PROBLEMS

Problem 6.1. Explain in words your understanding of the difference between phenomenological thermodynamics and statistical thermodynamics.

Problem 6.2. Show, by listing all of the macrostates, that the number of macrostates possible for a system composed of ten particles that may occupy three energy levels is 60.

Problem 6.3. Consider a system with two particles a and b that may each exhibit any of four energy levels, $\epsilon_1$, $\epsilon_2$, $\epsilon_3$, and $\epsilon_4$.
   a. How many microstates might this system exhibit?
   b. Enumerate its microstates.
   c. Use the list of microstates to generate a list of macrostates for this system.
   d. Identify the microstates corresponding to each macrostate.

Problem 6.4. Calculate the number of microstates corresponding to each of the following combinations:
   a. A system with three particles and four energy levels.
   b. A system with 15 particles and four energy levels.
   c. A system with four particles and 15 energy levels.
   d. A cluster of 50 particles each of which may reside in any of 30 energy levels.
   e. 1000 particles that may reside in 100 energy levels.

Problem 6.5. Consider a model in which the available energy levels are linearly spaced along the energy axis:

$$\epsilon_n = \left(n + \frac{1}{2}\right)\epsilon_0 \quad (n = 0, 1, 2, \ldots, 9)$$
The system contains ten particles. Consider two macrostates:

\[ \{0, 0, 1, 2, 4, 2, 1, 0, 0, 0\} \ldots \text{State I} \]
\[ \{0, 1, 1, 2, 2, 1, 0, 1, 0, 0\} \ldots \text{State II} \]

a. Which macrostate has the higher energy?
b. Which macrostate has the higher entropy?
c. Which macrostate is more likely to be observed?

**Problem 6.6.** Compute the factorials of the following numbers: 10; 30; 60,
   a. Directly.
   b. Using Stirling's approximation.
   c. In each case, compute the error in \( \ln n! \) that results from the approximation.

**Problem 6.7.** A system containing 500 particles and 15 energy levels is in the following macrostate:

\[ \{14, 18, 27, 38, 51, 78, 67, 54, 32, 27, 23, 20, 19, 17, 15\} \]

This system experiences a process in which the number of particles in each energy level changes by the following amounts:

\[ \{0, 0, -1, -1, -2, 0, +1, +1, +2, +2, +1, 0, -1, -1, -1\} \]

Estimate the change in entropy for this process.

**Problem 6.8.** Using a convenient computer applications package, calculate and
Answers:

**Problem 6.3**
(a) \(4^4 = 16\) microstates
(b) Enumerate systematically. There are 10 macrostates

**Problem 6.4**
(a) \(4^3 = 64\)
(b) \(4^{15} = 1.074 \times 10^9\)
(c) \(15^4 = 50,625\)
(d) \(30^{20} = 7.18 \times 10^{73}\)
(e) \(100^{1000} = (10^2)^{1000} = 10^{2000}\)

**Problem 6.5**
(a) \(\Delta U = 0\) (J/mol)
(b) \(\Omega_\|/\Omega_\perp = 12\)
(c) State II is more likely

**Problem 6.6**
(a) Calculator:
\[10! = 3.629 \times 10^6, 30! = 2.653 \times 10^{32}, 60! = 8.321 \times 10^{81}\]
(b) Stirling’s Formula: \(4.54 \times 10^5, 1.927 \times 10^{31}, 4.28 \times 10^{80}\)
(c) Errors in \(\ln x!\): 0.138, 0.035, 0.016

**Problem 6.7**
\[\Delta S = -13.05\text{ (J/mol K)} = -2.17 \times 10^{-23}\text{ (J/atom K)}\] (Applying Equation 6.9)
Problem 7.6. A relatively useful and simple integrated form of the Clausius–Clapeyron equation is obtained (Equation 7.39) if the temperature dependence of the heat of vaporization is neglected. Estimate the temperature interval over which this assumption is valid for a typical element such as nickel.

Problem 7.7. At 1 atm pressure, pure water ice melts at 0°C. At 10 atm, the melting point is found to be −0.08°C. The density of water at 0°C is 1.000 g/cc, while that of ice is 0.917 g/cc. From this information, estimate the entropy of fusion of ice.

Problem 7.8. Estimate the melting point of the HCP (c) phase form of pure titanium at 1 atm pressure. Note that c is metastable above 1155 K at 1 atm.

