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THE EFFICIENCY OF THERMOELECTRIC
GENERATORS

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Richard William Lowrie
1949

THESIS

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THE EFFICIENCY OF THERMOELECTRIC GENERATORS

By

Richard William Lowrie

A THESIS

Submitted to the School of Graduate Studies of Michigan
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Introduction

Thermocouples provide a means for converting heat energy directly to electrical energy. There are very few other phenomena which accomplish this.

The potential usefulness and scope of application of thermocouples is great since the energy conversion is direct, no rotating or moving parts being necessary. However, the efficiency is at present very low , and this limits the applications of thermocouples to heat measurement.

Research on the phenomena of the thermoelectric effects is now being pursued in various laboratories. Most of this work is experimental in nature, consisting of investigations into the physical properties of semiconductors. There is no satisfactory theory as yet to explain all the features of thermoelectricity. When the theory is complete; then the proper materials can be immediately selected which will give the optimum efficiency to a thermoelectric generator. In lieu of a complete theory, the method of approach has been to use the known facts as a guide to extensive experimental investigations.

Energy Conversions

Of the various types of energy or sources or power, the following must be included: heat, or radiation in general; mechanical, electrical, chemical, potential, and nuclear energy. Each of these sources of power have certain characteristics which limit their range of usefulness. This range is not entirely inherent in the nature of the energy, but may be expanded in many cases by new applications. For example, one would not expect to drive an ocean liner on its trip by the use of the electrical energy stored in a large condenser. Such a condenser would be enormous by present standards. Yet someday such sources of power may be commonplace, if research discloses a material with suitable properties. Such a material might be one like barium titanate, which has a dielectric constant of 11,000.⁽¹⁾ If this could be increased by a factor of 30, and if the dielectric strength could be increased by a factor of 20 and the resistivity by a factor of 100,000; then 100 kilowatt hours of electrical energy could be stored in a volume of 2 cubic feet for several weeks.⁽²⁾

Of the above listed forms of energy, the most versatile is electricity. Large amounts of electric

(1) Ref.#16,#19,#31,#33.

(2) Ref.#9.

power can be transmitted with small loss over long distances by small wires. The advantages of electricity to the production of motion are too well known to be mentioned. Electricity can be converted into heat with perfect efficiency. The desirability of having a large supply of electricity available is obvious. The best way to obtain the electricity is not, however, so obvious in every instance. If, near the user of electricity is a large waterfall or swift river, the economics of the situation immediately direct the consumer to the cheapest source, a hydro-electric plant or a steam turbine-alternator plant. If the consumer is only going to use an average of 5000 KWH a day, a diesel plant might be more economical. If the consumer is a farmer, isolated from a public utility power line, he may use a gasoline unit or a wind generator, or batteries. These are the main sources of electricity in use today.⁽¹⁾ Others are being developed, however, such as tides, geysers, solar heat, nuclear heat of reaction, and various electrochemical reactions including photosynthesis.

The nuclear pile as a source of heat energy has been considered for several years, and experimental units are now being tested.⁽²⁾ The advantages are that there is a very low fuel cost and a very slow rate of

(1) Ref.#22

(2) Ref.#7

fuel usage. The radiations make necessary heavy shielding, however.

Magnetostriction generators have been studied as a possible source of electricity. The efficiency is good, but very little research has been carried out on this method to determine the advantages or disadvantages.⁽¹⁾ The usual process suggested is to change the length of an iron bar by mechanical means or heat, and then utilize the corresponding change in magnetic properties to produce a voltage. Another similar idea, proposed by Edison, is the thermomagnetic generator in which the change in the permeability of an iron bar in a magnetic field, due to rapid heating and cooling, changes the flux linkages in a surrounding coil.⁽²⁾ Edison believed the efficiency could be pushed up to a reasonably high value, but he realized that such a generator would necessarily be relatively heavy.

A device for generating electricity from light by means of selenium cells has been described in the literature.⁽³⁾ Due to the high resistance of selenium, however, little current could be obtained.

Considerable work has been done on utilizing the rise and fall of water due to tides, and some work has

(1) Ref. # 5, # 10

(2) Ref. #123

(3) Ref. #116

been done on harnessing the force of the waves.(1)

Wind generators in small sizes are in wide use on farms and on aircraft. Large units are not widely used due to the fact that there are very few locations with a strong wind available.

Various means have been suggested for converting chemical energy to electrical energy.(2) Storage batteries are heavy and bulky. A storage battery which could efficiently store, 100 times as much energy as is now possible, could be very widely used in every place where electric power is utilized. About 1898, a great deal of discussion was given to the production of electricity from carbon in a carbon-metal heated cell.(3) At that time, an overall efficiency of 34% was thought to be quite easily attained, and some units were built which looked promising. It was eventually decided that such a method would not be commercially feasible, and the process has not been discussed in detail since.

Thermocouples provide an attractive means for converting heat directly into electricity. There are no rotating or reciprocating parts whatever to wear or to require lubrication. The application of thermocouples to electric power generation has been worked on by various

(1) Ref. # 135, section 2-31

(2) Ref. # 13, # 115

(3) Ref. # 115, # 117, # 118

investigators since at least 1890,⁽¹⁾ and is now being given considerable attention.⁽²⁾ The recent increase in interest in thermocouples is due to two factors, increased scope of potential usefulness and a better knowledge of the nature of semiconductors. The efficiency of thermoelectric generators is not, at the present time, high enough to make this type of converter commercially feasible. Future discussion of the efficiency and applications of thermoelectric generators will be discussed later.

- (1) Ref. #74, #89, #90, #99, #100, #104, #111, #117, #118, #120, #121.
(2) Ref. #8, #23, #29, #35, #57.

HISTORY

The thermoelectric effect was discovered in 1821 by T.J. Seebeck.⁽¹⁾ He found that if the junction of two dissimilar metals (or any conductors) was heated, a voltage was generated at the junction which could be measured by connecting a suitable meter to the other ends of the wires. Two different metals which are joined together at one end so as to be used for generating electricity by means of the thermoelectric effect is called a thermocouple. It was not long before thermocouples were widely used as a means of indicating temperature. Thermocouples can be installed in such places as furnaces or underground pipes, and the temperature of the couple can be read at some remote distance by means of a sensitive electric meter attached to the thermocouple wires.

The converse of the thermoelectric effect was detected by J. Peltier in 1834.⁽²⁾ He found that the flow of current through a thermocouple either heated or cooled the junction, depending on the direction of the current. The usual joule heating is a much larger effect, however. The cooling due to the Peltier effect is not large enough to be of commercial use.

If the Seebeck and Peltier effects were the only ones involved in thermoelectricity, the curve of emf versus

(1) Ref. # 128

(2) Ref. # 127

temperature would be a straight line. The fact that such a linear relationship was the exception rather than the rule, led W. Thomson to postulate and finally discover in 1851, a third effect, now called the Thomson effect.⁽¹⁾ The Thomson effect is simply this: wherever a thermal gradient exists in a conductor, an electric potential gradient also exists. The voltage produced in couples due to the Thomson effect is usually much smaller than the Seebeck voltage and is usually neglected in analyses of thermocouples when power generation is being considered. For a brief description of apparatus for demonstrating these effects, see references # 65 and # 71.

The first applications of thermocouples were in temperature measurement. Webster defines a thermocouple as a thermoelectric couple used for the measurement of heat. As a means for indicating temperature and radiation, in general, the thermocouple has received a great deal of attention.⁽²⁾ Some of the applications include measuring human body temperatures, air velocity, and stellar temperatures. A great deal has been written on various thermocouple alloys, thermocouple stability and linearity, protection from oxidation, thermocouple instruments to measure rf currents, potentiometers and millivoltmeters for thermocouples, thermoelectric temperature scales and

(1) Ref. # 126

(2) Ref. # 47

other applications.

The use of thermocouples for producing electric power from heat has been considered for nearly 100 years. The method is attractive because there are no moving parts and the conversion is direct. Until recently, an efficiency greater than 1% had not been achieved. The latest figure is 7%, obtained by using a PbS - ZnSb thermocouple. Due to the high electrical resistance of pure PbS however, a commercially usable thermoelectric generator made of such a couple would have to be quite large and bulky to maintain a low internal resistance. Research is being carried on continuously in an effort to improve the efficiency. This research is both experimental and theoretical in nature.

GENERAL DISCUSSION

There would be many applications for an efficient thermoelectric generator. In the automotive, railroad, farming, aircraft, mining, stationary power plants, and other industries such a generator would be most useful.

As a means for extracting power from a nuclear pile, thermocouples present a simplicity that cannot be duplicated. No complicated heat exchangers, turbine, and generator would be necessary. When a nucleus splits and gives up energy, the energy appears as radiation of various wave lengths, and as high velocity electrons, neutrons, protons, and other particles. To make use of this energy the only method seems to be to stop the particles by collisions and utilize the heat produced. The cross sections for neutron absorption, as well as the properties as a moderator, of the thermocouple materials must be considered, and also the melting points. Perhaps someday the thermocouple junctions themselves will be the source of the atom splitting, and the energy released would appear as an electric current with little harmful radiation loss.

Whenever there is a difference in temperature, there is a potential energy source able to energize a thermoelectric generator. Such sources of heat as the sun,

geysers, volcanos, earth heat, cold springs, and nuclear piles may someday be the energizers of thermoelectric generating units. Even the radiation from a distant star has been made to generate electricity by means of sensitive thermopiles.⁽¹⁾ A thermopile is a bunch of thermocouples connected in series and is really nothing other than a miniature thermoelectric generator operating at a very low temperature difference. The efficiency of thermopiles has been considered, but the analysis is different than for a generator since no power is desired.⁽²⁾ The usual thermopile efficiency is around .005 %.

The Army and Navy financed some research during the war to develop a small generator unit. Some of this research is still going on.⁽³⁾ The advantages of a thermoelectric generator fit in nicely with some of the military requirements; namely, simplicity, ruggedness, quiet operation, a source of pure D.C., and a source of heat to be used possibly for cooking or personnel comfort. A thermoelectric unit to attain maximum utility would also have to be compact and light, and fairly efficient. An efficiency of 8% or better would definitely be satisfactory. The PbS - ZnSb couple gives an efficiency of 7% but the size and weight of such a power couple is high due to

- (1) Ref. # 47 p. 395
- (2) Ref. # 47 p. 1284
- (3) Ref. #3, #131

the resistance of the materials.

