A PRIMER OF THERMOELECTRIC REFRIGERATION

by

L. A. Staebler, Philco Corporation

As presented to the Philadelphia Section of the ASRE, April 3, 1959, and the Central New York Chapters of ASHRAE, Syracuse, N. Y., April 15, 1959

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Scope

1. Advantages of thermoelectric refrigeration.
2. Non-technical explanation of the thermoelectric process with analogies to well-known principles of mechanical refrigeration.
3. Design and manufacturing problems.
4. Economic considerations.
5. Present applications and future possibilities.

April 9, 1959

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During the past few years, there has been an increasing amount of publicity concerning thermoelectricity and its application to refrigeration and electric power generation. If we as refrigerating engineers were to believe all of the "popular" articles on "electronic cooling", we would indeed expect a revolution in our industry and would have due cause to worry about our professional futures. It is therefore important for us to understand clearly, first, the inherent advantages of thermoelectric cooling which account for the intense interest in this subject, second, the mechanism of thermoelectric effects, and, third, the future of thermoelectric refrigeration and its possible impact on our industry.

Many technical articles have been written on this general subject, most of which have been either restricted to some phase of the total subject, or have been so technical that the average engineer has difficulty in understanding the subject matter. Thermoelectricity falls in the realm of solid state physics and most articles have required a solid state physicist to understand them. There is, therefore, a real need for a simple presentation of this subject that can be understood by the average engineer. I have attempted to achieve this objective by this article, and have accordingly called it "A Primer of Thermoelectric Refrigeration".

With this introduction, let us now see why there is so much interest at the present time in thermoelectric refrigeration.

Its Advantages

Figure 1 illustrates a conventional vapor compression refrigerating system which includes an electric motor, compressor, condenser, throttling valve, evaporator and a vapor refrigerant. To pump heat in the opposite direction, the heating and cooling functions of the condenser and evaporator can be interchanged by reversing the direction of refrigerant flow. This reversal, however, cannot be achieved without considerable difficulty and expense. Since the motor and compressor involve rotary and reciprocating motion, wearing of parts and noise may also be a problem. To contain the refrigerant, a hermetic system is necessary and refrigerant leakage cannot be tolerated. A further inherent limitation of this system is that it cannot be readily miniaturized to economically provide only a small amount of refrigeration.

Let us now look at Figure 2 and see the reason for all the excitement about thermoelectric refrigeration. Here we have a truly electronic refrigerator. There are no moving parts and we have replaced the motor, compressor, condenser, throttling valve, evaporator and vapor refrigerant with the simple arrangement shown. We now have only a thermoelectric couple (two dissimilar materials in contact) and a battery (or electric power supply). By passing a dc current through the thermoelectric couple, we get cooling at one end and heating at the other end. By merely reversing the polarity of the battery, we interchange the heating and cooling functions. In other words, we can pump heat in either direction by reversing the current flow.

Since there are no moving parts, there is nothing to wear out and nothing to generate noise. There is no refrigerant to contain and the tubing has been replaced with electrical wiring. The system can be readily miniaturized, for both low refrigerating capacity and to meet restricted space requirements.

Another important advantage, which may not be so obvious, is the simple process by which the refrigerating capacity can be modulated to meet the requirements placed on the system. This modulation is accomplished simply by varying the current flow through the couple. This is the equivalent of modulating the capacity of a conventional refrigerating system by varying the displacement or the RPM of the compressor.

Isn't this enough to stir one's imagination? But this is still only part of the story. Let us look at <u>Figure 3</u> and consider the possibilities for power generation. Here we are using the thermoelectric effect to generate electrical energy directly from thermal energy. This should make it possible to use one thermoelectric couple to generate electricity which can then be fed into another couple to produce refrigeration. This would be the equivalent of absorption refrigeration in which heat is used as a power source to provide refrigeration. According to some of the more optimistic writers, some day we may use thermoelectricity to air condition our cars directly from the waste heat in the exhaust!

These, then, are the advantages and possibilities of thermoelectric refrigeration that have stimulated so much popular interest and speculation.

That this interest is more than just a passing fancy is shown by the fact that it is estimated that approximately 80 companies and a few non-profit and government groups are active or at least very interested in the product potential of thermoelectricity for cooling and/or heating. The military budget alone is currently $3 million and is scheduled to go to $8 million in 1960 and $40 million in 1961.

Actually, the present state of the art is such that thermoelectric refrigeration is already practical for certain specialty applications, and there are indications that it may someday obsolete present methods of refrigeration for household appliances. Of equal importance, however, is the fact that thermoelectric refrigeration creates a real opportunity for the development of new products, not practical with conventional methods of refrigeration.

Since this is the situation that we, as refrigeration engineers, face today, it behooves us to become better acquainted with the facts of life. In the remaining portion of this presentation, I will accordingly discuss the following:

a) First will be a non-technical explanation of the thermoelectric process with analogies to well-known principles of refrigeration engineering.

b) Next will be a discussion of the design and manufacturing problems involved in device application.

c) A quick look at the economic aspects will then be in order and here we will look at both operating costs (C.O.P.) and manufacturing costs.

d) We will then take a quick look at the present possibilities and attempt to predict the future.

e) The presentation will be concluded by a few simple demonstrations, which may be of some interest to you.

What It Is

Thermoelectricity is by definition the direct conversion of electrical energy into thermal energy, or, vice versa. If a temperature difference is created across the ends of two different materials in contact, an electrical voltage is generated. This is known as the Seebeck Effect (see Figure 4). A common example of a practical application of this effect is the well-known thermocouple for measuring temperatures. Another common application is the thermoelectric generator used with pilot lights in gas furnaces, to serve as a safety device by closing a solenoid valve in the fuel line when the pilot light goes out. These are examples of power generation with thermoelectricity.

