

4 The Second Law: the concepts

Solutions to exercises

Discussion questions

- E4.1(b)** Trouton's rule is that the ratio of the enthalpy of vaporization of a liquid to its boiling point is a constant. Energy in the form of heat (enthalpy) supplied to a liquid manifests itself as turbulent motion (kinetic energy) of the molecules. When the kinetic energy of the molecules is sufficient to overcome the attractive energy that holds them together the liquid vaporizes. The enthalpy of vaporization is the heat energy (enthalpy) required to accomplish this at constant pressure. It seems reasonable that the greater the enthalpy of vaporization, the greater the kinetic energy required, and the greater the temperature needed to achieve this kinetic energy. Hence, we expect that $\Delta_{\text{vap}}H \propto T_b$, which implies that their ratio is a constant.
- E4.2(b)** The device proposed uses geothermal heat (energy) and appears to be similar to devices currently in existence for heating and lighting homes. As long as the amount of heat extracted from the hot source (the ground) is not less than the sum of the amount of heat discarded to the surroundings (by heating the home and operating the steam engine) and of the amount of work done by the engine to operate the heat pump, this device is possible; at least, it does not violate the first law of thermodynamics. However, the feasibility of the device needs to be tested from the point of view of the second law as well. There are various equivalent versions of the second law, some are more directly useful in this case than others. Upon first analysis, it might seem that the net result of the operation of this device is the complete conversion of heat into the work done by the heat pump. This work is the difference between the heat absorbed from the surroundings and the heat discharged to the surroundings, and all of that difference has been converted to work. We might, then, conclude that this device violates the second law in the form stated in the introduction to Chapter 4; and therefore, that it cannot operate as described. However, we must carefully examine the exact wording of the second law. The key words are "sole result." Another slightly different, though equivalent, wording of Kelvin's statement is the following: "It is impossible by a cyclic process to take heat from a reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir." So as long as some heat is discharged to surroundings colder than the geothermal source during its operation, there is no reason why this device should not work. A detailed analysis of the entropy changes associated with this device follows.

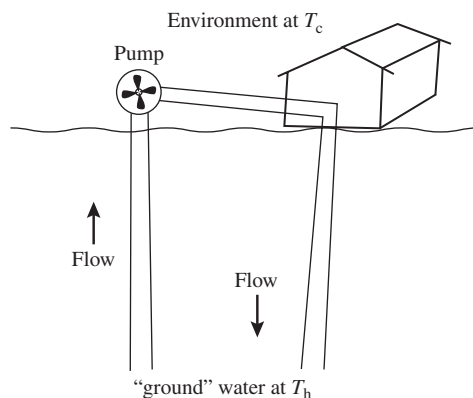


Figure 4.1 C_V and C_P are the temperature dependent heat capacities of water

Three things must be considered in an analysis of the geothermal heat pump: Is it forbidden by the first law? Is it forbidden by the second law? Is it efficient?

$$\Delta E_{\text{tot}} = \Delta E_{\text{water}} + \Delta E_{\text{ground}} + \Delta E_{\text{environment}}$$

$$\Delta E_{\text{water}} = 0$$

$$\Delta E_{\text{ground}} = -C_V(T_h)\{T_h - T_c\}$$

$$\Delta E_{\text{environment}} = -C_V(T_h)\{T_h - T_c\}$$

adding terms, we find that $\Delta E_{\text{tot}} = 0$ which means that the first law is satisfied for any value of T_h and T_c .

$$\Delta S_{\text{tot}} = \Delta S_{\text{water}} + \Delta S_{\text{ground}} + \Delta S_{\text{environment}}$$

$$\Delta S_{\text{water}} = 0$$

$$\Delta S_{\text{ground}} = \frac{q_{\text{ground}}}{T_h} = \frac{-C_p(T_h)\{T_h - T_c\}}{T_h}$$

$$\Delta S_{\text{environment}} = \frac{q_{\text{environment}}}{T_c} = \frac{C_p(T_c)\{T_h - T_c\}}{T_c}$$

adding terms and estimating that $C_p(T_h) \simeq C_p(T_c) = C_p$, we find that

$$\Delta S_{\text{tot}} = C_p\{T_h - T_c\} \left\{ \frac{1}{T_c} - \frac{1}{T_h} \right\}$$

This expression satisfies the second law ($\Delta S_{\text{tot}} > 0$) only when $T_h > T_c$. We can conclude that, if the proposal involves collecting heat from environmentally cool ground water and using the energy to heat a home or to perform work, the proposal cannot succeed no matter what level of sophisticated technology is applied. Should the “ground” water be collected from deep within the Earth so that $T_h > T_c$, the resultant geothermal pump is feasible. However, the efficiency, given by eqn 4.11, must be high to compete with fossil fuels because high installation costs must be recovered during the lifetime of the apparatus.

$$E_{\text{rev}} = 1 - \frac{T_c}{T_h}$$

with $T_c \sim 273$ K and $T_h = 373$ K (the highest value possible at 1 bar), $E_{\text{rev}} = 0.268$. At most, about 27% of the extracted heat is available to do work, including driving the heat pump. The concept works especially well in Iceland where geothermal springs bring boiling water to the surface.

E4.3(b) See the solution to exercises 4.3 (a).

Numerical exercises

E4.4(b)
$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{q}{T}$$

(a)
$$\Delta S = \frac{50 \times 10^3 \text{ J}}{273 \text{ K}} = \boxed{1.8 \times 10^2 \text{ J K}^{-1}}$$

(b)
$$\Delta S = \frac{50 \times 10^3 \text{ J}}{(70 + 273) \text{ K}} = \boxed{1.5 \times 10^2 \text{ J K}^{-1}}$$

E4.5(b) At 250 K, the entropy is equal to its entropy at 298 K plus ΔS where

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{V,m} dT}{T} = C_{V,m} \ln \frac{T_f}{T_i}$$

$$\text{so } S = 154.84 \text{ J K}^{-1} \text{ mol}^{-1} + [(20.786 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}] \times \ln \frac{250 \text{ K}}{298 \text{ K}}$$

$$S = \boxed{152.65 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\text{E4.6(b)} \quad \Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{p,m} dT}{T} = C_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S = (1.00 \text{ mol}) \times \left(\frac{5}{2} + 1\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{(100 + 273) \text{ K}}{273 \text{ K}} = \boxed{9.08 \text{ J K}^{-1}}$$

E4.7(b) However the change occurred, ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\Delta S_1 = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{p,m} dT}{T} = C_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S_1 = (2.00 \text{ mol}) \times \left(\frac{7}{2}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{(135 + 273) \text{ K}}{(25 + 273) \text{ K}} = 18.3 \text{ J K}^{-1}$$

and for the second

$$\Delta S_2 = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

$$\text{where } q_{\text{rev}} = -w = \int p dV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{p_i}{p_f}$$

$$\text{so } \Delta S_2 = nR \ln \frac{p_i}{p_f} = (2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{1.50 \text{ atm}}{7.00 \text{ atm}} = -25.6 \text{ J K}^{-1}$$

$$\Delta S = (18.3 - 25.6) \text{ J K}^{-1} = \boxed{-7.3 \text{ J K}^{-1}}$$

The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Or the ordering represented by confining the sample to a smaller volume in step 2 overcame the disordering represented by the temperature rise in step 1. A negative entropy change is allowed for a system as long as an increase in entropy elsewhere results in $\Delta S_{\text{total}} > 0$.

