**The Four Laws of Thermodynamics** There are four basic laws of thermodynamics that apply to any situation that meets the requirements of the specific laws. The laws start with the zeroth law and end with the third since the zeroth law was created later. **Zeroth Law of Thermodynamics**: "If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other." This law is rather self explanatory, but it can be represented in math as: if a=c and b=c , a=b (which is similar to the transitive property of equality). The zeroth law helps define the notion of temperature. **First law of thermodynamics**: "A change in the internal energy of a closed thermodynamic system is equal to the difference between the heat supplied to the system and the amount of work done by the system on its surroundings." This basically means that if a closed system receives more net heat than net work that it does, it would gain internal energy, and if the net work exceeds net heat intake, the closed system would lose energy (This can be represented in mathematics where i=change in internal energy, q=net heat intake, and w=net work as: i=q−w , and that means that when q>w , i>0 . In addition, i<0 when q<w , and i=0 when q=w .) One factor that supports this law is the Law of conservation of Energy. **Second Law of Thermodynamics**: "Heat cannot spontaneously flow from a colder location to a hotter location." This law explains entropy in that as the temperature of one object nears the temperature of another object, the amount of entropy increases, and this entropy must be decreased in order for work to be done. One example for this is a steam engine. As a steam engine is used, the metal and water in the steam engine will retain heat until the temperature of the metal and water is equivalent to the temperature of the fire that they are above. This waste heat can be removed by the usage of cooling water or another coolant, shutting the steam engine down, or any other cooling method, until it cools down to a fair temperature. **Third Law of Thermodynamics**: "The entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero, and as a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value." The importance of this law is that it proves that it is impossible for an object to reach absolute zero. The reason for this is that as an object reaches lower temperatures, the molecular/atomic process slow which decreases heat transfer while the amount of work done (In this case it is molecular in the form of heat transfer.) decreases in an asymptotic approach and exponential decay due to the First and Second Laws of Thermodynamics. One example of this is that if there was an object at absolute zero touching another object that is significantly warmer, the warmer object would lose temperature in ever decreasing amounts as there is less energy for the warmer object to give to the colder object (The colder object also gains energy due to the Law of Conservation of Energy and would have less of a potential to receive energy.). That allows both of the objects' temperatures to be tracked using an exponential decay graph for the warmer object and a graph of exponential growth for the colder object (with temperature as the y-axis and time as the x-axis), and both graphs would have an asymptotic approach toward a certain temperature value (This situation is like constantly dividing 1,000,000 in half in an attempt to reach zero.). That means that an object can never be at absolute zero unless an object can be at a temperature lower than that (which is impossible due to the definition of absolute zero). This also implies that two objects that start out at different temperatures will never reach exactly equal temperatures, but measurement tools don't necessarily have the accuracy to detect those small differences. In addition, the way heat transfers between objects is dependent on the composition of the objects that the heat is going between. **The Many Gas Laws** For more detailed information, see Chem Lab/Gas Laws Gay-Lussac’s Law: states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature. >PT=C , therefore P1T1=P2T2=P3T3... Boyle’s Law: states that the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure when the temperature and mass are constant. PV=C , therefore P1V1=P2V2=P3V3... Charles’ Law: states that the volume of a given amount of gas held at constant pressure is directly proportional to the Kelvin temperature. VT=C , therefore V1T1=V2T2=V3T3... Avogadro’s Law: Gives the relationship between volume and amount of gas when pressure and temperature are held constant Hess’ Law: states that the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps. This is also known as the law of constant heat summation. Le Châtelier's Principle: If a change is made to a system, then the system will react in such a way so as to absorb the force causing the change. Ideal Gas Law: A combination of all the gas laws, applicable to any gas. Relates temperature, volume, and pressure to each other. A further derivation of this law is called van der Waals' equation. PV=nRT OR PV=nKT van der Waals' Equation: As there are attractive forces between molecules, the pressure is lower than the ideal value. To account for this the pressure term is augmented by an attractive force term a/V2. Likewise, real molecules have a volume. The volume of the molecules is represented by the term b. The term b is a function of a spherical diameter d known as the van der Waals diameter. The van der Waals’ equation accounts for these inaccuracies. (P+n2aV2)(V−nb)=nRT Heat Theories There are two theories of heat, one obsolete, one valid. Caloric Theory of Heat The caloric theory of heat is an obsolete theory stating that heat is a fluid that flows from hot to cold substances. There are six assumptions of this caloric theory. 