There is good evidence that the thermoelectric effect is not entirely atomic or molecular in nature. The emf is affected by various mechanical changes in the metal such as impurities, heat treatment, drawing, rolling, pressure, tension, and magnetization.

Efforts to find an equation relating the thermoelectric voltage to the other constants of the atom or molecule have not yet been successful. Telkes⁽¹⁾ gives one equation which is not completely accurate as regards experimental confirmation. It is

$$\theta = \pm \left(\frac{\Delta E}{2Te_0} + \text{Const.} \right) \quad \text{where } \theta = \text{thermoelectric power,}$$

ΔE = energy level difference in electron volts, T = temperature in degrees Kelvin, e_0 = electronic charge, and the constant varies from 108×10^{-6} to 172×10^{-6} .

There appears to be no simple relationship between the emf and the other physical constants. Most investigators have consequently turned to long trial and error experiments to find the alloys and compounds which will give the highest efficiencies. The thermoelectric properties of most of the elements and many of the alloys are given in the International Critical Tables. A portion of these tables is given in a later section of this thesis.

The main factor determining the emf is some atomic property of the metal since there are wide variations

(1) Ref. # 23

among the metals. Comparing the thermoelectric properties of the elements to other properties of the elements does not show any relationship between the two, except that no metal which exhibits a high thermal emf is superconducting. The significance of this is problematical.

Assume that for a certain thermocouple the resistance drops to 10^{-15} ohms at 4°K , and assume the emf does not reach zero except at 0°K . In outer space one junction could easily be kept at very nearly 0°K . The other junction could have the radiation from the sun focused on it and the temperature kept at 4°K . If the couple wires were quite long, the heating of the cold junction would be unimportant. The current that could be so produced by the resulting voltage might be utilized through a transformer, the couple acting as a primary by a periodic variation of the hot junction temperature. Any heat engine that can work with 0°K as a lower limit of temperature and can expand to 0 psia will be very efficient. Actually, little is known about the thermoelectric effect at very low temperatures. A better knowledge of the atomic changes that take place to permit superconductivity may also reveal some of the causes of thermoelectricity. (1)

In the past, most of the thermocouple research has been done on metals which are relatively good conductors.

(1) Ref. # 71, P. 316.

It was realized that in order to obtain large currents, large conductors would be necessary due to the small thermoelectric voltage. For example, if the couples are large bars with a total resistance of .001 ohms, and the generated emf is 50 mv, the current will be 50 amps. A striking laboratory demonstration makes use of the large current to illustrate the thermoelectric effect. The current is used in an electromagnet to support very heavy weights.

If the metals are not good conductors then the size of the conductors becomes impractical, especially if the metal is expensive or heavy. For this reason, most of the metals considered in the past have been good conductors, even though some semiconductors give much higher voltages. Recent work has shown, however, that the conductor metals do not offer much opportunity for improvement as regards efficiency in a thermoelectric generator. This will be shown later in the mathematics.

The most fruitful area of work now seems to be with semiconductors such as lead sulfide, lead oxide, silicon, germanium, antimony, bismuth, carbon compounds, and certain plastics. The chief disadvantage in using a semiconductor is its electrical resistance. However, most substances which have a high electrical resistance also have a high thermal resistance, and a high thermal resistance is desirable to prevent heat conduction along

the couple. The relation between electrical and thermal conduction is known as the Weidmann-Franz-Lorenz Law which states that the ratio of thermal to electrical conductivity is equal to a constant times the absolute temperature. The lower the value of the constant, the better for thermocouple purposes. However, for most materials the value of the constant is the same, namely 2.45×10^{-8} . No materials show a lower value, but many show a higher value. The difference between 2.45×10^{-8} and the value for the material in question may be called the deviation, or D. The larger D, the less desirable the material as a thermocouple for a power generator. Papers on the subject often state "assuming the Weidmann-Franz Law to hold". This means the value of the ratio of thermal to electrical conductivity is a maximum, or 2.45×10^{-8} . This condition limits the number of suitable materials and serves as a useful criteria to judge whether or not a certain substance might serve as a power thermocouple.

Comparing a metal thermocouple to a semiconductor thermocouple, it is obvious that the metal thermocouple will have a lower resistance for a given size. However, there are two advantages for the semiconductor. First, the ϵ_{ef} is higher by a factor of 2 to 10; and second, the electrical resistance usually decreases as the temperature goes up. Also, there remains the possibility

that the resistance of a semiconductor may often be lowered considerably without affecting the other properties very much, by the addition of slight amounts of impurities.

Since the efficiency of metal thermocouples seems to be limited to below 2%, most of the work today is centering on semiconductors, the hope being to find a semiconductor with a good thermal emf, a low heat conductivity, and a low electrical resistivity. Recent work indicates that these properties might be attained by the addition of small amounts of "impurities", in some cases. For example, to improve the electrical conductivity of silicon without decreasing Q , a small amount of copper might be added. The type and amount of metal to add is found only by experimental work, however. See Ref. # 23.

The physical interpretation of conductivity and thermal emf in semiconductors is being developed, using the modern theory of solids as a basis. See references #18, # 20, #25, #53, #59, #64, and #73. So far, no one has come forth with a complete theory. The usual qualitative theory of thermoelectricity assumes an electron "gas" under pressure in the metal, the flow of which represents current. A thermocouple junction represents a semi-permeable membrane for the gas, which diffuses predominately in one direction to set up a local emf. It is known that the emf

originates at the junction. It seems reasonable to assume, consequently, that since the point of contact of two metals acts in such a peculiar manner, it is somewhat analagous to a semi-permeable membrane.

At the other junction, a local emf equal to the first is set up opposing it so that the net emf with the circuit at one temperature is zero. This junction emf is called the Peltier potential since a unit charge in crossing the junction will either gain or give up heat energy. The difference in the Peltier potentials at the junctions is the Seebeck voltage, often called the Peltier voltage, and is zero when there is no temperature gradient in the conductors. When any two metals are placed in contact, a potential is set up between the other two ends of the metals. This is called the contact potential. The absolute value of the contact potential is difficult to measure since it is a sensitive function of the surface condition of the metal. The contact potential is also called the volta effect, volta potential difference, or potential function.

There is a close relationship between the contact potential and the Peltier voltage. This relationship has been developed from thermodynamical considerations and states $\frac{\partial V}{\partial T} = -\frac{1}{T}P$ where V = contact potential,

T = temperature in degrees absolute, and P = the Peltier

coefficient plus a "surface heat of charging" coefficient.⁽¹⁾

According to the electron gas analogy, it appears that the thermoelectric properties of a substance would be quite different when in the liquid state. Very little research has been carried out investigating the thermoelectric properties of liquid - liquid junctions. To prevent the junction from becoming homogeneous by diffusion, some type of separating membrane should be used. The electro-chemical effects may become large when the substances are in the liquid state.

Experimentally, the electrical conductivity has no relation to the thermal emf. Now, $\sigma = \frac{e^2 N l v}{4 K T}$, where σ = electrical conductivity, e = electronic charge, N = the number of free electrons per cm, l = mean free path, v = average electron velocity, K = gas constant per particle, and T = the absolute temperature. Since $\sigma \propto N l v$ and since the thermal emf is not proportional to σ , the thermal emf is not proportional to $N l v$ as might be expected from the electron gas analogy.

A paper by Ellis states the most important characteristics of a thermocouple to be used for power purposes.⁽²⁾ They are "(1) maximum hot junction

(1) Ref. # 86, # 44

(2) Ref. # 8

temperature of 1000° F, (2) potential characteristic of 600 microvolts per degree C, (3) the structure should be mechanically strong, (4) low internal resistance, and (5) should resist oxidation over prolonged periods." Other desirable features are compactness, light weight, reliability, simplicity, and low cost. Ellis also states "The examination of the characteristics of metals indicates that a combination of metals would not produce such a couple. The best approach may be in the field of semiconductors, incorporating trace elements to adjust properly the thermal and electrical conductivity, and structural characteristics. The application of quantum mechanics and a complete review of materials by the application of the electron theory may result in a couple whose lattice structure has the optimum desired characteristics." He goes on to state that such a generator, with an efficiency of at least 8%, would revolutionize conversion units in the power field. The potential characteristic for metals is at present only about 1/10 of the desired $600 \mu\text{v}/^{\circ}\text{C}$.

When a desirable couple is found, the design of the generator unit presents itself. For small units such as 1 KW, exposure of the junctions directly to the heat source might be satisfactory. For larger units, in order to maintain a constant and even tem-

perature at all the junctions, a liquid could be used as a heat-transfer agent. The shape of the unit might be cylindrical, with the hot liquid on the inside flowing past the hot junctions. The external junctions could be exposed to a blast of cooling air or could be cooled by another liquid. This second liquid might be used to heat a second unit, in this way conserving more of the available heat. The design calculations of a small unit are given in detail in a later section.

There has not been a great deal published on thermoelectric generators. The bibliography lists most of the books and periodicals which contain any pertinent information.⁽¹⁾ The "Industrial Arts Index" and the "Engineering Index" contain numerous references to thermocouples, but most refer to the measurements applications. Such things as accuracy, stability, oxidation, and response time have been investigated thoroughly in relation to temperature measurement applications.

There are three laws often spoken of in describing thermocouple characteristics.⁽²⁾ The first is the law of the homogeneous circuit: a current cannot be initiated in any circuit of a single homogeneous metal by the application of heat alone. The second

(1) Ref. #8, #23, #29, #35, #57, #104, #117, #120, #121

(2) Ref. #47, p.80

law is as follows: the algebraic sum of the thermoelectric voltages in any circuit of dissimilar metals at a uniform temperature is zero. The third law states: the total emf of any number of thermojunctions in series, at any set of temperatures, is the algebraic sum of the individual junction emf's. The couples are all assumed to be of the same two metals. The second law is called the law of intermediate metals, and the third law is called the law of successive temperatures. These three laws have been repeatedly verified by experiment and are the physical basis upon which much of the present theory of thermoelectricity has been based.

