

Problem Set #6 solution, Chem 340, Fall 2013

– Due Friday, Oct 11, 2013

Please show all work for credit

To hand in:

Atkins

Chap 3 –Exercises: 3.3(b), 3.8(b), 3.13(b), 3.15(b)

Problems: 3.1, 3.12, 3.36, 3.43

Engel

Chap. 5: P5.14, P5.19, P5.20, P5.33

Extras :

Atkins

Chap 3 –Exercises: 3.4(b), 3.7 (b), 3.14(b)

Problems: 3.3, 3.7, 3.10, 3.11, 3.42, 3.45

To hand in :

Atkins

Exercises:

3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = 7/2 R$, is changed from 25° C and 1.50 atm to 135° C and 7.00 atm. How do you rationalize the sign of ΔS ?

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

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

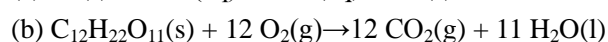
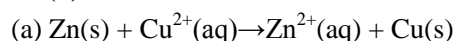
$$\text{where } q_{\text{rev}} = -w = \int p dV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{p_i}{p_f}$$

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

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

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 $\Delta S_{\text{total}} > 0$.

3.8(b) Calculate the standard reaction entropy at 298 K of



$$\begin{aligned} \text{(a)} \quad \Delta_r S^\ominus &= S_m^\ominus(\text{Zn}^{2+}, \text{aq}) + S_m^\ominus(\text{Cu}, \text{s}) - S_m^\ominus(\text{Zn}, \text{s}) - S_m^\ominus(\text{Cu}^{2+}, \text{aq}) \\ &= [-112.1 + 33.15 - 41.63 + 99.6] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-21.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

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

3.13(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm³ to 4.60 dm³ in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

$$\begin{aligned} \text{(a)} \quad \Delta S(\text{gas}) &= nR \ln \left(\frac{V_f}{V_i} \right) [3.13] = \left(\frac{21 \text{ g}}{39.95 \text{ g mol}^{-1}} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 2 \\ &= 3.029 \text{ J K}^{-1} = \boxed{3.0 \text{ J K}^{-1}} \end{aligned}$$

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

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

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

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

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

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

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

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

3.15(b) A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

$$\text{(a)} \quad \eta = 1 - T_c/T_h [\text{eqn 3.10}] = 1 - 500\text{K}/1000\text{K} = 0.500$$

$$\text{(b)} \quad \text{Maximum work} = \eta |q_h| = 0.500 \times 1.0 \text{ kJ} = 0.5 \text{ kJ}$$

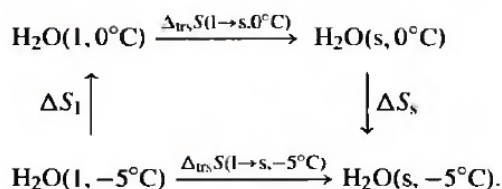
$$\text{(c)} \quad \eta_{\text{max}} = \eta_{\text{rev}} \quad \text{and} \quad |w_{\text{max}}| = |q_h| - |q_{c,\text{min}}|$$

$$|q_{c,\text{min}}| = |q_h| - |w_{\text{max}}| = 1.0 \text{ kJ} - 0.5 \text{ kJ} = 0.5 \text{ kJ}$$

Problems:

3.1 Calculate the difference in molar entropy (a) between liquid water and ice at -5°C , (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are $37.3\text{ J K}^{-1}\text{ mol}^{-1}$ and $-41.9\text{ J K}^{-1}\text{ mol}^{-1}$, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures. **Confusing since flip $T_f/T \rightarrow T/T_f$, later flip ΔT**

(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



Thus $\Delta_{\text{trs}}S(l \rightarrow s, -5^\circ\text{C}) = \Delta S_1 + \Delta_{\text{trs}}S(l \rightarrow s, 0^\circ\text{C}) + \Delta S_s$,

where $\Delta S_1 = C_{p,m}(l) \ln \frac{T_f}{T}$ [3.19; $\theta_f = 0^\circ\text{C}$, $\theta = -5^\circ\text{C}$]

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

$$\Delta S_1 + \Delta S_s = -\Delta C_p \ln \frac{T}{T_f} \quad \text{with } \Delta C_p = C_{p,m}(l) - C_{p,m}(s) = +37.3\text{ J K}^{-1}\text{ mol}^{-1}.$$

$$\Delta_{\text{trs}}S(l \rightarrow s, T_f) = \frac{-\Delta_{\text{fus}}H}{T_f} \quad [3.16].$$

Thus, $\Delta_{\text{trs}}S(l \rightarrow s, T) = \frac{-\Delta_{\text{fus}}H}{T_f} - \Delta C_p \ln \frac{T}{T_f}$.

$$\begin{aligned} \Delta_{\text{trs}}S(l \rightarrow s, 5^\circ\text{C}) &= \frac{-6.01 \times 10^3\text{ J mol}^{-1}}{273\text{ K}} - (37.3\text{ J K}^{-1}\text{ mol}^{-1}) \times \ln \frac{268}{273} \\ &= \boxed{-21.3\text{ J K}^{-1}\text{ mol}^{-1}}. \end{aligned}$$

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

$$\Delta_{\text{fus}}H(T) = -\Delta H_1 + \Delta_{\text{fus}}H(T_f) - \Delta H_s.$$

$$\Delta H_1 + \Delta H_s = C_{p,m}(l)(T_f - T) + C_{p,m}(s)(T - T_f) = \Delta C_p(T_f - T).$$

