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# THERMODYNAMICS
# AND
# THE DESIGN OF HEAT ENGINES

by

ROBERT W. CLARK JR.

> "He who speaks on his own does so to gain honor for himself, but he who works for the honor of the one who sent him is a man of truth."

The words of this book are the truth as God has given me the light to see the truth. If these words reveal some of the beauty and magnificence of His creation, it is because they do in fact reflect His light. If these words are found to contain elements of error, the fault lies in the vision of a mortal man and not in the perfection of the light He shed. Praise be to God!

# CHAPTER 1

# THERMODYNAMICS AND THE PERFECT GAS

by

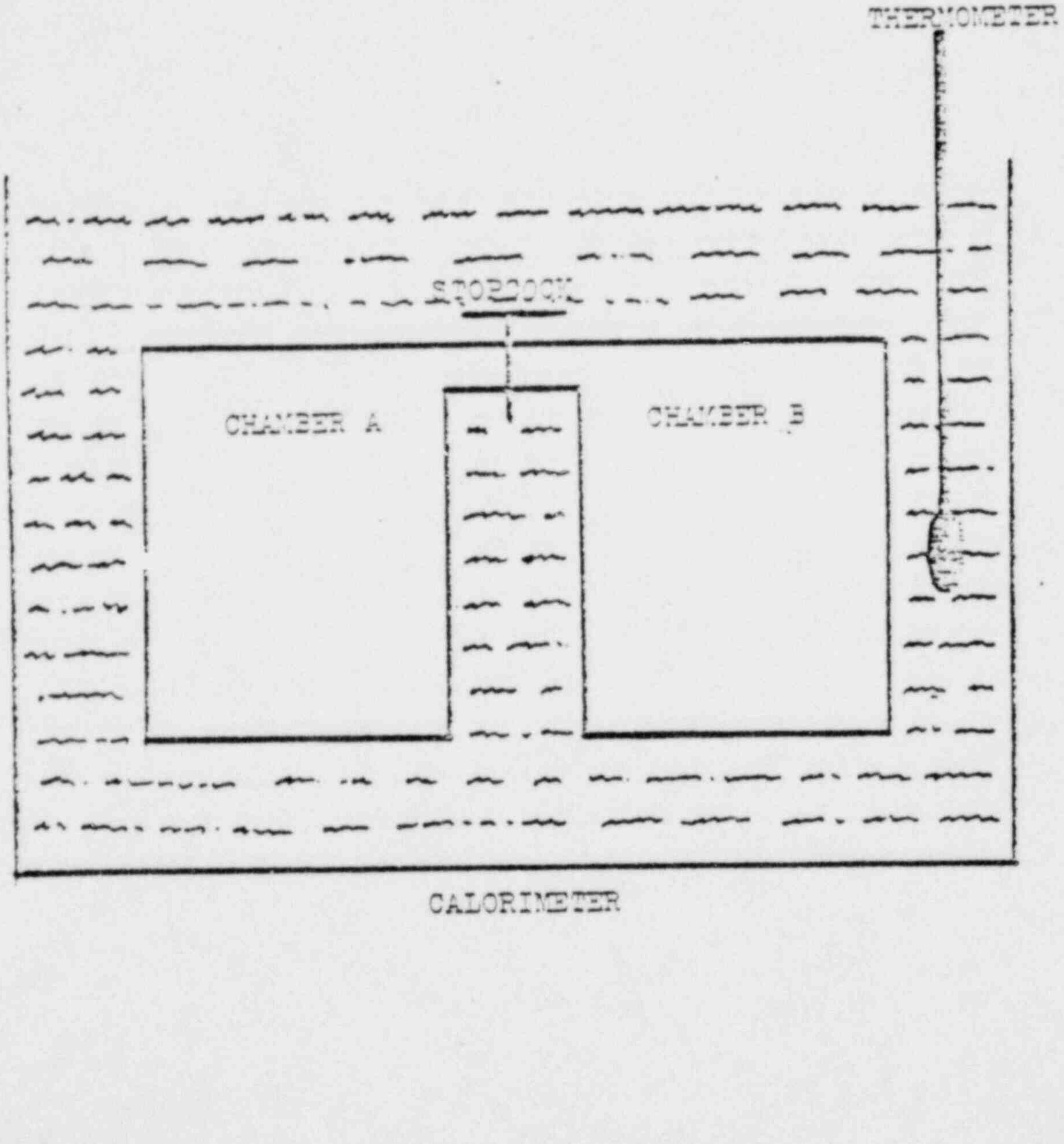
ROBERT W. CLARK JR.

Many centuries ago Aristotle considered two objects, one of which weighed more than the other, and concluded that the heavier object must of necessity fall faster than the lighter object because of its greater weight. This logic appeared to be so unquestionable that it was not until the 17th century that this false conclusion was corrected by the work and the experiments of Galileo Galilei. Galileo not only developed the law of motion of a falling body by means of his experiments but also contributed greatly to the development of scientific method, a method which requires that theories be validated by experiment.

History has a most uncomfortable way of repeating itself because men do not always learn from the lessons it teaches. Early in the 19th century James Prescott Joule did pioneer work in the field of thermodynamics for which he is justly famous. But one experiment he conducted was somewhat beyond the technology of his time and its results, falsely interpreted, led to the creation of the fictitious "Perfect Gas", a gas which does not exist and which therefore cannot be subjected to scientific experiment. This "Perfect Gas" and its imaginary qualities developed on the basis of Aristotlean logic form the basis for modern thermodynamic theory starting with the "First Law" of thermodynamics.

The purpose of the experiment was to confirm a theory regarding the fundamental nature of work. The experiment itself was a simple one. Joule placed a two chamber container into a calorimeter, the two chambers being connected by a tube with a stopcock. (See Exhibit A on page 2.) Chamber A was filled with a gas while Chamber B was evacuated. After thermal equilibrium had been established, as indicated by a thermometer, Joule opened the stopcock, thus permitting the gas to flow from Chamber A to Chamber B until the

## EXHIBIT A
## THE JOULE'S EXPERIMENT



CALORIMETER

pressure equalized within the two chambers. After a period of time he observed that there had been only a very slight change in the reading of the thermometer. He concluded that this meant that there had been practically no transfer of heat from the calorimeter to the container or vice versa. "It is assumed that if this experiment could be performed with an ideal gas there would be no temperature change at all." This quote is taken from Enrico Fermi's book, "THERMODYNAMICS", page 22, published by Dover Publications, Inc., 1936, in which Fermi cites this experiment as the proof of the "First Law of Thermodynamics".

The air conditioning industry is a development of the 20th century. This industry, of practical necessity, has contributed a great deal to man's knowledge of the behavior of gases under varying conditions of temperature, pressure and volume. One result of this contribution is that every air conditioning technician and engineer, simply by referring to an ASHRAE HANDBOOK, can very easily determine the drop in temperature which would occur if Joule's experiment were repeated today using any gas, including hydrogen, for which the thermodynamic properties have been determined. And it is a fact, scientifically determined by many, many experiments, that there would be a drop in the temperature of every known gas, every real world gas. TABLE 1, below, provides such data for two refrigerant gases for the benefit of those who do not have ready access to an ASHRAE HANDBOOK.

TABLE 1

| Ref. No. | Volume (Cu Ft/lb) | Pressure (PSIA) | Temperature (°F) | Enthalpy (BTU/lb) |
|---|---|---|---|---|
| 12 | 0.33408 → 0.58302 | 200 → 110 | 350 → 300 | 123.778 → 122.520 |
| 12 | 0.31100 → 0.39137 | 185 → 145 | 260 → 240 | 113.930 → 111.348 |
| 12 | 0.12331 → 0.45225 | 480 → 125 | 350 → 230 | 134.594 → 110.104 |
| 22 | 0.17879 → 0.29655 | 450 → 250 | 300 → 240 | 147.315 → 129.310 |
| 22 | 0.26525 → 0.49777 | 292 → 146 | 250 → 180 | 140.513 → 130.871 |
| 22 | 0.20873 → 0.52527 | 380 → 144 | 200 → 180 | 144.619 → 130.934 |

Why was it necessary to create the fictitious "Perfect Gas"? Why was it necessary for respected scientists to use Aristotlean logic to assume away the actual results of this experiment? Why is this Aristotlean logic instead of science taught at Universities today an a basic element of thermodynamic theory? Because this one experiment is a fundamental experimental test of the validity of many of the basic tenets of thermodynamic theory as it existed in Joule's day and as it exists today. It was and is today thought that these basic tenets are correct and as a consequence there should not be a drop in the temperature of the gas in Joule's two chamber experiment. The temperature of the gas *should* *not* change. But the temperature of the gas does in fact drop. Those who repeat Joule's experiment using any real world gas and the materials and technology available today will find that the temperature of the gas does in fact drop and will also find that the change in its temperature is in accord with published thermodynamic data for that particular gas. It does not matter greatly which gas you choose because all real world gases are imperfect according to current thermodynamic theory. None behave in the "logical" manner of the "Perfect Gas". As Table 1 and the data presented in that table makes evident, Joule's conclusion was in error and neither his conclusion nor the fictitious "Perfect Gas" agree with experimental data.

