

### Chapter 11 Problems: The Thermodynamic Definition of Entropy

1. Calculate the Carnot efficiency of a solar concentrator–Stirling engine system that operates at 700°C and 37°C.

*Answer:* The temperatures are 973 K and 310 K in kelvins. The efficiency is then

$$\xi = (973-310)/973 = 68.1\%$$

However, most companies stopped development research on solar concentrator–Stirling engine systems in the late 1990's, because the systems were not economically viable. The increase in petroleum and natural gas prices in 2007 caused a resurgence in interest.

2. Is it more efficient to fly in the summer or winter?

*Answer:* Given Eq. 11.2.14,  $\xi_{\max} = \left( \frac{T_H - T_L}{T_H} \right)$ ,  $T_L$  is lower in winter so  $\xi_{\max}$  is greater in winter.

[Also, air turbulence decreases in the winter, which probably has a bigger effect.]

3. On a really hot day, is it possible to cool the kitchen by opening the refrigerator door?

*Answer:* The temperature near the refrigerator will briefly drop, but the room temperature will subsequently steadily rise. The refrigerator acts as a heat pump, using electrical work to transfer heat from a low temperature reservoir to a high temperature reservoir. The best that can happen is that the room stays at constant temperature. This is because the low temperature reservoir is the area in front of the open refrigerator, and the high temperature reservoir is the area in back of the refrigerator, which is heated by the cooling coils on the back of the refrigerator. The temperature in fact must increase. You can argue this question using the First Law or the Second Law. Using the First Law: electrical energy enters the room to run the refrigerator, so  $\Delta U_{\text{room}} > 0$ , so  $\Delta T > 0$ . Using the Second Law: assume that the refrigerator runs on a battery, even then the temperature would increase. The reason is that no engine or heat pump can be 100% efficient, so some energy will be wasted and the temperature will increase.

4. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is 500. K and the initial volume is 4.00 L. For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to 300. K. What is the volume  $V_3$  after step II, and  $V_4$  after step III,? Step IV returns the system to the initial temperature and volume.

*Answer:* For step II, since the step is adiabatic and reversible:  $V_3 T_3^c = V_2 T_2^c$  with  $c = C_v/nR$ . For a monatomic gas  $C_v = 3/2 nR$ , giving  $c = 3/2$ :

$$V_3 = V_2 \left( \frac{T_2}{T_3} \right)^c = 8.00 \text{ L} \left( \frac{500.}{300.} \right)^{3/2} = 17.21 \text{ L}$$

For step III, we need to calculate  $V_4$  from  $V_1$  using step IV. Step IV is an adiabatic reversible step so that we can calculate  $V_4$  from  $V_1$  by  $V_4 T_4^c = V_1 T_1^c$ :

$$V_4 = V_1 \left( \frac{T_1}{T_4} \right)^c = 4.00 \text{ L} \left( \frac{500.}{300.} \right)^{3/2} = 8.606 \text{ L}$$

5. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is 500. K and the initial volume is 4.00 L. For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to 300. K. Notice that for a reversible cycle, the work done in steps II and IV is equal, but opposite in sign. (a) Calculate the work done in step I and step III. (b) Calculate the energy transferred from the high temperature reservoir,  $q_H$ . (c) Calculate the efficiency for the cycle.

*Answer:* (a) For step I,  $n = 1.00$  mol,  $T_H = 500.$  K,  $V_1 = 4.00$  L and  $V_2 = 8.00$  L as given in the problem. Since the expansion is isothermal and reversible:  $w_I = -nRT_H \ln(V_2/V_1)$  giving:

$$w_I = -(1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(500. \text{ K}) \ln(8.00/4.00) = -2881. \text{ J}$$

(b) Please see Problem 4 for the calculation of  $V_3 = 17.21$  L and  $V_4 = 8.606$  L. Since step III is isothermal reversible at  $T_L = 300.$  K:

$$w_{III} = -(1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300. \text{ K}) \ln(8.606/17.21) = 1729. \text{ J}$$

