{-1} + 6 \times 205.2\,\text{J K}^{-1}\,\text{mol}^{-1} - 6 \times 213.8\,\text{J K}^{-1}\,\text{mol}^{-1} - 6 \times 70.0\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -262.4\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta H_R^\circ = -1273.1\,\text{kJ mol}^{-1} - 6 \times 393.5\,\text{kJ mol}^{-1} - 6 \times 285.8\,\text{kJ mol}^{-1} = 2803\,\text{kJ mol}^{-1}$$

$$\Delta S_{surroundings}^\circ = \frac{-\Delta H_R^\circ (298.15\,\text{K})}{T} = \frac{-2802.7\,\text{kJ mol}^{-1}}{330.\,\text{K}} = -9.40 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S_{universe}^\circ = \Delta S_{surroundings}^\circ + \Delta S_R^\circ = -262.4\,\text{J K}^{-1}\,\text{mol}^{-1} - 9.40 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -9.66 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

To calculate ΔS for the system, the surroundings, and the universe at $T = 310.\,\text{K}$, we must take the heat capacities into account.

$$\Delta C_{p,m} = 6 \times 29.4\,\text{J K}^{-1}\,\text{mol}^{-1} + 219.2\,\text{J K}^{-1}\,\text{mol}^{-1} - 6 \times 37.1\,\text{J K}^{-1}\,\text{mol}^{-1} - 6 \times 75.3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -278.8\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S_R^\circ (310.\,\text{K}) = \Delta S_R^\circ (298.15\,\text{K}) + \Delta C_{p,m}\ \ln\frac{310.\,\text{K}}{298.15\,\text{K}}$$

$$= -262.4\,\text{J K}^{-1}\,\text{mol}^{-1} - 278.8\,\text{J K}^{-1}\,\text{mol}^{-1} \times \ln\frac{310.\,\text{K}}{298.15\,\text{K}} = -273.4\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta H_R^\circ (310.\,\text{K}) = \Delta H_R^\circ (298.15\,\text{K}) + \Delta C_{p,m}\Delta T$$

$$= 2802.7\,\text{kJ mol}^{-1} - 278.8 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1} \times (310. - 298.15)\text{K} = 2799\,\text{kJ mol}^{-1}$$

$$\Delta S_{surroundings}^\circ = \frac{-\Delta H_R^\circ (310.\,\text{K})}{T} = \frac{-2793.8\,\text{kJ mol}^{-1}}{310.\,\text{K}} = -9.03 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S_{universe}^\circ = \Delta S_{surroundings}^\circ + \Delta S_R^\circ = -273.4\,\text{J K}^{-1}\,\text{mol}^{-1} - 9.03 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -9.30 \times 10^3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

P5.2   The Chalk Point, Maryland, generating station supplies electrical power to the Washington, D.C., area. Units 1 and 2 have a gross generating capacity of 710. MW (megawatt). The steam pressure is 25×10^6 Pa, and the superheater outlet temperature (T_h) is 540.°C. The condensate temperature (T_c) is 30.0°C.

a.   What is the efficiency of a reversible Carnot engine operating under these conditions?

b.   If the efficiency of the boiler is 91.2%, the overall efficiency of the turbine, which includes the Carnot efficiency and its mechanical efficiency, is 46.7%, and the efficiency of the generator is 98.4%, what is the efficiency of the total generating unit? (Another 5.0% needs to be subtracted for other plant losses.)

c.   One of the coal burning units produces 355 MW. How many metric tons (1 metric ton $= 1 \times 10^6$ g) of coal per hour are required to operate this unit at its peak output if the enthalpy of combustion of coal is 29.0×10^3 kJ kg^{-1}?

(a) $\varepsilon = \dfrac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \dfrac{303\,\text{K}}{813\,\text{K}} = 0.627$

(b)   The efficiency of the generating plant is the product of the individual efficiencies.

$$\varepsilon = 0.912 \times 0.467 \times 0.984 \times 0.95 = 0.398$$

(c)   The energy output per hour is given by $355 \text{ MW} \times \dfrac{3600 \text{ s}}{\text{hr}} = 1.278 \times 10^{12} \text{ J hr}^{-1}$.

The heat required to output this energy is $q = \dfrac{E_{output}}{\varepsilon} = \dfrac{1.278 \times 10^{12} \text{ J hr}^{-1}}{0.398} = 3.211 \times 10^{12} \text{ J hr}^{-1}$.

The number of tons of coal needed is $\dfrac{3.211 \times 10^{12} \text{ J hr}^{-1}}{29.0 \times 10^{9} \text{ J ton}^{-1}} = 110.7 \text{ ton hr}^{-1}$.

P5.3   An electrical motor is used to operate a Carnot refrigerator with an interior temperature of 0.00°C. Liquid water at 0.00°C is placed into the refrigerator and transformed to ice at 0.00°C. If the room temperature is 300. K, what mass of ice can be produced in one day by a 0.50-hp motor that is running continuously? Assume that the refrigerator is perfectly insulated and operates at the maximum theoretical efficiency.

We need to find the amount of heat per unit time that can be removed from the interior of the refrigerator.

$$\frac{q}{t} = \eta_r \left(\frac{-w}{t} \right) = \frac{T_{cold}}{T_{hot} - T_{cold}} \left(\frac{-w}{t} \right)$$

$$= \frac{273.15 \text{ K}}{300. \text{ K} - 273.15 \text{ K}} \times 0.50 \text{ hp} \times \frac{746 \text{ W}}{\text{hp}} = 6046 \text{ W} = 6046 \text{ J s}^{-1}$$

The number of grams of ice that can be frozen in one day by this amount of heat extraction is

$$m_{ice} = \frac{q/t}{\Delta H_{fusion}} \times t = \frac{6046 \text{ J s}^{-1}}{6008 \text{ J mol}^{-1}} \times \frac{18.02 \text{ g}}{\text{mol}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} = 1.57 \times 10^{6} \text{ g}$$

P5.4   An air conditioner is a refrigerator with the inside of the house acting as the cold reservoir and the outside atmosphere acting as the hot reservoir. Assume that an air conditioner consumes 1.70×10^{3} W of electrical power, and that it can be idealized as a reversible Carnot refrigerator. If the coefficient of performance of this device is 3.30, how much heat can be extracted from the house in a day?

$$\eta_r = \frac{q_{cold}}{w} = 3.30; \quad q_{cold} = 3.30 w$$

$$q_{cold} = 3.30 \times 1.70 \times 10^{3} \text{ J s}^{-1} \times \frac{3600 \text{ s}}{\text{hr}} \times 24 \text{ hr} = 4.85 \times 10^{8} \text{ J}$$

P5.5   One mole of $H_2O(l)$ is compressed from a state described by $P = 1.00$ bar and $T = 350.$ K to a state described by $P = 590.$ bar and $T = 750.$ K. In addition, $\beta = 2.07 \times 10^{-4}$ K^{-1}, and the density can be assumed to be constant at the value 997 kg m^{-3}. Calculate ΔS for this transformation, assuming that $\kappa = 0$.

From Equation (5.24),

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V \beta \, dP \approx nC_{P,m} \ln \frac{T_f}{T_i} - nV_{m,i}\beta(P_f - P_i)$$

$$= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{750. \text{ K}}{350. \text{ K}} - 1 \text{ mol} \times \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{997 \text{ kg m}^{-3}}$$

$$\times 2.07 \times 10^{-4} \text{ K}^{-1} \times 589 \text{ bar} \times 10^{5} \text{ Pa bar}^{-1}$$

$$= 57.4 \text{ J K}^{-1} - 0.220 \text{ J K}^{-1} = 57.2 \text{ J K}^{-1}$$

P5.6   2.25 moles of an ideal gas with $C_{V,m} = 3/2 \, R$ undergoes the transformations described in the following list from an initial state described by $T = 310.$ K and $P = 1.00$ bar. Calculate $q, w, \Delta U, \Delta H,$ and ΔS for each process.

a.   The gas is heated to 675 K at a constant external pressure of 1.00 bar.

b.   The gas is heated to 675 K at a constant volume corresponding to the initial volume.

c.   The gas undergoes a reversible isothermal expansion at 310. K until the pressure is one third of its initial value.

(a)   The gas is heated to 675 K at a constant pressure of 1.00 bar.

$$V_i = \frac{nRT_i}{P_i} = \frac{2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K}}{10^5 \text{ Pa}} = 5.80 \times 10^{-2} \text{ m}^3$$

$$V_f = \frac{T_f}{T_i}V_i = \frac{675 \text{ K}}{310. \text{ K}} \times 5.80 \times 10^{-2} \text{ m}^3 = 0.126 \text{ m}^3$$

$$w = -P_{external}\Delta V = -10^5 \text{ Pa} \times (0.126 \text{ m}^3 - 5.80 \times 10^{-2} \text{ m}^3) = -6.83 \times 10^3 \text{ J}$$

$$\Delta U = nC_{V,m}\Delta T = 2.25 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times 365 \text{ K} = 10.2 \times 10^3 \text{ J}$$

$$q = \Delta H = \Delta U - w = 10.2 \times 10^3 \text{ J} + 6.83 \times 10^3 \text{ J} = 17.1 \times 10^3 \text{ J}$$

$$\Delta S = nC_{P,m}\ln\frac{T_f}{T_i} = 2.25 \text{ mol} \times \left(\frac{3}{2}+1\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{675 \text{ K}}{310. \text{ K}} = 36.4 \text{ J K}^{-1}$$

(b)   The gas is heated to 675 K at a constant volume corresponding to the initial volume. $w = 0$ because $\Delta V = 0$.

$$\Delta U = q = nC_{V,m}\Delta T = 2.25 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times 365 \text{ K} = 10.2 \times 10^3 \text{ J}$$

$$\Delta H = nC_{p,m}\Delta T = 2.25 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times 365 \text{ K} = 17.1 \times 10^3 \text{ J}$$

$$\Delta S = nC_{V,m}\ln\frac{T_f}{T_i} = 2.25 \text{ mol} \times \left(\frac{3}{2}\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{675 \text{ K}}{310. \text{ K}} = 21.8 \text{ J K}^{-1}$$

(c)   The gas undergoes a reversible isothermal expansion at 310. K until the pressure is one third of its initial value. $\Delta U = \Delta H = 0$ because $\Delta T = 0$.