Let us now examine the implications of Joule's two chamber experiment. The first law of thermodynamics is stated mathematically by Fermi and others by the general formula $\Delta U + W = Q$ where $\Delta U$ is the variation in the energy of the system, W is the work performed by the system, and Q is the amount of energy received by the system from its environment. In a thermally isolated system such as Joule's two chamber container within a calorimeter Q is equal to zero. Thus, for such a thermally isolated system the first law formula becomes $\Delta U + W = 0$. Fermi, again on page 22, states: "Since the volumes of the two chambers A and B composing our system do not change during the experiment, our system can perform no external work, that is, $W = 0$. Therefore, $\Delta U = 0$; the energy of the system, and, hence, the energy of the gas, do not change." Fermi continues this very logical line of reasoning on page 23 by saying: "Let us now consider the process as a whole. Initially the gas occupied volume A, and at the end of the process it filled the two chambers A and B; that is, the transformation resulted in a change in volume of the gas. The experiment showed, however, that there was no resultant change in the temperature of the gas. Since there was no variation in energy during the process, we must conclude that a variation in volume at constant temperature produces no variation in energy. In other words, the energy of an ideal gas is a function of the temperature only and not a function of the volume." (For the sake of accuracy it is necessary to note that Joule did in fact report a very slight change in temperature.)

In other words, the first law formula as stated in the form $\Delta U + W = Q$ requires $\Delta U$ to be zero if W is zero and Q is zero. Since it is a fundamental tenet of thermodynamics that the energy of a gas is determined solely by its temperature, if $\Delta U$ is zero there could not be a change in the temperature of the gas. There could not be a change in the temperature of the gas because W is zero and Q is zero. But there was a change in the temperature of the gas and there is a change in the temperature of the gas whenever this experiment is repeated. And this experimental fact denies the validity of the first law formula as it is now written $\Delta U + W = Q$. Rather than accept this experimental fact and its many implications it became logically necessary to create the imaginary "Perfect Gas" and to endow this "Perfect Gas" with the imaginary qualities that fit so nicely into generally accepted and recognized thermodynamic theory. One attribute of this "Perfect Gas" is quite comforting to those who prefer Aristotlean logic to scientific method: since the "Perfect Gas" does not exist it cannot be subjected to experimentation the results of which might prove to be contradictory to current theory.

Let us now confirm the fact that the first law of thermodynamics as written $\Delta U + W = Q$ is not valid by conducting a pair of experiments. Let us fill a small container having a volume of 0.012182 cubic foot with one pound of liquid refrigerant 12 having a temperature of 75°F and an enthalpy of 25.204 BTU/lb. Let us connect this small container by stopcock controlled tube to a larger evacuated container having a volume such that the total volume of both containers and the connecting tube is 0.29177 cubic foot. Let us next build into this apparatus the means to introduce a measured amount of heat. After allowing the apparatus to achieve thermal equilibrium with its external environment having a temperature of 75°F also let us next thermally insulate this system so that it cannot lose heat to the environment nor gain heat other than that heat deliberately introduced and measured. Now let us open the stopcock and introduce 105.885 BTUs into the system. Under these conditions the temperature of the refrigerant 12 will increase from 75°F to 360°F. At the same time the enthalpy of the gas will increase to 131.089 BTU/lb. Now let us repeat this experiment with an apparatus identical to this except that the volume of the large container is such that the total volume of both containers and the connecting tube is only 0.19247 cubic foot. Let us introduce 105.881 BTUs into this second system or 0.004 BTUs less than in the first case. Under these conditions the temperature of the refrigerant 12 will increase from 75°F to 370°F, 10°F higher than in the first case even though slightly less heat is introduced. At the same time the enthalpy of the gas will increase to 131.085 BTU/lb.

Since neither system can perform external work, Fermi's logic dictates that W in both cases is zero. Since less heat was introduced in the second experiment than in the first, $Q_2$ is slightly less than $Q_1$. If the first law formula $\Delta U + W = Q$ were valid, therefore, $\Delta U_1$ would be slightly higher than $\Delta U_2$. But it is not. $\Delta U_2$ is higher than $\Delta U_1$ because the temperature of the refrigerant 12 is 10°F higher in the second experiment than in the first. Mathematically the first law formula in the form $\Delta U + W = Q$ cannot be valid and this pair of experiments can be used as proof of that fact. It is also proof of the fact that the energy of a real world gas is a function of volume as well as of temperature. The first law of thermodynamics as it is currently written may very well be valid in some fictional world populated with "Perfect Gases" created with impeccable Aristotlean logic, but it is not valid in the beautiful real world populated with real gases created by God. In this beautiful real world created by God a heavier object does not fall faster than a lighter object and real gases can be subjected to experimentation.

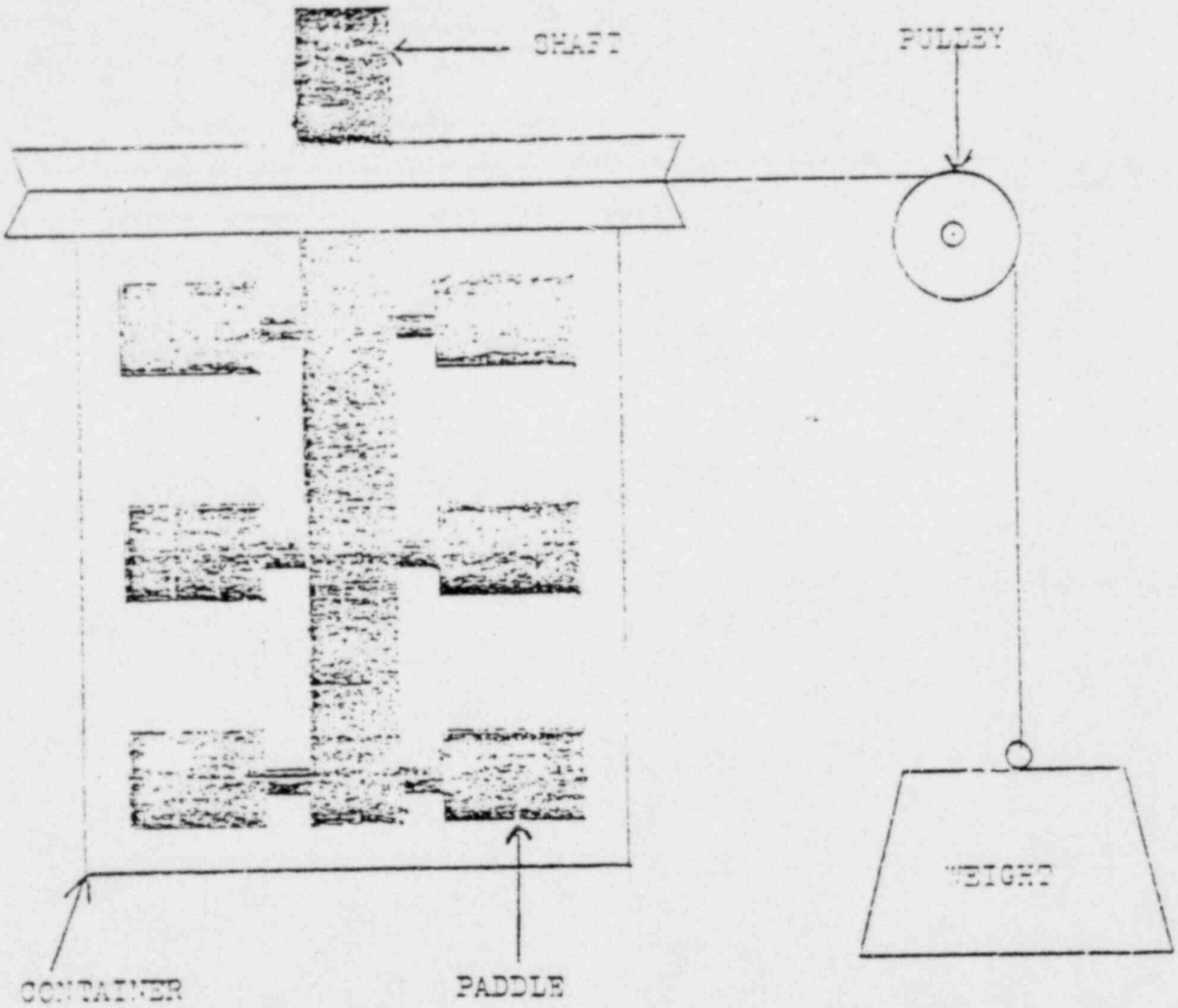
In this pair of experiments the only real difference between the two is volume. The temperature of the refrigerant 12 increased more in the second experiment because the volume of the large container is less. As a consequence of this smaller volume pressure becomes higher as the liquid refrigerant 12 is transformed into a gas. At the conclusion of the first experiment the pressure of the refrigerant 12 was 230 PSIA. At the conclusion of the second experiment the pressure of the refrigerant 12 was 360 PSIA. The thermodynamic data tables published by the air conditioning industry make it quite evident that it requires less heat to raise the temperature of a fluid at a given temperature and pressure to a higher temperature if the final pressure is higher than it does to raise the temperature of that fluid the same amount if the final pressure is lower. For example, it requires 83.145 BTUs to convert one pound of refrigerant 12 at a beginning temperature of 50°F under a beginning pressure of 61.394 PSIA to a gas at 200°F under a final pressure of 200 PSIA. But it requires 86.181 BTUs to convert that one pound of refrigerant 12 at the same beginning temperature and pressure to a gas at the same 200°F under a final pressure of 100 PSIA. The reader may verify the fact that this applies to all real world gases by simply referring to the published thermodynamic data tables or to an ASHRAE HANDBOOK. When this fact is applied to thermodynamical systems that cannot perform external work ($W_s = 0$), it means that if $\Delta U$s are held equal in terms of temperature, Qs are not equal; if heat input and therefore Qs are held equal, $\Delta U$s in terms of temperature are not equal. Thus, Joule's two chamber experiment, the above described pair of experiments, or published thermodynamic data tables for any real world gas may all be used to demonstrate that the first law of thermodynamics as written $\Delta U + W = Q$ is not valid. The logic behind the first law is impeccable; impeccable, but wrong.