EXPERIMENTAL INVESTIGATIONS

Several experiments suggested suitable research work. One was to measure the emf as a function of the distance across the face of the junction. This was readily done. The thermocouple wires were about 1/8" in diameter, of iron and constantan. One end of the iron wire was made flat and smooth. One end of the constantan wire was made pointed and sharp. These two ends were then placed together in a constant temperature water bath, and the thermal emf was measured as a function of the distance across the face of the iron wire. No detectable variation could be found. This was as expected since the iron wire was fairly homogeneous. As another experiment, the effect of pressure was tested. With the constantan point touching the iron wire at a fixed point, the pressure at the junction was increased. No change in emf was observed for a range of pressure from about 10 to 1000 psi.

Another experiment was to observe the effect on the emf when a current was passed transversely across the face of the iron. Fig. 1 shows a sketch of the apparatus. The effect observed for currents up to 15 amps is shown on graph 5. The upward curve of the current indicates that the slight increase in emf at

higher currents is probably due to joule heating at the face of the iron conductor. The use of transverse current to produce free electrons does not seem to have any appreciable effect on the emf. Reversal of the transverse current produced no change. The idea in this experiment was to see if the conduction electrons

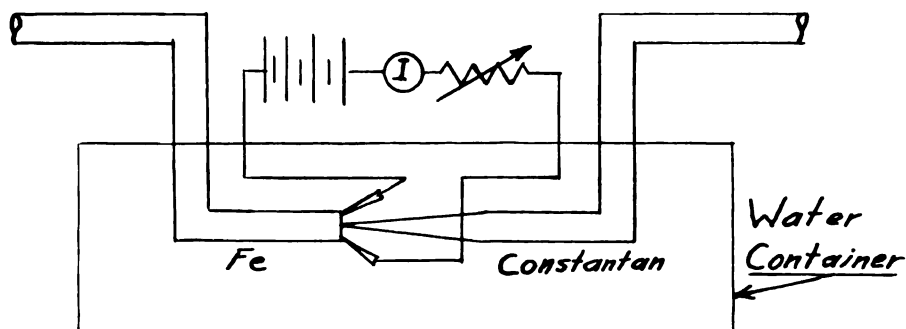


Fig. 1.

set in motion by the transverse current might act in reducing the potential barrier at the metal surface which limits the thermoelectric voltage.

In another experiment the iron was heated to a red heat and then touched to the cold constantan. The resultant emf observed was that corresponding to the average temperature of the two metals. This showed that the "gas" pressure set up in the hot conductor was freely dissipating on contact with the cold conductor. An equilibrium temperature was quickly reached as exhibited by the average temperature emf observed. There seems to be no possibility here for increasing the efficiency.

Since the efficiency of thermopiles is of the same order as for larger generators, the size of the junctions apparently has no effect on the efficiency.

The metal couple composed of Chromel P and constantan produces about 40 mv at a temperature of 1000°F, as shown on graph *13*. This voltage would be sufficient to energize an efficient thermoelectric generator if it were not for the high thermal conductivity of the metals. There are at least two methods of decreasing the thermal conductivity without decreasing the electrical conductivity a comparable amount. The first is to find a new metal or semiconductor with the desired characteristics. This is the present avenue of approach. The second possible method of preventing heat transmission is to remove a section of the metal and put in its place a heat insulator. However, this also decreases the electrical conductivity, except when the insulator is such a material as an ionized gas at low pressure. Such a gas will transmit the current, under certain conditions, without exhibiting an excessively high resistance. External means would be necessary to keep the gas ionized. The only heat passing through the gas would be by radiation and ion bombardment. This heat would probably not be so serious as the conduction heat, depending on the spacing and

temperature difference. To keep the resistance low, a short spacing and large areas would have to be used. It is doubtful, however, if the emf would be large enough to cause current to flow in the gas, even if a high electric field intensity were produced by using points and short spacing. Possibly a conducting liquid could be used in place of the ionized gas. If a solid were used as the insulator, the large temperature drop across the material would introduce a new emf which would have to be considered. It turns out that the thermoelectric properties of the insulator become the major factor and then the problem is back where it started; namely, to find a substance with high electrical and low thermal conductivity.

The efficiency of the PbS - ZnSb couple is 7%, as reported by Telkes.⁽¹⁾ This is the observed efficiency. The calculated efficiency is 10%. To increase this efficiency and reduce the size of the couples, a higher electrical conductivity for the PbS must be obtained. This may be done by adding small amounts of another metal such as silver or copper. The effect of such additions has not yet been fully determined. The best method of doing this would be to add the powdered metal to the powdered PbS at room temperature and then fuse the mixture in a ceramic boat.

(1) Ref. # 23

Due to the high melting point of PbS, 1800°C , it is difficult to work with it in the molten state.

Since the point of contact of two metals is the seat of the thermal emf, it might be worthwhile to investigate the effect of coating the face of one metal with various oxide films of other metals. This might permit a greater emf to be developed.

A useful investigation would be one to determine the relationship between the wavelength of the heating radiation and the thermal emf. This could be done using a light-ray apparatus as shown in Fig. 2, for frequencies near the visible region. The angle of

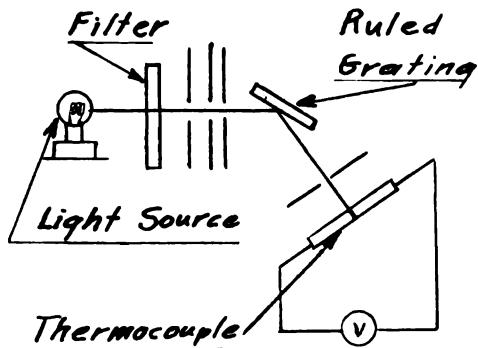


Fig 2.

inclination of the grating determines the wavelength by the formula $n\lambda = 2d \sin \theta$, where λ = wavelength, d = ruled line spacing, and θ = the angle of inclination from the horizontal. n = the order of the re-

flexion. For higher frequencies, an x-ray apparatus similar to the above light ray apparatus could be used. The per cent absorption would have to be measured by an ionization chamber and allowed for. The relation between intensity and emf would also have to be studied. Another interesting investigation would

be to determine the effect of various energy electron beams on a thermocouple.

A thermocouple responds to heat, which is an average motion of the atoms in the metal. It might be interesting to observe, if possible, the effect of a neutron beam on a thermocouple junction. Some of the neutrons would be absorbed and scattered, imparting a high velocity to some of the atoms. This would cause a temperature rise which might be measurable. If the two metals were of different atomic weights, there would be a flow of particles from the heavier to the lighter as shown in the following analysis.

Let v_r = recoil velocity of the atom

v_1 = initial neutron velocity

m_0 = mass neutron = 1

m = atomic weight of atom

N = number of neutron collisions

It can be shown from conservation of energy and momentum during an elastic collision that,

$$v_r = \frac{2m_0}{m + m_0} v_1 \quad (1)$$

Assuming the number of neutron collisions to be proportional to the atomic weight of the target, (the number may not be proportional due to the density or due to the resonance levels), then

$$N = Km \quad (2)$$

The flow of recoil atoms past the junction can be represented by i which equals the number times the velocity of the atoms, or

$$i = Nv_F \quad (3)$$

Substitute (1) and (2) into (3).

$$i = Km \frac{2m_0 v_1}{m + m_0} \quad (4)$$

The ratios of i for two different materials (a) and (b) become:

$$\frac{i_a}{i_b} = \frac{K_a m_a (m_b + m_0)}{K_b m_b (m_a + m_0)} \quad (5)$$

Let material (a) be carbon ($m = 12$) and material (b) be lead ($m = 206$). Then

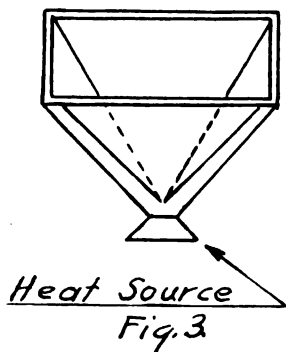
$$\frac{i_a}{i_b} = \frac{K_a}{K_b} \frac{12}{206} \frac{207}{13} = \frac{K_a}{K_b} 0.927$$

If K_a and K_b are equal, then the number of recoil atoms from (a) to (b) is 0.927 times the number from (b) to (a). This small flow from the heavier to the lighter metal might be detectable as a current in the wires. This method of detecting a neutron beam could not be as sensitive as the usual ionization chamber devices, but it might be useful in determining the neutron flux inside a pile or other inaccessible or small places.

Design of a Small Generator

The design of a small thermoelectric generator will now be considered. Short rectangular bars of

copper and constantan will be used as the couple materials. For copper-constantan, about 0.054 mv/°C, or 27 mv at 500°C is the developed voltage. To be useful, the total generator voltage should be at least 24 volts with no load. This would require 890 junction pairs. For a generator, one shape might be an inverted square pyramid as shown in fig. 3.



The sides would be made of some heat resistant material such as transite, with holes in the sides for the square rods of copper and constantan. The heat would flow on the outside. The

inside could contain water to provide a cold junction for the thermocouples. If 890 couples are required, 222 couples will be placed on each side of the pyramid. If the cross sectional area of the rods is 1 cm² and the length is 4 cm, the total area of the holes in a side of the pyramid is 222 cm². The sides of the pyramid will be triangles. Let the area of these triangles be 250 cm², then the ratio of holes to the total area will be 0.9. If the triangles are equilateral, they will be 24 cm on a side. Assuming the hot junctions to operate at a temperature of 1000°C, the electrical resistivity of copper at this temperature is 7.25 $\mu\Omega$ -cm. If the cold junctions

are kept near 0°C , the resistivity (ρ) of copper here is $1.72 \mu\Omega\text{-cm}$. The average value or ρ_{av} is 4.5. For constantan the average value is 50.2. The total resistance of one couple may now be calculated, knowing ρ , the area, and the length. The resistance is 2.13×10^{-4} ohms. For a total of 890 junctions, the overall hot resistance will be 0.194 ohms. The current delivered to a .194 ohm load will be 62 amps. At this load, the maximum power condition, the generator terminal voltage is 12 volts and the power delivered to the load is 746 watts or 1.0 hp. This is the output power. Next, the equivalent input power must be found. The thermal conductivity of copper (K_{Cu}) is 2660 BTU/hr/ft²/°F/inch. For constantan the figure is 186.⁽¹⁾ Converting the above values of K and using a temperature differential of 1000°C as a basis, the heat conducted by the copper is 3.55 BTU/min and by the constantan is 0.6 BTU/min, making a total of 9.15 BTU/min being lost by conduction to the cold junction. For 890 junctions, the total heat lost is 8150 BTU/min or 192 hp. This is effectively, the input. The efficiency is then $\frac{1}{192} = .52\%$. From this it is seen that the efficiency is about one half of one per cent. In practice, this might be increased to one or two

(1) Ref. # 135 Sec. 3-28

per cent, by using shorter bars, closer spacing, utilizing the heat absorbed by the cooling water, or by using other metals with a higher voltage. Such a thermoelectric generator with an output of 1 hp and an efficiency of 0.5% would have a volume of about 0.5 cubic feet, and weigh about 100 pounds.