E4.8(b) $q = q_{\text{rev}} = \boxed{0}$ (adiabatic reversible process)

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \boxed{0}$$

$$\begin{aligned} \Delta U &= nC_{V,m} \Delta T = (2.00 \text{ mol}) \times (27.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 - 250) \text{ K} \\ &= 2750 \text{ J} = \boxed{+2.75 \text{ kJ}} \end{aligned}$$

$$w = \Delta U - q = 2.75 \text{ kJ} - 0 = \boxed{2.75 \text{ kJ}}$$

$$\Delta H = nC_{p,m} \Delta T$$

$$C_{p,m} = C_{V,m} + R = (27.5 \text{ J K}^{-1} \text{ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 35.814 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{So } \Delta H = (2.00 \text{ mol}) \times (35.814 \text{ J K}^{-1} \text{ mol}^{-1}) \times (+50 \text{ K})$$

$$= 3581.4 \text{ J} = \boxed{3.58 \text{ kJ}}$$

- E4.9(b)** However the change occurred, ΔS has the same value as if the change happened by reversible heating at constant volume (step 1) followed by reversible isothermal expansion (step 2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\begin{aligned}\Delta S_1 &= \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{V,m} dT}{T} = C_{V,m} \ln \frac{T_f}{T_i} \quad [C_{V,m} = C_{p,m} - R] \\ &= (3.50 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{700 \text{ K}}{250 \text{ K}} = 44.9 \text{ J K}^{-1}\end{aligned}$$

and for the second

$$\Delta S_2 = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

$$\text{where } q_{\text{rev}} = -w = \int p dV = nRT \ln \frac{V_f}{V_i},$$

$$\text{so } \Delta S_2 = nR \ln \frac{p_i}{p_f} = (3.50 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{60.0 \text{ L}}{20.0 \text{ L}} = 32.0 \text{ J K}^{-1}$$

$$\Delta S = 44.9 + 32.0 \text{ J K}^{-1} = \boxed{76.9 \text{ J K}^{-1}}$$

- E4.10(b)** $\Delta S = \frac{q_{\text{rev}}}{T}$ If reversible $q = q_{\text{rev}}$

$$\begin{aligned}q_{\text{rev}} &= T \Delta S = (5.51 \text{ J K}^{-1}) \times (350 \text{ K}) \\ &= 1928.5 \text{ J}\end{aligned}$$

$$q = 1.50 \text{ kJ} \neq 19.3 \text{ kJ} = q_{\text{rev}}$$

$q \neq q_{\text{rev}}$; therefore the process is not reversible

- E4.11(b)** (a) The heat flow is

$$\begin{aligned}q &= C_p \Delta T = nC_{p,m} \Delta T \\ &= \left(\frac{2.75 \text{ kg}}{63.54 \times 10^{-3} \text{ kg mol}^{-1}} \right) \times (24.44 \text{ J K}^{-1} \text{ mol}^{-1}) \times (275 - 330) \text{ K} \\ &= \boxed{-58.2 \times 10^3 \text{ J}}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad \Delta S &= \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_p dT}{T} = nC_{p,m} \ln \frac{T_f}{T_i} \\ &= \left(\frac{2.75 \text{ kg}}{63.54 \times 10^{-3} \text{ kg mol}^{-1}} \right) \times (24.44 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{275 \text{ K}}{330 \text{ K}} = \boxed{-193 \text{ J K}^{-1}}\end{aligned}$$

- E4.12(b)** $\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$ where $q_{\text{rev}} = -w = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{p_i}{p_f}$
- $$\text{so } \Delta S = nR \ln \frac{p_i}{p_f} = \left(\frac{35 \text{ g}}{28.013 \text{ g mol}^{-1}} \right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{21.1 \text{ atm}}{4.3 \text{ atm}} = \boxed{17 \text{ J K}^{-1}}$$

E4.13(b) $\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$ where $q_{\text{rev}} = -w = nRT \ln \frac{V_f}{V_i}$

so $\Delta S = nR \ln \frac{V_f}{V_i}$ and $V_f = V_i \exp\left(\frac{\Delta S}{nR}\right)$

We need to compute the amount of gas from the perfect gas law

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT} = \frac{(1.20 \text{ atm}) \times (11.0 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (270 \text{ K})} = 0.596 \text{ mol}$$

$$\text{So } V_f = (11.0 \text{ L}) \exp\left(\frac{-3.0 \text{ J K}^{-1}}{(0.596 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}\right) = \boxed{6.00 \text{ L}}$$

E4.14(b) Find the final temperature by equating the heat lost by the hot sample to the heat gained by the cold sample.

$$-n_1 C_{p,m} (T_f - T_{i1}) = n_2 C_{p,m} (T_f - T_{i2})$$

$$T_f = \frac{n_1 T_{i1} + n_2 T_{i2}}{n_1 + n_2} = \frac{\frac{1}{M}(m_1 T_{i1} + m_2 T_{i2})}{\frac{1}{M}(m_1 + m_2)}$$

$$= \frac{m_1 T_{i1} + m_2 T_{i2}}{m_1 + m_2}$$

$$= \frac{(25 \text{ g}) \times (323 \text{ K}) + (70 \text{ g}) \times (293 \text{ K})}{25 \text{ g} + 70 \text{ g}} = 300.9 \text{ K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = n_1 C_{p,m} \ln\left(\frac{T_f}{T_{i1}}\right) + n_2 C_{p,m} \ln\left(\frac{T_f}{T_{i2}}\right)$$

$$= \left\{ \left(\frac{25 \text{ g}}{46.07 \text{ g mol}^{-1}}\right) \ln\left(\frac{300.9}{323}\right) + \left(\frac{70 \text{ g}}{46.07 \text{ g mol}^{-1}}\right) \times \ln\left(\frac{300.9}{293}\right) \right\} C_{p,m}$$

$$= \left\{ -3.846 \times 10^{-2} + 4.043 \times 10^{-2} \right\} C_{p,m}$$

$$= (0.196 \times 10^{-2} \text{ mol}) \times (111.5 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{0.2 \text{ J K}^{-1}}$$

E4.15(b) $\Delta H_{\text{total}} = 0$ in an isolated container.

Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures

$$T_f = \frac{1}{2}(200^\circ\text{C} + 25^\circ\text{C}) = 112.5^\circ\text{C}$$

$$nC_m = mC_s \quad \text{where } C_s \text{ is the specific heat capacity}$$

$$\Delta S = mC_s \ln\left(\frac{T_f}{T_i}\right) \quad 200^\circ\text{C} = 473.2 \text{ K}; \quad 25^\circ\text{C} = 298.2 \text{ K}; \quad 112.5^\circ\text{C} = 385.7 \text{ K}$$

$$\Delta S_1 = (1.00 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{385.7}{298.2}\right) = 115.5 \text{ J K}^{-1}$$

$$\Delta S_2 = (1.00 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{385.7}{473.2}\right) = -91.802 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = \boxed{24 \text{ J K}^{-1}}$$

E4.16(b) (a) $q = 0$ [adiabatic]

(b) $w = -p_{\text{ex}}\Delta V = -(1.5 \text{ atm}) \times \left(\frac{1.01 \times 10^5 \text{ Pa}}{\text{atm}}\right) \times (100.0 \text{ cm}^2) \times (15 \text{ cm}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right)$
 $= -227.2 \text{ J} = \boxed{-230 \text{ J}}$

(c) $\Delta U = q + w = 0 - 230 \text{ J} = \boxed{-230 \text{ J}}$

(d) $\Delta U = nC_{V,m}\Delta T$

$$\Delta T = \frac{\Delta U}{nC_{V,m}} = \frac{-227.2 \text{ J}}{(1.5 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$= \boxed{-5.3 \text{ K}}$$

(e) $\Delta S = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$

$$T_f = 288.15 \text{ K} - 5.26 \text{ K} = 282.9 \text{ K}$$

$$V_i = \frac{nRT}{p_i} = \frac{(1.5 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (288.2 \text{ K})}{9.0 \text{ atm}}$$

$$= 3.942 \text{ L}$$

$$V_f = 3.942 \text{ L} + (100 \text{ cm}^2) \times (15 \text{ cm}) \times \left(\frac{1 \text{ L}}{1000 \text{ cm}^3}\right)$$

$$= 3.942 \text{ L} + 1.5 \text{ L} = 5.44 \text{ L}$$

$$\Delta S = (1.5 \text{ mol}) \times \left\{ (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{282.9}{288.2}\right) \right.$$

$$\left. + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{5.44}{3.942}\right) \right\}$$

$$= 1.5 \text{ mol}(-0.5346 \text{ J K}^{-1} \text{ mol}^{-1} + 2.678 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{3.2 \text{ J K}^{-1}}$$

E4.17(b) (a) $\Delta_{\text{vap}}S^\ominus = \frac{\Delta_{\text{vap}}H^\ominus}{T_b} = \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{(64.1 + 273.15) \text{ K}} = +104.58 \text{ J K}^{-1} = \boxed{104.6 \text{ J K}^{-1}}$

(b) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad \text{so} \quad \Delta S_{\text{sur}} = \boxed{-104.6 \text{ J K}^{-1}}$$

E4.18(b) (a) $\Delta_r S^\ominus = S_m^\ominus(\text{Zn}^{2+}, \text{aq}) + S_m^\ominus(\text{Cu}, \text{s}) - S_m^\ominus(\text{Zn}, \text{s}) - S_m^\ominus(\text{Cu}^{2+}, \text{aq})$
 $= [-112.1 + 33.15 - 41.63 + 99.6] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-21.0 \text{ J K}^{-1} \text{ mol}^{-1}}$

(b) $\Delta_r S^\ominus = 12S_m^\ominus(\text{CO}_2, \text{g}) + 11S_m^\ominus(\text{H}_2\text{O}, \text{l}) - S_m^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12S_m^\ominus(\text{O}_2, \text{g})$
 $= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)] \text{ J K}^{-1} \text{ mol}^{-1}$
 $= \boxed{+512.0 \text{ J K}^{-1} \text{ mol}^{-1}}$

E4.19(b) (a) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f H^\ominus(\text{Cu}^{2+}, \text{aq})$
 $= -153.89 - 64.77 \text{ kJ mol}^{-1} = -218.66 \text{ kJ mol}^{-1}$

$$\Delta_r G^\ominus = -218.66 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (-21.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-212.40 \text{ kJ mol}^{-1}}$$

$$\begin{aligned} \text{(b)} \quad \Delta_r H^\ominus &= \Delta_c H^\ominus = -5645 \text{ kJ mol}^{-1} \\ \Delta_r G^\ominus &= -5645 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (512.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-5798 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{E4.20(b)} \quad \text{(a)} \quad \Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f G^\ominus(\text{Cu}^{2+}, \text{aq}) \\ = -147.06 - 65.49 \text{ kJ mol}^{-1} = \boxed{-212.55 \text{ kJ mol}^{-1}}$$

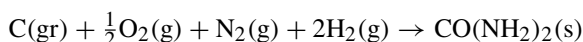
$$\text{(b)} \quad \Delta_r G^\ominus = 12\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 11\Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f G^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) \\ = [12 \times (-394.36) + 11 \times (-237.13) - (-1543)] \text{ kJ mol}^{-1} = \boxed{-5798 \text{ kJ mol}^{-1}}$$

Comment. In each case these values of $\Delta_r G^\ominus$ agree closely with the calculated values in Exercise 4.19(b).

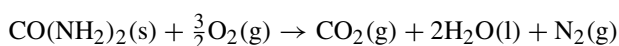


$$\begin{aligned} \Delta_r H^\ominus &= \sum v_j \Delta_f H^\ominus(\text{J}) \\ &= -484.5 \text{ kJ mol}^{-1} - (-238.66 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1}) \\ &= -135.31 \text{ kJ mol}^{-1} \\ \Delta_r S^\ominus &= \sum v_j S^\ominus(\text{J}) \\ &= 159.8 \text{ J K}^{-1} \text{ mol}^{-1} - 126.8 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -164.67 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_r G^\ominus &= \Delta_r H^\ominus - T \Delta_r S^\ominus \\ &= -135.31 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-164.67 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -135.31 \text{ kJ mol}^{-1} + 49.072 \text{ kJ mol}^{-1} = \boxed{-86.2 \text{ kJ mol}^{-1}} \end{aligned}$$

E4.22(b) The formation reaction of urea is



The combustion reaction is



$$\Delta_c H = \Delta_f H^\ominus(\text{CO}_2, \text{g}) + 2\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\ominus(\text{CO(NH}_2)_2, \text{s})$$

$$\begin{aligned} \Delta_f H^\ominus(\text{CO(NH}_2)_2, \text{s}) &= \Delta_f H^\ominus(\text{CO}_2, \text{g}) + 2\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_c H(\text{CO(NH}_2)_2, \text{s}) \\ &= -393.51 \text{ kJ mol}^{-1} + (2) \times (-285.83 \text{ kJ mol}^{-1}) - (-632 \text{ kJ mol}^{-1}) \\ &= -333.17 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S^\ominus &= S_m^\ominus(\text{CO(NH}_2)_2, \text{s}) - S_m^\ominus(\text{C}, \text{gr}) - \frac{1}{2}S_m^\ominus(\text{O}_2, \text{g}) - S_m^\ominus(\text{N}_2, \text{g}) - 2S_m^\ominus(\text{H}_2, \text{g}) \\ &= 104.60 \text{ J K}^{-1} \text{ mol}^{-1} - 5.740 \text{ J K}^{-1} \text{ mol}^{-1} - \frac{1}{2}(205.138 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - 2(130.684 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -456.687 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f H^\ominus - T \Delta_r S^\ominus \\ &= -333.17 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-456.687 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -333.17 \text{ kJ mol}^{-1} + 136.093 \text{ kJ mol}^{-1} \\ &= \boxed{-197 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{E4.23(b) (a)} \quad \Delta S(\text{gas}) = nR \ln\left(\frac{V_f}{V_i}\right) = \left(\frac{21 \text{ g}}{39.95 \text{ g mol}^{-1}}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 2$$

$$= 3.029 \text{ J K}^{-1} = \boxed{3.0 \text{ J K}^{-1}}$$

$$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = \boxed{-3.0 \text{ J K}^{-1}} \text{ [reversible]}$$

$$\Delta S(\text{total}) = \boxed{0}$$

(b) (Free expansion)

$$\Delta S(\text{gas}) = \boxed{+3.0 \text{ J K}^{-1}} \text{ [S is a state function]}$$

$$\Delta S(\text{surroundings}) = \boxed{0} \text{ [no change in surroundings]}$$

$$\Delta S(\text{total}) = \boxed{+3.0 \text{ J K}^{-1}}$$

$$\text{(c)} \quad q_{\text{rev}} = 0 \quad \text{so} \quad \Delta S(\text{gas}) = \boxed{0}$$

$$\Delta S(\text{surroundings}) = \boxed{0} \text{ [No heat is transferred to the surroundings]}$$

$$\Delta S(\text{total}) = \boxed{0}$$

E4.24(b) Because entropy is a state function, we can choose any convenient path between the initial and final states.