Now let us examine another implication of Joule's two chamber experiment and the experimental fact that the energy level of a gas filled system is a function of volume as well as of temperature. It is a fundamental tenet of thermodynamics that the absolute temperature for equal masses of the same substance is directly proportional to the Qs. Let us therefore repeat the pair of experiments involving containers with unequal volumes in terms of absolute temperatures. Let us assume that in both cases the small containers are each filled with one pound of liquid refrigerant 22 having a temperature of $32^{\circ}F$ or $273.1^{\circ}K$, a volume of 0.012468 cubic foot and an enthalpy of 19.169 BTU/lb. Under these conditions the starting point for this pair of experiments is absolutely the same in terms of Q because temperature, volume and enthalpy are identical. Let us now assume that the volume of the first large container is such that the total volume of the containers and connecting tube of the first system is 0.69668 cubic foot and assume that the volume of the second large container is such that the total volume of the containers and connecting tube of the second system is 0.38756 cubic foot. Let us now add precisely 132.978 BTUs to the one pound of liquid refrigerant 22 in each system. Having started at the same point in terms of Q and having added the same amount of heat to the identical masses in each system, according to existing thermodynamic theory there <u>should</u> be no difference in temperature. In both cases the enthalpy of the gas is increased to 152.147 BTU/lb. However, in the first case the temperature of the refrigerant 22 increases to $290^{\circ}F$ ($416.4^{\circ}K$) at a pressure of 128 PSIA and in the second case the temperature of the refrigerant 22 increases to $300^{\circ}F$ ($421.99^{\circ}K$) at a pressure of 226 PSIA. Quite obviously the absolute temperature for equal masses of the same substance is <u>not</u> directly proportional to the Qs. This tenet of thermodynamics is not true for refrigerant 22. This tenet of thermodynamics is not true for refrigerants 12 or 11. Indeed, this tenet of thermodynamics is not true for any real world gas. It is of course true of the imaginary "Perfect Gas" with its imaginary qualities which cannot be subjected to experiment by virtue of the fact that it doesn't exist. The reader may verify the fact that the absolute temperature for equal masses of the same substance is not directly proportional to the Qs by referring to published thermodynamic data tables in an ASHRAE HANDBOOK. The data presented above can be verified at the same time.

This tenet of thermodynamics that the absolute temperature for equal masses of the same substance is directly proportional to the Qs is also not valid for liquids. This can be illustrated by examining the definition of a unit of heat. The British thermal unit (Btu) is defined as the quantity of heat which must be supplied to one pound of water to raise its temperature through one fahrenheit degree, specifically between 63°F and 64°F, at one atmosphere of pressure. It is necessary to specify the pressure because it would take less heat to raise the temperature of one pound of water through one fahrenheit degree if the pressure were 500 atmospheres and even less heat if the pressure were 1000 atmospheres. The range of error in this tenet of thermodynamics is less for liquids than for gases, but it is not a valid tenet in either case. It is also not valid for solids although the range of error is less for solids than for liquids.

The first law of thermodynamics and its mathematical expression in the general form $\Delta U + W = Q$ purports to be a statement of the conservation of energy for thermodynamical systems. As such it is also a statement of the equivalence of work and heat. That is, if $\Delta U$ is zero but $Q$ is positive, then $W$ must of mathematical necessity be positive and there must as a consequence be equivalence between $W$ and $Q$. In 1843 James Prescott Joule conducted another famous experiment that proved that a given quantity of work was equivalent to a given quantity of heat. The apparatus he used for this experiment was essentially a friction calorimeter and it is illustrated in Exhibit B on the next page. A 26 kilogram weight, attached to a string which was passed over a pulley, was used to rotate a shaft and with it a set of paddles that churned a measured amount of water in a container. The weight was repeatedly raised and dropped 1.6 meters. When the experiment was concluded Joule found that there had been a slight rise in the temperature of the water in the container, about 0.3°C. Joule computed the mechanical

# EXHIBIT B
# JOULE'S FRICTION CALORIMETER



work done and the heat produced by it, finding that 838 foot pounds were equivalent to one BTU. Later, more accurate experiments have found this conversion factor (which is symbolized by the letter J in his honor) is precisely 778.3 ft-lb/BTU or 4.186 joules/gm-cal. It is, of course, necessary to add to this: at one atmosphere of pressure. It would take less than 778.3 foot pounds of work to raise the temperature of one pound of water through one fahrenheit degree if the water were under a pressure of 500 atmospheres.

As you will see in chapter 2 devoted to the nature of work much of the error that can be found in thermodynamic theory today can be traced to this experiment of Joule and to the work of Sadi Carnot.

On page 8 of his book Fermi states: "Equation (6) is called the equation of state of an ideal or perfect gas; it includes the laws of Boyle, Guy-Lussac, and Avogadro. No real gas obeys equation (6) exactly. An ideal substance that obeys equation (6) exactly is called an ideal or a perfect gas." (Note: I have added the underlining to emphasize this portion of Fermi's statement and the same is true for the statements below.)

On page 10 Fermi states: "We can now state Dalton's law for gas mixtures in the following form: The pressure exerted by a mixture of gases is equal to the sum of the partial pressures of all the components present in the mixture. This law is only approximately obeyed by real gases, but it is assumed to hold exactly for ideal gases."

On page 21 Fermi states: "In the case of a gas, we can express the dependence of the energy on the state variables explicitly. We choose T and V as the independent variables, and prove first that the energy is a function of the temperature T only and does not depend on the volume V. This, like many other properties of gases, is only approximately true for real gases and is assumed to hold exactly for ideal gases."

There is a common thread of error throughout thermodynamic theory as it exists today. That common thread of error may not be evident yet but with God's help my words in the next chapter may contribute to the elimination of this error and to a better understanding of this beautiful world He created. Had it not been for the creation of the imaginary "Perfect Gas" this error would have been found and corrected by others long ago. Logic, no matter how sound it appears to be, is not a valid substitute for experimental facts and scientific methods. Today, any air conditioning technician with an ASHRAE HANDBOOK can supply the detail evidence to prove conclusively that every major tenet of the science of thermodynamics, including the first and the second laws of thermodynamics, is in error and the extent of this error increases as pressure and temperature increase. Fermi and many other noted scientists fell victim to the seductive logic of the "Perfect Gas" theory, just as Aristotle's logic seduced earlier scientists into believing that a hea vier object would fall faster than a lighter one. The logic in both cases was impeccable - and in both cases wrong.

The fact that the magnitude of the error throughout existing thermodynamic theory increases as temperature and pressure increase points out a danger not recognized by the general public nor even by the scientific community. Thermodynamic theory provided the basis for the design and operation of nuclear power generating plants, generating plants that operate at both high temperatures and high pressures. More importantly, when something unexpected occurs, as did occur at Three Mile Island, thermodynamic theory must provide the answers as to what corrective action should be taken. Since existing thermodynamic theory is rampant with error, and since the gases in a nuclear power generating plant are not the "Perfect Gases" Fermi and others have created to develop the existing theory of thermodynamics, the corrective action taken in the event of an accident may not be corrective. Three Mile Island was proof that the margin for error is quite small if we are to avoid a nuclear disaster. That margin for error may be a good deal less than the error that can be found in the major tenets of the science of thermodynamics as it exists today.

# CHAPTER 2

# THE NATURE OF WORK

by

ROBERT W. CLARK JR.

The work of Sadi Carnot in the early years of the 19th century relating to the theory of heat engine operation and to the fundamental nature of work preceeded the experiments of Joule. Much of Carnot's work became a basic part of modern thermodynamic theory either directly or indirectly through its inclusion in the work of others. He is most famous for his formula for determining the maximum efficiency (E) of a theoretically perfect heat engine, $E = (T_2 - T_1) / T_2$, the temperature values being absolute scale temperatures. This formula, like the first law of thermodynamics, is based upon the false assumption that the energy level of a gas filled system is a function of temperature only and not a function of volume; that is, that heat is *directly* related to temperature. This formula, like the first law of thermodynamics, is also based upon the false assumption that heat is *directly* related to external work. This is exactly the meaning of the first law formula $\Delta U + W = Q$ when this formula is broken into its two logical components: when $W = 0$, then $\Delta U = Q$, and when $\Delta U = 0$, then $W = Q$. The two experiments of Joule cited in the first chapter were intended to prove these separate elements of both Carnot's formula and the first law of thermodynamics.

