Lecture 1
Phys 404, Spring 2011

Newton's laws of motion and the Schrodinger equation in quantum mechanics are not well suited to describe the macroscopic properties of common objects (e.g. a block of copper, a glass of water, etc.) at finite temperature. It is too cumbersome to use these equations to understand the behavior of a collection of Avagodro's number ($N_A \sim 6.02\ 10^{23}$) of particles. We need another approach.

Thermodynamics describes the macroscopic properties of a system. Macroscopic properties are things that you can feel with your hand, see with your eyes, etc. The laws of thermodynamics are empirical observations about macroscopic systems that cannot be proven from first principles. They are observations about the properties of a great number of individual objects acting together in a collective manner.

Statistical Mechanics starts from the quantum mechanical properties of individual particles and builds up a quantitative framework in which to understand the properties of a collection of a large number of identical particles. Eventually it produces predictions for the macroscopic thermodynamic properties of a system. Thermodynamics is a set of empirical statements about the macroscopic properties of such systems.

Thermodynamic Variables are defined as the properties that must be specified in order to duplicate the macroscopic state of a system uniquely. Note that there are many microscopic states of the system that have essentially the same macroscopic state, and that thermodynamics does not concern itself with these microscopic issues. The thermodynamic state of a system can be completely specified (as far as macroscopic thermodynamics is concerned) by specifying the values of a minimal set of state variables. If the system starts from a point in this state space (e.g. $\{x_1^0, x_2^0, \ldots, x_c^0\}$) and goes on an excursion in state space, but then returns to the same point, the system will have macroscopic properties that are indistinguishable from those that it started with.

There are two types of state variables; intensive and extensive. Extensive thermodynamic variables depend on how much "stuff" is present. Examples include mass (m), volume (V), entropy (σ) and free energy (F). If you have a system with thermodynamic variable x, consider what happens when the system is cut in half. If the variable x associated with each piece is half of the original value then it is an extensive thermodynamic variable. Intensive variables do not depend on the extent of the system. Examples include temperature (T, later τ), pressure (P) and chemical potential (μ). Thermodynamic variables frequently appear as "conjugate pairs" in expressions for free energy. One variable is extensive while the other is intensive. Examples include temperature and entropy, pressure and volume, and chemical potential and particle number.

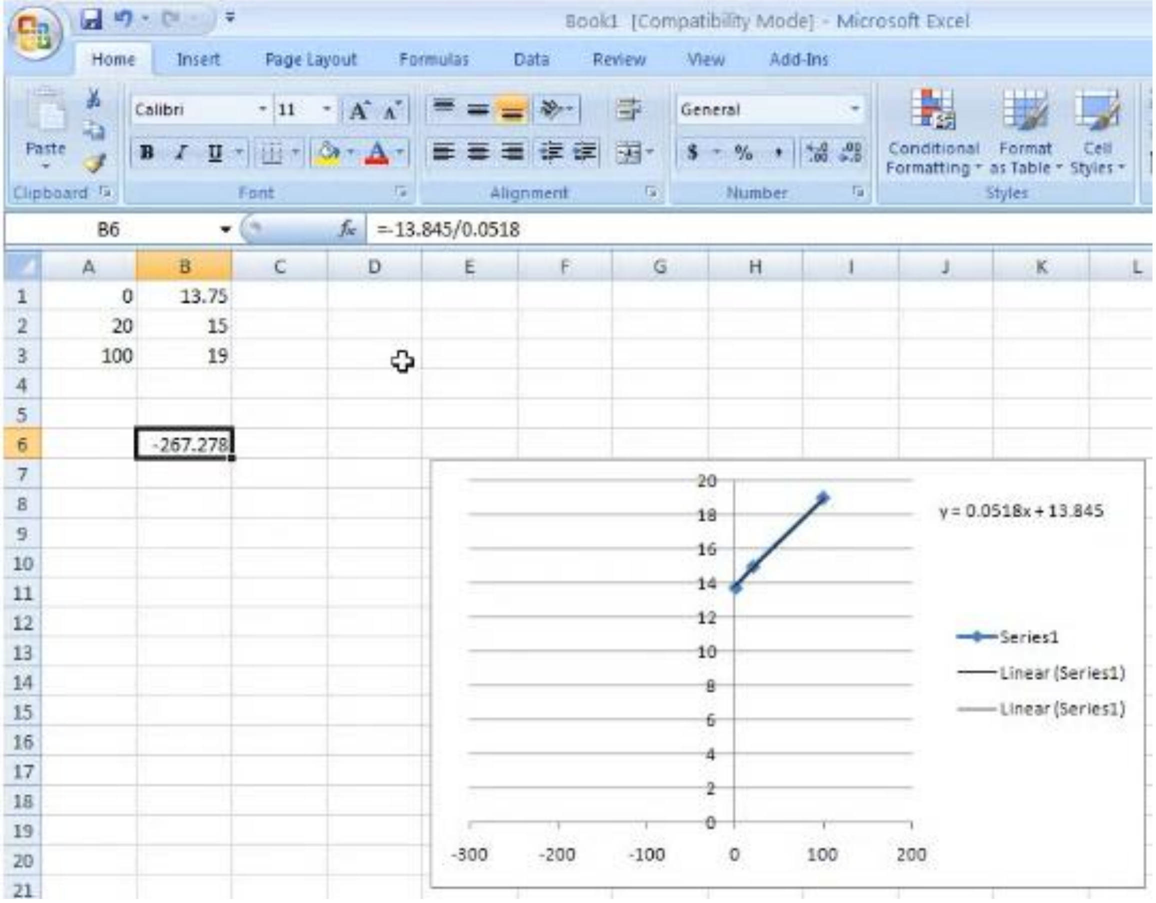
The 0^2 Law of Thermodynamics says that an isolated system will eventually come to thermodynamic equilibrium. Thermodynamic equilibrium is achieved when 3 other equilibria are achieved:

