Homework Assignment 7; Due 03/11/08
22.5, 22.6, 22.15, 22.18, 23.1
Additional problems

22.5
Suppose that you draw a card from a standard deck of 52 cards. What is the probability of drawing:
a) an ace of any suit?
b) the ace of spades?
c) How would your answers to parts (a) and (b) change if you were allowed to draw three times, replacing the card drawn back into the deck after each draw?

a) In a deck of 52 cards there are four aces, therefore:
\[ P_E = \frac{E}{N} = \frac{4}{52} \]

b) There is only one card that corresponds to the event of interest, therefore:
\[ P_E = \frac{E}{N} = \frac{1}{52} \]

c) By replacing the card, the probability for each drawing is independent, and the total probability is the sum of probabilities for each event. Therefore, the probability will be 3\(P_E\) with \(P_E\) as given above.

22.6
You are dealt a hand consisting of 5 cards from a standard deck of 52 cards. Determine the probability of obtaining the following hands.
a) a flush (five cards of the same suit)

b) a king, queen, jack, ten, and ace of the same suit (a “royal flush”)

a) The first card specifies the suit, and the remaining four cards must be of that suit in order to obtain a flush:

$$P = \frac{\binom{52}{1} \binom{12}{1} \binom{11}{1} \binom{10}{1} \binom{9}{1}}{52} \approx 0.002$$

b) A royal flush requires that one receive a K, Q, J, 10, or A of any suit in the first card. If that card is obtained, only the other four cards of the suit will result in a royal flush:

$$P = \frac{\binom{20}{1} \binom{4}{1} \binom{2}{1} \binom{1}{1}}{52} \approx 1.52 \times 10^{-5}$$

22.15

Consider the following energy-level diagrams:

a) At what temperature will the probability of occupying the second energy level be 0.15 for the states depicted in part (a) of the figure?

b) Perform the corresponding calculation for the states depicted in part (b) of the figure. Before beginning the calculation, do you expect the temperature to be higher or lower than that determined in part (a) of this problem? Why?

a) According to the energy-level diagram, there is one state at \( \epsilon = 0 \) and one state at \( \epsilon = 300 \text{ cm}^{-1} \). Therefore:

$$0.15 = P_1 = \frac{e^{-\beta \epsilon}}{g} = \frac{e^{-\beta (300 \text{ cm}^{-1})}}{1 + e^{-\beta (300 \text{ cm}^{-1})}}$$

$$0.15 + 0.15 \left( e^{-\beta (300 \text{ cm}^{-1})} \right) = e^{-\beta (300 \text{ cm}^{-1})}$$

$$0.15 = 0.85 \left( e^{-\beta (300 \text{ cm}^{-1})} \right)$$

$$0.176 = e^{-\beta (300 \text{ cm}^{-1})}$$

$$1.74 = \beta (300 \text{ cm}^{-1}) = \left( \frac{1}{0.695 \text{ cm}^{-1} K^{-1} T} \right) (300 \text{ cm}^{-1})$$

$$T = 248 \text{ K}$$

b) According to the energy-level diagram, there is one state at \( \epsilon = 0 \) and two states at \( \epsilon = 300 \text{ cm}^{-1} \). Therefore:
0.15 = \rho_1 = \frac{2e^{-β_a}}{q} = \frac{2e^{-β(300 \text{ cm}^{-1})}}{1 + 2e^{-β(300 \text{ cm}^{-1})}}

0.15 + 0.30\left(e^{-β(300 \text{ cm}^{-1})}\right) = 2e^{-β(300 \text{ cm}^{-1})}

0.15 = 1.70\left(e^{-β(300 \text{ cm}^{-1})}\right)

0.088 = e^{-β(300 \text{ cm}^{-1})}

2.43 = β(300 \text{ cm}^{-1}) = \frac{1}{\left(0.695 \text{ cm}^{-1} \text{ K}^{-1}\right)(T)}(300 \text{ cm}^{-1})

T = 178 \text{ K}

The temperature at which \rho_1 = 0.15 is lower for case b since the presence of two states at the higher energy provides more opportunity for the system to populate the higher energy state.

22.18

A set of 13 particles occupies states with energies of 0, 100, and 200 cm\(^{-1}\). Calculate the total energy and number of microstates for the following configurations of energy:

a) \(a_0 = 8, a_1 = 5,\) and \(a_2 = 0\)

b) \(a_0 = 9, a_1 = 3,\) and \(a_2 = 1\)

c) \(a_0 = 10, a_1 = 1,\) and \(a_2 = 2\)

Do any of these configurations correspond to the Boltzmann distribution?