However, the thermoelectric effect of greatest interest to refrigerating engineers is the Peltier Effect (see Figure 5), in which the passage of a current through the junction of two different materials results in either the absorption or evolution of heat at the junction. The Peltier Effect was discovered by the Frenchman, Peltier, in 1834.

How It Works

Now, you will ask, what is the explanation for the thermoelectric phenomenon and why did 125 years pass before it could be put to practical use? To answer these questions requires, first, an understanding of the mechanism of these related effects, i.e., the mechanism by which either heat or electricity flows through a material.

Materials, particularly metals, contain a certain distribution of electrons that are free to move in response either to temperature differences or to an electric field. Thus, if heat is applied at one end of a metal rod, it will cause a drift of electrons toward the cold end, transporting heat in so doing. This is the main means of heat transport in a metal. Now, since each electron also carries a unit of electrical charge, this flow of heat is capable of producing an electrical current as well. See Figure 6.

This, then, is the key to the thermoelectric phenomenon. Because the flow of electrons is involved in transport of both heat and electricity, it is possible to transport heat directly by means of an electrical current or conversely, to cause a flow of electrical current through the application of heat.

Refrigerating System Analogies

Before we go into a discussion of thermoelectric materials and the design of the thermoelectric couple, let us look at Figure 7 and discuss certain similarities or analogies between the vapor compression refrigeration cycle and the thermoelectric refrigeration cycle. We can at once see the following similarities:

Vapor Compression		Thermoelectric	
(1)	Refrigerant gas	(1)	Electron "gas"
(2)	Leak tight tubing	(2)	Electrical wiring
(3)	Motor-compressor	(3)	Electric power supply
(4)	Condenser	(4)	Hot junction
(5)	Evaporator	(5)	Cold junction
(6)	Throttling valve	(6)	"Energy level relationships"
(7)	Motor losses	(7)	Power supply losses
(8)	Compressor losses	(8)	Losses in TE materials
(9)	Reverse cycle valve	(9)	Reverse cycle switch
(10)	Capacity modulation mechanism	(10)	Capacity modulation by varying the electrical current

The key to the successful operation of each system is the means for obtaining a change in "energy level" relationships at the hot and cold sides of the system. In the case of the vapor compression cycle, this is possible through use of a throttling valve between the condenser and evaporator. Without this valve, there would be a constant pressure and a uniform refrigerant enthalpy (energy level) throughout the system and no heat pumping would occur. The same thing may occur in the thermoelectric circuit. If Materials A and B are identical, the energy level of the electron gas would be the same throughout the system and there would be no heat pumping. However, by selecting materials with different available electron energy levels, the electron "gas" flowing across the barrier or "junction" must undergo an energy change which results in either the absorption or rejection of heat energy at the junction, depending on the direction of the current flow. Figure 8 illustrates simplified energy level diagrams for the two systems.

Parameters of Thermoelectric Materials

It is apparent that the concept of "energy level" is important to a simple explanation of thermoelectric refrigeration. It will also be apparent that for the best operation, the difference in energy levels in the two materials should be as great as possible. The parameters of thermoelectric materials which affect the energy level will now be described. In this description, it will be helpful to refer to Figure 9 which shows the similarities between these parameters and corresponding characteristics of compressor design and performance.

(1) The first of these parameters is the thermal conductivity, K, of the material, which results in backward flow of heat through the couple. This loss should be kept to a minimum by striving for a low K.

Analogy: This is similar to the backward flow of gas in a compressor due to piston blow-by and valve leakage.

(2) The second is the electrical resistivity, ρ, which determines the I^2R losses. To limit this loss, ρ should be of a low value.

Analogy: This loss is similar to the friction losses in a compressor and to other factors which increase the temperature of the gas in the cylinder of a compressor.

(3) The third parameter is thermoelectric power, S, which describes the interdependence of electrical and thermal effects in a material. It is described mathematically as $S = \Delta E/\Delta T$ and is equal to the ratio of Seebeck voltage to the temperature difference between the junctions. More simply, it may be described as the quantity of

electrons pumped for a given temperature difference. A high thermoelectric power is essential to good performance.

Analogy: A parallel concept in compressor performance is the weight (number of molecules) of refrigerant gas pumped by the compressor per unit volume of piston displacement, as influenced only by the reexpansion losses due to head clearance. For a high pumping rate, the head clearance should be as low as possible.

(4) The figure of merit, Z, is the most important parameter for describing a thermoelectric material since it involves all three factors previously discussed. It is defined mathematically as $Z = S^2/\rho K$. To obtain maximum Z, S^2/ρ should be maximized and K minimized. It should be noted that S, ρ and K are interrelated and are all dependent on the concentration of free electrons. See Figure 10.

Analogy: A similar concept to figure of merit in compressor performance is the volumetric efficiency as affected by all three characteristics already discussed, i.e., piston blow-by and valve leakage, friction losses contributing to gas superheating, and reexpansion losses. This may not be mathematically rigorous, but all factors are in the right direction.

(5) A very useful relationship may be derived from the figure of merit. This is the maximum temperature difference that can be developed under no-load conditions between the hot and cold junction of a

couple. It is defined as Max $\Delta T = 1/2\ ZT_c^2$, where T_c is the cold junction temperature in degrees Kelvin.

Analogy: This is similar in concept to the maximum pressure difference - or maximum compression ratio - obtainable in a compressor, also in an unloaded condition. It is similarly dependent on the volumetric efficiency and the suction pressure.

It is hoped that explaining the characteristics of the thermoelectric materials in terms of these well-known characteristics of compressor performance will remove some of the mystery surrounding thermoelectric refrigeration.