These are all only analytical values and not actual test data, although some of the units that have been built show approximately these same values.⁽¹⁾ It should be noted that the emf and the resistance are both proportional to the number of junctions. Therefore the current is approximately independent of the number of junctions. The power is proportional to the total number of junctions.

(1) Ref. # 15, # 28, # 35, # 57, # 120

MATHEMATICAL ANALYSIS

In 1821 Seebeck observed the fundamental thermoelectric phenomena, namely, that heating the junction of two dissimilar metals caused an emf to be developed. This voltage was found to be proportional to (1) the temperature difference between the hot and cool ends of the wires, (2) the metals being used, and (3) to a lesser extent, the absolute temperature of the cold junction. For chromel and constantan the emf is about 70 microvolts per degree centigrade.

In 1834, Peltier found the inverse Seebeck effect, namely, the cooling or heating of a junction of dissimilar metals by a current. The direction of the current determines whether the effect is cooling or heating at a particular junction. This effect is separate from and much smaller than the usual joule heating, due to the resistance.

A third thermoelectric effect was discovered by Thompson in 1851. He found that a temperature gradient in a homogeneous conductor set up a potential gradient along the conductor. For most metals, the magnitude of the Thompson voltage is much smaller than the Seebeck voltage.

A Peltier potential π will be used which represents the change in heat energy at a junction for a

given charge passing through the junction.

Thus,

$$\pi = \frac{dH}{dq} = \frac{d(Vq)}{dq} = \frac{V dq}{dq} = V \quad (1)$$

The coefficient π represents a voltage V as shown above. To discuss the Thompson effect, a coefficient σ will be introduced which may be thought of as the specific heat of the free electrons in the metal. It represents the heat per unit charge necessary to cause a unit change in temperature, or

$$\frac{dH}{q} = \sigma dT \quad (2)$$

This may be rewritten as

$$H = \int \sigma q dT \quad (3)$$

to show the energy associated with the heat by the Thompson effect.

A circuit to illustrate these effects may be drawn as follows:

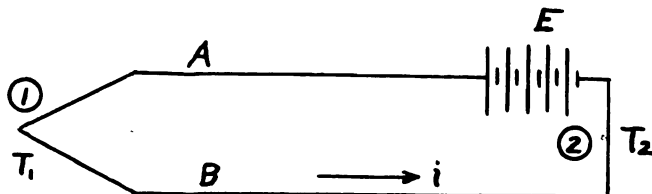


Fig. 4.

The battery is sending current through the circuit composed of two different con-

ductors, A and B. Due to the Peltier effect, heat will be absorbed at junction 2 and liberated at junction 1, and a Peltier voltage will be set up at these points. Due to the resulting temperature gradient along A and

P, a Thompson emf will be established. The total result may be expressed in an energy equation as

$$E q = \int_{T_2}^{T_1} q \sigma_A dT + \pi_{T_1} q - \int_{T_1}^{T_2} q \sigma_B dT - \pi_{T_2} q \quad (4)$$

or

$$E = \int_{T_2}^{T_1} \sigma_A dT + \pi_{T_1} - \int \sigma_B dT - \pi_{T_2} \quad (5)$$

The following diagram may assist in visualizing the effects.

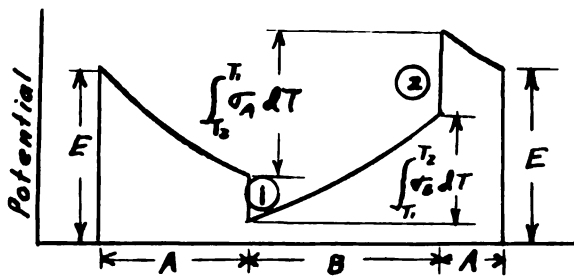


Fig. 5.

Thus the battery energy is considered equal to the difference of the two Thompson energies plus the

difference of the

two Peltier energies. The resistance of the conductors is neglected and the joule heating is considered zero. The entire process may be considered to be reversible since the Peltier and Thompson effects are believed to be completely reversible. Neglecting the joule heating does not introduce a serious error in the analysis. This error is discussed quite completely in Bridgeman, p. 53.⁽¹⁾ Since the entire

(1) Ref. # 86

thermoelectric phenomena is reversible, the net change in entropy of the system must equal zero by the second law of thermodynamics.

It remains to find π and $\sigma_A - \sigma_B$ or $\Delta\sigma$ in terms of the temperature and E. Equation (5) gives one relationship between π and σ . A simpler relation is obtained by differentiating (5) as follows:

$$\frac{dE}{dT} = \frac{d\pi}{dT} + \Delta\sigma \quad (6)$$

where $\Delta\sigma = \sigma_A - \sigma_B$; T_2 is constant, and T_1 is considered variable.

To find π and $\Delta\sigma$ separately, another independent equation besides (6) is necessary. This other equation can be obtained from relations involving the second law of thermodynamics, as follows: From elementary thermodynamics,

$$Q = \Delta U + W \quad (7)$$

where Q = heat, U = internal energy, and W = work.

Equation (7) may be rewritten as

$$\Delta Q = \Delta U + \Delta W \quad (8)$$

It is also known that the difference in entropy S is represented by

$$S_2 - S_1 = \int \frac{\Delta Q}{T}$$

$$\text{or} \quad dS = \frac{dQ}{T} \quad (9)$$

Substituting (8) into (9) gives

$$dS = \frac{dU + \Delta W}{T} \quad (10)$$

which may be rewritten as

$$dU = T dS - \Delta W \quad (11)$$

Now, applying the Legendre transformation to eliminate $T dS$ gives

$$\begin{aligned} dU - d(TS) &= T dS - \Delta W - d(TS) \\ d(U - TS) &= T dS - \Delta W - T dS - S dT \\ \Delta(U - TS) &= -\Delta W - S dT \\ \text{or } \Delta(\Psi) &= -\Delta W - S dT \\ \text{where } \Psi &= U - TS \quad (1) \end{aligned} \quad (12)$$

A chart of the various symbols used by various authors in thermodynamics is given for clarity.

	Technical Thermodynamics Epstein	Clausius Kelvin Planck	GIBBS	Lewis & Randall & Others	Kieffer & Stuart & Others	Wenner
Internal Energy	U	U	E	E	U	E
Enthalpy	X	X	X	H	H	H
Entropy	S	S	η	S	S	S
Work Function, Free Energy, U-TS	Ψ	F	Ψ	A	Ψ	$\Delta F = \Delta H - T\Delta S$
Thermodynamic Potential Free Energy U-TS+PV	ϕ	$-T\phi$	$\mathcal{F}$	F		

Fig. 6

The thermodynamic energy function (12) may be applied to find an independent relation between π and $\Delta\sigma$. Ψ

in (12) is the "work function", sometimes called the "free energy", or the "thermal potential". In connection with the thermoelectric effect, ψ may be used to represent the heat liberated at a junction due to the passing of current.

$$\text{Thus } \psi = \pi \quad (13)$$

The internal energy U represents the difference in the electron specific heats of the two metals, times the absolute temperature T .

$$U = \Delta\sigma T \quad (14)$$

This may be seen more clearly from the following diagram. Consider an electron passing from conduc-

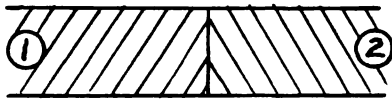


Fig. 7

tor 1 to 2, with a random velocity v . Then the internal energy of 1 due to the electron is $U_1 = v_1 T_1 \sigma_1$

The internal energy of 2 due to the electron is

$U_2 = v_2 T_2 \sigma_2$. Therefore,

$$U_1 - U_2 = v_1 T_1 (\sigma_1 - \sigma_2) = U \quad (15)$$

$U_1 - U_2$ represents the net internal energy. The random velocity will average out to be unity, hence

$$U = \Delta\sigma T \quad (16)$$

$$\text{From (12) } d\psi = -dW = S dT \quad (17)$$

If the work is zero, $W = 0$, and

$$d\psi = -SdT, \text{ or} \quad (18)$$

$$\frac{d\psi}{dT} = -S \quad (1) \quad (19)$$

Substituting (19) into (12) gives

$$\psi = U + T \frac{d\psi}{dT} \quad (2)$$

which is called the Gibbs-Helmholtz equation.

Now the equation $\psi = U - TS$ may be rewritten, upon substituting equations (13), (16), and (19), as

$$\begin{aligned} \pi &= \Delta\sigma T - T \left(- \frac{d\psi}{dT} \right) \\ \pi &= \Delta\sigma T + T \frac{d\pi}{dT} \end{aligned} \quad (20)$$

$$\text{or,} \quad \Delta\sigma T = \pi - T \frac{d\pi}{dT} \quad (21)$$

$$\text{Also,} \quad \frac{dE}{dT} = \frac{d\pi}{dT} + \Delta\sigma \quad (6)$$

From equations (6) and (21) the values of π and $\Delta\sigma$ can be found. From (6),

$$\Delta\sigma = \frac{dE}{dT} - \frac{d\pi}{dT} \quad (22)$$

Substituting (22) into (21) gives

$$T \frac{dE}{dT} - T \frac{d\pi}{dT} = \pi - T \frac{d\pi}{dT}$$

from which

$$\pi = T \frac{dE}{dT} \quad (23)$$

This gives the expression for the Peltier coefficient π . Experimental values substituted in for

(1) Ref. # 75 eqn. 5.26

(2) Ref. # 75 eqn. 5.58

$\frac{dE}{dT}$ and T give results proving this equation within

the accuracy limits of the experiment. The value of π can be determined directly by experiment, but precautions must be taken to neutralize the Thompson emf.