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

Thus, $\Delta S_{\text{sur}} = \frac{\Delta_{\text{fus}}H(T)}{T} = \frac{\Delta_{\text{fus}}H(T_f)}{T} + \Delta C_p \frac{(T - T_f)}{T}$.

$$\begin{aligned} \Delta S_{\text{sur}} &= \frac{6.01\text{ kJ mol}^{-1}}{268\text{ K}} + (37.3\text{ J K}^{-1}\text{ mol}^{-1}) \times \left(\frac{268 - 273}{268} \right) \\ &= \boxed{+21.7\text{ J K}^{-1}\text{ mol}^{-1}}. \end{aligned}$$

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

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 vapor at 95°C . However, since the transformation here is to the high temperature state (vapor) 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.

$$\begin{aligned}\Delta_{\text{trs}}S(1 \rightarrow g, T) &= \Delta_{\text{trs}}S(1 \rightarrow g, T_b) + \Delta C_p \ln \frac{T}{T_b} \\ &= \frac{\Delta_{\text{vap}}H}{T_b} + \Delta C_p \ln \frac{T}{T_b}, \quad \Delta C_p = -41.9 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\Delta_{\text{trs}}S(1 \rightarrow g, T) &= \frac{40.7 \text{ kJ mol}^{-1}}{373 \text{ K}} - (41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{368}{373} \right) \\ &= \boxed{+109.7 \text{ J K}^{-1} \text{ mol}^{-1}}.\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{sur}} &= \frac{-\Delta_{\text{vap}}H(T)}{T} = -\frac{\Delta_{\text{vap}}H(T_b)}{T} - \frac{\Delta C_p(T - T_b)}{T} \\ &= \left(\frac{-40.7 \text{ kJ mol}^{-1}}{368 \text{ K}} \right) - (-41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{368 - 373}{368} \right) \\ &= \boxed{-111.2 \text{ J K}^{-1} \text{ mol}^{-1}}.\end{aligned}$$

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

Since $\Delta S_{\text{total}} < 0$, the reverse transition, $g \rightarrow 1$, is spontaneous at 95°C .

3.12 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. Assume that the heat capacities are constant over the temperature range involved.

$$\Delta_r H^\circ = \sum_{\text{products}} \nu \Delta_f H^\circ - \sum_{\text{reactants}} \nu \Delta_f H^\circ \quad [2.34\text{a}]$$

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

$$\Delta_r S^\circ = \sum_{\text{products}} \nu S_m^\circ - \sum_{\text{reactants}} \nu S_m^\circ \quad [3.25\text{a}]$$

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

$$\Delta_r H^\circ(398 \text{ K}) = \Delta_r H^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{398 \text{ K}} \Delta_r C_p^\circ dT \quad [2.36\text{a}]$$

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

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

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

For each substance in the reaction

$$\Delta S_m = C_{p,m} \ln\left(\frac{T_f}{T_i}\right) = C_{p,m} \ln\left(\frac{398 \text{ K}}{298 \text{ K}}\right) \quad [3.23]$$

Thus,

$$\begin{aligned} \Delta_r S^\circ(398 \text{ K}) &= \Delta_r S^\circ(298 \text{ K}) + \sum_{\text{products}} \nu C_{p,m}^\circ \ln\left(\frac{T_f}{T_i}\right) - \sum_{\text{reactants}} \nu C_{p,m}^\circ \ln\left(\frac{T_f}{T_i}\right) \\ &= \Delta_r S^\circ(298 \text{ K}) + \Delta_r C_p^\circ \ln\left(\frac{398 \text{ K}}{298 \text{ K}}\right) \\ &= (42.08 \text{ J K}^{-1} \text{ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{398 \text{ K}}{298 \text{ K}}\right) \\ &= (42.08 - 0.93) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+41.15 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

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

3.36 The protein lysozyme unfolds at a transition temperature of 75.5°C and the standard enthalpy of transition is 509 kJ mol^{-1} . Calculate the entropy of unfolding of lysozyme at 25.0°C , given that the difference in the constant-pressure heat capacities upon unfolding is $6.28\text{ kJ K}^{-1}\text{ mol}^{-1}$ and can be assumed to be independent of temperature. *Hint.* Imagine that the transition at 25.0°C occurs in three steps: (i) heating of the folded protein from 25.0°C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0°C . Because the entropy is a state function, the entropy change at 25.0°C is equal to the sum of the entropy changes of the steps.

Taking the hint, we have

$$\Delta_{\text{trs}}S^\circ(25^\circ\text{C}) = \Delta S_{\text{i}} + \Delta S_{\text{ii}} + \Delta S_{\text{iii}}$$

We are not given the heat capacity of either the folded or unfolded protein, but if we let $C_{p,m}$ be the heat capacity of the folded protein, the heat capacity of the unfolded protein is $C_{p,m} + 6.28\text{ kJ K}^{-1}\text{ mol}^{-1}$. So, for the heating and cooling steps, we have:

$$\Delta S_{\text{i}} = C_p \ln\left(\frac{T_f}{T_i}\right) = C_{p,m} \ln\left(\frac{348.7\text{ K}}{298.2\text{ K}}\right) \quad [3.23]$$

and $\Delta S_{\text{iii}} = (C_{p,m} + 6.28\text{ kJ K}^{-1}\text{ mol}^{-1}) \ln\left(\frac{298.2\text{ K}}{348.7\text{ K}}\right)$, so

$$\begin{aligned} \Delta S_{\text{i}} + \Delta S_{\text{iii}} &= C_{p,m} \ln\left(\frac{348.7\text{ K}}{298.2\text{ K}}\right) + (C_{p,m} + 6.28\text{ kJ K}^{-1}\text{ mol}^{-1}) \ln\left(\frac{298.2\text{ K}}{348.7\text{ K}}\right) \\ &= (6.28\text{ kJ K}^{-1}\text{ mol}^{-1}) \ln\left(\frac{298.2\text{ K}}{348.7\text{ K}}\right) = -0.983\text{ kJ K}^{-1}\text{ mol}^{-1} \end{aligned}$$