Semiconductors

We will now more carefully examine the various thermoelectric materials to determine the reason for the recent acceleration in development. In this connection, refer to the chart of Figure 11 which shows the progress in thermoelectric cooling since 1834. Pure metals have an inherently low thermoelectric power. Also the relationship between thermal and electrical conductivity is fixed. Because of this, metals are not suitable materials for thermoelectric refrigeration and progress was at a standstill until post-war advances in solid state physics gave us a new class of thermoelectric materials known as "semiconductors", which have properties particularly suitable for thermoelectric applications. (As a point of interest, transistors are a result of this post-war activity in semiconductor physics.)

What is a semiconductor? It is almost self-explanatory. Metals are good heat and electrical conductors due to a plentiful supply of "free" electrons.

Insulating materials, as the name implies, are poor conductors because their electrons are tightly bound. A semiconductor, therefor, is a material with an electrical conductivity somewhere between that of a conductor and an insulator. However, its thermal conductivity is due to the properties of both conductors and insulators, but is more closely associated with those of an insulator. In other words, lattice vibration, or the vibration of the atom, which is the principal method of heat transport in an insulator, also contributes to thermal conductivity.

The total thermal conductivity of a semiconductor, unlike that of metals, is thus made up of two components: (a) electronic and (b) non-electronic or lattice vibration. It is possible to independently adjust the lattice vibration component without affecting either the electronic component of the thermal conductivity or the electrical conductivity itself. Considerable improvement in the figure of merit is thus possible in semiconductors through an independent adjustment of the thermal conductivity, K. In metals, thermal conductivity K, and electrical resistivity, ρ , are related by the Wiedemann-Franz law which says that the product $K\rho$ is a constant. This means that K or ρ cannot be independently adjusted, which limits the thermoelectric effect in metals.

Also, semiconductors are the most promising thermoelectric materials because their concentration of charge carriers (free electrons) are of a magnitude where S^2/ρ is a maximum. See Figure 10.

Semiconductors possess still another thermoelectric advantage over metals. This is due to the fact that electrical and thermal currents may result from a flow of either electrons or positively charged "holes" vacated by electrons. The two types of semiconductors are known as "N-type" and "P-type", respectively. Hence, instead of subtracting thermoelectric powers between the two materials forming a junction as in a metallic couple, we add them when forming a junction of N and P type materials.

These are the reasons why semiconductor materials are playing such an important part in making thermoelectric refrigeration a practical reality.

It may be of some interest to note that bismuth telluride, Bi_2Te_3, is presently the most commonly used semiconductor for thermoelectric refrigeration. The N-type material usually has a small excess of tellurium to provide free electrons, or negative charge carriers. The P-type material is likewise bismuth telluride; however, it has a small excess of bismuth to give positive charge carriers.

Engineering Problems

One can best appreciate the manufacturing and engineering problems only when he actually becomes involved in the design and development of devices. Problems that must be solved include:

(1) Economical production of good thermoelectric materials.

(2) Determination of the best physical configuration of the couple as influenced by considerations of refrigerating capacity, space limitations, cost per couple, cost per Btu and power supply requirements.

(3) Fabrication of the individual couples, which involves considerations of cutting to size, plating and soldering.

(4) Assembly of multiple-couple panels to provide the total amount of cooling required. This involves considerations of physical structure, thermal insulation between the couples, heat conduction to attached extended surfaces, and electrical circuitry.

(5) Satisfactory means for efficient removal of heat from the hot junction and rejecting it to the air.

(6) Design of efficient, low cost power supplies to furnish low voltage, high amperage dc output.

There are problems that are being tackled vigorously by industry and for which many solutions have already been found. No attempt will be made here to go into further detail concerning these matters.

Economic Considerations

As to the economics of the situation, the questions most frequently asked are (1) how good is thermoelectric refrigeration; (2) how does it compare with conventional refrigeration in terms of manufacturing cost and cost of operation; and (3) when will it become competitive to conventional methods of refrigeration?

Let us first consider the question, "how good is thermoelectric refrigeration?" This can best be answered in terms of the maximum temperature difference presently available. Present day materials are capable of reaching a maximum temperature difference of about 145°F in an unloaded condition, which is just about the temperature difference encountered by a conventional refrigeration system in maintaining a 0°F evaporator air temperature in a 110° ambient. Note, however, that the 145° temperature difference is obtainable in the thermoelectric system only when the couple is not loaded, i.e., is perfectly insulated and not picking up any heat. If a reasonable load is put on the couple, the operating temperature difference may drop to, say, 70°F. To obtain the desired temperature difference in a loaded condition, it would be necessary to design a cascade system. Thus it does not appear that present-day materials are good enough to permit us to build a practical and economical conventional household refrigerator capable of maintaining a zero freezer in a 110° ambient refrigerator. There are, however, many other appliances and specialty items not requiring such a high temperature difference which can be more readily powered by a thermoelectric system.

The cost of operation is also an important consideration, particularly where a large refrigerating capacity is involved. Thermoelectric couples are presently relatively inefficient compared with the vapor compressor cycle. As a rough estimate, it may be said that the C.O.P. of the thermoelectric system is perhaps only 10% to 50% of that obtainable from conventional systems. This means, of course, that it may cost 2 to 10 times as much to operate. This would be prohibitive for major appliances, particularly room air conditioners and household refrigerators, but would be of less consequence with the smaller appliances and with specialty items.

Present manufacturing costs likewise present a somewhat discouraging picture. Currently, a sufficient amount of material to provide 100 Btu per hour of cooling may cost between $20 and $40. As production techniques are refined and production volume increases, this can reasonably be expected to fall to perhaps $3 per 100 Btu. Bear in mind, however, that the thermoelectric materials represent only a portion of the total costs involved.

