THE APPLICATION OF THERMOELECTRIC THEORY TO
POWER GENERATION AND REFRIGERATION

by

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STATEMENT BY AUTHOR

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ABSTRACT

The student, after an extensive literature survey, designed and fabricated two applications of the principles of thermoelectricity. The power level of both devices was in the low range of less than one watt. A brief account of the early history in this field is given, with a somewhat broader report on the underlying thermodynamics and the present state of the art.

At a very light load, the thermoelectric refrigerator achieved its maximum COP, equal to 0.202. The maximum cooling capacity of the device was equivalent to a rate of 0.41 watts, at which load the COP was 0.049. Principal causes of these low figures were the high rate of Joule heat evolved at the cold junctions, and the low film coefficients at all inner and outer junction heat transfer surfaces. These adverse effects resulted in a performance of the refrigerator as a whole equivalent to only about one-fourth that predicted for the individual elements.

When functioning as an electric generator, the maximum output obtained was 0.0079 watts at 93.8 millivolts. Under these conditions the thermal efficiency of the generator as a whole was only 0.0113%. At a part load of 0.0047 watts, the efficiency was slightly lower, or 0.0106%. These effi-
ciencies are approximately one-ninth those predicted for the individual components. The inadequate insulating properties of the heat chamber permitted the greater portion of the input thermal energy to escape through the chamber walls without doing any work. One of the chief reasons for the low conversion efficiencies of the couples themselves was the unsuitable resistance ratio, external to internal.
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CHAPTER 1  
INTRODUCTION TO THERMOELECTRIC PHENOMENA

1.1 Scope of Present Study

Energy conversion processes have occupied the attention of the engineer and the student of engineering since the earliest days of this profession. Power producing devices have contributed immensely to an ever-improving standard of living. More recently, refrigeration and environmental control apparatus have helped make life more comfortable.

It is appropriate, therefore, that a close examination be made of an increasingly important method of power generation and refrigeration. This is the field of thermoelectricity. In the present study, thermoelectric phenomena were reviewed theoretically and experimentally. Two specific applications, i.e., a thermoelectric generator and a thermoelectric refrigerator, were thoroughly investigated.

To provide a firm and adequate basis for the experimental work to follow, a comprehensive review of selected literature dealing with thermoelectric effects was made by the degree candidate. To complete the undertaking, experimental working models of each of the two devices were designed, fabricated, tested, and evaluated. The evaluation phase consisted of an appraisal of thermoelectric devices in
the energy conversion field as compared to other methods currently used. Of particular importance also is the comparison of actual performance characteristics with the predicted design characteristics. The power level of the apparatus fabricated in this analysis was in the low range of less than one watt.

1.2 The History of Thermoelectricity

In 1822 Thomas Seebeck discovered that a current will flow in a circuit composed of two different metals provided the circuit is closed and the junctions of the metals are at different temperatures. He further observed that the magnitude of the current depended upon the difference in temperature.

An exactly opposite effect, the creation of a difference in temperature between two junctions as the result of a flow of current, was observed by Jean Peltier in 1834. It was proved that heat was being absorbed at one junction and given off at the other when Lenz succeeded in freezing water at one junction in such a circuit. This was over 120 years ago, so we can see that thermoelectric phenomena are nothing new.

It might be interesting to locate these events historically with other discoveries in the fields of electricity and thermodynamics about that time.

<table>
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<td>1822</td>
<td>Seebeck. Thermoelectric voltage pro-</td>
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portional to temperature difference.

<table>
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<th>Year</th>
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<td>1824</td>
<td>Carnot's paper on the &quot;motive power of heat.&quot;</td>
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<td>1827</td>
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<td>1844</td>
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Then, for almost a hundred years nothing significant developed in the field of thermoelectricity until physicists in Russia and at Westinghouse achieved efficiencies in the neighborhood of 7%.

More recently, A. F. Ioffe, (Ref. 1) director of the Institute for Semiconductors of the U.S.S.R. Academy of Sciences, observed that the thermal efficiency of the materials originally tested by Seebeck was, theoretically, about 3%, and that this constituted the most efficient source of electric power at that time and for fifty years until the advent of the steam-driven electric generator. Ioffe reckons that rather startling differences might exist today had Seebeck's discoveries been pursued. Such a conclusion is debatable.
1.3 The Physics of Thermoelectricity

It is necessary to have a basic understanding of the mechanism of thermoelectricity in order to compare it with conventional power generation. First of all, let us imagine a block of solid material containing some free electrons. These electrons can be made to move under the influence of a thermal field. If heat is applied to one side of the solid the electrons will tend to behave somewhat as humans might. They will drift away from the hotter region. This leads to an electrical gradient. To take advantage of this electrical gradient the circuit is closed externally, and the electrons flow through the external circuit. This could be called the pumping of electrons with thermal energy, (see Fig. 1.1).

A more sophisticated explanation involves the use of the "hole" concept where the current carriers in one arm of the couple are positively charged holes and in the other are electrons. Thus, the p and n designations of semiconductor physics apply, and the most efficient couples will be based on a junction of such materials (see Chapter 2).

As a comparison, recall that the steam boiler and turbine pump water and steam molecules, but since they are not charged particles, no electrical work is done directly. Thermoelectricity by-passes the "mechanical generator" step by causing charged particles to be pumped directly through a circuit.

The thermoelectric material efficiency depends upon
Heat Pumping of Electrons

Fig. 1.1
three parameters: \( \alpha = \) Seebeck coefficient expressed in microvolts per degree temperature difference.\(^1\)

\[ \sigma = \text{Electrical conductivity} \]

\[ \kappa = \text{Thermal conductivity} \]

These are combined into an expression which is a measure of electrical generating efficiency, and is called the "figure of merit."

\[ z = \frac{\alpha^2 \sigma}{\kappa} \]

The basic considerations that govern the efficiency of a thermoelectric generator are, however, essentially the same as those that govern any heat-power cycle. The Carnot cycle gives the maximum efficiency attainable in cyclic processes.

In the thermoelectric generator the material serves as its own heat exchanger. The highest acceptable temperature is applied to the hot junction and the heat which is not converted to electricity is exchanged at the cold junction. For the steam or gas power cycle, the operation of stages in series in the turbine is analogous to elements in series in a thermoelectric generator.

The foregoing serves to introduce the reader to this energy conversion process which is currently experiencing a

\(^1\)The Seebeck coefficient is given with respect to lead, except in certain rare cases with respect to platinum. See reference 17, pages 2638 and 2639.
rebirth. The topics of performance and efficiency will be more closely examined in a later chapter. Chapter 2 deals with the basic phenomena underlying thermoelectric effects and their origin in the structure and behavior of semiconductors.
CHAPTER 2

STRUCTURE AND BEHAVIOR OF SEMICONDUCTORS

2.1 General

In the era of Seebeck and Peltier, 130 years ago, the science of solid state physics was unknown. The progressively better understanding of the atomic phenomena in solids, notably since the original postulation of the existence of the electron, has advanced the art of composing substances for various purposes by providing the proper atomic conditions to create the desired results.

What do we want in a thermoelectric material? Obviously, to be at all effective, the process must cause a relatively high electrical potential to be created per degree of temperature difference between the junctions. Secondly, the material must have a low electrical resistivity while simultaneously exhibiting low heat conductivity characteristics. In the first instance, the potential mentioned is brought about when the electrons in the two dissimilar substances have greatly different energies. The underlying fact which makes thermoelectricity possible at all is that the difference in electron energy is either absorbed or liberated as heat at the junction boundary by interchange of kinetic energy with the atomic lattice.
2.2 Crystal Structure of Covalent Solids.

In a covalent solid, all four valence electrons of every atom are required to form the crystal. These covalent bonds are very strong, so that at low temperatures each electron is held very securely to the two atoms sharing it. Hence, there are no free electrons as there are in metals. Because of this, electric conduction is not possible. As the temperature is raised, the atoms begin to vibrate. At relatively high temperatures the thermal vibration may become so intense that the bonds occasionally break. When this occurs, free electrons result. Electrical conduction is now possible since charges are available to move in response to an applied electric field. The region of the ruptured bond is called a "hole".

Perfect covalent materials without imperfections of any kind are called intrinsic semiconductors. Since semiconductors do not conduct electricity at absolute zero, the valence-energy band must be thought of as being completely filled with electrons. (The reader is cautioned to distinguish carefully between "band" and "bond". The former designates any energy level, while the latter is synonymous with "union".) Electrical conduction in semiconductors results only when enough heat is added to break one of the bonds. This occurs at a fairly definite temperature.

In our model, therefore, we recognize two possible energy bands, conveniently separated by a "forbidden zone".
The two permissible bands are called (1) conduction band and (2) valence band. The width of the forbidden zone is different for different materials. The amount of energy required to break a bond equals the width of the forbidden zone in the band theory model.

Before any rupture of bonds occurs, however, there exist two bands, one completely filled and the other completely empty. After bonds break, we have a few free electrons in the conduction band while the valence band now contains "holes". Thanks to this situation, electrical conduction is now possible.

From elementary electrical theory, resistivity

\[ \rho = \frac{1}{Ne\mu} \]

where

- \( N \) = density of free charges
- \( e \) = charge per electron (quantitative)
- \( \mu \) = mobility of the charges.

Perhaps a little clarification of the concept of mobility would be in order. It should be recalled that as the temperature of a substance such as a metal is increased from absolute zero, the internal energy of the material causes the electrons to move about in a completely random fashion. In a configuration such as a wire, probably as many would be moving in one direction as would be traveling toward
the other end. Their motion could be compared to the random motion of the molecules of a gas in a closed vessel.

When an electric field is applied, the free electrons are accelerated in a direction opposite to the direction of the electric field. Two simultaneous movements are now present. The free electrons cannot have a fixed and uniform velocity in the direction opposite to the field because of the random motion tendencies brought about by the internal or thermal energy. In all likelihood, the electron quite often moves in such a direction as to have a velocity component in the same direction as the electric field.

Nevertheless, there is a component of "drift" velocity in the opposite direction. Mobility is defined as the ratio of this drift velocity to the magnitude of the electric field intensity. In most cases (see Ref. 5, P. 155) the mobility is a constant of the material and is independent of the electric field intensity.

Since \( N \) increases with temperature, \( \rho \) must, as a result, have a negative temperature coefficient of resistance. In contrast, pure metals have positive temperature coefficients of resistance.

2.3 Electrical Conduction in an Intrinsic Semiconductor.

In an intrinsic semiconductor the number of conduction electrons always equals the number of holes. Under the stimulus of an applied electric field, a hole will be filled by
an electron from an adjoining valence bond, which creates a new hole as a result. In contrast to the situation in metals, these moving electrons are not free, but pass from valence bond to valence bond, progressively filling holes.

Or looked at in another way, as the electrons move from bond to bond, the hole apparently moves in the reverse direction. We get the impression of hole movement. This is called "hole conduction" to distinguish it from the conventional electronic conduction of free electrons in metallic substances. The holes seem to act as though they had a positive charge equal to the charge on an electron.

2.4 Effect of Impurities in the Crystal.

The presence of impurities greatly affects the characteristics of a semiconductor. The effect can be considerable even when only 1 part in $10^7$ is present. Now suppose that germanium or silicon of valence 4 is crystallized with a few impurities of valence 5 such as arsenic, antimony, or phosphorous. However, only four of the five valence electrons of the impurity enter into the interatomic valence bonds.

When this occurs, the fifth electron hangs sort of loosely to its basic nucleus. It does not take much thermal vibration to jar it loose from its original home. When loose, it can wander about as a free electron.