For the transition itself, use Trouton's rule (eqn 3.20):

$$\Delta S_{\text{ii}} = \frac{\Delta_{\text{trs}}H^\circ}{T_{\text{trs}}} = \frac{509\text{ kJ mol}^{-1}}{348.2\text{ K}} = 1.46\bar{0}\text{ kJ K}^{-1}\text{ mol}^{-1}$$

Hence, $\Delta_{\text{trs}}S^\circ = (1.46\bar{0} - 0.983)\text{ kJ K}^{-1}\text{ mol}^{-1} = 0.47\bar{7}\text{ kJ K}^{-1}\text{ mol}^{-1} = \boxed{47\bar{7}\text{ J K}^{-1}\text{ mol}^{-1}}$

3.43 The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A, $V = 4.00 \text{ dm}^3$, $p = 1.00 \text{ atm}$, and $T = 300 \text{ K}$, that $V_A = 10V_B$, $p_C/p_B = 5$, and that $C_{p,m} = 7/2 R$.

The Otto cycle is represented in Fig. 3.5. Assume one mole of air.

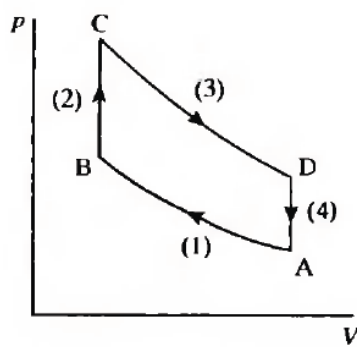


Figure 3.5

$$\varepsilon = \frac{|w|_{\text{cycle}}}{|q_2|} \quad [3.8].$$

$$w_{\text{cycle}} = w_1 + w_3 = \Delta U_1 + \Delta U_3 \quad [q_1 = q_3 = 0] = C_V(T_B - T_A) + C_V(T_D - T_C) \quad [2.27].$$

$$q_2 = \Delta U_2 = C_V(T_C - T_B).$$

$$\varepsilon = \frac{|T_B - T_A + T_D - T_C|}{|T_C - T_B|} = 1 - \left(\frac{T_D - T_A}{T_C - T_B} \right).$$

We know that

$$\frac{T_A}{T_B} = \left(\frac{V_B}{V_A} \right)^{1/c} \quad \text{and} \quad \frac{T_D}{T_C} = \left(\frac{V_C}{V_D} \right)^{1/c} \quad [2.28a].$$

Since $V_B = V_C$ and $V_A = V_D$, $\frac{T_A}{T_B} = \frac{T_D}{T_C}$, or $T_D = \frac{T_A T_C}{T_B}$.

$$\text{Then } \varepsilon = 1 - \frac{\frac{T_A T_C}{T_B} - T_A}{T_C - T_B} = 1 - \frac{T_A}{T_B} \quad \text{or} \quad \boxed{\varepsilon = 1 - \left(\frac{V_B}{V_A} \right)^{1/c}}.$$

Given that $C_{p,m} = \frac{7}{2}R$, we have $C_{v,m} = \frac{5}{2}R$ [2.26] and $c = \frac{2}{5}$.

$$\text{For } \frac{V_A}{V_B} = 10, \quad \varepsilon = 1 - \left(\frac{1}{10}\right)^{2/5} = \boxed{0.47}.$$

$$\Delta S_1 = \Delta S_3 = \Delta S_{\text{sur},1} = \Delta S_{\text{sur},3} = \boxed{0} \quad [\text{adiabatic reversible steps}].$$

$$\Delta S_2 = C_{v,m} \ln \left(\frac{T_C}{T_B}\right).$$

$$\text{At constant volume } \left(\frac{T_C}{T_B}\right) = \left(\frac{p_C}{p_B}\right) = 5.0.$$

$$\Delta S_2 = \left(\frac{5}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (\ln 5.0) = \boxed{+33 \text{ J K}^{-1}}.$$

$$\Delta S_{\text{sur},2} = -\Delta S_2 = \boxed{-33 \text{ J K}^{-1}}.$$

$$\Delta S_4 = -\Delta S_2 \left[\frac{T_C}{T_D} = \frac{T_B}{T_A}\right] = \boxed{-33 \text{ J K}^{-1}}.$$

$$\Delta S_{\text{sur},4} = -\Delta S_4 = \boxed{+33 \text{ J K}^{-1}}.$$

Engel

P5.14 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 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 500°C .

b. Calculate ΔH for the transformation $\text{Pb}(s, 25^\circ\text{C}) \rightarrow \text{Pb}(l, 500^\circ\text{C})$.

