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MAE 431: ENERGY SYSTEM

Research Paper

Title: Entropy and the Second Law of Thermodynamic.

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ABSTRACT:

This research paper introduces the concepts of Entropy and Second Law of Thermodynamic, their origins, and the formulation for second law of thermodynamic. We also discuss the two statements formulated for second law of thermodynamic, which are the Kelvin-Planck statement that is based on observation of heat engine and Clausius statement that is based on the observation of refrigerator or heat pump. Finally, we will prove that these two statements of second law of thermodynamic are indeed equivalent by proving that violation of one statement will lead to the violation of the other statement.

INTRODUCTION:***Entropy and Second Law of Thermodynamic:***

The first law of thermodynamic deals with the energy balance during a given process. The first law cannot tell us the direction of the process that will take place. A process cannot take place unless it satisfies both the first law and the second law of thermodynamic. The first law is based on the conservation of energy principle, however, satisfying the first law does not mean that the process will actually take place. For example, a cup of hot coffee will eventually cool off. This process satisfies the first law of thermodynamic since the amount of heat lost by the coffee is equal to the amount of energy gained by the surroundings. The reverse process, where a cup of coffee becomes hotter and hotter in a room as a result of heat transfer from the surroundings to the cup, will not take place yet the process satisfies the conservation of energy, the first law of thermodynamic. But we all know that this will not happen in real life. This example shows us that a process must take place only in a certain direction; this rule is given in the second law of thermodynamic. This is why sometimes the second law is called the time arrow.

An important property called the internal energy was found to arise as a consequence of the first law of thermodynamics. Another important property, called the entropy, follows from the second law. The second law of thermodynamic and the concept of entropy that is related to it is a very interesting topic. There are many applications of second law of thermodynamic, for example in information science, computer science, communications theory and etc [1]. The term entropy, which is closely related to the second law, was created by Clausius. He invented the term in 1865 when he had noticed that a certain ratio was constant in reversible, or ideal, heat cycles. The ratio was heat exchanged to absolute temperature. Clausius decided that the conserved ratio must correspond to a real, physical quantity, and he named it "entropy".

Today, the *American Heritage Dictionary* gives as the first definition of entropy, "For a closed system, the quantitative measure of the amount of thermal energy *not available to do work*" (emphasis added). So it's a negative kind of quantity, the opposite of available energy. In mathematical formulation, we formulate the entropy change of a system as:

$$S_2 - S_1 = \left(\int_{rev}^2 \frac{\delta Q}{T} \right)_{int} \quad \text{[Equation 1]}$$

Where the integration is carried out for any internally reversible process linking the two states. The prove of entropy is a property can be shown by proving the quantity:

$$\left(\oint \frac{\delta Q}{T} \right)_{int, rev} = 0$$

This proves can be found in reference [5]. The entropy is a state property that it only depends only on the ends states and not the path followed between the states (Jones 329).

There is another definition given to the entropy where entropy is also use to mean disorganization and disorder. This is so called the logical entropy. In the *American Heritage Dictionary*, gives this second definition of entropy, "a measure of disorder or randomness in a closed system." Again, it's a negative concept, this time the opposite of organization or order [1].

Now we know that a system cannot undergo a process if the process does not satisfy both the first law and also the second law of thermodynamic. And the second law shows the direction of the process, that is, the tendency of the process will proceed. We will now discuss two common statements for the formulation of second law of thermodynamic, which are Clausius Statement and Kelvin-Planck Statement. However, before this, we need to introduce the concept of heat engine and refrigerator.

ORIGIN OF SECOND LAW OF THERMODYNAMICS:

There are two important concepts that related to the formulation of the second law of thermodynamic, which is Heat engine and Refrigerator. The concept of Heat engine forms the basic of Kelvin-Planck expression for the second law of thermodynamic. On the other hand, the concept of refrigerator or heat pump forms the basic of Clausius expression of the second law of thermodynamic. We shall later proof that this two statements of second law are actually equivalent to each other.

Heat engine:

Work is easy to convert to other form of energy but converting other form of energy to work is not easy. Work can be converted to heat easily but converting heat to work we need heat engine. A schematic diagram showing the heat engine is shown in Figure 1. Heat engines have the following characteristic:

- a. They received heat from a high-temperature source.
- b. They convert part of the heat to work.
- c. The reject the remaining waste heat to a low temperature sink.
- d. They operate on a cycle.