The logic upon which carnot's formula is based seems to be not only valid but also unquestionable. Carnot insisted that a steam engine converted heat into work by means of a temperature drop between the heat source and the heat sink. Logically, therefore, work (W) equals heat input ($Q_2$) at the boiler minus heat rejected ($Q_1$) at the condenser, or $W = Q_2 - Q_1$. Since the efficiency (E) of any heat engine is equal to work output (W) divided by work input ($Q_2$), then $E = W/Q_2$ or by substitution the $E = (Q_2 - Q_1)/Q_2$. This logical reasoning then continues as follows: *Since the absolute temperature for equal masses of the same substance is directly* proportional to the Qs, then absolute temperatures can be substituted for the Qs. Thus, by substituting the Ts for the Qs, the formula becomes $E = (T_2 - T_1)/T_2$. It follows from this logic that work is accomplished in a heat engine solely as a consequence of the temperature drop. It also follows from this logic that the temperature difference is the only determinant of efficiency in a theoretically perfect heat engine.

The statement that is underlined was and is today a major tenet of thermodynamic theory. But it is not a scientifically valid statement for any real gas for reasons that were discussed in Chapter 1. The thermodynamic data tables for all real world gases provide the experimentally determined proofs that it takes more heat to raise the temperature of any fluid under conditions of low pressure than under conditions of high pressure. The data in volume after volume is readily available to any air conditioning technician. Thus substituting Ts for Qs is not scientifically valid. This is one major error in Carnot's famous formula but it is not the most important error.

The Carnot Formula states that the temperatures are the only determinant of efficiency. If this were in fact so in the real world then one gas would be as efficient as any other for any temperature range when used as the working substance in the theoretically perfect heat engine. One gas would also be as efficient as any other in the theoretically perfect air conditioning system because the theoretically perfect air conditioning system is nothing more than the theoretically perfect heat engine operating in reverse. But this is simply not true as any air conditioning technician with access to an ASHRAE HANDBOOK can determine for himself. If this formula were true there would be no reason for the existance of a variety of refrigerants. If this formula were true, any one refrigerant would be as useful and as afficient as any other refrigerant for every temperature range. Specifically, if this formula were true then all refrigerants would require the same horsepower per ton of refrigeration and all refrigerants would have the same coefficient of performance for the standard temperature range of 40°F to 105°F if used as the working substance in the theoretically perfect air conditioning system. But this is quite simply not true as Table 2 below illustrates and as every air conditioning technician and engineer knows. Temperature is not the only determinant of efficiency and for that very reason air conditioning technicians and engineers use different refrigerants and the choice will vary as the temperature range varies. It is appropriate at this point to comment that on a practical basis more valid thermodynamics is taught today at air conditioning tradeschools than is taught at any large university.

TABLE 2

| REFRIGERANT NUMBER | THEORETICAL HORSEPOWER PER TON (40°F-105°F) | COEFFICIENT OF PERFORMANCE |
|---|---|---|
| R 11 | 0.676 | 6.95 |
| R 113 | 0.70 | 6.74 |
| R 114 | 0.722 | 6.52 |
| R 12 | 0.736 | 6.39 |
| R 500 | 0.747 | 6.31 |
| R 22 | 0.75 | 6.29 |
| R 502 | 0.806 | 5.86 |

(Data taken from "System Design Manual, Part 4" published by Carrier Air Conditioning Company, Syracuse, N. Y. 1969)

The data in Table 2 makes it obvious that one or more factors other than temperature influence the efficiency of even a theoretically perfect heat engine. We could arrive at the same conclusion logically by carrying the logic supporting the Carnot Formula to a logical extreme. If work is accomplished in a heat engine solely as a result of a temperature drop as Carnot believed and as his formula states, then the pressure or pressures at which the theoretically perfect heat engine is operated is of no consequence. It is possible to heat a gas under conditions of constant pressure. It would likewise be possible to operate a simple single piston heat engine under conditions of constant pressure for a given temperature range. The heat added on the power stroke would increase the temperature and also the volume of the gas and would therefore do some work. But when the heat source is removed at the end of the power stroke, it would take at least as much work to return the piston to its original position on the return stroke as the power stroke accomplished. Even the theoretically perfect heat engine could not be operated efficiently under the condition of constant pressure regardless of the temperature range involved. Obviously pressure is a factor in determining the efficiency of a heat engine. But pressure is not a factor included in the Carnot Formula. The Carnot Formula, like the first law of thermodynamics, is not valid.

As the reader may have noticed by this time each of the major tenets of thermodynamics as it exists today has a major flaw that renders it invalid and in each case that major flaw is related to volume or to the counterpart of volume, pressure. This common thread of error stems from a faulty understanding of the nature of work. Let us now begin to correct that which has been proven to be wrong and develop in the process a new theory of work.

To better understand the process involved in the conversion of heat into work it will be most helpful to return to the two chamber experiment of Joule shown in Exhibit A on page 2. To begin let us assume Chamber A is filled with refrigerant 12, assume Chamber A has a volume of 0.33408 cubic foot and Chamber B has a volume of 0.24974 cubic foot, assume the temperature of the gas is 350°F under a pressure of 200 PSIA, and assume Chamber B is evacuated initially. The enthalpy of the refrigerant 12 gas under these conditions is 129.778 BTU/lb. When the stopcock is opened the total volume occupied by the gas is increased to 0.58382 cubic foot, the pressure of the gas drops to 110 PSIA, the temperature of the gas drops 50°F to 300°F, and the enthalpy of the gas drops to 122.520 BTU/lb. This data can be verified by referring to published data on the thermodynamic properties of refrigerant 12. Other real gases behave in the same manner.

Fermi was right when he stated that no external work was done by this thermally isolated two chamber system. But Fermi and others have been wrong in assuming that no work was done. Work was in fact done. Joule proved that heat is equivalent to mechanical work within a system. As a consequence of the work that was done in the two chamber experiment the energy level of the system dropped as evidenced by the decrease in both the temperature and the enthalpy of the gas. Consequently, since there was a drop in the energy level of the system as evidenced by this decrease in temperature and enthalpy, of logical necessity some mechanical work had to be done. And since the gas itself is the only substance in the two chambers, of logical necessity the work that was done was in fact done on the gas itself. It does, as Table 1 on page 3 indicates, take work in the form of heat to cause an increase in the diameter of a gas atom or molecule. That is why it does, as Table 1 indicates, take more heat to raise the temperature of a fluid under conditions of low pressure than under conditions of high pressure. Under conditions of low pressure more of the heat that is added goes into the mechanical work of increasing the diameter of the gas atom or molecule and less into raising the temperature of the fluid. Under conditions of high pressure less of the heat that is added goes into the mechanical work of increasing the diameter of the gas atom or molecule and more goes into raising the temperature of the fluid. As stated previously, the thermodynamic data tables published by the air conditioning industry offer voluminous proofs that this is true. Fermi was right when he stated that no external work was done by Joule's thermally isolated two chamber system. But Fermi was wrong is assuming that no work was done. Internal work was done and that work was done of the gas itself.

The mechanism through which this work was accomplished was pressure and specifically the pressure drop from 140 PSIA to 70 PSIA in our example. The temperature drop that occurred was the result of this drop in pressure and not the cause of that drop in pressure. The most important error in Carnot's famous formula is that he confused cause and effect. For almost two centuries the science of thermodynamics has repeated this error, this confusion of cause and effect. The result is a "science" based upon the fiction of the "Perfect Gas", a science based upon a multiplicity of "laws" that must be qualified with a statement such as: "This law is only approximately obeyed by real gases.". In this two chamber experiment of Joule filled with refrigerant 12 heat is converted into internal work by means of a pressure drop, not by means of a temperature drop; the pressure drop is the cause, the temperature drop is the effect.