From (23)

$$\frac{dE}{dT} = \frac{\pi}{T} \quad (24)$$

Substitute (24) into (6). Then

$$\frac{\pi}{T} = \frac{d\pi}{dT} + \Delta\sigma$$

or

$$\frac{d\pi}{dT} = \frac{\pi}{T} - \Delta\sigma \quad (25)$$

From (23)

$$\frac{d\pi}{dT} = T \frac{d^2E}{dT^2} + \frac{dE}{dT} \quad (26)$$

Substituting (25) into (26) gives

$$T \frac{d^2E}{dT^2} + \frac{dE}{dT} = \frac{\pi}{T} - \Delta\sigma \quad (27)$$

Since

$$\frac{\pi}{T} = \frac{dE}{dT} \quad (24)$$

Equation (27) becomes

$$T \frac{d^2E}{dT^2} = -\Delta\sigma$$

or

$$\Delta\sigma = -T \frac{d^2E}{dT^2} \quad (28)$$

This is the final expression for $\Delta\sigma$. The two

coefficients π and $\Delta\sigma$ are usually obtained by thermal measurements but may be found from the curve of E vs T by equations (23) and (28).

Usually the voltage E can be expressed as a quadratic function of the temperature, or

$$E = \alpha (T_1 - T_2) + \frac{1}{2}\beta (T_1 - T_2)^2 \quad (29)$$

This may be carried further, and is sometimes given as

$$E = \alpha (T_1 - T_2) + \frac{1}{2}\beta (T_1 - T_2)^2 + \frac{1}{6}\gamma (T_1 - T_2)^3$$

The constants α , β , and γ can be found from the experimental data once three values of E and the corresponding values of temperature are known. A simultaneous solution will then give α and β or α , β , and γ . Assuming α and β to be known, to find π or $\Delta\sigma$ it is necessary to find the first and second derivatives of voltage with respect to the temperature. π and $\Delta\sigma$ are usually evaluated at a fixed temperature such as 0°C . In such a case $T_1 - T_2 = 0$, and $\frac{dE}{dT} = \alpha$ and

$$\frac{d^2E}{dT^2} = \beta \text{ from which } \pi = T\alpha \text{ and } \Delta\sigma = -T\beta.$$

The numerical values of π and $\Delta\sigma$ are usually given in microvolts per degree centigrade. The difference in the values of π for two different temperatures is approximately equal, if $\Delta\sigma$ is small, to the value of E. For example, the emf of a Zn - Pb couple at 0°C

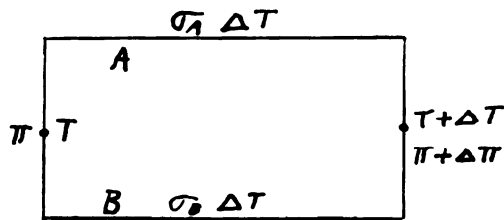
and 100°C as found from $E = a t + \frac{1}{2} b t^2 \times 10^{-2}$
 ($a = 3.18$, $b = -.113$) is 312.5 microvolts. The value
 of π for Zn, with Pb as a reference metal, at 0°C ,
 as found from a and b , is $\pi_1 = 273 \times 3.068 = 837$.
 At 100°C , $\pi_2 = 373 \times 3.068 = 1142$. The difference
 between π_1 and π_2 is 305 microvolts, which is only
 about 2% different from the value found by formula.

The Peltier heat coefficient, or π , gives an
 indication of the emf generated at a junction for
 a given temperature of the junction. If the Thomp-
 son effect were zero, the curve of E vs T would be a
 straight line, and the value of $\pi_2 - \pi_1$ would
 equal E . π , whether found from heat measurements
 or by calculation, gives a fair approximation to the
 attainable emf of a thermocouple, for most metals.
 Where the Thompson coefficient is large, the curve
 of E vs T will be curved and $\pi_1 - \pi_2$ will not equal
 E . In the above example, $\sigma_1 = T_1 b = 273(-.113) = -30.8$
 and $\sigma_2 = T_2 b = 373(-.113) = -42.1$,
 or $\Delta\sigma = 11.3$. Now $\pi + \Delta\sigma$ gives $305 + 11.3 = 316.3$,
 which is closer to the value of E (312) as found by
 the quadratic formula. The quadratic equation express-
 es the true emf versus T . The values of π and $\Delta\sigma$ are
 a first and second approximation to this E .

Another derivation for π and $\Delta\sigma$ starts with a

closed circuit of two dissimilar metals with no emf. (1)

There is a temperature difference, however.



$$E = \pi_2 - \pi_1 = \Delta\pi \quad (29)$$

$$\frac{\pi_2}{T_2} = \frac{\pi_1}{T_1} \quad (30)$$

$$\frac{\pi_2 - \pi_1}{\pi_1} = \frac{T_2 - T_1}{T_1} \quad (31)$$

Fig. 8

Substituting (29) into (31),

$$E = \pi_1 \frac{T_2 - T_1}{T_1} \quad (32)$$

Adding the emf's around the circuit,

$$\Delta E = \pi + \Delta\pi - \pi + \Delta\sigma \Delta T - \sigma_B \Delta T \quad (33)$$

$$= \Delta\sigma + (\sigma_A - \sigma_B) \Delta T \quad (34)$$

$$\frac{dE}{dT} = \frac{d\pi}{dT} (\sigma_A - \sigma_B) \quad (35)$$

From the second law of thermodynamics,

$$\sum \frac{Q}{T} = 0$$

$$\frac{q(\pi + \Delta\pi)}{T + \Delta T} - \frac{q\pi}{T} - \frac{q\sigma_A \Delta T}{T + \frac{\Delta T}{2}} - \frac{q\sigma_B \Delta T}{T + \frac{\Delta T}{2}} = 0 \quad (36)$$

where q = unit charge

$$4 \left(\frac{\pi}{T} \right) \frac{(\sigma_A - \sigma_B) \Delta T}{T + \frac{\Delta T}{2}} = 0 \quad (37)$$

$$\frac{d}{dT} \left(\frac{\pi}{T} \right) - \frac{1}{T} (\sigma_A - \sigma_B) = 0 \quad (38)$$

(1) Ref. #47 p. 80

$$\sigma_A - \sigma_B = \frac{\pi}{T} - \frac{1}{T} \frac{d\pi}{dT} \quad (39)$$

Eliminating $\sigma_A - \sigma_B$ in (35) and (39) gives

$$\pi = T \frac{dE}{dT} \quad (40)$$

and

$$\sigma_A - \sigma_B = \Delta\sigma = - T \frac{d^2 E}{dT^2} \quad (41)$$

There are the final values of π and $\Delta\sigma$, and are the same as found by the previous analysis.

EFFICIENCY ANALYSIS

This analysis assumes the generator to be composed of only one couple, but the analysis is the same regardless of the number. Considerable credit for this analysis must go to M. Telkes (Ref. 93); and to R. Papet (Ref. 11), who pointed out a lack of generality in Telkes' paper. Telkes assumed the internal resistance to be equal to the external resistance; the condition for maximum power. Graphs 1 and 10 show the efficiency for this condition. Papet pointed out this was not the condition for maximum efficiency, however, since the maximum efficiency occurs when the external resistance is much larger than the internal. The present analysis gives the values of the ratio of external to internal resistance for maximum efficiency; for various temperature differences, for various thermoelectric powers, and for various deviations from the Wiedemann-Franz Law.

The following symbols will be used:

W_e = Total heat input to couple

P_{out} = Output or load power

P_{int} = Internal or lost power

Q_c = heat lost by conduction

R_i = internal resistance

R_2 = external resistance

E = total output emf

T_2 = hot junction temp.

T_1 = cold junction temp.

$$\Delta T = T_2 - T_1$$

η = overall efficiency

η_r = thermal efficiency

ρ', ρ'' = average specific resistance of couples

K', K'' = average specific heat conduction of couples

S', S'' = cross sectional area of couples

L = length of both couples

The first step is to find a simple relation for the efficiency.

$$P_{out} = I^2 R_2 \quad (1)$$

$$P_{int} = I^2 R_1 = \frac{E^2 R_1}{(R_1 + R_2)^2} \quad (2)$$

$$W_e = (P_{out} + P_{int}) \frac{T_2}{\Delta T} + Q_c \quad (3)$$

From (1) and (2)

$$P_{out} + P_{int} \frac{R_2}{R_1} P_{int} + P_{int} = P_{int} \frac{R_1 + R_2}{R_1} \quad (4)$$

Substitute (4) into (3)

$$W_e = \frac{R_1 + R_2}{R_1} P_{int} \frac{T_2}{\Delta T} + Q_c \quad (5)$$

Now,

$$\eta = \frac{P_{out}}{W_e} = \frac{\frac{R_2}{R_1} P_{int}}{\frac{R_1 + R_2}{R_1} P_{int} \frac{T_2}{\Delta T} + Q_c} = \frac{1}{\frac{R_1 + R_2}{R_2} \frac{T_2}{\Delta T} + \frac{R_1 Q_c}{R_2 P_{int}}}$$

$$\text{or, } \eta = \frac{1}{\frac{R_1 + R_2}{R_2} \frac{T_2}{\Delta T} - \frac{(R_1 + R_2)^2}{R_2} \frac{Q_c}{E^2}} \quad (6)$$

From (6), if $Q_c = 0$,

$$\eta = \frac{R_2 \Delta T}{(R_1 + R_2) T_2}$$

which is the usual efficiency relationship. Since Q_c cannot even be approximated to zero, however, it cannot be said at once that the larger $\frac{R_2}{R_1}$ the greater the efficiency. The best value of $\frac{R_2}{R_1}$ will be considered later.