Impurities of this kind are called donors since they donate free electrons to the semiconductor. Notice that
holes are not created in this process. There results a material we call "n-type" or negative type since electrons carry a negative charge.

The opposite result can be obtained. Impurities of valence 3 such as boron, aluminum, indium, and gallium can enter the crystal structure of a valence 4 element. At low temperatures, there results a stable configuration which contains a hole, or absent electron. As the temperature is increased and thermal vibrations begin, an electron is jarred loose from a bond and jumps into the vacancy or hole. This leaves a hole in the valence bond structure. The only free charges are the positive holes. Electric current results from the motion of the positively charged holes. This semiconductor material would be called "p-type". The impurity is called an acceptor since it accepts electrons from the basic material. This deliberate introduction of impurities is called "doping". Usually a thermoelectric material contains both donor and acceptor impurities, but the density of one ordinarily exceeds that of the other. The majority rules when the material is given a name.

It is important to remember that when a dangling electron of the n-type semiconductor separates from its impurity atom, a hole is not produced, since the electron does not come from the covalent bond. Compared to the energy required to cause an electron in a pure semiconductor to "jump across" the forbidden zone, the energy required to shake
loose the fifth electron in the n-type material is not large; hence lower temperatures may be used.

With a p-type material, free electrons are not produced because to be free they must exist in the conduction band. What happens is that the acceptor atoms acquire an electron, leaving a hole at the point the electron originated. The resulting negative ions do not contribute to the current, as one might think, since they are rigidly bound in position with the crystal structure.

Summarizing, then, in the n-type semiconductors we have electronic conduction originating from the flow of free electrons in the conduction band; in the p-type materials, hole type flow of electric current results when holes apparently flow in a direction opposite to that of the jumping electrons, whose movement results from the thermal vibrations of the atomic structure as the temperature is increased, and electrons are set free temporarily, or just long enough for them to go to the nearest hole, but, of course, in so doing create another hole.

2.5 Thermal Conduction in Metals and Semiconductor Materials

In order that the flow of heat take place, there must first exist suitable carriers free to move, and secondly, there must exist a temperature difference.

In metals, which are excellent conductors of both heat and electric charge, the free electrons constitute the principal class of carrier for both of these properties.
That there is a direct relationship between the thermal and the electrical conductivity of metals was first demonstrated experimentally by Wiedemann and Franz in 1853. A theoretical derivation was given by Lorenz in 1872, who further showed that the ratio of the thermal conductivity to the electrical conductivity was directly proportional to the absolute temperature.

Ioffe (page 56 of ref. 1) says, "An exact theory of thermal conductivity has not yet been evolved". Nevertheless, we do know that the cloud of mobile electrons which gives to a metal its power to conduct electricity is also largely instrumental in transporting heat. A secondary mechanism available for heat transfer in solid metals is the so-called Debye waves or lattice vibrations. These are vibrations of the molecules about their equilibrium positions. This phenomenon is associated with a set of standing acoustical waves the velocity of which depends on the elastic moduli of the material concerned.

Since the electrical conductivity of a semiconductor is dependent upon the movement of electrons (or the holes left in a filled band of electrons), it is to be expected that there will be an associated thermal conductivity related to the electrical conductivity through the Wiedemann-Franz law. This would mean an electronic thermal conductivity increasing rapidly with increase in temperature. Recorded values for the thermal conductivities of such
semiconductors as carbon and graphite show, however, that the thermal conductivity decreases as the temperature increases (Ref. 18, page 74). This result occurs since in a semiconductor at low temperatures, the electronic contribution to the thermal conductivity is completely outweighed by the lattice contribution. With increase in temperature, however, the increased number of free electrons means a rapid increase in the electronic contribution which at very high temperatures may outstrip the lattice contribution, and from there on the semiconductor acts as a metal.
CHAPTER 3
SEMICONDUCTOR MATERIALS FOR THERMOELECTRIC APPLICATIONS

Research by R C A and Westinghouse has shown that no one material gives the desired figure of merit for good efficiency over the range of temperatures from, say, 25 to 700°C. R C A has done some work with thermocouple branches constructed in a "sandwich-type" arrangement, where materials are selected to provide a high figure of merit "Z" over relatively narrow temperature ranges. In this setup, the various materials are joined in series from the hot junction to the cold junction, and in cross-section would resemble a section of the wall of a boiler furnace, beginning with refractory firebrick, insulating firebrick, and then a layer of 85% magnesia insulation, each material possessing a most suitable temperature range.

In the thermoelectric branch, one obtains an envelope of $Z$ vs. $T$ curves which represent the best average $Z$ value over the entire operating temperature range from $T_h$ down to $T_c$.

In R C A's investigations the data on the thermal and electrical properties of the materials were obtained in the following ways: The electrical resistivity $\rho$ was determined by an a-c scanning method; the thermoelectric power $\alpha$
and thermal conductivity $K$ were measured simultaneously by
the technique of establishing a small temperature gradient
across the specimen placed between a heater and sink; and
the carrier concentration $n$ and mobility $\mu$ were obtained from
measurements of the Hall constant (see Ref. 2).

A power-generating thermocouple was constructed at
RCA in 1958, from n- and p-type alloys having the follow­
ing compositions:

n-type, $\text{Bi}_2 \text{Te}_3 - 25\% \text{Bi}_2 \text{Se}_3$

p-type, $\text{Bi}_2 \text{Te}_3 - 40\% \text{Sb}_2 \text{Te}_3 - 10\% \text{Sb}_2 \text{Se}_3$

The n-type material was doped with Cu Br, and the p-type
material with excess Bi. The junctions were made by solder­
ing with Bi - 20\% Sb alloy.

Heat was supplied to the hot junction by a resistance
heater, and the cold junction temperature was fixed at 25°C
by circulating water. The variation in generating efficiency
(watts output / watts input) with temperature difference $T_h - T_c$ followed a straight line up to about 200°C of $\Delta T$ and
then gradually the rate of increase fell off until a maximum
efficiency of about 6.5\% was obtained at a $\Delta T$ of 300°C.
A plot of efficiency vs. temperature difference showed how
the figure of merit varied with temperature. Measurements
made revealed that in their evaluation the p-type branch was
not operating as efficiently as the n-type branch. In addi­
tion, metallographic examinations showed that the soldered
junctions were beginning to break down at $T_h = 325°C$. RCA
concluded from these observations that with a slight improve-
ment in the metal-to-semiconductor junction as well as a
better adjustment of the electrical conductivity of the
p-type branch, it should be possible to obtain a power-
generating efficiency up to 10% with these alloys while oper-
ating with a Δ T of 300 °C. (Carnot efficiency under these
temperatures would be 50.2%).

Exploratory research on the properties of ternary
compounds has shown that this new class of materials includes
semiconductors that could be useful for power generation at
intermediate temperatures. Of particular interest seems to
be the observation that the "rock Salt" structure has been
found for Ag Sb S₂, Ag Sb Te₂, Ag Bi S₂, and Ag Bi Se₂. Of
the ternary compounds examined to date, Ag Sb Te₂ was found
to be the most promising for both refrigeration and power
generation, since it has a low lattice thermal conductivity,
an estimated band gap ≥ 0.2 eV, a reasonably high thermo-
electric power (≥ 200 microvolts per degree), and a corre-
spondingly low electrical resistivity. The main deterrent
to the use of the silver-antimony-telluride alloy is the
present inability to adjust its electrical properties
through controlled impurity additions. To determine the
possible usefulness of this compound as a power generating
material, however, measurements of the thermoelectric power
and electrical resistivity have been made (see Ref. 2).

Also, solid-solution alloys of Ag Sb Te₂ with
compounds such as Pb Te, Sn Te, and Ge Te have been studied. (In aqueous solutions and in most common solutions the solvent freezes out as a pure solid. However, there are solutions in which the solid solvent which freezes out contains the solid solute dissolved in it. A homogeneous mixture of two or more crystalline solids in varying proportions is known as a solid solution. The attainment of equilibrium in solid solutions is much slower than in liquid solutions.)

Preliminary work has shown that the useful temperature range of the Ag Sb Te$_2$ - 90% Ge Te alloy will be 50 to 100 C higher than the pure Ag Sb Te$_2$. Furthermore, there seems to be a striking improvement in the figure of merit of Ge Te over the temperature range, 25 to 550 C, by alloying with 10% Ag Sb Te$_2$. The data of the R C A investigators also suggest that above 600 C, pure Ge Te is superior to any of the alloys.

A general consideration of the thermoelectric properties of semiconductors suggests that this class of materials can be useful for thermocouples up to at least 700 C; and that construction of generating units in a sandwich-type arrangement will be necessary to obtain high figures of merit over a wide temperature range and, therefore, high efficiencies. Both Westinghouse and R C A have done considerable evaluation with power-generating devices with hot junction temperatures as high as 325 C using alloys of (Bi Sb)$_2$ (Te Se)$_3$ with efficiencies running about 5.5 to 6.5%.
Thermoelectric data as a function of temperature up to 600 °C have been obtained on the p-type ternary compound, Ag Sb Te₂ and alloys of this compound with Ge Te. The results show that Ag Sb Te₂ and the alloy, Ag Sb Te₂ - 90% Ge Te, are the most promising p-type materials for power generation. An average figure of merit (\( \propto \frac{2}{\varphi \kappa} \)) of about 1.75 \( \times 10^{-3} \) per degree was obtained with Ag Sb Te₂; up to about 500 °C. Thermoelectric data as a function of temperature up to 700 °C have also been obtained for certain In As - Ga As alloys, which are capable of giving figures of merit up to 1 \( \times 10^{-3} \) per degree at a temperature of 700 °C.

Additional data on semiconductor materials can be found in references 2, 3, 13, 14, and 15.
4.1 The Four Basic Effects

There are four interrelated effects which must be considered in any analysis of the phenomenon of thermoelectricity. Two of these were briefly mentioned in chapter one; i.e., Seebeck and Peltier effects. In this chapter, these four effects together with thermal and electrical conduction will be examined more closely.

In Figure 4.1 is depicted a thermocouple circuit existing between two reservoirs, one at temperature $T_h$ and the other at a lower temperature $T_c$. The Seebeck coefficient, or thermoelectric power as it is sometimes called, is the open circuit voltage developed in the thermoelement per degree temperature difference between the hot and cold ends. The elements A and B represent the thermoelectric couple connected in a circuit with the aid of metal junction pieces and the external load $R_L$.

The Peltier effect is the evolution or absorption of heat when an electric current passes from one material to a different one at the same temperature, e.g. $\Pi I$ in Figure 4.1. The rate at which heat is evolved at the junction when a current passes from A to B is $\Pi_{AB} I$, where $\Pi_{AB}$ is the
Basic Concepts of Thermoelectricity

\[ V = \alpha (\Delta T) \]
\[ \Pi = \alpha T \]
\[ \text{Peltier Heat} = (\Pi I)_{T=C} \]
\[ \text{Thomson Heat} = \mu I (\Delta T) \]

Seebeck Coefficient = \( \alpha \)

Peltier Coefficient = \( \Pi \)

Thomson Coefficient = \( \mu \)
Peltier coefficient. If the current is reversed, then heat will be absorbed at the rate $\frac{\text{Peltier heat}}{\text{current}}$.

The third effect, or Thomson effect, is the evolution or absorption of heat when a current passes along a conductor having a temperature gradient. The rate at which heat is evolved is $\mu I (\Delta T)$, where $\mu$ is the Thomson coefficient, and the current passes from the higher to the lower temperature.