a)

$$\begin{aligned} S_m^\circ(\text{Pb},l,773 \text{ K}) &= S_m^\circ(\text{Pb},s,298.15 \text{ K}) + \int_{298.15 \text{ K}}^{600.55 \text{ K}} \frac{C_{p,m}}{[\text{T/K}]} d[\text{T/K}] + \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} + \int_{600.55 \text{ K}}^{773.15 \text{ K}} \frac{C_{p,m}}{[\text{T/K}]} d[\text{T/K}] \\ &= \int_{298.15 \text{ K}}^{600.55 \text{ K}} \frac{(22.13) + (0.01172)[\text{T/K}] + (1.00 \times 10^{-5})[\text{T}^2/\text{K}^2]}{[\text{T/K}]} d[\text{T/K}] + \frac{(4770 \text{ J mol}^{-1})}{(600.55 \text{ K})} \\ &+ \int_{600.55 \text{ K}}^{773.15 \text{ K}} \frac{(32.51) - (0.00301)[\text{T/K}]}{[\text{T/K}]} d[\text{T/K}] \\ &= (64.80 \text{ J mol}^{-1} \text{ K}^{-1}) + (20.40 \text{ J mol}^{-1} \text{ K}^{-1}) + (7.94 \text{ J mol}^{-1} \text{ K}^{-1}) + (7.69 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= \underline{100.8 \text{ J mol}^{-1} \text{ K}^{-1}} \end{aligned}$$

b)

$$\begin{aligned} \Delta H_{\text{total}} &= \int_{298.15 \text{ K}}^{600.55 \text{ K}} C_{p,m}^{\text{solid}} d[\text{T/K}] + \Delta H_{\text{fusion}} + \int_{600.55 \text{ K}}^{773.15 \text{ K}} C_{p,m}^{\text{liquid}} d[\text{T/K}] \\ &= (8918 \text{ J mol}^{-1}) + (4770 \text{ J mol}^{-1}) + (5254 \text{ J mol}^{-1}) \\ &= \underline{18.94 \times 10^3 \text{ J mol}^{-1}} \end{aligned}$$

P5.19) Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$. Thermodynamic data at $T = 298\text{ K}$ for glucose and lactic acid are given here:

	ΔH_f° (kJ mol ⁻¹)	C_p° (J K ⁻¹ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
Glucose	-1273.1	219.2	209.2
Lactic acid	-673.6	127.6	192.1

Calculate the entropy of the system, the surroundings, and the universe at $T = 310\text{ K}$. Assume the heat capacities are constant between $T = 298\text{ K}$ and $T = 330\text{ K}$.

The standard entropy and enthalpy and heat capacity for this reaction are: *note: here $C_{p,rxn}^\circ = \Delta C_p^\circ$*

$$\Delta S_{\text{reaction}}^\circ(298\text{ K}) = \sum_i \nu_i S_{f,i}^\circ = 2 \times (192.1\text{ J K}^{-1}\text{ mol}^{-1}) + (-1) \times (209.2\text{ J K}^{-1}\text{ mol}^{-1}) = 175.0\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta H_{\text{reaction}}^\circ(298\text{ K}) = \sum_i \nu_i H_{f,i}^\circ = (2) \times (-673.6\text{ kJ mol}^{-1}) + (-1) \times (-1273.1\text{ kJ mol}^{-1}) = -74.1\text{ kJ mol}^{-1}$$

$$C_{p,\text{reaction}}^\circ(298\text{ K}) = (2) \times (127.6\text{ J K}^{-1}\text{ mol}^{-1}) + (-1) \times (219.2\text{ J K}^{-1}\text{ mol}^{-1}) = 36.0\text{ J K}^{-1}\text{ mol}^{-1}$$

At 310 K the entropy and enthalpy for this reaction are then:

$$\begin{aligned} \Delta S_{\text{reaction}}^\circ(310\text{ K}) &= \Delta S_{\text{reaction}}^\circ(298\text{ K}) + C_{p,\text{reaction}}^\circ \ln\left(\frac{T_f}{T_i}\right) \\ &= (175.0\text{ J K}^{-1}\text{ mol}^{-1}) + (36.0\text{ J K}^{-1}\text{ mol}^{-1}) \times \ln\left(\frac{310\text{ K}}{298.15\text{ K}}\right) = \underline{176.4\text{ J K}^{-1}\text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ(310\text{ K}) &= \Delta H_{\text{reaction}}^\circ(298\text{ K}) + C_{\text{reaction}}^\circ (T_f - T_i) \\ &= (-74.1\text{ kJ mol}^{-1}) + (36.0\text{ J K}^{-1}\text{ mol}^{-1}) \times (310\text{ K} - 298.15\text{ K}) = \underline{-73.7\text{ kJ mol}^{-1}} \end{aligned}$$

And the entropies for the surroundings and universe:

$$\Delta S_{\text{surroundings}} = \frac{-dq}{T} = \frac{-\Delta H_{\text{reaction}}^\circ}{T} = \frac{(73.7\text{ kJ mol}^{-1})}{(310\text{ K})} = \underline{237.7\text{ J mol}^{-1}\text{ K}^{-1}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{reaction}} + \Delta S_{\text{surroundings}} = (176.4\text{ J K}^{-1}\text{ mol}^{-1}) + (237.7\text{ J mol}^{-1}\text{ K}^{-1}) = \underline{414.1\text{ J mol}^{-1}\text{ K}^{-1}}$$

P5.20) Consider the formation of glucose from carbon dioxide and water, that is, the reaction of the following photosynthetic process: $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$. The following table of information will be useful in working this problem:

$T = 298 \text{ K}$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	$\text{O}_2(\text{g})$
$\Delta H_f^\circ \text{ kJ mol}^{-1}$	-393.5	-285.8	-1273.1	0.0
$S^\circ \text{ J mol}^{-1} \text{ K}^{-1}$	213.8	70.0	209.2	205.2
$C_{P,m}^\circ \text{ J mol}^{-1} \text{ K}^{-1}$	37.1	75.3	219.2	29.4

Calculate the entropy and enthalpy changes for this chemical system at $T = 298 \text{ K}$ and $T = 330. \text{ K}$. Calculate also the entropy of the surrounding and the universe at both temperatures.