The materials must be fabricated into couples, the couples assembled into panels, heat exchange surfaces added, and a suitable dc power supply made available.

When all these factors are taken into consideration, it will be seen that although the thermoelectric system may actually be more economic for capacities of about 100 Btu per hour or less, it is now prohibitively expensive for major appliances, particularly room air conditioners.

Figure 12 tabulates some hypothetical application data which will aid in bringing the foregoing discussion into sharp focus. Figure 13 provides additional information concerning relative product costs of refrigerating systems.

What of Tomorrow?

The last question is "when will thermoelectric refrigeration become competitive to conventional refrigeration?" As shown by Figures 12 and 13, thermoelectric refrigeration is already competitive for special applications and specialty items where the Btu requirements are low, or where manufacturing costs and cost of operation are not important, or where conventional refrigeration cannot be satisfactorily used because of space limitations or other reasons. Therefore, the most promising uses for thermoelectric refrigeration in the near future are in the military, for instrument application, and for certain specialty items in the appliance market where only a moderate amount of cooling is necessary. However, as materials improve and manufacturing techniques are refined, thermoelectric refrigeration can be expected to invade the household refrigerator market. It is not expected, however, that it will ever be a serious contender in the air conditioner market.

What is needed to make thermoelectric refrigeration commonplace in the home is invention - better materials than those now available, plus solutions to the many engineering problems besetting us. The road will be long and tortuous, but the stakes are high. But with all the effort and money that is being spent by government and industry on this project, who knows - we may be there before some of us know what has happened!

In this presentation, I have attempted to outline the inherent advantages of thermoelectric refrigeration, to explain simply the mechanism of thermoelectric effects, to outline some of the design and manufacturing problems involved, and to predict the future of thermoelectric refrigeration and its possible impact on our industry. If, as a result of this discussion, you now see thermoelectric refrigeration in its true perspective, this article will have achieved its purpose.

