Exploring Thermodynamics

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I. Thermo-Physics

1. Introduction. Thermodynamics is the study of energy change. It is concerned with the equilibrium states of a system, and not by the path with which the system arrives at these states. Yet, once a specific material is selected for the system, how that materials state variables (pressure, volume, temperature, etc.) relate to its equilibrium states, and the work done to move between these states, are also of interest. State variable relationships and work-energy relationships, in some cases, depend on specific processes undergone by the system (path functions), and in other cases depend only on the initial and final states of the system (point functions, or state functions), not on how the system arrives at its final state.

The seeds of thermodynamics, in this authors' opinion, were planted by the engineers first concerned with the dream of a heat engine. The dream was to create a device, which would in one cycle, consume a quantity of heat and produce an equal quantity of work. Today, although we understand that it is impossible to produce an EQUAL amount of work, the study of this "heat to work" energy conversion creates the basis of the science of classical thermodynamics.

It is possible to derive the concepts of thermodynamics entirely by sound mathematical reasoning, and many authors do so. Here, we will attempt to include physical models, both MACRO and MICRO, to impart a deeper understanding of the topic.

We start with a brief discussion of temperature

2. Temperature. One can hardly hear the word thermodynamics with out seeing a thermometer in one's mind. Truly, this device is fundamental in the experimental world of heat. But rarely do we consider what the device is actually measuring. Here, we will explore that question.

The name of Gabriel Fahrenheit (1686-1736) is associated with temperature in the minds of most people. Fahrenheit, a medical doctor, explored the correlation between a patients' state of health and the value of the temperature. There was no well-established temperature scale at that time, and Fahrenheit was attempting to discover an integer numerical scale, which would correlate to the various afflictions of the human body. Early in his experiments, Fahrenheit saw the need for the establishment of reputable temperature standards, which could be used to calibrate his thermometer. Mouth of a healthy male, the freezing point of water, the freezing point of a saturated ice-salt bath (still zero F today), and the boiling point of water were among some of the reference points he explored. The

numerical values on his thermometer underwent many revisions over the years he experimented and these numerical values have NO BASIS in science. They were merely assigned.

Carolus Linnaeus (1707-1778), a professor of physics, astronomy, and botany at the University of Upsula, is in fact the inventor of the temperature scale that uses as its temperature standards, the freezing point and boiling point of pure water, and subdivides that range into 100%. Zero was assigned to freezing water and 100 assigned to boiling water. The scale was named *Centigrade* (indicating "centi" or one hundred graduations between the two references). It was around 1968, when System International mistakenly renamed the centigrade unit as Celsius. Celsius was an astronomer at the same university. It is assumed that because of the roman numerical **C** on the scale, taken for the letter C, that Celsius was erroneously credited with the invention of the scale. It is important to understand that like the Fahrenheit scale, the number values on the "Celsius |Linnaeus" scale have no basis in science. They were assigned.

It was J. Charles (1748-1823) whom was to discover the "absolute" scale although he would not realize the true impact of that discovery. Charles was experimenting to determine the temperature vs. volume relationship of a gas. He discovered through experiment that, for all other variables held constant, the volume occupied by a gas was proportional to the temperature of a gas. The relationship was linear. To mathematically express this relationship, the slope intercept form of a straight line (V= mT + b) may be used. This equation was cumbersome to Charles since one cannot do ratio and proportion when there is an additive constant (b). Thus, great was his surprise when he discovered that for ALL gasses, when their volume temperature relationships are extrapolated toward lower temperatures, they have the SAME horizontal (T) intercept. On the centigrade scale, this value is -273 C. Charles and others then adopted a new (absolute) scale which placed its zero at -273 C for the sole purpose of removing the additive constant (b=0) from the linear relationship. Charles would not understand the full significance of this discovery. The discovery would remain for Lord Kelvin, after which the scale is named.

What then does a thermometer measure? Consider a thermometer made with a small hollow glass bulb (the probe) connected by a rigid hose to a U-tube manometer containing a liquid inside (the scale readout). The remainder of the apparatus is filled with a gas. We put the probe in a gas environment to measure its temperature. The observed effect is a shift in the liquid inside the manometer. We measure the height difference and assign it a temperature value. Let us now examine this situation from a micro point of view.

The gas for which we seek its temperature consists of many molecules moving with random speeds and in random directions. Some of these molecules strike our thermometer probe. In doing so, the collision transfers kinetic energy of the molecules center of mass to the probe. The probe accepts this energy by

increasing the amplitude of vibration of the molecules from which it is made. None of the incident gas molecules' rotational energy however is transferred to the probe since that would require them to apply a torque on the probe molecules and angularly displace them, changing their rotational speeds. The probe molecules are rigidly bound in solid form. The now increased energy contained in the amplitude of vibration in the probe molecules is delivered to the gas contained within the probe by the same mechanism discussed. Thus, the kinetic energy of the gas within the thermometer is increased. These internal gas molecules, now moving faster, impact the liquid surface of the manometer and their change in momentum supplies an increased force to the liquid that causes the liquid height difference to increase. We call it temperature. It would appear that what we have measured is *related to the average translational kinetic energy of the particles* of gas. This is what the thermometer measures: this is temperature. This definition has a basis in science.

From the above perspective, the lowest temperature that one may conceive would occur when all the particles are at a relative speed of zero with respect to the thermometer; that is when the average kinetic energy of all the particles is zero. This is absolute zero, -273 C, or Zero Kelvin as we call it today. Lord Kelvin is accredited with the explanation.

Only the zero point on the Kelvin scale has basis in science, the remainder of the scale is simply assigned.

3. Work. Work is defined in physics as the accomplishment of a task. Mathematically, it is computed by
$$Work = \int \vec{F} \bullet d\vec{x}$$
It is the scalar product of a force times a distance. It is learned in physics that work is a path function since the value of work depends on how the force varies along the displacement path. In a beginning physics class, the student is likely to associate work with a change in kinetic energy. Formally, work done by the net force on an object of constant mass is equal to the change in kinetic energy of the objects center of mass.
$$Work_{ByFnet} = \Delta KE_{cm}$$
From this fundamental relationship, the student first encounters the point function of kinetic energy.

In thermodynamics however, especially when analyzing a heat engine, the work done by an expanding gas is of more general concern. This work, often called *expansion work*, is better represented in terms of pressure and volume rather than in terms of force and displacement.

Consider a gas confined in a cylinder with a movable piston. Let the piston displace to the right by an increment dx against the external force $F_{external}$.
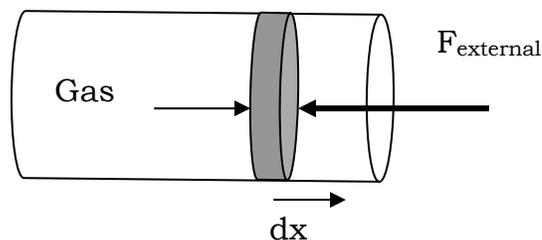
Figure 1. Gas contained in a cylinder with movable piston.

The expansion work is given by:

$$W = \int \vec{F}_{ex} \bullet d\vec{x} = -\int P_{ex} A dx = -\int P_{ex} dV$$

The minus sign is necessary because the direction of dx is opposite that of $F_{external}$.

The above result is often adapted further by restricting the expansion to a reversible *equilibrium* expansion. That is, the pressure of the gas contained within the cylinder is assumed nearly equal to the external pressure opposing the expansion, $P_{gas} = -P_{ex}$. With this assumption, the Expansion Work becomes,

$$W = \int P_{gas} dV$$

The minus sign is lost since the force of the gas is in the direction of the increase in volume, dV.