Choose isothermal compression followed by constant-volume heating

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) + nC_{V,m} \ln\left(\frac{T_f}{T_i}\right)$$

$$= -nR \ln 3 + nC_{V,m} \ln 3$$

$$= n(C_{V,m} - R) \ln 3 \quad C_{V,m} = \frac{5}{2}R \text{ for a diatomic perfect gas}$$

$$\boxed{\Delta S = \frac{3}{2}nR \ln 3}$$

E4.25(b) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$

$$\Delta_r G^\ominus = 3\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 4\Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f G^\ominus(\text{C}_3\text{H}_8, \text{g}) - 0$$

$$= 3(-394.36 \text{ kJ mol}^{-1}) + 4(-237.13 \text{ kJ mol}^{-1}) - 1(-23.49 \text{ kJ mol}^{-1})$$

$$= -2108.11 \text{ kJ mol}^{-1}$$

The maximum non-expansion work is $\boxed{2108.11 \text{ kJ mol}^{-1}}$ since $|w_e| = |\Delta_r G|$

$$\text{E4.26(b) (a)} \quad \varepsilon = 1 - \frac{T_c}{T_h}$$

$$= 1 - \frac{500 \text{ K}}{1000 \text{ K}} = \boxed{0.500}$$

$$\text{(b)} \quad \text{Maximum work} = \varepsilon|q_h| = (0.500) \times (1.0 \text{ kJ}) = \boxed{0.50 \text{ kJ}}$$

$$\text{(c)} \quad \varepsilon_{\text{max}} = \varepsilon_{\text{rev}} \quad \text{and} \quad |w_{\text{max}}| = |q_h| - |q_{c,\text{min}}|$$

$$|q_{c,\text{min}}| = |q_h| - |w_{\text{max}}|$$

$$= 1.0 \text{ kJ} - 0.50 \text{ kJ}$$

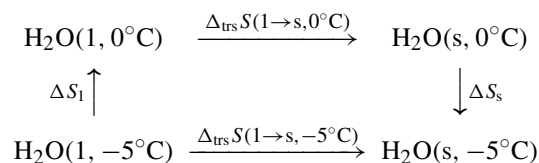
$$= \boxed{0.5 \text{ kJ}}$$

Solutions to problems

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

Solutions to numerical problems

- P4.1** (a) Because entropy is a state function $\Delta_{\text{trs}}S(l \rightarrow s, -5^\circ\text{C})$ may be determined indirectly from the following cycle



$$\Delta_{\text{trs}}S(l \rightarrow s, -5^\circ\text{C}) = \Delta S_l + \Delta_{\text{trs}}S(l \rightarrow s, 0^\circ\text{C}) + \Delta S_s$$

$$\Delta S_l = C_{p,m}(l) \ln \frac{T_f}{T} \quad [\theta_f = 0^\circ\text{C}, \theta = -5^\circ\text{C}]$$

$$\Delta S_s = C_{p,m}(s) \ln \frac{T}{T_f}$$

$$\Delta S_l + \Delta S_s = -\Delta C_p \ln \frac{T}{T_f} \quad \text{with } \Delta C_p = C_{p,m}(l) - C_{p,m}(s) = +37.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{trs}}S(l \rightarrow s, T_f) = \frac{-\Delta_{\text{fus}}H}{T_f}$$

$$\begin{aligned} \text{Thus, } \Delta_{\text{trs}}S(l \rightarrow s, T) &= \frac{-\Delta_{\text{fus}}H}{T_f} - \Delta C_p \ln \frac{T}{T_f} \\ &= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} - (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{268}{273} \\ &= \boxed{-21.3 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\Delta S_{\text{sur}} = \frac{\Delta_{\text{fus}}H(T)}{T}$$

$$\Delta_{\text{fus}}H(T) = -\Delta H_l + \Delta_{\text{fus}}H(T_f) - \Delta H_s$$

$$\Delta H_l + \Delta H_s = C_{p,m}(l)(T_f - T) + C_{p,m}(s)(T - T_f) = \Delta C_p(T_f - T)$$

$$\Delta_{\text{fus}}H(T) = \Delta_{\text{fus}}H(T_f) - \Delta C_p(T_f - T)$$

$$\begin{aligned} \text{Thus, } \Delta S_{\text{sur}} &= \frac{\Delta_{\text{fus}}H(T)}{T} = \frac{\Delta_{\text{fus}}H(T_f)}{T} + \Delta C_p \frac{(T - T_f)}{T} \\ &= \frac{6.01 \text{ kJ mol}^{-1}}{268 \text{ K}} + (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{268 - 273}{268} \right) \\ &= \boxed{+21.7 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\Delta S_{\text{total}} = (21.7 - 21.3) \text{ J K}^{-1} \text{ mol}^{-1} = +0.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since $\Delta S_{\text{total}} > 0$, the transition $l \rightarrow s$ is spontaneous at -5°C

- (b) A similar cycle and analysis can be set up for the transition liquid \rightarrow vapour at 95°C . However, since the transformation here is to the high temperature state (vapour) from the low temperature

state (liquid), which is the opposite of part (a), we can expect that the analogous equations will occur with a change of sign.

$$\begin{aligned}\Delta_{\text{trs}}S(l \rightarrow g, T) &= \Delta_{\text{trs}}S(l \rightarrow g, T_b) + \Delta C_p \ln \frac{T}{T_b} \\ &= \frac{\Delta_{\text{vap}}H}{T_b} + \Delta C_p \ln \frac{T}{T_b}, \quad \Delta C_p = -41.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{trs}}S(l \rightarrow g, T) &= \frac{40.7 \text{ kJ mol}^{-1}}{373 \text{ K}} - (41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{368}{373} \\ &= +109.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta S_{\text{sur}} &= \frac{-\Delta_{\text{vap}}H(T)}{T} = -\frac{\Delta_{\text{vap}}H(T_b)}{T} - \frac{\Delta C_p(T - T_b)}{T} \\ &= \left(\frac{-40.7 \text{ kJ mol}^{-1}}{368 \text{ K}} \right) - (-41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{368 - 373}{368} \right) \\ &= \boxed{-111.2 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

$$\Delta S_{\text{total}} = (109.7 - 111.2) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-1.5 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Since $\Delta S_{\text{total}} < 0$, the reverse transition, $g \rightarrow l$, is spontaneous at 95°C .