From (6), if $R_1 \ll R_2$ or $R_1 \approx 0$, then

$$\eta = \frac{1}{\frac{T_2}{\Delta T} + \frac{R_2 Q_c}{E^2}}$$

The significance of this is that the efficiency is inversely proportional to R_2 , not directly proportional as might be assumed.

$$\text{Let } R_2 = K_2 R_1 \quad \text{or} \quad K_2 = \frac{R_2}{R_1} \quad (7)$$

Then (6) becomes

$$\eta = \frac{1}{\frac{1 + K_2}{K_2} \frac{T_2}{\Delta T} - \frac{(1 + K_2)^2}{K_2} \frac{R_1 Q_c}{E^2}} \quad (8)$$

A new expression for $\frac{R_1 Q_c}{E^2}$ will now be found and substituted into (8)

$$\text{Let } d' = \frac{S'}{L} \quad \text{and} \quad d'' = \frac{S''}{L} \quad d' \text{ and } d'' \text{ are form}$$

factors.

$$\text{Since } Q_c = \Delta T (K' d' + K'' d'') \quad (9)$$

$$\text{and } R_1 = \frac{\rho'}{d'} + \frac{\rho''}{d''} \quad (10)$$

and since the best form factors result when

$$K' d' = K'' d'' \text{ and } \frac{\rho'}{d'} = \frac{\rho''}{d''}, \text{ the following}$$

$$\text{relations hold: } \frac{d''}{d'} = \frac{K'}{K''} \quad (11)$$

$$\frac{d''}{d'} = \frac{\rho''}{\rho'} \quad (12)$$

Also, from (11) and (12),

$$\frac{d''}{d'} = \left(\frac{K' \rho''}{K'' \rho'} \right)^{1/2} \quad (13)$$

From (9) and (10)

$$\frac{R_1 Q_c}{E^2} = \frac{\Delta T (K' d' + K'' d'')}{e^2 (\Delta T)^2} \left(\frac{\rho'}{d'} + \frac{\rho''}{d''} \right) \quad (14)$$

Since $E = e \Delta T$ by definition.

Equation (14) may be rewritten as,

$$\frac{R_1 Q_c}{E^2} = \frac{K' \rho' + K'' \rho'' + \frac{K' \rho'' d'}{d''} + \frac{\rho' K'' d''}{d'}}{e^2 \Delta T} \quad (15)$$

Substitute (13) into (15)

$$\frac{R_1 Q_c}{E^2} = \frac{K' \rho' + K'' \rho'' + 2 \sqrt{K' K'' \rho' \rho''}}{e^2 \Delta T} = \frac{[(K'' \rho'')^{1/2} + (K' \rho')^{1/2}]^2}{e^2 \Delta T} \quad (16)$$

Substitute (16) into (8)

$$\eta = \frac{1}{\frac{1+K_2}{K_2} \frac{T_2}{\Delta T} + \frac{(1+K_2)^2}{K_2} \frac{[(K'' \rho'')^{1/2} + (K' \rho')^{1/2}]^2}{e^2 \Delta T}} \quad (17)$$

From the Wiedemann-Franz-Lorenz law, taking the average temperature,

$$K'' \rho'' = K' \rho' = 2.45 \times 10^{-8} \frac{1}{(T_2 + T_1)} \quad (18)$$

Placing the numerical value of (13) into (17) gives

$$\eta = \frac{K_2 \Delta T}{[1 + K_2] \left[T_2 + \frac{1 + K_2}{e^2} (4.9 \times 10^{-8})(T_2 + T_1) \right]} \quad (19)$$

This is the final equation for efficiency, involving only the temperatures, the thermoelectric power e , and K_2 . The value of K_2 will be discussed shortly. A plot of η versus ΔT for various values of e is given on graph 1. Graph 1 is plotted from equation (19) and the curves agree with a similar plot made by Telkes. (Ref. 23) K_2 is assumed to be unity, which is the maximum power condition.

To find the relation between R_1 and R_2 to give maximum efficiency, take $\frac{d\eta}{dK_2}$ and let it equal zero.

$$K_2 = R_2/R_1$$

First, simplify (19) slightly.

$$\text{Let } K_3 = \frac{4.9 \times 10^{-8}(T_2 + T_1)}{e^2}$$

Then

$$\begin{aligned} \eta &= \frac{K_2 \Delta T}{(1 + K_2)(T_2 + K_3 + K_2 K_3)} \\ &= \frac{K_2 \Delta T}{T_2 + K_3 + K_2(2K_3 + T_2) + K_2^2 K_3} = \frac{K_2 \Delta T}{D_1} \\ \frac{d\eta}{dK_2} &= \frac{D_1 \Delta T - K_2 \Delta T(2K_3 + T_2 + 2K_2 K_3)}{D_1^2} \end{aligned}$$

$$\text{Let } \frac{d\eta}{dK_2} = 0$$

$$D_1 - K_2(2K_3 + T_2 + 2K_2 K_3) = 0$$

$$T_2 + K_3 - K_2^2 K_3 = 0$$

$K_2 = \sqrt{\frac{T_2 + K_3}{K_3}}$ Replacing K_3 by its value gives

$$K_2^2 = \frac{e^2 T_2}{4.9 \times 10^{-8} (T_1 + T_2)} \quad (20)$$

This is the value of K_2 which will give, for known values of T_1 , T_2 , and e , the maximum efficiency when substituted in equation (19). A plot of K_2 versus ΔT for various values of e is given on graph 3. For small values of e , K_2 is nearly equal to one. A plot of the efficiency versus temperature difference for various values of e , with K_2 equal to the value specified by formula (20), is given on graph 2. The values of η are slightly greater than on graph 1. The effect of changes in the ratio of R_2 to R_1 on the efficiency indicate that previously published calculated values of efficiency have been slightly too low. The efficiency is usually calculated for $R_1 = R_2$; but, as shown above, the maximum efficiency will always be slightly greater than this. Since K_2 turns out to be nearly equal to one, which is also the maximum power condition, the fortunate situation is present where the maximum efficiency and maximum power points nearly coincide.

The higher values of efficiency calculated by equation (19) are not attained in practice due to the joule heating of the cold junction, heat losses by

radiation and convection, or a deviation from the Wiedemann-Franz-Lorenz law from which the constant 4.9×10^{-8} comes. Equation (18) introduced this law, which states:

$K\rho = 2.45 \times 10^{-8}T$. This law holds for most metals. Some metals show a higher value than 2.45×10^{-8} but none show a lower value. Since low values of K and ρ are to be preferred, the larger the value or the larger the deviation (D) from the normal value, the less advantageous the metal for a couple. The deviation D can be represented by $D = \frac{\rho K}{2.45 \times 10^{-8}T}$. The

smaller D the better a particular metal or semi-conductor will be in a thermocouple. Graphs 1, 2 and 3 were plotted assuming the W-F law to hold. The effects of deviations from this law are shown on graphs 10 and 11. Equation (21) shows equation (19) rewritten to include D .

$$\eta = \frac{K_2 \Delta T}{(1+K_2) \left[T_2 + \frac{1+K_2}{e^2} (D \times 4.9 \times 10^{-8})(T_1 + T_2) \right]} \quad (21)$$

$$\text{where } K_2 = \frac{e^2 T_2 + 2D(2.45 \times 10^{-8})(T_1 + T_2)}{2D(2.45 \times 10^{-8})(T_1 + T_2)} = \sqrt{\frac{e^2 T_2 + 4K\rho}{4K\rho}},$$

$$(K\rho)_{\min} = 2.45 \times 10^{-8} \frac{(T_2 + T_1)}{2} \quad \text{and} \quad D = \frac{K\rho}{K'\rho'}$$

Plots of K_2 versus T are given on graphs 3,4,5,6,7,8,9 for various values of D and e . From these graphs, for a given value of D , e , and T ; K_2 can be found. This value of K_2 is then used in equation 21, and the effi-

iciency calculated from this equation. The efficiency calculated in this way is shown in graph 11. Graph 10 is for the case when $K_2=1$, which is the maximum power condition.

From the graph, an efficiency of 6% would result when $e=1200$ and $D=45$. With $D=45$ and assuming $K=.01$ which is a fairly low value, the value of ρ would be about .001. Thus any material with $D=45$, $K=.01$, and ρ greater than .001 could not have an efficiency greater than 6% unless e were greater than 1200×10^{-6} , or the temperature difference were greater than 400°C . The larger the value of e , the greater deviation possible from the Wiedemann-Franz-Lorenz law before the efficiency drops to low values.

With D between 1 and 2, as for most metals, the efficiency is given on graph 1 or 2 fairly accurately. From these graphs it is seen that in order to obtain an efficiency of at least 5%, e must equal at least $150 \mu\text{v}/^\circ\text{C}$. One of the best metal thermocouples, Chromel P versus constantan, has a value of e or Q of 76. Thus it appears that due to the low e of most metals the efficiency is limited to low values.

With a semiconductor, however, which has a value of $e=800$ or more, and with $T=400^\circ\text{C}$, the efficiency would be 10% even if the deviation were as large as 10. It is readily seen, therefore, that semiconductors,

because of their higher value of α , are more promising as regards efficient power generation by means of the thermoelectric effect.

The ideal couple would have a thermoelectric power of $800\mu\text{v}/^\circ\text{C}$, operate at at least 400°C , and have a deviation no greater than 3 from the Wiedemann-Franz law. The electrical resistance should be at least as low as that of iron or constantan. The cost of the couple should not be great and this eliminates many possible substances. Such a couple would have an overall efficiency of about 20%; would be compact, inexpensive, and reliable.

TABLES AND GRAPHS

A list of the values of a , b , c , and d for several elements and alloys is given in the next table. From this table, E , Q , and Q_0 can be found from the following formulas:

$$E = aT + \frac{1}{2} bT^2 \times 10^{-6} + cT^3 \times 10^{-9} + d$$

E is in microvolts. T represents $T - T_0$ or T .

$$Q = \frac{dE}{dT} = \text{thermoelectric "power"}$$

$$= a + bT \times 10^{-6} + 3cT^2 \times 10^{-9}$$

Q is in microvolts per degree C.

$$= TQ = T \frac{dE}{dT}$$

$$= T \frac{dQ}{dT} = - T \frac{d^2 E}{dT^2}$$

For a more complete listing of a , b , c , and d , see Vol. VI of the International Critical Tables.