The standard entropy and enthalpy and heat capacity for this reaction are:

$$\begin{aligned} \Delta S_{\text{reaction}}^\circ (298 \text{ K}) &= \sum_i \nu_i S_{f,i}^\circ \\ &= (1) \times (209.2 \text{ J K}^{-1} \text{ mol}^{-1}) + (6) \times (205.2 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &+ (-6) \times (70.0 \text{ J K}^{-1} \text{ mol}^{-1}) + (-6) \times (213.8 \text{ J K}^{-1} \text{ mol}^{-1}) = -262.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ (298 \text{ K}) &= \sum_i \nu_i H_{f,i}^\circ \\ &= (1) \times (-1273.1 \text{ kJ mol}^{-1}) + (6) \times (0 \text{ kJ mol}^{-1}) \\ &+ (-6) \times (-285.8 \text{ kJ mol}^{-1}) + (-6) \times (-393.5 \text{ kJ mol}^{-1}) \\ &= 2802.7 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} C_{p,\text{reaction}}^\circ (298 \text{ K}) &= (1) \times (219.2 \text{ J K}^{-1} \text{ mol}^{-1}) + (6) \times (29.4 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &+ (-6) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) + (-6) \times (37.1 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -278.8 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

At 310 K the entropy and enthalpy for this reaction are then:

$$\begin{aligned} \Delta S_{\text{reaction}}^\circ (310 \text{ K}) &= \Delta S_{\text{reaction}}^\circ (298 \text{ K}) + C_{p,\text{reaction}}^\circ \ln \left(\frac{T_f}{T_i} \right) \\ &= (-262.4 \text{ J K}^{-1} \text{ mol}^{-1}) + (-278.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{330 \text{ K}}{298.15 \text{ K}} \right) = \underline{-290.7 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ (310 \text{ K}) &= \Delta H_{\text{reaction}}^\circ (298 \text{ K}) + C_{\text{reaction}}^\circ (T_f - T_i) \\ &= (2802.7 \text{ kJ mol}^{-1}) + (-278.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times (330 \text{ K} - 298.15 \text{ K}) = \underline{2793.8 \text{ kJ mol}^{-1}} \end{aligned}$$

And the entropies for the surroundings and universe:

$$\Delta S_{\text{surroundings}} = \frac{-dq}{T} = \frac{-\Delta H_{\text{reaction}}^\circ}{T} = \frac{(-2793.8 \text{ kJ mol}^{-1})}{(330 \text{ K})} = \underline{-8.47 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}}$$

$$\begin{aligned} \Delta S_{\text{universe}} &= \Delta S_{\text{reaction}} + \Delta S_{\text{surroundings}} = (-290.47 \text{ J K}^{-1} \text{ mol}^{-1}) + (-8.47 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= \underline{-8.76 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}} \end{aligned}$$

P5.33) 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 20°C, what mass of ice can be produced in 1 min by a 0.25-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.

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

$$= \frac{(273 \text{ K})}{(293 \text{ K} - 273 \text{ K})} \times (0.25 \text{ hp}) \times (746 \text{ W hp}^{-1}) = 2546 \text{ J s}^{-1}$$

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

$$\frac{q/t}{\Delta H_{\text{fusion}}} t M_{\text{ice}} = \frac{(2546 \text{ J s}^{-1})}{(6008 \text{ J mol}^{-1})} \times (60 \text{ s min}^{-1}) \times (18.02 \text{ g mol}^{-1}) = \underline{4.5 \times 10^2 \text{ g min}^{-1}}$$

Extras :

Atkins

Exercises:

3.4(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS . – *note: this is an unusual C_V looks like C_P , but do problem as written anyway*

$$q = q_{\text{rev}} = 0 \text{ [adiabatic reversible process]}$$

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

$$\Delta U = nC_{V,m}\Delta T = (2.00 \text{ mol}) \times (27.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 - 250) \text{ K}$$

$$= 2750 \text{ J} = \boxed{+2.75 \text{ kJ}}$$

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

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

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

$$\text{So } \Delta H = (2.00 \text{ mol}) \times (35.814 \text{ J K}^{-1} \text{ mol}^{-1}) \times (+50 \text{ K}) = 3581.4 \text{ J} = \boxed{3.58 \text{ kJ}}$$

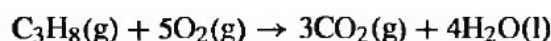
3.7(b) The enthalpy of vaporization of methanol is $35.27 \text{ kJ mol}^{-1}$ at its normal boiling point of 64.1° C . Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

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

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

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

3.14(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K. (*for next week!*)



$$\begin{aligned} \Delta_{\text{r}}G^{\ominus} &= 3\Delta_{\text{f}}G^{\ominus}(\text{CO}_2, \text{g}) + 4\Delta_{\text{f}}G^{\ominus}(\text{H}_2\text{O}, \text{l}) - \Delta_{\text{f}}G^{\ominus}(\text{C}_3\text{H}_8, \text{g}) - 0 \\ &= 3(-394.36 \text{ kJ mol}^{-1}) + 4(-237.13 \text{ kJ mol}^{-1}) - 1(-23.49 \text{ kJ mol}^{-1}) \\ &= -2108.11 \text{ kJ mol}^{-1} \end{aligned}$$

The maximum non-expansion work is $\boxed{2108.11 \text{ kJ mol}^{-1}}$ since $|w_{\text{add}}| = |\Delta G|$.