a) Thermal Equilibrium. Two objects in thermal contact (meaning that they are exchanging energy) will eventually adopt a common value for a thermodynamic quantity known as temperature.
b) Mechanical Equilibrium. Two systems in mechanical contact (meaning that they can exchange volume) will eventually adopt a common value for a thermodynamic quantity known as pressure.
c) Diffusive Equilibrium. Two systems in diffusive contact (meaning that they can exchange particles) will eventually adopt a common value for a thermodynamic quantity known as chemical potential.

The 0^{th} Law of Thermodynamics says that there exists a parameter whose value is common to two or more systems in thermodynamic equilibrium with each other. This is the concept of temperature. We demonstrated this in class with demo I2-27 Thermal Equilibrium between Cu and Al.

The ideal gas is a low density gas (this precise condition will be derived later) that has 4 thermodynamic state variables; pressure (P, measured in Pascals or N/m^2), volume (V, measured in m^3), number of particles (N, typically on the order of Avogadro's number $N_A = 6.02\ 10^{23}$) and temperature (T, measured in Kelvin). There is an equation of state relating these thermodynamic quantities (which we will derive from statistical mechanics, along with corrections) called the ideal gas law: $P\ V = N\ k_B\ T$, where the fudge factor is called Boltzmann's constant, $k_B = 1.381\ 10^{-23}$ J/K. The equation of state is a constraint on the possible values of the thermodynamic variables of the system.

Using statistical mechanics we will later show that the average kinetic energy of a monatomic ideal gas is simply related to its temperature as $\overline{\frac{1}{2}mv^2} = \frac{3}{2}k_BT$, where m is the mass of the atom. We know that kinetic energy is bounded below by zero, therefore the temperature must also be bounded below by zero. Pressure is a convenient way to determine the temperature of an ideal gas since from the equation of state $P = \left(\frac{Nk_B}{V}\right)T$, and the quantity in brackets is a constant for a fixed volume and number of particles. Hence a measurement of pressure is indirectly a measurement of temperature, for an ideal gas. We exploited this property in demo I3-52 Constant Volume Gas Thermometer – Absolute Zero, where we extrapolated a series of pressure measurements taken at 0°C, 20°C and 100°C to the point where the pressure of the gas fell to zero. This turned out to be at a temperature of roughly -267°C (see graph below), which is quite close to the known value of -273.15°C, the absolute zero of temperature. We will use the Kelvin temperature scale that defines this point to be T = 0 K. The temperature in Kelvin is equal to that in Celsius plus 273.15.



B6 =-13.845/0.0518

	A	B
1	0	13.75
2	20	15
3	100	19
4		
5		
6		-267.278