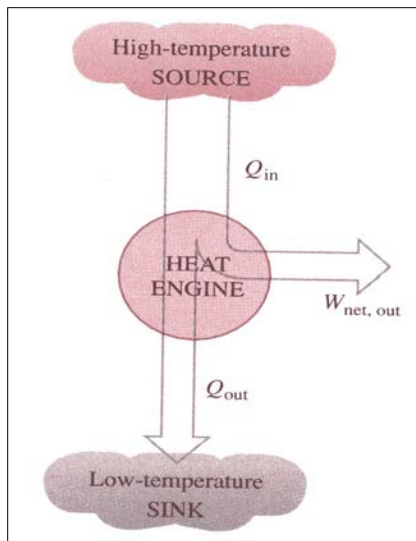


Figure 1. A heat engine. Q_{in} is the heat from the high-temperature reservoir, and Q_{out} is the temperature reject by the heat engine to the low-temperature reservoir. The amount of work produce by this heat engine is $W_{net, out}$.

The work-producing device that fits into the definition of a heat engine is the steam power plant, which is an external-combustion engine. A heat engine must have some thermal efficiency, where this thermal efficiency must be less than unity. This means that some heat must be rejected from the process. The thermal efficiency of a heat engine is defined as:

Thermal efficiency= Net Work output/ Total heat input

$$\eta = W_{net,out}/Q_{in}$$

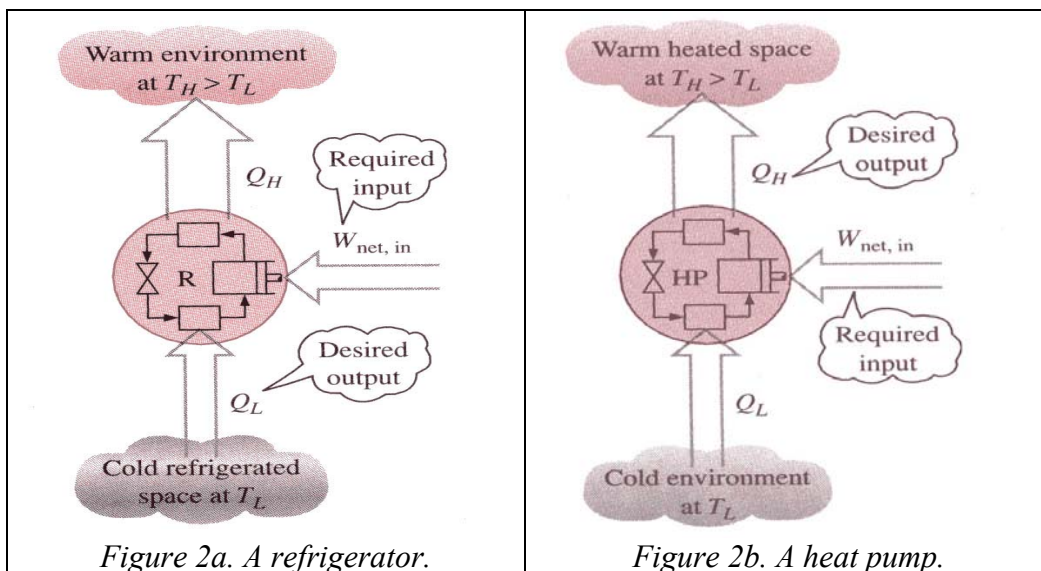
We cannot have a 100 percent thermal efficiency for a heat engine. Some heat must be rejecting to a sink. For example, a steam power plant rejects heat as a form of water in a lower temperature, say 80C then its entrance temperature, say, 100C. We cannot save this form of heat back to the reservoir at 100C because the temperature of the water will not flow into the 100C reservoir by itself, some work must be done to raise its temperature. For this reason, this is called the wasted energy. Now it is clear that this limitation on the heat engine form the basic of the Kelvin-Planck statement of second law of thermodynamic. One of these statements is:

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. [1]

That is, a heat engine must exchange heat with a low-temperature sink as well as a high temperature source to keep operating. We will then collect few definitions from different thermodynamic textbook and compare them, which will be done in the following section.

Refrigerator and Heat Pump.