$$w_{reversible} = -q = -nRT\ln\frac{V_f}{V_i} = -2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln 3 = -6.37 \times 10^3 \text{ J}$$

$$\Delta S = -nR\ln\frac{P_f}{P_i} + nC_p \ln\frac{T_f}{T_i}$$

$$= -2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{1}{3} + 2.25 \text{ mol} \times \left(\frac{5}{2}\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \ln 1$$

$$= 20.6 \text{ J K}^{-1}$$

P5.7   Consider the reversible Carnot cycle shown in Figure 5.2 with 1.25 mol of an ideal gas with $C_V = 5/2R$ as the working substance. The initial isothermal expansion occurs at the hot reservoir temperature of $T_{hot} = 740. \text{ K}$ from an initial volume of 3.75 L (V_a) to a volume of 12.8 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to $T_{cold} = 310. \text{ K}$. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by $T_a = 740. \text{ K}$ and $V_a = 3.75 \text{ L}$ is reached.

a.   Calculate V_c and V_d.

$$V_c = V_b\left(\frac{T_c}{T_b}\right)^{\frac{1}{1-\gamma}} = 12.8 \text{ L} \times \left(\frac{310. \text{ K}}{740. \text{ K}}\right)^{\frac{1}{1-1.4}} = 113 \text{ L}$$

$$V_d = V_a\left(\frac{T_d}{T_a}\right)^{\frac{1}{1-\gamma}} = 3.75 \text{ L} \times \left(\frac{310. \text{ K}}{740. \text{ K}}\right)^{\frac{1}{1-1.4}} = 33.0 \text{ L}$$

b.   Calculate w for each step in the cycle and for the total cycle.

$$w_{ab} = -nRT_a \ln\frac{V_b}{V_a} = 1.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{12.8 \text{ L}}{3.75 \text{ L}} = -9.44 \times 10^3 \text{ J}$$

$$w_{bc} = nC_{V,m}(T_c - T_b) = 1.25 \text{ mol} \times 2.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (310. \text{ K} - 740. \text{ K}) = -11.2 \times 10^3 \text{ J}$$

$$w_{cd} = -nRT_c \ln\frac{V_d}{V_c} = 1.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{33.0 \text{ L}}{113 \text{ L}} = 3.96 \times 10^3 \text{ J}$$

$$w_{da} = nC_{V,m}(T_a - T_d) = 1.75 \text{ mol} \times \frac{5}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (740. \text{ K} - 310. \text{ K}) = +11.2 \times 10^3 \text{ J}$$

$$w_{total} = -9.44 \times 10^3 \text{ J} - 11.2 \times 10^3 \text{ J} + 3.96 \times 10^3 \text{ J} + 11.2 \times 10^3 \text{ J} = -5.49 \times 10^3 \text{ J}$$

c.   Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{310. \text{ K}}{740. \text{ K}} = 0.581 \quad q = \frac{w}{\varepsilon} = \frac{1.00 \times 10^3 \text{ J}}{0.581} = 1.72 \times 10^3 \text{ J}$$

P5.8   The average heat evolved by the oxidation of foodstuffs in an average adult per hour per kilogram of body weight is $7.20 \text{ kJ kg}^{-1} \text{ hr}^{-1}$. Assume the weight of an average adult is 62.0 kg. Suppose the total heat evolved by this oxidation is transferred into the surroundings over a period lasting one week. Calculate the entropy change of the surroundings associated with this heat transfer. Assume the surroundings are at $T = 293 \text{ K}$.

$$q(\text{per day, 62.0 kg}) = 7.20 \text{ kJ kg}^{-1} \text{ hr}^{-1} \times 24 \text{ h day}^{-1} \times 7 \text{ day week}^{-1} \times 62.0 \text{ kg}$$
$$= 44.6 \times 10^4 \text{ kJ week}^{-1}$$

$$\Delta S = \frac{q}{T} = \frac{44.6 \times 10^4 \text{ kJ day}^{-1}}{293 \text{ K}} = 256 \text{ kJ K}^{-1} \text{ week}^{-1}$$

P5.9   Calculate ΔS, ΔS_{total}, and $\Delta S_{surroundings}$ when the volume of 150. g of CO initially at 273 K and 1.00 bar increases by a factor of two in (a) an adiabatic reversible expansion, (b) an expansion against $P_{external} = 0$, and (c) an isothermal reversible expansion. Take $C_{P,m}$ to be constant at the value $29.14 \text{ J mol}^{-1} \text{ K}^{-1}$ and assume ideal gas behavior. State whether each process is spontaneous. The temperature of the surroundings is 273 K.

a.   An adiabatic reversible expansion $\Delta S_{surroundings} = 0$ because $q = 0$. $\Delta S = 0$ because the process is reversible.

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 0$. The process is not spontaneous.

b.   An expansion against $P_{external} = 0$. ΔT and $w = 0$. Therefore $\Delta U = q = 0$.

$$\Delta S = nR \ln\frac{V_f}{V_i} = \frac{150. \text{ g}}{28.01 \text{ g mol}^{-1}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln 2 = 30.9 \text{ J K}^{-1}$$

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 30.9 \text{ J K}^{-1} + 0 = 30.9 \text{ J K}^{-1}$. The process is spontaneous.

c.   An isothermal reversible expansion $\Delta T = 0$. Therefore $\Delta U = 0$.

$$w = -q = -nRT \ln\frac{V_f}{V_i} = -\frac{150. \text{ g}}{28.01 \text{ g mol}^{-1}} \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 273 \text{ K} \times \ln 2 = -8.43 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{reversible}}{T} = \frac{8.43 \times 10^3 \text{ J}}{273 \text{ K}} = 30.9 \text{ J K}^{-1}$$

$$\Delta S_{surroundings} = \frac{-q}{T} = \frac{-8.43 \times 10^3 \text{ J}}{273 \text{ K}} = -30.9 \text{ J K}^{-1}$$

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 30.9 \text{ J K}^{-1} - 30.9 \text{ J K}^{-1} = 0$. The system and surroundings are at equilibrium.

P5.10   The maximum theoretical efficiency of an internal combustion engine is achieved in a reversible Carnot cycle. Assume that the engine is operating in the Otto cycle and that $C_{V,m} = 5/2\,R$ for the fuel–air mixture initially at 273 K (the temperature of the cold reservoir). The mixture is compressed by a factor of 6.9 in the adiabatic compression step. What is the maximum theoretical efficiency of this engine? How much would the efficiency increase if the compression ratio could be increased to 15? Do you see a problem in doing so?

$$T_f = T_i \left(\frac{V_f}{V_i} \right)^{1-\gamma} = T_i \left(\frac{1}{7.5} \right)^{1-\frac{7}{5}} = 273\,\text{K} \times \left(\frac{1}{6.9} \right)^{-0.4} = 591\,\text{K}$$

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{273\,\text{K}}{591\,\text{K}} = 0.538$$

$$T_f = T_i \left(\frac{V_f}{V_i} \right)^{1-\gamma} = T_i \left(\frac{1}{15} \right)^{1-\frac{7}{5}} = 298\,\text{K} \times \left(\frac{1}{15} \right)^{-0.4} = 806\,\text{K}$$

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{273\,\text{K}}{806\,\text{K}} = 0.661$$

It would be difficult to avoid ignition of the fuel–air mixture before the compression was complete.

P5.11   2.25 moles of an ideal gas with $C_{V,m} = 5/2\,R$ is transformed from an initial state $T = 680.\,\text{K}$ and $P = 1.15$ bar to a final state $T = 298.\,\text{K}$ and $P = 4.75$ bar. Calculate ΔU, ΔH, and ΔS for this process.

$$\Delta U = nC_{V,m}\Delta T = 2.25\,\text{mol} \times \frac{5 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times (298\,\text{K} - 680.\,\text{K}) = -17.9 \times 10^3\,\text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 2.25\,\text{mol} \times \frac{7 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times (298\,\text{K} - 680.\,\text{K}) = -25.0 \times 10^3\,\text{J}$$

$$\Delta S = -nR\ln\frac{P_f}{P_i} + nC_{P,m}\ln\frac{T_f}{T_i}$$

$$= -2.25\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\frac{4.75\,\text{bar}}{1.15\,\text{bar}} + 2.25\,\text{mol} \times \frac{7 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times \ln\frac{298\,\text{K}}{680.\,\text{K}}$$

$$= -26.5\,\text{J K}^{-1} - 54.0\,\text{J K}^{-1} = -80.5\,\text{J K}^{-1}$$

P5.12   1.10 moles of N_2 at 20.5°C and 6.20 bar undergoes a transformation to the state described by 215°C and 1.75 bar. Calculate ΔS if

$$\frac{C_{P,m}}{\text{J mol}^{-1}\,\text{K}^{-1}} = 30.81 - 11.87 \times 10^{-3}\frac{T}{K} + 2.3968 \times 10^{-5}\frac{T^2}{K^2} - 1.0176 \times 10^{-8}\frac{T^3}{K^3}$$

$$\Delta S = -nR\,\ln\frac{P_f}{P_i} + n\int_{T_i}^{T_f}\frac{C_{P,m}}{T}dT$$

$$= -1.10\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\frac{1.75\,\text{bar}}{6.20\,\text{bar}}$$

$$+ \int_{293.65}^{488.15} \frac{\left(30.81 - 11.87 \times 10^{-3}\frac{T}{K} + 2.3968 \times 10^{-5}\left(\frac{T}{K}\right)^2 - 1.0176 \times 10^{-8}\left(\frac{T}{K}\right)^3 \right)}{T}d\frac{T}{K}\,\text{J K}^{-1}$$

$$= 11.6\,\text{J K}^{-1} + \left[30.81\,\ln\frac{T}{K} - 0.01187\frac{T}{K} + 1.1984 \times 10^{-5}\frac{T^2}{K^2} - 0.3392 \times 10^{-8}\left(\frac{T}{K}\right)^3 \right]_{288.35}^{468.15}\,\text{J K}^{-1}$$

$$= 11.6\,\text{J K}^{-1} + 17.2\,\text{J K}^{-1} - 2.54\,\text{J K}^{-1} + 2.00\,\text{J K}^{-1} - 0.34\,\text{J K}^{-1} = 27.9\,\text{J K}^{-1}$$

P5.13   Calculate ΔS for the isothermal compression of 1.75 mol of Cu(s) from 2.15 bar to 1250. bar at 298 K. $\beta = 0.492 \times 10^{-4}$ K^{-1}, $\kappa = 0.78 \times 10^{-6}$ bar^{-1}, and the density is 8.92 g cm^{-3}. Repeat the calculation assuming that $\kappa = 0$.

$$\Delta S = -\int_{P_i}^{P_f} V_i (1 - \kappa P) \beta \, dP$$

$$= -\int_{2.15 \times 10^5}^{1.25 \times 10^8} \frac{63.55 \times 10^{-3} \text{ kg mol}^{-1}}{8.92 \times 10^3 \text{ kg m}^3} (1 - 0.780 \times 10^{-11} \text{ Pa}^{-1} \times P) 0.492 \times 10^{-4} \text{ K}^{-1} dP$$

$$= -0.0765 \text{ J K}^{-1}$$

Repeating the calculation for $\kappa = 0$, we see no change because $1 \gg \kappa P$.