Problem 7.9. At 1 atm pressure pure germanium, melts at 1232 K and boils at 2980 K. The pressure at the triple point (S,L,G) is $8.4 \times 10^{-8}$ atm. Estimate the heat of vaporization of germanium.

Problem 7.10. Assuming that the pressure dependence of the transformation temperatures may be neglected below 1 atm, calculate the pressures at the triple points (α, γ, L), (γ, δ, G) and (δ, L, G) for pure iron. Assume also that all heats of transformation are temperature independent.

Problem 7.11. Thallium exists in the following forms: vapor (V), liquid (L), face centered cubic (α), body centered cubic (β) and hexagonal (δ). Estimate and plot a phase diagram for thallium from the following information:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>ΔH (J/mole)</th>
<th>ΔS (J/mole K)</th>
<th>ΔV (cc/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L → V</td>
<td>152,000</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>β → L</td>
<td>4300</td>
<td>7.4</td>
<td>0.39</td>
</tr>
<tr>
<td>δ → β</td>
<td>380</td>
<td>0.75</td>
<td>−0.02</td>
</tr>
<tr>
<td>α → δ</td>
<td>−320</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>α → β</td>
<td>60</td>
<td>0.92</td>
<td>0.08</td>
</tr>
</tbody>
</table>

At 1 atm the stable phase forms are:
- α (0–500 K); β (500–576 K); L (576–1730 K); above 1730 K (vapor). (The FCC α form is stable only at low temperatures and high pressures.)
1. List all of the possible two phase equilibria that could exist in this system.
2. Compute and plot the unary phase diagram for thallium in the range from $10^{-15}$ to 1 atm and from 300 to 2000 K. For the part of the diagram above 1 atm plot (T, P) axes. Below 1 atm plot the axes as $(-1/T, \log P)$.
Assume $Δc_p = 0$ for all transformations. Consider only the following equilibria: (α + β), (α + δ), (β + δ), (β + L), (δ + V), (δ + V) and (L + V); the others are metastable.
Answers:

**Problem 7.6**
The error in log $P$ is about 1.5% at the melting point (over a range of about 1500 K)

**Problem 7.7**
$\Delta S = 18.6 \, (J/mol \, K)$

**Problem 7.8**
$T^{eL} = 1710 \, K$

**Problem 7.9**
$\Delta H_v = 269,000 \, (J/mol)$

**Problem 7.10**

\[ P_{\text{ayG}} = 2.6 \times 10^{-10} \, (\text{atm}); \quad P_{\text{hyG}} = 9.0 \times 10^{-6} \, (\text{atm}); \quad P_{\text{h}LG} = 7.0 \times 10^{-5} \, (\text{atm}) \]

**Problem 7.11**

\[ (T, P)_{\text{y}LG} = (576 \, K, 6.38 \times 10^{-10} \, (\text{atm})); \quad (T, P)_{\text{h}LG} = (500 \, K, 4.47 \times 10^{-12} \, \text{atm}) \]
Chapter 8

**Problem 8.2.** Review the consequences of the definition of partial molal properties that make it a convenient measure of the contribution of each component to the total value of the thermodynamic properties of a solution.

**Problem 8.3.** Given that the volume change on mixing of a solution obeys the relation

\[ \Delta V_{\text{mix}} = 2.7X_1X_2^2 \left( \frac{\text{cc}}{\text{mol}} \right) \]

a. Derive expressions for the partial molal volumes of each of the components as functions of composition.

b. Demonstrate that your result is correct by using it to compute \( \Delta V_{\text{mix}} \), demonstrating that the equation above is recovered.

**Problem 8.4.** Use the partial molal volumes computed in Problem 8.3 to demonstrate that the Gibbs–Duhem equation holds for these properties in this system.

**Problem 8.5.** In the system Pandemonium (Pn)–Condominium (Cn), the partial molal heat of mixing of Pandemonium may be fitted by the expression

\[ \Delta H_{\text{Pn}} = 12.500X_{Pn}^2X_{Cn} \left( \frac{\text{J}}{\text{mol}} \right) \]

Calculate and plot the function that describes the variation of the heat of mixing with composition for this system.

**Problem 8.6.** For an ideal solution it is known that, for component 2,

\[ \Delta G_2 = RT \ln X_2 \]

Use the Gibbs–Duhem integration to derive corresponding relation for component 1.

