

All of thermodynamics is based upon three statements of fact, or laws. None of the three can be "proved" ... yet no exception to any of them has ever been observed. The order of the laws is fixed by tradition, and reference to any of them by name conjures up specific ideas and limitations. The laws are:

The first law of thermodynamics..."Energy is conserved."

Specifically, this means the total energy of the universe is a constant, i.e., energy cannot be created nor can it be destroyed. It can, however, be manipulated. For example, we can put heat into an engine and cause it to do work. Heat and work, in fact, are the two most common ways to interpret energy.

Early in the studies of this field, it was found that not all of the heat ("random" energy) could be converted to work ("directed" energy). If we think of the engine as being "the system" and heat (Q) and work (W) as appearing and disappearing in the rest of the universe ("the surroundings"), then the difference between the two quantities must be surely be *somewhere*, that is, it must be inside the engine.

We would say that we have increased the internal energy of the system, U (or in some textbooks, E). The equation that represents this fact is

$$\Delta U = |Q|_{in} - |W|_{out}$$

where the "bars" about each quantity represent absolute magnitudes.

Because the discipline was brought to maturity during the industrial revolution, there is particular interest in engines (or "systems") that do work by the expansion and compression of pistons, what is commonly called pressure-volume work, or PV-work. In these systems, an applied pressure leads to an increase in volume of the fluid (usually air) within the piston, moving the piston forward and driving the various components attached to the piston head into motion.

## State functions versus Path functions:

State functions: the internal energy is an example of what is called a "state function." It has a magnitude dependent only upon the state parameters, and not upon the particular order in which a process is carried out. Specifically, the internal energy of the fluid within a piston is composed of its kinetic energy (the energy of motion) and the potential energy (the energy of attraction):

$$U = KE + PE$$

Let us say that we have pure carbon monoxide as our fluid, not a mixture of nitrogen and oxygen, which we refer to as "air." It will make it a little easier for us to speak of the specific properties of a fluid. Within the piston, the individual molecules are translating, rotating, and vibrating. Any change of a state function, say the temperature, can alter the speed of the molecule (translation), the period of revolution (rotation), and the frequency of movement within the molecule of the individual atoms with respect to one another (vibration),

$$KE = KE_{\text{trans}} + KE_{\text{rot}} + KE_{\text{vib}}$$

Physics has provided an equation for each one of these motions of nitrogen, i.e.,

$$KE_{\text{trans}} = 1/2 m v^2$$

$$KE_{\text{rot}} = 1/2 I \omega^2$$

$$KE_{\text{vib}} = 1/2 k x^2$$

where,  $m$  = mass of the molecule

$I$  = moment of inertia of the molecule

$k$  = vibrational force constant of the molecule

$v$  = linear velocity of translation of the molecule

$\omega$  = angular velocity of the rotation of the molecule

$x$  = amount of linear displacement of the atoms about center of the bond length between them

The mass, moment of inertia, and force constant of such a molecule is unique to that molecule and can be pulled out of a table, but  $v$ ,  $\omega$ , and  $x$  can vary with a change in a state parameter, such as the temperature. If we increase the temperature, while holding the pressure and volume constant, the linear velocity, the angular velocity, and the amount of displacement of the atoms within the molecule with respect to one another will increase as well, and the kinetic energy will go up.

Similar equations exist for the potential energy. The atoms will be attracted to the earth (where Newton's law of gravitation applies) and to one another. The change in distance from the center of the earth is so small, relatively, for each molecule that we normally ignore the change in internal energy due to Newton's law, but such is not the case for the attraction between the molecules.

Because oxygen and carbon have different electronegativities, the electrons forming the bond between them spend more time around oxygen than around carbon. Up close and personal, there appears to be a slight excess of "negative" charge on oxygen and a subsequent "positive" charge on carbon. This separation leads to what is called the permanent dipole moment of carbon monoxide, once again specific for the molecule and available in tables. The energy of attraction (PE) between molecules is a variation on Coulomb's law of attraction between charged ions, which is applicable to solids, solutions, and plasmas.

Suffice to say that this energy of attraction is directly proportional to the dipole moment squared and inversely proportional to the distance squared between the two molecules. Thus the higher the dipole moment and the shorter the distance between the molecules, the stronger the attraction and the higher the potential energy.

This is why real gases appear to be "ideal" in a large container, for the potential energy drops off sharply with distance and the kinetic energy dominates. If further, the molecule has little or no internal structure (rotation and vibration almost disappear), then translation alone controls the kinetic energy.

Since an "ideal" gas is a point mass and has no interactions (mimicked by an inert gas like neon), its total internal energy,  $U$ , is simply

$$U = KE + PE = KE_{\text{tran}} = 1/2 m v^2$$

Path functions: unlike the internal energy, both the heat and the work appearing and disappearing in the surroundings do depend upon how the process is carried out. As far as a "system" is concerned, neither heat nor work even exist until a process is carried out. They are part of the surroundings, and unlike the internal energy, they do not impact the system's world until a process occurs. For that reason, we do not speak of a "change" in heat or a "change" in work, but simply describe them as specific amounts. A system possesses an internal energy; it does not possess "heat" or "work."

Heat and work belong to the surroundings.

The system may, however, receive heat or have work done on it and give off heat or do work.