The Thomson heat and the Peltier heat are reversible and are in addition to the irreversible Joule heat.

The fourth effect, while not limited to thermoelectricity, plays an important role, and is this irreversible Joule heat. If the thermal emf is not balanced exactly by an external emf, a current will flow, whose value may be adjusted by varying the external emf. If there is no external circuit, but instead the cold ends are put in direct contact to form a closed loop, all the electrical energy developed by the couple is dissipated into internal energy.

$$\text{Joule Heat} = I^2 R$$

4.2 The Origin and Nature of Thermoelectricity

The reader's attention is again directed to Figure 1.1. Before "heat" is applied, we have a more or less uniform concentration of electrons in each of the two elements. Upon being heated, the situation immediately changes. The electrons at each hot end will diffuse more readily than
those at the cold ends, and as a result, more of the hot electrons will move to the cold ends than vice versa. In the figure, one element is an n-type and the other a p-type semiconductor.

Now, consider one leg of the couple only, say the n-type element. There is a pileup of electrons at one end, giving rise to a back emf which prevents further flow of charge. In an open-circuit equilibrium situation, hot electrons keep flowing to the cold end, while cold electrons flow to the hot end because of the voltage gradient. Thus there is no net-flow of charge. Under the influence of a temperature gradient there exists then a heat flow together with a tendency for electric flow, the latter being just balanced by the back emf. (This counterpotential would have opposite signs for electrons and holes, if the other element were being considered).

The above may be thought of as the tendency of heat to drag along electricity. We shall now consider the tendency of an electric current to drag along heat. Let an electric current flow through a conductor. The electrons in flowing from one end to the other carry along some internal energy and some entropy. This "entropy of transport" can be shown to be related to the specific heat, which has the dimensions of entropy. Now, if a current passes from one material to a second material with a different entropy of transport, heat must be evolved or absorbed at the junction
to make up the difference. This is what the Peltier effect is, and from this occurrence comes the equation

\[ \Pi_{AB} = (\alpha_A - \alpha_B) T, \]

where \( \alpha_A \) is the absolute Seebeck coefficient of A, \( \alpha_B \) of B, and the relative coefficient between the two elements is \( \alpha_A - \alpha_B \).

In the same way, in a homogeneous material with a temperature gradient, one can think of two adjacent pieces of material at a temperature \( T \) and a temperature \( T + dT \) as being slightly different materials. Thus the Thomson effect can be thought of as a differential Peltier effect within a given material.

4.3 Efficiency and the Figure of Merit

The following is a summary of symbols used throughout the following analyses, with the subscript \( n \) indicating negative element and \( p \) the positive element, \( c \) the cold temperature and \( h \) the hot temperature:

- cross sectional area \( A \)
- length \( L \)
- resistance, internal \( r \)
- resistance, load \( R \)
- resistivity \( \rho \)
- thermal conductivity \( \kappa \)
- thermal conductance \( K \)
- Seebeck coefficient \( \alpha \)
Without doubt, the best analysis of thermoelectric performance published anywhere is to be found in Chapter 2 of reference 1. Ioffe, the "father of thermoelectricity", has done an excellent job in presenting this study of efficiency.

When one investigates actual and theoretical performance, it is soon apparent that since we are dealing with a cyclic process, the inescapable authority of the Carnot efficiency must be recognized. We shall find that, as in all other real processes, the Carnot efficiency is unattainable because of the reduction in efficiency dictated by the irreversible losses of heat conduction and Joule heat.

Let us, then, first examine these two forces which detract from performance. In section 2.5 was presented a brief microscopic approach to the phenomenon of heat conduction. Looked at macroscopically, this process certainly holds no mysteries. We learn quite young that thermal energy will flow from a high temperature region to a colder one, and that the reverse is impossible without the aid of outside forces supplying work to the system. The process is irrever-
sible simply because dissipative effects make some of the energy unavailable.

A similar situation exists with regard to the Joule heat. The heat rejected to the surrounding cold reservoir cannot be recovered cyclically. Nevertheless, as Ioffe points out on page 38 of reference 1, in some thermoelectric applications, however, half the Joule heat flows back to the high temperature reservoir. This is beneficial in that it means less heat must be supplied to this reservoir from an outside source to keep it at \( T_h \). The remainder of the Joule heat is wasted, however, as far as delivering useful power to the load is concerned. Where a large current is flowing, this Joule heat loss can be appreciable.

As in any electric power producing device, the efficiency is the ratio of the useful load to the energy supplied to the source of thermal energy to keep its temperature constant.

\[
\text{Efficiency} = \frac{\text{Work}}{\text{Peltier heat} + \text{conducted heat} - \frac{1}{2} \text{Joule heat}}
\]

\[
\text{Work} = I^2 R_L
\]

Following Ioffe, letting \( m = \frac{\text{Load Resistance}}{\text{Internal Resistance}} \)
\[ \eta = \frac{\alpha^2 (T_h - T_c)^2}{r(m+1)} x \frac{m}{(m+1)^2} \]

\[ \eta = \frac{\alpha^2 T_h (T_h - T_c)}{r(m+1)} + K(T_h - T_c) - \frac{\alpha^2 (T_h - T_c)^2}{2r(m+1)^2} \]

Note that this differs from Ioffe's equation at the bottom of page 38 in Ref. 1, which is believed in error.

The first term is readily seen to be simply the Carnot Efficiency. The reciprocal of \( \frac{Kr}{\alpha^2} \) is called \( Z \). This topic of efficiency will be analyzed in greater detail in the next chapter.

Efficiency of the thermocouple depends on:

1 - hot and cold junction temperatures
2 - the Z factor or "figure of merit"
3 - the ratio of resistances.

On page 39 of reference 1, it is shown that \( Kr \) is
minimized if \( Kr = \left( \sqrt{\frac{\kappa}{r}} + \sqrt{\frac{\kappa}{z}} \right)^2 \)

and optimum ratio of \( \frac{R}{r} \) for maximum \( \eta \) is

\[
M = \sqrt{1 + \frac{Z (T_h + T_c)}{2}}
\]

Figures 4 and 4a on page 42 of reference 1 show how the maximum theoretical thermoelectric efficiency is a function of only two quantities (assuming \( T_c \) to be a constant), these being the figure of merit and the temperature of the hot junction. Actual efficiencies will, of course, be much lower than the high of 32% shown, due principally to the fact that suitable materials are not yet available and also because of the fabrication problems involved.

4.4 Coefficient of Performance

In 1850, Clausius made his statement of the Second Law; i.e., "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". In other words, there is no refrigerator capable of functioning without requiring a power input. The purpose of any refrigerator is to extract as much heat as possible from the cold reservoir while keeping work input requirement to a minimum. The quantity which indicates the ability of the refrigeration system to do its job is called the coefficient of performance, and equals heat extracted from the cold region divided by
work required.

In a thermoelectric refrigerator, which, of course, has no refrigerant, no compressor, and no compressor drive motor, the input work is simply the electric power supplied.

\[
\text{C.O.P.} = \frac{\text{Heat Extracted}}{\text{Electrical Work Input}}
\]

Peltier heat \( = \Pi I \)

and since \( \Pi = \alpha T \)

Peltier heat \( = \alpha I T_c \)

Joule heat \( = I^2 r \), half of which goes to the hot junction and half to the cold junction.

Heat transfer by conduction \( Q_h \) is given, per unit area, as

\[ Q_h = K (T_h - T_c) \]

Also, since the Seebeck effect would be working against us, there is a power consumption

\[ \alpha I (T_h - T_c) \]

Net heat extracted from cold region =

\[ \alpha I T_c - \left[ \frac{I^2 r}{2} + K (T_h - T_c) \right] \]

Total power input = \( I^2 r + \alpha I (T_h - T_c) \)
\[
\alpha I T_c - \frac{I^2 r}{2} - K (T_h - T_c)
\]

\[
COP = \frac{I^2 r + \alpha I (T_h - T_c)}{\frac{V}{2} - \frac{Kr (T_h - T_c)}{V}}
\]

where \(V\) equals the \(I r\) drop.

Maximum COP

\[
\text{Maximum COP} = \frac{\frac{T_c}{T_h - T_c} \times \frac{M}{M + l}}{\frac{T_h}{T_c}}
\]

where \(M = \sqrt{1 + \frac{Z (T_h + T_c)}{2}}\)

The main condition governing the efficiency of a refrigerator (as well as of a generator) is the heat flux across the thermopile. In a generator this depends mainly on heat conduction. The amount of heat transferred to the hot junction is only slightly greater than that removed from the cold junction, since useful work output is low. These conditions are somewhat different for the refrigerator, however. To the heat extracted from the space to be chilled is added electric
energy which usually exceeds the heat extraction by a considerable amount. The hot end heat rejection is then

\[ Q_h = Q_c + W \]

\[ W = \frac{Q_c}{\text{COP}} \]

\[ Q_h = Q_c + \frac{Q_c}{\text{COP}} = Q_c \left( 1 + \frac{1}{\text{COP}} \right) \]

For example, when \( \text{COP} = \frac{2}{10} \),

\[ Q_h = Q_c \left( 1 + \frac{10}{2} \right) = 6 Q_c \]

4.5 Coupled Flows and the Entropy Transport Parameter.

For a period of approximately eighty years beginning with the era of Lord Kelvin at the middle of the nineteenth century, considerable thought has been given to difficulties surrounding the interrelationship between the reversible and irreversible effects in thermoelectricity.

About thirty years ago in the United States, Onsager made a definite contribution to solving the problem with his macroscopic treatment of irreversible coupled flows. Sections 10.14 and 14.10 in reference 6 contain an excellent summary of this analysis. It is illustrated how entropy must be conceived of as being generated in the conductor, the ends of which are at different temperatures. This is the case of heat conduction, which as we have seen is an irreversible effect.
With an applied potential difference instead of the previous temperature difference, entropy is again produced within the wire since none goes in but the Joule heat causes an entropy current out.

Zemansky states that "If departure from equilibrium is not too great, the entropy (or heat) and electricity flows are coupled in a simple manner". "Onsager proved by means of the microscopic point of view, that the coupling coefficients are equal, which is now known as Onsager's reciprocal relation".

From Onsager's equations is formed a ratio of the entropy current to the electric current when the \( \Delta T \) is equal to zero. This ratio is given the name "entropy transport parameter".

It is further demonstrated on pages 304 and 305 of reference 6 that the Seebeck voltage between the hot and cold junction of a thermocouple made up of two legs A and B is equal to:

\[
\text{Seebeck Voltage} = \int_{T_c}^{T_h} (S^*_A - S^*_B) \,dT
\]

where \( S^* \) indicates the entropy transport parameter.

The analyses of this present chapter will serve to help in the design studies of Chapter 5.
5.1 Power Generation

Let us consider a simple thermoelectric generator consisting of an n-type leg and a p-type leg. Both legs are of cylindrical cross section, of equal diameters and equal lengths. (German scientists have recently shown that the performance is not improved by making the legs in a noncylindrical shape. See Ref. 12).

