

Chemistry 163C Problem Set #2
Due Thursday, 4/17 at the beginning of class

- 1) If you roll five dice at the same time, how much more likely are you to roll the numbers {1 2 3 4 5} than {2 2 4 4 4}? (You can assume that it is equally probable to observe any one of the six sides of a single die.) Why is this so? We showed in class that entropy S is given by the expression $S = k \ln W$, where k is Boltzmann's constant and W is the weight of the most probable configuration. What is the "entropy" for each of the two outcomes?
- 2) Consider a two level system where the ground state is nondegenerate and the excited state of energy ϵ is four fold degenerate. Write down the partition function and mathematical expressions for the populations of the two levels. Plot the partition function and the populations as a function of temperature from $T = 0$ to $T \rightarrow \infty$. What value do you get for q at $T \rightarrow \infty$?
- 3) Given N dice, show that the number of ways of observing n_1 ones, n_2 twos, etc. is given by the formula:

$$W = \frac{N!}{n_1! n_2! n_3! n_4! n_5! n_6!}$$

Hint: Consider a product of binomial expressions $\frac{N!}{n!(N-n)!}$

for n_1 ones from N dice, n_2 twos from $N - n_1$ dice, n_3 threes from $N - n_1 - n_2$ dice, etc.

- 4) Look up Stirling's approximation for $N!$ in your text. Compute $\ln(N!)$ and Stirling's approximation for $\ln(N!)$ for $N = 10, 20, 30, 40, 50$ and 60 and plot the outcomes against each other. Does the approximation work for large N ?

From Engel & Reid 3rd Edition, Chapter 13: 2, 7, 8, 9, 12, 13, 15, 20, 21, 25