The amount of heat, then, must have a definition, and that definition is controlled by two things, namely, a difference in temperature and the ability of some object to absorb the heat that is passed. If two objects possess the same temperature, then heat cannot be exchanged between them. The greater the difference between the two objects, the larger the amount of heat that can be exchanged...if indeed the colder object is *capable* of accepting heat. A metal has a high ability to accept heat; asbestos has a low ability to accept heat. We call this ability to accept heat the heat capacity (C) of the object, and the pertinent definition is

$$Q = C \Delta T.$$

If the system gives off this heat, energy is lost from the system and we assign a "negative" value to the magnitude. We say the process is exothermic, i.e., "heat out." If the system accepts heat, energy is gained, and we assign a "positive" value to the magnitude. Such a process is endothermic, i.e., "heat in."

Note that we must consciously assign a positive or negative sign to this quantity.

In the case of a pure material, at a given pressure, temperature, and volume, the heat capacity depends only upon the amount of material present. We represent this by,

$$Q = m C_{sp} \Delta T,$$

where  $m$  = mass of material  
 $C_{sp}$  = specific heat of the material.

Chemists like to think of moles of material rather than masses of material, so it is convenient for us to express the heat capacity to reflect this. We will pull off a simple math stunt by multiplying by "one" in the form of (MM/MM), where MM is the molecular mass (or molecular weight) of the material.

$$C = m C_{sp} = (m/MM) (MM \times C_{sp}) = n \bar{C}$$

where  $\bar{C}$  is called the molar heat capacity. Again, this is a specific table value at a given T, P, and V.

Note that we continue to refer to amount of material, temperature, pressure, and volume. In fact, for the systems we will study, these are the four parameters that will always define the "state" of a system. They are the "state variables:" any function that depends only upon them is called a "state function" and any equation that depends only upon them is called an "equation of state."

Probably the most obvious example of an equation of state is the ideal gas equation,

$$P V = n R T.$$

Similarly, work must have a definition, and again we turn to physics,

$$W = \text{force} \times \text{change in distance} = f \Delta d$$

We (the surroundings) can exert as much force against a wall as we want, but if the wall (the system) does not move, no work has been done on the system. As with heat, we must be able to tell whether the system does work or has work done on it.

Unlike work, we will build this into the definition. If the system does work, energy is lost and  $W$  must be negative. If work is done on the system, energy is gained and  $W$  must be positive. This is easily kept track of by simply placing a "negative" sign in front of the definition for  $W$ ,

$$W = - f \Delta d.$$

If  $\Delta d$  is positive, then  $W$  is automatically negative and the system does work.

With this in mind, we will use the more common form of the first law found in textbooks,

$$\Delta U = Q + W = C \Delta T - f \Delta d.$$

The heat,  $Q$ , must still be assigned a positive or negative value, but  $W$  will take care of itself.

**PV-work:** As we stated at the onset, the early thermodynamicists were particularly interested in the work done by and on a piston. Typically, a constant external pressure is exerted on the piston head, and a heated fluid causes the piston head to move forward. By definition, the external pressure on the piston head is given by the force exerted spread across the area of the piston head, that is,

$$P_{\text{ext}} = f/A, \text{ or } f = P_{\text{ext}} \times A.$$

If we place this back into the equation,

$$W = - (P_{\text{ext}} \times A) \times \Delta d.$$

We call this change in distance for a piston head the “stroke.” The fluid (the system) will push against the piston head, increasing the “stroke” and doing work. Again we will re-group the terms in the equation, to yield

$$W = - P_{\text{ext}} \times (A \times \Delta d).$$

Obviously, the term  $(A \times \Delta d)$  represents a change in volume for the fluid, and we can recast the equation as

$$W_{\text{system}} = - P_{\text{ext}} \Delta V, \quad \text{and the first law becomes}$$

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = Q - P_{\text{ext}} \Delta V.$$

$$U_{\text{final}} - U_{\text{initial}} = Q - P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}}).$$

The Enthalpy: this early work on pistons revealed a surprising result. To show this, we will rearrange the first law to solve for the heat,  $Q$ ,

$$Q = \Delta U + P_{\text{ext}} \Delta V = U_{\text{final}} - U_{\text{initial}} + P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}})$$

$$Q = U_{\text{final}} - U_{\text{initial}} + P_{\text{ext}} V_{\text{final}} - P_{\text{ext}} V_{\text{initial}}$$

$$Q = (U_{\text{final}} + P_{\text{ext}} V_{\text{final}}) - (U_{\text{initial}} + P_{\text{ext}} V_{\text{initial}})$$

Since the external pressure is constant (an isobaric process) and the same for both the initial and final states, we could write,

$$Q = (U_{\text{final}} + P_{\text{final}} V_{\text{final}}) - (U_{\text{initial}} + P_{\text{initial}} V_{\text{initial}}).$$

Notice that everything on the right-hand-side is either a state function ( $U$ ) or a combination of state variables ( $P$  and  $V$ ). This is characteristic of an "equation of state", and whatever it describes is a "state function."

The thermodynamicists named this term in parenthesis the enthalpy (from the Greek work, *enthalpe*, "to heat") and gave it the symbol,  $H$ .

$$H = U + PV,$$

such that at constant pressure,

$$Q_p = H_{\text{final}} - H_{\text{initial}} = \Delta H = n \bar{C}_p \Delta T$$

Thus, by restricting the path (only at constant pressure), they had changed a "path" function into a "state" function.

More surprising, as they studied other systems, this same quantity was found to be a state function for them as well.



With this in mind, they considered the possibility of holding the volume constant (an isochoric process),

$$Q_V = \Delta U + f \Delta d.$$

Now it does not matter whether the force applied is constant or variable, there is no change in the distance if there is no change in volume. The second term on the right-hand-side is zero, and we obtain

$$Q_V = \Delta U = n \bar{C}_V \Delta T$$

We have restricted the path (only at constant volume) and again changed a "path" function into a "state" function.