Problems:

3.3 A block of copper of mass 2.00 kg ($C_{p,m} = 24.44 \text{ J K}^{-1} \text{ mol}^{-1}$) and temperature 0° C is introduced into an insulated container in which there is 1.00 mol $\text{H}_2\text{O}(\text{g})$ at 100° C and 1.00 atm.

(a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapor is present at equilibrium. From the vapor pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies.

(*Hint.* You will need to make plausible approximations.)

$$\text{(a)} \quad q(\text{total}) = q(\text{H}_2\text{O}) + q(\text{Cu}) = 0; \text{ hence } -q(\text{H}_2\text{O}) = q(\text{Cu}).$$

$$q(\text{H}_2\text{O}) = n(-\Delta_{\text{vap}}H) + nC_{p,m}(\text{H}_2\text{O}, \text{l}) \times (\theta - 100^\circ \text{C})$$

where θ is the final temperature of the water and copper.

$$q(\text{Cu}) = mC_s(\theta - 0) = mC_s\theta, \quad C_s = 0.385 \text{ J K}^{-1} \text{ g}^{-1}.$$

Setting $-q(\text{H}_2\text{O}) = q(\text{Cu})$ allows us to solve for θ .

$$n(\Delta_{\text{vap}}H) - nC_{p,m}(\text{H}_2\text{O}, \text{l}) \times (\theta - 100^\circ \text{C}) = mC_s\theta$$

Solving for θ yields:

$$\begin{aligned}\theta &= \frac{n\{\Delta_{\text{vap}}H + C_{p,m}(\text{H}_2\text{O}, \text{i}) \times 100^\circ\text{C}\}}{mC_s + nC_{p,m}(\text{H}_2\text{O}, \text{l})} \\ &= \frac{(1.00 \text{ mol}) \times (40.656 \times 10^3 \text{ J mol}^{-1} + 75.3 \text{ J}^\circ\text{C}^{-1}\text{mol}^{-1} \times 100^\circ\text{C})}{2.00 \times 10^3 \text{ g} \times 0.385 \text{ J}^\circ\text{C}^{-1}\text{g}^{-1} + 1.00 \text{ mol} \times 75.3 \text{ J}^\circ\text{C}^{-1}\text{mol}^{-1}} \\ &= 57.0^\circ\text{C} = 330.2 \text{ K}.\end{aligned}$$

$$q(\text{Cu}) = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times (57.0 \text{ K}) = 4.39 \times 10^4 \text{ J} = \boxed{43.9 \text{ kJ}},$$

$$q(\text{H}_2\text{O}) = \boxed{-43.9 \text{ kJ}}.$$

$$\Delta S(\text{total}) = \Delta S(\text{H}_2\text{O}) + \Delta S(\text{Cu}).$$

$$\begin{aligned}\Delta S(\text{H}_2\text{O}) &= \frac{-n\Delta_{\text{vap}}H}{T_b} [3.16] + nC_{p,m} \ln\left(\frac{T_f}{T_i}\right) [3.19] \\ &= -\frac{(1.00 \text{ mol}) \times (40.656 \times 10^3 \text{ J mol}^{-1})}{373.2 \text{ K}} \\ &\quad + (1.00 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{330.2 \text{ K}}{373.2 \text{ K}}\right) \\ &= -108.9 \text{ J K}^{-1} - 9.22 \text{ J K}^{-1} = \boxed{-118.1 \text{ J K}^{-1}}.\end{aligned}$$

$$\begin{aligned}\Delta S(\text{Cu}) &= mC_s \ln\frac{T_f}{T_i} = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{330.2 \text{ K}}{273.2 \text{ K}}\right) \\ &= \boxed{145.9 \text{ J K}^{-1}}.\end{aligned}$$

$$\Delta S(\text{total}) = -118.1 \text{ J K}^{-1} + 145.9 \text{ J K}^{-1} = \boxed{28 \text{ J K}^{-1}}.$$

This process is spontaneous since $\Delta S(\text{surroundings})$ is zero and, hence,

$$\Delta S(\text{universe}) = \Delta S(\text{total}) > 0.$$

(b) The volume of the container may be calculated from the perfect gas law.

$$V = \frac{nRT}{p} = \frac{(1.00 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (373.2 \text{ K})}{1.00 \text{ atm}} = 30.6 \text{ dm}^3$$

At 57°C the vapor pressure of water is 130 Torr (*Handbook of Chemistry and Physics*). The amount of water vapor present at equilibrium is then

$$n = \frac{pV}{RT} = \frac{(130 \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}}\right) \times (30.6 \text{ dm}^3)}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (330.2 \text{ K})} = 0.193 \text{ mol}.$$

This is a substantial fraction of the original amount of water and cannot be ignored. Consequently the calculation needs to be redone taking into account the fact that only a part, n_1 , of the vapor condenses

into a liquid while the remainder ($1.00 \text{ mol} - n_1$) remains gaseous. The heat flow involving water, then, becomes

$$q(\text{H}_2\text{O}) = -n_1 \Delta_{\text{vap}}H + n_1 C_{p,m}(\text{H}_2\text{O}, \text{l}) \Delta T(\text{H}_2\text{O}) \\ + (1.00 \text{ mol} - n_1) C_{p,m}(\text{H}_2\text{O}, \text{g}) \Delta T(\text{H}_2\text{O}).$$