It should be seen that although the above discussion was based on an expanding gas, no equation of state was incorporated. The work relationship is thus valid for any expanding material; solid, liquid, or gas.

It is often useful to plot pressure as a function of volume to visualize a given process. The area bounded under such a plot is the work done in that process.
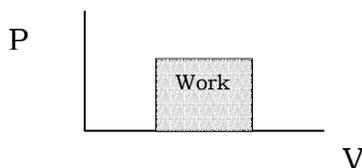

Figure 2. Constant pressure process showing expansion work as the area under the P vs. V graph.

For a process of constant pressure, the pressure can be removed from the integral as constant and the resulting work function becomes,

$$W = P_{gas} \Delta V$$

4. Heat. It was originally said, "Heat is *that* which can be made to flow as a result of a temperature difference alone". At that time in history, heat was

misunderstood as being a fluid, due to the fact that its "flow" was describable with equations derived for fluid flow. In the early 1800's, it was found by Count Rumford (a.k.a. Benjamin Thompson, 1753-1814) that heat and work were related. Heat was not a fluid but a form of work. Experimental results showed that work could be converted into an equal amount of heat (although for the reverse conversion, this is not possible).   The terminology of "flow" is however often retained.   Today, we may expand this statement to: _heat is that fraction of the total microscopic energy of a collection of particles, which can be made to transfer as a result of a temperature difference alone._   This _flow_ or _transfer_ does not necessarily imply that matter must displace from one point to another. It is Energy that transfers. Heat is a form of work; it is MICRO Work. Objects do not "have" heat but rather heat enters or leaves an object. Heat implies a process; it is not a state of being.

Heat is often associated with temperature change using the relationship,
$$Q = n\, c\Delta T$$

where n is the amount of material and c is the specific heat capacity for the material. (It should be pointed out here that while the relationship $Q = n\, c\Delta T$ is valid for many processes, it is not necessary for a system to change temperature in order to accept or reject heat.)

The specific heat capacity, or "specific heat" (c) is an experimentally measured constant. In both the calorie and BTU systems of energy measurement, the specific heat of water is assigned the value of unity.

$$C_{H_2O, liq @ 15C} \equiv 1\frac{cal}{gram \bullet C} \equiv 1\frac{BTU}{Lb \bullet F}$$

Specific heat values for other materials are found from experiment similar to the following.

Example. Consider a metal object of mass 20 grams and initially at 100C. This object is placed in a well-insulated container (of negligible mass and small specific heat) containing 100 grams of liquid water at 25 C. The mixture is allowed to reach a new equilibrium temperature, measured at 28 C.   We apply conservation of heat energy to the process Heat lost (-) by the hot metal must equal the heat gained (+) by the cooler water.

$$Q_{metal} + Q_{water} = 0$$
$$(n\, c\, \Delta T)_{metal} + (n\, c\, \Delta T)_{water} = 0$$
$$(20\text{ g})\, c_{metal}(28 - 100)C + (100\text{g})\,(1\frac{cal}{g\, C})(28 - 25)C = 0$$

C_{metal}=.208 cal/g C

5. Internal Energy. If objects do not "have" heat, then what do they have? It is called Internal Energy (or thermal energy). *Internal Energy is the total MICRO energy (kinetic, rotational, vibrational, etc.) of a collection of particles*; the *ability* of those particles to do work by virtue of their microscopic speeds and configurations. Internal energy is what a system "has", and is what changes when heat only is added to an object. This total micro energy is never computed; only changes in Internal Energy are computed. It will be shown that Internal Energy is a condition of state, a point function, and does not depend on the path used to arrive at that state.

6. First Law of Thermodynamics. The first law of thermodynamics is an accounting relationship between work (W), heat (Q), and a systems change in internal energy (ΔU). In business accounting, there are many ways that a business may choose to organize its various accounts. This is also true in the science of thermodynamics. Chemists, Physicists, and various engineering fields have used various methods to classify these quantities and relationships. So much so that without a detailed breakdown of the symbols and sign convention, it becomes difficult for people well versed in thermodynamics to communicate. Attempts have been made to standardize symbols and sign convention. These attempts for the most part have resulted in further divergence and confusion. Here, the more traditional sign conventions and symbols will be used. We will adopt the sign convention, which was used by the engineers who had the dream of the heat engine. Heat will be Positive when entering the system. Work will be positive when the system does work on its surroundings.
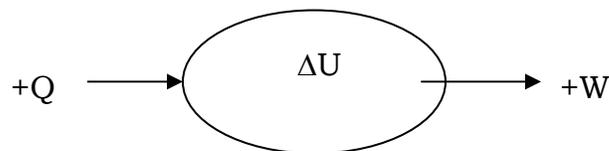

Figure 3. Schematic representation of the first law of thermodynamics.

Consider a system of constant mass. We wish to put heat into this system (positive) and to extract useful work out of this system (also positive).

The First Law of Thermodynamics becomes:

$$\Delta U = Q - W$$

$$dU = dq - dw$$

The heat into the system, minus the work out of the system, equals the change in internal energy of the system. This is an accounting principle. The first law does not dictate that a process is possible, it only keeps track of the work, heat, and energy changes.

It is important to remind ourselves that both Q and W are path functions. Their substitution will depend on the details of the process under consideration. The change in Internal Energy on the other hand, is a point function. **ΔU** depends only on the initial and final states and not on the path or process that connects them. This statement is verified in a later section.

7. The Gas Equation of State. To realize further relationships for processes, which accept heat and produce work, an equation relating the state variables of our material must be acquired. <u>In the discussions to follow, we will assume that our material is a gas.</u> This choice is made because the state equation for a gas is mathematically simpler than that of solids and liquids. We will adopt the Ideal Gas Law as our equation of state.

The ideal gas law is given by:

$$PV = nRT$$

where:

P is the absolute pressure of the gas,
V is the volume of the container holding the gas molecules,
n is the number of moles of gas molecules,
R is the universal gas constant {8.314 J/(mol K) , .08205 (liter atm)/(mol K), etc},
T is the absolute Kelvin temperature.

The origin of the ideal gas law lies in the empirical studies of Boyle, Charles, and Gay-Lussac. Their experiments involved holding all but two quantities constant, and seeing how the remaining two variables were related.

The ideal gas law defines a surface in P, V, T space. An ideal gas can only exist on this surface. The following figure illustrates this surface.
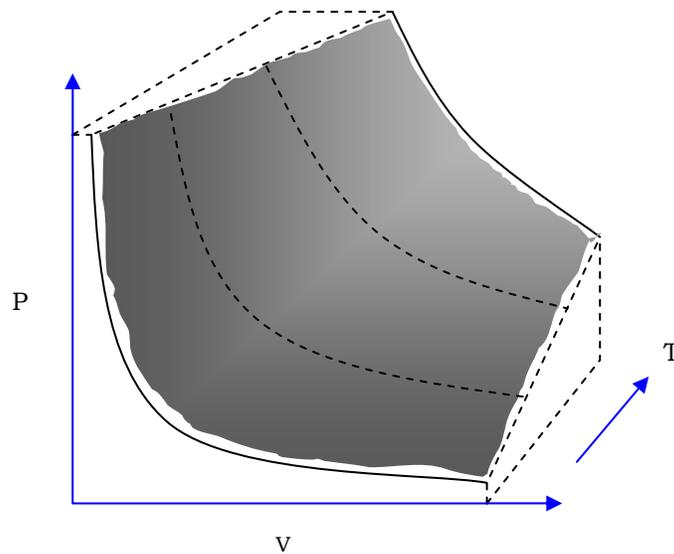
Figure 4. Illustration of the surface defined by the ideal gas law.
Shown are dashed lines of constant temperature.