**Calorimetry:** these same thermodynamicists immediately applied these ideas to the heat given off by the combustion of various fuels, particularly the hydrocarbons. The hydrocarbon was introduced into a piston with excess pure oxygen, so that carbon dioxide and water were the only products. The piston was immersed in water and combustion initiated by a spark. The heat given off passed into the water in a thermally-insulated container (so that there was no heat leak into the larger surroundings) and the temperature increase of the water measured. Since specific heat capacities were based upon water, amounts of heat released into a known mass of water by the combustion could be measured.

Later, they learned to calibrate these containers, known as calorimeters, to include the heat absorbed by the piston, the walls of the container, the thermometer, and any stirrers necessary to insure even distribution of the heat. Here, they simply referred to the total heat capacity of that particular calorimeter,  $C_{cal}$ , and needed only to measure the temperature change.

$$Q_{\text{absorbed}} = C_{\text{cal}} \Delta T_{\text{cal}}$$

If the piston was allowed to expand or contract against a constant external pressure, then

$$\Delta H_{\text{comb}} = - Q_{\text{absorbed (P)}} = - C_{\text{cal}} \Delta T_{\text{cal}}$$

If instead, the piston was not allowed to expand (constant volume), the heat evolved is the change in the internal energy,

$$\Delta U_{\text{comb}} = - Q_{\text{absorbed (V)}} = - C_{\text{cal}} \Delta T_{\text{cal}}$$

This latter type of calorimeter ( $\Delta V = 0$ ) is called a "bomb" calorimeter. Obviously, nothing keeps us from studying other reactions of special interest, and tables were put together for heats of atomization, heats of neutralization, heats of formation (the formation of a compound from its elements), heats of vaporization, etc.

The first law has given us two state functions, U and H, and shown how they are related to two path functions, Q and W. During the study, it was found that even if a process were carried through a cycle (where the final state is the same as the initial state) so that  $\Delta U$  is equal to zero, and

$$Q = - W,$$

caution must be taken in interpreting this result.

Though it is true that directed energy (W) can completely be degraded to chaotic energy (Q), the reverse is not true. In a cycle only a fraction of the heat put into a system can be taken out as work. The remainder is simply wasted. If this were not so, these cycles could be endlessly repeated and a perpetual motion machine could be constructed. Though not predicted by the first law, the development of the first law did lead to the assertion

"a perpetual motion machine is an impossibility."

$\bar{C}_V$ ,  $\bar{C}_P$ , and the internal structure of a molecule: If we study the rather straight-forward case of a gas molecule absorbing heat, we can quickly zero in on how a molecule might use the energy.

We will begin with  $\bar{C}_V$ . It was early found that monatomic gases (such as the inert gases, mercury, and metallic vapors) had a  $\bar{C}_V$  value of  $3/2 R$ , where  $R$  is the gas constant, and they held on to this value as the temperature rose.

At high temperatures in a constant volume container, only the kinetic energy is significant, but each atom is free to move in three dimensions.

To these studies, we have added two other observations:

- (a) a monatomic gas trapped on a surface (where it can move in only two dimensions), has a  $\bar{C}_V$  value of  $R$ .
- (b) a uni-directional gas (electrons in a wire, ion beams), has a  $\bar{C}_V$  of  $1/2 R$

For many linear gaseous molecules,  $\bar{C}_V$  at low temperatures was close to  $5/2 R$ , and for non-linear molecules,  $3 R$ . As the temperature rose, however, these values continued to rise, and

for diatomic gases, the value of  $\bar{C}_V$  caps out at  $7/2 R$  at high  $T$ .

The interpretation of these results is following:

- (a) for a any gas, there is a contribution to  $\bar{C}_{V(\text{trans})}$  of  $1/2 R$  for every direction in which the molecule is allowed to translate.
  
- (b) for a linear molecule, there is a contribution to  $\bar{C}_V$  of  $1/2 R$  for every axis around which it can rotate about its center of gravity, but it cannot store rotational energy along the axis through the bond length.  $\bar{C}_{V(\text{rot})} = 2 (1/2) R = R$ .
  
- (c) for a non-linear molecule, three axes of rotation about the center of gravity are possible, and  $\bar{C}_{V(\text{rot})} = 3 (1/2) R = 3/2 R$ .
  
- (d) diatomic molecules have only a single vibration, and if at high temperature they cap out at  $7/2 R$ , then  $\bar{C}_{V(\text{vib})}$  must equal to a full  $R$  for every vibration fully obtained. This value is reached when all diatomics in the container are vibrating.

The degrees of freedom: the total number of ways a molecule can store kinetic energy is known as "the degrees of freedom." These ways of course are translation, rotation, and vibration. As the temperature rises, first translation is activated, then rotation, and finally vibration. Physics tells us that the number of degrees of freedom should be  $3 N$ , where  $N$  is the number of atoms in the molecule. Let us apply this to a diatomic molecule, where  $N = 2$ .

$$3 N = 6 = \# \text{ of translations} + \# \text{ of rotations} + \# \text{ of vibrations.}$$

# translations = 3, for it can move freely in the x, y, and z, directions

# rotations = 2, for it cannot store rotational energy along the axis through the bond.

As a result,

$$\# \text{ vibrations} = 3 N - \# \text{ translations} - \# \text{ rotations} = 6 - 3 - 2 = 1.$$