(c) The total work is  $w = w_I + w_{III}$  for a reversible cycle:

$$w = -2881. \text{ J} + 1729. \text{ J} = -1152. \text{ J}$$

For isothermal step I,  $\Delta U = 0$ , so that  $q_H = -w_I = 2881. \text{ J}$  giving the efficiency, using Eq. 11.1.5:

$$\xi = \frac{-w}{q_H} = \frac{-(-1152.)}{2881.} = 0.400$$

We can check our calculation using Eq. 11.2.14 giving:

$$\xi_{\max} = \left( \frac{T_H - T_L}{T_H} \right) = \left( \frac{500. - 300.}{500.} \right) = 0.400$$

So our calculations are correct. Notice that the comparison of the results from Eq. 11.1.5 and Eq. 11.2.14 shows that the maximum efficiency for a process operating in a cycle is an exclusive function of the operating temperatures. We chose a process where the volume doubles in step I. However, this choice does not, in the end, have an effect on the efficiency.

6. A 0.200-mol sample of a monatomic ideal gas is used as the working substance in a reversible Carnot cycle that operates between 700 K and 300 K. The starting volume is 0.500 L. The heat transferred into the gas from the high temperature reservoir is 1000. J. (a) Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta S$  for each of the steps in the Carnot cycle. (b) Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta S$  for the complete cycle.

*Answer:* (a) For step I,  $n = 0.200$  mol,  $q_H = 1000.$  J,  $T_H = 700.$  K,  $T_L = 300.$  K, and  $V_1 = 0.500$  L as given in the problem. For this isothermal step,  $\Delta U = 0$ , so that  $w_I = -q_H = -1000.$  J and

$$\Delta S = q_{\text{rev}}/T_H = 1000. \text{ J}/700. \text{ K} = 1.429 \text{ J K}^{-1}$$

For the subsequent step we will need to know  $V_2$ . Since the expansion is isothermal and reversible:  $w = -nRT \ln(V_2/V_1)$  giving:

$$w_I = -1000 \text{ J} = -(0.200 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(700. \text{ K}) \ln(V_2/V_1)$$

or  $\ln(V_2/V_1) = 0.8591$  and finally:

$$V_2 = 0.500 \text{ L } e^{0.8591} = 1.181 \text{ L}$$

For step II, since the step is adiabatic and reversible,  $q = q_{\text{rev}} = 0$ ,  $\Delta S = 0$ , and for a monatomic gas  $C_v = 3/2 nR$ :

$$w_{\text{II}} = \Delta U = C_v \Delta T = \frac{3}{2} nR(T_L - T_H) = \frac{3}{2} (0.200 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300. - 700. \text{ K})$$

$$w_{\text{II}} = \Delta U = -997.7 \text{ J}$$

For the subsequent step we will need to know  $V_3$ . Since the expansion is adiabatic and reversible:  $V_3 T_3^c = V_2 T_2^c$  with  $c = C_v/nR$ . For a monatomic gas  $C_v = 3/2 nR$ , giving  $c = 3/2$ :

$$V_3 = V_2 \left( \frac{T_2}{T_3} \right)^c = 1.181 \text{ L} \left( \frac{700.}{300.} \right)^{3/2} = 4.208 \text{ L}$$

For step III, which is again isothermal,  $\Delta U = 0$  so that  $w_{\text{III}} = -q_L$  and  $w = -nRT_L \ln(V_4/V_3)$ . We need to calculate  $V_4$ . Step IV is an adiabatic reversible step so that we can calculate  $V_4$  from  $V_1$  by  $V_4 T_4^c = V_1 T_1^c$ :

$$V_4 = V_1 \left( \frac{T_1}{T_4} \right)^c = 0.500 \text{ L} \left( \frac{700.}{300.} \right)^{3/2} = 1.782 \text{ L}$$

So the work in step III is:

$$w_{\text{III}} = -nRT \ln(V_4/V_3) = -(0.200 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300. \text{ K}) \ln(1.782/4.208) \\ = 428.6 \text{ J}$$

with  $q_L = q_{\text{rev}} = -w_{\text{III}} = -428.6 \text{ J}$  and  $\Delta S = q_{\text{rev}}/T_L = -428.6 \text{ J}/300. \text{ K} = -1.429 \text{ J K}^{-1}$  which is the same absolute value as for step I.