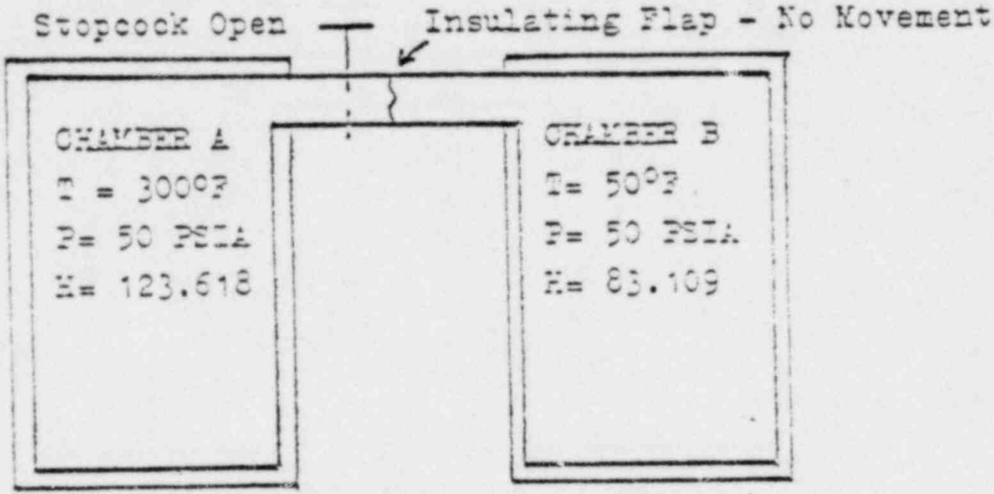
One proof that heat is converted into internal work by means of a pressure drop in this two chamber experiment of Joule rather than by means of a temperature drop is provided by the very method Joule used to conduct the experiment. Before the stopcock was opened the entire apparatus was allowed to achieve a state of thermal equilibrium. The gas in the one chamber and the entire apparatus had the same temperature. No difference in temperature existed between the two chambers or between the two chambers and the surrounding environment. Thus, without a difference in the temperature, no temperature drop could occur to initiate change. But a pressure difference did exist before the stopcock was opened. When the stopcock was opened, a pressure drop did occur in Chamber A and it was this pressure drop that converted heat into internal work and that caused the drop in the temperature of the gas. Thus, Joule's method itself provides one proof that in this experiment heat is converted into internal work by means of a pressure drop. The following experiments are designed to provide additional proofs that pressure, not temperature, is the mechanism by means of which heat is converted into internal work.

Let us build a two chamber apparatus consisting of two very well insulated chambers connected to each other with clear plastic tubing. Let us substitute recording thermocouples in both chambers for the thermometer used by Joule and provide a stopcock for flow control. Let us also provide an insulating flap of very flexible material such as Teflon tape within the clear plastic tubing in such a manner that it offers zero or negligible resistance to flow if there is flow from one chamber to the other but does provide some insulation between the gas in the two chambers. This apparatus is illustrated in Figure C on the next page.

# EXHIBIT C

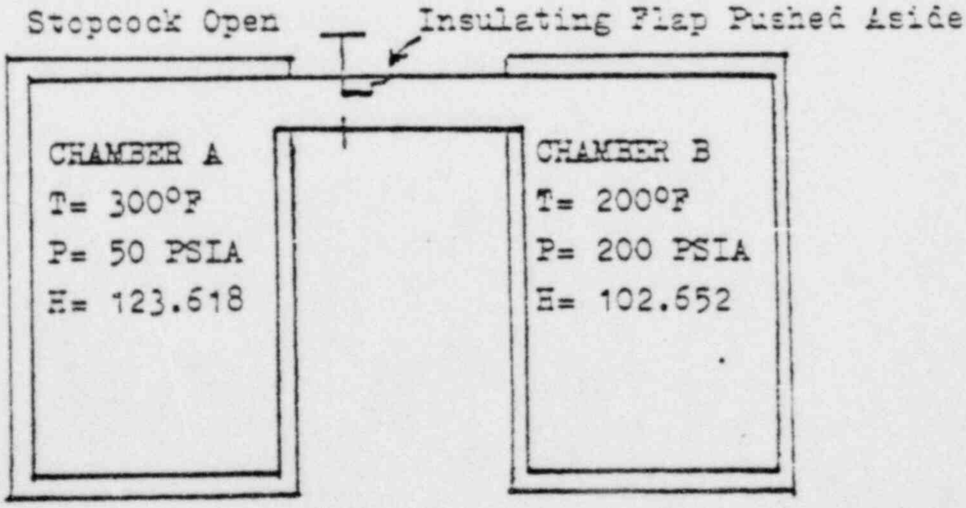
## TWO CHAMBER EXPERIMENT OF JOULE - MODIFIED

FIGURE C-1



(No flow occurs when the stopcock is opened.)

FIGURE C-2



(Flow occurs from Chamber B to Chamber A when stopcock is opened.)

To begin our first experiment with this apparatus let us close the stopcock and evacuate both chambers. Next let us fill Chamber A with refrigerant 12 gas having a temperature of 300°F, a pressure of 50 PSIA, a volume of 1.3197 cubic foot per pound, and an enthalpy of 123.618 BTU/lb. Then let us fill Chamber B with refrigerant 12 gas having a temperature of 50°F, a pressure of 50 PSIA, a volume of 0.82502 cubic foot per pound, and an enthalpy of 83.109 BTU/lb. Under these conditions, illustrated in Figure C-1, there exists a significant temperature difference of 250°F, a significant difference in enthalpy of 40.509 BTU/lb., but no difference in pressure. The gas in Chamber A has a much higher energy level than the gas in Chamber B. But when the stopcock is opened, nothing happens. There is no flow of gas from Chamber A to Chamber B. Indeed, there is no flow of gas in either direction for there is no difference in pressure between the two chambers. Quite obviously neither a significant difference in temperature nor a significant difference in energy level is the mechanism through which heat is converted into work.

Having evacuated both chambers and closed the stopcock, let us now use this same apparatus for a second experiment. Let us again fill Chamber A with refrigerant 12 gas having a temperature of 300°F, a pressure of 50 PSIA, a volume of 1.3197 cubic foot per pound, and an enthalpy of 123.618 BTU/lb., the same conditions for Chamber A as in the first experiment. Let us next fill Chamber B with refrigerant 12 gas having a temperature of 200°F, a pressure of 200 PSIA, a volume of 0.24869 cubic foot per pound, and an enthalpy of 102.652 BTU/lb. Under these conditions, illustrated in Figure C-2, the temperature of the gas in Chamber A is 100°F higher than the temperature of the gas in Chamber B and the enthalpy of the gas in Chamber A is 20.966 BTU/lb greater. Thus the gas in Chamber A has both a higher temperature and a higher energy level than the gas in Chamber B, just as it did in the first experiment above. But the gas in Chamber B is now under greater pressure than the gas in Chamber A. Thus, when the stopcock in opened gas will flow from Chamber B to Chamber A and this flow can be observed through the clear plastic tubing by watching the movement of the of the insulating flap. The flow of gas from Chamber B to Chamber A continues until the pressures in the two chambers are equal at which point the temperatures of the gas in the two chambers will not be equal. Thus pressure, not temperature, is the mechanism by means of which heat is converted into work. Pressure, in the form of an initial pressure differential and a subsequent pressure drop in the high pressure chamber, accomplishes in this experiment work that temperature and energy level could not accomplish in the first experiment. And those who mistakingly believe that the second law of thermodynamics is valid should take note of the fact that the temperature of the gas in Chamber B is lower than the temperature of the gas in Chamber A not only at the start of the experiment but also at the conclusion of the experiment. A much more conclusive proof that the second law of thermodynamics is not valid will be presented in a later chapter devoted to gravitational engines.

Needless to say these two experiments furnish additional proof that Carnot's famous formula and his theories are not valid. They also furnish additional proof that the theory of work inherent in the first law of thermodynamics is not valid. But a third experiment is necessary to complete the process for the work that has been performed in the thermally isolated systems so far has been internal work and not external work. For this third experiment let us again use the apparatus illustrated in Exhibit C with a slight modification. Let us replace the insulating flap with a small turbine-generator so that our thermally insulated system can accomplish some external work. Let us fill the two chambers in the same manner as in the second experiment. Thus the gas in Chamber A will have a temperature 100°F higher than the gas in Chamber B and will also have an enthalpy 20.966 BTU/lb. greater. The gas in Chamber B will be under a greater pressure than the gas in Chamber A, 150 PSIA greater pressure. When the stopcock is opened the gas will again flow from Chamber B to Chamber A and in the process this flow of gas will accomplished some external work by causing the turbine to turn. For the moment it is helpful not to quantify how much external work can be done - it is only important to specify the fact that external work as well as internal work is accomplished and that pressure is the mechanism through which heat is converted into work, both internal work and external work.

It can now be stated as a general rule that whenever a pressure difference within a fluid filled system exists or can be created by the addition of heat, by the withdrawal of heat, or by any other means, this pressure difference can be utilized to accomplish mechanical work. It may be helpful at this point to explain how heat is related to pressure. Heat alters the structure of matter by causing matter to expand or contract; expansion causes pressure to increase, contraction causes pressure to decrease. The expansion of an atom or a molecule is endothermic in nature; that is, the expansion of an atom or a molecule requires the addition of heat or it results in a decrease in the temperature and the energy level of the substance itself when expansion takes place as a result of a decrease in pressure or both if the addition of heat is not sufficient by itself when expansion takes place as a result of a decrease in pressure. Likewise, expansion in the form of an increase in the distance between atoms or molecules is endothermic in nature and such expansion requires the addition of heat or it results in a decrease in the temperature and the energy level of the substance itself when expansion takes place as a result of a decrease in pressure or both if the addition of heat is not sufficient by itself when expansion takes place as a result of a decrease in pressure. The contraction or reduction in size of an atom or a molecule is exothermic in nature; that is, the contraction of an atom or a molecule requires the withdrawal of heat or it results in an increase in the temperature and the energy level of the substance itself when contraction is caused by an increase in pressure or both if the withdrawal of heat is not sufficient by itself when contraction takes place as a result of an increase in pressure. In like manner a decrease in the distance between atoms or molecules requires the withdrawal of heat or it results in an increase in the temperature and the energy level of the substance itself when contraction is caused by an increase in pressure or both if the withdrawal of heat is not sufficient by itself when contraction takes place as a result of an increase in pressure. These are the basic relationships that tie heat, volume, temperature and pressure together.