For a non-linear triatomic molecule,

$$\# \text{ translations} = 3$$

# rotations = 3, for now rotational energy can be stored along all three rotational axes,

and

$$\# \text{ vibrations} = 3 N - \# \text{ translations} - \# \text{ rotations} = 9 - 3 - 3 = 3$$

Thus, for a non-linear triatomic molecule,  $\bar{C}_{V(\max)}$ , with all vibrations fully activated at high temperature, would be:

$$\bar{C}_{V(\max)} = \bar{C}_{V(\text{trans})} + \bar{C}_{V(\text{rot})} + \bar{C}_{V(\text{vib})}$$

$$\bar{C}_{V(\max)} = 3 (1/2 R) + 3 (1/2 R) + 3 (R) = 6 R.$$

Finally, it was observed for many gases that the difference between  $\bar{C}_p$  and  $\bar{C}_v$  was roughly equal to R

$$\bar{C}_p - \bar{C}_v = R,$$

and for an ideal gas this was exactly so.

Special case of an ideal gas: because an ideal gas is such a unique entity (point mass and no attractions), it should not surprise us that it might have also unique thermodynamic properties. In fact, it does, specifically:

$$\Delta U = n \bar{C}_V \Delta T$$

and

$$\Delta H = n \bar{C}_p \Delta T.$$

Thus, for an ideal gas, if the temperature does not change (an isothermal process), then neither does  $\Delta U$  nor  $\Delta H$ .

Moreover, if we go to the defining equation for the enthalpy,

$$H = U + PV$$

consider a change,

$$\Delta H = \Delta U + \Delta(PV)$$

and substitute what we now know about ideal gases,

$$n \bar{C}_p \Delta T = n \bar{C}_V \Delta T + \Delta(n R T)$$

$$\cancel{n \bar{C}_p \Delta T} = \cancel{n \bar{C}_V \Delta T} + \cancel{n R \Delta T}.$$

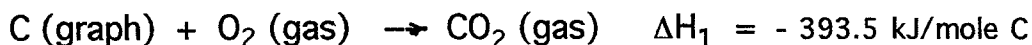
Cancelling common terms on both sides,

$$\bar{C}_p - \bar{C}_V = R, \text{ just what was asserted above.}$$

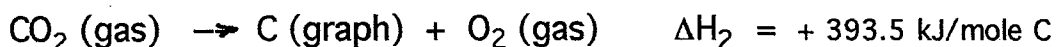
Hess's Laws: In 1840 a Russian scientist, G. H. Hess, proposed a way to take advantage of the various tables of enthalpy changes which had been compiled. His proposals were based on the fact that the enthalpy is a "state function," and thus does not depend on "how" a process is carried out. His proposals were three-fold, namely,

- (a) if one reverses the direction of a reaction, then one is doing nothing but changing what constitutes the initial and the final states. The magnitude of the enthalpy change should be the same, and only the sign associated with it would be reversed.

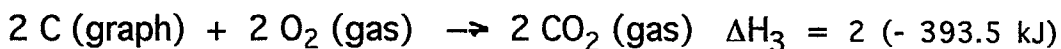
Consider the combustion of graphite to yield carbon dioxide



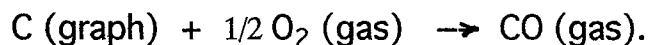
If we choose instead to determine the reverse of this reaction, we need only change the sign,



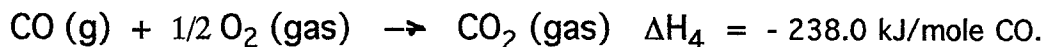
- (b) Note that this is a per mole of C quantity, so that if we use twice that amount of carbon, we should release twice the heat.



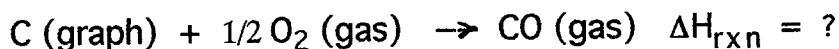
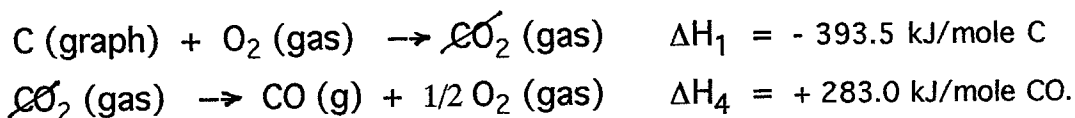
(c) Suppose you wish to know  $\Delta H$  for the reaction,



This is hard to do in a calorimeter, for you are almost certain to get a mixture of CO and  $\text{CO}_2$ , so let us look at the combustion of carbon monoxide, for which the tables give:



Look what happens if we combine the reaction of  $\Delta H_1$  with the reverse of  $\Delta H_4$ ,



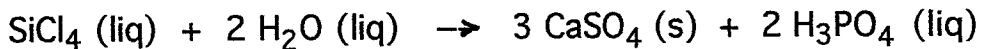
Carbon dioxide “cancels out” and half of the oxygen on the left-hand-side.

Hess stated: for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the **sum** of the enthalpy changes for the **individual** steps.