P5.14   Calculate $\Delta S°$ for the reaction $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$ at 725 K. Omit terms in the temperature-dependent heat capacities higher than T^2/K^2.

From Table 2.4,

$$C_P°(H_2, g) = 22.66 + 4.38 \times 10^{-2} \frac{T}{K} - 1.0835 \times 10^{-4} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_P°(N_2, g) = 30.81 - 1.187 \times 10^{-2} \frac{T}{K} + 2.3968 \times 10^{-5} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_P°(NH_3, g) = 29.29 + 1.103 \times 10^{-2} \frac{T}{K} + 4.2446 \times 10^{-5} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_P° = 2 \left(29.29 + 1.103 \times 10^{-2} \frac{T}{K} + 4.2446 \times 10^{-5} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1} \right)$$

$$- \left(30.81 - 1.187 \times 10^{-2} \frac{T}{K} + 2.3968 \times 10^{-5} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1} \right)$$

$$- 3 \left(22.66 + 4.38 \times 10^{-2} \frac{T}{K} - 1.0835 \times 10^{-4} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1} \right)$$

$$\Delta C_P° = -40.21 - 0.0975 \frac{T}{K} + 3.860 \times 10^{-4} \frac{T^2}{K^2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S° = 2S°_{298.15}(NH_3, g) - S°_{298.15}(N_2, g) - 3S°_{298.15}(H_2, g)$$

$$= 2 \times 192.8 \text{ J K}^{-1} \text{ mol}^{-1} - 191.6 \text{ J K}^{-1} \text{ mol}^{-1} - 3 \times 130.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -198.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S°_T = \Delta S°_{298.15} + \int_{298.15}^{T} \frac{\Delta C_P°}{T'} dT'$$

$$= -198.1 \text{ J K}^{-1} \text{ mol}^{-1} + \int_{298.15}^{725} \frac{\left(-40.21 - 0.0975 \frac{T}{K} + 3.860 \times 10^{-4} \frac{T^2}{K^2} \right)}{\frac{T}{K}} d\frac{T}{K} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -198.1 \text{ J K}^{-1} \text{ mol}^{-1} - 31.34 \text{ J K}^{-1} \text{ mol}^{-1} - 41.62 \text{ J K}^{-1} \text{ mol}^{-1} + 84.28 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -191.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.15   Using the expression $dS = \frac{C_P}{T} dT - V\beta \, dP$, calculate the decrease in temperature that occurs if 2.25 moles of water at 310. K and 1650. bar is brought to a final pressure of 1.30 bar in a reversible adiabatic process. Assume that $\kappa = 0$.

$$dS = \frac{C_P}{T}dT - V\beta\, dP$$

$$\Delta S = \int dS = C_P \ln\frac{T_f}{T_i} - V\beta(P_f - P_i)$$

Because the process is reversible and adiabatic, $\Delta S = 0$.

$$C_P \ln\frac{T_f}{T_i} = V\beta(P_f - P_i) \qquad \ln T_f = \frac{V\beta(P_f - P_i) + C_P \ln T_i}{C_P}$$

$$= \frac{\dfrac{18.02 \times 10^{-3}\ \text{kg}}{998\ \text{kg m}^3} \times 2.04 \times 10^{-4}\ \text{K}^{-1} \times (1.30 \times 10^5\ \text{Pa} - 1.65 \times 10^8\ \text{Pa}) + 75.3\ \text{J K}^{-1}\,\text{mol}^{-1} \times \ln 310.}{75.3\ \text{J K}^{-1}\,\text{mol}^{-1}}$$

$$= 5.72851$$

$$T_f = 307.5\ \text{K}$$

$$\Delta T = -2.5\ \text{K}$$

P5.16   3.75 moles of an ideal gas with $C_{V,m} = 3/2\,R$ undergoes the transformations described in the following list from an initial state described by $T = 298\ \text{K}$ and $P = 4.50$ bar. Calculate q, w, ΔU, ΔH, and ΔS for each process.

   a.   The gas undergoes a reversible adiabatic expansion until the final pressure is one third its initial value.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{T_f}{T_i}\right)^{1-\gamma}\left(\frac{P_i}{P_f}\right)^{1-\gamma}; \quad \left(\frac{T_f}{T_i}\right)^{\gamma} = \left(\frac{P_i}{P_f}\right)^{1-\gamma}; \quad \frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_f = T_i\left(\frac{4.50\ \text{bar}}{1.50\ \text{bar}}\right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = 298\ \text{K} \times (3.00)^{-\frac{2}{5}} = 192\ \text{K}$$

$$\Delta U = w = nC_{V,m}\Delta T = 3.75\ \text{mol} \times \frac{3 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1}}{2} \times (192\ \text{K} - 298\ \text{K}) = -4.96 \times 10^3\ \text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 3.75\ \text{mol} \times \frac{5 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}{2} \times (192\ \text{K} - 298\ \text{K}) = -8.26 \times 10^3\ \text{J}$$

$\Delta S = 0$ because $q_{reversible} = 0$.

   b.   The gas undergoes an adiabatic expansion against a constant external pressure of 1.50 bar until the final pressure is one third its initial value.

$q = 0$ because the process is adiabatic.

$$nC_{v,m}(T_f - T_i) = -nRP_{external}\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{v,m} + \frac{nRP_{external}}{P_f}\right) = T_i\left(nC_{v,m} + \frac{nRP_{external}}{P_i}\right)$$

$$T_f = T_i\left(\frac{C_{v,m} + \dfrac{RP_{external}}{P_i}}{C_{v,m} + \dfrac{RP_{external}}{P_f}}\right) = 298\ \text{K} \times \left(\frac{1.5 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 1.50\ \text{bar}}{4.50\ \text{bar}}}{1.5 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} + \dfrac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 1.50\ \text{bar}}{1.500\ \text{bar}}}\right)$$

$$T_f = 218.5\ \text{K}$$

$$\Delta U = w = nC_{V,m}\Delta T = 3.75\,\text{mol} \times \frac{3 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times (218.5\,\text{K} - 298\,\text{K}) = -3.72 \times 10^3\,\text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 3.75\,\text{mol} \times \frac{5 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times (218.5\,\text{K} - 298\,\text{K}) = -6.19 \times 10^3\,\text{J}$$

$$\Delta S = -nR\ln\frac{P_f}{P_i} + nC_{P,m}\ln\frac{T_f}{T_i}$$

$$= -3.75\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\frac{1.50\,\text{bar}}{4.50\,\text{bar}} + 3.75\,\text{mol} \times \frac{5 \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}{2} \times \ln\frac{218.5\,\text{K}}{298\,\text{K}}$$

$$= 34.3\,\text{J K}^{-1} - 24.2\,\text{J K}^{-1} = 10.1\,\text{J K}^{-1}$$

c.   The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to one third of its initial value.

ΔT and $w = 0$. Therefore $\Delta U = \Delta H = 0$ and $q = \Delta U - w = 0$.

$$\Delta S = -nR\;\ln\frac{P_f}{P_i} = -3.75\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times \ln\frac{1.50\,\text{bar}}{4.50\,\text{bar}} = 34.3\,\text{J K}^{-1}$$

P5.17   The interior of a refrigerator is typically held at 36°F and the interior of a freezer is typically held at 0.00°F. If the room temperature is 65°F, by what factor is it more expensive to extract the same amount of heat from the freezer than from the refrigerator? Assume that the theoretical limit for the performance of a reversible refrigerator is valid in this case.

From Equation (5.44)

$$\eta_r = \frac{T_{cold}}{T_{hot} - T_{cold}}$$

$$T_{room} = \frac{5}{9}(65 - 32) + 273.15 = 291.5\,\text{K}$$

$$T_{freezer} = \frac{5}{9}(0.00 - 32) + 273.15 = 255.4\,\text{K}$$

$$T_{refrigerator} = \frac{5}{9}(36 - 32) + 273.15 = 275.4\,\text{K}$$

For the freezer $\eta_r = \dfrac{255.4\,\text{K}}{291.5\,\text{K} - 255.4\,\text{K}} = 7.1.$

For the refrigerator $\eta_r = \dfrac{275.4\,\text{K}}{291.5\,\text{K} - 275.4\,\text{K}} = 17.$

The freezer is more expensive to operate than the refrigerator by the ratio $17/7.1 = 2.4$.

P5.18   Using your results from Problem P5.7, calculate q, ΔU, and ΔH for each step in the cycle and for the total cycle described in Figure 5.2.

$a \rightarrow b$	$\Delta U = \Delta H = 0$ because $\Delta T = 0$	$q = -w = 9.44 \times 10^3\,\text{J}$
$b \rightarrow c$	$\Delta U = w = -1.12 \times 10^4\,\text{J}$ because $q = 0$	$\Delta H = \Delta U + nR\Delta T = -15.6 \times 10^3\,\text{J}$
$c \rightarrow d$	$\Delta U = \Delta H = 0$ because $\Delta T = 0$	$q = -w = -3.96 \times 10^3\,\text{J}$
$d \rightarrow a$	$\Delta U = w = 1.12 \times 10^4\,\text{J}$ because $q = 0$	$\Delta H = \Delta H + nR\Delta T = 15.6 \times 10^3\,\text{J}$

$$q_{total} = 9.44 \times 10^3\,\text{J} - 3.96 \times 10^3 = 5.49 \times 10^3\,\text{J} = -w_{total}$$

$$\Delta U_{total} = \Delta H_{total} = 0$$

P5.19 At the transition temperature of 95.4°C, the enthalpy of transition from rhombic to monoclinic sulfur is $0.38\,\text{kJ mol}^{-1}$.

    a.   Calculate the entropy of transition under these conditions.

    b.   At its melting point, 119°C, the enthalpy of fusion of monoclinic sulfur is $1.23\,\text{kJ mol}^{-1}$. Calculate the entropy of fusion.

    c.   The values given in parts (a) and (b) are for 1 mol of sulfur; however, in crystalline and liquid sulfur, the molecule is present as S_8. Convert the values of the enthalpy and entropy of fusion in parts (a) and (b) to those appropriate for S_8.

    (a) $\Delta S_{transition} = \dfrac{\Delta H_{transition}}{T_{transition}} = \dfrac{0.38\,\text{kJ mol}^{-1}}{(273.15 + 95.4)\,\text{K}} = 1.0\,\text{J K}^{-1}\,\text{mol}^{-1}$

    (b) $\Delta S_{fusion} = \dfrac{\Delta H_{fusion}}{T_{fusion}} = \dfrac{1.23\,\text{kJ mol}^{-1}}{(273.15 + 119)\,\text{K}} = 3.14\,\text{J K}^{-1}\,\text{mol}^{-1}$

    (c)   Each of the ΔS in parts (a) and (b) should be multiplied by 8.

