Review and Mathematical Tools

1. Combinatorics

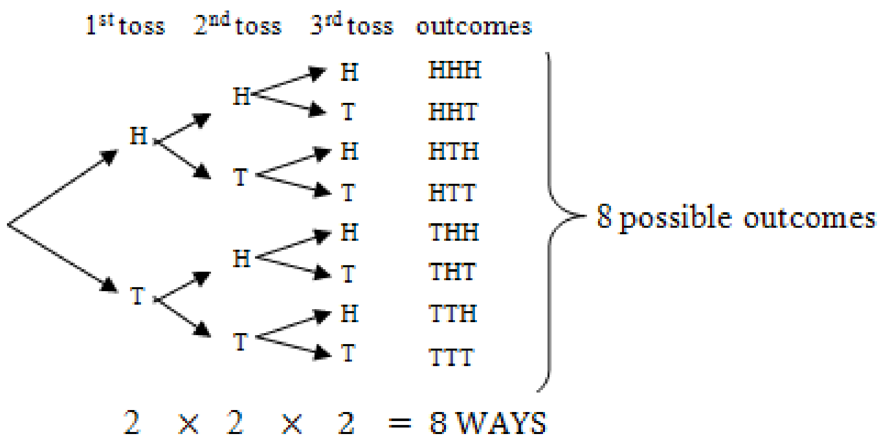
One thing we will be discussing in this class is the topic of **entropy.** Entropy is essentially the measure of disorder in a system and governs whether certain thermodynamic processes, such as a gas contracting or a ligand binding to a protein, will occur. Quantitatively speaking, entropy is somewhat proportional to the number of different arrangements of a system of molecules.

The Basic Counting Principle

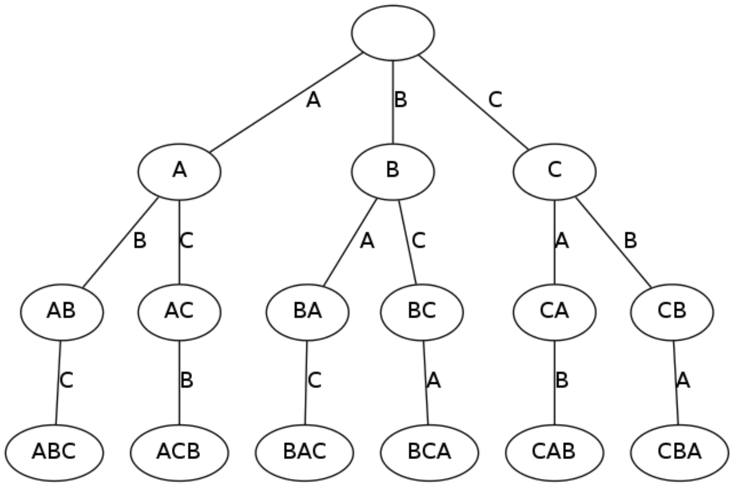
Counting is a very important life skill. It is also particularly relevant to a branch of mathematics know as **combinatorics**, which broadly aims to enumerate (count) the different arrangements and combinations of a set of elements. Here is the statement of the Basic Counting Principle:

> Suppose two experiments are performed. If there are m possible outcomes in Experiment 1, and n possible outcomes in Experiment 2, then there are $m \cdot n$ possible outcomes of the two experiments.

Suppose that there we toss three fair coins. A coin can either land heads-up (H) or tails-up (T). To restate, we are performing 3 experiments (tossing three coins). In tossing the first coin, we have 2 possible outcomes. In tossing the second coin, we have 2 outcomes. In tossing the third coin, we have—surprise—2 outcomes. Thus, there are $2 \cdot 2 \cdot 2 = 8$ possible outcomes of tossing 3 coins. I also like to think of this statement visually:



This leads me into my main lesson: **permutations**. A permutation is a particular arrangement of a set of elements in which the order in which they are arranged matters. For example, let's say I want to figure out how many different ways I can arrange the letters *a, b,* and *c*. We could easily arrange and rearrange these 3 letters and count all the unique arrangements. But an easier way would be to use the Basic Counting Principle. Let's say we have 3 spots in which to put letters. In the first spot, we have 3 letters to choose from (*a*, *b*, or *c*). In the next spot, we have 2 letters to choose from (since we already put a letter in the first spot). Then in the last spot we only have 1 letter to choose from. Thus, by the Basic Counting Principle, we have 3·2·1 = 6 possible permutations of the letters *abc*.