$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_4 = -393.5 \text{ kJ} + 283.0 \text{ kJ} = -110.5 \text{ kJ/mole C}$$



Heats of combustion suffer from always containing oxygen, and it cannot always cancel out. For that reason, it is more common to use heats of formation in a Hess's law treatment. A Hess's law treatment of a series of heat of formation reactions can yield something like the following:



$$\Delta H_{\text{rxn}} = [ 3 \Delta \bar{H}_{\text{f}}(\text{CaSO}_4) + 2 \Delta \bar{H}_{\text{f}}(\text{H}_3\text{PO}_4) ] - [ 3 \Delta \bar{H}_{\text{f}}(\text{SiCl}_4) + 2 \Delta \bar{H}_{\text{f}}(\text{H}_2\text{O}) ]$$

Had we expressed  $\Delta H_{\text{rxn}}$  in terms of the absolute molar enthalpies (H) of the reactants and products, then

$$\Delta H_{\text{rxn}} = H_{\text{final}} - H_{\text{initial}} = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

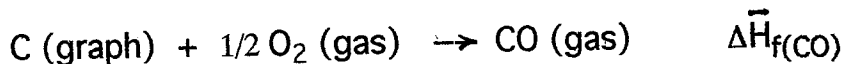
$$\Delta H_{\text{rxn}} = [ 3 \bar{H}_{(\text{CaSO}_4)} + 2 \bar{H}_{(\text{H}_3\text{PO}_4)} ] - [ 3 \bar{H}_{(\text{SiCl}_4)} + 2 \bar{H}_{(\text{H}_2\text{O})} ]$$

A comparison the last equation with the first equation, suggests that

$$\bar{H}_{\text{molecule}} = \Delta \bar{H}_{\text{f}}(\text{molecule}),$$

and that is exactly what our clever thermodynamicists have maneuvered !

Return to our reaction,



Using absolute enthalpies,

$$\Delta \bar{H}_{\text{f}}(\text{CO}) = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}} = \bar{H}_{\text{CO}} - \bar{H}_{\text{C}} - 1/2 \bar{H}_{\text{O}_2}$$

The thermodynamicists arbitrarily assign the absolute enthalpy of every element in its most stable form at 25 °C and 1 atm of pressure, as having a value of zero, so under these conditions our relationship becomes

$$\Delta \bar{H}_{\text{f}}(\text{CO}) = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}} = H_{\text{CO}} - (0) - 1/2 (0)$$

and at standard conditions, 25 °C and 1 atm of pressure,

$$\Delta \bar{H}_{\text{f}}(\text{CO}) = \bar{H}_{\text{CO}} .$$

This assignment to the elements does not hold at any other temperatures of pressures, but we have ways of dealing with that.

**Reversible versus Irreversible Processes:** An important point to make again and again is that a state function is independent of how the process is carried out, so the early thermodynamicists quickly homed in on what would result from a process that could take as long as we wished as opposed to one that takes place in real time.

All real processes take place in finite amount time and the change disturbs the system in such a way that it cannot be re-created by simply stepping back to a previous state. We describe these system as irreversible. This does not mean that we cannot back-track; it simply recognizes that we should not expect all the molecules in a system to return to their original positions. Natural processes are not like a movie reel in which we can simply return to a previous frame and find nothing unchanged.

The mathematical opposite to this is called a reversible process, for in this case we make the individual steps in the process infinitesimally small, so that a reversal would freeze-frame all previous steps. Obviously this is an impossibility, and it would require an infinitely long amount of time to move from the initial state to the final state. What, then, is to be gained by investigating such approaches? As it turns out, quite a lot, including some new state functions.

**Reversible work:** Let us begin by considering the expansion of an ideal gas. The ideal gas represents a unique case of point masses (no internal structure) combined with no interactions between the molecules (no potential energy other than the force of gravity). To illustrate our point, we will place the process, pictorially, on a Boyles Law PV-plot at constant temperature.

Let us begin by placing the gas in a container with a piston, surmounted by a block with a mass,  $m$ , atop it. Further, we will let the mass of the block correspond to the same mass of the piston head. These masses correspond to a weight (a force), equal to  $2 m \times g$ , where  $g$  is the force of gravity. The constant pressure above the gas is now

$$P_{\text{ext}} = f/A = \text{weight}/A_{\text{piston head}} = (2 m \times g) / A_{\text{piston head}}$$

For convenience, let the internal pressure of the gas,  $P_1$ , be twice the external pressure (thus,  $P_{\text{ext}} = P_1/2$ ), so that we must introduce a stop at the top of the piston.

Since we wish to visually display our process, we will represent the external pressure by

$$P_{\text{ext}} = \text{weight}/A_{\text{piston head}} = (2 m \times g) / A_{\text{piston head}} = P_1/2,$$

and use the graph to record the change. Let the initial state variables for the ideal gas be  $P_1$ ,  $V_1$ ,  $T_1$ , and  $n_1$ . Now we remove the stop. If the number of moles and the temperature are held constant, the gas will expand until the internal pressure,  $P_2 = P_{\text{ext}} = P_1/2$ , and Boyles Law states that

$$P_1 V_1 = P_2 V_2 = (P_1/2) V_2, \quad \text{or}$$

$$V_2 = 2 V_1.$$

Using our definition for work, remembering that we are expanding against a constant external pressure