Now let us proceed to the next step in understanding more completely the basic nature of work, specifically how heat is converted into mechanical work by a heat engine. To accomplish this task it will be most helpful first to explain the current theory and in the process to point out the fallacies inherent in this current theory. Current theory is based upon the work of Sadi Carnot. To explain how a heat engine converted heat into work Carnot developed an Ideal Engine Cycle and this Carnot Cycle is the basis of current theory. The separate components of this Ideal Engine Cycle are illustrated in Figures D-1, D-2 and D-3 of Exhibit D on the next page.

Carnot imagined a cylinder filled with a working substance such as steam at the heat source temperature $T_2$, pressure $P_1$, and volume $V_1$ as illustrated in Figure D-1. He then imagined that an amount of heat ($Q_2$) was added causing the working substance to expand isothermally, that is at the same temperature. When this step is complete the working substance would have a new, lower pressure ($P_2$) and a new, greater volume ($V_2$). With the heat source removed, the working substance was allowed to continue to expand adiabatically (without a loss of heat) by supposing that no heat could escape from the cylinder. This expansion would continue until the temperature of the working substance falls to the heat sink temperature $T_1$ at which point the pressure would be $P_3$ and the volume $V_3$. During both of these expansions the heat engine will have done work by lifting the loaded piston and this work can be represented by the shaded area in Figure D-1.

Next Carnot assumed the working substance was compressed isothermally by applying a force to the piston, the heat of compression being rejected to the heat sink. At the end of this step an amount of heat ($Q_1$) is rejected and the working substance has a higher pressure ($P_4$) and a smaller volume ($V_4$). Next, the working substance is again compressed, this time adiabatically,

# EXHIBIT D
# CARNOT'S IDEAL ENGINE CYCLE

FIGURE D-1

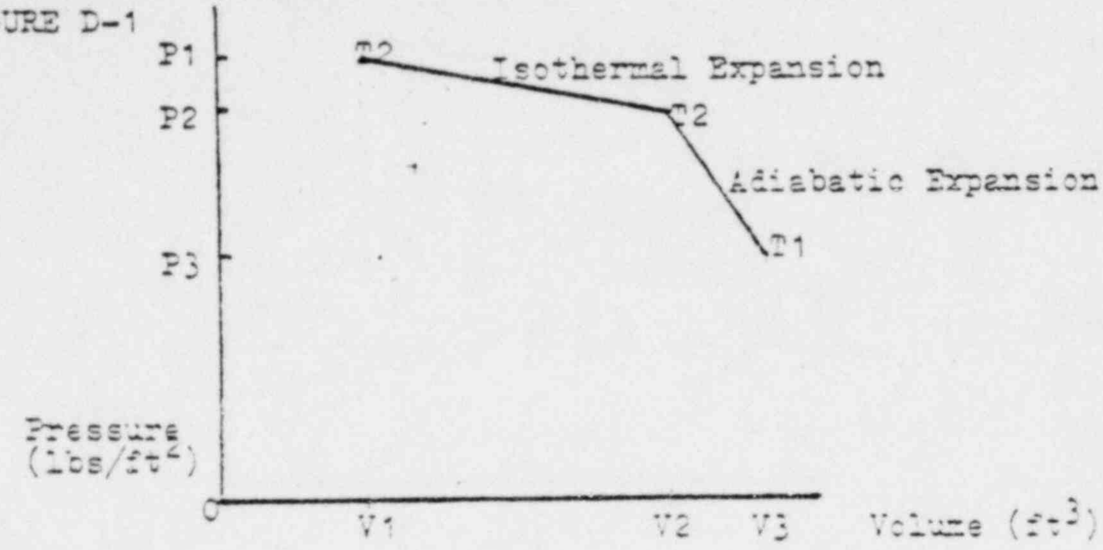


FIGURE D-2

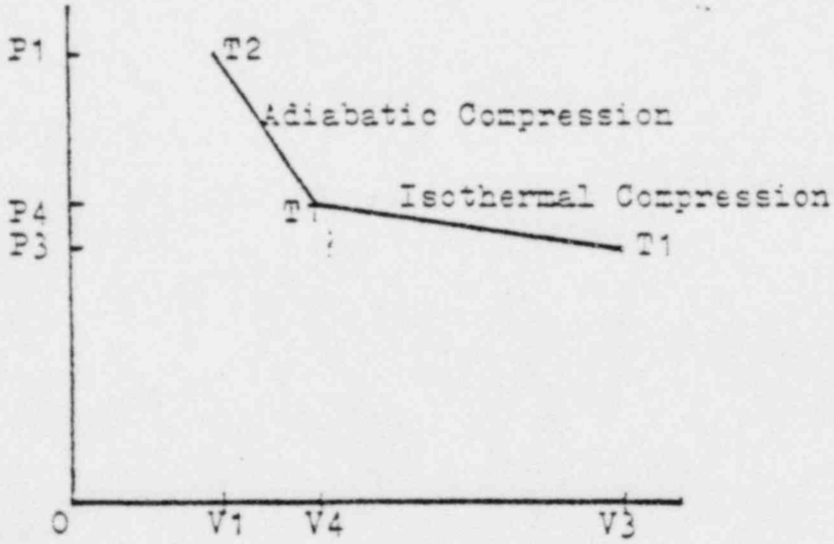
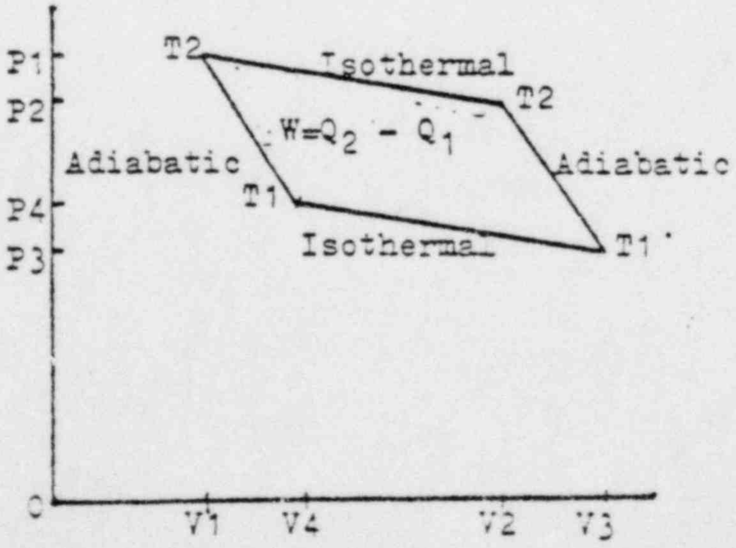
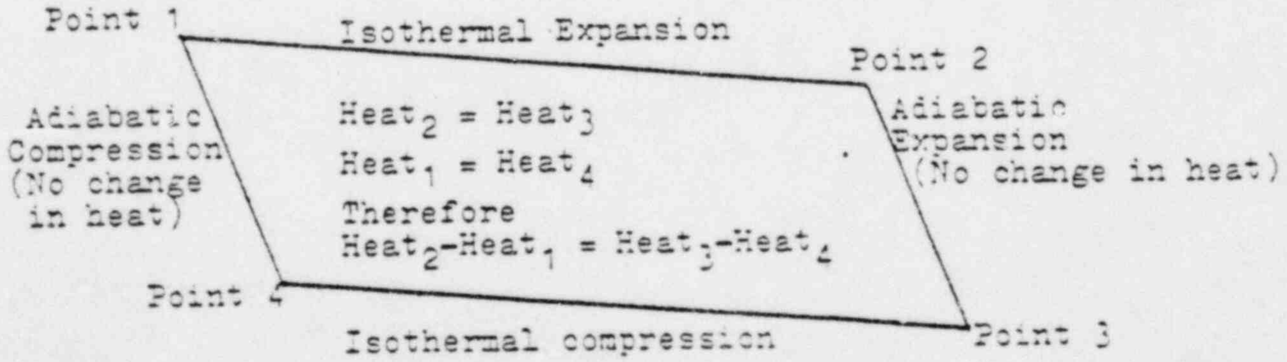


FIGURE D-3



without allowing any of the heat of compression to pass into the sink, until conditions of temperature, pressure and volume are the same as when the entire process started. The work done on the working substance during these two separate compressions is shown by the shaded area under the curve in Figure D-2. By superimposing one curve upon the other, the net work done during this Ideal Engine Cycle can be represented as illustrated in Figure D-3. Since care was taken to restore the working substance to its original conditions of temperature, pressure and volume, no energy was supposedly gained or lost during the cycle within the ideal engine. It has been concluded, therefore, that the source of the net work done must of necessity be the amount of heat that was converted into work, or $W = Q_2 - Q_1$.