The properties of an "ideal gas" are:
- That it consists of identical particles in random motion.
- That there are a large number of particles.
- The volume of a particle is ZERO.
- No external force acts on the collection of particles other than the force exerted by the walls of the container.
- F=ma is obeyed, collisions are elastic, momentum is conserved, and the time of the collision is short.
- The gas is in EQUILIBRIUM. As such, the statistical quantities of pressure and temperature are well defined in the volume region of concern.

Reviewing the above properties, it would seem that this list is restrictive to the extent that it would be impossible to find a gas satisfying these criteria. "No net force…" implies that we may not use the ideal gas law in a gravitational field! As it turns out, scientists and engineers violate many of the above properties on a regular basis and the ideal gas law is still an excellent model of the behavior of the gas. This excellent modeling is due to the fact that the number of molecules involved in the process is so very large, that if thousands of molecules misbehave, they will represent only a tiny fraction of the total number of molecules. However, as the density of the gas becomes larger, the property demanding the volume of the particle be zero creates a significant misbehavior since the true volume of the gas molecules is significant when compared to the volume of the container.

On occasion, it is useful to introduce the gas law using the quantities density and molecular weight (mass). This is easily done with a few substitutions as follows:

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$P = \frac{\rho}{mw} RT$$

This can be verified by unit analysis of the ratio n/V. In SI units,

$$\text{moles/m}^3 \ = \ \text{kg/m}^3 * \text{moles/kg} \ = \text{density} / mw$$

The ideal gas law will enable us to derive many different relationships for various processes.

8. Speed Distribution of an Ideal Gas. Although it is not necessary to know how the speeds within molecules vary in order to do thermodynamic calculations, it will help understand the statistical nature of many thermodynamic state variables such as temperature, pressure, and entropy. James Maxwell, in 1852, derived the probability distribution function for the speeds of gas molecules. This function has become known as *Maxwell's speed distribution law.* It is:

$$n(v) / N = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 \exp\left(\frac{-Mv^2}{2RT} \right)$$

where:

M is the molecular mass (kg/mole),
R is the gas constant (8.314 j/mole K),
T is the Kelvin temperature,
v is the molecular speed (m/s),
n(v)/N, is the fraction of molecules per unit speed interval (having the units of $1/\Delta v$), in the interval between v and v+dv.

The product, n(v)/N * dv, is the fraction of molecules having speeds in the interval between v and v+dv.

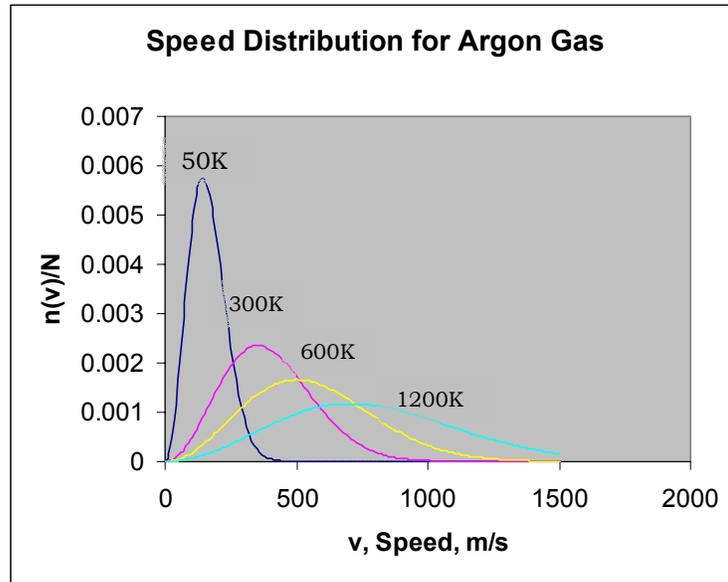This equation is plotted for Argon gas at various temperatures below.

Figure 5. Velocity distribution curves for argon at various temperatures.

One can see from the above figure how the peak of the speed distribution curve shifts toward larger velocity values as the temperature increases. Also notice how the spread of the speed distribution curve increases as the temperature increases. Finally, notice that even at low temperatures, a few gas particles are moving very fast.

9. Internal Energy of a Gas, a Micro View. Consider a mono-atomic gas confined in a cubical box. We wish to find an expression for the force exerted by the box wall on a particle. Starting in the horizontal dimension, looking only at the "x" component velocity of the particle we apply impulse momentum to the elastic collision of a particle with the right face of the box.
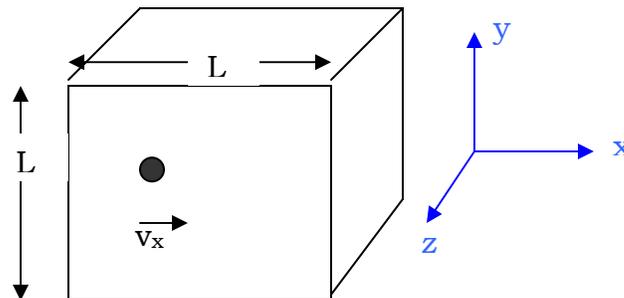

Figure 6. Schematic representation of a mono atomic particle moving in a box.

$$F_{ave}\Delta t = \Delta(mv_x)$$

Since the collision is elastic, the magnitude of the velocity of the particle does not change, only the direction of the velocity.

$$F_{ave}\Delta t = (-mv_x) - (mv_x) = -2mv_x$$

The force desired in the above equation is a steady state force; the average must be computed over a sufficiently long time, the time required to repeat the collision. In that amount of time, a particle of zero volume, moving at a speed v_x, will travel twice the length of the box.

$$\Delta t = \frac{2L}{v_x}$$

Substituting, we have

$$F_{ave} \frac{2L}{v_x} = -2mv_x$$

$$F_{ave} = -m \frac{v_x^2}{L}$$

This is the average force on a particle.

We now assert that the average force on the box wall is equal the sum of all the collision forces over that period, and in the opposite direction. For N particles, the force on the box wall becomes,

$$F_{ave} = \frac{m}{L} \sum_{i=1}^{N} (v_x^2)_i$$

If N is quite large, a number of "on the average" assumptions can be made. Since there are no external forces on the particles (other than the box wall), it is "on the average" true that v_x, v_y, and v_z , are all about the same in value. The velocity of a particle can now be found from its component velocities. We deduce the actual velocity of a particle as,

$$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$$

Substituting for v_x, we have

$$F_{ave} = \frac{m}{3L} \sum_{i=1}^{N} v_i^2$$

We now recall that the pressure on the box wall is this average force, divided by the box wall area L^2. Therefore, $F_{ave} = P\, L^2$. We substitute and solve for pressure.

$$P_{ave} = \frac{m}{3L^3} \sum_{i=1}^{N} v_i^2$$

We rearrange noting that L^3 is the volume of the box V.

$$PV = \frac{m}{3} \sum_{i=1}^{N} v_i^2$$

From the Ideal gas law, PV=nRT, we replace PV.

$$nRT = \frac{m}{3} \sum_{i=1}^{N} v_i^2$$

We now divide both sides by 2, and multiply by 3 to yield,

$$\frac{3}{2}nRT = \frac{m}{2}\sum_{i=1}^{N} v_i^2$$

Notice that the expression on the right side of the above equation is the TOTAL Kinetic Energy of the group of particles. Since a mono atomic gas can only have translational kinetic energy (zero moment of inertia), this also must represent the Internal Energy of that gas! For a mono atomic gas,

$$\Delta U = \frac{3}{2}nR\Delta T$$

This fact gives us one of the most powerful substitutions available.