$$W_1 = - P_{\text{ext}} \Delta V = - P_{\text{ext}} (V_2 - V_1).$$

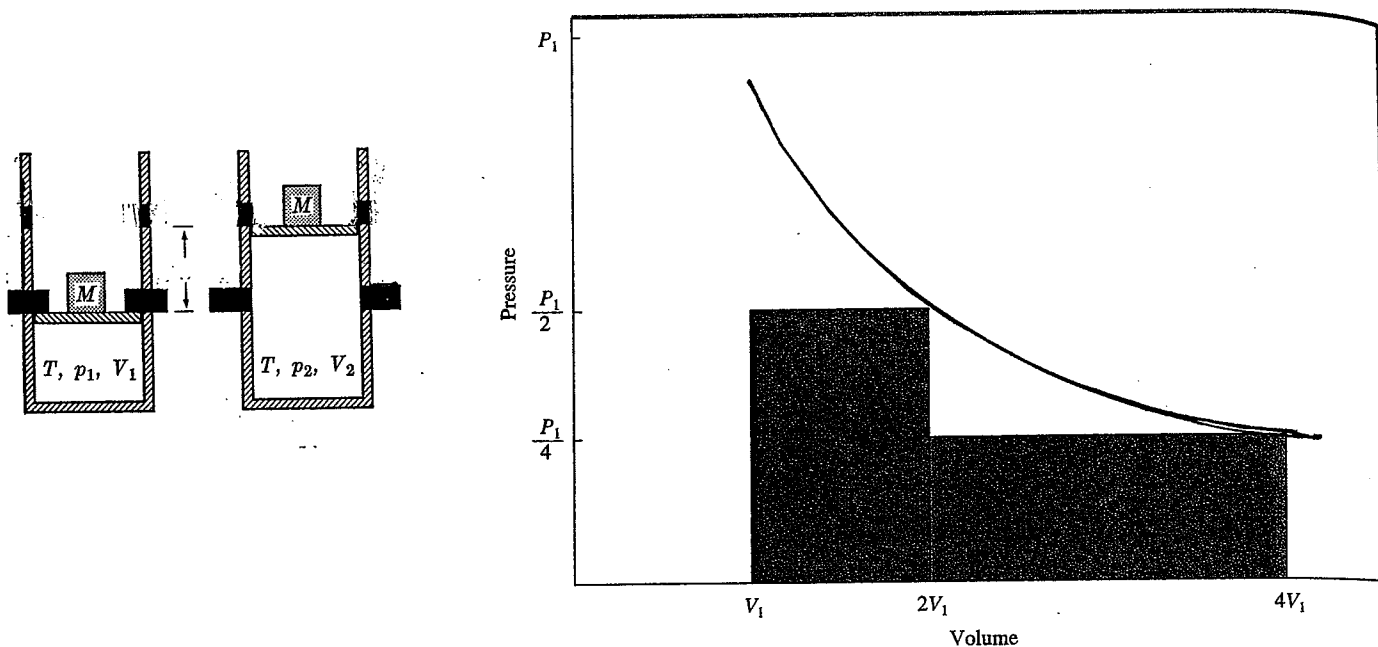
Substituting the relevant quantities,

$$W_1 = - P_{\text{ext}} (V_2 - V_1) = - (P_1/2) (2 V_1 - V_1),$$

$$W_1 = - (P_1/2) (V_1) = - P_1 V_1 / 2 .$$

This is a natural process occurring in real time, thus it represents what we call an irreversible process, and the work is irreversible work.

On our graph, this is represented by the area of the first rectangle.



Now we remove the mass on the top of the piston head, and let the piston expand freely. The external pressure has been reduced to one-fourth of the original internal pressure, and the piston expands until the final volume is  $4 V_1$ . Again we put the quantities into the equation, yielding

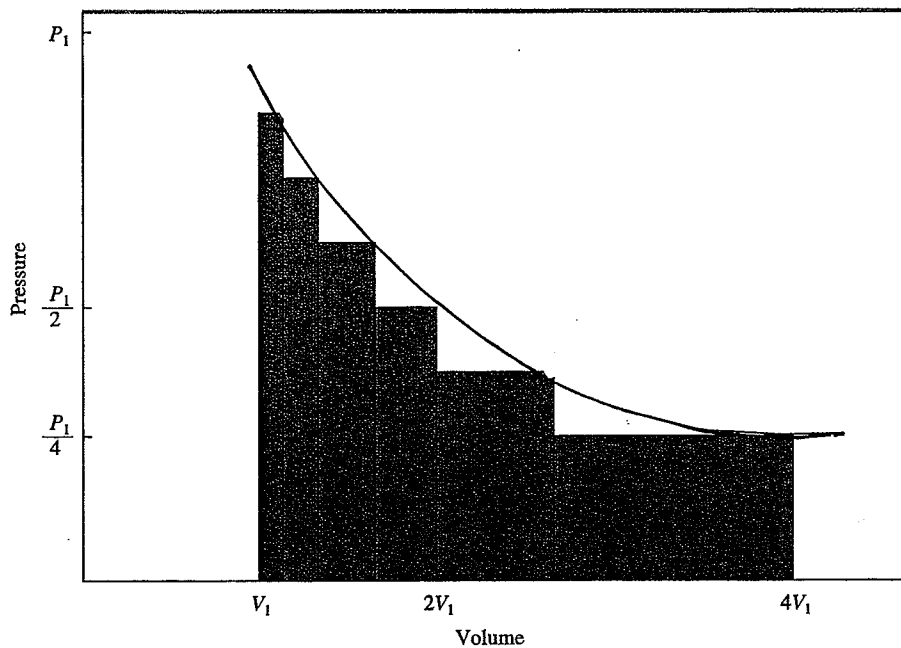
$$W_2 = - (P_1/4) (4 V_1) = - P_1 V_1$$

The total work done by the gas is simply the sum of the two works,

$$W_{\text{tot}} = W_1 + W_2 = - (P_1 V_1 / 2 + P_1 V_1)$$

$$W_{\text{tot}} = - 3/2 (P_1 V_1) .$$

Now let us envision this process as occurring with many small weights on the top of the piston head (so that  $P_{\text{ext}}$  is much closer to the internal pressure), and each of them will be removed sequentially. We will expand from the original  $V_1$  to  $4V_1$ , but notice that a much greater area is swept out, and much more work is done.