For step IV, since the step is adiabatic and reversible,  $q = q_{\text{rev}} = 0$ ,  $\Delta S = 0$ , and for a monatomic gas  $C_v = 3/2 nR$ :

$$w_{\text{IV}} = \Delta U = C_v \Delta T = \frac{3}{2} nR(T_H - T_L) = \frac{3}{2} (0.200 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(700. - 300. \text{ K})$$

giving  $w_{\text{IV}} = \Delta U = 997.7 \text{ J}$  which is just the negative of step II, as expected.

(b) The results and totals are summarized in the following table.

Step	q (J)	w (J)	$\Delta U$ (J)	$\Delta S$ (J K <sup>-1</sup> )
I: isothermal, $T_H$	1000.	-1000.	0	1.429
II. adiabatic	0	-997.7	-997.7	0
III. isothermal, $T_L$	-428.6	428.6	0	-1.429
IV. adiabatic	0	997.7	997.7	0
<b>totals</b>	<b>571.4</b>	<b>-571.4</b>	<b>0</b>	<b>0</b>

We can check our results by calculating the overall efficiency using the numbers from the table and comparing with Eq. 11.2.14. Using  $w$  and  $q_H$ , explicitly from the table, and using Eq. 11.1.5 gives:

$$\xi = \frac{-w}{q_H} = \frac{-(-571.4 \text{ J})}{1000. \text{ J}} = 0.5714$$

Now using Eq. 11.2.14 gives:

$$\xi_{\text{max}} = \left( \frac{T_H - T_L}{T_H} \right) = \left( \frac{700. - 300.}{700.} \right) = 0.5714$$

So our calculations are correct. Note that the overall change in  $\Delta S$  for this cyclic process is zero, since the cycle is reversible.

7. The peak sun solar flux that reaches a surface pointed directly at the sun is about  $1.00 \text{ kW m}^{-2}$ . Using a solar collector of area  $10.0 \text{ m}^2$ , calculate the collector temperature that would be necessary to produce  $4.00 \text{ kW}$  of power using a steam turbine coupled to an electric generator at peak sun flux. Assume the discharge temperature of the turbine is  $35^\circ\text{C}$  and that the combined steam turbine and electrical generator operate at  $60.0\%$  of the maximum theoretical efficiency (due to frictional losses, etc.). Neglect radiative losses from the solar collector absorber surface.

*Answer:* The final output power,  $P$ , is:

$$P = J_{\text{solar}} A \xi_{\text{max}} (0.600)$$

using the fact that the combined steam turbine and electrical generator operate at  $60\%$  of the maximum theoretical efficiency. The required power is  $4 \text{ kW}$ :

$$P = 4 \text{ kW} = (1.00 \text{ kW m}^{-2})(10.0 \text{ m}^2) \xi_{\text{max}} (0.600)$$

solving for  $\xi_{\text{max}}$  gives  $\xi_{\text{max}} = 0.667$

Using  $\xi_{\text{max}}$  and solving for  $T_{\text{H}}$  from Eq. 11.2.14 using  $T_{\text{L}} = 35 + 273. \text{ K} = 308. \text{ K}$ :

$$\xi_{\text{max}} = 0.667 = \left( \frac{T_{\text{H}} - T_{\text{L}}}{T_{\text{H}}} \right) = \left( \frac{T_{\text{H}} - 308. \text{ K}}{T_{\text{H}}} \right)$$

or  $0.667 T_{\text{H}} = T_{\text{H}} - 308 \text{ K}$

gives  $T_{\text{H}} = 925. \text{ K}$

8. In problem 7, we neglected radiative losses from the solar collector absorber surface. Assuming the same conditions and operating temperatures as in problem 7, calculate the output power when radiative losses from the solar collector absorber surface are taken into account. Assume that the absorber surface is  $0.1 \text{ m}^2$  (this concentration ratio is  $A/a = 100$ ).