P4.2

$$\begin{aligned}\Delta S_m &= \int_{T_1}^{T_2} \frac{C_{p,m} dT}{T} [19] = \int_{T_1}^{T_2} \left(\frac{a + bT}{T} \right) dT = a \ln \left(\frac{T_2}{T_1} \right) + b(T_2 - T_1) \\ a &= 91.47 \text{ J K}^{-1} \text{ mol}^{-1}, \quad b = 7.5 \times 10^{-2} \text{ J K}^{-2} \text{ mol}^{-1} \\ \Delta S_m &= (91.47 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{300 \text{ K}}{273 \text{ K}} \right) + (0.075 \text{ J K}^{-2} \text{ mol}^{-1}) \times (27 \text{ K}) \\ &= 10.7 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Therefore, for 1.00 mol, $\Delta S = +11 \text{ J K}^{-1}$

P4.8

	ΔS	ΔS_{surr}	ΔH	ΔT	ΔA	ΔG
Process (a)	$+5.8 \text{ J K}^{-1}$	-5.8 J K^{-1}	0	0	-1.7 kJ	-1.7 kJ
Process (b)	$+5.8 \text{ J K}^{-1}$	-1.7 J K^{-1}	0	0	-1.7 kJ	-1.7 kJ
Process (c)	$+3.9 \text{ J K}^{-1}$	0	$-8.4 \times 10^2 \text{ J}$	-41 K	?	?

Process (a)

$$\boxed{\Delta H = \Delta T = 0} \quad [\text{isothermal process in a perfect gas}]$$

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

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) [4.17] = (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{20 \text{ L}}{10 \text{ L}} \right) = \boxed{+5.8 \text{ J K}^{-1}}$$

$$\Delta S_{\text{surr}} = -\Delta S = \boxed{-5.8 \text{ J K}^{-1}}$$

$$\Delta A = \Delta U - T \Delta S [36] \quad \Delta U = 0 \quad [\text{isothermal process in perfect gas}]$$

$$\Delta A = 0 - (298 \text{ K}) \times (5.76 \text{ J K}^{-1}) = \boxed{-1.7 \times 10^3 \text{ J}}$$

$$\Delta G = \Delta H - T \Delta S = 0 - T \Delta S = \boxed{-1.7 \times 10^3 \text{ J}}$$

Process (b)

$$\Delta H = \Delta T = 0 \quad [\text{isothermal process in perfect gas}]$$

$$\Delta S = +5.8 \text{ J K}^{-1} \quad [\text{Same as process (a); } S \text{ is a state function}]$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \quad q_{\text{surr}} = -q = -(-w) = w \quad [\text{First Law with } \Delta U = 0]$$

$$w = -p_{\text{ex}} \Delta V$$

$$= -(0.50 \text{ atm}) \times (1.01 \times 10^5 \text{ Pa atm}^{-1}) \times (20 \text{ L} - 10 \text{ L}) \times \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right) = -5.05 \times 10^2 \text{ J}$$

$$= q_{\text{surr}}$$

$$\Delta S_{\text{surr}} = \frac{-5.05 \times 10^2 \text{ J}}{298 \text{ K}} = -1.7 \text{ J K}^{-1}$$

$$\Delta A = -1.7 \times 10^3 \text{ J}$$

$$\Delta G = -1.7 \times 10^3 \text{ J} \quad [\text{same as process (a); } A \text{ and } G \text{ are state functions}]$$

Process (c)

$$\Delta U = w \quad [\text{adiabatic process}]$$

$$w = -p_{\text{ex}} \Delta V = -5.05 \times 10^2 \text{ J} \quad [\text{same as process (b)}]$$

$$\Delta U = nC_{V,m} \Delta T \quad \Delta T = \frac{\Delta U}{nC_{V,m}} = \frac{-5.05 \times 10^2 \text{ J}}{(1.00 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})} = -40.6 \text{ K}$$

$$T_f = T_i - 40.6 \text{ K} = 298 \text{ K} - 40.6 \text{ K} = 257 \text{ K}$$

$$\Delta S = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) [20] + nR \ln\left(\frac{V_f}{V_i}\right) [17]$$

$$= (1.00 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{257 \text{ K}}{298 \text{ K}}\right) + (1.00 \text{ mol}) \\ \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{20 \text{ L}}{10 \text{ L}}\right) = +3.9 \text{ J K}^{-1}$$

$$\Delta S_{\text{surr}} = 0 \quad [\text{adiabatic process}]$$

ΔA and ΔG cannot be determined from the information provided without use of additional relations developed in Chapters 5 and 19.

$$\Delta H = nC_{p,m} \Delta T \quad C_{p,m} = C_{V,m} + R = \frac{5}{2} R$$

$$= (1.00 \text{ mol}) \times \left(\frac{5}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-40.6 \text{ K}) = -8.4 \times 10^2 \text{ J}$$

P4.9

$$S_{\text{m}}^{\ominus}(T) = S_{\text{m}}^{\ominus}(298 \text{ K}) + \Delta S$$

$$\Delta S = \int_{T_1}^{T_2} C_{p,m} \frac{dT}{T} = \int_{T_1}^{T_2} \left(\frac{a}{T} + b + \frac{c}{T^3} \right) dT = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) - \frac{1}{2} c \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right)$$

$$\begin{aligned}
 \text{(a)} \quad S_{\text{m}}^{\ominus}(373 \text{ K}) &= (192.45 \text{ J K}^{-1} \text{ mol}^{-1}) + (29.75 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{373}{298}\right) \\
 &\quad + (25.10 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}) \times (75.0 \text{ K}) \\
 &\quad + \left(\frac{1}{2}\right) \times (1.55 \times 10^5 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{(373.15)^2} - \frac{1}{(298.15)^2}\right) \\
 &= \boxed{200.7 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad S_{\text{m}}^{\ominus}(773 \text{ K}) &= (192.45 \text{ J K}^{-1} \text{ mol}^{-1}) + (29.75 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{773}{298}\right) \\
 &\quad + (25.10 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}) \times (475 \text{ K}) \\
 &\quad + \left(\frac{1}{2}\right) \times (1.55 \times 10^5 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{773^2} - \frac{1}{298^2}\right) \\
 &= \boxed{232.0 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

P4.10 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,m} \ln \frac{T_f}{T_i}$ [4.20]

$$\text{Since } q = nC_{p,m}(T_f - T_i), T_f = T_i + \frac{q}{nC_{p,m}} = T_i + \frac{I^2 R t}{nC_{p,m}} \quad (q = ItV = I^2 R t)$$

$$\text{That is, } \Delta S = nC_{p,m} \ln\left(1 + \frac{I^2 R t}{nC_{p,m} T_i}\right)$$

$$\text{Since } n = \frac{500 \text{ g}}{63.5 \text{ g mol}^{-1}} = 7.87 \text{ mol}$$

$$\begin{aligned}
 \Delta S &= (7.87 \text{ mol}) \times (24.4 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(1 + \frac{(1.00 \text{ A})^2 \times (1000 \Omega) \times (15.0 \text{ s})}{(7.87) \times (24.4 \text{ J K}^{-1}) \times (293 \text{ K})}\right) \\
 &= (192 \text{ J K}^{-1}) \times (\ln 1.27) = \boxed{+45.4 \text{ J K}^{-1}}
 \end{aligned}$$