The change in internal energy is only a function of change in temperature.

We may substitute for the change in internal energy of a specific process, the change in internal energy for *any other* process that would undergo the same change in temperature. We have developed this result for a mono atomic gas however the statement is true for any gas.

In general, for any Ideal gas, the change in internal energy can be represented with the below relationship,

$$\Delta U = \frac{\#}{2}nR\Delta T$$

where the symbol # represents the number of degrees of freedom for the gas; the number of ways the gas can store energy.
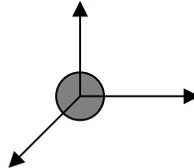

Figure 7. Schematic representation of a monoatomic particle
showing 3 KE degrees of freedom.

For a mono atomic gas (a point mass), there are 3 directions that can contain kinetic energy. #=3.
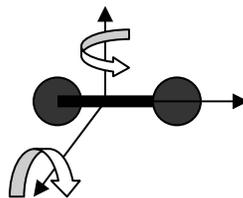

Figure 8. Schematic representation of a diatomic particle
showing 3 KE and 2 RE degrees of freedom.

For a diatomic gas (linear molecule), in addition to the three kinetic energy directions, the molecule exhibits a non-zero moment of inertia about two of these

directions and can therefore carry rotational energy about each axis as well. # = 3 translation + 2 rotation = 5.

   A polyatomic gas (non-linear molecule) would have # = 3 translation + 3 rotation = 6.

   These numbers: 3, 5, and 6 *do not* consider vibrational energy storage.

   10. Specific Heat Capacities of a Gas. Early in the study of heat and temperature, experimenters found that the heat added to a material was proportional to that objects change in temperature. The relationship,
$$Q = n\, c\Delta T$$
was found to relate the heat and the change in temperature. The variable n represents the amount of material (grams, pounds, moles, etc) and c is the materials specific heat capacity (or specific heat). It was thought at that time, the specific heat was a material constant. Through the years however, it was discovered that the specific heat was not at all constant, but a function of both temperature and process!

   Perhaps it would have been wise at this point to abandon the above equation in search of an equation of more general worth. Surely, many scientists and engineers explored just that thought, and did in fact arrive at an alternative way to represent heat, yet much specific heat data had, and is still collected for materials. The concept and associated equation seems to provide science with useful relationships; and as such, remains entrenched in the toolbox of thermodynamics.

   Let us now pose a thought experiment; consider two containers, which contain equal amounts of the same kind of gas at the same temperature. What is different about the two containers is that one container must remain at a constant volume while the other must remain at a constant pressure. We now add the same amount of heat to both containers and ask the question, "Will the temperature within each container change by the same amount?"

   One answer, considering the equation $Q = n\, c\Delta T$, would suggest that both containers should increase temperature by the same amount.

   Experimental evidence however shows that the constant volume container will have the larger increase in temperature. This fact can be explained using the first law of thermodynamics, $\Delta U = Q - W$.

The constant volume container is rigid. The change in volume is zero and thus so is the work. All heat entering the container goes to an increase in Internal Energy and thus an increase in temperature. In the constant pressure container, the gas expands and work is done. The resulting change in Internal Energy is less than in the constant volume container and thus the change in temperature is also less.

So why did Q = n c ΔT fail? The reason is that the value of the specific heat is different for each process! We now "patch" the failed relationship by defining two specific heat capacities for a single gas:

c_p, the specific heat for the constant pressure process.
c_v, the specific heat for the constant volume process.

Values for both these variables are tabled in many sources, including how they vary with temperature.

We now set out to explore the relationship between c_p and c_v.   Consider two containers, which contain equal amounts of the same kind of gas at the same temperature. What is different about the two containers is that one container must remain at a constant volume while the other must remain at a constant pressure.   In *this* experiment, we put differing amounts of heat into each container in an attempt to achieve *the same change in temperature.*

For the constant volume process, the work is zero and the first law becomes,
$$\Delta U = Q = nc_v\Delta T$$
For the constant pressure process, the work is W=PΔV and the first law becomes,
$$\Delta U = Q - W = nc_p\Delta T - P\Delta V$$
Since the change in temperature for both processes is the same, we equate the change in Internal Energy to obtain,
$$nc_v\Delta T = nc_p\Delta T - P\Delta V$$
For the constant pressure process, the ideal gas law evaluated between two states is,
$$P\Delta V = nR\Delta T$$

Substituting for PΔV, we arrive at
$$nc_v\Delta T = nc_p\Delta T - nR\Delta T$$
After cancellation, we arrive at the desired relationship,

$$R = c_p - c_v$$

This relationship (for a gas) is in excellent agreement with experimental results.

11. Reversible Gas Processes. There are four processes that are frequently used to model more complicated processes in engineering and science. They are:
- Isometric process. A constant volume process.

- Isobaric process. A constant pressure process.
- Isothermal process. A constant temperature process.
- Adiabatic process. A process with zero heat flow.

Here, we will examine how these processes look on a pressure vs. volume graph, how the first law relates to these processes, and the details of expressing the heat and work for these processes when the material is an ideal gas. We are considering here only equilibrium processes for which the values of pressure and temperature are well defined.

11.1 Isometric Process. The Isometric process is viewed as a vertical line on the P vs. V graph. Since dV=0, the work done for this process is also zero as evidenced by the lack of area under the trajectory as viewed.
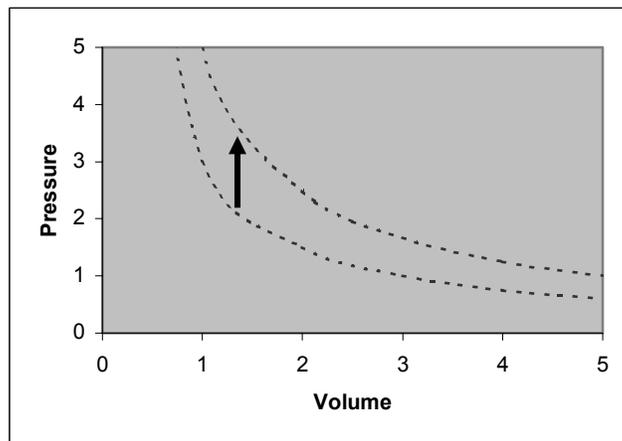

Figure 9. Gas undergoing an isometric process.

The first law is therefore, $\Delta U = Q$. All heat for the process changes the internal energy of the gas, and a corresponding change in temperature is expected. For a gas, the heat may be expressed using $Q = n\, c_v\, \Delta T$, and the first law is therefore,

$$\Delta U = n\, c_v\, \Delta T$$

We are also in a position to predict c_v for an *Ideal* gas. Equating $\Delta U = \dfrac{\#}{2} nR\Delta T$ to the above relationship, $c_v = \dfrac{\#}{2} R$

11.2 Isobaric Process. The Isobaric process is viewed as a horizontal line on the P vs. V graph. As can be seen, the temperature will change in an isobaric process and we would expect an associated change in the internal energy for a gas.
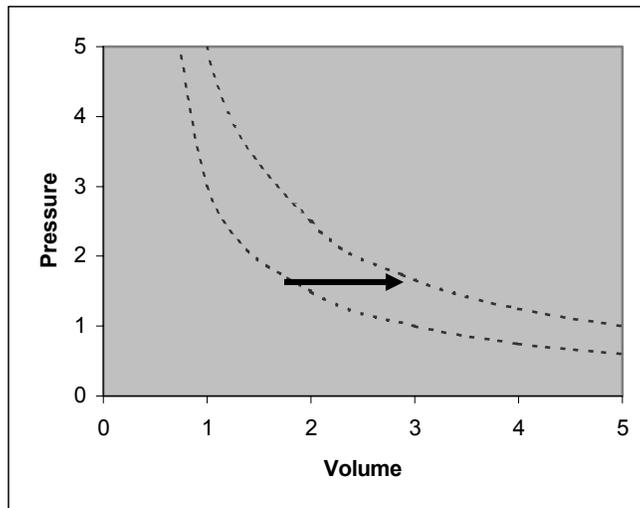
Figure 10. Gas undergoing an isobaric process.