        $\Delta S_{transition} = 8.24\,\text{J K}^{-1}\,\text{mol}^{-1}$

        $\Delta S_{fusion} = 25.1\,\text{J K}^{-1}\text{mol}^{-1}$

P5.20 One mole of a van der Waals gas at $25.0°\text{C}$ is expanded isothermally and reversibly from an initial volume of $0.010\,\text{m}^3$ to a final volume of $0.095\,\text{m}^3$. For the van der Waals gas, $(\partial U/\partial V)_T = a/V_m^2$. Assume that $a = 0.556\,\text{Pa m}^6\,\text{mol}^{-2}$, and that $b = 64.0 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$. Calculate q, w, ΔU, ΔH, and ΔS for the process.

$$\Delta U = \int_{V_i}^{V_f}\left(\frac{\partial U}{\partial V}\right)_T dV$$

For a van der Waals gas

$\Delta U = n^2 a\left(\dfrac{1}{V_i} - \dfrac{1}{V_f}\right)$ as shown in Example Problem 3.5

$$\Delta U = 0.556\,\text{Pa m}^6\,\text{mol}^{-2}\left(\frac{1}{0.010\,\text{m}^3} - \frac{1}{0.095\,\text{m}^3}\right) \times 1\,\text{mol}^2 = 49.7\,\text{J}$$

$$w = -\int_{V_i}^{V_f} P\,dV = -RT\int_{V_i}^{V_f}\frac{n\,dV}{V_m - b} + n^2 a\int_{V_i}^{V_f}\frac{dV}{V^2}$$

$$= -nRT\ln\frac{(V_f - b)}{(V_i - b)} - n^2 a\left(\frac{1}{V_f} - \frac{1}{V_i}\right)$$

$$= 1\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}\,\ln\frac{0.095\,\text{m}^3 - 64 \times 10^{-6}\,\text{m}^3}{0.010\,\text{m}^3 - 64 \times 10^{-6}\,\text{m}^3}$$

$$-\,0.556\,\text{Pa m}^6\,\text{mol}^{-2}\left(\frac{1}{0.095\,\text{m}^3} - \frac{1}{0.010\,\text{m}^3}\right) \times 1\,\text{mol}^2$$

$$= -5.595 \times 10^3\,\text{J} + 49.75\,\text{J} = -5.55 \times 10^3\,\text{J}$$

$$P_i = \frac{nRT}{V_i - b} - \frac{n^2 a}{V_i^2} = \frac{1\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}}{0.010\,\text{m}^3 - 64 \times 10^{-6}\,\text{m}^3} - \frac{1\,\text{mol}^2 \times 0.556\,\text{Pa m}^6\,\text{mol}^{-2}}{(0.010\,\text{m}^3)^2}$$

$$= 2.44 \times 10^5\,\text{Pa}$$

$$P_f = \frac{nRT}{V_f - b} - \frac{n^2 a}{V_f^2} = \frac{1\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}}{0.095 - 64 \times 10^{-6}} - \frac{1\,\text{mol}^2 \times 0.566\,\text{Pa m}^6\,\text{mol}^{-2}}{(0.095\,\text{m}^3)^2}$$

$$= 2.60 \times 10^4\,\text{Pa}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i$$

$$= 49.7\ \text{J} + (2.60 \times 10^4\ \text{Pa} \times 0.095\ \text{m}^3 - 2.44 \times 10^5\ \text{Pa} \times 0.010\ \text{m}^3) = 79.7\ \text{J}$$

$$q = \Delta U - w = 49.7\ \text{J} + 5.55 \times 10^3\ \text{J} = 5.59 \times 10^3\ \text{J}$$

$$\Delta S = \frac{q_{reversible}}{T} = \frac{5.59 \times 10^3\ \text{J}}{298.15\ \text{K}} = 18.8\ \text{J K}^{-1}$$

P5.21 From the following data, derive the absolute entropy of crystalline glycine at $T = 300.\ \text{K}$. You can perform the integration numerically using either a spreadsheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.9).

Temperature (K)	$C_{P,m}(\text{J K}^{-1}\ \text{mol}^{-1})$
10.	0.3
20.	2.4
30.	7.0
40.	13.0
60.	25.1
80.	35.2
100.	43.2
120.	50.0
140.	56.0
160.	61.6
180.	67.0
200.	72.2
220.	77.4
240.	82.8
260.	88.4
280.	94.0
300.	99.7
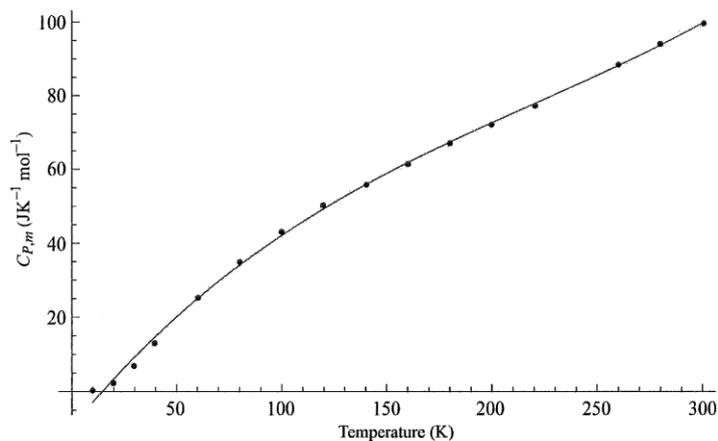
The line in the graph above of $C_{P,m}$ (vertical axis) against T is the best fit to the data of a polynomial of the form $a + bx + cx^2 + dx^3$ given by $-9.4109 + 0.67903 \, x - 0.0019301 \, x^2 + 2.93185 \times 10^{-6} \, x^3$.

$$S_m^\circ(300. \, \text{K}) = \int_{10.00 \, \text{K}}^{300.0 \, \text{K}} \frac{-9.4109 + 0.67903T - 0.0019301T^2 + 2.93185 \times 10^{-6}T^3}{T} = 104.5 \, \text{J K}^{-1} \, \text{mol}^{-1}$$

We have integrated from 10 K rather than 0 K because the integrand is not well defined at 0 K and because the contribution to S below 10 K is very small.

P5.22   Calculate ΔH and ΔS if the temperature of 1.75 moles of Hg(l) is increased from $0.00°C$ to $75.00°C$ at 1 bar. Over this temperature range, $C_{P,m} = 30.093 - 4.944 \times 10^{-3} \, T \, \text{J mol}^{-1} \, \text{K}^{-1}$.

$$\Delta H = 1.75 \, \text{mol} \times \int_{273.15 \, \text{K}}^{348.15 \, \text{K}} (30.093 - 4.944 \times 10^{-3} T) \, \text{J mol}^{-1} \, \text{K}^{-1} \, dT$$

$$= 1.75 \times (30.093(348.15 \, \text{K} - 273.15 \, \text{K}) - 2.472 \times 10^{-2}(348.15 \, \text{K} - 273.15 \, \text{K})^2) \, \text{J}$$

$$= 3.75 \times 10^3 \, \text{J}$$

$$\Delta S = 1.75 \, \text{mol} \times \int_{273.15 \, \text{K}}^{348.15 \, \text{K}} \left(\frac{30.093 - 4.944 \times 10^{-3} T \, \text{J mol}^{-1} \, \text{K}^{-1}}{T} \right) dT$$

$$= 1.75 \times \left(-4.944 \times 10^{-3}(T_f - T_i) + 30.093 \, \ln \frac{T_f}{T_i} \, \text{J K}^{-1} \right) = 12.1 \, \text{J K}^{-1}$$

P5.23   Calculate ΔS if the temperature of 2.50 mol of an ideal gas with $C_V = 5/2R$ is increased from 160. to 675 K under conditions of (a) constant pressure and (b) constant volume.

a.   at constant pressure

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} = 2.50 \, \text{mol} \times \left(\frac{5}{2} + 1 \right) \times 8.314 \, \text{J mol}^{-1} \, \text{K}^{-1} \times \ln \frac{675 \, \text{K}}{160. \, \text{K}} = 105 \, \text{J K}^{-1}$$

b.   at constant volume

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} = 2.50 \, \text{mol} \times \frac{5}{2} \times 8.314 \, \text{J mol}^{-1} \, \text{K}^{-1} \times \ln \frac{675 \, \text{K}}{160. \, \text{K}} = 74.8 \, \text{J K}^{-1}$$

P5.24   Beginning with Equation (5.5), use Equation (5.6) to eliminate V_c and V_d to arrive at the result $w_{cycle} = nR(T_{hot} - T_{cold}) \ln V_b / V_a$.

$$w_{ab} = -nRT_{hot} \ln \frac{V_b}{V_a}$$

$$w_{bc} = nC_{V,m}(T_{cold} - T_{hot})$$

$$w_{cd} = -nRT_{cold} \ln \frac{V_d}{V_c}$$

$$w_{da} = nC_{V,m}(T_{hot} - T_{cold}) = -w_{bc}$$

$$w_{total} = -nRT_{hot} \ln \frac{V_b}{V_a} - nRT_{cold} \ln \frac{V_d}{V_c}$$

$$T_{hot}V_c^{\gamma-1} = T_{cold}V_b^{\gamma-1} \quad \text{and} \quad T_{cold}V_a^{\gamma-1} = T_{hot}V_d^{\gamma-1}$$

Solving the last two equations for T_{hot} and equating the results,

$$T_{hot} = T_{cold} \frac{V_b^{\gamma-1}}{V_c^{\gamma-1}} = T_{cold} \frac{V_a^{\gamma-1}}{V_d^{\gamma-1}}$$

Therefore,

$$\frac{V_b}{V_c} = \frac{V_a}{V_d} \quad \text{or} \quad \frac{V_c}{V_d} = \frac{V_b}{V_a}$$

and

$$w_{total} = -nRT_{hot}\ln\frac{V_b}{V_a} - nRT_{cold}\ln\frac{V_d}{V_c} = -nR(T_{hot} - T_{cold})\ln\frac{V_b}{V_a}$$

P5.25   Calculate ΔS_R° for the reaction $H_2(g) + Cl_2(g) \to 2\,HCl(g)$ at 870. K. Omit terms in the temperature-dependent heat capacities higher than T^2/K^2.