Heat transfer in the nature is always from a high temperature medium to low temperature medium. The transfer of heat from high temperature medium to low temperature medium does not require any device. However, the reverse process cannot happen in nature and the transfer of heat from low temperature to high temperature medium requires a special device, which is called refrigerator. A refrigerator is also a cyclic device like heat engine. A refrigerator is shown schematically in Figure 2a.



A heat pump is also a device that transfers heat from low-temperature medium to high temperature medium. The heat pump and refrigerator operate in the same cycle but they differ in the objective. The objective of a refrigerator is to maintain the refrigerated space in a low temperature by removing heat from it. On the other hand, the purpose of a heat pump is to maintain a heat space in high temperature by absorbing heat from a low temperature source. A refrigerator is shown schematically in Figure 2b.

The performance of the refrigerator is called the COP, coefficient of performance. Where:

$$\text{COP}_R = Q_L / W_{\text{net,in}}$$

Also, by conservation of energy, we have:

$$W_{\text{net, out}} = Q_H - Q_L \quad \text{[Equation 1]}$$

The COP of refrigerator can be greater than unity.

The performance of the heat pump in term of COP is,

$$\text{COP}_{\text{HP}} = Q_H / W_{\text{net,in}}$$

Where the coefficient of heat pump is always greater than unity. [1]

Now, from the idea of refrigerator and heat pump that heat cannot transfer from a low temperature reservoir to a high temperature reservoir without doing work to the system we are able to write the Clausius statement of the second law of thermodynamic as:

It is impossible for a heat engine to produce a net work output in a complete cycle if it exchanges heat only with a single energy reservoir. [1]

This statement does not mean that it is impossible to construct a cyclic device that transfers heat from a cold medium to a warmer one. It means that a refrigerator will not operate unless its compressor is driven by an external power source. That is, in order to transfer heat from low temperature to a high temperature one, work must be done.

Now we have discussed the heat engine, refrigerator and heat pump. By doing this, we are able to explain the two equivalence statement of second law of thermodynamic. We must remember that the Kelvin-Planck statement and Clausius statement of second law is a negative statement and a negative statement cannot be proved. The second law is base on experimental observation, and no experiment has been conducted contradicts the second law.

In the following section, we collect few definitions of the two statements from different source. Then, we will prove that they are actually two equivalent statements for the second law of thermodynamic.

DEFINITION OF SECOND LAW OF THERMODYNAMIC FROM DIFFERENT SOURCES:

The Kelvin-Planck statement has the advantage that it provides an effective means for bringing out important second law deductions related to systems undergoing thermodynamic cycles. However, the Clausius statement inequality lead directly to the property entropy and to formulations of the second law convenient for the analysis of closed system and control volumes as they undergo process that are not necessarily cycle. [2]. Some of the two statements from different source are listed below:

1. Base on Yunas A. Cengel & Michael A. Boles. "Thermodynamic, An engineering Approach." [3].

Kelvin-Planck Statement:

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

Also can be expressed as:

No heat engine can have a thermal efficiency of 100 percent, or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.

Clausius Statement:

It is impossible to construct a device that operates in a cycle and produce no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

2. Base on Eastop & Mcconkey. "Applied Thermodynamics for Engineering Technologist". [4]

Kelvin-Planck Statement:

It is impossible for a heat engine to produce a net work output in a complete cycle if it exchanges heat only with a single energy reservoir.

Clausius Statement:

It is impossible to construct a device that operating in a cycle will produce no effect other than the transfer of heat from a cooler to a hotter body.

3. Base on Michael J. Moran & Howard N. Shapiro, “Fundamental of Engineering Thermodynamic”

Kelvin-Planck Statement:

It is impossible for any system to operate in any thermodynamic cycle and deliver a net amount of work to its surrounding while receiving energy by heat transfer from a single thermal reservoir.

This statement does not rule out the possibility of a system developing a net amount of work from a heat transfer drawn from a single reservoir. It only denies the possibility if the system undergoes a thermodynamic cycle.

Clausius Statement:

It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

4. Base on J.B Jones & R.E. Dugan. “Engineering Thermodynamics”.

Kelvin-Planck Statement:

It is impossible for any device to operate in a cycle and produce work while exchanging heat only with bodies at a single fixed temperature.