The work done for this process is W = P ΔV, which is easily seen as the rectangular area under the P vs. V graph.

The first law is therefore,

$$\Delta U = Q - W$$
$$\Delta U = Q - P\Delta V$$

Heat is also associated with this process. The heat can be expressed using $Q = n\, c_p\, \Delta T$, and on substitution to the first law, we have

$$\Delta U = n\, c_p\, \Delta T - P\Delta V$$

For an isobaric process, one can also incorporate the ideal gas law at the initial and final states of the gas:

$$P_f V_f = nRT_f$$
$$P_i V_i = nRT_i$$

Subtracting the initial from the final, and noting $P_f = P_i$, we arrive at

$$P\Delta V = nR\Delta T$$

This relationship may also be substituted for the isobaric work term to give

$$\Delta U = n\, c_p\, \Delta T - nR\Delta T$$
$$\text{or}$$
$$\Delta U = n\, (c_p - R)\, \Delta T$$

11.3 Isothermal Process. The Isothermal process is a process of constant temperature and as such will follow an isotherm on the P vs. V graph. Since there is no change in temperature, there is also no change in internal energy for this process.
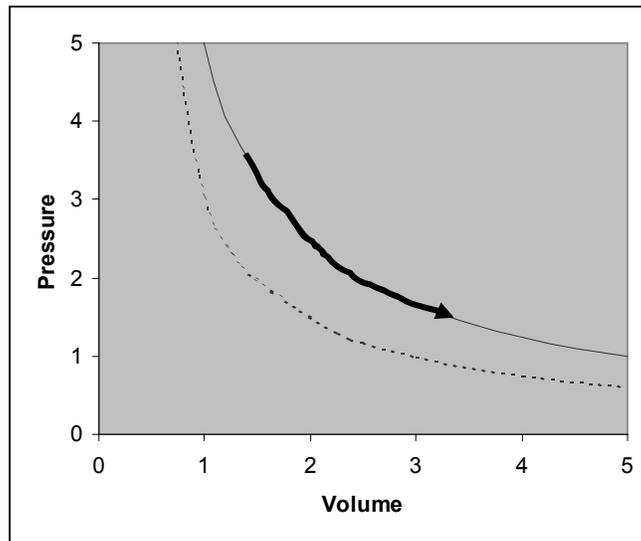
Figure 11. Gas undergoing an isothermal process.

The first law is therefore, $\Delta U = Q - W$, where $\Delta U = 0$, so $Q = W$!

It should be noted that, for an isothermal expansion, the first law would indicate that all the heat entering the system could be converted to useful work. This would make this process 100% efficient! An isothermal process would not violate the first law of thermodynamics, *but it does violate the second law!*   This raises the question, "why do we consider the process"? In principle, the isothermal process *could* be executed if it were to be done infinitely slow. Thus, slow processes, which have only small deviations from constant temperature, may be modeled with this process.

The work done for this process, for a gas, is obtained using the ideal gas law as follows:

$$W = \int P dV$$

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

On substitution into the integral,

$$W = nRT \int \frac{1}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

There is no c_T. The relationship $Q = n c \Delta T$ does NOT apply to a constant temperature processes.

11.4 Adiabatic Process. An adiabatic process is a process in which no heat crosses the system boundary. This process could occur if a system were well insulated, or as a result of a rapid process where there was insufficient time for the heat to cross the system boundary. We wish to determine how the gas state

variables, pressure, temperature, and volume are related for a process of this kind. We will derive this trajectory for the case where the number of moles of gas is a constant.

Since the material is a gas, any process involving a gas must obey the ideal gas law. We start with the ideal gas law, and differentiate both sides assuming a constant number of moles.

$$PV = nRT$$

$$PdV + VdP = nRdT$$

The result is a differential equation describing the ideal gas law.

Our tactic is to use the first law to create the adiabatic constraint, then to insert that constraint into the above differential equation, and finally, solve the modified differential equation for the adiabatic process trajectory.

The first law, with zero heat is,

$$dU = dq - dw$$

$$dU = -dw$$

Since dw = PdV, we substitute

$$dU = -PdV$$

We now need a replacement for dU. This will be done by considering another process that has the same change in temperature; a constant volume process.

For the constant volume process, the first law is,

$dU = dq = nc_v dT$

Equating dU's we have,

$$nc_v dT = -PdV$$

Now we insert the above constraint into the differential equation by substituting for dT.

$$PdV + VdP = nR\frac{(-PdV)}{nc_v}$$

We rearrange the above to get

$$\left(1 + \frac{R}{c_v}\right)PdV + VdP = 0$$

Before we solve this equation, let us examine the quantity in brackets above. This can be simplified as follows:

$$\left(1 + \frac{R}{c_v}\right) = \left(\frac{c_v}{c_v} + \frac{R}{c_v}\right) = \left(\frac{c_v + R}{c_v}\right) = \frac{c_p}{c_v} \equiv \gamma$$

Here, we define γ as the ratio of the specific heat at constant pressure, to the specific heat at constant volume. Our differential equation is:

$$\gamma PdV + VdP = 0$$

We divide both sides by PV,

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

Integrating both sides,

$$\gamma \int \frac{dV}{V} + \int \frac{dP}{P} = \int 0$$

This gives,

$$\gamma \ln V + \ln P = const.$$

Absorbing γ into (ln V) as an exponent, and exponentiation of both sides we arrive at the adiabatic trajectory.

$$\ln V^\gamma + \ln P = const.$$
$$\exp\{\ln V^\gamma + \ln P\} = \exp\{const.\}$$
$$\exp(\ln V^\gamma)\exp(\ln P) = const.$$

$$PV^\gamma = \text{constant}$$
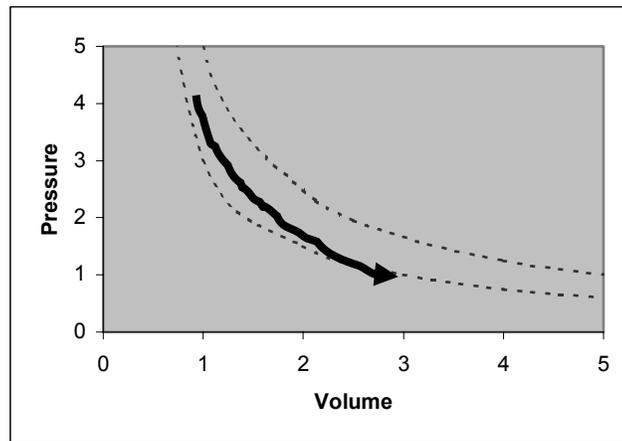
Figure 12. Gas undergoing an adiabatic process.

The adiabatic process produces work at the expense of internal energy as evidenced by the area under the curve and the corresponding change in temperature.