The total energy is equal to the sum of energy associated with a given level times the number of particles in that level. For the occupation numbers in a:

\[ E = \sum_n \varepsilon_n a_n = \varepsilon_0 a_0 + \varepsilon_1 a_1 + \varepsilon_2 a_2 \]

\[ = (0 \text{ cm}^{-1})(8) + (100 \text{ cm}^{-1})(5) + (200 \text{ cm}^{-1})(0) = 500 \text{ cm}^{-1} \]

Repeating the calculation for the occupation numbers in (b) and (c) yields the same energy of 500 cm\(^{-1}\). The number of microstates associated with each distribution is given by the weight:
\[ W_a = \frac{N!}{\prod_n a_n!} = \frac{N!}{a_0!a_1!a_2!} = \frac{13!}{(8!)(5!)(0!)} = 1287 \]

\[ W_b = \frac{13!}{(9!)(3!)(1!)} = 2860 \]

\[ W_c = \frac{13!}{(10!)(1!)(2!)} = 858 \]

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

\[ \frac{a_i}{a_j} = e^{-\beta(e_i-e_j)} = e^{-\left(\frac{e_i-e_j}{k}\right)/T} \]

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. For set (b), comparing the occupation numbers for level 2 and level 0 results in:

\[ \frac{a_2}{a_0} = e^{-\left(\frac{200 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)/T} \]

\[ \frac{1}{9} = e^{-\left(\frac{200 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)/T} \]

\[ T = 131 \text{ K} \]

Repeating the same calculation for level 1 and level 0:

\[ \frac{a_1}{a_0} = e^{-\left(\frac{100 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)/T} \]

\[ \frac{3}{9} = e^{-\left(\frac{100 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)/T} \]

\[ T = 131 \text{ K} \]

The distribution of energy in (b) is in accord with the Boltzmann distribution.
1) We have used quantum mechanical expressions for the translational, rotational, and vibrational energy to calculate the partition function. The translational partition function can be and was calculated classically. The expression for the classical partition function for one dimensional translation within a box of length a is:

\[
\Lambda = \left( \frac{\hbar^2}{2\pi mkT} \right) = \left( \frac{6.626 \times 10^{-34} \text{ J s}^2}{2\pi \left( \frac{0.002 \text{ kg mol}^{-1}}{0.0106 \text{ m}^3} \right)(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right) = 7.15 \times 10^{-11} \text{ m}
\]

\[
q_T(H_2) = \frac{V}{\Lambda^3} = \frac{100 \text{ cm}^3}{(7.15 \times 10^{-11} \text{ m})^3} = 2.74 \times 10^{26}
\]

\[
q_T(N_2) = \frac{V}{\Lambda^3(N_2)} = \left( \frac{m(N_2)}{m(H_2)} \right) = \left( \frac{28.014 \text{ g mol}^{-1}}{20.16 \text{ g mol}^{-1}} \right) = 51.8
\]

\[
q_T(N_2) = 51.8 (q_T(H_2)) = 1.42 \times 10^{32}
\]
Answer: The sum over states over-counts, unless corrected for the uncertainty principle, i.e. the fact that position and momentum cannot be known to arbitrarily high accuracy. The partition function, i.e. the sum over states, must be corrected for this fact.

2) It is common to tabulate the ratios \( \Theta_v = \frac{h \nu}{k_B} \) and \( \Theta_R = \frac{h^2}{2Ik_B} \) so that the single particle partition functions for vibration and rotation can be written as:

\[
q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)e^{-\Theta_R(J+1)/T} \quad \text{and} \quad q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\frac{n+\frac{1}{2}}{\Theta_v}/T}
\]

a) Show that the vibrational contribution to the energy is

\[
U_{\text{vib}} = Nk_B \left( \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right)
\]

Solution: \( q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\frac{n+\frac{1}{2}}{\Theta_v}/T} = e^{-\Theta_v/2T} \sum_{n=0}^{\infty} e^{-n\Theta_v/T} = \frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}} = e^{-\Theta_v/2T} \left( 1 - e^{-\Theta_v/T} \right)^{-1}
\]

\[
U_{\text{vib}} = \frac{Nk_B T^2}{q_{\text{vib}}} \frac{\partial q_{\text{vib}}}{\partial T} = \frac{Nk_B T^2}{e^{-\Theta_v/2T}} \left( 1 - e^{-\Theta_v/T} \right) \frac{\partial}{\partial T} \left[ e^{-\Theta_v/2T} \left( 1 - e^{-\Theta_v/T} \right)^{-1} \right]
\]