L. A. Staebler

4/9/59

FIGURE 1

VAPOR COMPRESSION SYSTEM

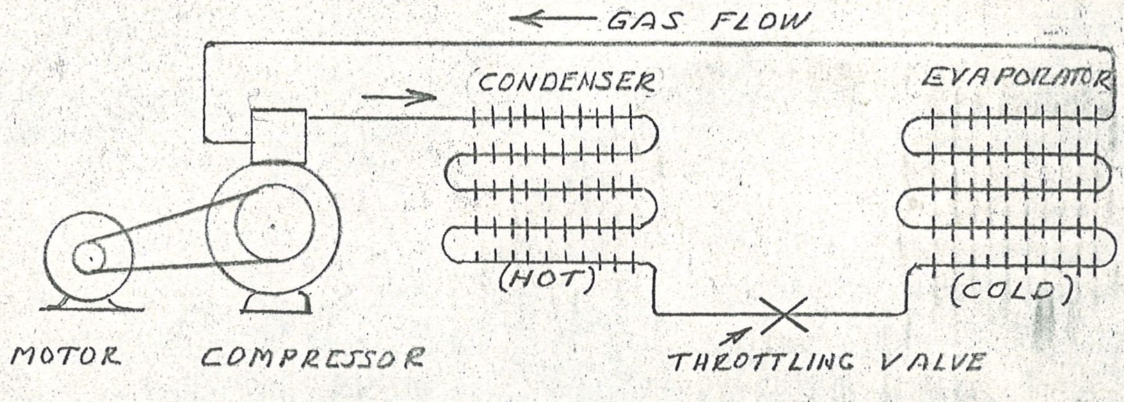


FIGURE 2

THERMOELECTRIC SYSTEM

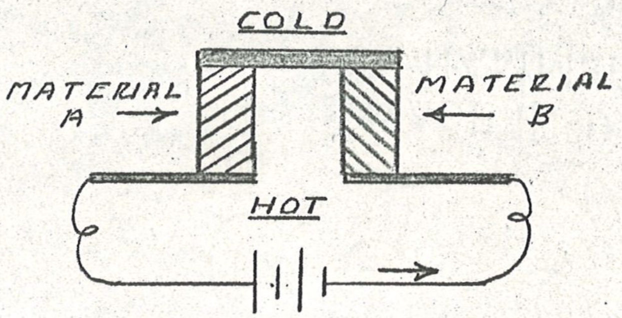


FIGURE 3

ELECTRICAL POWER GENERATION

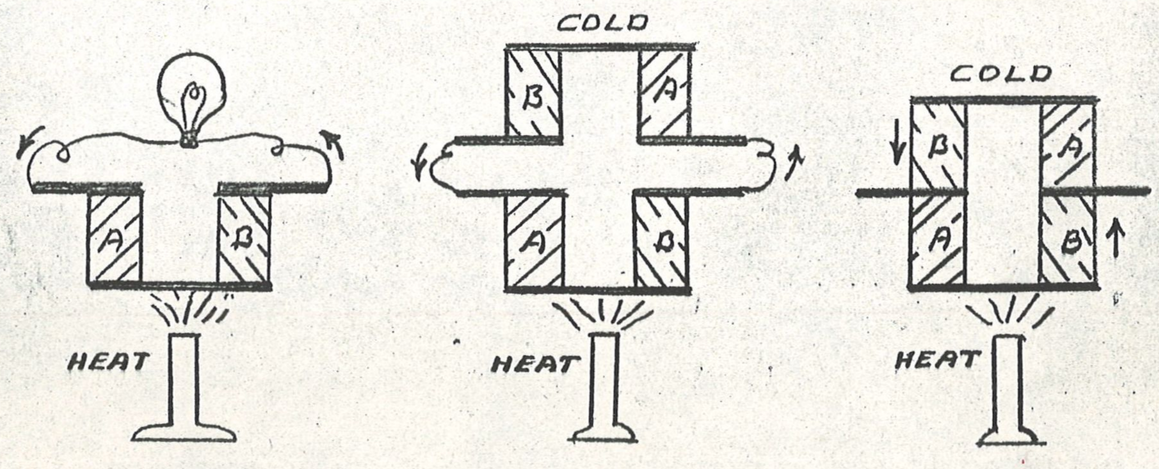
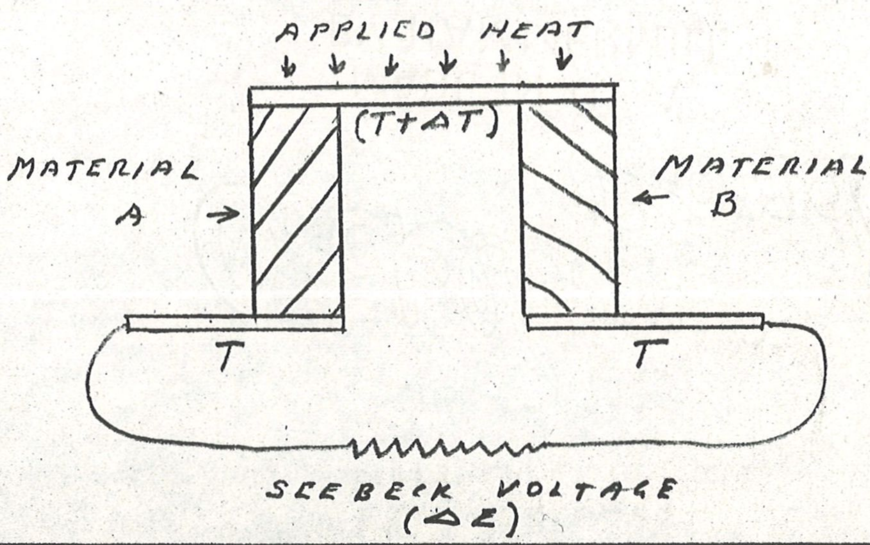


FIGURE 4

THE SEEBECK EFFECT

THE GENERATION OF AN E.M.F. BY A TEMPERATURE DIFFERENCE BETWEEN THE JUNCTIONS IN A CIRCUIT COMPOSED OF TWO DISSIMILAR ELECTRICALLY CONDUCTING HOMOGENEOUS PHASES.



$$\Delta E = S \Delta T$$

FIGURE 5

THE PELTIER EFFECT

THE REVERSIBLE ABSORPTION OR EVOLUTION OF THERMAL ENERGY AT THE JUNCTION BETWEEN TWO DISSIMILAR PHASES WHICH IS PRODUCED BY THE PASSAGE OF AN ELECTRICAL CURRENT THROUGH THE JUNCTION.

$$Q = \pi I$$

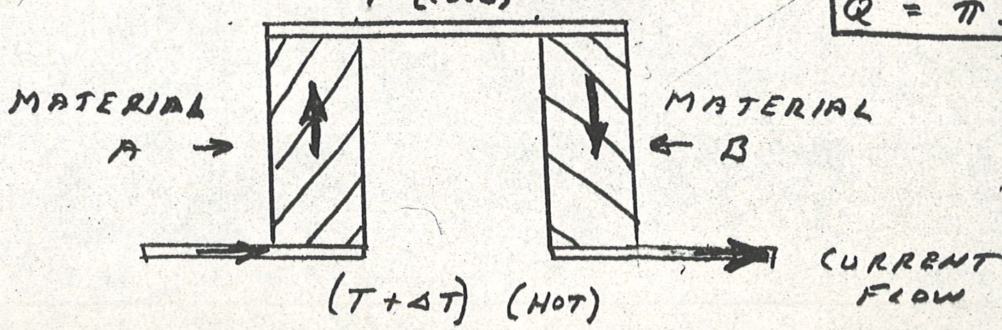
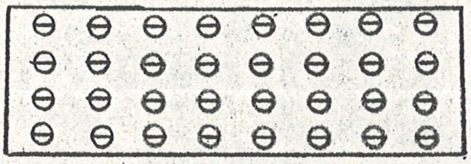
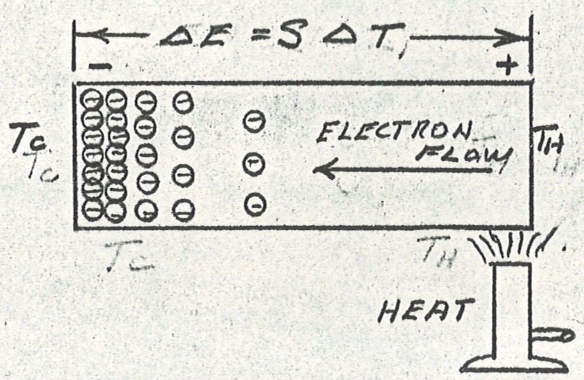


FIGURE 6

ELECTRON TRANSPORT OF ELECTRICAL AND THERMAL ENERGY



UNIFORM DISTRIBUTION OF FREE ELECTRONS IN A MATERIAL.



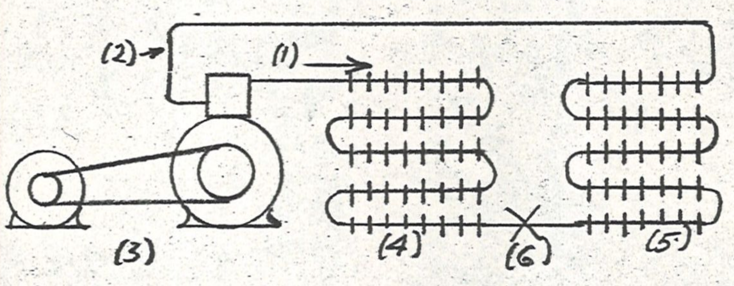
REDISTRIBUTION OF FREE ELECTRONS DUE TO APPLICATION OF HEAT.