For the second experiment, no change in state occurs for the copper; hence, $\Delta S(\text{copper}) = 0$. However, for the water, considered as a large heat sink

$$\Delta S(\text{water}) = \frac{q}{T} = \frac{I^2 R t}{T} = \frac{(1.00 \text{ A})^2 \times (1000 \Omega) \times (15.0 \text{ s})}{293 \text{ K}} = \boxed{+51.2 \text{ J K}^{-1}}$$

$$[1 \text{ J} = 1 \text{ A V s} = 1 \text{ A}^2 \Omega \text{ s}]$$

P4.12 (a) Calculate the final temperature as in Exercise 4.14(a)

$$T_f = \frac{n_1 T_{i1} + n_2 T_{i2}}{n_1 + n_2} = \frac{1}{2}(T_{i1} + T_{i2}) = 318 \text{ K} \quad [n_1 = n_2]$$

$$\begin{aligned}
 \Delta S &= n_1 C_{p,m} \ln \frac{T_f}{T_{i1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i2}} = n_1 C_{p,m} \ln \frac{T_f^2}{T_{i1} T_{i2}} \quad [n_1 = n_2] \\
 &= \left(\frac{200 \text{ g}}{18.02 \text{ g mol}^{-1}}\right) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{318^2}{273 \times 363}\right) = \boxed{+17.0 \text{ J K}^{-1}}
 \end{aligned}$$

(b) Heat required for melting is

$$n_1 \Delta_{\text{fus}} H = (11.1 \text{ mol}) \times (6.01 \text{ kJ mol}^{-1}) = 66.7 \text{ kJ}$$

The decrease in temperature of the hot water as a result of heat transfer to the ice is

$$\Delta T = \frac{q}{nC_{p,m}} = \frac{66.7 \text{ kJ}}{(11.1 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1})} = 79.8 \text{ K}$$

At this stage the system consists of 200 g water at 0°C and 200 g water at $(90^\circ\text{C} - 79.8^\circ\text{C}) = 10^\circ\text{C}$ (283 K). The entropy change so far is therefore

$$\begin{aligned} \Delta S &= \frac{n\Delta H_{\text{fus}}}{T_f} + nC_{p,m} \ln \frac{283 \text{ K}}{363 \text{ K}} \\ &= \left(\frac{(11.1 \text{ mol}) \times (6.01 \text{ kJ mol}^{-1})}{273 \text{ K}} \right) + (11.1 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{283 \text{ K}}{363 \text{ K}} \right) \\ &= 244 \text{ J K}^{-1} - 208.1 \text{ J K}^{-1} = +35.3 \text{ J K}^{-1} \end{aligned}$$

The final temperature is $T_f = \frac{1}{2}(273 \text{ K} + 283 \text{ K}) = 278 \text{ K}$, and the entropy change in this step is

$$\Delta S = nC_{p,m} \ln \frac{T_f^2}{T_{i1}T_{i2}} = (11.1) \times (75.3 \text{ J K}^{-1}) \times \ln \left(\frac{278^2}{273 \times 283} \right) = +0.27 \text{ J K}^{-1}$$

Therefore, overall, $\Delta S = 35.3 \text{ J K}^{-1} + 0.27 \text{ J K}^{-1} = \boxed{+36 \text{ J K}^{-1}}$

P4.15

$$\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J) \quad [2.41]$$

$$\begin{aligned} \Delta_r H^\ominus(298 \text{ K}) &= 1 \times \Delta_f H^\ominus(\text{CO}, \text{g}) + 1 \times \Delta_f H^\ominus(\text{H}_2\text{O}, \text{g}) - 1 \times \Delta_f H^\ominus(\text{CO}_2, \text{g}) \\ &= \{-110.53 - 241.82 - (-393.51)\} \text{ kJ mol}^{-1} = \boxed{+41.16 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J) \quad [4.22]$$

$$\begin{aligned} \Delta_r S^\ominus(298 \text{ K}) &= 1 \times S_m^\ominus(\text{CO}, \text{g}) + 1 \times S_m^\ominus(\text{H}_2\text{O}, \text{g}) - 1 \times S_m^\ominus(\text{CO}_2, \text{g}) - 1 \times S_m^\ominus(\text{H}_2, \text{g}) \\ &= (197.67 + 188.83 - 213.74 - 130.684) \text{ kJ mol}^{-1} = \boxed{+42.08 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\Delta_r H^\ominus(398 \text{ K}) = \Delta_r H^\ominus(298 \text{ K}) + \int_{298 \text{ K}}^{398 \text{ K}} \Delta_r C_p \, dT \quad [2.44]$$

$$= \Delta_r H^\ominus(298 \text{ K}) + \Delta_r C_p \Delta T \quad [\text{heat capacities constant}]$$

$$\begin{aligned} \Delta_r C_p &= 1 \times C_{p,m}(\text{CO}, \text{g}) + 1 \times C_{p,m}(\text{H}_2\text{O}, \text{g}) - 1 \times C_{p,m}(\text{CO}_2, \text{g}) - 1 \times C_{p,m}(\text{H}_2, \text{g}) \\ &= (29.14 + 33.58 - 37.11 - 28.824) \text{ J K}^{-1} \text{ mol}^{-1} = -3.21 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta_r H^\ominus(398 \text{ K}) = (41.16 \text{ kJ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}) = \boxed{+40.84 \text{ kJ mol}^{-1}}$$

For each substance in the reaction

$$\Delta S = C_{p,m} \ln \left(\frac{T_f}{T_i} \right) = C_{p,m} \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \quad [4.20]$$

Thus

$$\begin{aligned}\Delta_r S^\ominus(398\text{ K}) &= \Delta_r S^\ominus(298\text{ K}) + \sum_{\text{J}} \nu_{\text{J}} C_{p,m}(\text{J}) \ln\left(\frac{T_f}{T_i}\right) \\ &= \Delta_r S^\ominus(298\text{ K}) + \Delta_r C_p \ln\left(\frac{398\text{ K}}{298\text{ K}}\right) \\ &= (42.01\text{ J K}^{-1}\text{ mol}^{-1}) + (-3.21\text{ J K}^{-1}\text{ mol}^{-1}) = (42.01 - 0.93)\text{ J K}^{-1}\text{ mol}^{-1} \\ &= \boxed{+41.08\text{ J K}^{-1}\text{ mol}^{-1}}\end{aligned}$$

Comment. Both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ changed little over 100 K for this reaction. This is not an uncommon result.

P4.17

$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m} dT}{T} \quad [4.19]$$

Perform a graphical integration by plotting $C_{p,m}/T$ against T and determining the area under the curve.