From Table 2.4,

$$C_P^\circ(H_2, g) = 22.66 + 4.38 \times 10^{-2}\frac{T}{K} - 1.0835 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}$$

$$C_P^\circ(Cl_2, g) = 22.85 + 6.543 \times 10^{-2}\frac{T}{K} - 1.2517 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}$$

$$C_P^\circ(HCl, g) = 29.81 - 4.12 \times 10^{-3}\frac{T}{K} + 6.2231 \times 10^{-6}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}$$

$$\Delta C_P^\circ = 2\left(29.81 - 4.12 \times 10^{-3}\frac{T}{K} + 6.2231 \times 10^{-6}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}\right)$$

$$-\left(22.66 + 4.38 \times 10^{-2}\frac{T}{K} - 1.0835 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}\right)$$

$$-\left(22.85 + 6.543 \times 10^{-2}\frac{T}{K} - 1.2517 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}\right)$$

$$\Delta C_P^\circ = 14.11 - 0.117\frac{T}{K} + 2.460 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}$$

$$\Delta S^\circ = 2S_{298.15}^\circ(HCl, g) - S_{298.15}^\circ(Cl_2, g) - S_{298.15}^\circ(H_2, g)$$

$$= 2 \times 186.9\,J\,K^{-1}\,mol^{-1} - 223.1\,J\,K^{-1}\,mol^{-1} - 130.7\,J\,K^{-1}\,mol^{-1} = 20.0\,J\,K^{-1}\,mol^{-1}$$

$$\Delta S_T^\circ = \Delta S_{298.15}^\circ + \int_{298.15}^{T}\frac{\Delta C_p^\circ}{T'}\,dT'$$

$$= 20.0\,J\,K^{-1}\,mol^{-1} + \int_{298.15}^{870.}\frac{\left(14.11 - 0.117\frac{T}{K} + 2.460 \times 10^{-4}\frac{T^2}{K^2}\,J\,K^{-1}\,mol^{-1}\right)}{\frac{T}{K}}\,d\frac{T}{K}\,J\,K^{-1}\,mol^{-1}$$

$$= 20.0\,J\,K^{-1}\,mol^{-1} + 15.11\,J\,K^{-1}\,mol^{-1} - 66.91\,J\,K^{-1}\,mol^{-1} + 82.16\,J\,K^{-1}\,mol^{-1} = 50.1\,J\,K^{-1}\,mol^{-1}$$

P5.26   A 22.0 g mass of ice at 273 K is added to 136 g of $H_2O(l)$ at 310 K at constant pressure. Is the final state of the system ice or liquid water? Calculate ΔS for the process. Is the process spontaneous?

Assume initially that the final state is water. If this is not the case, the calculated temperature will be below 273 K. Calculate ΔS for the ice and water separately, and add them to get the overall ΔS for the process.

$$n_{ice}\Delta H_{fusion}^{ice} + n_{ice}C_{P,m}^{H_2O}(T_f - T_i^{ice}) + n_{H_2O}C_{P,m}^{H_2O}(T_f - T_i^{H_2O}) = 0$$

$$T_f = \frac{n_{ice}C_{P,m}^{H_2O}T_i^{ice} + n_{H_2O}C_{P,m}^{H_2O}T_i^{H_2O} - n_{ice}\Delta H_{fusion}^{ice}}{n_{ice}C_{P,m}^{H_2O} + n_{H_2O}C_{P,m}^{H_2O}} =$$

$$\frac{\frac{22.0\,g\,ice}{18.02\,g\,ice\,mol^{-1}} \times 75.3\,J\,K^{-1}\,mol^{-1} \times 273\,K + \frac{136\,g\,H_2O}{18.02\,g\,H_2O\,mol^{-1}} \times 75.3\,J\,K^{-1}\,mol^{-1}}{\frac{22.0\,g\,ice}{18.02\,g\,ice\,mol^{-1}} \times 75.3\,J\,K^{-1}\,mol^{-1} + \frac{136\,g\,H_2O}{18.02\,g\,H_2O\,mol^{-1}} \times 75.3\,J\,K^{-1}\,mol^{-1}}$$

$$\frac{\times 310.\,K - \frac{22.0\,g\,ice}{18.02\,g\,ice\,mol^{-1}} \times 6010\,J\,mol^{-1}}{}$$

$$T_f = 294\,K$$

ΔS is calculated for the ice. It consists of melting the ice at 273 K and heating the resulting water to 336 K.

$$\Delta S = n\frac{\Delta H_{fusion}}{T_{fusion}} + nC_{P,m} \quad \ln\frac{T_f}{T_{fusion}}$$

$$= \frac{22.0 \, g \text{ ice}}{18.02 \, g \text{ ice mol}^{-1}} \times \frac{6010 \text{ J mol}^{-1}}{273 \text{ K}} + \frac{22.0 \, g \text{ ice}}{18.02 \, g \text{ ice mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \ln\frac{294 \text{ K}}{273 \text{ K}}$$

$$= 33.6 \text{ J K}^{-1}$$

ΔS is calculated for the water. It consists of cooling the water from 360 K to 309 K.

$$\Delta S = nC_{P,m} \quad \ln\frac{T_f}{T_{initial}} = \frac{136 \, g}{18.02 \, g \text{ mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{294 \text{ K}}{310. \text{ K}} = -30.6 \text{ J K}^{-1}$$

$\Delta S_{total} = 33.6 \text{ J K}^{-1} - 30.6 \text{ J K}^{-1} = 3.0 \text{ J K}^{-1}$. $\Delta S_{total} > 0$, hence the process is spontaneous.

P5.27 Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction: $C_6H_{12}O_6(s) \rightarrow 2CH_3CHOHCOOH(s)$. Thermodynamic data at $T = 298$ K for glucose and lactic acid are given below.

	ΔH_f° (kJ mol^{-1})	C_P° (J K^{-1} mol^{-1})	S° (J K^{-1} mol^{-1})
Glucose(s)	−1273.1	219.2	209.2
Lactic Acid(s)	−673.6	127.6	192.1

Calculate ΔS for the system, the surroundings, and the universe at $T = 325.$ K. Assume the heat capacities are constant between $T = 298$ K and $T = 330.$ K.

At 298.15 K

$$\Delta S_R^{\circ} = 2 \times 192.1 \text{ J K}^{-1} \text{ mol}^{-1} - 209.2 \text{ J K}^{-1} \text{ mol}^{-1} = 175.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_R^{\circ} = -2 \times 673.6 \text{ kJ mol}^{-1} + 1273.1 \text{ kJ mol}^{-1} = -74.2 \text{ kJ mol}^{-1}$$

To calculate ΔS for the system, the surroundings, and the universe at $T = 325$ K, we must take the heat capacities into account.

$$\Delta C_{p,m} = 2 \times 127.6 \text{ J K}^{-1} \text{ mol}^{-1} - 219.2 \text{ J K}^{-1} \text{ mol}^{-1} = 36.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_R^{\circ}(325 \text{ K}) = \Delta S_R^{\circ}(298.15 \text{ K}) + \Delta C_{p,m} \ln\frac{325 \text{ K}}{298.15 \text{ K}}$$

$$= 175.0 \text{ J K}^{-1} \text{ mol}^{-1} + 36.0 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{325 \text{ K}}{298.15 \text{ K}} = 175 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_R^{\circ}(325 \text{ K}) = \Delta H_R^{\circ}(298.15 \text{ K}) + \Delta C_{p,m}\Delta T$$

$$= -74.1 \text{ kJ mol}^{-1} + 36.0 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 26.85 \text{ K} = -73.1 \text{ kJ mol}^{-1}$$

$$\Delta S_{surroundings}^{\circ} = \frac{-\Delta H_R^{\circ}(310. \text{ K})}{T} = \frac{73.1 \text{ kJ mol}^{-1}}{325 \text{ K}} = 225 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{total}^{\circ} = \Delta S_{surroundings}^{\circ} + \Delta S_R^{\circ} = 225 \text{ J K}^{-1} \text{ mol}^{-1} + 175 \text{ J K}^{-1} \text{ mol}^{-1} = 400. \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.28 The amino acid glycine dimerizes to form the dipeptide glycylglycine according to the reaction

$$2\text{Glycine}(s) \rightarrow \text{Glycylglycine}(s) + H_2O(l)$$
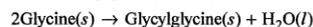
Calculate $\Delta S, \Delta S_{surroundings}$, and $\Delta S_{universe}$ at $T = 298$ K. Useful thermodynamic data follow:

	Glycine	Glycylglycine	Water
ΔH_f° (kJ mol^{-1})	−537.2	−746.0	−285.8
S_m° (J K^{-1} mol^{-1})	103.5	190.0	70.0

$$\Delta S_R^\circ = -2 \times 103.5 \text{ J K}^{-1} \text{ mol}^{-1} + 190.0 \text{ J K}^{-1} \text{ mol}^{-1} + 70.0 \text{ J K}^{-1} \text{ mol}^{-1} = 53.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_R^\circ = 2 \times 537.2 \text{ kJ mol}^{-1} - 746 \text{ kJ mol}^{-1} - 285.8 \text{ kJ mol}^{-1} = 42.6 \text{ kJ mol}^{-1}$$

$$\Delta S_{surroundings} = \frac{-\Delta H_R^\circ}{T} = \frac{-42.6 \text{ kJ mol}^{-1}}{298.0 \text{ K}} = -143 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{total} = -142.95 \text{ J K}^{-1} \text{ mol}^{-1} + 53.0 \text{ J K}^{-1} \text{ mol}^{-1} = -90.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.29   One mole of $H_2O(l)$ is supercooled to $-3.75°C$ at 1 bar pressure. The freezing temperature of water at this pressure is $0.00°C$. The transformation $H_2O(l) \rightarrow H_2O(s)$ is suddenly observed to occur. By calculating ΔS, $\Delta S_{surroundings}$, and ΔS_{total}, verify that this transformation is spontaneous at $-3.75°C$. The heat capacities are given by $C_{P,m}(H_2O(l)) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_{P,m}(H_2O(s)) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{fusion} = 6.008 \text{ kJ mol}^{-1}$ at $0.00°C$. Assume that the surroundings are at $-3.75°C$. [*Hint:* Consider the two pathways at 1 bar: (a) $H_2O(l, -3.75°C) \rightarrow H_2O(s, -3.75°C)$ and (b) $H_2O(l, -3.75°C) \rightarrow H_2O(l, 0.00°C) \rightarrow H_2O(s, 0.00°C) \rightarrow H_2O(s, -3.75°C)$. Because S is a state function, ΔS must be the same for both pathways.]