Or

It is impossible for any device to operate in a cycle to absorb heat from a single reservoir and produce an equivalent amount of work.

Clausius Statement:

It is impossible for any device to operate in such manner that it produces no effect other than the transfer of heat from one body to another body at a higher temperature.

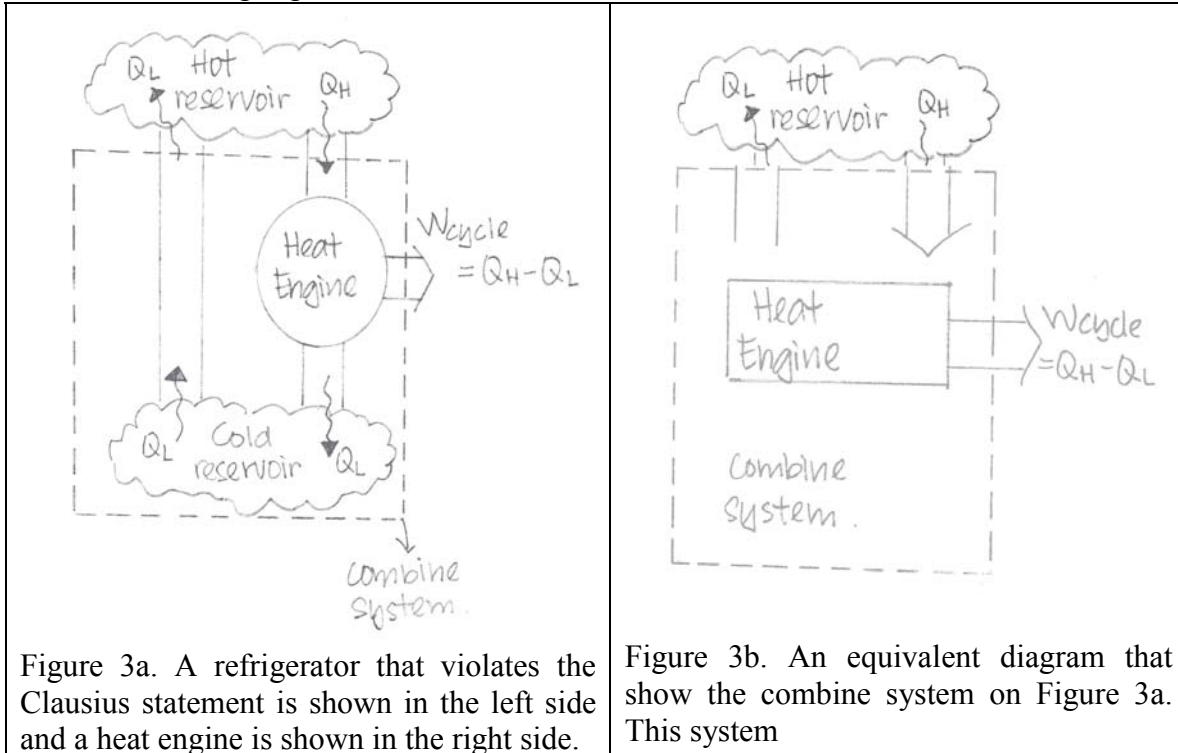
Obviously, the Kelvin-Planck statement is formulated base on the observation of the heat engine and the Clausius statement is formulated base on the observation of the refrigerator and heat pump. As we explain in previous paragraph.

DEMONSTRATING THE EQUIVALENT OF KELVIN-PLANCK AND CLAUSIUS STATEMENTS.

The equivalence of the Kelvin-Planck statement and the Clausius statement is proved by showing that violation of one statement implies the violation of the other. (We are not proving that they are valid, as we have said in previous paragraph, the second law is negative statement, which cannot be proved) In this section, we will prove in both ways, that is, we will show that the violation of the Clausius statement will lead to the violation of the Kelvin-Planck statement; also, we will show that the violation of the Kelvin-Planck statement will lead to the violation of the Clausius statement. This is shown separately below:

A. Demonstrates the violation of the Clausius statement leads to the violation of the Kelvin-Planck statement.

This is done using Figure 3a and 3b shown below.