Thermoelectric Constants

Metal Pair	a	b	c	d	Applicable Temp. Range
Ag-Pb	3.34	.85	-	-	0-200
Ag-Pt	3.04	.01	-	-	0-900
Al-Pb	-.495	.173	-	-	0-200
Al-Pt	-.798	.91	-.67	-	0-800
Au-Pb	2.9	.93	-	-	0-200
Bi-Pb	-43.7	-46.5	-33.7	-	0-100
Bi-Pt	15.	-	-	-17900.	300-800
Bi-Cu	60.	2 to 10 (varies with crystal)			0-100
C-Pb	11.06	3.58	5.38	-	0-100
C-Pt	-6.	16.9	-.23	-	0-550
Cd-Pb	2.85	3.89	-	-	0-100
Cd-Pt	1.5	-	-	-164.	320-700
Co-Pt	-10.7	-5.7	7.5	-	0-1200
Cu-Pb	2.76	1.22	-	-	0-100
Cu-Pt	3.13	2.46	-	-	0-900
Fe-Pb	16.65	-2.96	-26.75	-	-230 to 100
Fe-Pt	Q 19.5 at 0°C, 10.8 at 600°C, 19 at 900°C				
Fe-Cu	13.7	-7.8	6.6	-	0-700
Ge-Pt	302.	72.5	-	-	-200 to 125
Ge-Pt	-219.	776.	-2391.	26716.	135 to 275
Ge-Pt	1422.	-702.	762.	-87460.	275 to 500
Ge-Pt	-362.	31.2	-	204.9	500 to 700
Hg-Pb	-3.81	-3.33	-	-	0-200
Li-Pt	14.4	8.76	-	-	-200 to 50
Li-Pt	16.7	4.08	-	-	50 to 168
Li-Pt	20.57	5.39	-	-	183 to 300
Mg-Pb	-.2	.26	-1.67	-	0-100
Mg-Pt	5.	1.44	-	-	0-700
Mo-W	4.61	.872	-	-	0-1060
Mo-W	24.5	-133.6	-	-12400.	950 to 2250
Mo-Pb	5.9	4.3	-7.5	-	0-100
Mo-Pt	13.	2.96	-	-	0-1200
Ag-Pb	-.2	.26	-	-	-200 to 100
Na-Pb	-4.16	-1.44	-	-	-133 to 0
Ni-Pb	19.	-3.	-	-	0-200
Ni-Pt	-17.12	2.46	-2.19	-	0-1200
Pt-Pb	-3.04	-3.24	8.41	-	-200 to 300
Sb-Pt	46.2	6.36	-14.3	-	0-630
Sb-Pt	-	Q 2100	-	-	650-711
Sb-Pb	35.6	14.5	-	-	0-100
Se-Pb	b 99000 to 114,000 for Q only				10-100
Si-Pb	-403.	-47.	351.	-	0-350
Sn-Pb	-.168	.187	-	-	0-200
Sn-Pt	13.	-	-	-2200.	415-600
W-Pb	1.6	3.41	-	-	0-100
W-Cu	-1.12	1.695	-	-	0-630

Thermoelectric Constants

Metal Pair	a	b	c	d	Applicable Temp. Range
W-Pt	9.4	3.7	-	-	0-1200
Zn-Pb	3.096	3.2	11.	-	-260 to 0
Zn-Cu	.232	.97	-	-	20-100
Zn-Pb	3.151	-.113	-	-	0-250
Zn-Pt	5.74	3.3	-	-	0-450
Zn-Pt	-17.	-	-	1820.	450-700

Alloys

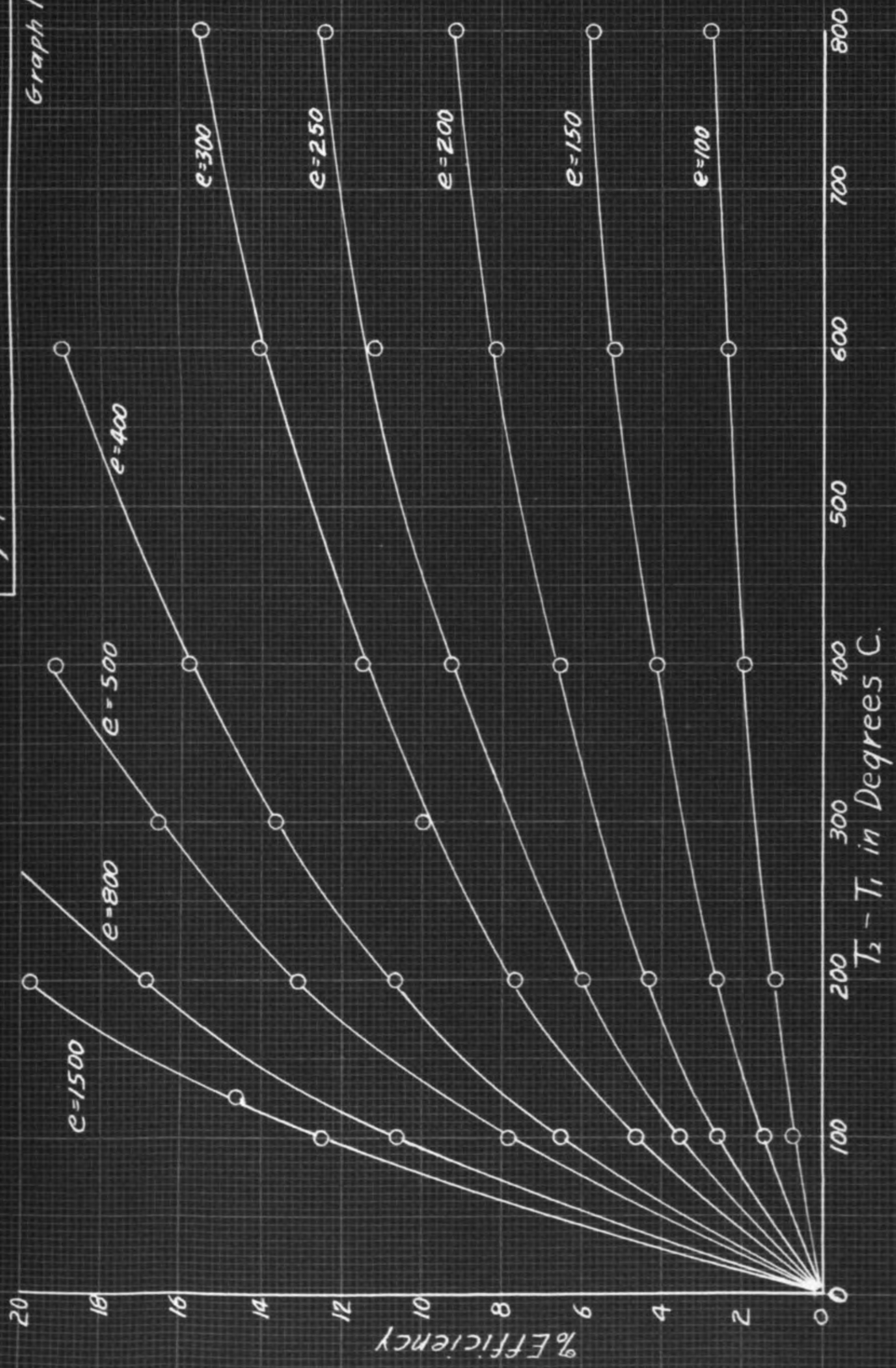
Reference Metal	Alloy	a	b	c	d	Applicable Temp. Range
Pb	Ag-Al	4.03	1.54	-	-	
Pb	Ag ₃ Al ₂ -AlCu ₃	a 9.56,	b 2.47	-	-	
Cu	Ag-Au	-2.7	-.4	-	-	
Cu	Ag-Cd	-1.42	-.38	-	-	
Pt	Ag-Pd	-26.8	-6.7	3.7	-	
Pt	Ag-Pt	-3.375	-.94	-	-	
Cu	Ag-Sb	Q 32 max	-	-	-	
Pb	Al-Cu	11.8	2.65	-	-	
Cu	Constantan	-38.1	-8.88	8.57	-	0-400
Pb	Constantan	Q max	38.8	-	-	
Pb	Al-Mn	10.4	-.24	-	-	
Cu	Fe-Mn	Q 29	451M	-	-	0-48
Hg	Hg-Pb	E	746.7 max at 180°C	-	-	
Hg	Tl	E	1001.1 max at 180°C	-	-	
Cu	Se-Te	Q 630	-	-	-	18°C

Oxides

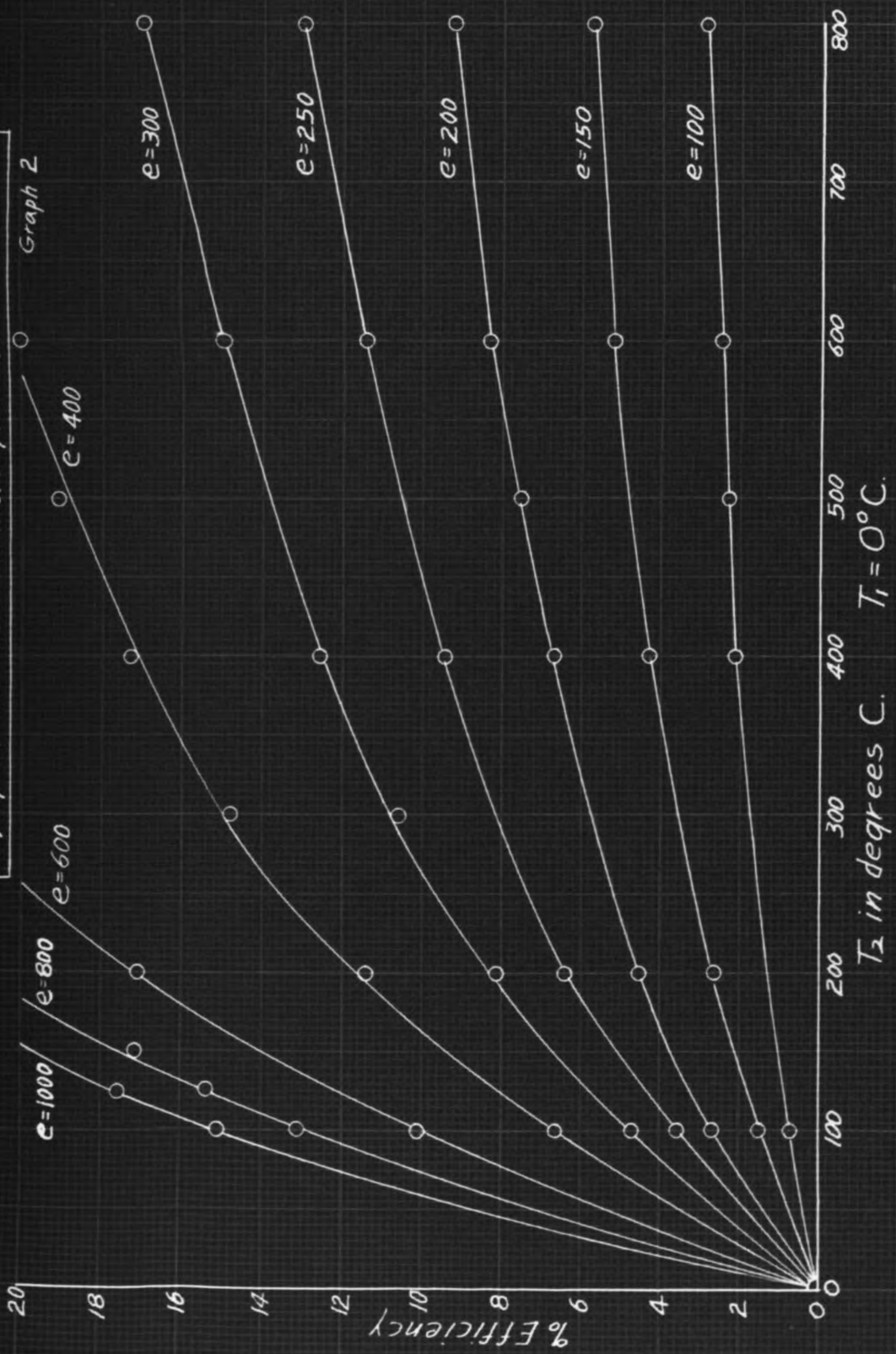
Pb	Bi ₂ O ₃	1946	-1.86	-	-	500-800
Pb	CuO	-1029	1.7	-	-	70-350
Pb	PbO	-48300.	117.	-	-	250-390
Pb	PbO	-6000.	9.22	-	-	390-550
Pb	PbO	3914	5.	-	-	550-850