**Problem 8.7.** Recall the definitional relationship for the enthalpy function:

\[ H' = U' + PV' \]

Use the partial molal operator and the definition of the properties of the pure components to derive the analogous relationship,

\[ \Delta H_k = \Delta U_k + P\Delta V_k \]
Problem 8.8. The excess free energy of mixing in face-centered cubic solid solutions of aluminum and zinc is well described by the relation:

$$\Delta G_{mix}^e = X_{Al}X_{Zn}(9600X_{Zn} + 13200X_{Al})\left(1 - \frac{T}{4000}\right)$$

Compute and plot curves for $\Delta G_{mix}$ as a function of composition for a sequence of temperatures ranging from 300 to 700 K.

Problem 8.9. Using the relation given in Problem 8.8, calculate and plot the activity of Zn in an FCC solid solution of these elements at 500K.

Problem 8.10. The excess Gibbs free energy of mixing of the system A–B is given

$$\Delta G_{mix}^e = a(1 - bT)(1 - cP)X_A X_B$$

where $a = 12,500 \text{ (J/mol)}$, $b = 2 \times 10^{-4} \text{ K}^{-1}$ and $c = 7 \times 10^{-5} \text{ (atm)}^{-1}$.

a. Derive expressions for all of the mixing properties for this system.

b. Use these relations to evaluate all of the properties of the solution at 100 atm pressure, 550 K and a composition $X_B = 0.35$.

Problem 8.11. Criticize the following reported finding: “The system A–B forms a regular solution at high temperatures with the heat of mixing found to obey the relation,

$$\Delta H_{mix} = -14,500X_A X_B \left(1 - \frac{350}{T}\right)$$

Problem 8.12. Given that Henry’s law holds for the solute in a dilute real solution, derive Raoult’s law for the solvent.

Problem 8.13. The system A–B forms a regular solution with the heat of mixing given by:

$$\Delta H_{mix} = -13,500X_A X_B \left(\frac{J}{\text{mol}}\right)$$

a. Derive expressions for the Henry’s law constant for A as a solute in B and B as a solute in A.

b. Plot both Henry’s law constants as a function of temperature.

Problem 8.14. The system A–B may be described by the quasichemical model. The heat of vaporization of pure A is 98,700 (J/mol); that of pure B is 127,000 (J/mol). At a solution composition $X_B = 0.40$ at 750 K the activity of component B is found to be 0.53. Estimate the energy of an AB bond in this system.
Answers

**Problem 8.3**

Benchmark:

\[ \Delta V_2 = 54X_2^2X_2; \quad \Delta V_1 = 27X_1X_2^2 \]

**Problem 8.5**

Plot the results of a Gibbs–Duhem integration:

\[ \Delta H_{\text{fn}} = 12,500 X_{\text{Cu}}^2 \left( X_{\text{Cu}} - \frac{1}{2} \right); \quad \Delta H_{\text{mix}} = 6250X_{\text{Cu}}^2X_{\text{Pn}} \]

**Problem 8.9**

Plot the activity of zinc obtained from

\[ RT \ln a_{\text{Zn}} = \left( 1 - \frac{T}{4000} \right) X_{\text{Al}}^2 \left[ 13,200(X_{\text{Al}} - X_{\text{Zn}}) + 19,200X_{\text{Zn}} \right] \]

\[ + RT \ln X_{\text{Zn}} \]

**Problem 8.10**

<table>
<thead>
<tr>
<th>Total Properties</th>
<th>PMP of A</th>
<th>PMP of B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta C_{\text{mix}}^\alpha ) (J/mol)</td>
<td>2513</td>
<td>1353</td>
</tr>
<tr>
<td>( \Delta S_{\text{mix}}^\alpha ) (J/mol K)</td>
<td>0.565</td>
<td>0.304</td>
</tr>
<tr>
<td>( \Delta V_{\text{mix}} ) (cc/mol)</td>
<td>-1.749</td>
<td>-0.942</td>
</tr>
<tr>
<td>( \Delta H_{\text{mix}} ) (J/mol)</td>
<td>2824</td>
<td>1521</td>
</tr>
<tr>
<td>( \Delta U_{\text{mix}} ) (J/mol)</td>
<td>2842</td>
<td>1511</td>
</tr>
<tr>
<td>( \Delta F_{\text{mix}}^\alpha ) (J/mol)</td>
<td>2531</td>
<td>1363</td>
</tr>
</tbody>
</table>

**Problem 8.13**

Plot as a function of temperature

\[ \gamma_A^0 = \gamma_B^0 = e^{-13,500/RT} \]