FIGURE 6 REFRIGE

FIGURE 7

REFRIGERATION SYSTEM ANALOGIES

VAPOR COMPRESSION



(1) REFRIGERANT GAS

(2) LEAK-TIGHT TUBING

(3) MOTOR-COMPRESSOR

(4) CONDENSER

(5) EVAPORATOR

(6) THROTTLING VALVE

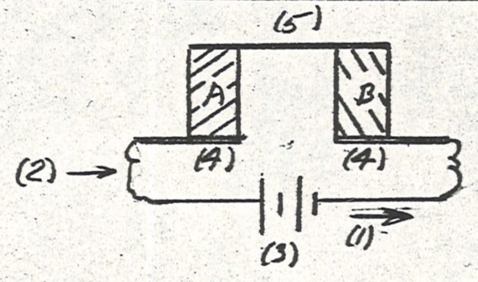
(7) MOTOR LOSSES

(8) COMPRESSOR LOSSES

(9) REVERSE CYCLE VALVE

(10) CAPACITY MODULATION MECHANISM

THERMOELECTRIC



(1) ELECTRON GAS

(2) ELECTRICAL CONDUCTORS

(3) BATTERY

(4) HOT JUNCTION

(5) COLD JUNCTION

(6) "ENERGY LEVEL RELATIONSHIPS"