Because n_1 depends on the equilibrium temperature through $n_1 = 1.00 \text{ mol} - \frac{pV}{RT}$, where p is the vapor pressure of water, we will have two unknowns (p and T) in the equation $-q(\text{H}_2\text{O}) = q(\text{Cu})$. There are two ways out of this dilemma: (1) p may be expressed as a function of T by use of the Clapeyron equation (Chapter 4), or (2) by use of successive approximations. Redoing the calculation yields:

$$\theta = \frac{n_1 \Delta_{\text{vap}}H + n_1 C_{p,m}(\text{H}_2\text{O}, \text{l}) \times 100^\circ\text{C} + (1.00 - n_1) C_{p,m}(\text{H}_2\text{O}, \text{g}) \times 100^\circ\text{C}}{mC_s + nC_{p,m}(\text{H}_2\text{O}, \text{l}) + (1.00 - n_1) C_{p,m}(\text{H}_2\text{O}, \text{g})}.$$

With

$$n_1 = (1.00 \text{ mol}) - (0.193 \text{ mol}) = 0.807 \text{ mol}$$

(noting that $C_{p,m}(\text{H}_2\text{O}, \text{g}) = 33.6 \text{ J mol}^{-1} \text{ K}^{-1}$ [Table 2.7]), $\theta = 47.2^\circ\text{C}$. At this temperature, the vapor pressure of water is 80.41 Torr, corresponding to

$$n_1 = (1.00 \text{ mol}) - (0.123 \text{ mol}) = 0.877 \text{ mol}.$$

This leads to $\theta = 50.8^\circ\text{C}$. The successive approximations eventually converge to yield a value of $\theta = 49.9^\circ\text{C} = 323.1 \text{ K}$ for the final temperature. (At this temperature, the vapor pressure is 0.123 bar.) Using this value of the final temperature, the heat transferred and the various entropies are calculated as in part (a).

$$q(\text{Cu}) = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(\text{H}_2\text{O}).$$

$$\Delta S(\text{H}_2\text{O}) = \frac{-n \Delta_{\text{vap}}H}{T_b} + n C_{p,m} \ln \left(\frac{T_f}{T_i} \right) = -119.8 \text{ J K}^{-1}.$$

$$\Delta S(\text{Cu}) = m C_s \ln \frac{T_f}{T_i} = 129.2 \text{ J K}^{-1}.$$

$$\Delta S(\text{total}) = -119.8 \text{ J K}^{-1} + 129.2 \text{ J K}^{-1} = 9 \text{ J K}^{-1}.$$

3.7 The standard molar entropy of $\text{NH}_3(\text{g})$ is $192.45 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K, and its heat capacity is given by eqn 2.25 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100° C and (b) 500° C .

equation 2.25 and Table 2.2:

Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + c/T^2$

	a	$b/(10^{-3} \text{ K})$	$c/(10^5 \text{ K}^2)$
C(s, graphite)	16.86	4.77	-8.54
$\text{CO}_2(\text{g})$	44.22	8.79	-8.62
$\text{H}_2\text{O}(\text{l})$	75.29	0	0
$\text{N}_2(\text{g})$	28.58	3.77	-0.50

* More values are given in the *Data section*.

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

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

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

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

3.10 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1 + Bp)$. Initially at 373 K, it undergoes Joule - Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = 5/2 R$, $\mu = 0.21 \text{ K atm}^{-1}$, $B = -0.525(\text{K}/T) \text{ atm}^{-1}$, and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

Consider the temperature as a function of pressure and enthalpy: $T = T(p, H)$

$$\text{so } dT = \left(\frac{\partial T}{\partial p} \right)_H dp + \left(\frac{\partial T}{\partial H} \right)_p dH$$

The Joule-Thomson expansion is a constant-enthalpy process (Section 2.12). Hence,

$$dT = \left(\frac{\partial T}{\partial p} \right)_H dp = \mu dp$$

$$\begin{aligned} \Delta T &= \int_{p_i}^{p_f} \mu dp = \mu \Delta p \quad [\mu \text{ is constant}] \\ &= (0.21 \text{ K atm}^{-1}) \times (1.00 \text{ atm} - 100 \text{ atm}) \\ &= \boxed{-21 \text{ K}} \end{aligned}$$

$$T_f = T_i + \Delta T = (373 - 21) \text{ K} = 352 \text{ K} \quad [\text{Mean } T = 363 \text{ K}]$$

Consider the entropy as a function of temperature and pressure: $S = S(T, p)$.

$$\text{Therefore, } dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp$$

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad [\text{Table 3.5}]$$

$$\text{For } V_m = \frac{RT}{p}(1 + Bp)$$

$$\left(\frac{\partial V_m}{\partial T} \right)_p = \frac{R}{p}(1 + Bp)$$

$$\text{Then, } dS_m = \frac{C_{p,m}}{T} dT - \frac{R}{p}(1 + Bp) dp$$

$$\text{or } dS_m = \frac{C_{p,m}}{T} dT - \frac{R}{p} dp - RB dp$$

On integration

$$\begin{aligned} \Delta S_m &= \int_1^2 dS_m = C_{p,m} \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right) - RB(p_2 - p_1) \\ &= \frac{5}{2} R \ln \left(\frac{352}{373} \right) - R \ln \left(\frac{1}{100} \right) - R \left(-\frac{0.525 \text{ atm}^{-1}}{363} \right) \times (-99 \text{ atm}) \\ &= \boxed{+35.9 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

3.11 The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
$C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4
T/K	70	100	150	200	250	298
$C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0°C and (b) 25°C .

$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m} dT}{T} \quad [3.18].$$

From the data, draw up the following table.