*Answer:* From Eq. 11.2.20, and using  $T_{\text{H}} = 925. \text{ K}$  and  $T_{\text{L}} = 308. \text{ K}$  from problem 7:

$$\begin{aligned} \xi_{\text{max}} &= \left( \frac{T_{\text{H}} - T_{\text{L}}}{T_{\text{H}}} \right) \left( \frac{J_{\text{solar}} A - a \sigma T_{\text{H}}^4}{J_{\text{solar}} A} \right) \\ &= (0.667) \left( \frac{1000 \text{ W m}^{-2} (10.0 \text{ m}^2) - 0.1 \text{ m}^2 (5.6704 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4})(925.)^4}{1000 \text{ W m}^{-2} (10.0 \text{ m}^2)} \right) \\ &= (0.667) \left( \frac{1.00 \times 10^4 - 4151.3 \text{ W}}{1.00 \times 10^4 \text{ W}} \right) = (0.667)(0.585) = 0.390 \end{aligned}$$

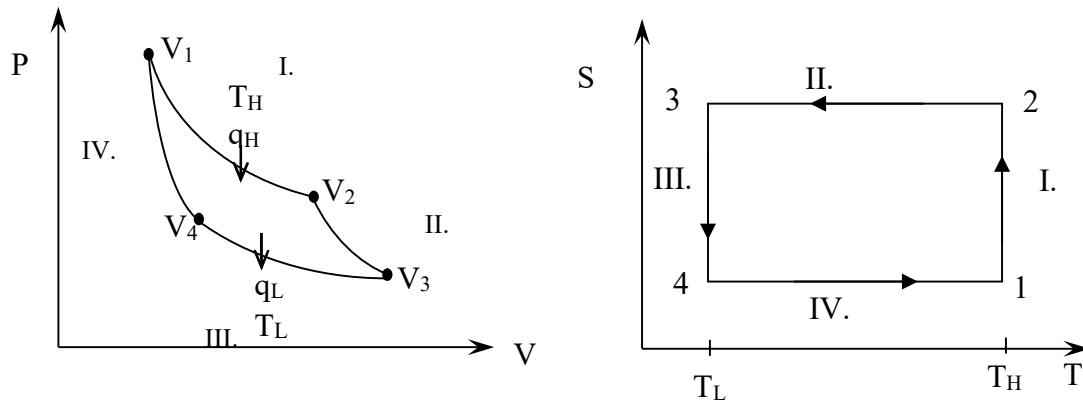
The radiative loss from the absorber area is significant. Then the final output power is decreased almost by a factor of two:

$$P = J_{\text{solar}} A \xi_{\text{max}} (0.600) = (1.00 \text{ kW m}^{-2})(10.0 \text{ m}^2)(0.390)(0.600) = 2.34 \text{ kW}$$

The implication for chemists from this example is that many diverse energy sources must be found to decrease our dependence on fossil fuels. Solar power alone will not solve the problem; the materials requirements are too large.

9. Give a rough sketch of the progress for a reversible Carnot cycle on a plot of entropy versus temperature. Label the steps I-IV so that you can compare with Figure 11.2.1. Also indicate the starting point.

*Answer:* Please review problem 4, for explicit example numbers. The starting point in Figure 11.2.1 is chosen at  $T_H$ . Step I is isothermal with an increase in entropy, since  $\Delta S = q_{rev}/T_H$  with  $q_{rev} > 0$ . Step II is adiabatic reversible, so  $\Delta S$  is zero and then  $S$  is constant. The temperature drops from  $T_H$  to  $T_L$ . Step III is isothermal, again, but with a decrease in entropy since  $q_L < 0$ . Step IV is adiabatic again, but the temperature increases from  $T_L$  to  $T_H$ .



10. The solar concentration ratio of a solar collector is defined as the total collector area divided by the absorber area,  $c = A/a$ . The solar collection area for a very large “power tower” is on the order of 200.  $m^2$ . For a small solar absorber area of 0.1  $m^2$  ( $\sim 1$   $ft^2$ ), the corresponding concentration ratio is 2000. Plot the solar thermal efficiency for this concentration ratio as a function of absorber temperature,  $T_H$ , including the Carnot efficiency and radiative losses. Assume that the low temperature reservoir for the solar thermal process is at 300. K and the solar flux is 1000.  $W m^{-2}$ .