We now calculate the work done in an adiabatic expansion. We start with the general expression for expansion work,

$$W = \int_i^f PdV$$

Since pressure is a function of volume for this process, we arrange a suitable substitution using the adiabatic trajectory, where the constant is evaluated at the initial point,

$$PV^\gamma = P_i V_i^\gamma$$

$$P = P_i V_i^\gamma V^{-\gamma}$$

This is now substituted in the work integral to give,

$$W = P_i V_i^\gamma \int_i^f V^{-\gamma} dV$$

The above integral is now evaluated,

$$W = P_i V_i^\gamma \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_i^f$$

$$W = \frac{P_i V_i^\gamma}{1-\gamma} \left[V_f^{1-\gamma} - V_i^{1-\gamma} \right]$$

Since $P_i V_i^\gamma = P_f V_f^\gamma$, we distribute this within the brackets to give,

$$W = \frac{1}{1-\gamma} \left[P_f V_f^\gamma V_f^{1-\gamma} - P_i V_i^\gamma V_i^{1-\gamma} \right]$$

Cleaning up the exponents,

$$W = \frac{1}{1-\gamma} \left[P_f V_f - P_i V_i \right]$$

We arrive at our result,

$$W = \frac{\Delta(PV)}{1-\gamma}$$

the expansion work done in an adiabatic process.

12. Peculiar Results; Entropy. Through out history, scientists have done experiments, which, when the data was examined, interesting trends emerged. Working with the collisions of balls, it was noticed that peculiar relationships existed between the velocities of the balls before, and after those collisions. For example, if a single ball was rolled into a string of other balls of the same mass at rest, that ball stopped and one ball from the other end of the string emerged with the same velocity! Today, we all but take that result for granted as we profess the reason: conservation of momentum and energy. Momentum – Impulse being developed by Newton around 1687 A.D. However, prior to Newton, the fact that it took place in the way that it did was, peculiar. Much the same peculiar fact was often noticed involving the square of the velocities, a peculiar conservation fact that today, we explain with conservation of kinetic energy. Peculiar results, path independent results, conservation results, they draw our focus.

So when Sadi Carnot (1792-1832), while studying the efficiency of his now famous hypothetical heat engine cycle, saw that the ratio of Q/T , summed over all legs of the Carnot Cycle, summed to zero, this too must have been noticed as, peculiar.

Recalling statements made earlier, the equation in use for the relationship between heat and temperature, $Q = n\,c\,\Delta T$, clearly had some problems. Its foundation lie in empirical experiment, still, it presented no particular insight toward a physical law of nature. The specific heat constant was not much more than a fudge factor chosen for the particular material and process. For the quantity Work, at least it was well founded with the variables of force and displacement.

Eventually, the question would arise, "is there an equation, similar to work, that can be used to describe heat?" This equation would require a heat "force variable" and a heat "coordinate variable". Now the heat "force variable", the CAUSE variable, would seem obvious – "…as a result of temperature difference only" – the force variable must be temperature, T. But what is the coordinate variable? It would have to be *invented!* The letter "S" is used in modern thermodynamics as the heat "coordinate variable" – and its name, Entropy.

This invention would now provide a way of computing heat with the same sort of integral as work.

$$W = \int \vec{F} \bullet d\bar{x} \quad \text{Definition of work}$$

$$W = \int P\,dV \qquad \text{Expansion work}$$

$$Q = \int T\,dS \qquad\qquad \text{Heat}$$

We may plot T as a function of S, and extract the area under the curve as heat.
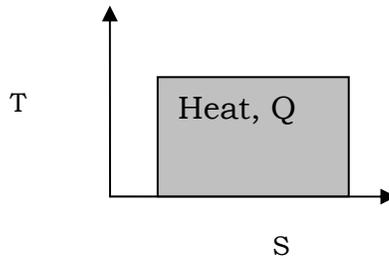

Figure 13. Temperature as a function of entropy. Area bounded represents heat.

This invention Entropy (S) was formalized by Rudolph Clausius (1822-1888) as the peculiar coordinate variable for heat. Let us rearrange this relationship,

$$Q = \int T\,dS$$

$$dq = T\,dS$$

$$dS = \frac{dq}{T}$$

In this form, we notice the same peculiar ratio that Carnot also noticed.

Now this "Entropy" is a coordinate variable you say, but what kind of coordinate is it? What *IS* Entropy? The answer could be " It doesn't really mater". We can do experiments, compute the Entropy, put the values in a table, and when we need it, we can look it up. True as this statement is, the concept of entropy doesn't seem to be much of an improvement over specific heat; but this Entropy is, peculiar. Since it is a coordinate, we can represent it on a number line. Its' value is, *what it is.* Like pressure, volume, and temperature (also coordinates), Entropy seems to be a state variable.

There is yet another peculiar idea to discuss. If an unyielding and thermally insulated sheet of armor plate suddenly stops a speeding bullet, all the kinetic energy of the bullets center of mass is converted into Internal Energy and manifests itself in a rise of temperature. Why then do we never observe a stopped bullet, when heated to a high temperature, spontaneously reduce its temperature and speed off with a large center of mass kinetic energy? The first law of thermodynamics does not prohibit an event of this kind. There seems to be a direction for spontaneous change, and that direction is not reversible. Irreversible and spontaneous changes are seen throughout nature.

So, when Sadi Carnot and Rudolph Clausius, while studying a hypothetical REVERSABLE (never to far from equilibrium) heat engine cycle found that for the cycle,

$$\oint \frac{1}{T}dq = \oint dS = \Delta S \equiv 0$$

, and for an IRREVERSIBLE cycle, the same computation resulted in

$$\Delta S \succ 0$$

, this result must have surpassed – peculiar. *That was discovery.* Here is a state variable, which will point the direction of spontaneous change; it will provide a mathematical foundation for *no spontaneous change – equilibrium! That is discovery.*

We will now author a definition of reversibility and equilibrium. The condition of reversibility between a system and its surroundings exists when the intensity factors of system (pressure, temperature, electric potential, etc.), differ by no more than an infinitesimal amount from the surroundings. Equilibrium is when they are equal. The difference is indistinguishable.

13. The Second Law of Thermodynamics and Efficiency. We now define Entropy with, and introduce the Second Law of Thermodynamics as:

$$dq_{rev} = T\,dS$$

where we use any hypothetically reversible path between states. All entropy computations *MUST* use Kelvin temperature.

In words, the Second Law of Thermodynamics can be stated *"For any process that proceeds from one equilibrium state to another, the sum of the change in entropy for the system and the change in entropy for its surroundings must be positive or zero. No natural process ever produces a zero result".* It is possible, for a given system, to undergo a process that will increase entropy, decrease entropy, or for the entropy to remain constant. We must remember however that the piston producing this process has two sides. For the other side of the piston, the universe side, we also produce a process and *that* process is never reversible. The Entropy of the universe will always increase.

Perhaps a more practical statement of the second law of thermodynamics incorporates the concept of efficiency. The efficiency of any process is the ratio of "what you want out of the process" to "the cost of getting what you want". For a cyclic heat engine, we want work and its cost is fuel (heat). We define the efficiency of the engine as,

$$Eff = \frac{\text{Work for the cycle}}{\text{Heat into engine}}$$

Real heat engines not only consume fuel, the byproducts of the fuel are ejected as exhaust. This exhaust is negative heat … it represents a loss of efficiency. We now formulate an alternative statement of the Second Law of Thermodynamics:

No cyclic heat engine will convert heat into work at an efficiency of 100%.

