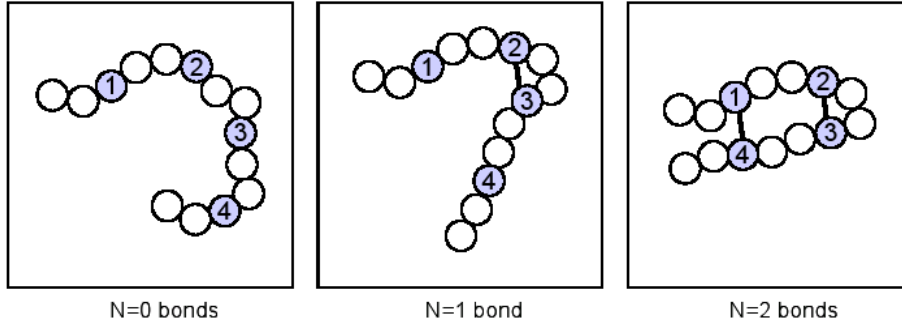


**Probability of Disulfide Bond Formation (2005 Final):**

A protein has four cysteines, any two of which can bind together to form disulfide links. The protein can have a number of disulfide bonds, where  $N = 0, 1, 2$ . Examples of each type of configuration are shown in the pictures below:



where a thick black line indicates the formation of a disulfide bond.

1. Calculate  $\Omega$  for  $N = 0, 1$ , and 2 bonds.
2. Assume that the energy of each macrostate is  $E_N = 2 E_0 - N E_0$ . Therefore, if the protein has two disulfide bonds, its energy is 0. Fill in the table, labeling the energy levels with their value of  $E_N$ , and also indicate the degeneracy of each level.
3. Write an expression for the partition function,  $q$ , as a function of  $E_0$  and  $T$ .
4. What is the value of  $q$  as  $T \rightarrow \infty$ ? As  $T \rightarrow 0$ ?
5. Sketch a probability distribution for the system at equilibrium at a temperature of  $T = \frac{E_0}{k}$ .
6. Calculate the average energy  $\langle E \rangle$  at  $T = \frac{E_0}{k}$ . Express your answer in units of  $E_0$ .

### Equilibrium (2005 Final):

Consider the reaction  $CO(g) + 2H_2(g) = CH_3OH(g)$

Use the following thermodynamic data:

$$\Delta \bar{H}_f^\circ(CH_3OH) = -200.7 \text{ kJ}$$

$$\Delta \bar{H}_f^\circ(CO) = -110.5 \text{ kJ}$$

$$\Delta \bar{S}^\circ(CH_3OH) = 239.8 \text{ J/K}$$

$$\Delta \bar{S}^\circ(H_2) = 130.6 \text{ J/K}$$

$$\Delta \bar{S}^\circ(CO) = 197.7 \text{ J/K}$$

1. Find  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  for the reaction above.
2. Find  $\Delta G_{rxn}^\circ$  and  $K_p$  at 500K for the reaction. You may assume that  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  are independent of T.
3. 1 mole of CO(g) and 1 mole of  $H_2(g)$  are allowed to react to form  $CH_3OH(g)$  at 500K and at a constant total pressure  $p_T$ . What is  $p_T$  if at equilibrium 0.25 moles of  $CH_3OH(g)$  are formed?
4. Suppose that the yield of  $CH_3OH(g)$  needs to be increased to 0.3 moles. Should the pressure be increased, decreased, or not changed compared to the pressure in the previous question? Explain. (No calculation is required.)

### The third law entropy:

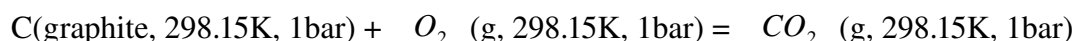
In Table C.2 of your textbook, you will find for  $T = 298.15\text{K}$  and  $p = 1\text{bar}$ , the following thermodynamic information for  $\text{CO}_2(\text{g})$

$$\Delta \bar{H}_f^\circ = -393.509 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta \bar{G}_f^\circ = -394.359 \frac{\text{kJ}}{\text{mol}}$$

$$\bar{S}^\circ = 213.74 \frac{\text{J}}{\text{K mol}}$$

1. What is  $\Delta S^\circ$  for the reaction:



2. If your answer to the previous question is *not*  $\bar{S}^\circ = 213.74 \frac{\text{J}}{\text{K mol}}$ , what is the definition of  $\bar{S}^\circ$  and why is it *not the same as*  $\Delta S^\circ$ ? For full credit you should write down the equation that specifies the process which defines  $\bar{S}^\circ$  for  $\text{CO}_2(\text{g})$ .

### Residual entropy:

1. Suppose that we arrange different kinds of atoms A and B on the  $N$  sites of a crystal. If  $N_A$  is the number of A atoms and  $N_B$  is the number of B atoms, then  $N_A + N_B = N$  is the total number of sites (as well as the total number of atoms). At  $T = 0\text{K}$ , what is the entropy of the mixture? Is this answer consistent with the third law of thermodynamics?

Hint: Use Stirling's Formula  $\ln(N!) \approx N \ln(N) - N$  to simplify your answer.

2. Suppose now that the residual entropy of the A/B crystal at  $T = 0\text{K}$  is known to be  $3.4 \text{ J/K}$ . What can you conclude about the relative abundances of A and B? Express your answer in the ratio A:B.

**One-component phase equilibrium (2001, Exam III):**

Near the triple point of iodine, the equilibrium vapor pressure of the solid and the liquid are well represented by:

$$\ln(p_s) = 16.8 - \frac{7312}{T}$$

$$\ln(p_l) = 12.0 - \frac{5452}{T}$$

where the temperature and pressure are expressed in Kelvin and bar units.

1. Calculate the temperature  $T_{tp}$  and pressure  $p_{tp}$  of the triple point.
2. Consider the functional form of the integrated Clausius-Clapeyron equation (assume  $\Delta H$  is constant) to state the molar heat of sublimation and the molar heat of vaporization for iodine.
3. Once again, consider  $\Delta H$  to be independent of temperature. Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the melting of one mole of solid iodine at the triple point. Does the sign of  $\Delta S$  make sense? Explain.