\[
= \frac{Nk_B T^2}{e^{-\Theta_v/2T}} \left( 1 - e^{-\Theta_v/T} \right) \left[ \left( \frac{\Theta_v}{2T^2} \right) e^{-\Theta_v/2T} \left( 1 - e^{-\Theta_v/T} \right)^{-1} - \left( \frac{\Theta_v}{T^2} \right) e^{-\Theta_v/2T} \left( 1 - e^{-\Theta_v/T} \right)^{-2} \right]
\]

\[
= Nk_B \left[ \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right] \frac{e^{\Theta_v/T}}{\left( e^{\Theta_v/T} - 1 \right)^2}
\]

b) Show that the vibrational heat capacity is

\[
C_v = Nk_B \left( \frac{\Theta_v}{T} \right)^2 e^{\Theta_v/T} \left( e^{\Theta_v/T} - 1 \right)^2
\]

Solution: Differentiate \( U_{\text{vib}} \) wrt \( T \)...Chain rule again...

c) For H\(_2\) \( \Theta_v = 6215K \) and for I\(_2\) \( \Theta_v = 310K \). Calculate the vibrational energies and heat capacities for H\(_2\) and I\(_2\) and 300K and 1000K. How well do these numbers agree with the predictions of the equipartition principle?

Solution:
For hydrogen:

T=300K

\[
Nk_B \left[ \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right] = Nk_B (6215K) \left[ \frac{1}{2} + \frac{1}{e^{6215/300} - 1} \right] = Nk_B (6215K) \left[ \frac{1}{2} + \frac{1}{e^{6215/300} - 1} \right] \approx \frac{Nk_B (6215K)}{2}
\]

T=1000K

\[
Nk_B \left[ \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right] = Nk_B (6215K) \left[ \frac{1}{2} + \frac{1}{e^{6215/1000} - 1} \right] = Nk_B (6215K) \left[ \frac{1}{2} + \frac{1}{e^{6215/1000} - 1} \right] \approx \frac{Nk_B (6215K)}{2}
\]

For iodine:
For the heat capacity just use
\[ C_v = Nk_B \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T} - 1\right)^2} \]

d) For H\(_2\) and I\(_2\) at 300K and 1000K, calculate the fraction of molecules not in the
ground vibrational state.
\[ q_{vib} = e^{-\Theta_v/T} \left(1 - e^{-\Theta_v/T}\right)^{-1} = e^{-6215/600} \left(1 - e^{-6215/300}\right)^{-1} \]
\[ P_0 = \frac{e^{-\Theta_v/T}}{q_{vib}} = e^{-\Theta_v/T} \left(1 - e^{-\Theta_v/T}\right) = 1 - e^{-\Theta_v/T} \]

For hydrogen at T=300K
\[ P_0 = 1 - e^{-\Theta_v/T} = 1 - e^{-6215/300} \approx 1 \] Therefore the probability (i.e. fraction) that a molecule is not in the ground state is \( 1 - P_0 \approx 0 \)

For hydrogen at T=1000K
\[ P_0 = 1 - e^{-\Theta_v/T} = 1 - e^{-6215/1000} \approx 1 \] So same result.

For iodine at T=300K
\[ P_0 = 1 - e^{-\Theta_v/T} = 1 - e^{-310/300} \approx 1 - 0.36 = 0.64 \] Therefore the probability (i.e. fraction) that a molecule is not in the ground state is \( 1 - 0.64 \approx 0.36 \)

For hydrogen at T=1000K
\[ P_0 = 1 - e^{-\Theta_v/T} = 1 - e^{-6215/1000} \approx 1 \]

2) Consider the dimerization of sodium vapor:
\[ 2Na(g) \rightleftharpoons Na_2(g) \]
For Na\(_2\) \( \Theta_v = 229K, \Theta_r = 0.221K, \varepsilon_D = 72.3kJmol^{-1} \).

a) Calculate the translational partition functions \( q_{trans} \) for Na and Na\(_2\) at T=1000K