Power output, as before = $I^2R$

Total emf, $\alpha_{np} = \alpha_n + \alpha_p$ per degree $\Delta T$

$r_{np} = r_p + r_n = (\frac{\rho_p}{A_p} + \frac{\rho_n}{A_n})L$ (in series)

$K_{np} = K_p + K_n = (\frac{\kappa_p A_p}{\kappa_n A_n}) / L$ (in parallel)

Where the temperature difference from hot to cold is not very great, the variation in the Seebeck coefficient is not large (see Ref. 12), so in this analysis we shall assume

$\alpha_{ph} = \alpha_{pc}$ and $\alpha_{nh} = \alpha_{nc}$

From Ohm's Law, $I = \frac{E}{R + r} = \frac{\alpha (T_h - T_c)}{R + r}$
Since useful work = $I^2 R$, we have

$$work = \frac{\alpha^2 (T_h - T_c)^2}{(R + r)^2} \times R$$

Resistance Ratio \( m = \frac{R}{r} \)

or \( R = m r \)

Therefore, \( W = \frac{\alpha^2 (T_h - T_c)^2}{(m r + r)^2} \times m r \)

\( W = \frac{\alpha^2 (T_h - T_c)^2}{r^2 (m + 1)^2} \times m r \)

\( W = \frac{\alpha^2 (T_h - T_c)^2}{r (m + 1)^2} \times \frac{m}{r} \)

Also, \( Z = \frac{\alpha^2}{K \rho} \) (by definition)

but \( K = \frac{KL}{A} \) and \( \rho = \frac{rA}{L} \), and \( K \rho = Kr \)

So, \( Z = \frac{\alpha^2}{K \rho} = \frac{\alpha^2}{Kr} \)

Then \( Kr = (K' \rho A + K \rho A) \left( \frac{\rho^2}{A} \right) \left( \frac{\rho A}{A} \right) \)
\[
Kr = \frac{A}{A} \left( \kappa_p + \kappa_n \right) \left( \rho_p + \rho_n \right)
\]

\[
= \kappa_p \rho_p + \kappa_n \rho_n + \kappa_p \rho_n + \kappa_n \rho_p
\]

Therefore 
\[
Z = \frac{\left| \alpha_n \right| + \left| \alpha_p \right|}{\kappa_p \rho_p + \kappa_n \rho_n + \kappa_p \rho_n + \kappa_n \rho_p} \]^{2}

This equation for the composite figure of merit for two legs of equal areas and equal lengths depends only on the physical properties of the two legs of the couple. As previously demonstrated in Chapter Four, we are now able to predict an expected efficiency since we can specify or measure the hot and cold junction temperatures, the external and internal electrical resistances, and we can calculate the figure of merit. Of course, knowledge of the two temperatures also permits us to calculate the Carnot efficiency, which sets a limit on the highest attainable actual efficiency.

To examine a typical case, let us picture a couple which is composed of two elements with the following properties:

<table>
<thead>
<tr>
<th>n-type</th>
<th>p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>-173 microvolts / deg. C</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$5.5 \times 10^{-4}$ ohm cm</td>
</tr>
<tr>
<td>$K$</td>
<td>0.020 watt / cm deg. C</td>
</tr>
<tr>
<td>Length</td>
<td>0.5 inch</td>
</tr>
<tr>
<td>Diameter</td>
<td>0.5 inch</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>$10.4 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>
The theoretical figure of merit,

\[ Z_{np} = \frac{(173 + 194)^2 (10^{-12})}{0.02 (10.4 + 5.5 + 5.5 + 10.4) (10^{-4})} \]

\[ = \frac{134500 \times 10^{-12}}{0.636 \times 10^{-4}} = \frac{2.12 \times 10^{-3}}{\text{deg C}} \]

Length = Diameter = 0.5 \times 2.54 = 1.27 \text{ cm}

\[ r_{np} = \left( \frac{\rho_p}{A_p} + \frac{\rho_n}{A_n} \right) L \]

but since \( L = D \),

\[ A = 0.785 L^2 \]

\[ r_{np} = \left( \frac{\rho_p}{A_p} + \frac{\rho_n}{A_n} \right) L / 0.785 L^2 \]

\[ r_{np} = 1.595 \times 10^{-3} \text{ ohm} \]

Assuming \( R = 1.0 \text{ ohm} \), (a readily available experimental load)

\[ m = \frac{R}{r} = \frac{1.0}{0.001595} = 627 \]

Assume \( T_c = 27 \text{ C} = 300 \text{ K} \)

And \( T_h = 227 \text{ C} = 500 \text{ K} \)
Then, \[ W = \propto 2(T_h - T_c)^2 \frac{m}{r (m + 1)^2} \]

\[ W = 0.00535 \text{ watts} \]

Carnot Efficiency = \[ \frac{500-300}{500} = \frac{200}{500} = 40\% \]

To determine how much this ideal cycle efficiency is reduced as a result of irreversible losses due to heat conduction and Joule heat entering into the expression for figure of merit, and to the choice of the ratio \( m \); we use the previously-given equation for the thermocouple efficiency:

\[ \eta_{t.c.} = \frac{m}{m + 1} \]

\[ = 0.00168 \]

Overall Efficiency = \[ 0.40 \times 0.00168 = 0.067\% \]

An immediate observation is the relative unimportance of the internal Joule heat, but the great part played by the resistance ratio.

In the above example, had \( m \) been equal to unity, with
all other parameters unchanged,

\[ \eta = 0.40 \times \frac{1/2}{1 + \frac{2}{0.00212 \times 500} = \frac{200}{4 \times 500}} = 7.18\% \]

This gives a theoretical thermal efficiency a hundred times greater than in the previous example.

It is, naturally, of the utmost importance to know how we can achieve the maximum efficiency for any power conversion apparatus. Following Ioffe (pages 39 and 40 of reference 1), the expression for maximum efficiency can be obtained by taking the partial derivative of the efficiency with respect to the resistance ratio, setting equal to zero, finding the optimum value of this ratio, and then inserting in the previous equation for efficiency. This process leads to:

\[ \eta_{\text{max}} = \frac{T_h - T_c}{T_h} \times \frac{M - 1}{M + T_c/T_h} \]

where \( M = \sqrt{1 + \frac{Z(T_h + T_c)}{2}}. \)

"The greater is \( M \) in comparison with unity, i.e., the larger the values of \( Z \) and \( T_h + T_c \), the smaller is the reduction of the efficiency due to irreversible losses. Therefore,
an increase of the hot junction temperature increases the efficiency not only by increasing the value of the efficiency of a reversible engine, but also because of the simultaneous increase of M at a given figure of merit." (Ref. 1, page 40)

Therefore, using the figure of merit of the above example; i.e.,

\[ Z = \frac{2.12 \times 10^{-3}}{\text{deg C}} \]

\[ M_{\text{max}} = \sqrt{1 + \frac{0.00212 \times (500 + 300)}{2}} \]

\[ M_{\text{max}} = \sqrt{1 + 0.848} = 1.36 \]

Then,

\[ \eta_{\text{max}} = \frac{500 - 300}{500} \times \frac{1.36 - 1}{1.36 + \frac{300}{500}} \]

\[ \eta_{\text{max}} = 7.33\% \]

5.2 Thermoelectric Refrigeration

As stated in chapter four,

\[ \text{COP} = \frac{\propto I T_c - K (T_h - T_c) - 1/2 I^2 r}{I^2 r + \propto (T_h - T_c) I} \]
where the second term in the denominator corresponds to the Seebeck power of the refrigerator.

This equation is adequate to determine the COP of any thermoelectric cooling device since calculation of the component parameters is straightforward, i.e.,

\[ \alpha_{np} = \alpha_n + \alpha_p \]

\[ K = \frac{K_p + K_n}{L} = \left( \frac{\kappa_p A_p + \kappa_n A_n}{L} \right) \]

\[ r = r_p + r_n = \left( \frac{\rho_p}{A_p} + \frac{\rho_n}{A_n} \right) L \]

The other quantities are directly measurable.

As an illustrative example consider the following, using the same couple as in section 5.1.

\[ \alpha = (173 + 194) \times 10^{-6} = 367 \times 10^{-6} \text{ volts} \]

\[ K = \frac{0.020}{L} \times (2A) = \frac{0.04 \times 0.785 L^2}{L} \]

\[ K = 0.04 \times 0.785 \times 1.27 \]

\[ = 0.0399 \text{ watt/deg C} \]

\[ r_{np} = r_p + r_n = 1.595 \times 10^{-3} \text{ ohm} \]

Assume:

\[ T_c = 27 \text{ C} = 300 \text{ K} \]

\[ T_h = 32 \text{ C} = 305 \text{ K} \]

\[ I = 20 \text{ amperes} \]
Then, using the equation for COP,

\[
COP = \frac{(367 \times 10^{-6}) (20 \times 300) - (0.0399 \times 5) - (200) (1.595 \times 10^{-3})}{(400 \times 1.595 \times 10^{-3}) + (367 \times 10^{-6} \times 5 \times 20)}
\]

\[
COP = \frac{2.2 - 0.1995 - 0.319}{0.638 + 0.0367} = 1.682
\]

\[
COP = \frac{1.682}{0.675} = 2.49
\]

In another example, with all conditions remaining the same except that the temperature difference = 20°C instead of the previous 5°C; i.e., \(T_h = 320\) K,

\[
COP = \frac{2.2 - 0.798 - 0.319}{0.638 + 0.147} = 1.38
\]

It is apparent that decreased performance results as the refrigerator chilled space temperature is brought down increasingly below ambient.

The refrigeration required in a realistic situation can be calculated from the product \(UA\Delta T\), for the walls of the cooled space. The overall thermal conductance through the walls, \(U\), consists of the two film coefficients plus the con-
ductivity of the wall material. Or, more precisely,

\[
\frac{1}{U} = \frac{1}{h_0} + \frac{L}{k} + \frac{1}{h_1}
\]

\(h_0\) and \(h_1\) are the outside and inside coefficients, \(L\) the thickness of the wall, and \(k\) its thermal conductivity.

One way of determining the heat transfer through the boundaries of the refrigerator would be to pass a steady electric current into the interior of the box to an internal resistance heater, permit a steady temperature to develop within the space, and then assume that under stabilized conditions, the heat leakage through the boundaries equals the Joule heat created in the resistance. In this manner, it is easily possible to establish the value of the product "UA".

This procedure will be further described in the next chapter.
CHAPTER 6
TEST EQUIPMENT AND PROCEDURES

6.1 Introduction

The first five chapters of this thesis deal with the preparatory studies and surveys made prior to the actual fabrication of experimental equipment to be used to evaluate and demonstrate two applications of thermoelectric phenomena. Chapter six describes the apparatus, test equipment, and circuits assembled in the laboratory for the purpose of examining and appraising these applications.

During the period of preliminary planning which preceded the construction of the experimental devices, many manufacturers of electrical, chemical, and semi-conductor materials were contacted. It was learned that the majority of the production and custom designed units were extremely expensive, ranging up to a price of several thousand dollars for relatively low-power equipment.

One exception to this was the model TA-11 thermo-cell produced by Ohio Semiconductors, Inc. A device of this type was purchased for incorporation in the test apparatus. It proved to be a practical, efficient thermoelectric device, with semiconductor material made of bismuth telluride alloys. The unit can be used to heat or cool a small thermal load; or
by maintaining a temperature difference between the two junctions, it can be used for power generation.

The configuration of the TA-11 thermo cell provided the basic idea for construction of additional devices by the author. Preliminary testing of the purchased unit revealed the importance of a low resistance joint at the hot and cold junctions. It was also observed that adequate heat transfer surface had to be provided at both junctions to help compensate for the rather low film coefficient resulting from the flow of heat to and from the still ambient air. Consequently, the various couples assembled in the University shops were provided with 3" by 3" copper plates inside the box, and finned external junctions.