Multi-step processes of this type are represented by

$$W_{\text{tot}} = - \sum_{i=1}^n P_i \Delta V_i$$

where  $P_i$  = external pressure for each step  
 $\Delta V_i$  = change in volume for each step  
 $n$  = number of steps in the process.

Now envision what would happen if the internal pressure is only infinitesimally larger than the external pressure

$$P_{\text{int}} = P_{\text{ext}} + dP,$$

or  $P_{\text{ext}} = P_{\text{int}} - dP,$

and that the volume changes are infinitesimally small

$$\Delta V = dV .$$

If this is put back into our equation for  $W_{\text{tot}}$ ,

$$W_{\text{tot}} = - \sum_{i=1}^n (P_{\text{int}} - dP)_i (dV)_i$$

then in the limit that  $dV \rightarrow 0$ , we obtain what we learned in calculus is the definition of an integral, that is,

$$W_{\text{tot}} = - \int_{V_1}^{V_2} P_{\text{int}} dV .$$

for an ideal gas,  $P_{\text{int}} = (nRT/V)$ , and

$$W_{\text{tot}} = - \int_{V_1}^{V_2} (nRT/V) dV$$

Because, this is an isothermal process, the number of moles of gas does not change, and  $R$  is a constant, all of these terms may be brought outside the integral sign, and we integrate  $(dV/V)$  over the range  $V_{\text{initial}}$  to  $V_{\text{final}}$ . The result for this reversible work is,

$$W_{\text{tot}} = W_{\text{rev}} = - n R T \ln (V_f/V_i).$$

The reversible work thus represents all the work under the isotherm (constant T) from  $P_1, V_1$  to  $P_2, V_2$ , and enables us to predict the maximum amount of work that can be done by the gas under these expansion conditions.

If we wish to compress the gas back to the initial conditions, then the area under the curve also represents the minimum amount of work that need be done on the gas to compress it.

An ideal gas does the greatest amount of work possible for any kind of gas, primarily because we waste none of the energy pulling the molecules apart from one another. More importantly, if we have a gas law for a real gas (such as the van der Waal equation), we can find its maximum work by simply carrying out an integration of its  $P_{int}dV$  such as that above.

The Second Law of Thermodynamics: It follows that if work can be calculated for a reversible process, then  $Q_{rev}$  should be available from the first law, that is,

$$Q_{rev} = \Delta U - W_{rev}.$$

An even easier case is that for a cycle, where one eventually returns to the initial state, and all of the state functions are equal to zero.  $\Delta U = 0$ , and

$$Q_{rev} = -W_{rev}.$$

The significance of the reversible heat was first recognized by Sadi Carnot, a French scientist, in 1824. Carnot envisioned the reversible expansion and contraction of an ideal gas by a four-step process:

- (a) an isothermal expansion at a high  $T$  from  $P_1, V_1$  to  $P_2, V_2$
- (b) an adiabatic expansion ( $Q = 0$ ) to a lower  $T$  from  $P_2, V_2$  to  $P_3, V_3$
- (c) an isothermal compression at the lower  $T$  from  $P_3, V_3$  to  $P_4, V_4$
- (d) an adiabatic compression ( $Q = 0$ ) from the lower  $T$  to the higher  $T$  from  $P_4, V_4$  to  $P_1, V_1$

An adiabatic process ( $Q = 0$ ) occurs when the system is thermally-wrapped so that heat can neither be put into the system or escape from the system. Since this is a cyclic process,  $\Delta U = 0$ .

Obviously, in steps (b) and (d), heat does not exist. He could, however, calculate  $Q_{rev}$  in steps (a) and (c), and he obtained an interesting result, namely,

$$[Q_{rev(a)} / T_a] + [Q_{rev(c)} / T_c] = 0.$$

When a van der Waal gas is sent through the same cycle, the same result is realized. This led Carnot to suggest it would be true of any gas, and that if this quantity always sums to zero in a cyclic process, then it must represent a state function. The function is given the symbol,  $S$ , and labeled the entropy.

Thus, for an isothermal process,

$$\Delta S = Q_{rev}/T .$$



What happens, however, when the temperature varies? In that case, we consider very small changes and remember our definition for work, i.e.,

$$dS = \delta Q_{\text{rev}}/T.$$

where we are using  $\delta$  to represent that  $Q$  is not a state function under all conditions.

If, for example, the process is carried out at constant pressure,

$$\delta Q_{\text{rev}} = n \bar{C}_p dT, \quad \text{and}$$

$$dS = (n \bar{C}_p dT)/T = n \bar{C}_p (dT/T).$$

If the temperature change is so small that  $\bar{C}_p$  stays essentially constant,

$$\Delta S = n \bar{C}_p \ln (T_f/T_i)$$

If the change in temperature is significant, one can always use empirical equations such as

$$\bar{C}_p = a + bT + cT^2 + dT^3 + \dots$$

where "a, b, c, and d" are table-values listed for most gases at a given pressure. The actual pressure is not critically important for the majority of the gases, so one frequently goes to the tables for  $P = 1 \text{ atm}$  (or  $1 \text{ bar}$ ).

A secondary benefit of Carnot's work was the ability to calculate the efficiency of the cycle and show that it was less than 1.0, that is, not all of the heat could be converted to work. No perpetual motion in that machine !