Solution:
\[ q_{Na} = \left(\frac{2\pi m k_BT}{\hbar^2}\right)^{3/2} V = \left(\frac{2\pi \times 0.023 \times 1.66 \times 10^{-24} \times 1.38 \times 10^{-23} \times 10^3}{(6.62)^2 \times 10^{-68}}\right)^{3/2} = 6.54 \times 10^{26} V \]
\[ q_{Na_2,trans} = \left(\frac{2\pi m k_BT}{\hbar^2}\right)^{3/2} V = \left(\frac{2\pi \times 0.046 \times 1.66 \times 10^{-24} \times 1.38 \times 10^{-23} \times 10^3}{(6.62)^2 \times 10^{-68}}\right)^{3/2} = (2.83)6.54 \times 10^{26} = 1.85 \times 10^{27} \]

b) Calculate the rotational and vibrational partition functions for Na\(_2\) at T=1000K.
State any assumptions you make and justify them.
Solution:
\[ q_{Na_{2},rot} = \frac{T}{2\Theta_{rot}} = \frac{1000}{2(0.221)} = 2262 \]

\[ q_{vib}^{rot} = \frac{e^{\frac{\epsilon_f}{RT}}}{1 - e^{\frac{\Theta}{T}}} = (4.88)(5960) = 29,085 \]

c) Calculate the total partition functions for Na and \(Na_2\) at \(T=1000\)K. Assume the ground electronic state for Na is doubly degenerate i.e. \(g_{0,\text{Na}} = 2\), and \(g_{0,\text{Na}_2} = 1\) and assume only the ground electronic states are populated.

Solution: \(q_{Na,\text{total}} = q_{Na,\text{trans}}q_{Na,\text{elec}} = (6.54 \times 10^{26} V)(2) = 1.31 \times 10^{27} V\)

\(q_{Na_2} = q_{Na_{2,\text{trans}}}q_{Na_{2,\text{rot}}}q_{Na_{2,\text{vib}}}q_{Na_{2,\text{elec}}} = (1.85 \times 10^{27} V)(2260)(29085) = 1.22 \times 10^{35} V\)

d) Calculate the equilibrium constant for the dimerization of sodium vapor at \(T=1000\)K. Assume the volume \(V=1\)m\(^3\). In your calculation treat the equilibrium constant as a ratio of number densities \(N/V\).

\[ K = \left( \frac{q_{Na_2}}{q_{Na}} \right)^2 = \frac{1.22 \times 10^{35}}{(1.31 \times 10^{27})^2} = 7.11 \times 10^{-20} \]

3) Using the Sackur-Tetrode equation,

a) Calculate the entropy of one mole of argon gas at a temperature of 300K and a pressure of 1 atm. Assume argon behaves ideally.

Solution:

\[ q_{trans} = \left( \frac{2\pi mk_BT}{h^2} \right)^{3/2} V = \left( \frac{2\pi Mk_BT}{N_A h^2} \right)^{3/2} V = \left( \frac{2\pi (0.04\text{ kg/mole})(1.38 \times 10^{-23} \text{ J/K})(300\text{ K})}{(6.02 \times 10^{23} \text{ / mole})(6.62 \times 10^{-34} \text{ J/s})^2} \right)^{3/2} V \]

\[ = 2.47 \times 10^{32} V \]

\[ S = Nk_B \ln \left( \frac{q_{trans}^{5/2}}{N} \right) = R \ln \left( \frac{2.47 \times 10^{32} V}{N} \right) = R \ln \left( \frac{2.47 \times 10^{32}}{N} \right) k_B T^5/2 \]

\[ = R \ln \left( \frac{2.47 \times 10^{32}}{10^5 N / m^2} (1.38 \times 10^{-23} \text{ J/K})(300\text{ K}) e^{5/2} \right) = 154.8 \text{ J/mole} \cdot \text{K} \]

b) Using the Sackur-Tetrode equation, calculate the entropy change \(\Delta S\) when one mole of argon changes its temperature from 300K to 1000K. Assume the volume remains constant and that argon behaves ideally.

\[ S = Nk_B \ln \left( \frac{q_{trans}^{5/2}}{N} \right) = Nk_B \ln \left( \frac{2\pi mk_BT}{h^2} \right)^{3/2} V e^{5/2} \]

\[ = \frac{3Nk_B}{2}(\cos t \tan t + \ln T) \]

\[ \therefore \Delta S = S(T_2) - S(T_1) = \frac{3Nk_B}{2} \ln \left( \frac{T_2}{T_1} \right) = \frac{3R}{2} \ln \left( \frac{T_2}{T_1} \right) = (1.5)(8.31)(\ln 1000 - \ln 300) = 15 \text{ J/Kmole} \]

\[ S = \]
c) Using the Sackur-Tetrode equation, calculate the entropy change $\Delta S$ when one mole of argon changes its volume from $1\text{m}^3$ to $10\text{m}^3$. Assume the temperature remains constant.

Solution:
Same reasoning...

$$\Delta S = S(V_2) - S(V_1) = Nk_B \ln \left( \frac{V_2}{V_1} \right) = R \ln \left( \frac{V_2}{V_1} \right) = (8.31) \ln \left( \frac{10}{1} \right) = 19.1 \text{ J} / \text{mole}$$