For pathway (b) $H_2O(l, -3.75°C) \rightarrow H_2O(l, 0.00°C) \rightarrow H_2O(s, 0.00°C) \rightarrow H_2O(s, -3.75°C)$.

$$\Delta S = nC_{P,m}(l) \ln \frac{273.15 \text{ K}}{269.40 \text{ K}} - n \frac{\Delta H_{fusion}}{273.15 \text{ K}} + nC_{P,m}(s) \ln \frac{269.40 \text{ K}}{273.15 \text{ K}}$$

$$= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{273.15 \text{ K}}{269.40 \text{ K}} - 1 \text{ mol} \times \frac{6008 \text{ J mol}^{-1}}{273.15 \text{ K}}$$
$$+ 1 \text{ mol} \times 37.7 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{269.40 \text{ K}}{273.15 \text{ K}}$$

$$= 1.041 \text{ J K}^{-1} - 22.00 \text{ J K}^{-1} - 0.521 \text{ J K}^{-1} = -21.48 \text{ J K}^{-1}$$

To calculate $\Delta S_{surroundings}$, we first calculate $\Delta H_P = q$.

$$\Delta H(-3.75°C) = \Delta H(0.00°C) + (C_P(solid) - C_P(liquid))\Delta T$$

$$\Delta H(-3.75°C) = 1 \text{ mol} \times [-6008 \text{ J mol}^{-1} + (37.7 \text{ J mol}^{-1} \text{ K}^{-1} - 75.3 \text{ J mol}^{-1} \text{ K}^{-1}) \times (-3.75 \text{ K})] = -5867 \text{ J} = q$$

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{5867 \text{ J}}{269.40 \text{ K}} = 21.78 \text{ J K}^{-1}$$

$\Delta S_{total} = 21.78 \text{ J K}^{-1} - 21.48 \text{ J K}^{-1} = 0.30 \text{ J K}^{-1} > 0$. The process is spontaneous.

P5.30   Calculate ΔS, $\Delta S_{surroundings}$, and $\Delta S_{universe}$ per day for the air conditioned house described in Problem 5.4. Assume that the interior temperature is $65°F$ and the exterior temperature is $99°F$.

32.0, 70.0, and 104 degrees Fahrenheit correspond to 0, 21.1, and 40.6 degrees Centigrade, respectively.

$$q_{cold} = \eta \times power \times time = 3.30 \times 1.70 \times 10^3 \text{ J s}^{-1} \times 3600 \text{ S hr}^{-1} \times 24 \text{ hr day}^{-1} = 4.85 \times 10^8 \text{ J}$$

$$q_{hot} = q_{cold}\left(\frac{1}{\eta} + 1\right) = 6.31 \times 10^8 \text{ J}$$

$$\Delta S = -\frac{q_{cold}}{T_{cold}} = \frac{4.85 \times 10^3 \text{ J}}{291.48 \text{ K}} = -1.66 \times 10^6 \text{ J K}^{-1}$$

$$\Delta S_{surroundings} = -\frac{q_{hot}}{T_{hot}} = \frac{6.32 \times 10^8 \text{ J s}^{-1}}{310.37 \text{ K}} = 2.03 \times 10^6 \text{ J K}^{-1}$$

$$\Delta S + \Delta S_{surroundings} = -1.66 \times 10^6 \text{ J K}^{-1} + 2.03 \times 10^6 \text{ J K}^{-1} = 3.72 \times 10^5 \text{ J K}^{-1}$$

P5.31   The following heat capacity data have been reported for L-alanine:

T(K)	10.	20.	40.	60.	80.	100.	140.	180.	220.	260.	300.
$C^\circ_{P,m}$ (J K^{-1} mol^{-1})	0.49	3.85	17.45	30.99	42.59	52.50	68.93	83.14	96.14	109.6	122.7

By a graphical treatment, obtain the molar entropy of L-alanine at $T = 300.$ K. You can perform the integration numerically using either a spread sheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.9).

The data is graphed below with the heat capacity and temperature on the vertical and horizontal axes, respectively. The best fit to the data has the form

$$C_{P,m} = -9.160 + 0.7761\,T - 0.001951\,T^2 + 0.000002764\,T^3$$
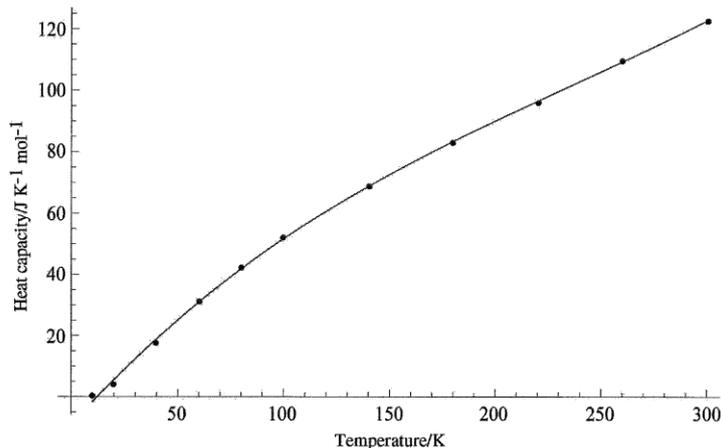
To obtain the entropy at 300. K, we evaluate the integral

$$S°(300.\,\text{K}) = \int_{10}^{300} \frac{-9.160 + 0.7761\,T - 0.001951\,T^2 + 0.000002764\,T^3}{T}\,dT$$

$$= [0.7761\,T - 0.0009756\,T^2 + 9.213 \times 10^{-7}\,T^3 - 9.160\,\text{Log}[T]]_{10.\,\text{K}}^{300.\,\text{K}}$$

$$= 131.1\,\text{J mol}^{-1}\,\text{K}^{-1}$$

We have neglected the contribution to S from temperatures below 10. K as the data is not available. This contribution is very small.

P5.32   Calculate $\Delta S_{surroundings}$ and ΔS_{total} for the processes described in parts (a) and (b) of Problem P5.16. Which of the processes is a spontaneous process? The state of the surroundings for each part is at 298 K, 1.50 bar. $\Delta S_{surroundings} = 0$ for (a) and (b) because $q = 0$.

a. $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 0 + 0 = 0$. The process is not spontaneous.

b. $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 10.1\,\text{J K}^{-1} + 0 = 10.1\,\text{J K}^{-1}$. The process is spontaneous.

P5.33   A refrigerator is operated by a 0.25-hp (1 hp = 746 watts) motor. If the interior is to be maintained at 4.50°C and the room temperature is 38°C, what is the maximum heat leak (in watts) that can be tolerated? Assume that the coefficient of performance is 50.% of the maximum theoretical value. What happens if the leak is greater than your calculated maximum value?

The coefficient of performance is

$$\eta_r = 0.500 \times \frac{T_{cold}}{T_{hot} - T_{cold}} = 0.500 \times \frac{277.65\,\text{K}}{311.15\,\text{K} - 277.65\,\text{K}} = 4.14$$

The maximum heat that can be removed from the cold reservoir is given by

$$\text{Input power} \times \text{coefficient of performance} = 0.25 \text{ hp} \times \frac{746 \text{ W}}{\text{hp}} \times 4.14 = 773 \text{ W} = 773 \text{ J s}^{-1}$$

If the heat leak is greater than this value, the temperature in the refrigerator will rise.

P5.34 Using your results from Problems P5.18 and P5.7, calculate ΔS, $\Delta S_{surroundings}$, and ΔS_{total} for each step in the cycle and for the total Carnot cycle described in Figure 5.2.

$a \rightarrow b$ $\qquad \Delta S = -\Delta S_{surroundings} = \dfrac{q_{reversible}}{T} = \dfrac{9.44 \times 10^3 \text{ J}}{740. \text{ K}} = 12.8 \text{ J K}^{-1}$ $\qquad \Delta S_{total} = 0$

$b \rightarrow c$ $\qquad \Delta S = -\Delta S_{surroundings} = 0$ because $q_{reversible} = 0$ $\qquad \Delta S_{total} = 0$

$c \rightarrow d$ $\qquad \Delta S = -\Delta S_{surroundings} = \dfrac{q_{reversible}}{T} = \dfrac{-3.96 \times 10^3 \text{ J}}{310. \text{ K}} = -12.8 \text{ J K}^{-1}$ $\qquad \Delta S_{total} = 0$

$d \rightarrow a$ $\qquad \Delta S = -\Delta S_{surroundings} = 0$ because $q_{reversible} = 0$ $\qquad \Delta S_{total} = 0$

For the cycle, $\Delta S = \Delta S_{surroundings} = \Delta S_{total} = 0$.

P5.35 Between $0°C$ and $100°C$, the heat capacity of $Hg(l)$ is given by

$$\frac{C_{P,m}(\text{Hg, } l)}{\text{J K}^{-1} \text{ mol}^{-1}} = 30.093 - 4.944 \times 10^{-3} \frac{T}{\text{K}}$$

Calculate ΔH and ΔS if 2.25 moles of $Hg(l)$ is raised in temperature from $0.00°$ to $88.0°C$ at constant P.

$$\Delta H = n \int_{273.15}^{361.15} C_{P,m} d[T/K]$$

$$= 2.25 \text{ mol} \times [30.093 \times (361.15 - 273.15) - 2.472 \times 10^{-3}(361.15^2 - 273.15^2)]\text{J mol}^{-1}$$

$$= 5.65 \times 10^3 \text{ J}$$

$$\Delta S = n \int_{273.15}^{361.15} \frac{C_{P,m}}{[T/K]} d[T/K]$$

$$= 2.25 \text{ mol} \times \left[30.093 \ln \frac{T_f}{T_i} - 4.944 \times 10^{-3}(348.15 - 273.15) \right] \text{J K}^{-1} \text{ mol}^{-1}$$

$$= 17.9 \text{ J K}^{-1}$$

P5.36 Calculate $\Delta S_{surroundings}$ and ΔS_{total} for part (c) of Problem P5.6. Is the process spontaneous? The state of the surroundings is $T = 310. \text{ K}$, $P = 0.333$ bar.

The gas undergoes a reversible isothermal expansion at $310. \text{ K}$ until the pressure is one third of its initial value.

$$w_{reversible} = -q = -nRT \ln \frac{V_f}{V_i} = -2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310. \text{ K} \times \ln 3 = -6.37 \times 10^3 \text{ J}$$

$$\Delta S_{surroundings} = \frac{-q}{T} = \frac{-6.37 \times 10^3 \text{ J}}{310. \text{ K}} = -20.55 \text{ J K}^{-1}$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} + nC_{P,m} \ln \frac{T_f}{T_i}$$

$$= -2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{1}{3} + 2.25 \text{ mol} \times \left(\frac{5}{2}\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \ln 1$$

$$= 20.55 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 20.55 \text{ J K}^{-1} - 20.55 \text{ J K}^{-1} = 0$$

There is no natural direction of change in this process because it is reversible.

