Statistical thermodynamics exercises with answers

Configurations, weights and entropy:

1) For the two instantaneous configurations: A: {400, 50, 20, 10} and B: {300, 100, 50, 30}. Calculate which configuration has the greatest weight. Calculate the associate entropy of these configurations.

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$\ln W_A = 288.3 \qquad \ln W_B = 494.1 \qquad W_B > W_A$$

$$S = k_b \ln(W)$$

$$S_A = 3.98 \cdot 10^{-21} J/K \text{ or } 2397\, J/(K\, mol) \qquad S_B = 6.82 \cdot 10^{-21} J/K \text{ or } 4108\, J/(K\, mol)$$

2) Consider the following two configurations with the same energy. Configuration A: {150, 150, 320, 180, 50, 25, 15} and configuration B: {160, 140, 340, 160, 40, 35, 15}. Calculate which configuration has the greatest weight. Discuss which configuration is most probable.

$$lnW_A = 1443$$

$$lnW_B = 1433$$

$$W_A > W_B$$

$S = k_B lnW$ Thus, $S_A > S_B$ and consequently the configuration A is the most probable

3) We have a system of 3 levels at 20ºC with the corresponding energies (e0=1 kJ/mol, e1=2 kJ/mol and e2=3 kJ/mol). a) Calculate the energy of the following configurations: {9, 6, 1}, {10, 4, 2}, {11, 2, 3} and {12, 0, 4}. b) Calculate the weight and the entropy of the previous configurations. Discuss which configuration is the most probable.

a) $E=e_0*n_0+e_1*n_1+e_2*n2$

$$E_{\{9,6,1\}}=E_{\{10,4,2\}}=E_{\{11,2,3\}}=E_{\{12,0,4\}}=24\,kJ/mol$$

b)

$$W=\frac{N!}{n_0!n_1!n_2!} \qquad S=k_b\ln(W)$$

$$W_{\{9,6,1\}}=\frac{16!}{9!6!1!}=80080 \qquad W_{\{10,4,2\}}=120120 \qquad W_{\{11,2,3\}}=43680 \qquad W_{\{12,0,4\}}=1820$$

$$S_{\{9,6,1\}}=1.56\cdot10^{-22}J/K \qquad S_{\{10,4,2\}}=1.61\cdot10^{-22}J/K \qquad S_{\{11,2,3\}}=1.48\cdot10^{-22}J/K$$

$$S_{\{12,0,4\}}=1.04\cdot10^{-22}J/K$$

4) Consider a four level system that could be populated with two different instantaneous configurations. Configuration A: {420, 60, 24, 11} and configuration B: {310, 110, 60, 35}. a) Calculate which configuration has the greatest weight. b) Calculate the associate entropy of these configurations.

For both configurations, the total number of particles, N=515

$$lnW_A = 330$$

$$lnW_B = 550$$

Thus, $W_B > W_A$

b)

$S = k_B lnW$

$$S_A = 4.5610^{-21}\,J/K$$

$$S_B = 7.6010^{-21}\,J/K$$

It is also valid to use R constant and to give the entropies in terms of J/Kmol.

5) Calculate the entropy of a system of 7500 particles distributed as indicated with the following configuration {4000, 2000, 1000, 500}. If the particles were uniformly distributed among the four levels, calculate also the entropy associated with this new configuration. Comment the observed differences.

Boltzmann distribution

1) Consider a three-level system with energy levels: 0, 2 kJ/mol and 4 kJ/mol. a) Calculate the population (probability) corresponding to these energy levels at T=25ºC and T= 100ºC.

Temperature 25 C Population p0: 0.61 Population p1: 0.27 Population p2: 0.12

Temperature 100 C Population p0: 0.56 Population p1: 0.29 Population p2: 0.15

2) The conformational variability of a macromolecule could be studied at certain conditions with a three-level system. It has been determined that the energy of the most stable levels (e 0 and e1) are 0 kJ/mol and 1.2 kJ/mol, respectively. An experiment determined the population of the most stable level to be p0=0.54 (that is 54%) at 75ºC. Calculate the energy and population of the last level (level 2). Comment what happens with the population of the last level if the temperature is increased.

$$q=1/p_0=1/0.54=1.85$$

$$p_1=\exp\left(-1200\,\text{J/mol}/(RT)\right)/q=0.357$$

$$p_2=1-p_0-p_1=0.103$$

Isolate E_2 from $p_2=\left(-E_2/(RT)\right)/q$ E_2 = 4788 J/mol

If the temperature is increased the population of the last level will increase. In the limit, the population of the tree levels will be 1/3.