1. Heat is a fluid that flows from hot to cold substances 2. Heat has a strong attraction to matter, which can hold a lot of heat. 3. Heat is conserved. 4. Sensible heat causes an increase in the temperature of a system 5. Latent heat combines with particles in matter, which causes substances to melt or boil. 6. Heat is weightless. This is the ONLY true assumption. Antoine Lavoisier came up with the caloric heat theory in the 1770’s. Heat was called “caloric”, and cold was called “frigoric”, or lack of caloric. Kinetic Theory of Heat The kinetic theory is a valid theory that states that matter is comprised of molecules in constant, random motion. It comprises of the following assumptions: 1. The gas consists of very small particles, so the average distance between the gas particles is comparatively large. 2. These particles have the same mass. 3. The number of molecules is so large that statistical treatment can be applied. 4. These molecules are in constant, random, and rapid motion. 5. The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic. This means the molecules are considered to be perfectly spherical in shape and elastic in nature. 6. Except during collisions, the interactions among molecules are negligible. (That is, they exert no forces on one another.) This implies the dynamics of the molecules can be treated classically. This means the equations of motion of the molecules are time-reversible. "The average kinetic energy of the gas particles is proportional to the temperature of the system and depends only on it." 7. The time during collision of molecule with the container's wall is negligible as compared to the time between successive collisions. All the gas laws are derivable by the kinetic theory of heat. The first version of the kinetic theory of heat was put out by August Krönig in 1856. He made a simple gas-kinetic model that only considered translational movement. A later model was conceived by James Clerk Maxwell. In all technicalities, he is the father of the kinetic theory. Carnot Cycle One of the important things that helped with the creation of the Four Laws of Thermodynamics is the Carnot Cycle, a heat engine with the theoretical maximum efficiency. A picture of the Carnot Cycle is shown below. The Carnot Cycle In the above image, Q stands for heat, and W stands for work. What is happening in the picture is that heat is being transferred from the warmer red square (at temperature T1 ) to the neutral white square where some of the heat remains in the form of work. The rest of the heat moves to the colder blue square (at temperature T2 ). Due to the Law of Conservation of Energy (which has the implication that energy can't be created or destroyed and is sometimes stated as that), the amount of work done in the middle square must be equivalent to the heat transferred from the red square to the white square minus the heat transferred from the white square to the blue square. That can be mathematically represented as: W=Q1−Q2 . In addition, the amount of heat transferred and the amount of work done are proportional to temperature by the equation W=Q1(1−T2T1) . This makes logical sense in that as the temperatures of two objects near each other, the potential and amount of heat transfer decreases which would also decrease the amount of work done on the white square due to the Second and Third Laws of Thermodynamics. In addition, that equation can be altered so that you can find Q2 . The new equation would be: Q2=T2T1Q1 . That can be further altered to show the proportion between temperature difference and heat transfer, and the equation for that is: Q2Q1=T2T1 . That can then be written as 0=T2T1−Q2Q1 , and then it can be changed to 0=Q1T1−Q2T2 . Since Q2 is a measure of heat output from the white square, it can be written as a negative number by using the white square as a reference point. That means that the equation can be turned into the inequality Q1T1+Q2T2>0 or the equality S=Q1T1+Q2T2 (where S equals entropy). The function of that equation and the inequality is entropy since it represents the part that is not work in the equation W=Q1−Q2 , because it is based off of the equation Q2=T2T1Q1 . If you go back to the equation Q2Q1=T2T1 , you can alter it so that you can find any of those variables. The equations to do that are as follows: Q2=T2T1Q1 , T1=T2Q2/Q1 , Q1=Q2T2/T1 , T2=Q2Q1T1 Importance Studies of the Carnot Cycle have caused the creation of the First and Second Laws of Thermodynamics. If you look at the equation W=Q1−Q2 , you can see that it shows heat flow in and out of the white square in the picture, and work in thermodynamics refers to energy transferred to a system that changes the system. This was restated later as the **First** **Law** of **Thermodynamics**. If you look at the equation for finding entropy, Q1T1+Q2T2=S , and apply it to the Carnot Cycle while including the progression of time, you can see that as the Carnot Cycle goes on for longer periods of time, T1 decreases towards T2 which increases. In addition, Q1 and Q2 would decrease. This became the Second Law of Thermodynamics. Examples of Usage The equations in the Carnot Cycle can be used to determine the values for all 6 of the variables so long as you have the value for one temperature variable, one heat variable, and one other variable that is not the value for entropy. Lets suppose in the Carnot Cycle that W is 10 joules, Q1 is 40 joules, and T1 is 400 degrees Kelvin. We can make a table of our information which is: Information about variables in the Carnot Cycle variable W (work) Q1 (heat) Q2 (heat) T1 (temperature) T2 (temperature) S (entropy) value 10 Joules 40 Joules 400 degrees Kelvin From there we can use formulas to find out the rest of the variables. The equation: Q1=W+Q2 can be used to find the value for Q2 . The equation with values for the variables is: 40=10+Q2 , and that can be simplified to 30=Q2 . The new table would therefore be: Information about variables in the Carnot Cycle variable W (work) Q1 (heat) Q2 (heat) T1[ (temperature) T2 (temperature) S (entropy) value 10 Joules 40 Joules 30 Joules 400 degrees Kelvin Then, the equation: Q2=T2T1Q1 can be used to find the value for T2 . The equation with values for the variables is: 30=40T2400 . The equation can then be simplified to: 0.75=T2400 , and that can be simplified to: 300=T2 . This answer can be verified by checking it with the equation: W=1−T2T1Q1 , and the equation with values for the variables is: 10=401−300400 . That can be simplified to 10=40(1−0.75) which is equal to 10=0.25⋅40 . That is equal to 10=10 which means that 225=T2 . Therefore, the new table is: Information about variables in the Carnot Cycle variable W (work) Q1 (heat) Q2 (heat) T1 (temperature) T2 (temperature) S (entropy) value 10 Joules 40 Joules 30 Joules 400 degrees Kelvin 300 degrees Kelvin Finally, the equation S=Q1T1+Q2T2 can be used to find the value for S, and the equation with values for the variables is: S=40400+30300 . That can be simplified toS=0.1+0.1 , which is equivalent to S=0.2 . Therefore all of the values for the variables in a table is: Information about variables in the Carnot Cycle variable W (work) Q1 (heat) Q2 (heat) T1 (temperature) T2 (temperature) S (entropy) value 10 Joules 40 Joules 30 Joules 400 degrees Kelvin 300 degrees Kelvin 0.2 Joules per Kelvin Maxwell's Daemon Maxwell's Daemon is an imaginary creature that the mathematician James Clerck Maxwell created to contradict the second law of thermodynamics. Suppose that you have a box filled with a gas at some temperature. This means that the average speed of the molecules is a certain amount depending on the temperature. Some of the molecules will be going faster than average and some will be going slower than average. Suppose that a partition is placed across the middle of the box separating the two sides into left and right. Both sides of the box are now filled with the gas at the same temperature. Maxwell imagined a molecule-sized trap door in the partition with his minuscule creature poised at the door who is observing the molecules. When a faster than average molecule approaches the door he makes certain that it ends up on the left side (by opening the tiny door if it's coming from the right) and when a slower than average molecule approaches the door he makes sure that it ends up on the right side. So after these operations, he ends up with a box in which all the faster than average gas molecules are in the left side and all the slower than average ones are in the right side. So the box is hot on the left and cold on the right. Then one can use this separation of temperature to run a heat engine by allowing the heat to flow from the hot side to the cold side. Another possible action of the demon is that he can observe the molecules and only open the door if a molecule is approaching the trap door from the right. This would result in all the molecules ending up on the left side. Again this setup can be used to run an engine. This time one could place a piston in the partition and allow the gas to flow into the piston chamber thereby pushing a rod and producing useful mechanical work. This imaginary situation seemed to contradict the second law of thermodynamics. To explain the paradox scientists point out that to realize such a possibility the demon would still need to use energy to observe the molecules (in the form of photons for example). And the demon itself (plus the trap door mechanism) would gain entropy from the gas as it moved the trap door. Thus the total entropy of the system still increases. The demon is trying to create more useful energy from the system than there was originally. Equivalently he was decreasing the randomness of the system (by ordering the molecules according to a certain rule) which is decreasing the entropy. No such violation of the second law of thermodynamics has ever been found. Joule's Laws Joule's Laws are two laws created by James Prescott Joule that describe the heat dissipation of components in an electrical circuit and how the internal energy of an ideal gas relates to temperature, pressure, and volume. Joule's First Law: Q=tRI2 In that equation, Q is the heat dissipation of the component while I is the electrical current through the component, and R is the electrical resistance of the component while t is the time that the electricity ran through the component. If the time is measured in seconds (s is oftentimes used as the variable for seconds.), the variable Q will represent an answer in Joules (j ). Joule's first Law provides one way in which Electrical Engineering and Thermodynamics relate. In Electrical Engineering, the equation for finding the power in a circuit/component is: P=VI (where P is power in watts, V is volts, and I is current or amperes.) which can be written as P=RI2 (where R is the electrical resistance). That means that: J=Ps (W can also be used in place of P .). This can be further proven by one definition of a volt (V=JC where C represents Coulombs). One Ampere (amp) is equivalent to one Coulomb per second which means that the equation can be changed to: V=JIs or J=VIs which is equal to J=Ps . The main importance of Joule's First Law is that it allows people to calculate the heat dissipation of electrical circuits/components. Joule's