All of the literature reviewed during the period before laboratory work began stressed the importance of a high-grade bond between the semiconductor elements and the copper plates forming the junctions. Similar advice was given in correspondence from Messrs. Eichhorn of the Whirlpool Corporation and Zemansky of the City College of New York. Mr. Eichhorn was so kind as to send free of charge two p-type and two n-type samples of bismuth telluride material. These thermoelements had been nickel plated and had the following properties: (information supplied by Mr. Eichhorn)

\[ n\text{-type } \alpha = -180 \text{ microvolts/}^{\circ}\text{C} \]
\[ \rho = 0.0009 \text{ ohm cm} \]
\[ \kappa = 0.02 \text{ watt cm/cm}^2 \text{/}^{\circ}\text{C} \]
p-type $\alpha = 170$ microvolts /°C
$\rho = 0.0009$ ohm cm
$\kappa = 0.02$ watt cm/cm²  °C

The n-type material had been doped with cuprous sulphide. The p-type was actually one of the materials discussed in chapter three, bismuth-antimony-telluride with mercury for a dope. The properties stated above are not very different from those of the thermoelements in Ohio Semiconductor's TA-ll. These are:

- Seebeck Coefficient: 160 to 180 microvolts per deg C
- Electrical Resistivity: 0.0008 to 0.0012 ohm cm
- Thermal Conductivity: 0.012 to 0.021 watts/cm deg C

In the latter case, the n-type alloy is doped with cuprous bromide, instead of the sulphide, while the p-type element is not doped at all.

The two pairs of elements supplied by the Whirlpool Corporation Research Laboratories served as practice material in the soldering process. RCA publications suggested the use of Wood's metal, which consists of 50% Bi, 25% Pb, 12.5% Sn, and 12.5% Cd, for effecting a good bond between the semiconductor elements and copper. Since it was noted that the melting point temperature of this alloy was 70°C, it was decided not to use this as a solder as the refrigeration chamber was later to be used as a housing for the heating space in the power generation phase of the experiment. Testing was carried out with various techniques of soldering using a
60-40 tin-lead solder. In addition to the 1/2" by 1/2" cylindrical ingots previously mentioned, five pairs of 3/16" by 1/4" elements were available. These latter thermoelements, however, were not nickel plated. Efforts made in tinning these smaller ingots were not too successful.

This semiconductor material is polycrystalline with the crystallites oriented so that the principal cleavage planes are parallel to the axis of the ingot. It was soon discovered that extreme care had to be exercised in the bonding operation to prevent damage to the element through splitting or cracking. Any undue pressure used in the process of making the joint was certain to fracture the material. Sudden and/or extreme temperature changes also cracked the bismuth telluride. Several instances of a good electrical bond but a rather weak structural union were observed during this period of becoming familiar with the proper techniques of assembling the devices. Only when the use of the soldering iron was discontinued, and the heating done in an electric oven or over an electric range, was success attained in the fabrication of suitable thermoelectric couples.

When sufficient skill in the art of making good semiconductor-to-copper junctions was acquired by the author, four additional pairs of bismuth telluride elements were procured, this time from the Electronic Chemicals Division of Merck and Company, who generously refused payment for this material.
The properties of this material were given as follows:

**p-type**

Lot L579, 381-0-595
Net weight 6.0 grams
Thermoelectric power, microvolts / deg C 194
Electrical resistivity, ohm cm. \(10.4 \times 10^{-4}\)

**n-type**

Lot L579, 380-0-548
Net weight 6.0 grams
Thermoelectric power, microvolts / deg C -173
Electrical resistivity, ohm cm. \(5.5 \times 10^{-4}\)

As will be remembered from the earlier discussions of the characteristics of semiconductor materials, the thermoelectric power, or Seebeck voltage, is not entirely independent of the electrical properties. The value of this voltage increases slightly with increasing resistivity. Thus the variation in the figure of merit is less than would be indicated by the variations in the individual parameters. Merck gives the relationship for the subject materials as:

\[
\frac{\kappa^2}{\rho} \quad \text{p-type} \quad 3.53
\]

\[
\frac{\kappa^2}{\rho} \quad \text{n-type} \quad 5.40
\]
Although the thermal conductivity was not given, it no doubt was close to that of the material of other suppliers; i.e., 0.020 watt / cm deg C.

The figure of merit is:

\[ z = \frac{\alpha^2}{\kappa} \]

Checking dimensions,

\[ z = \frac{(\text{volts})^2 \times 10^{-12}}{\text{deg}^2} \]

\[ z = \frac{(\text{cm})^2 \text{deg}}{\text{watt cm} \times \text{Ohm cm}} \]

\[ z = \frac{(\text{volts})^2 \times 10^{-12}}{\text{deg watt ohm}} \]

but, watt = volt x amp

so, \[ z = \frac{(\text{volt})^2 \times 10^{-12}}{\text{deg volt amp ohm}} \]

and since amp ohm = volt,

\[ Z \text{ is measured in reciprocal degrees.} \]

p-type: \[ Z_p = \frac{(194)^2 \times 10^{-12}}{0.020 \times 10.4 \times 10^{-4}} \]

\[ Z_p = 1.81 \times 10^{-3} / \text{deg C} \]
n-type: \[ z_n = \frac{(-173)^2 \times 10^{-12}}{0.020 \times 5.5 \times 10^{-4}} \]

\[ z_n = 2.72 \times 10^{-3} / \text{deg C} \]

Since in the present work temperatures were measured in degrees Fahrenheit, these values would be

\[ z_p = \frac{1.81 \times 10^{-3}}{1.8} = 1.0 \times 10^{-3} / \text{deg F} \]

\[ z_n = \frac{2.72 \times 10^{-3}}{1.8} = 1.51 \times 10^{-3} / \text{deg F} \]

6.2 Experimental Refrigeration Application.

One of the purposes of this project was to fabricate a small refrigerator utilizing the principles of thermoelectricity. Consequently, a box approximately 6" x 7" x 7" was made of a 1" thick sugar cane fibrous material called "Canec". The density of this Celotex product is fourteen pounds per cubic foot, with a thermal conductivity equal to 0.34 btu per hour, square foot, and temperature gradient of one degree Fahrenheit per inch of thickness (information given by manufacturer).

To facilitate assembly and disassembly and the necessary modifications, the four walls and top and bottom were
Wiring Diagram for Refrigeration  FIG. G.1
made to fit perfectly and then held together with rubber bands. "Stepped" joints were made at all wall edges to minimize thermal leakage. In the final design, consisting of two shop-made thermoelectric couples and the purchased TA-11 device, the walls contained the semiconductor elements, fixed in place by the soldering on of the inner copper junction plate (see Fig. 6.3). Adjacent devices were connected in series with insulated No. 6 wire, of negligible resistance. Resistances of connected wires, leads, and of the couples themselves were determined in the Electronics Laboratory on the impedance bridge, which instrument is capable of reading to 0.0005 ohm.

Individual resistances for the two shop-made couples were 0.0030 ohms each, and 0.0025 ohms for the TA-11. The total resistance when connected in series was found to be 0.0085 ohms.

All temperatures were read using thermocouples, plus a mercury thermometer for quick indication of the temperature of the air space within the box.

The yardstick of performance of the refrigerator is, of course, the achieving of a chilled space at the expenditure of the least amount of electrical power input. The coefficient of performance gives us the answer. From the analysis of the previous chapter, it is known that the following data are required to calculate a predicted COP:

1. Physical properties of the materials used; i.e., Seebeck coefficient, electrical resistivity, and
thermal conductivity.

2 - direct current, amperes.
3 - hot and cold temperatures

With an efficiently designed and competently fabricated thermocouple for refrigeration service, it is relatively simple to obtain a cold junction temperature about 50 F below ambient (Ref. 1 and sales literature describing the TA-11 device). Ohio Semiconductor bulletin TA-11 shows that at an input current of twenty amperes, the expected temperature difference between junctions is approximately 58 F.

To calculate the COP for the TA-11 purchased couple, (previous calculations neglected the junction resistance), we proceed as follows, first converting the values of the given physical properties to degrees Fahrenheit, since this scale was used in the experimental work:

\[ \alpha_{np} = \frac{340}{1.8} = 189 \text{ microvolts per deg F} \]

\[ r_{np} = 0.0025 \text{ ohm (measured in laboratory)} \]

\[ K = \frac{0.0399}{1.8} = 0.0222 \text{ watt per deg F} \]

Assuming a current of 20 amps, a \( T_h = 600 \text{ R} \), a \( T_c = 542 \text{ R} \),

\[ \text{COP} = \frac{\alpha I T_c - K (T_h - T_c) - 0.5 I^2 r}{I^2 r + \alpha (T_h - T_c) I} \]
Here, low C 0 P is chiefly the result of the adverse effect of a rather high Joule heat and thermal conduction.

As mentioned previously, two of the three couples used in the fabrication of the refrigerator were assembled in the University shop from the elements obtained from the Merck Company. To predict a C 0 P for either of these two couples, we make use of the following information:

\[ \alpha_{np} = \frac{367}{1.8} = 204 \text{ microvolts per deg F} \]

\[ r_{np} = 0.0030 \text{ ohm (measured in laboratory)} \]

\[ K_{np} = \frac{0.0399}{1.8} = 0.0222 \text{ watt per deg F} \]

Assuming the same 20 ampere current and the same hot and cold temperatures,

\[ C 0 P = \frac{0.32}{1.44} = 0.222 \]

It is seen that the predicted C 0 P of each of the shop-assembled couples is slightly higher than that of the purchased TA-11. This, of course, is due to the fact that the higher Seebeck coefficient of the Merck elements more than offsets the slightly higher resistances of these couples when assembled.
Several facts stand out from an examination of the equation for COP. It is apparent that the heat removal as the result of the Peltier effect is reduced by the heat conducted along both semiconductor legs because of the temperature difference from the hot to cold ends, and by the internal Joule heat. Both effects detract from the efficiency of the operation by creating a heat load in addition to the heat transfer through the walls of the refrigeration chamber.

As the temperature difference increases, the denominator of the equation, or work input, increases also. In any application, therefore, a compromise must be reached between temperature difference and the expected COP. Besides, the COP of the elements may be considerably different from the refrigerator taken as a whole.

Let us now determine the product "UA" for the refrigerator. With the three thermoelectric couples in place in the walls of the box, but not interconnected for either power generation or refrigeration, a small resistance load inside the enclosed space (0.025 amps at 15.0 volts = 0.375 watts) caused the temperature of the interior to rise to a steady 3.9 degrees F above the existing ambient air. At four times this heat input, or 1.5 watts, the temperature rose 16.0 degrees F. This gives an average of about 10.5 degrees per watt of electric power supplied.

Considering heat transfer on a one-hour basis,

\[ Q = UA \Delta T \]
1 watt = $3.413 \frac{\text{Btu}}{\text{hr}} = 10.5 \text{ UA}$

or, $\text{UA} = \frac{3.413}{10.5} = 0.325 \frac{\text{Btu}}{\text{hr deg}}$

This figure gives us an idea of the insulation properties of the assembled refrigerator.

Many test runs were made for the purpose of observing the performance of the experimental refrigerator as the input electrical power was gradually increased. The resulting temperatures combined with the physical data previously known enables the COP to be calculated. Furthermore, a distinction can be made between the COP of any one thermoelement and that of the box as a whole.

For a single unit, steady state

$$\text{COP} = \frac{\alpha IT_c - K (T_h - T_c) - 0.5 I^2 r}{I^2 r + \alpha (T_h - T_c) I}$$

where $T_h$ and $T_c$ are junction temperatures.