(7) BATTERY LOSSES

(8) LOSSES IN TE MATERIALS

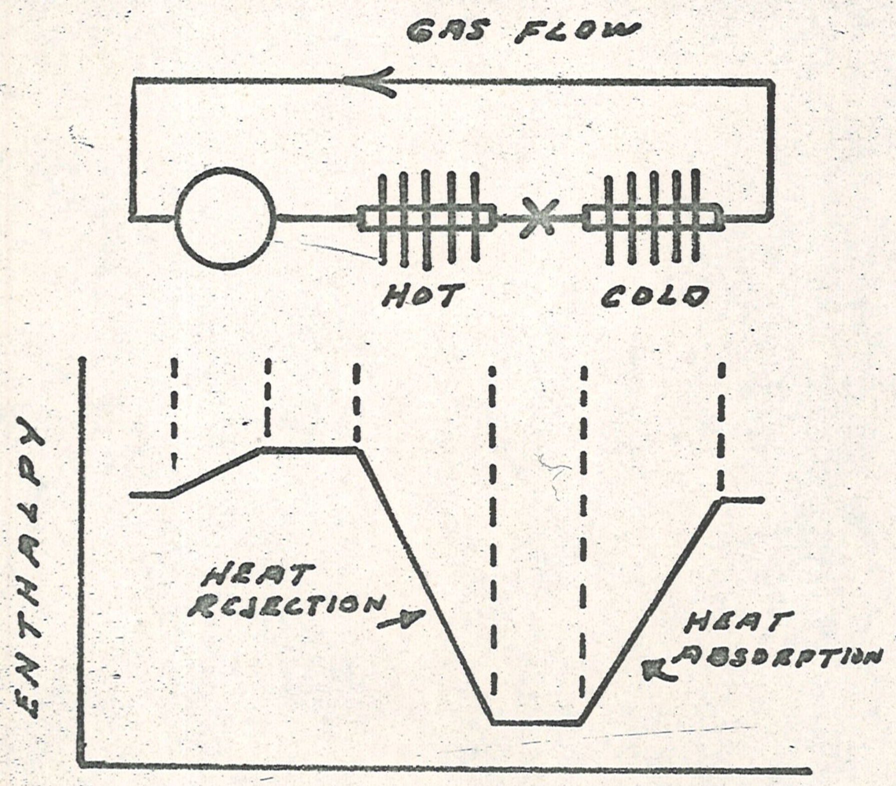
(9) REVERSE CYCLE SWITCH

(10) CAPACITY MODULATION BY VARYING ELECTRIC CURRENT

FIGURE 8

ENERGY LEVEL DIAGRAMS

VAPOR COMPRESSION



THERMOELECTRIC

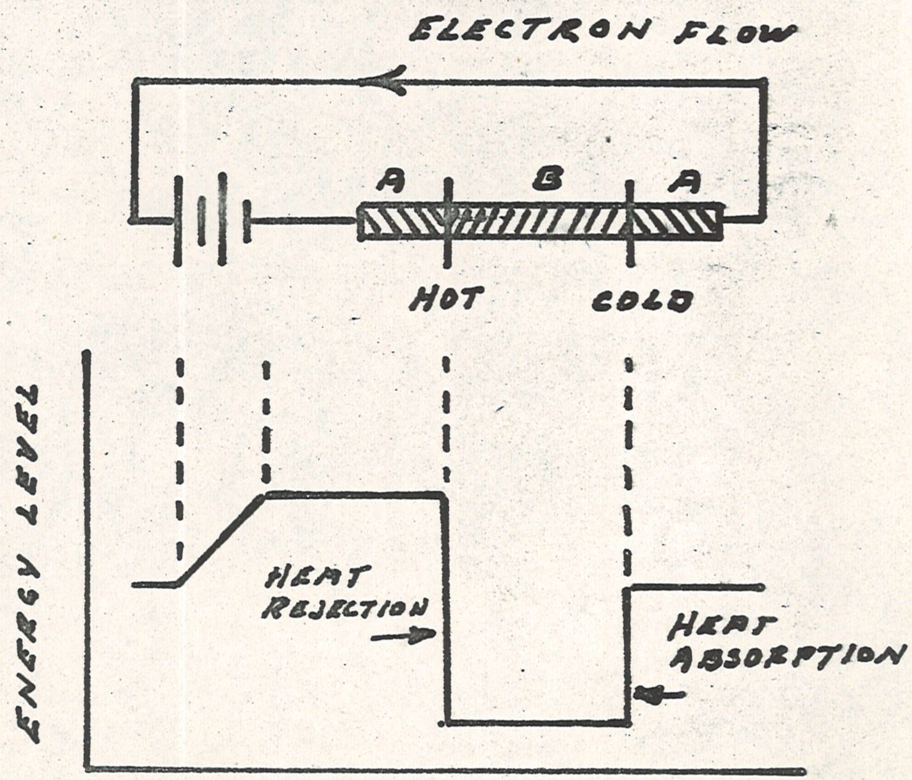
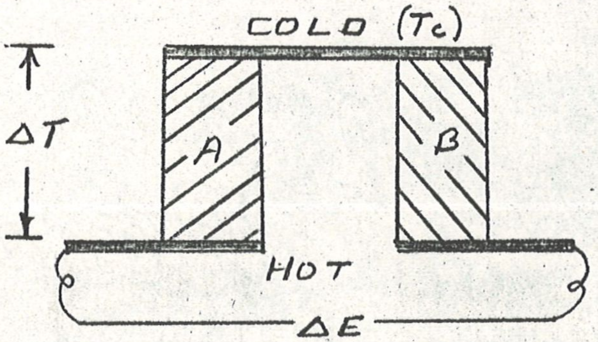


FIGURE 9

PARAMETERS OF TE MATERIALS

ANALOGIES

THERMOCOUPLE



(1) THERMAL CONDUCTIVITY, K (RESULTS IN BACKWARD FLOW OF HEAT)

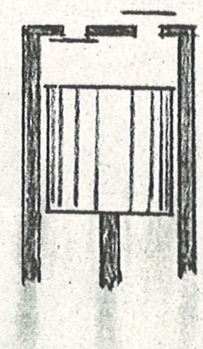
(2) ELECTRICAL RESISTIVITY, ρ (RESULTS IN I^2R LOSSES)

(3) THERMOELECTRIC POWER
$S = \Delta E / \Delta T$

(4) FIGURE OF MERIT
$Z = S^2/\rho \cdot K$

(5) MAXIMUM TEMP. DIFFERENCE
$\Delta T_{MAX} = \frac{1}{2} Z \, T_c^2$

COMPRESSOR



(1) LOSSES DUE TO GAS LEAKAGE

(2) LOSSES DUE TO MECHANICAL FRICTION

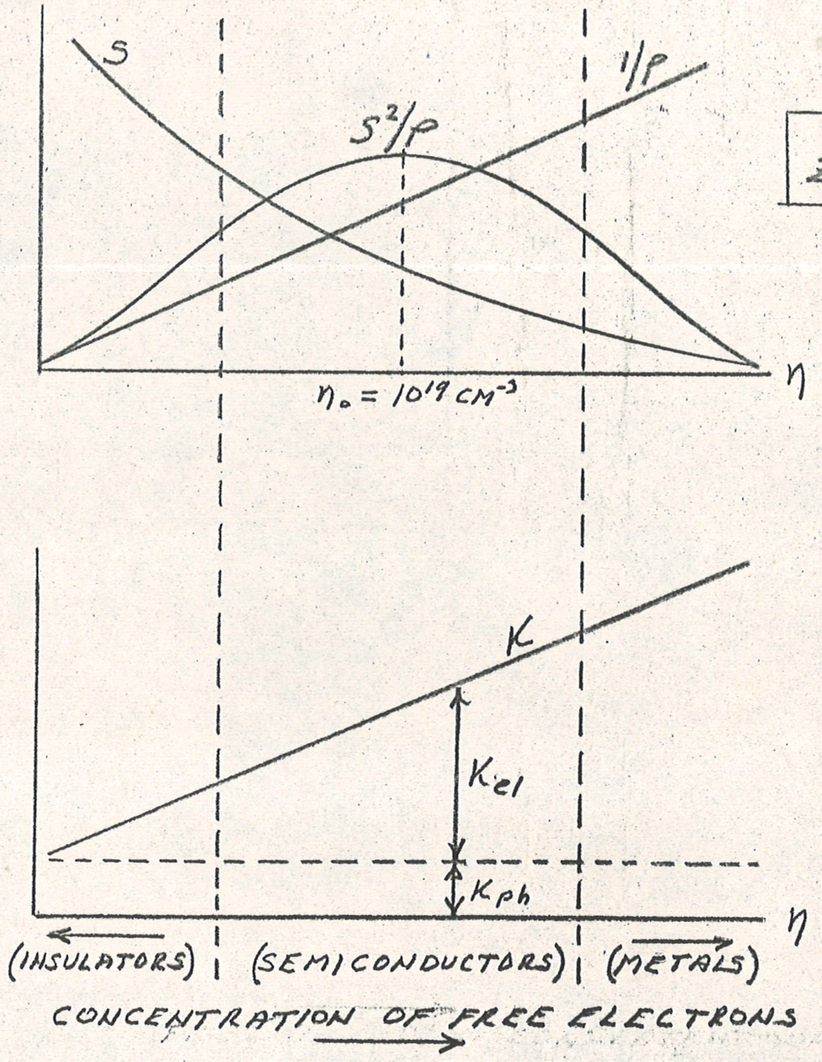
(3) PUMPING CAPACITY AS AFFECTED BY HEAD CLEARANCE

(4) VOLUMETRIC EFFICIENCY AS AFFECTED BY (1), (2), (3)

(5) MAXIMUM PRESSURE DIFFERENCE (OR MAX. COMPRESSION RATIO) AS AFFECTED BY VOLUMETRIC EFFICIENCY AND SUCTION PRESSURE.