P5.37   Calculate the entropy of one mole of water vapor at 175°C and 0.625 bar using the information in the data tables.

$$S(175°C, 0.625 \text{ bar}) = S°(298.15 \text{ K}) - nR \ln \frac{P_f}{P_i} + nC_P \ln \frac{T_f}{T_i}$$

$$= 1 \text{ mol} \times 188.8 \text{ J K}^{-1} \text{ mol}^{-1} - 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{0.625 \text{ bar}}{1 \text{ bar}}$$

$$+ 1 \text{ mol} \times 33.58 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{448.15 \text{ K}}{298.15 \text{ K}} = 206 \text{ J K}^{-1}$$

P5.38   The heat capacity of α-quartz is given by

$$\frac{C_{P,m}(\alpha\text{-quartz},s)}{\text{J K}^{-1} \text{ mol}^{-1}} = 46.94 + 34.31 \times 10^{-3} \frac{T}{\text{K}} - 11.30 \times 10^5 \frac{T^2}{\text{K}^2}$$

The coefficient of thermal expansion is given by $\beta = 0.3530 \times 10^{-4} \text{ K}^{-1}$ and $V_m = 22.6 \text{ cm}^3 \text{ mol}^{-1}$. Calculate ΔS_m for the transformation α-quartz (15.0°C, 1 atm) → α-quartz (420.°C, 925 atm). From Equations (5.23) and (5.24)

$$\Delta S_m = \int_{T_i}^{T_f} C_{P,m} \frac{dT}{T} - V\beta(P_f - P_i)$$

$$= \int_{288.15}^{693.15} \frac{\left(46.94 + 34.31 \times 10^{-3} \frac{T}{\text{K}} - 11.3 \times 10^{-5} \left(\frac{T}{\text{K}} \right)^2 \right)}{T/\text{K}} d\frac{T}{\text{K}} \text{ J K}^{-1} \text{ mol}^{-1} - V\beta(P_f - P_i)$$

$$= \left[\begin{array}{l} 46.94 \times \ln \frac{693.15 \text{ K}}{288.15} + 34.31 \times 10^{-3} \times (693.15 - 288.15) \\ -5.65 \times 10^{-5} \times (693.15^2 - 288.15^2) \end{array} \right] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$- 22.6 \text{ cm}^3 \text{ mol}^{-1} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \times 0.3530 \times 10^{-4} \text{ K}^{-1} \times 924 \text{ atm} \times \frac{1.0125 \times 10^5 \text{ Pa}}{\text{atm}}$$

$$= 41.20 \text{ J K}^{-1} \text{ mol}^{-1} + 13.896 \text{ J K}^{-1} \text{ mol}^{-1} - 22.455 \text{ J K}^{-1} \text{ mol}^{-1} - 0.0746 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 32.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.39   a.   Calculate ΔS if 1.00 mol of liquid water is heated from 0.00°C to 10.0°C under constant pressure if $C_{P,m} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

　　　　b.   The melting point of water at the pressure of interest is 0.00°C and the enthalpy of fusion is 6.010 kJ mol^{-1}. The boiling point is 100.°C and the enthalpy of vaporization is 40.65 kJ mol^{-1}. Calculate ΔS for the transformation $H_2O(s, 0.00°C) \rightarrow H_2O(g, 100.°C)$.

　　　　(a)   The heat input is the same for a reversible and an irreversible process.

$$dq = dq_{reversible} = nC_{P,m} \, dT$$

$$\Delta S = n \int \frac{C_{P,m}}{T} \, dT = nC_{P,m} \ln \frac{T_f}{T_i}$$

$$= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{283.15 \text{ K}}{273.15 \text{ K}}$$

$$= 2.71 \text{ J K}^{-1}$$

　　　　(b) $$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} = \frac{1 \text{ mol} \times 6010 \text{ J mol}^{-1}}{273.15 \text{ K}} = 22.00 \text{ J K}^{-1}$$

$$\Delta S_{vaporization} = \frac{\Delta H_{vaporization}}{T_{vaporization}} = \frac{1 \text{ mol} \times 40650. \text{ J mol}^{-1}}{373.15 \text{ K}} = 108.94 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{fusion} + \Delta S_{vaporization} + \Delta S_{heating} = (22.00 + 108.94 + 2.71) \text{ J K}^{-1} = 133.65 \text{ J K}^{-1}$$

P5.40   21.05 g of steam at 373 K is added to 415 g of $H_2O(l)$ at 298 K at a constant pressure of 1 bar. Is the final state of the system steam or liquid water? Calculate ΔS for the process.

Assume that the final state is liquid water. If this is not the case, the calculated temperature will be greater than 373 K.

$$-n_{steam}\Delta H_{vaporization}^{H_2O} + n_{steam}C_{P,m}^{H_2O}(T_f - T_i^{steam}) + n_{H_2O}C_{P,m}^{H_2O}(T_f - T_i^{H_2O}) = 0$$

$$T_f = \frac{n_{steam}C_{P,m}^{H_2O}T_i^{steam} + n_{H_2O}C_{P,m}^{H_2O}T_i^{H_2O} + n_{steam}\Delta H_{vaporization}^{H_2O}}{n_{steam}C_{P,m}^{H_2O} + n_{H_2O}C_{P,m}^{H_2O}} =$$

$$\frac{\dfrac{21.05 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 373 \text{ K} + \dfrac{415 \text{ g } H_2O(l)}{18.02 \text{ g } H_2O \text{ mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} + \dfrac{21.05 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 40650 \text{ J mol}^{-1}}{\dfrac{21.05 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} + \dfrac{415 \text{ g } H_2O(l)}{18.02 \text{ g } H_2O \text{ mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 328 \text{ K}$$

ΔS is calculated for the steam. It consists of condensing the steam at 373 K and cooling the resulting water to 328 K.

$$\Delta S = -n\frac{\Delta H_{vaporization}}{T_{vaporization}} + nC_{P,m}\ln\frac{T_f}{T_{vaporization}}$$

$$= -\frac{21.05 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times \frac{40650 \text{ J mol}^{-1}}{373 \text{ K}} + \frac{21.05 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{328 \text{ K}}{373 \text{ K}}$$

$$= -138.6 \text{ J K}^{-1}$$

ΔS is calculated for the water. It consists of heating the water from 298 K to 328 K.

$$\Delta S = nC_{P,m}\ln\frac{T_f}{T_i} = \frac{415 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{328 \text{ K}}{298 \text{ K}} = 164.7 \text{ J K}^{-1}$$

$\Delta S_{total} = 164.7 \text{ J K}^{-1} - 138.6 \text{ J K}^{-1} = 26.0 \text{ J K}^{-1}$. The process is spontaneous.

P5.41   Using your result from Problem 5.31, extrapolate the absolute entropy of L-alanine to physiological conditions, $T = 310. \text{ K}$. Assume the heat capacity is constant between $T = 300. \text{ K}$ and $T = 310. \text{ K}$.

We can either extrapolate the curve to 310. K using the same functional form or assume that the heat capacity is constant at its 300. K value between 300. K and 310. K.

$$S°(310. \text{ K}) = \int_{10. \text{ K}}^{310. \text{ K}} \frac{-9.1602 + 0.77610T - 0.0019511T^2 + 2.76403 \times 10^{-6}T^3}{T} = 135.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S°(310. \text{ K}) = S°(300. \text{ K}) + C_P \ln\frac{T_f}{T_i}$$

$$= 135.2 \text{ J K}^{-1} \text{ mol}^{-1} + 122.7 \text{ J K}^{-1} \text{ mol}^{-1} \ln\frac{310. \text{ K}}{300. \text{ K}} = 135.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.42   The mean solar flux at the Earth's surface is $\sim 2.00 \text{ J cm}^{-2} \text{ min}^{-1}$. In a nonfocusing solar collector, the temperature reaches a value of 79.5°C. A heat engine is operated using the collector as the hot reservoir and a cold reservoir at 298 K. Calculate the area of the collector needed to produce 1000. watts. Assume that the engine operates at the maximum Carnot efficiency.

$$\varepsilon = 1 - \frac{T_{hot}}{T_{cold}} = 1 - \frac{298 \text{ K}}{352.65 \text{ K}} = 0.155$$

The area required for the solar panal is

$$\frac{\text{power}}{\text{efficiency} \times \text{flux}} = \frac{1000.\,\text{J s}^{-1}}{0.155 \times 2.00\,\text{J cm}^{-2}\,\text{min}^{-1} \times 1\,\text{min}/60\,\text{s} \times 10^{4}\,\text{cm}^{2}/\text{m}^{2}} = 19.4\,\text{m}^{2}$$

P5.43 An ideal gas sample containing 1.75 moles for which $C_{V,m} = 5/2R$ undergoes the following reversible cyclical process from an initial state characterized by $T = 275$ K and $P = 1.00$ bar:

a.   It is expanded reversibly and adiabatically until the volume triples.

b.   It is reversibly heated at constant volume until T increases to 275 K.

c.   The pressure is increased in an isothermal reversible compression until $P = 1.00$ bar. Calculate $q, w, \Delta U, \Delta H,$ and ΔS for each step in the cycle, and for the total cycle.

(a)   The temperature at the end of the adiabatic reversible expansion is calculated.

$$T_f = T_i \left(\frac{V_f}{V_i}\right)^{1-\gamma} = 275\,\text{K} \times (3)^{1-\frac{7}{5}} = 275\,\text{K} \times (3)^{-2/5} = 177\,\text{K}$$

The initial and final volume and the final pressure are calculated.

$$V_i = \frac{nRT_i}{P_i} = \frac{1.75\,\text{mol} \times 8.314\,\text{J mol}^{-1}\text{K}^{-1} \times 275\,\text{K}}{10^5\,\text{Pa}} = 2.18 \times 10^{-3}\,\text{m}^3$$

$$V_f = 3V_i = 6.55 \times 10^{-3}\,\text{m}^3$$

$$P_f = P_i \frac{V_i}{V_f}\frac{T_f}{T_i} = 1.00\,\text{bar} \times \frac{1}{3} \times \frac{177\,\text{K}}{275\,\text{K}} = 0.215\,\text{bar}$$

$q = 0$ because the expansion is adiabatic.

$$\Delta U = w = nC_{V,m}\Delta T = 1.75\,\text{mol} \times \frac{5 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1}}{2} \times (177\,\text{K} - 275\,\text{K}) = -3.56 \times 10^3\,\text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 1.75\,\text{mol} \times \frac{7 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1}}{2} \times (177\,\text{K} - 275\,\text{K}) = -4.98 \times 10^3\,\text{J}$$

$\Delta S = 0$ because $q_{reversible} = 0$. $\Delta S_{surroundings} = 0$ because $q = 0$. $\Delta S_{total} = 0$.