Let us begin our analysis of this Ideal Engine Cycle by examining it logically and mathematically. Adiabatic means without loss or gain of heat. The Ideal Engine Cycle, as illustrated very simply below, consists of four distinct steps, two of which are isothermal and two of which are adiabatic. If heat content at Point 1 is equal to heat content at Point 4, whatever value that content may have in terms of BTUs, and if heat content at Point 2 is equal to heat content at Point 3, whatever value that content may have in terms of BTUs, then the BTUs of heat added between Point 1 and Point 2 must of logical and arithmetic necessity equal the BTUs of heat rejected between Point 3 and Point 4. Logically and mathematically it cannot be otherwise. Thermodynamics as taught at Harvard and other universities is fiction but logic as taught at Harvard is a true science.



If a theoretical thermodynamic cycle includes both an adiabatic expansion and an adiabatic compression, as does the Ideal Engine Cycle of Carnot, then heat input and heat rejected are of logical and arithmetic necessity equal by definition. And please note that the Ideal Engine Cycle of Carnot is theoretical because the only gas that can be expanded adiabatically or compressed adiabatically is the fictional perfect gas which does not exist. As the two container experiments described earlier proved the expansion of a real gas is endothermic in nature. Such expansion requires either the addition of heat to maintain constant enthalpy while temperature decreases or it results in a decrease in both the temperature and the enthalpy of the gas. In like manner the compression of a real gas is exothermic in nature. Such compression requires either the rejection of heat to maintain constant enthalpy while temperature increases or it results in an increase in both the temperature and the enthalpy of the gas. A real gas may be expanded at constant enthalpy _if_ heat is added. A real gas may also be compressed at constant enthalpy _if_ heat is rejected. But the adiabatic expansion and the adiabatic compression of a real gas without the gain or loss of heat are both fictions.

By substituting expansion and compression at constant enthalpy for adiabatic expansion and adiabatic compression, the theoretical Ideal Engine Cycle of Carnot can be duplicated in the real world. Now let us proceed to calculate the work that can be done by this modified cycle using refrigerant 12 as the working substance. In the process of doing this calculation let us at the same time challenge another basic tenet of thermodynamics. Fermi states on page 16 of his book: "We assume, however, that work can be exchanged between the system and its environment (for example, by enclosing the system in a cylinder with non-conducting walls but with a movable piston at one end). The exchange of energy between the inside and the outside of the container can now occur only in the form of work, and _from the principle of the conservation of energy it follows that the amount of work performed by the system during any transformation depends only on the initial and the final states of the transformation_." The statement underlined is not valid. It is very important to understand why it is invalid because it affects the design of efficient heat engines.

The current method of calculating the work that can be done by a piston is stated as follows: The amount of work that is done by a piston is given by the product of the force on the piston and the distance that it travels. The force on the piston is the product of its cross-sectional area, A, and the <u>average</u> pressure within the cylinder, P. The distance of travel is found by dividing the change of volume within the cylinder $(V_2 - V_1)$ by A. Thus the work done is given by the formula PA x $(V_2 - V_1)/A$ or more simply by $P(V_2 - V_1)$. The use of <u>average</u> pressure in this method of calculation is consistent with Fermi's statement that the amount of work performed by the system during any transformation depends only on the initial and the final states of the transformation.

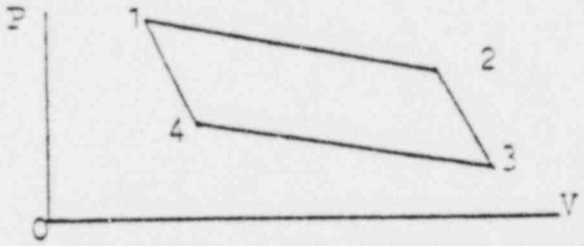
Let us begin our calculations with 10 pounds of refrigerant 12 having a pressure of 58363 pounds per square foot gravity (PSFG), a temperature of 210°F, a volume of 0.88791 cubic foot and an enthalpy of 95.3 BTU/ lb within the single cylinder of the perfect heat engine. Let us expand this gas isothermally until it has a pressure of 49723 PSFG, a volume of 1.1659 cubic feet, and an enthalpy of 98.54 BTU/lb. Since this expansion is isothermal the temperature remains at 210°F. In the second step of our cycle the gas is expanded at constant enthalpy until it has a volume of 3.0020 cubic feet, a temperature of 170°F and a pressure of 20923 PSFG. The two expansions are now complete so let us use the current method of calculating work to determine how much work the expansions can accomplish.

During these two expansions pressure dropped from 58363 PSFG to 20923 PSFG and volume increased from 0.88791 to 3.0020 cubic feet. Average pressure is thus 39643 PSFG and the net change in volume is 2.11409 cubic feet. A piston with an area of one square foot would thus travel 2.11409 feet. If this method of calculation were correct, and if the statement of Fermi were correct, work done would be equal to average pressure times the change in volume, 39643 x 2.11409, or 83809 ft. lbs.

Let us now do the same calculation for each expansion separately and then add the two results. During the isothermal expansion pressure changes from 58363 PSFG to 49723 PSFG and volume changes from 0.88791 to 1.1659 cubic feet. Therefore the work done during this expansion, using the same formula $P(V_2-V_1)$, is equal to 54043 x 0.27799 or 15023 ft. lbs. During the second expansion pressure changes from 49723 PSFG to 20923 PSFG and volume changes from 1.1659 to 3.0020 cubic feet. Thus the work done during this expansion, using the same formula, is equal to 35323 x 1.8361 or 64857 ft. lbs. Calculated by individual steps the work done by the piston is equal to 15023 + 64857 or a total of 79880 ft. lbs.

Why the difference? The use of average pressure for these two expansions combined is not mathematically valid. Such use of an average pressure would be valid only if the expansion of the gas per unit of pressure were uniform throughout the entire transition, that is, if the change in volume per unit of pressure were the same during the isothermal expansion as it is during the expansion at constant enthalpy. That this condition is not true is evidenced by the change in the slope of the line on the pressure-volume diagram at the point where isothermal expansion ends. Isothermal expansion, expansion at constant pressure, expansion at constant enthalpy, and expansion due to a change in volume are different from each other in terms of volumetric change per unit of pressure. The slope of the line on the pressure-volume diagram changes accordingly. Work must therefore be calculated separately for each step in the thermodynamic cycle and the use of average pressure for two or more steps is not valid. For the same reason Fermi's statement of the thermodynamic principle that the amount of work performed by a system during any transformation depends only on the initial and the final states of the transformation is not valid. How you get from one point to another through engine design, and how you get back does make a difference in the amount of work that can be performed by an engine. The very fact that separate calculations lead to a different conclusion is also proof that the use of average pressure for two expansions combined is not mathematically valid. If it were valid, separate calculations using the same formula would yield the same result.

Logic by itself can be used to prove these same conclusions even more convincingly. If Fermi's statement of this thermodynamic principle and this use of average pressure for the two expansions combined were valid, and if they were applied consistently not only to determine the work done by the piston on its power stroke but also to determine the work done on the piston on its return stroke, they they could be used to prove that no heat engine could produce net work if the engine were operated in a complete thermodynamic cycle. The difference in pressure between point 1 and point 3 on the power stroke as illustrated in the pressure-volume diagram below is quite obviously the same as the difference in pressure

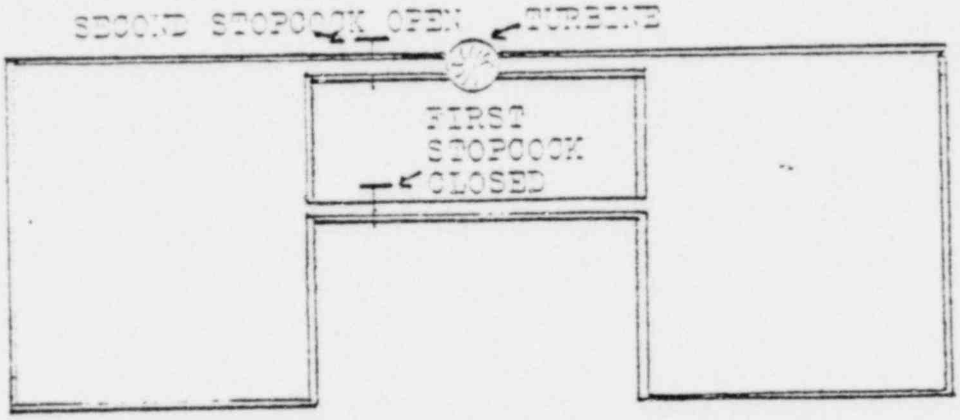


between point 3 and point 1 on the return stroke. Likewise, the difference in volume between point 1 and point 3 on the power stroke is quite obviously the same as the difference in volume between point 3 and point 1 on the return stroke. Thus, if Fermi's statement of this thermodynamic principle and this use of average pressure were valid, the amount of work that would be required to return the piston to its starting point would always be exactly equal to the amount of work the piston produced on the power stroke if the engine were operated in a complete thermodynamic cycle. Applying this principle of thermodynamics consistently and this use of average pressure consistently to the entire heat engine cycle makes it obvious that both are fallacious. Which side of the piston is pushed does not change the amount of work accomplished or required.