For the box as a whole, steady state

$$\text{COP} = \frac{Q_c}{W} = \frac{UA \Delta T}{W}$$

where $\Delta T$ represents the temperature difference from the inner space to the outside air.
At each power input setting, the following readings were taken:

- Ambient temperature, deg F
- Current input, amps
- Voltage, volts
- Power input (calculated E*I), watts
- Junction temperatures, deg F
- Space temperature, deg F

Following these preliminary tests, it was decided to try to improve the efficiency of refrigeration by effecting a modification to the Ohio Semiconductor TA-11 device. The original cold junction consisted of an oval-shaped thin copper plate of overall dimensions at the center lines of half inch by one inch. The rather small surface area restricted heat travel from the air within the box to the metal surface. To improve heat flux, the original plate was removed and a large copper plate, 1/16" x 3" x 3" was installed. Unfortunately, the quality of the soldering operation proved to be poor. As a result, the improvement in heat transfer produced by the increased area was offset considerably by the inferior quality of the soldered joint.

As a matter of fact, a better refrigeration capacity existed before the change was made. This result emphasizes the importance of a high caliber, low resistance junction. The resistance of this couple was 0.0025 ohm originally, and 0.0035 ohm following the modification made by the author.
Figure 6.1 shows the wiring diagram for the refrigeration testing.

6.3 Power Generation Test Procedures.

Upon completion of the evaluation of the simple refrigeration experiment, the arrangement of the components was altered to permit utilization of as much of the existing apparatus as possible in the second phase of the task; i.e., electric power generation. An electric soldering iron tip was used as a source of thermal energy. (See Fig. 6.2)

As is the case with any power conversion apparatus, it is desirable also in this instance to predict an anticipated thermal efficiency before the equipment is assembled and tested. We recall from section 5.1 that of primary importance to efficiency in a thermoelectric generator is the figure of merit, which, in turn, depends on the physical properties of the semiconductor material and the quality of assembly.

Considering the modified TA-11 device,

\[ Z_{np} = \frac{(189)^2 \times 10^{-12}}{0.0222 \times 0.0035} \]

\[ Z_{np} = 0.46 \times 10^{-3} \text{ per deg } ^\circ F \]

Making the following assumptions, we shall calculate an efficiency:

Let \( m = 100, \ T_h = 860 \text{ R}, \ T_c = 540 \text{ R} \)
Wiring Diagram for Power Generation Fig. 6.2
First, Carnot Efficiency = \( \frac{860 - 540}{860} = 37.2\% \)

\[
\eta = \frac{T_h - T_c}{T_h} \times \frac{m}{m+1} \cdot \frac{1}{1 + \frac{1}{Z} \times \frac{m+1}{T_h} - \frac{T_h - T_c}{T_h} \times \frac{1}{2(m+1)}}
\]

\[
\eta = 0.372 \times \frac{100}{101}
\]

\[
\eta = 0.372 \times \frac{0.99}{1 + 255 - 0.00184}
\]

\[\eta = 0.144\% \text{ at } m = 100\]

Let us next find M, the value of m giving the highest efficiency, for the temperatures given. (Reference 1, chapter 2)

\[
M = 1 + \frac{Z (T_h + T_c)}{2}
\]

\[
M = 1 + \frac{0.46 \times 10^{-3} (860 + 540)}{2}
\]

\[M = 1.15, \text{ for maximum efficiency.}\]
TEST EQUIPMENT AND CIRCUITS

FIG. 6.3
\[ \eta_{\text{max}} = \frac{\text{Th} - \text{T}_c}{\text{Th}} \times \frac{\text{M} - 1}{\text{M} + \text{T}_c/\text{Th}} \]

\[ \eta_{\text{max}} = 0.372 \times \frac{0.15}{1.778} = 3.14\% \]

This is the predicted maximum efficiency for the TA-11 couple in the electric power generation testing.

The figure of merit for the shop-fabricated couples is

\[ z_{np} = \frac{(204)^2 \times 10^{-12}}{0.0222 \times 0.0030} = 0.625 \times 10^{-3} \text{ per deg F} \]

At a resistance ratio equal to 100 (and same temperatures as before)

\[ \eta = 0.372 \times \frac{0.99}{1 + 188 - 0.00184} \]

\[ \eta = 0.195\% \text{ at } m = 100 \]

In a like manner,

\[ \text{M} = 1.2 \]

At this optimum value of \( m \),

\[ \eta_{\text{max}} = 0.372 \times \frac{0.2}{1.828} = 4.07\% \]

The importance of a good figure of merit and the significance of the proper choice of the load are readily seen in the above four examples.
Expressions developed in chapters four and five have shown how the efficiency of electric power generation can be predicted. Examples in the present chapter have given us an idea of what to expect as to probable values of these efficiencies. In any actual power conversion operation, however, the ascertaining of thermal efficiency is quite easy to determine, whether it be for the entire plant or process or for some particular phase of the operation. It is simply output divided by input.

Therefore, in the present experiment, since we are creating a high temperature region by sending a current through a resistance, our tests should be aimed at giving watts input and watts output, plus the various temperatures of interest, such as interior space and ambient and thermocouple hot and cold junction temperatures.

In the original power generation test runs, the interior air temperatures were limited to 250 F and the supply alternating current voltage to about 100 volts. As the external junctions of the generating couples were not too well finned to promote good heat transfer to the ambient air, and since the semiconductor elements themselves were only one-half inch long, the maximum temperature difference produced was only 52.0 degrees F, sufficient for creation of only a rather small emf.

The low-resistance soldering heating tip was replaced, therefore, with one capable of producing thermal
energy at a greater rate. At 140 volts, the input A.C. power read 69.8 watts. This voltage was applied to the resistance of the tip and allowed to remain for about 1 1/2 hours, at the end of which time the temperature within the thermoelectric generator test chamber had stabilized at 440 F. Potential in millivolts was read across each of the three couples. (This phase of the program was carried out after the refrigeration experimentation, during which the purchased couple had been modified, as will be recalled, with adverse effects to its capacity as a thermoelectric device.)

A D.C. milliammeter, Weston model 741 of a range up to 100 milliamperes served as the load on the experimental generator. The measured resistance was found to be 1.108 ohms. Previously, a microammeter was used to record the output current (and act as a load), but its high resistance, 2330 ohms, made it almost useless for this test. At an input power of 17.80 watts, the output was only 0.1875 microwatts, giving an infinitesimal efficiency of conversion. (Following the final analysis of the data, it was then seen that even the 1.108 ohms of the milliammeter was much too great a resistance load, resulting in a value of m of 116, or about a hundred times that value found to be optimum.)

At conditions of maximum applied A.C. power and again at an intermediate point, complete readings were taken. At other values of power input, the no-load voltage was recorded at various intervals down to an input power of 3.57 watts.
The results obtained in these two experiments are discussed in the final chapter, and some conclusions are drawn.
7.1 The Refrigeration Application

The ultimate objective in the refrigeration phase of this program was the ascertaining of \( C_0 P \), the coefficient of performance. Following is a summary listing of the parameters which are part of the equation for this indicator of performance and of the required properties of the thermoelectric elements used.

\[
\begin{align*}
\alpha & \quad \text{the Seebeck coefficient} \\
r & \quad \text{the electrical resistance} \\
K & \quad \text{the thermal conductance} \\
I & \quad \text{the current flow} \\
T_h & \quad \text{the hot junction temperature} \\
T_c & \quad \text{the cold junction temperature}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Modified TA-11 Couple</th>
<th>Shop-made Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{np} ) = 189 microvolts per deg F</td>
<td>204 microvolts per deg F</td>
</tr>
<tr>
<td>( r_{np} ) = 0.0035 ohm</td>
<td>0.0030 ohm</td>
</tr>
<tr>
<td>( K_{np} ) = 0.0222 watt per deg F</td>
<td>0.0222 watt per deg F</td>
</tr>
</tbody>
</table>

In the refrigeration testing, in addition to the current flow and junction temperatures, other variables recorded were:

ambient temperature, deg F
A summary of readings taken for the first of the shop-made thermoelements is as follows:

<table>
<thead>
<tr>
<th>Ambient Temp.</th>
<th>Amps</th>
<th>Total Volts</th>
<th>Total Watts</th>
<th>Junction Cold</th>
<th>Junction Hot</th>
<th>Δ T</th>
<th>Space Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.1</td>
<td>7.3</td>
<td>0.09</td>
<td>0.657</td>
<td>64.5</td>
<td>100.0</td>
<td>35.5</td>
<td>82.7</td>
</tr>
<tr>
<td>84.2</td>
<td>8.9</td>
<td>0.11</td>
<td>0.978</td>
<td>64.5</td>
<td>102.0</td>
<td>37.5</td>
<td>82.6</td>
</tr>
<tr>
<td>84.2</td>
<td>11.1</td>
<td>0.13</td>
<td>1.443</td>
<td>61.5</td>
<td>99.0</td>
<td>37.5</td>
<td>82.5</td>
</tr>
<tr>
<td>84.2</td>
<td>14.5</td>
<td>0.18</td>
<td>2.61</td>
<td>57.5</td>
<td>99.0</td>
<td>41.5</td>
<td>82.1</td>
</tr>
<tr>
<td>84.2</td>
<td>19.2</td>
<td>0.25</td>
<td>4.80</td>
<td>53.5</td>
<td>100.0</td>
<td>46.5</td>
<td>81.4</td>
</tr>
<tr>
<td>84.2</td>
<td>20.0</td>
<td>0.26</td>
<td>5.20</td>
<td>52.5</td>
<td>103.0</td>
<td>51.5</td>
<td>80.7</td>
</tr>
<tr>
<td>84.2</td>
<td>21.0</td>
<td>0.27</td>
<td>5.67</td>
<td>53.5</td>
<td>106.5</td>
<td>53.0</td>
<td>80.1</td>
</tr>
<tr>
<td>84.2</td>
<td>25.0</td>
<td>0.34</td>
<td>8.50</td>
<td>54.0</td>
<td>108.0</td>
<td>54.0</td>
<td>79.9</td>
</tr>
<tr>
<td>84.2</td>
<td>26.9</td>
<td>0.36</td>
<td>9.68</td>
<td>58.5</td>
<td>114.0</td>
<td>55.5</td>
<td>80.0</td>
</tr>
<tr>
<td>84.2</td>
<td>28.6</td>
<td>0.37</td>
<td>10.58</td>
<td>62.5</td>
<td>117.0</td>
<td>54.5</td>
<td>80.6</td>
</tr>
<tr>
<td>84.2</td>
<td>30.6</td>
<td>0.42</td>
<td>12.85</td>
<td>66.5</td>
<td>120.5</td>
<td>54.0</td>
<td>80.9</td>
</tr>
<tr>
<td>84.2</td>
<td>32.9</td>
<td>0.44</td>
<td>14.47</td>
<td>75.0</td>
<td>126.0</td>
<td>51.0</td>
<td>81.8</td>
</tr>
<tr>
<td>84.3</td>
<td>36.3</td>
<td>0.50</td>
<td>18.15</td>
<td>84.0</td>
<td>132.0</td>
<td>48.0</td>
<td>82.7</td>
</tr>
</tbody>
</table>
The following temperatures were recorded for the second of the two shop-made devices while the current as indicated was flowing in series through the system of three thermoelectric couples:

<table>
<thead>
<tr>
<th>Junction Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amps</strong></td>
</tr>
<tr>
<td>7.3</td>
</tr>
<tr>
<td>8.9</td>
</tr>
<tr>
<td>11.1</td>
</tr>
<tr>
<td>14.5</td>
</tr>
<tr>
<td>19.2</td>
</tr>
<tr>
<td>20.0</td>
</tr>
<tr>
<td>21.0</td>
</tr>
<tr>
<td>25.0</td>
</tr>
<tr>
<td>26.9</td>
</tr>
<tr>
<td>28.6</td>
</tr>
<tr>
<td>30.6</td>
</tr>
<tr>
<td>32.9</td>
</tr>
<tr>
<td>36.3</td>
</tr>
</tbody>
</table>