But "What *is* Entropy?" Well, what is force? What is energy? The beauty in all this is that we do not need to know! We may still use these concepts to formulate relationships, which lead to the solution of engineering problems. These concepts are not dependent on the specifics of any material or object. Still, we find it satisfying to interpret force and energy. In the case of Internal energy, we <u>interpret</u> it as *the total micro energy of a group of particles.*

14. We Interpret Entropy. Entropy is the measure of *disorder.* For a gas seen as a collection of particles, this Entropy (disorder) manifests itself in two forms: disorder of position (configuration entropy), and disorder of energy (or velocity).

Consider a library. If all the books are on the shelf in their correct position, such that when we locate a particular book in the card catalog, we go to the correct stack, and to the correct shelf, and to the correct position on that shelf, and blindly grab, and the probability of selecting the desired book is 100%, this for any desired book, we would say that the library is in perfect order. If however, we must select an entire shelf of books to insure the desired book is also selected, the library is in disorder. In this case, the disorder can be measured by the ratio of the volume selected, to the volume of the library.

We could use much the same argument in selecting a particle with a given speed. If all the particles have the same speed, it is easy to select a particle with that speed on a blind grab. As the speeds of the particles become increasingly more random, the probability of selecting a particle in a certain speed range becomes more difficult. The disorder of velocity (energy) has increased. Thus, entropy can be interpreted as related to the spread of the position and velocity distributions of the gas molecules.

For solids, liquids, and mixtures, additional forms of Entropy are possible. Is the crystal perfect or does it have defects? Is it two separate piles of material, salt and sugar, or a mixture of both? We may interpret Entropy in a number of ways; *however,* the real beauty is that we do not need to interpret entropy to use entropy. That is discovery.

Computing Changes in Entropy. To compute the change in entropy for a particular process, whether reversible of irreversible, it is only necessary to devise a _reversible_ path between the initial and final equilibrium states and compute the change in entropy for that path. Starting with

$$dS = \frac{dq_{rev}}{T}$$

, we require a suitable replacement for dq$_{rev}$. One suitable replacement may be obtained from differentiation of the original heat equation, Q = n c ΔT. In doing so, we may take advantage of years of tabulation of specific heat data. Another useful replacement for dq$_{rev}$ is often obtained from the first law. Some examples follow.

The change of entropy for a reversible constant pressure process. We assume both the specific heat as constant, and the number of moles as constant.

$$Q = nc_p \Delta T$$
$$dq = nc_p dT$$

$$dS = \frac{nc_p dT}{T}$$

$$\int dS = nc_p \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S = nc_p \ln\left(\frac{T_f}{T_i}\right)$$

Again, temperatures must be in Kelvin.

The change of entropy for a reversible constant volume process. We assume both the specific heat as constant, and the number of moles as constant.

$$Q = nc_v \Delta T$$

$$dq = nc_v dT$$

$$dS = \frac{nc_v dT}{T}$$

$$\int dS = nc_v \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S = nc_v \ln\left(\frac{T_f}{T_i}\right)$$

The change of entropy for a reversible constant temperature process for a gas. We assume both the specific heat as constant, and the number of moles as constant. Here we start with the first law,

$$dU = dq - dw$$

For this process, the change in internal energy is zero. The first law becomes,

$$dq = dw = PdV$$

Substitution gives,

$$dS = \frac{PdV}{T}$$

From the ideal gas law,

$$\frac{P}{T} = nR\frac{1}{V}$$

Substitution gives,

$$dS = nR\frac{1}{V}dV$$

Integration of both sides,

$$\int dS = nR \int_{V_i}^{V_f} \frac{1}{V}dV$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

The change in entropy for a reversible adiabatic process. We start with the Second Law,

$$dq = T\,ds$$

Since, for the adiabatic process, dq=0, and T is not zero, ds must equal zero. Thus, for the adiabatic process,

$$\Delta S = 0$$

This process is often called an isentropic process.

<u>Change in Entropy of a Pure Ideal Gas, Any Process</u>. For a pure substance (no mixing), its change in Entropy is a function of both temperature and volume (pressure). We now set out to compute a general relationship for the change in entropy which connects any two equilibrium states of an ideal gas, as a function of the temperatures and pressures of those initial and final states.

Our strategy is based on the fact that the change in entropy, a state variable, is path independent as long as we choose some reversible path. We choose a reversible constant temperature path, followed by a reversible constant pressure path, to connect the initial and final states of the ideal gas as shown in the diagram below. The change in entropy for this "combination" process is just the sum of the changes in entropies of its parts; each previously derived.
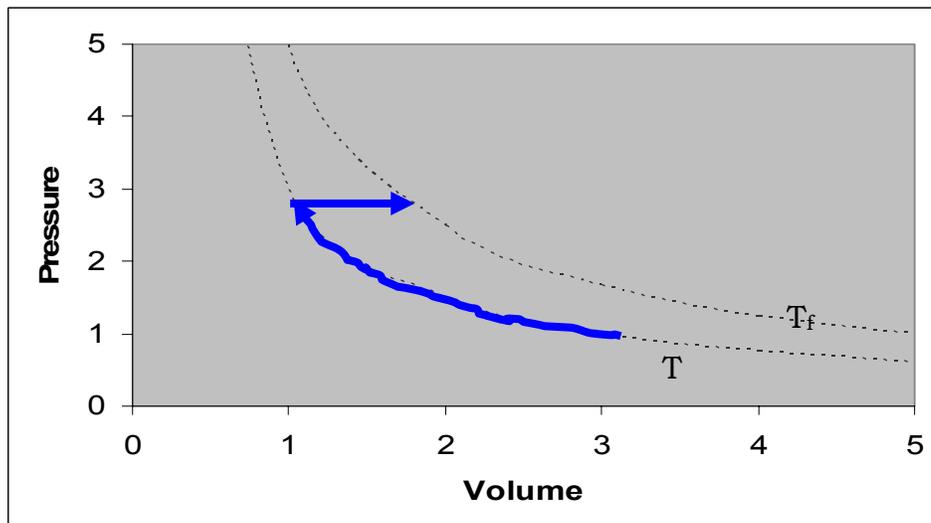
$$\Delta S = \Delta S_{T=const} + \Delta S_{P=const} = nR\ln\!\left(\frac{V_f}{V_i}\right) + nc_P\ln\!\left(\frac{T_f}{T_i}\right) \quad \text{(considering C}_P\text{ as constant)}$$

For the constant temperature portion of the process, $\dfrac{V_f}{V_i} = \dfrac{P_i}{P_f}$. Substitution into the above gives:

$$\Delta S = nc_P\ln\!\left(\frac{T_f}{T_i}\right) - nR\ln\!\left(\frac{P_f}{P_i}\right)$$

<u>Change in Entropy for an Equilibrium Phase Transformation.</u> Equilibrium phase transformations occur at constant temperature. Starting from dq=T dS,

$$dS = \frac{1}{T} dq$$

$$\Delta S_{phase} = \frac{1}{T_{phase}} \int dq = \frac{Q_{phase}}{T_{phase}}$$

Thermodynamic tables tabulate the latent heat of phase transformations per amount of material, L (in units of energy/mole), thus for a given number of moles of material, Q_{phase}=n L_{phase}. Thus, for example, a phase transformation from liquid to vapor,

$$\Delta S_{vap} = \frac{nL_{vap}}{T_{vap}}$$

15. Other Functions of State, Point Functions. The first law, with all of its' power, is but a law of accounting. It does not dictate feasibility. It is the second law that contains a statement of feasibility. These two laws may be combined via substitution to yield a statement of both accountability, and feasibility; the <u>combined first and second law of thermodynamics</u>.

$$\Delta U \equiv Q - W = \int TdS - \int PdV$$

The first and second law combined can be used as is, or can be further rearranged using the calculus procedure "integration by parts", to yield three additional state functions.