T/K	10	15	20	25	30	50
$\frac{C_{p,m}}{T}/(\text{J K}^{-2} \text{mol}^{-1})$	0.28	0.47	0.540	0.564	0.550	0.428
T/K	70	100	150	200	250	298
$\frac{C_{p,m}}{T}/(\text{J K}^{-2} \text{mol}^{-1})$	0.333	0.245	0.169	0.129	0.105	0.089

Plot $C_{p,m}/T$ against T (Fig. 3.1). This has been done on two scales. The region 0 to 10 K has been constructed using $C_{p,m} = aT^3$, fitted to the point at $T = 10 \text{ K}$, at which $C_{p,m} = 2.8 \text{ J K}^{-1} \text{ mol}^{-1}$, so $a = 2.8 \times 10^{-3} \text{ J K}^{-4} \text{ mol}^{-1}$. The area can be determined (primitively) by counting squares. Area A = $38.28 \text{ J K}^{-1} \text{ mol}^{-1}$.

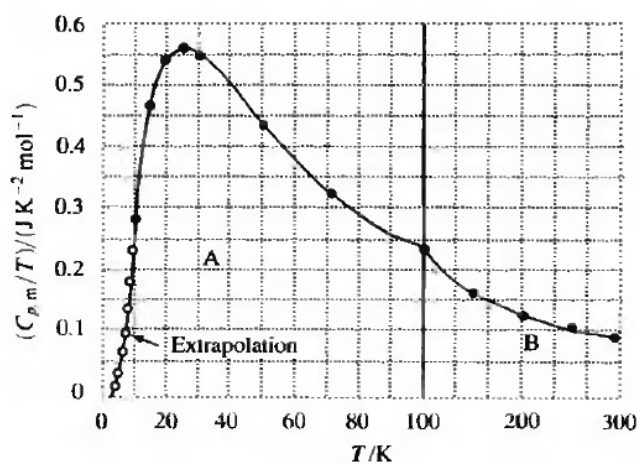


Figure 3.1

Area B up to $0^\circ \text{C} = 25.60 \text{ J K}^{-1} \text{ mol}^{-1}$; area B up to $25^\circ \text{C} = 27.80 \text{ J K}^{-1} \text{ mol}^{-1}$. Hence

(a) $S_m(273 \text{ K}) = S_m(0) + \boxed{63.88 \text{ J K}^{-1} \text{ mol}^{-1}}$,

(b) $S_m(298 \text{ K}) = S_m(0) + \boxed{66.08 \text{ J K}^{-1} \text{ mol}^{-1}}$.

3.42 Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is $-5512 \text{ kJ mol}^{-1}$ and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000° C and the exit temperature is 800° C ?

In effect, we are asked to compute the maximum work extractable from a gallon of octane, assuming that the internal combustion engine is a reversible heat engine operating between the specified temperatures, and to equate that quantity of energy with gravitational potential energy of a 1000-kg mass. The efficiency is

$$\eta = \frac{|w|}{|q_h|} [3.8] = \frac{|w|}{|\Delta H|} = \eta_{\text{rev}} = 1 - \frac{T_c}{T_h} [3.10], \quad \text{so } |w| = |\Delta H| \left(1 - \frac{T_c}{T_h} \right)$$

$$|\Delta H| = 5512 \times 10^3 \text{ J mol}^{-1} \times 1.00 \text{ gal} \times \frac{3.00 \times 10^3 \text{ g}}{1 \text{ gal}} \times \frac{1 \text{ mol}}{114.23 \text{ g}} = 1.44\bar{8} \times 10^8 \text{ J}$$

$$\text{so } |w| = 1.44\bar{8} \times 10^8 \text{ J} \times \left(1 - \frac{1073 \text{ K}}{2273 \text{ K}} \right) = 7.64\bar{2} \times 10^7 \text{ J}$$

If this work is converted completely to potential energy, it could lift a 1000-kg object to a height h given by $|w| = mgh$, so

$$h = \frac{|w|}{mg} = \frac{7.64\bar{2} \times 10^7 \text{ J}}{(1000 \text{ kg})(9.81 \text{ m s}^{-2})} = 7.79 \times 10^3 \text{ m} = \boxed{7.79 \text{ km}}$$

3.45 The expressions that apply to the treatment of refrigerators also describe the behavior of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.

In case (a), the electric heater converts 1.00 kJ of electrical energy into heat, providing $\boxed{1.00 \text{ kJ}}$ of energy as heat to the room. (The Second Law places no restriction on the complete conversion of work to heat—only on the reverse process.) In case (b), we want to find the heat deposited in the room $|q_h|$:

$$|q_h| = |q_c| + |w| \quad \text{where} \quad \frac{|q_c|}{|w|} = c = \frac{T_c}{T_h - T_c} \text{ [Impact 13.1]}$$

$$\text{so } |q_c| = \frac{|w|T_c}{T_h - T_c} = \frac{1.00 \text{ kJ} \times 260 \text{ K}}{(295 - 260)\text{K}} = 7.4 \text{ kJ.}$$

The heat transferred to the room is $|q_h| = |q_c| + |w| = 7.4 \text{ kJ} + 1.00 \text{ kJ} = \boxed{8.4 \text{ kJ}}$. Most of the thermal energy the heat pump deposits into the room comes from outdoors. Difficult as it is to believe on a cold winter day, the intensity of thermal energy (that is, the absolute temperature) outdoors is a substantial fraction of that indoors. The work put into the heat pump is not simply converted to heat, but is 'leveraged' to transfer additional heat from outdoors.