Readings taken simultaneously for the modified TA-11 couple:

<table>
<thead>
<tr>
<th><strong>Amps</strong></th>
<th><strong>Cold</strong></th>
<th><strong>Hot</strong></th>
<th><strong>Δ T</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>74.0</td>
<td>101.0</td>
<td>27.0</td>
</tr>
<tr>
<td>8.9</td>
<td>74.0</td>
<td>98.0</td>
<td>24.0</td>
</tr>
<tr>
<td>11.1</td>
<td>72.0</td>
<td>98.0</td>
<td>26.0</td>
</tr>
<tr>
<td>14.5</td>
<td>69.0</td>
<td>100.0</td>
<td>31.0</td>
</tr>
<tr>
<td>19.2</td>
<td>66.0</td>
<td>103.5</td>
<td>37.5</td>
</tr>
</tbody>
</table>
To calculate the COP corresponding to these data, we use the now familiar expression:

$$\text{COP} = \frac{\alpha T_0 I - K \Delta T - 0.5 I^2r}{I^2r + \alpha \Delta TI}$$

In the case of the first shop-made couple, simple calculations produce the following:

<table>
<thead>
<tr>
<th>Amps</th>
<th>$\alpha IT_0$</th>
<th>$K \Delta T$</th>
<th>$0.5I^2r$</th>
<th>$I^2r$</th>
<th>$\alpha \Delta TI$</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>0.781</td>
<td>0.788</td>
<td>0.080</td>
<td>0.160</td>
<td>0.0528</td>
<td>-0.408</td>
</tr>
<tr>
<td>8.9</td>
<td>0.952</td>
<td>0.832</td>
<td>0.119</td>
<td>0.238</td>
<td>0.0681</td>
<td>+0.003</td>
</tr>
<tr>
<td>11.1</td>
<td>1.180</td>
<td>0.832</td>
<td>0.185</td>
<td>0.370</td>
<td>0.0850</td>
<td>0.358</td>
</tr>
<tr>
<td>14.5</td>
<td>1.528</td>
<td>0.921</td>
<td>0.316</td>
<td>0.632</td>
<td>0.1228</td>
<td>0.385</td>
</tr>
<tr>
<td>19.2</td>
<td>2.01</td>
<td>1.030</td>
<td>0.552</td>
<td>1.104</td>
<td>0.1820</td>
<td>0.335</td>
</tr>
<tr>
<td>20.0</td>
<td>2.09</td>
<td>1.140</td>
<td>0.600</td>
<td>1.200</td>
<td>0.210</td>
<td>0.248</td>
</tr>
</tbody>
</table>
(Continued)

<table>
<thead>
<tr>
<th>Amps</th>
<th>$\propto IT_c$</th>
<th>$K \Delta T$</th>
<th>$0.5I^2r$</th>
<th>$I^2r$</th>
<th>$\propto \Delta T_I$</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.0</td>
<td>2.20</td>
<td>1.178</td>
<td>0.661</td>
<td>1.322</td>
<td>0.227</td>
<td>0.232</td>
</tr>
<tr>
<td>25.0</td>
<td>2.62</td>
<td>1.200</td>
<td>0.938</td>
<td>1.876</td>
<td>0.276</td>
<td>0.224</td>
</tr>
<tr>
<td>26.9</td>
<td>2.85</td>
<td>1.232</td>
<td>1.09</td>
<td>2.18</td>
<td>0.305</td>
<td>0.212</td>
</tr>
<tr>
<td>28.6</td>
<td>3.05</td>
<td>1.210</td>
<td>1.23</td>
<td>2.46</td>
<td>0.318</td>
<td>0.218</td>
</tr>
<tr>
<td>30.6</td>
<td>3.28</td>
<td>1.200</td>
<td>1.405</td>
<td>2.81</td>
<td>0.337</td>
<td>0.214</td>
</tr>
<tr>
<td>32.9</td>
<td>3.59</td>
<td>1.132</td>
<td>1.625</td>
<td>3.25</td>
<td>0.342</td>
<td>0.231</td>
</tr>
<tr>
<td>36.3</td>
<td>4.03</td>
<td>1.065</td>
<td>1.98</td>
<td>3.96</td>
<td>0.356</td>
<td>0.228</td>
</tr>
</tbody>
</table>

For the second of the shop-made units, one obtains:

<table>
<thead>
<tr>
<th>Amps</th>
<th>$\propto IT_c$</th>
<th>$K \Delta T$</th>
<th>$0.5I^2r$</th>
<th>$I^2r$</th>
<th>$\propto \Delta T_I$</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>0.792</td>
<td>0.644</td>
<td>0.080</td>
<td>0.160</td>
<td>0.043</td>
<td>0.335</td>
</tr>
<tr>
<td>8.9</td>
<td>0.967</td>
<td>0.622</td>
<td>0.119</td>
<td>0.238</td>
<td>0.051</td>
<td>0.782</td>
</tr>
<tr>
<td>11.1</td>
<td>1.204</td>
<td>0.622</td>
<td>0.185</td>
<td>0.370</td>
<td>0.063</td>
<td>0.898</td>
</tr>
<tr>
<td>14.5</td>
<td>1.560</td>
<td>0.722</td>
<td>0.316</td>
<td>0.632</td>
<td>0.096</td>
<td>0.718</td>
</tr>
<tr>
<td>19.2</td>
<td>2.05</td>
<td>0.910</td>
<td>0.552</td>
<td>1.104</td>
<td>0.160</td>
<td>0.465</td>
</tr>
<tr>
<td>20.0</td>
<td>2.12</td>
<td>1.010</td>
<td>0.600</td>
<td>1.200</td>
<td>0.186</td>
<td>0.368</td>
</tr>
<tr>
<td>21.0</td>
<td>2.23</td>
<td>1.065</td>
<td>0.661</td>
<td>1.322</td>
<td>0.206</td>
<td>0.330</td>
</tr>
<tr>
<td>25.0</td>
<td>2.65</td>
<td>1.190</td>
<td>0.938</td>
<td>1.876</td>
<td>0.273</td>
<td>0.243</td>
</tr>
<tr>
<td>26.9</td>
<td>2.86</td>
<td>1.288</td>
<td>1.09</td>
<td>2.18</td>
<td>0.319</td>
<td>0.193</td>
</tr>
<tr>
<td>28.6</td>
<td>3.05</td>
<td>1.322</td>
<td>1.23</td>
<td>2.46</td>
<td>0.347</td>
<td>0.178</td>
</tr>
<tr>
<td>30.6</td>
<td>3.27</td>
<td>1.422</td>
<td>1.405</td>
<td>2.81</td>
<td>0.400</td>
<td>0.138</td>
</tr>
<tr>
<td>32.9</td>
<td>3.52</td>
<td>1.565</td>
<td>1.625</td>
<td>3.25</td>
<td>0.470</td>
<td>0.089</td>
</tr>
<tr>
<td>36.3</td>
<td>3.90</td>
<td>1.733</td>
<td>1.98</td>
<td>3.96</td>
<td>0.577</td>
<td>0.041</td>
</tr>
</tbody>
</table>
Similarly for the modified TA-11 device,

<table>
<thead>
<tr>
<th>Amps</th>
<th>$\Delta ITc$</th>
<th>$K \Delta T$</th>
<th>$0.5I^2r$</th>
<th>$I^2r$</th>
<th>$K \Delta TT$</th>
<th>CO P</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>0.738</td>
<td>0.600</td>
<td>0.0932</td>
<td>0.1864</td>
<td>0.0373</td>
<td>0.201</td>
</tr>
<tr>
<td>8.9</td>
<td>0.900</td>
<td>0.532</td>
<td>0.138</td>
<td>0.277</td>
<td>0.0403</td>
<td>0.725</td>
</tr>
<tr>
<td>11.1</td>
<td>1.114</td>
<td>0.577</td>
<td>0.194</td>
<td>0.388</td>
<td>0.0545</td>
<td>0.777</td>
</tr>
<tr>
<td>14.5</td>
<td>1.450</td>
<td>0.688</td>
<td>0.368</td>
<td>0.737</td>
<td>0.0850</td>
<td>0.478</td>
</tr>
<tr>
<td>19.2</td>
<td>1.910</td>
<td>0.832</td>
<td>0.645</td>
<td>1.290</td>
<td>0.1360</td>
<td>0.304</td>
</tr>
<tr>
<td>20.0</td>
<td>1.986</td>
<td>0.432</td>
<td>0.700</td>
<td>1.400</td>
<td>0.1588</td>
<td>0.228</td>
</tr>
<tr>
<td>21.0</td>
<td>2.08</td>
<td>1.032</td>
<td>0.771</td>
<td>1.542</td>
<td>0.1845</td>
<td>0.160</td>
</tr>
<tr>
<td>25.0</td>
<td>2.48</td>
<td>1.155</td>
<td>1.095</td>
<td>2.19</td>
<td>0.246</td>
<td>0.094</td>
</tr>
<tr>
<td>26.9</td>
<td>2.67</td>
<td>1.266</td>
<td>1.27</td>
<td>2.54</td>
<td>0.290</td>
<td>0.047</td>
</tr>
<tr>
<td>28.6</td>
<td>2.83</td>
<td>1.343</td>
<td>1.43</td>
<td>2.86</td>
<td>0.327</td>
<td>0.018</td>
</tr>
<tr>
<td>30.6</td>
<td>3.04</td>
<td>1.432</td>
<td>1.64</td>
<td>3.28</td>
<td>0.374</td>
<td>-0.008</td>
</tr>
<tr>
<td>32.9</td>
<td>3.29</td>
<td>1.510</td>
<td>1.90</td>
<td>3.80</td>
<td>0.423</td>
<td>-0.028</td>
</tr>
<tr>
<td>36.3</td>
<td>3.67</td>
<td>1.554</td>
<td>2.31</td>
<td>4.62</td>
<td>0.480</td>
<td>-0.037</td>
</tr>
</tbody>
</table>

We have calculated the CO P for each of the three couples under varying conditions of power input. These figures furnish an indication of the performance of these individual components of the refrigerator, but do not, in themselves, give the experimenter the full story. Referring to page 56 for a moment, we see that for our particular refrigeration chamber, an effective heating or cooling power of one watt was capable of maintaining a temperature difference of approximately 10.5°F between the space inside and the outside ambient air temperature.
With this known, the rate of heat removal for the box taken as a whole can be established simply by knowing the temperature difference across the walls. These values of $\Delta T$ are obtainable at each load condition from the first table of data in this chapter.

