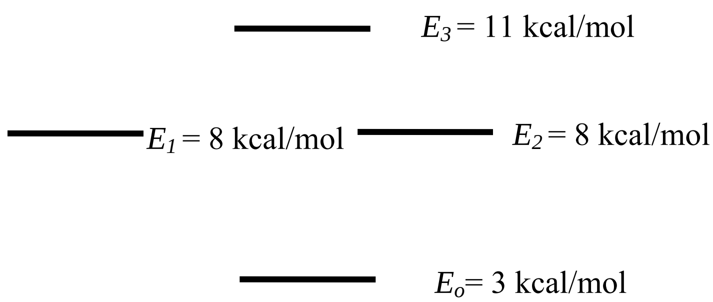
10.40 Thermodynamics **Fall 2003**
Exam 2

Problem 1

1. (20 points) For a 1 mole molecular system that can only occupy any of 4 different states:



(a) (4 points) What is U at T = 300 K?

(b) (4 points) What is the probability that a given snapshot of the system will have an energy of 3 kcal/mol at 300 K?

(c) (4 points) If each energy state is increased by 2 kcal/mol, what is the probability that a given snapshot of the system will have an energy of 3 kcal/mol at 300 K?

(d) (4 points) What is U as T gets very large?

(e) (4 points) What is U as T gets very small?

Solution:

(a)
Since the number of moles, the temperature, and the volume is constant, we can use the canonical ensemble. Start with Equation (10-17) for the ensemble average of the energy:

$$U = \langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{\sum_i E_i e^{-\beta E_i}}{Q_N} \qquad (10\text{-}17)$$

Some students used the expression

$$U = \langle E \rangle = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_{\underline{V},N}$$

This was a longer route, but as long as the derivative was performed correctly, the result was the same expression as Equation (10-17).

For this system, there are four <u>distinguishiable</u> energy states, E_o, E_1, E_2, and E_3. Noting that since we are working in terms of the intensive energy:

$\beta = RT = 0.5961$ kcal/mol

$$Q_N = e^{-3/\ 0.5961} + 2e^{-8/\ 0.5961} + e^{-11/\ 0.5961} = 0.006524$$

$$\sum_i E_i e^{-\beta E_i} = 3e^{-3/\ 0.5961} + (2)8e^{-8/\ 0.5961} + 11e^{-11/\ 0.5961} = 0.019587$$

Plugging the values into Equation (10-17), we get:

$\underline{U = 3.00229 \text{ kcal/mol}}$.

(b)

From Equation (10-16):

$$P_N(E_o = 3 \text{ kcal/mol}) = \frac{e^{-\beta E_o}}{Q_N} = \underline{0.99954}, \text{ or } \underline{99.954\%}, \text{a very high probability.}$$

(c)

If each energy state is increased by 2 kcal/mol, then the possible energy states will be E_o = 5 kcal/mol, E_1 = E_2 = 10 kcal/mol, and E_3 = 13 kcal/mol. Therefore, the lowest possible energy state the system can attain is 5 kcal/mol, and the system can never have E = 3 kcal/mol. By Equation (10-16):

$\underline{P_N(E = 3 \text{ kcal/mol}) = 0}$.

(d)

As T→∞, the term $e^{-\beta E}$ goes to 1, so that by Equation (10-16), all energy states are equally likely to be filled. Therefore, the ensemble average energy is the average of all possible energy states:

$\underline{U = \langle E \rangle = 7.5 \text{ kcal/mol}}$.

(e)

As T→0, the term $e^{-\beta E}$ goes to 0. However, it goes to zero more quickly for the higher energy states than the lower ones, so that by Equation (10-16), the only energy state that is likely to be filled is the lowest energy state. Therefore, the ensemble average energy is equal to the energy of the ground state, or:

$\underline{U = E_o = 3 \text{ kcal/mol}}$.