3) It is observed that one drug could bind to its protein target in two different places (site A and site B). The energy associated to the binding of the drug when it is attached to site A is of -15.5 kJ/ mol, and when it is attached to the site B is of -13.7 kJ/mol. Determine at which temperature the population of the drug binding the site A is double than the population of the drug binding the site B.

$$p_i=\exp(-E_i/RT)/q$$

$$p_A/p_B=\exp(-E_A/RT)/\exp(-E_B/RT)=2$$

$$T=312.3\,K=39\,C$$

4) Consider a three-level system with energy levels: 0, 2 kJ/mol and 3 kJ/mol. Calculate the population corresponding to these energy levels at T=60ºC. Comment what happens with the population of highest level (3 kJ/mol) if the temperature is increased.

$$p_0=\frac{e^{-\beta e_i}}{q}=0.55 \qquad p_1=\frac{e^{-\beta e_1}}{q}=0.27 \qquad p_2=\frac{e^{-\beta e_2}}{q}=0.18$$

If the temperature is increased, the population of the highest energetic level increases. In the limit of high temperature, the three states will have a population of 1/3.

5) Obtain the energy difference between the levels of a two-level systems if the fraction of molecules being in the most stable energy level (0 kJ/mol) is 0.9 at T=50ºC.

5903 J/mol

6) Consider a three-level system with energy levels: 0, 1.5 kJ/mol and 2.5 kJ/mol. Calculate the population corresponding to these energy levels at T=35ºC. Comment what happens with the population of the most stable level (0 kJ/mol) if the temperature is increased.

5) p{0}=0.52; p{1}=0.29; p{2}=0.19

7) In a four-level system at T= 100°C the population of the four levels is: 50%, 30%, 15% and 5%. Calculate the population of these four levels at T= -200ºC. Comment if there is any temperature at which the population of the last two levels could be the same.

8) A system has energy levels at $\varepsilon 0=0$, $\varepsilon 1=1.5$, $\varepsilon 2=2.2$ kJ/mol. a) Calculate the partition function and the relative population of the energy levels at a temperature of 300K. b) At what temperature is the population of the energy level at 1.5 kJ/mol equal to the population of the energy level at 2.2 kJ/mol .

9) Depending of the degree of opening of a channel, a macromolecule could be in three different conformations. One experiment at 25ºC determines the population of these three states to be 60%, 35% and 5%, for opened, semi-opened and closed conformations, respectively. a) Determine the relative energies of these three states.

10) It has been seen that a transmembrane protein could make conformational changes to adopt an active or inactive states. The estimated free energy for the active state of the protein is -200.5 kJ/mol. The degeneration of the inactive state is 2 with a free energy of -198.1 kJ/mol. a) If a cell has around of 105 of those transmembrane proteins, calculate the number of active and inactive proteins at 37ºC. b) Discuss which proportions will be obtained at 0K and at infinity temperature.

11) An enzyme with a flexible inner cavity could adopt three different macromolecular conformations: open, semi-open or closed conformations. One experiment carried out at 37°C determined the following populations 55%, 45% and 5%, for open, semi-open and closed conformations, respectively. a) Calculate the relative energy of these conformations. b) Calculate the proportions of these conformations if we make a new experiment at 4°C.

12) One polysaccharide could adopt three different conformations (A, B and C). At 42ºC degrees, the populations of A, B and C were determined to be 80%, 15% and 5%, respectively. Determine the populations of these three conformations of the polysaccharide at 2ºC. Indicate clearly the values of the energetic levels with appropriated units.

13) An experiment determined that a transmembrane macromolecule could adopt three different conformations (A, B and C) at 37ºC degrees. The corresponding populations for A, B and C were determined to be 40%, 35% and 25%. Determine the populations of the three conformations of the macromolecule at 5ºC