FIGURE 10

EFFECT OF FREE ELECTRON CONCENTRATION ON THE PARAMETERS OF THERMOELECTRIC MATERIALS

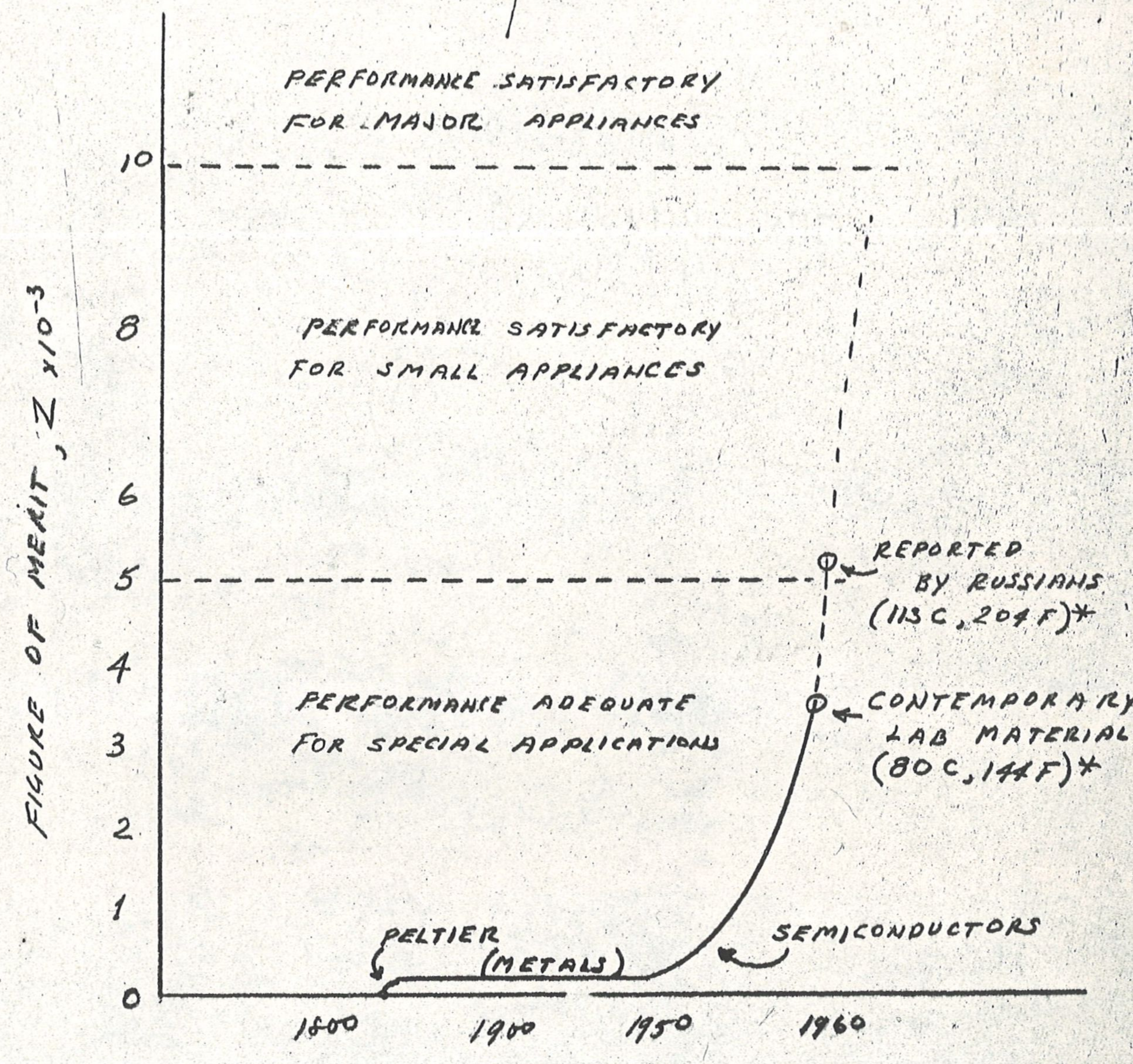


$$Z = S^2/\rho K$$

(FROM A.F. IOFFE)

FIGURE 11

PROGRESS IN THERMOELECTRIC COOLING



* NOTE: MAXIMUM ΔT
OF COUPLE.

FIGURE 12

HYPOTHETICAL APPLICATION DATA

APPLIANCE	AIR CONDITIONER	SMALL REFRIG.	SMALL ICE MAKER
T_H	125° F	120° F	80° F
T_C	45°	35°	15°
BTU/HR	12,000 (1-TON)	150	50
VAPOR COMPRESSION			
C.O.P.	2.3	1.0	0.5
WATTS INPUT	1,500	45	30
MFG. COST	$100	$25	$20
THERMOELECTRIC			
* C.O.P.	0.4	0.4	0.6
WATTS INPUT	8,600	110	25
* NO. OF JUNCTIONS	4,000	50	15
** COST OF JUNCTIONS, $	$400	$5	$2
" " STRUCTURE	$2,000	$25	$8
" " POWER SUPPLY	$35	$20	$15
TOTAL MFG. COST	$2,435	$50	$25

ASSUMPTIONS:

* $Z = 3 \times 10^{-3}$; DESIGNED FOR AVERAGE C.O.P. = MAX, H_L = MAX.

** ULTIMATE TOTAL COSTS PER COUPLE, FABRICATED AND ASSEMBLED IN PANELS — $0.50

FIGURE 13

COMPARATIVE PRODUCT COSTS

(VAPOR COMPRESSION VS. THERMOELECTRIC)