This graph of Figure 3a shows two systems operating between two temperature reservoirs. On the left side of Figure 3a is a refrigerator and at the right side is a heat engine. Let the system on the left side violate the Clausius statement that the process can transfer heat from the cold reservoir without doing any work. On the other hand, the system on the right side is a heat engine that received heat Q_H from the hot reservoir, output work as W_{cycle} , and rejects the remaining heat to the cold reservoir. The right system does not violate the second law. However, if we consider a system that is shown by the dotted line in Figure 3a, which includes the two systems and only the cold reservoir, called the combine system (also shown in Figure 3b). In this case, we will see an

interesting system, this new system received heat and reject heat ($Q_H - Q_L$) from the hot reservoir and produce a net amount of work (also $Q_H - Q_L$). This new system obviously violates the Kelvin-Planck statement that:

It is impossible for a heat engine to produce a net work output in a complete cycle if it exchanges heat only with a single energy reservoir.

Thus, shown here is the violation of the Clausius statement also leads to the violation of the Kelvin-Planck statement of second law of thermodynamic. Note also that in this case, if we does not violates the Clausius statement, the new system will not show up to violates the Kelvin-Planck statement.

B. Demonstrates the violation of the Kelvin-Planck statement leads to the violation of the Clausius statement.

This demonstration is done with the help of Figure 4 below.

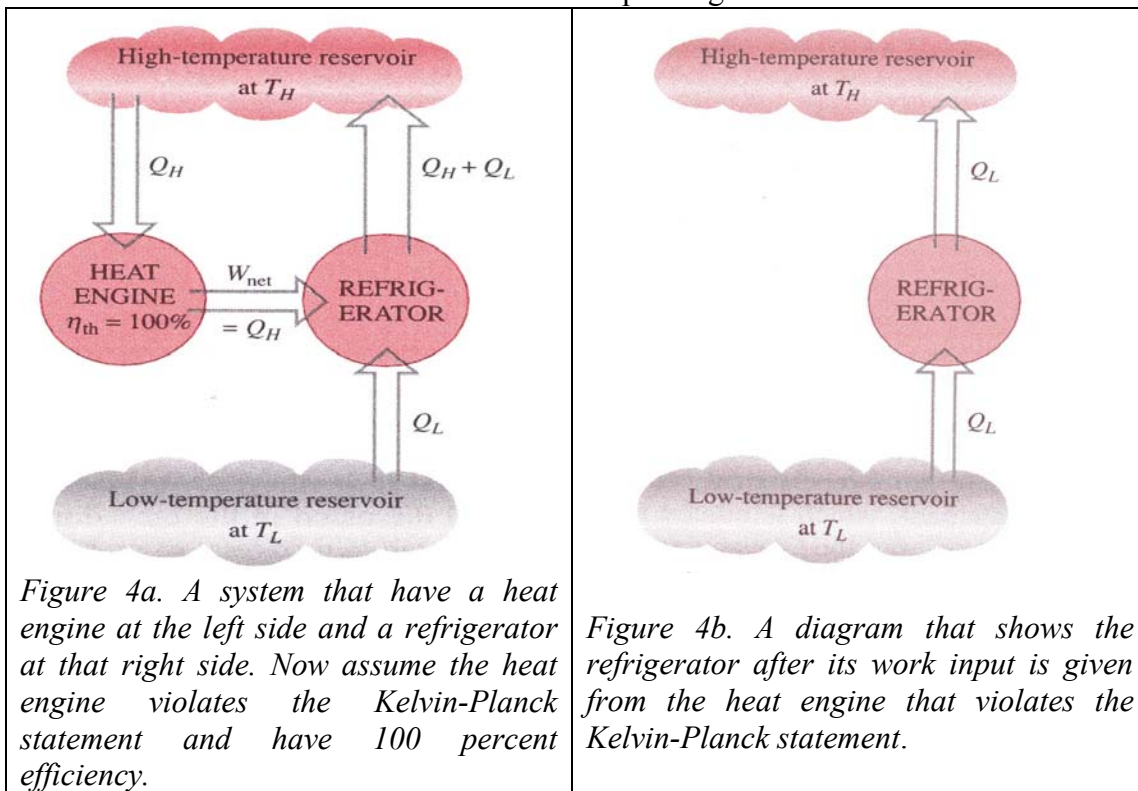


Figure 4 shows a heat engine and a refrigerator operating between two reservoirs. Now, let the heat engine violates the Kelvin-Planck statement that it can operate using a single reservoir and having a 100 percent of thermal efficiency. This is shown in the graph that W_{net} of the heat engine is equal to Q_H , the heat draw from the hot reservoir. On

the other hand, the right side of the diagram shows a refrigerator that does not violate the Clausius.