*Answer:* Using Eq. 11.2.20:

$$\xi_{\max} = \left( \frac{T_H - T_L}{T_H} \right) \left( \frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right)$$

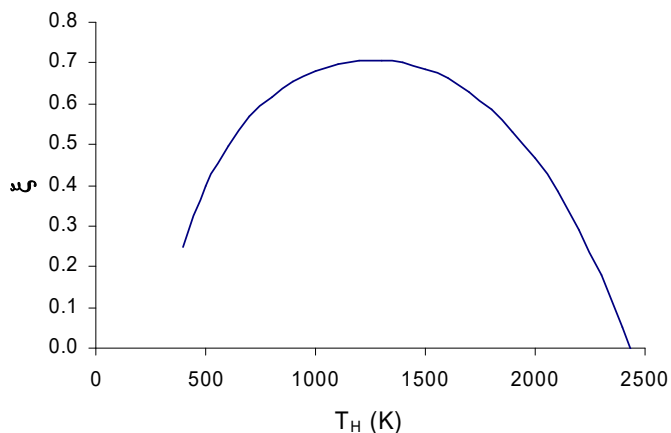
where the first term in brackets is the Carnot efficiency. With the given values:

$$\xi_{\max} = \left( \frac{T_H - 300. \text{ K}}{T_H} \right) \left( \frac{1000 \text{ W m}^{-2} (200. \text{ m}^2) - 0.1 \text{ m}^2 (5.6704 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}) T_H^4}{1000 \text{ W m}^{-2} (200. \text{ m}^2)} \right)$$

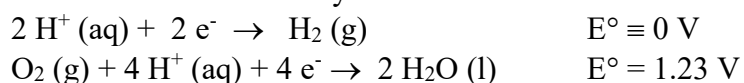
The following table lists the calculated values. The efficiency peaks at 1300 K. The chemical importance of this problem is that, even for very large collection areas, the maximum temperature available to drive chemical fuel cycles is limited. Additionally, finding materials that are robust at these temperatures is an important research area in materials chemistry.

$T_H$	Carnot	SB*	efficiency
400	0.250	0.999	0.250
500	0.400	0.998	0.399
600	0.500	0.996	0.498
700	0.571	0.993	0.568
800	0.625	0.988	0.618
900	0.667	0.981	0.654
1000	0.700	0.972	0.680
1100	0.727	0.958	0.697
1200	0.750	0.941	0.706
1300	0.769	0.919	0.707
1400	0.786	0.891	0.700
1500	0.800	0.856	0.685
1600	0.813	0.814	0.662
1700	0.824	0.763	0.629
1800	0.833	0.702	0.585
1900	0.842	0.631	0.531
2000	0.850	0.546	0.464

\* SB = Stefan-Boltzmann factor



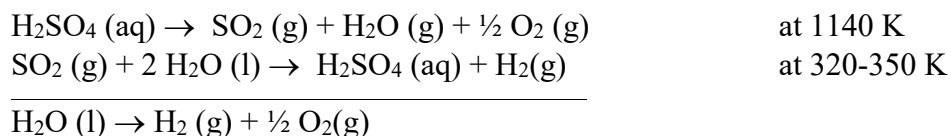
11. The electrolysis of water is a potential source of hydrogen for use as a transportation fuel. However,  $H_2$  production is very costly. From your General Chemistry course, you might remember that the direct electrolysis of water is based on the two standard reduction half-cells:



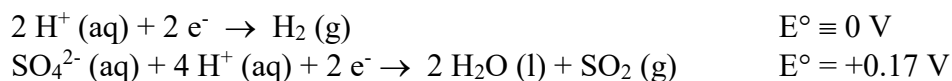
with the standard cell potential:



This cell potential is large and unfavorable. The Westinghouse-S cycle was developed in the 1970s to use solar thermal energy to lower the cost of the production of hydrogen.<sup>17</sup> The Westinghouse-S cycle consists of two reactions, the net result of which is the production of  $H_2$ :