Second Law: "The internal energy of an ideal gas is independent of its volume and pressure, depending only on its temperature." Note: The wording of the laws is the specific wording used in the Wikipedia article for Joule's Laws. Important Concepts Thermodynamic Systems A thermodynamic system is a region of the Universe with specific boundaries that is analyzed using thermodynamic theories, principles, and laws. Everything that is not part of a thermodynamic system is said to be in the surroundings. The system and surroundings are separated by a boundary that may be fixed (always stays in the same spot), movable (location can change), imaginary (There is nothing separating the surroundings and the system, and the boundary is merely a designated space.), or real (The boundary is a physical object.) There are five types of thermodynamic system, and each type allows different things to pass through the boundary. The types are: Open System: In open systems, matter, heat, and work can cross the boundary to enter or exit the system. The First Law of Thermodynamics when applied to an open system is (quoting from Wikipedia): "the increase in the internal energy of a system is equal to the amount of energy added to the system by matter flowing in and by heating, minus the amount lost by matter flowing out and in the form of work done by the system." Closed System: In a closed system, heat and work can cross the boundary, but matter can't cross the boundary. In addition, there is a type of boundary that may be in a closed system that heat can't cross, adiabatic, and one that work can't cross, rigid. Isolated system: In an isolated system, neither matter, heat, or work can cross the boundary. Therefore, differences in thermal energy will typically lessen until the system reaches thermodynamic equilibrium. Diathermic Systems: In a diathermic system, heat can cross the boundary, but nothing else. Adiabatic Systems: In an adiabatic system, heat may not cross the boundary, but everything else can. Thermodynamic Processes An isobaric process occurs at constant pressure. An example would be to have a movable piston in a cylinder, so that the pressure inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere. In other words, the system is dynamically connected, by a movable boundary, to a constant-pressure reservoir. An isochoric process is one in which the volume is held constant, meaning that the work done by the system will be zero. It follows that, for the simple system of two dimensions, any heat energy transferred to the system externally will be absorbed as internal energy. An example would be to place a closed tin can containing only air into a fire. To a first approximation, the can will not expand, and the only change will be that the gas gains internal energy, as evidenced by its increase in temperature and pressure. We may say that the system is dynamically insulated, by a rigid boundary, from the environment. An isochoric process is also known as an isometric process or an isovolumetric process. An isothermal process occurs at a constant temperature. An example would be to have a system immersed in a large constant-temperature bath. Any work energy performed by the system will be lost to the bath, but its temperature will remain constant. In other words, the system is thermally connected, by a thermally conductive boundary to a constant-temperature reservoir. An adiabatic process is a process in which there is no energy added or subtracted from the system by heating or cooling. For a reversible process, this is identical to an isentropic process. We may say that the system is thermally insulated from its environment and that its boundary is a thermal insulator. If a system has an entropy which has not yet reached its maximum equilibrium value, the entropy will increase even though the system is thermally insulated. Under certain conditions, two states of a system may be considered adiabatically accessible. An isentropic process occurs at constant entropy. For a reversible process, this is identical to an adiabatic process. If a system has an entropy value which has not yet reached its maximum equilibrium value, a process of cooling may be required to maintain that value of entropy. Branches of Thermodynamics There are several branches of thermodynamics, and each branch is about a specific aspect of thermodynamics. Classical Thermodynamics This is thermodynamics on a large or macroscopic scale. This branch of thermodynamics is used to model states and processes that are based on properties that can be measured, defined, and examined in a laboratory. These models include models based on the Four Laws of Thermodynamics and include: energy, mass, work, and heat exchanges. Statistical Thermodynamics This is thermodynamics on the molecular/atomic scale. This branch of thermodynamics explains how microscopic events, properties, and interactions influence Classical Thermodynamics. Chemical Thermodynamics This branch of thermodynamics is about how energy, within the subject of thermodynamics, influences chemicals and chemical reactions. Equilibrium Thermodynamics This branch of thermodynamics is about how matter and energy in a system change as the system approaches thermal equilibrium. One main goal in Equilibrium Thermodynamics is to figure out what a system will be like when it reaches thermodynamic equilibrium if you know the starting parameters for the system and the laws/forces that will act upon it. Non-Equilibrium Thermodynamics This branch of thermodynamics is the study of systems that aren't in thermal equilibrium, and many of the laws/theories/concepts are more general than the ones in Equilibrium Thermodynamics.