We can generalize this:

> Suppose we have n objects. Then there are
>
> $$n(n-1)(n-2)\cdots 3\cdot 2\cdot 1 = n!$$
>
> different permutations of those n objects

What if one or more of those n elements are identical? For example, how many unique permutations are there of the letters *PEPPER*? We know from the Basic Counting Principle that there are 6! Permutations of the letters $P_1E_2P_2P_3E_2R$ if we consider the 3 P's and 2 E's different from each other. Now consider the permutation, for instance, $P_1P_2E_2P_3E_2R$. If we permutate the P's among themselves and the E's among themselves, then the resulting permutations will still be in the form *PPEPER*. That is, all 3!2! permutations

$$\begin{array}{ll}
P_1P_2E_1P_3E_2R & P_1P_2E_2P_3E_1R \\
P_1P_3E_1P_2E_2R & P_1P_3E_2P_2E_1R \\
P_2P_1E_1P_3E_2R & P_2P_1E_2P_3E_1R \\
P_2P_3E_1P_1E_2R & P_2P_3E_2P_1E_1R \\
P_3P_1E_1P_2E_2R & P_3P_1E_2P_2E_1R \\
P_3P_2E_1P_1E_2R & P_3P_2E_2P_1E_1R
\end{array}$$

are of the form *PPEPER*. Since we do not consider the 3P's and 2E's to be different from one another, we divide out these extra permutations from the total 6! Permutations to account for overcounting. Thus, there are 6!/(3!2!) = 60 different permutations of the letters in *PEPPER*. In general:

> Suppose we have n objects. Then there are
>
> $$\frac{n!}{n_1!\,n_2!\cdots n_r!}$$
>
> different permutations of those objects, of which n_1 are alike, n_2 are alike, ⋯, n_r are alike.

2. Partial Derivatives

(Note: I am an engineer, not a mathematician. I will only give a brief introduction to partial derivatives and teach you how to use them for the purposes of this class. Thus, the material here may not be the most mathematically rigorous)

You should have taken some form of calculus before taking this class. Recall that a derivative is the rate of change of a function with respect to a variable. For instance:

$$Let\ y(x) = 2x^2$$

Then

$$\frac{dy}{dx} = 4x$$

$\frac{dy}{dx}$ is the derivative of y with respect to the variable x. This is also known as a **total derivative**.

Unless you have already taken multivariable calculus, all the functions you have worked with have only depended on <u>one variable</u>. For example:

$$f(x) = 8x + 4$$

$$T(h) = \sin(2h)$$

In many different applications, including thermodynamics, a quantity (such as pressure, volume, energy) may depend on more than one variable. For example, the Ideal Gas Law, which we will talk about in the class, can be used to describe the pressure of a gas as a function of volume V, temperature T, and number moles of gas n:

$$P(n, V, T) = \frac{nRT}{V}$$

Where $\boldsymbol{R = 8.314\frac{J}{mol*K}}$ is a constant.

So, how do we describe the rate of change of something when it depends on multiple variables? When working with functions of more than one variable, we can no longer assume that there is a single derivative that describes how a function is changing. Now, we must be explicit and describe how a function is changing **with respect to a certain variable.**

Enter the **partial derivative**!

A partial derivative describes the rate of change of a multivariate (multivariable) function with respect to one variable, holding the other variables of that function constant.

For instance, let's say we want to find the partial derivative of pressure with respect to temperature. In other words, how does pressure change if we change temperature, but hold the number of moles and volume constant?

What we do is treat the variables V and n as **constants** (in other words, like numbers rather than variables) and take the derivate of pressure with respect to T as we would with a single-variable function.

$$P(n,V,T) = \frac{nRT}{V}$$

$$\frac{\partial P}{\partial T} = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V}$$

We introduce some new notation. Notice how instead of writing $\frac{dP}{dT}$ we used some fancy curly symbol ∂ known as the **partial differential**. This is used to indicate that we are taking the derivative of a function that depends on more than one variable.

Now we have an expression that gives us the rate of change of pressure with respect to changing temperature, holding volume and the number of moles constant.

What if we instead wanted to find how pressure changes with respect to volume, holding temperature and number of moles constant? We differentiate with respect to volume!

$$\frac{\partial P}{\partial V} = \frac{\partial}{\partial V}\left(\frac{nRT}{V}\right) = nRT \ln V$$

As you can see, taking partial derivatives is not too different than the regular derivatives that you all know and love (at least for the purposes of this class).

I also want to introduce some additional notation that is used in thermodynamics. We are usually working with functions of several variables, so we want to keep track of which variables we are differentiating with respect to and which variables we are holding constant. This is because some variables may be non-independent (i.e. functions of other variables in the equations). Thus, we always put parentheses around our partial differential $\frac{\partial P}{\partial T}$ and denote the variables that we are holding constant as a subscript to the right of the parentheses. So instead of writing

$$\frac{\partial P}{\partial V} = nRT \ln V$$

We write

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = nRT \ln V$$