Draw up the following table

T/K	10	20	30	40	50	60	70	80
$(C_{p,m}/T)/(\text{J K}^{-1}\text{ mol}^{-1})$	0.209	0.722	1.215	1.564	1.741	1.850	1.877	1.868

T/K	90	100	110	120	130	140	150	160
$(C_{p,m}/T)/(\text{J K}^{-1}\text{ mol}^{-1})$	1.837	1.796	1.753	1.708	1.665	1.624	1.584	1.546

T/K	170	180	190	200
$(C_{p,m}/T)/(\text{J K}^{-1}\text{ mol}^{-1})$	1.508	1.473	1.437	1.403

Plot $C_{p,m}/T$ against T (Fig. 4.2(a)). Extrapolate to $T = 0$ using $C_{p,m} = aT^3$ fitted to the point at $T = 10\text{ K}$, which gives $a = 2.09\text{ mJ K}^{-2}\text{ mol}^{-1}$. Determine the area under the graph up to each T and plot S_m against T (Fig. 4.2(b)).

T/K	25	50	75	100	125	150	175	200
$\{S_m^\ominus - S_m^\ominus(0)\}/(\text{J K}^{-1}\text{ mol}^{-1})$	9.25	43.50	88.50	135.00	178.25	219.0	257.3	293.5

The molar enthalpy is determined in a similar manner from a plot of $C_{p,m}$ against T by determining the area under the curve (Fig. 4.3)

$$H_m^\ominus(200\text{ K}) - H_m^\ominus(0) = \int_0^{200\text{ K}} C_{p,m} dT = \boxed{32.00\text{ kJ mol}^{-1}}$$

Solutions to theoretical problems

P4.20

Refer to Fig. 4.5 of the text for a description of the Carnot cycle and the heat terms accompanying each step of the cycle. Labelling the steps (a), (b), (c), and (d) going clockwise around the cycle starting from state A, the four episodes of heat transfer are

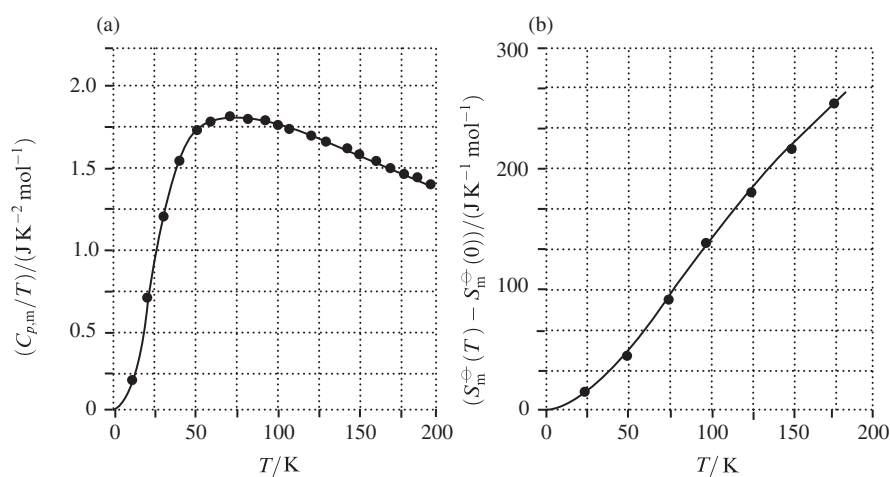


Figure 4.2

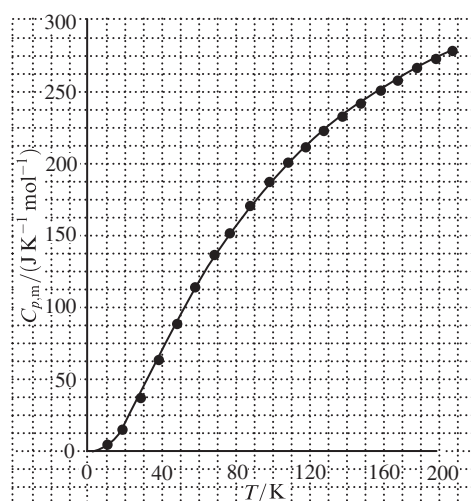


Figure 4.3

$$(a) \quad q_h = nRT_h \ln \frac{V_B}{V_A} \quad \frac{q_h}{T_h} = nR \ln \frac{V_B}{V_A}$$

$$(b) \quad 0 \text{ [adiabatic]}$$

$$(c) \quad q_c = nRT_c \ln \frac{V_D}{V_C} \quad \frac{q_c}{T_c} = nR \ln \frac{V_D}{V_C}$$

$$(d) \quad 0 \text{ [adiabatic]}$$

$$\text{Therefore } \oint \frac{dq}{T} = \frac{q_h}{T_h} + \frac{q_c}{T_c} = nR \ln \frac{V_B V_D}{V_A V_C}$$

$$\text{However, } \frac{V_B V_D}{V_A V_C} = \frac{V_B V_D}{V_C V_A} = \left(\frac{T_c}{T_h}\right)^c \times \left(\frac{T_h}{T_c}\right)^c \text{ [2.34 of Section 2.6]} = 1$$

$$\text{Therefore } \oint \frac{dq}{T} = 0$$

If the first stage is replaced by isothermal, irreversible expansion against a constant external pressure, $q = -w = p_{\text{ex}}(V_B - V_A)$ ($\Delta U = 0$, since this is an isothermal process in a perfect gas)

Therefore, $\frac{q_h}{T_h} = \left(\frac{p_{\text{ex}}}{T_h}\right) \times (V_B - V_A)$

However, $p_{\text{ex}}(V_B - V_A) < nRT_h \ln \frac{V_B}{V_A}$ because less work is done in the irreversible expansion, so

$$\oint \frac{dq}{T} < nR \ln \frac{V_B}{V_A} + nR \ln \frac{V_D}{V_C} = 0. \quad \text{That is, } \oint \frac{dq}{T} < 0$$

Comment. Whenever an irreversible step is included in the cycle the above result will be obtained.

Question. Can you provide a general proof of this result?

P4.22

The isotherms correspond to $T = \text{constant}$, and the reversibly traversed adiabats correspond to $S = \text{constant}$. Thus we can represent the cycle as in Fig. 4.4.

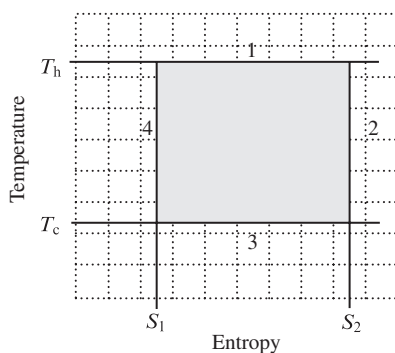


Figure 4.4

In this figure, paths 1, 2, 3, and 4 correspond to the four stages of the Carnot cycle listed in the text following eqn 4.7

The area within the rectangle is

$$\text{Area} = \oint T dS = (T_h - T_c) \times (S_2 - S_1) = (T_h - T_c) \Delta S = (T_h - T_c) nR \ln \frac{V_B}{V_A}$$

(isothermal expansion from V_A to V_B , stage 1)

$$\text{But, } w(\text{cycle}) = \varepsilon q_h = \left(\frac{T_h - T_c}{T_h}\right) nRT_h \ln \frac{V_B}{V_A} \quad [\text{Fig. 4.5}] = nR(T_h - T_c) \ln \frac{V_B}{V_A}$$

Therefore, the area is equal to the net work done in the cycle.