However, we now let the net work output W_{net} supply to the refrigerator. This work is used to remove heat from the cold reservoir to the hot reservoir. Now this will be our combine system. So, for the refrigerator, now the energy rejected to the hot reservoir is, from Equation 1, Q_H+Q_L . We can now see for the high temperature reservoir received a net amount of heat of:

$$\begin{aligned}\text{Heat} &= Q_H+Q_L - Q_H \\ &= Q_L\end{aligned}$$

The refrigerator system will now be shown as a separate system as in Figure 4b. Obviously, this refrigerator system violates the Clausius statement of second law of thermodynamic (provided the heat engine violates the Kelvin-Planck Statement), that:

It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

So, we can see that if we violate the Kelvin-Planck statement, we will also violate the Clausius statement of the second law of thermodynamic.

From these two demonstrations, we have concluded that the Kelvin-Planck statement and the Clausius statement of the second law of thermodynamic are indeed equivalent. A diagram that shows these two demonstrations is given below:

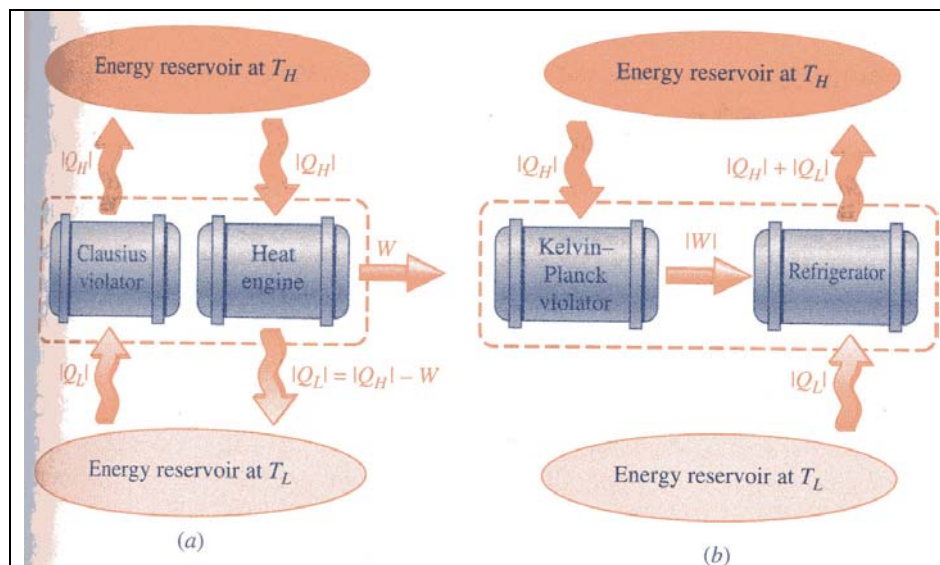


Figure 5. schematic diagram shows the violation of Clausius statement will lead to the violation of Kelvin-Planck statement (a), and violation of Kelvin-Planck statement will lead to the violation of the Clausius statement of the second law of thermodynamic.

REFERENCES:

[1] <http://www.panspermia.org/seconlaw.htm>

[2] Michael J. Moran & Howard N. Shapiro, "Fundamental of Engineering Thermodynamic". 4th edition. John Willey & Sons Inc. 2000.

[3] Yunas A. Cengel & Michael A. Boles. "Thermodynamic, An engineering Approach." 3rd edition. McGraw-Hill Inc. 1998.

[4] Eastop & Mcconkey. "Applied Thermodynamics for Engineering Technologist". 5th edition. Longman Inc. 1998.

[5] J.B Jones & R.E. Dugan. "Engineering Thermodynamics". 1st edition. Prentice Hall, Inc. 1996.

APPENDICES:

1. A copy of the pages that use in this paper from source [1].
2. A copy of the pages that use in this paper from source [2].
3. A copy of the pages that use in this paper from source [3].
4. A copy of the pages that use in this paper from source [4].
5. A copy of the pages that use in this paper from source [5].