Now let us continue with our calculation by determining the amount of work that is required on the piston to complete the thermodynamic cycle. To accomplish the isothermal compression of step 3 the pressure of the refrigerant 12 is increased from 20923 PSFG to 32443 PSFG and the volume of the gas is reduced from 3.0020 to 1.7948 cubic feet. This isothermal compression thus requires 26683 x 1.2072 or 32212 ft. lbs. of work. The final compression at constant enthalpy requires an increase in pressure from 32443 PSFG to 58363 PSFG and a decrease in volume from 1.7948 cubic feet to 0.88791 cubic foot. This final compression thus requires 45403 x 0.90689 or 41176 ft. lbs. of work. The total work that must be done on the piston during these two compressions is thus equal to 32212 + 41176 or 73388 ft. lbs. During the two expansions the piston did 79880 ft. lbs. of work. Net work accomplished is thus 79880-73388 or 6492 ft. lbs.

The net work that is accomplished by a heat engine is simply the result of the fact that the work done by the piston is accomplished at a relatively high pressure while the work done on the piston is accomplished at relatively low pressure. Volumetric change as reflected by the distance of travel is the same for both the power stroke and the return stroke when the heat engine is operated in a complete thermodynamic cycle. The key element in heat engine efficiency is thus the difference in pressure that can be created by either the addition of heat or the withdrawal of heat. Since the pressure-volume relationships per unit of heat for any given temperature range vary significantly for the many real fluids that exist in this marvelous world, one conclusion that can be drawn from this is that for every temperature range within which a heat engine operates there is one fluid that is superior to all others as a working fluid within that specific range. And since it does matter how you get from point 1 to point 3 and back, and because how is determined by heat engine design as well as by mode of operation, there may be - and there are - more efficient thermodynamic cycles than the Ideal Engine Cycle of Carnot. These will be discussed in later chapters.

As the next step in understanding the basic nature of work let us perform a series of experiments with two thermally isolated containers. Let us connect the two containers to each other by means of two separate tubes as illustrated in the figure below. One tube simply has a stopcock to control flow through that tube. The second tube, which also has a stopcock to control flow through that tube, leads from one container to a pelton wheel turbine and from that turbine to the second container. The turbine is arranged so that various loads can be placed upon it so that external work can be accomplished by the flow of gas from the first container to the second container. Thermocouples and pressure gauges with external readouts are placed within both containers so that the conditions of temperature and pressure can be monitored and recorded. Both containers and tubes are thermally insulated.



With both stopcocks closed and after evacuating both containers let us fill container one with a gas under high pressure and then allow thermal equilibrium to become established. The first of this set of experiments involves simply the opening of the first stopcock to allow the gas to expand and to flow from the first container to the second without passing through the turbine. Then record the results in terms of the temperatures and the pressures in both containers. This experiment merely duplicates the two chamber experiments conducted earlier and the results will be similar to those shown in Table 1 on page 3. This experiment establishes the base condition, specifically the volumetric expansion of a gas during which no external work is performed. Internal work is performed as described earlier and the purpose of this set of experiments is to find out if there is a specific relationship between internal work and external work.

Again evacuate both containers with the stopcocks closed and then recharge the first container with gas under the same conditions of temperature and pressure. Under the same final conditions place an appropriate load on the turbine and open the stopcock on the tube that controls gas flow to the turbine. When the turbine stops turning, close that stopcock and record the temperatures and pressures in the two containers. Now open the second stopcock so that the gas can continue to expand until the pressures in the two containers are equal. Again record the temperatures and pressures in the two containers. This completes the second experiment of this set of experiments.

For the third experiment repeat the second experiment with one exception. When the turbine stops turning under the identical load, lighten the load and permit more external work to be done. When the turbine stops turning for a second time, close the stopcock that controls flow to the turbine, record the temperatures and pressures in the two containers, and then open the second stopcock so that the gas can continue to expand until the pressures in the two containers are equal. Again record the temperatures and pressures in the two containers. Now calculate the amount of external work done by the turbine in the second and third experiments. The reader may wish to repeat this experiment for a fourth time, lightening the load each time the turbine stops so that the turbine can do even more external work each time the load is reduced.

Now please note the following results of these experiments:
(1) The conditions of temperature and pressure are the same at the conclusion of each experiment because the same amount of internal work is done in all cases;
(2) No external work was performed during the first experiment, some external work was performed during the second experiment, more external work was performed during the third experiment, and even more external work was performed during the fourth experiment but the external work that was performed in varying amount did not in any way alter or influence the final conditions of temperature and pressure.

Let us now repeat this set of experiments keeping the size of the first container the same but doubling the size of the second container. Because the volume of the second container has been doubled, the pressure drop will be greater and the decrease in temperature and enthalpy will greater because more internal work will be performed on the gas itself. Again the conditions of temperature, enthalpy and pressure will be the same at the conclusion of each experiment. Again the amount of external work performed will vary. Additionally it will be found that more external work can be performed during this second set of experiments than was performed during the first set using the same turbine loads in both cases.

When a gas is allowed to expand as a result of a change in volume and without the addition of heat, the pressure drop that occurs causes internal work to be performed on the gas itself resulting in a decrease in the temperature and the enthalpy of the gas. During this expansion external work can be - but need not necessarily be - performed. So long as the full pressure drop permitted by the change in volume is not prevented, the amount of external work performed does not alter or influence in any way the final conditions of temperature, enthalpy and pressure. The greater the amount of internal work performed, the greater is the potential for external work. Even if a perfect turbine in terms of zero resistance and zero friction were assumed to exist, the amount of external work performed cannot exactly equal the amount of internal work performed because the equality of gas pressure and load resistance would prevent expansion of the gas. To maximize the amount of external work performed by a turbine under these conditions, the load upon the turbine (plus turbine resistance) must be variable and slightly less than the difference in pressure between the two chambers. Needless to say the results of these experiments and these conclusions drawn from those results do not conform to the currently recognized and accepted first law of thermodynamics.

Let us now investigate what happens when volumetric expansion occurs as the result of the addition of heat.

For the first of a pair of experiments let us assume we have two thermally insulated containers connected to each other by a tube fitted with a stopcock to control flow. Let us assume the size of the first container is 0.13337 cubic foot and the size of the second container is 1.95393 cubic feet. The total volume of the two containers is thus 2.0873 cubic feet. Let us evacuate both containers, close the stopcock, and then fill the first container with ten pounds of liquid refrigerant 22 having a temperature of 73.68°F, a pressure of 18619.8 PSFG, and an enthalpy of 31.211 BTU/lb. Let us now open the stopcock and add 113.408 BTU/lb to the ten pounds of refrigerant 22. The liquid will become a gas that will have a temperature of 280°F, an enthalpy of 144.619 BTU/lb, and a pressure of 52603.8 PSFG. No external work is performed during this experiment.

Let us now assume the existance of a cylinder with a vertical piston having an area of one square foot and let us assume the minimum volume of this piston is 0.13337 cubic foot. Let us assume this piston is filled with ten pounds of liquid refrigerant 22 having a temperature of 73.68°F and an enthalpy of 31.211 BTU/lb. Let us also assume that a load of 18619.8 pounds rests upon the piston. The initial condition of this cylinder with a piston is therefore identical to the initial condition of the first container in the first of this pair of experiments described above.

Let us now add a 33984 pound weight to the load upon the piston making the total load 52603.8 pounds. No change occurs in the liquid because we assumed the minimum volume of the piston to be 0.13337 cubic foot and so we must also assume that this added weight rests upon the walls of the cylinder. Let us now add heat to this liquid until the pressure of the liquid becomes slightly less than 52603.8 PSFG. During this addition of heat no external work is performed because the pressure of the liquid must very slightly exceed 52603.8 PSFG before the piston will move. But some internal work is done. The heat causes an increase in the size of the refrigerant 22 molecule. Since total volume cannot change, this change in the size of the molecule causes a decrease in the distance between molecules. The former is endothermic in nature; the latter is exothermic in nature; but since some net heat is required the two changes are not thermally balanced in relation to each other.

When a total of 113.408 BTU/lb has been added to the ten pounds of refrigerant 22 it will have become a gas with a temperature of 280°F, an enthalpy of 144.619 BTU/lb, a pressure of 52603.8 PSFG, and a volume of 0.20873 cubic foot per pound. The ten pounds of refrigerant will now occupy a volume of 2.0873 cubic feet and the piston under load will have moved 1.95393 feet. Thus the work - external work - done as a result of the expansion of a gas caused by the addition of heat is equal to 1.95393 x 52603.8 or 102764 ft. lbs.

The first of this pair of experiments accomplished no external work. The second experiment accomplished 102784 ft. lbs. of external work. The conditions at the start of the two experiments were identical. The conditions at the end of the two experiments are identical. The same amount of heat was added in both cases. Clearly, the previous finding that during the expansion of a gas external work can be - but need not necessarily be - performed has been confirmed.

Internal work has to do with the structure of the working substance and changes in that structure. The relationships of that structure to heat, temperature, pressure and volume are finite, measureable and fixed.

The energy level of a substance when properly defined is also finite, measureable and fixed in terms structure and hence in terms of heat, temperature, pressure and volume.

External work in the form of mechanical work exchanged between systems is relative in nature. Work potential is also relative in nature. The relative nature of external work and work potential is the subject of the next chapter.