**Entropy and Spontaneity:** Because entropy is defined in terms of reversible heat, a disorderly or chaotic form of energy, entropy came to thought of in terms of disorder. The higher the entropy, the higher should be the disorder. Thus, if we looked at a pure material, we would expect that

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

The key architect for the specific statement of the first and second laws was the 19th-c German physicist, Rudolf Clausius, who stated "The energy of the universe is a constant; the entropy tends to a maximum," although the German physicist Hermann von Helmholtz independently proposed the first law and William Thomson, Lord Kelvin, a British physicist, was instrumental in the full realization of the second law.

Specifically, Clausius gives the second law of thermodynamics as:

"In all natural, or spontaneous, processes, change leads to an increase in disorder (entropy) for the universe."

Thus, although a natural process might lead to a decrease in entropy for the system, it must be compensated by an increase in entropy for the surroundings:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 .$$

Although this may be an intellectually satisfying statement, it leaves much to be desired in practice. We may be able to calculate the entropy change for a system, but how are we do the same for the entropy of the surroundings (the rest of the universe)? We cannot.

Clausius, therefore, tried to consider all the things that were happening in some of the common systems being studied. Prominent among these were the combustion experiments, all of which gave off heat at constant pressure and all of which could be identified with  $\Delta H$ . These were obviously spontaneous processes, and it appeared that the system was trying to lower its energy. (The entropy may or may not be increased.)

When he considered the condensation of a gas or the freezing of a liquid, he saw a decrease in entropy, but also an absorption of heat from the more chaotic form of the substance. The system has lowered both its entropy and its energy.

At constant pressure and temperature, he suggested that a state function existed that would incorporate both a need to decrease energy and to increase entropy. If we could find it, then we would need only to concentrate on the system, and let the surroundings take care of itself. He proposed that the pertinent quantity was

$$\Delta G = \Delta H - T \Delta S.$$

In the best of all possible worlds, the change would lead to a decrease in the energy and an increase in entropy, such that

$$\Delta G = (-) - T (+) = \text{negative value}$$

In the worst of cases, the energy would go up and the entropy would go down, or

$$\Delta G = (+) - T (-) = \text{positive value.}$$

What if the pressure remained constant (a common constraint on the system), but the temperature changed? Then, he would look at a refinement of equation, namely,

$$\Delta G = \Delta H - \Delta(TS), \text{ or}$$

$$G = H - TS.$$

This quantity is known as the Gibbs free energy, named for the American scientist, J. Willard Gibbs, who was one of the most important theoretical thermodynamicists of the late 19th- and early 20th-century.

Clausius proposed that, at constant pressure, if

$\Delta G_{\text{system}} < 0$  (that is, negative), then the process is spontaneous

$\Delta G_{\text{system}} > 0$  (that is, positive), then the process is non-spontaneous

$\Delta G_{\text{system}} = 0$  then the process is at equilibrium

*Thus, we only have to consider the system is making a prediction.*

Can the same thing be said at constant volume? Yes, if we recognize that the pertinent energy term is U.

We define a quantity known as the Helmholtz free energy, A,

$$A = U - TS,$$

and the conditions at constant temperature are the same as for the Gibbs free energy, namely,

$\Delta A_{\text{system}} < 0$  (that is, negative), then the process is spontaneous

$\Delta A_{\text{system}} > 0$  (that is, positive), then the process is non-spontaneous

$\Delta A_{\text{system}} = 0$  then the process is at equilibrium.

The Helmholtz free energy is also sometimes called the "maximum work function," for it represents the

*maximum  $W_{\text{rev}}$  of all kinds that can be done by the system.*

Similarly, the Gibbs free energy is also a reversible work, but it excludes PV-work. Thus, the Gibbs free energy represents the

*maximum  $W_{\text{rev}}$  over and above PV-work that can be done by the system.*

Thus, three of our state functions (U, H, and S) can be related to special forms of Q, and the other two (G and A) can be related to forms of the reversible work.

Third law of thermodynamics: the final law of thermodynamics also speaks to the entropy. In 1913, Max Planck, a German physicist who is probably better known for laying the foundations of quantum mechanics, proposed that

“the entropy of a pure, perfectly crystalline solid is zero at the absolute zero of temperature.”

The immediate consequence of the third law is that the absolute entropy of a substance can be calculated for the first time. Since we can determine a change in entropy for a substance using our earlier equations, such as when the molar heat capacity does not change significantly with temperature,

$$\Delta \bar{S} = \bar{C}_p \ln (T_f/T_i),$$

$$\text{then } \Delta \bar{S} = \bar{S}_T - \bar{S}_{(T=0K)} = \bar{S}_T - 0 = \bar{S}_T.$$

Obviously over wide ranges, we would need to introduce equations such as

$$\bar{C}_p = a + bT + cT^2 + dT^3 + \dots$$

but that is simple enough to do.

Phase changes involve a significant increase or decrease in entropy, and we must include this as well in determining  $\bar{S}_T$ . Since, by its very nature,  $\Delta H$  represents reversible heat at constant pressure, we need only add to the above determinations the sum of all the phase changes divided by the temperature of the phase change.

$$\Delta \bar{S}_{\text{tot, phase change}} = \sum (\Delta \bar{H}_i/T_i).$$

For a gas at room temperature, we would add

$$\Delta \bar{S}_{\text{tot, phase change}} = \Delta \bar{H}_{\text{fusion}}/T_{\text{fusion}} + \Delta \bar{H}_{\text{vaporization}}/T_{\text{vaporization}}$$

Tables of absolute entropies have been compiled for most substances, especially at  $P = 1 \text{ atm}$  (or  $1 \text{ bar}$  in the modern system) and  $T = 298.15 \text{ }^\circ\text{K}$ .