A brief review of "integration by parts" may be helpful. Here, we will apply the procedure to the definite integral: $\int_{V_i}^{V_f} PdV$. Figure 14a below shows two rectangles, one of area P_fV_f, and one of area P_iV_i. Subtracting the two areas gives us the area of an "L" shaped region. Notice that this area is independent of how we may chose to connect the points P_fV_f and P_iV_i.
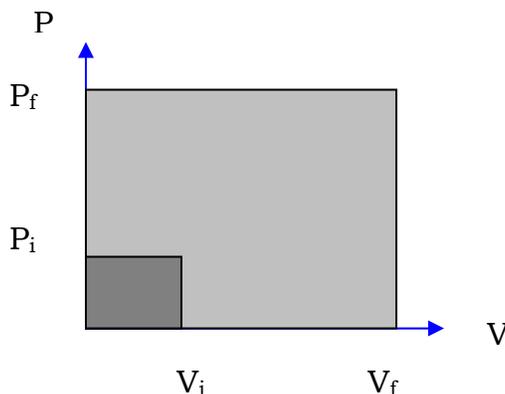

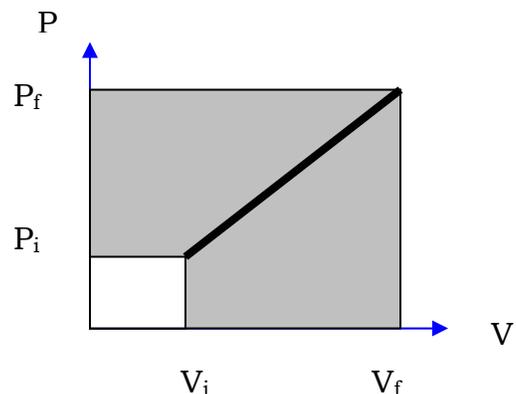Figure 14a showing the difference of two rectangular areas.

Figure 14b showing further subdivision into parts.

Once a path is chosen, as in figure 14b, the path further subdivides the "L" shaped area into two regions. The region under the curve described in general by $\int_{V_i}^{V_f} PdV$, and the region to the left of the curve described by $\int_{P_i}^{P_f} VdP$. Integration by parts is thus seen as an accounting of the areas involved:

Difference in rectangular area = area under + area to left of curve.

$$\Delta(PV) \equiv \int PdV + \int VdP$$

Of important interest is the fact that $\Delta(PV)$ is a "point function"; a function of state. It does not depend on how we get from the initial to the final point. We now proceed to develop the remaining three state functions.

15.1 Enthalpy. We start with the first and second law combined,

$$\Delta U = \int TdS - \int PdV$$

We apply integral by parts to the second integral.

$$\Delta U = \int TdS - (\Delta PV - \int VdP)$$

Since $\Delta(PV)$ is independent of path, we move it to the left side of the equation and redefine the results as the change in Enthalpy.

$$\Delta H \equiv \Delta U + \Delta(PV) = \int TdS + \int VdP$$

15.2 **Helmholtz Energy.** We start with the first and second law combined,

$$\Delta U = \int TdS - \int PdV$$

We apply integral by parts to the first integral.

$$\Delta U = \left(\Delta(TS) - \int SdT\right) - \int PdV$$

Since $\Delta(TS)$ is independent of path, we move it to the left side of the equation and redefine the results as the change in Helmholtz Energy.

$$\Delta A \equiv \Delta U - \Delta(TS) = -\int SdT - \int PdV$$

15.3 Gibbs Energy. We start with the first and second law combined,

$$\Delta U = \int TdS - \int PdV$$

We apply integral by parts to both integrals.

$$\Delta U = \left[\Delta(TS) - \int SdT\right] - \left[\Delta(PV) - \int VdP\right]$$

Since Δ(PV) and Δ(TS) are independent of path, we move them to the left side of the equation and redefine the results as the change in Gibbs Energy.

$$\Delta G \equiv \Delta U + \Delta(PV) - \Delta(TS) = -\int SdT + \int VdP$$

$$\Delta G \equiv \Delta A + \Delta(PV)$$

$$\Delta G \equiv \Delta H - \Delta(TS)$$

16. Interpretations of Enthalpy, Helmholtz Energy, and Gibbs Energy.
Once again the statement is made; "I can see the formula, <u>but what is it</u>?" And again, we answer the question by "it", is something that does not depend on how *it* gets there. That fact alone makes a state function interesting. We now however, embark on the mission of interpretation. We seek to connect the concept with the familiar. In the attempt, we must agree that the visualizations to follow are but shadows of the concepts themselves; interpretations under restricted conditions. These interpretations may however give insight as to the prudent use of these state functions.

16.1 Enthalpy. Reviewing the definition,

$$\Delta H \equiv \Delta U + \Delta(PV) = \int TdS + \int VdP$$

, one may wonder how this function would look for a constant pressure process. We impose the restriction to arrive at

$$\Delta H = \Delta U + P\Delta V = \int TdS$$

Interpretation of the remaining integral is crystal clear – it is heat. The change in Enthalpy for a constant pressure process is the heat, Q. The chemist often interchanges the phrases "heat of the reaction" and "change in enthalpy of the reaction"; these reactions occurring in a constant pressure environment. Constant pressure Enthalpy changes may be easily measured from calorimetric experiments or calculated from a large wealth of specific heat data.
 Consider two equilibrium states, which may be connected with a constant pressure process. The change in Enthalpy may be computed from,

$$\Delta H = Q = \int nc_P dT$$

If either n, or c_P may be considered constant, the integral is easier to evaluate. Once the Enthalpy change has been determined for *that* process, the value is correct for *any* process that connects those two equilibrium states.
 In a more general sense, ΔH = ΔU + Δ(PV) is often used when a process is such that only PV work and Internal energy changes are present.

16.2 Helmholtz Energy. Given the definition,

$$\Delta A \equiv \Delta U - \Delta(TS) = -\int SdT - \int PdV$$

one may view it under the conditions of constant temperature. This view produces,

$$\Delta A = \Delta U - T\Delta S = -\int P dV = -work$$

We may interpret the change in Helmholtz Energy under conditions of constant temperature as the negative of the maximum possible work, which can be extracted when moving from one equilibrium state to another along that path. Since the state of equilibrium between a system and its surroundings is achieved when no more work may be extracted, the Helmholtz Energy points the way to the criteria for equilibrium, and spontaneity.

$\Delta A < 0$, for the process indicates a spontaneous process.
$\Delta A = 0$, the system and surroundings are in equilibrium.

16.3 Gibbs Energy. Again, we review the definition,
$$\Delta G \equiv \Delta A + \Delta(PV),$$
we see that the Gibbs energy is, for a constant temperature process: *-(work)$_{max}$ + expansion work = -work$_{net}$* for the process. The Gibbs Energy also points the way to spontaneous change and equilibrium for a system and its surroundings.

$\Delta G < 0$, for the process indicates a spontaneous process.
$\Delta G = 0$, the system and surroundings are in equilibrium.

When a system is not in equilibrium, it has available energy (or what is often called *FREE* energy) to do work. In moving toward equilibrium, the system releases this energy in the form of work as it lowers its energy state. In chemical systems, open to the atmosphere, this is usually PV work.