(b) $w = 0$ because $\Delta V = 0$.

$$\Delta U = q = nC_{V,m}\Delta T = 1.75\,\text{mol} \times \frac{5 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1}}{2} \times (275\,\text{K} - 177\,\text{K}) = 3.56 \times 10^3\,\text{J}$$

$$\Delta H = nC_{P,m}\Delta T = 1.75\,\text{mol} \times \frac{7 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1}}{2} \times (275\,\text{K} - 177\,\text{K}) = 4.98 \times 10^3\,\text{J}$$

The pressure at the end of the process is calculated in order to calculate ΔS.

$$P_f = P_i \frac{T_f}{T_i} = 0.215\,\text{bar} \times \frac{275\,\text{K}}{177\,\text{K}} = 0.333\,\text{bar}$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} + nC_{P,m}\ln\frac{T_f}{T_i}$$

$$= -1.75\,\text{mol} \times 8.314\,\text{J mol}^{-1}\text{K}^{-1} \times \ln\frac{0.333\,\text{bar}}{0.215\,\text{bar}} + 1.75\,\text{mol} \times \frac{7 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1}}{2} \times \ln\frac{275\,\text{K}}{177\,\text{K}}$$

$$= -6.39\,\text{J K}^{-1} + 22.38\,\text{J K}^{-1} = 16.0\,\text{J K}^{-1}$$

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{-3.56 \times 10^3\,\text{J}}{275\,\text{K}} = -12.9\,\text{J K}^{-1}$$

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 16.0\,\text{J K}^{-1} - 12.9\,\text{J K}^{-1} = 3.1\,\text{J K}^{-1}$$

(c) $\Delta H = \Delta U = 0$ because $\Delta T = 0$.

$$w = -q = -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f}$$

$$= -1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 275 \text{ K} \times \ln \frac{0.333}{1} = 4.40 \times 10^3 \text{ J}$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} = -1.75 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{1.00 \text{ bar}}{0.333 \text{ bar}} = -16.0 \text{ J K}^{-1}$$

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{4.40 \times 10^3 \text{J}}{275 \text{ K}} = 16.0 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S = -16.0 \text{ J K}^{-1} + 16.0 \text{ J K}^{-1} = 0$$

For the entire cycle,

$$w_{cycle} = -3.56 \times 10^3 \text{ J} + 0 + 4.40 \times 10^3 \text{ J} = 840 \text{ J}$$

$$q_{cycle} = 0 + 3.56 \times 10^3 \text{ J} - 4.40 \times 10^3 \text{ J} = -840 \text{ J}$$

$$\Delta U_{cycle} = -3.56 \times 10^3 \text{ J} + 3.56 \times 10^3 \text{ J} + 0 = 0$$

$$\Delta H_{cycle} = -4.98 \times 10^3 \text{ J} + 4.98 \times 10^3 \text{ J} + 0 = 0$$

$$\Delta S_{cycle} = 0 + 16.0 \text{ J K}^{-1} - 16.0 \text{ J K}^{-1} = 0$$

$$\Delta S_{surrounging\ cycles} = 0 - 12.9 \text{ J K}^{-1} + 16.0 \text{ J K}^{-1} = 3.1 \text{ J K}^{-1}$$

$$\Delta S_{total\ cycle} = 3.1 \text{J K}^{-1}$$

P5.44   For protein denaturation, the excess entropy of denaturation is defined as $\Delta S_{den} = \int_{T_1}^{T_2} \frac{\delta C_P^{trs}}{T} dT$, where δC_P^{trs} is the

transition excess heat capacity. The way in which δC_P^{trs} can be extracted from differential scanning calorimetry (DSC) data is discussed in Section 4.6 and shown in Figure 4.7. The following DSC data are for a protein mutant that denatures between $T_1 = 288 \text{ K}$ and $T_2 = 318 \text{ K}$. Using the equation for ΔS_{den} given previously calculate the excess entropy of denaturation. In your calculations, use the dashed curve as the heat capacity base line which defines δC_P^{trs} as shown in Figure 4.8. Assume the molecular weight of the protein is 14000. grams.
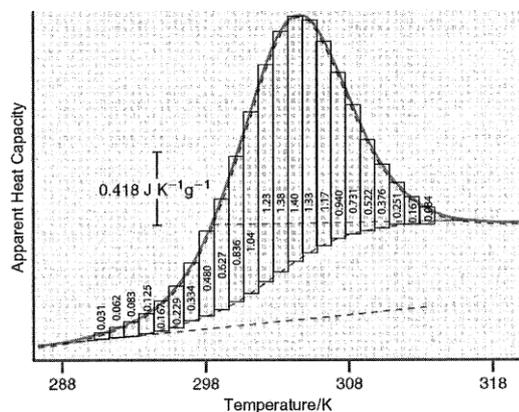
You can perform the integration numerically using either a spreadsheet program or a curve-fitting routine and a graphing calculator (see Example Problem 5.9).

We break up the area under the curve into rectangles and evaluate the area which is $C_P \times \Delta T$. We then divide by T for each rectangle and sum the contributions and finally multiply by the molar mass. This estimate approaches the value of the integral as the ΔT value approaches zero. The result is $620 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\Delta S_{den} = \int_{T_1}^{T_2} \frac{\delta C_P^{trs}}{T} dT = \sum_i \left(\frac{\delta C_P^{trs}}{T} \right)_i$$

$$= M \times \begin{pmatrix} \dfrac{0.031 \text{ J K}^{-1} \text{ g}^{-1}}{291 \text{ K}} + \dfrac{0.062 \text{ J K}^{-1} \text{ g}^{-1}}{292 \text{ K}} + \dfrac{0.083 \text{ J K}^{-1} \text{ g}^{-1}}{293 \text{ K}} + \dfrac{0.125 \text{ J K}^{-1} \text{ g}^{-1}}{294 \text{ K}} + \dfrac{0.167 \text{ J K}^{-1} \text{ g}^{-1}}{295 \text{ K}} \\[2mm] + \dfrac{0.229 \text{ J K}^{-1} \text{ g}^{-1}}{296 \text{ K}} + \dfrac{0.334 \text{ J K}^{-1} \text{ g}^{-1}}{297 \text{ K}} + \dfrac{0.480 \text{ J K}^{-1} \text{ g}^{-1}}{298 \text{ K}} + \dfrac{0.627 \text{ J K}^{-1} \text{ g}^{-1}}{299 \text{ K}} + \dfrac{0.836 \text{ J K}^{-1} \text{ g}^{-1}}{300 \text{ K}} \\[2mm] + \dfrac{1.04 \text{ J K}^{-1} \text{ g}^{-1}}{301 \text{ K}} + \dfrac{1.23 \text{ J K}^{-1} \text{ g}^{-1}}{302 \text{ K}} + \dfrac{1.38 \text{ J K}^{-1} \text{ g}^{-1}}{303 \text{ K}} + \dfrac{1.40 \text{ J K}^{-1} \text{ g}^{-1}}{304 \text{ K}} + \dfrac{1.33 \text{ J K}^{-1} \text{ g}^{-1}}{305 \text{ K}} \\[2mm] + \dfrac{1.17 \text{ J K}^{-1} \text{ g}^{-1}}{306 \text{ K}} + \dfrac{0.940 \text{ J K}^{-1} \text{ g}^{-1}}{307 \text{ K}} + \dfrac{0.731 \text{ J K}^{-1} \text{ g}^{-1}}{308 \text{ K}} + \dfrac{0.522 \text{ J K}^{-1} \text{ g}^{-1}}{309 \text{ K}} + \dfrac{0.376 \text{ J K}^{-1} \text{ g}^{-1}}{310 \text{ K}} \\[2mm] + \dfrac{0.251 \text{ J K}^{-1} \text{ g}^{-1}}{311 \text{ K}} + \dfrac{0.167 \text{ J K}^{-1} \text{ g}^{-1}}{312 \text{ K}} + \dfrac{0.084 \text{ J K}^{-1} \text{ g}^{-1}}{313 \text{ K}} \end{pmatrix}$$

$$= 627 \approx 620 \text{ J mol}^{-1} \text{ K}^{-1}$$

P5.45   The standard entropy of Pb(s) at 298.15 K is $64.80 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that the heat capacity of Pb(s) is given by

$$\frac{C_{P,m}(\text{Pb},s)}{\text{J mol}^{-1} \text{ K}^{-1}} = 22.13 + 0.01172\frac{T}{\text{K}} + 1.00 \times 10^{-5}\frac{T^2}{\text{K}^2}$$

The melting point is 327.4°C and the heat of fusion under these conditions is $4770. \text{ J mol}^{-1}$. Assume that the heat capacity of Pb(l) is given by

$$\frac{C_{P,m}(\text{Pb},l)}{\text{J K}^{-1} \text{ mol}^{-1}} = 32.51 - 0.00301\frac{T}{\text{K}}$$

a.   Calculate the standard entropy of Pb(l) at 725°C.

b.   Calculate ΔH for the transformation Pb(s, 25.0°C) → Pb(l, 725°C).

(a) $S_m^\circ(\text{Pb}, l, 998.15 \text{ K}) = S^\circ(\text{Pb}, s, 298.15 \text{ K})$

$$+ \int_{298.15}^{600.55} \frac{C_{P,m}}{[T/\text{K}]} d[T/\text{K}] + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{600.55}^{998.15} \frac{C_{P,m}}{[T/\text{K}]} d[T/\text{K}]$$

$$= 64.80 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$+ \int_{298.15}^{600.55} \frac{22.13 + 0.01172[T/\text{K}] + 1.00 \times 10^{-5}[T/\text{K}]}{[T/\text{K}]} d[T/\text{K}]$$

$$+ \frac{4770 \text{ J mol}^{-1}}{600.55 \text{ K}}$$

$$+ \int_{600.55}^{998.15} \frac{32.51 - 0.00301[T/\text{K}]}{[T/\text{K}]} d[T/\text{K}]$$

$$= 64.80 \text{ J mol}^{-1} \text{ K}^{-1} + 20.40 \text{ J mol}^{-1} \text{ K}^{-1} + 7.94 \text{ J mol}^{-1} \text{ K}^{-1} + 15.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 108.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

(b) $$\Delta H_{total} = \int_{298.15}^{600.55} C_{P,m}^{solid} d[T/\text{K}] + \Delta H_{fusion} + \int_{600.55}^{773.15} C_{P,m}^{liquid} d[T/\text{K}]$$

$$= 8.92 \times 10^3 \text{ J mol}^{-1} + 4770. \text{ J mol}^{-1} + 11.97 \times 10^3 \text{ J mol}^{-1}$$

$$= 25.7 \times 10^3 \text{ J mol}^{-1}$$