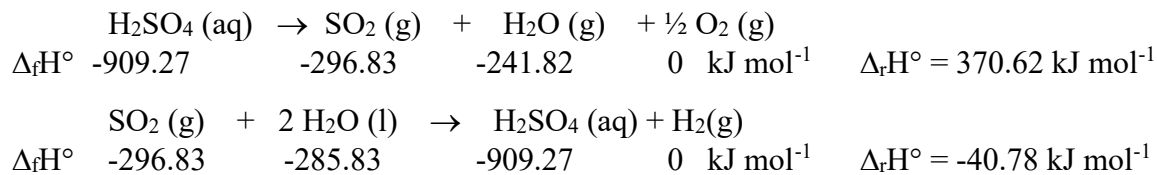


The first step, the dehydration of sulfuric acid, is run in a concentrating solar collector. The second step is run in an electrolytic cell with the standard reduction half reactions:



giving the standard cell potential  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.17 \text{ V}$ . Even though this cell potential is still negative, the energy requirement is greatly diminished from the direct hydrolysis. Of course, electrical energy is required to run the second step, which must be obtained from conventional sources. The solar thermal efficiency for this process covers only the production of  $\text{SO}_2(\text{g})$ . (a) Calculate the change in enthalpy for both steps in the Westinghouse-S cycle. (b) Calculate the maximum solar thermal efficiency for the production of  $\text{SO}_2(\text{g})$  for the thermal part of the process operating between 1140 K and 350 K. Neglect radiative losses. (c) Calculate the electrical work necessary to produce one mole of  $\text{H}_2$  for  $E^\circ_{\text{cell}}$  at  $-1.23 \text{ V}$  and  $-0.17 \text{ V}$ . [Hint: for electrochemical cells  $z_i$  is given by the number of electrons transferred in the balanced cell reaction.]

*Answer:* (a) Using the thermochemical tables in the appendix, the standard enthalpies of formation are listed below:



The reaction enthalpy change is  $\Delta_r H^\circ = [\text{products}] - [\text{reactants}] = \sum v_i \Delta_f H^\circ_i$

The first reaction is highly endothermic, requiring a significant input of thermal energy.

(b) The Carnot efficiency for the production of  $\text{SO}_2$  is:

$$\xi_{\text{max}} = \left( \frac{T_H - T_L}{T_H} \right) = \left( \frac{1140 - 350}{1140} \right) = 0.693$$

The question is if the value of the  $\text{H}_2$  as a replacement for fossil fuels is sufficient to outweigh the production costs.

(c). The electrical work is given by  $w = -z_i F \Delta\phi$ . For this electrochemical cell to produce one mole of  $\text{H}_2$ ,  $z_i = 2 \text{ mol}$  of electrons. The difference in electric potential  $\Delta\phi$  is the cell voltage,  $\Delta\phi = E_{\text{cell}}$ . For the direct production of hydrogen by electrolysis,

$$w = - (2 \text{ mol})(96,485 \text{ C mol}^{-1})(-1.23 \text{ V})(1 \text{ J/1 C V})(1 \text{ kJ/1000 J}) = 237. \text{ kJ mol}^{-1}$$

For the Westinghouse-S cycle, the electrolysis requires:

$$w = - (2 \text{ mol})(96,485 \text{ C mol}^{-1})(-0.17 \text{ V})(1 \text{ J/1 C V})(1 \text{ kJ/1000 J}) = 32.8 \text{ kJ mol}^{-1}$$

Even though the process still requires electrical energy, the electrical energy required is greatly decreased by providing the difference from the sun.

12. In Eq. 11.2.20:

$$\xi_{\text{max}} = \left( \frac{T_H - T_L}{T_H} \right) \left( \frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right)$$

The second term in brackets is the correction for the efficiency caused by radiative loss from the absorber surface. This correction results from the Stefan-Boltzmann equation, Eq. 11.2.16.

Derive this radiative loss correction from Eq. 11.2.16.

*Answer:* The flux is the power gain or loss per unit area. Given the solar collector area,  $A$ , the incident power from the sun is  $J_{\text{solar}} A$ . From Eq. 11.2.16,  $J_{\text{blackbody}} = \sigma T^4$ :  $J_{\text{blackbody}}$  is the flux emitted by the absorber surface. Given the absorber surface area,  $a$ , the emitted power from the surface at temperature  $T_H$  is

$$\text{emitted power} = J_{\text{blackbody}} a = a \sigma T_H^4$$

The net power absorbed is the difference:  $J_{\text{solar}} A - a \sigma T_H^4$ . The efficiency of the net absorption is the ratio of the net power absorbed to the incident power:

$$\xi_{\text{absorb}} = \left( \frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right)$$

The overall efficiency is  $\xi_{\text{max}} = \xi_{\text{Carnot}} \xi_{\text{absorb}}$