P4.23

$$\Delta S = \left[nC_{p,m} \ln \frac{T_f}{T_h} + nC_{p,m} \ln \frac{T_f}{T_c} \right] \quad [4.20] \quad [T_f \text{ is the final temperature, } T_f = \frac{1}{2}(T_h + T_c)]$$

In the present case, $T_f = \frac{1}{2}(500 \text{ K} + 250 \text{ K}) = 375 \text{ K}$

$$\begin{aligned} \Delta S &= nC_{p,m} \ln \frac{T_f^2}{T_h T_c} = nC_{p,m} \ln \frac{(T_h + T_c)^2}{4T_h T_c} = \left(\frac{500 \text{ g}}{63.54 \text{ g mL}^{-1}} \right) \times (24.4 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times \ln \left(\frac{375^2}{500 \times 250} \right) = \boxed{+22.6 \text{ J K}^{-1}} \end{aligned}$$

P4.26

$$g = f + yz$$

$$dg = df + y dz + z dy = a dx - z dy + y dz + z dy = a dx + y dz$$

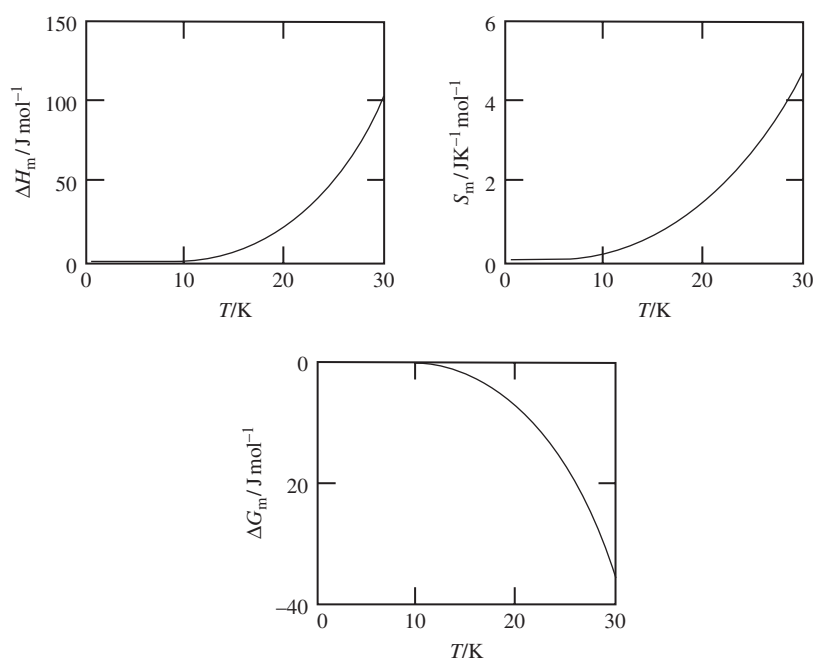
Comment. This procedure is referred to as a Legendre transformation and is essentially the method used in Chapter 5 to express the differentials of H , G , and A in terms of the differential of U .

P4.27 (a) According to eqns 2.43, 4.19, and 4.39:

$$\Delta H_m(T) = H_m(T) - H_m(0) = \int_{0\text{K}}^{30\text{K}} C_p(T) dT \quad \text{where } C_p(T) = aT^3 (1 - e^{-\beta/T^2})$$

$$S_m(T) = \int_{0\text{K}}^{30\text{K}} \frac{C_p(T)}{T} dT \quad \text{and} \quad \Delta G_m(T) = G_m(T) - G_m(0) = \Delta H_m(T) - T S_m(T)$$

The integral computations are easily performed with the built-in numerical integration capabilities of a scientific calculator or computer software spreadsheet. Computations at ten or more equally spaced temperatures between 0 K and 30 K will produce smooth-looking plots.



(b) According to the law of Dulong and Petit the constant pressure heat capacity of $\text{Ce}_2\text{Si}_2\text{O}_7$ (11 moles of atoms per mole of compound) is approximately equal to $11 \times 3 \times R = 274 \text{ J K}^{-1} \text{ mol}^{-1}$. The experimental value at 900 K equals $287 \text{ J K}^{-1} \text{ mol}^{-1}$. The law of Dulong and Petit gives a reasonable estimate of the heat capacity at very high temperature.

Solutions to applications

P4.29

(a) $\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{sec-C}_4\text{H}_9) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9)$$

$$= (67.5 - 51.3) \text{ kJ mol}^{-1} = 16.2 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta_r S^\ominus &= S_m^\ominus(\text{sec-C}_4\text{H}_9) - S_m^\ominus(\text{tert-C}_4\text{H}_9) \\ &= (336.6 - 314.6) \text{ J K}^{-1} \text{ mol}^{-1} = 22.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_r G^\ominus &= 16.2 \text{ kJ mol}^{-1} - (700 \text{ K}) \times (22.0 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{0.8 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{C}_3\text{H}_6) + \Delta_f H^\ominus(\text{CH}_3) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) \\ \Delta_r H^\ominus &= (20.42 + 145.49 - 51.3) \text{ kJ mol}^{-1} = 114.6 \text{ kJ mol}^{-1} \\ \Delta_r S^\ominus &= (267.05 + 194.2 - 314.6) \text{ J K}^{-1} \text{ mol}^{-1} = 146.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_r G^\ominus &= 114.6 \text{ kJ mol}^{-1} - (700 \text{ K}) \times (0.1467 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{11.9 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(c)} \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{C}_2\text{H}_4) + \Delta_f H^\ominus(\text{C}_2\text{H}_5) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) \\ \Delta_r H^\ominus &= (52.26 + 121.0 - 51.3) \text{ kJ mol}^{-1} = 122.0 \text{ kJ mol}^{-1} \\ \Delta_r S^\ominus &= (219.56 + 247.8 - 314.6) \text{ J K}^{-1} \text{ mol}^{-1} = 152.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_r G^\ominus &= 122.0 \text{ kJ mol}^{-1} - (700 \text{ K}) \times (0.1528 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{15.0 \text{ kJ mol}^{-1}}\end{aligned}$$

P4.32

The minimum power output that is needed to maintain the temperature difference $T_h - T_c$ occurs when $dp/dT_c = 0$

$$\begin{aligned}p &= \frac{d|w|}{dt} = \frac{d}{dt} (|q_h| - |q_c|) \quad [9-11] \\ &= \frac{d}{dt} \left(|q_c| \left\{ \frac{|q_h|}{|q_c|} - 1 \right\} \right) = \frac{d}{dt} \left(|q_c| \left\{ \frac{T_h}{T_c} - 1 \right\} \right) \\ &= \left(\frac{T_h}{T_c} - 1 \right) \frac{d|q_c|}{dt} = \left(\frac{T_h}{T_c} - 1 \right) kAT_c^4\end{aligned}$$

At constant T_h

$$\frac{dp}{dT_c} = \left(-\frac{T_h}{T_c^2} \right) (kAT_c^4) + 4kAT_c^3 \left(\frac{T_h}{T_c} - 1 \right)$$

This is a minimum when equal to zero. Simplifying yields

$$-\frac{T_h}{T_c} + 4 \left(\frac{T_h}{T_c} - 1 \right) = 0$$

$$\frac{T_h}{T_c} = \boxed{\frac{4}{3}}$$