From these figures, one obtains:

<table>
<thead>
<tr>
<th>Amps</th>
<th>Input Watts</th>
<th>Temperatures Ambient</th>
<th>ΔT</th>
<th>Refrigeration Watts</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>0.657</td>
<td>84.1</td>
<td>1.4</td>
<td>0.133</td>
<td>0.202</td>
</tr>
<tr>
<td>8.9</td>
<td>0.978</td>
<td>84.2</td>
<td>1.6</td>
<td>0.152</td>
<td>0.155</td>
</tr>
<tr>
<td>11.1</td>
<td>1.443</td>
<td>84.2</td>
<td>1.7</td>
<td>0.162</td>
<td>0.112</td>
</tr>
<tr>
<td>14.5</td>
<td>2.61</td>
<td>84.2</td>
<td>2.1</td>
<td>0.200</td>
<td>0.077</td>
</tr>
<tr>
<td>19.2</td>
<td>4.80</td>
<td>84.2</td>
<td>2.8</td>
<td>0.267</td>
<td>0.056</td>
</tr>
<tr>
<td>20.0</td>
<td>5.20</td>
<td>84.2</td>
<td>3.5</td>
<td>0.333</td>
<td>0.064</td>
</tr>
<tr>
<td>21.0</td>
<td>5.67</td>
<td>84.2</td>
<td>4.1</td>
<td>0.390</td>
<td>0.068</td>
</tr>
<tr>
<td>25.0</td>
<td>8.50</td>
<td>84.2</td>
<td>4.3</td>
<td>0.410</td>
<td>0.049</td>
</tr>
<tr>
<td>26.9</td>
<td>9.68</td>
<td>84.2</td>
<td>4.2</td>
<td>0.400</td>
<td>0.041</td>
</tr>
<tr>
<td>28.6</td>
<td>10.58</td>
<td>84.2</td>
<td>3.6</td>
<td>0.343</td>
<td>0.032</td>
</tr>
<tr>
<td>30.6</td>
<td>12.85</td>
<td>84.2</td>
<td>3.3</td>
<td>0.314</td>
<td>0.024</td>
</tr>
<tr>
<td>32.9</td>
<td>14.47</td>
<td>84.2</td>
<td>2.4</td>
<td>0.228</td>
<td>0.016</td>
</tr>
<tr>
<td>36.3</td>
<td>18.15</td>
<td>84.3</td>
<td>1.6</td>
<td>0.152</td>
<td>0.008</td>
</tr>
</tbody>
</table>

It is apparent from the values in the column of COP that the efficiency of our apparatus is acceptable at low operating power, but rapidly decreases as the power is increased.
That inadequate provision was made for heat transfer at the junctions is obvious from the foregoing tabulations. Too great a temperature difference between the inside space and the cold junctions indicates a poor film coefficient at the "working" surface. Outside, the hot junctions were exactly that. Temperatures reached 144°F at full load. Under these conditions, it was increasingly difficult for the refrigerating devices to do their job. The product $K \Delta T$ became a formidable obstacle to any cooling effort.

The results of the refrigeration experimentation are summarized in Figure 7.1.

Since the only function of a refrigerator is to remove thermal energy from a designated space, any process which generates heat is detrimental to the objective. A principal offender in our case is the Joule heat evolved at the cold junction unions. In a properly made junction, the sum of the two resistances at the cold ends must be negligible. Otherwise, the heat created due to $I^2r$ at that point, which is inside the box, becomes a serious problem.

For example, the increase in resistance of the TA-11 couple as the result of soldering on a different cold end plate was 0.001 ohm. At first glance this seems small but at a current flow of twenty amperes, the added heat equals $20 \times 20 \times 0.001 = 0.4$ watt, which is appreciable for the size refrigerator constructed for this evaluation. Not only does
Thermoelectric Refrigeration

Figure 7.1
the thermoelectric couple have to pull out the heat which penetrates the walls of the box, but it also must carry the added burden of extracting this Joule heat which has its origin at the poor bonds.

Two factors, it was observed, contributed to the extra resistance; i.e., oxidation and other impurities at the surface to be soldered, and difficulty in obtaining a connection in which the solder covered the entire area at the end of the semiconductor element.

Finally, a few remarks are appropriate concerning the reliability of the equation for the C O P of an individual couple when used as a forecaster of the overall performance of the refrigerator. In the present experiment, the results were disappointing. As seen from the tabulations, the refrigerator C O P was roughly only one-fourth that of its components.

This situation can be likened to that of a three-cylinder reciprocating engine. The indicated or internal horsepower of any of the three cylinders can easily be calculated from the PLAN / 33000 formula, as can the C O P for any of our three couples be calculated from the equation of this chapter. The B.H.P. of the engine may, however, prove to be a disappointment if the frictional losses of the engine and inefficiencies of the attached ancillary equipment are excessive.

In our refrigerator, excessive heat leakage through the walls of the box prevented the creating of an acceptable
temperature difference from ambient air to interior space. This adverse result is not predicted by the equation.

7.2 The "Canec" Box Generator

The electric power generation testing can be summarized using the following tabulation:

<table>
<thead>
<tr>
<th>A.C. Input Watts</th>
<th>Space Temp. deg F</th>
<th>Generated Voltages Plate 1 mv</th>
<th>Plate 2 mv</th>
<th>Modified TA-11 mv</th>
<th>D. C. Output ma</th>
<th>Actual watts</th>
<th>Active Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.8</td>
<td>440</td>
<td>36.8</td>
<td>24.0</td>
<td>33.0</td>
<td>84.0</td>
<td>0.0079</td>
<td>0.0133</td>
</tr>
<tr>
<td>60.7</td>
<td>419</td>
<td>33.7</td>
<td>20.9</td>
<td>30.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.3</td>
<td>398</td>
<td>30.8</td>
<td>18.1</td>
<td>26.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.3</td>
<td>377</td>
<td>27.8</td>
<td>15.2</td>
<td>24.1</td>
<td>70.0</td>
<td>0.0047</td>
<td>0.0106</td>
</tr>
<tr>
<td>38.0</td>
<td>341</td>
<td>26.5</td>
<td>11.7</td>
<td>21.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.3</td>
<td>320</td>
<td>23.7</td>
<td>11.6</td>
<td>19.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.4</td>
<td>299</td>
<td>20.9</td>
<td>9.7</td>
<td>16.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.75</td>
<td>275</td>
<td>18.9</td>
<td>6.9</td>
<td>12.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.28</td>
<td>264</td>
<td>17.7</td>
<td>6.4</td>
<td>11.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.30</td>
<td>253</td>
<td>15.8</td>
<td>5.8</td>
<td>10.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.92</td>
<td>242</td>
<td>13.3</td>
<td>5.0</td>
<td>8.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.57</td>
<td>222</td>
<td>9.8</td>
<td>3.6</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.2 shows graphically the efficiency corresponding to the two check points at which the actual electric power output was recorded.
In section three of the previous chapter, the author predicted component thermal efficiencies at a resistance ratio of 100 as follows:

Merck couples: \(0.195\%\)

TA - 11 couple (modified) \(0.144\%\)

when \(T_h = 860R\) and \(T_c = 540R\).

In the actual test, with the three couples connected in series electrically,

\[ m = \frac{1.108}{0.0095} = 116 \]

At the two points where efficiency of operation was checked, the following conditions existed, at 75.0F ambient:

<table>
<thead>
<tr>
<th></th>
<th>Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TA - 11</td>
</tr>
<tr>
<td>Th</td>
<td>Tc</td>
</tr>
<tr>
<td>Th</td>
<td>Tc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Merck Couple 1</th>
<th>Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>Tc</td>
</tr>
<tr>
<td>Space Temp:</td>
<td></td>
</tr>
<tr>
<td>440F</td>
<td></td>
</tr>
<tr>
<td>399F</td>
<td>129F</td>
</tr>
<tr>
<td>411F</td>
<td>149F</td>
</tr>
<tr>
<td>Space Temp:</td>
<td></td>
</tr>
<tr>
<td>377F</td>
<td></td>
</tr>
<tr>
<td>329F</td>
<td>129F</td>
</tr>
<tr>
<td>338F</td>
<td>140F</td>
</tr>
</tbody>
</table>

Previously calculated values of \(Z\) are:

TA-11 couple: \(0.46 \times 10^{-3}\) per deg F

Merck couples: \(0.625 \times 10^{-3}\) per deg F

Comparing theoretical efficiencies with actual overall efficiencies in the following tabulation, we observe how poorly the experimental box performed as a generator of electrical D.C. power:
The efficiency of the thermoelectric generator is:

\[
\text{Efficiency} = \frac{\text{D.C. electrical load, watts}}{\text{heat leaving hot junctions, watts}}
\]

As will be recalled from Chapter 4, the denominator is found by subtracting one-half the Joule heat from the sum of the Peltier heat absorbed at the hot junctions and the conducted heat. Consider the maximum load condition of the experiment, when the electrical heat source was 69.8 watts. Simple calculations reveal that the D.C. Joule heat is negligible, that the Peltier heat is but a small fraction of a watt, and that the conducted heat from the three hot junctions is approximately \(0.06 \times 270 = 16.2\) watts.

It is clear that less than one-fourth of the A.C. heat supplied to the generator enters the hot junctions of the thermoelectric elements. The remainder is lost through the walls of the box. Therefore, the equation for predicting the efficiency of a thermoelectric device is only partially helpful, in a manner analogous to the previous comments on the formula for COP.

<table>
<thead>
<tr>
<th>Couple</th>
<th>At Full Load</th>
<th>At Part Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merck No. 1</td>
<td>0.148%</td>
<td>0.105%</td>
</tr>
<tr>
<td>(No. 2 quite similar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA-11</td>
<td>0.102%</td>
<td>0.077%</td>
</tr>
<tr>
<td>Generator, actual overall</td>
<td>0.0113%</td>
<td>0.0106%</td>
</tr>
</tbody>
</table>
It is apparent that improved design and fabrication techniques and materials would have aided in achieving an overall generator efficiency more closely approaching the predicted efficiencies of the individual components.

Summarizing, efficient power generation through thermoelectricity requires:

1. Selection of the proper load conditions to fit a given generator, or, conversely, design of the device for a particular load. This will result by first ascertaining the value of the resistance ratio for maximum efficiency.

2. Competent fabrication of the components and assembly of the apparatus.

3. Adequate provision for good heat transfer rates at all junctions.

4. High figure of merit of the semiconductor elements.

5. A hot chamber well insulated to minimize heat transfer through the walls.

6. As for any heat-power cycle, a high $T_h$ and a low $T_c$. 
APPENDIX

Equipment and Instrumentation

A. Power Generation Phase

1. Variac Autotransformer - General Radio Company - Type W 5 M T - Inlet voltage approximately 115 volts A.C. - Outlet voltage from 0 to 150 volts A.C.

2. A.C. Voltmeter - General Electric Company - Type A P 9 - Range 0 to 150 volts - Least count 1 volt.

3. A.C. Ammeter - Triplett, model 430 C - Range 0 to 500 ma. - Least count 10 ma.

4. D.C. Voltmeter - General Electric Company - Type D P 9 - Range 0 to 100 mv - Least count 0.1 mv.

5. D.C. Ammeter - Weston, model 741 - Range 0 to 100 ma - Least count 2 ma.

6. Thermometer, 40 F to 580 F - Least count 2 deg F.

7. Thermocouple Potentiometer - General Electric Company - Type P J 1 B 4, No. 3246043 - Least count 2 deg F.

8. Impedance Bridge (for resistance measurements) - General Radio Company - Type No. 1650-A - Serial No. 932.

9. Soldering Iron (heat source) - rated at 47 ½ watts at 110 volts A.C.
APPENDIX

EQUIPMENT and INSTRUMENTATION

B. Refrigeration Phase


2. D.C. Voltmeter - Simpson model 260, series 111, Range 0 to 2.5 volts - Least count 0.05 volts.

3. D.C. Ammeters - G E type DP 9, 0 to 30 amps, Least count 0.2 amps; and G E type D 040, 0 to 30 amps, Least count 1 amp.

4. Thermocouple Potentiometer - General Electric Company - Type P J 1 B 4, No. 3246043 - Least count 2 deg F.

5. Thermometers, 45 F to 110 F - L.C. 0.1 deg F, and 26 F to 220 F - L.C. 0.2 deg F.

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REFERENCES


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