Efficiency VS ΔT . $e = \text{thermo. e.l. Power}$
in $\mu\text{W}/^\circ\text{C}$. $K_2 = 1$. $D = 1$.

Graph 1

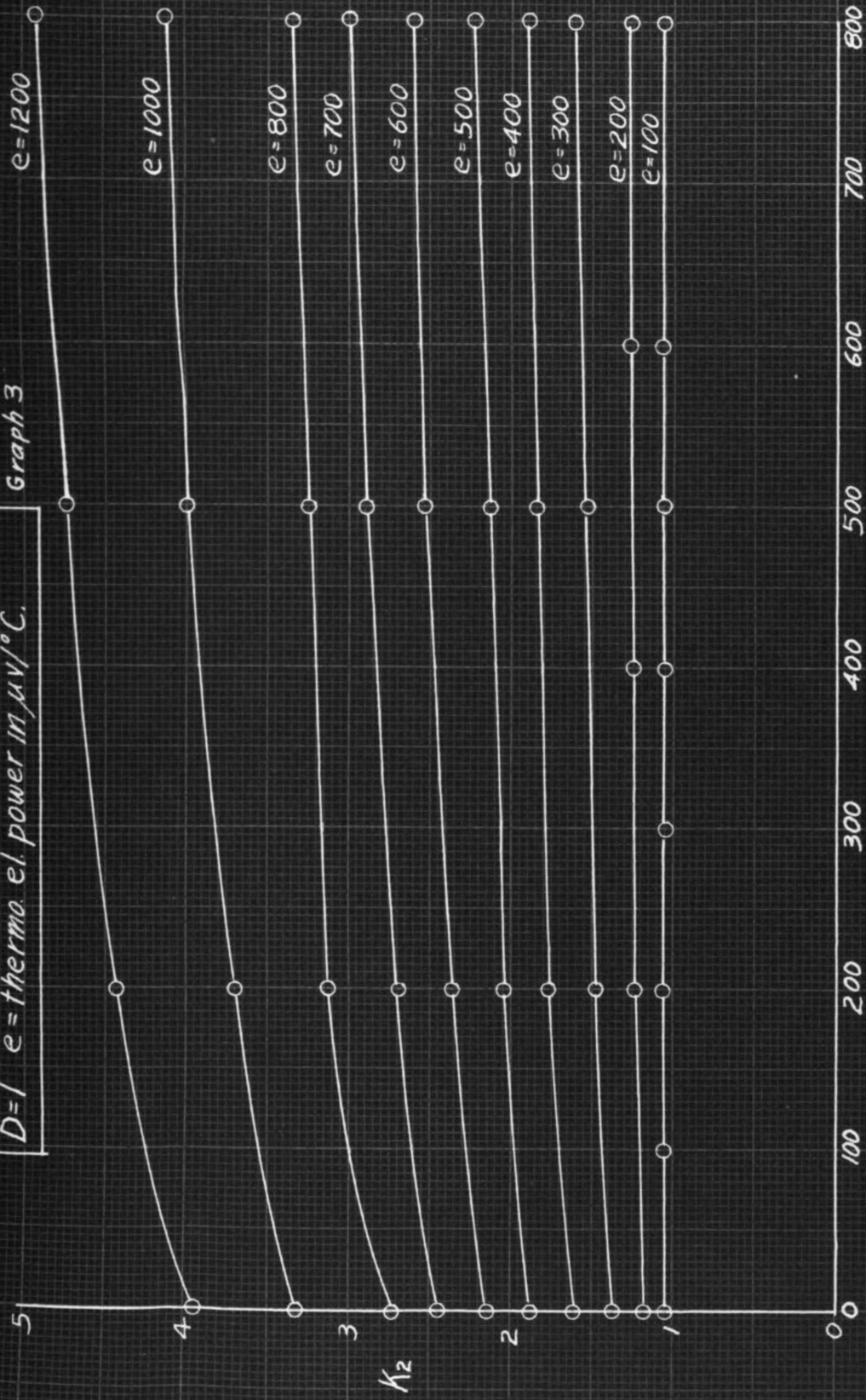


Original Curve of Effy. VS T_2 . $e = \text{thermo. el. power in } \mu\text{V}/^\circ\text{C}$. $K_2 = \text{value for max. } \eta$. $D = 1$

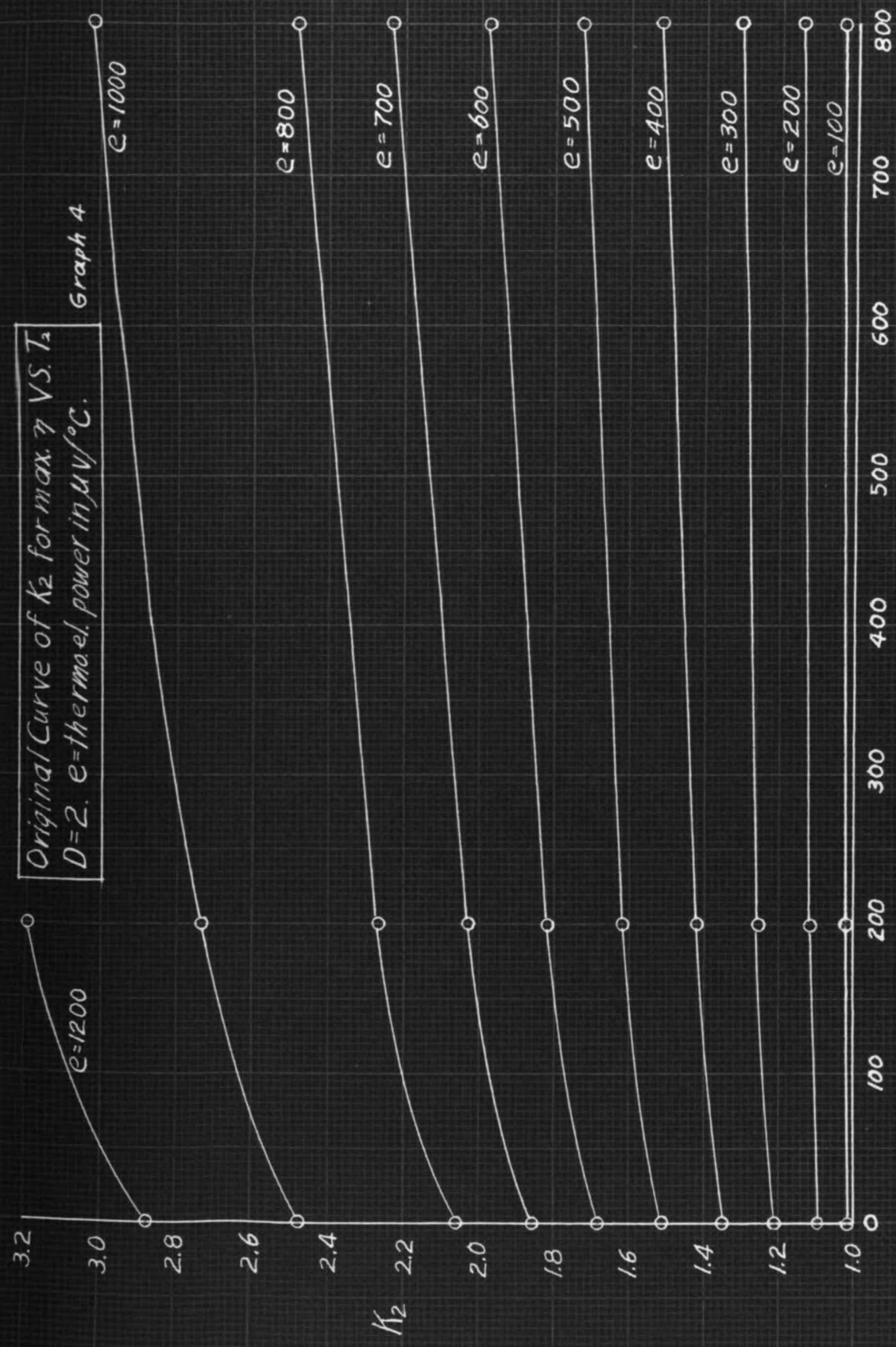


Original Curves of k_2 for max. η , VS T_2 .
 $D=1$ e = thermo el. power in $\mu V/^{\circ}C$.

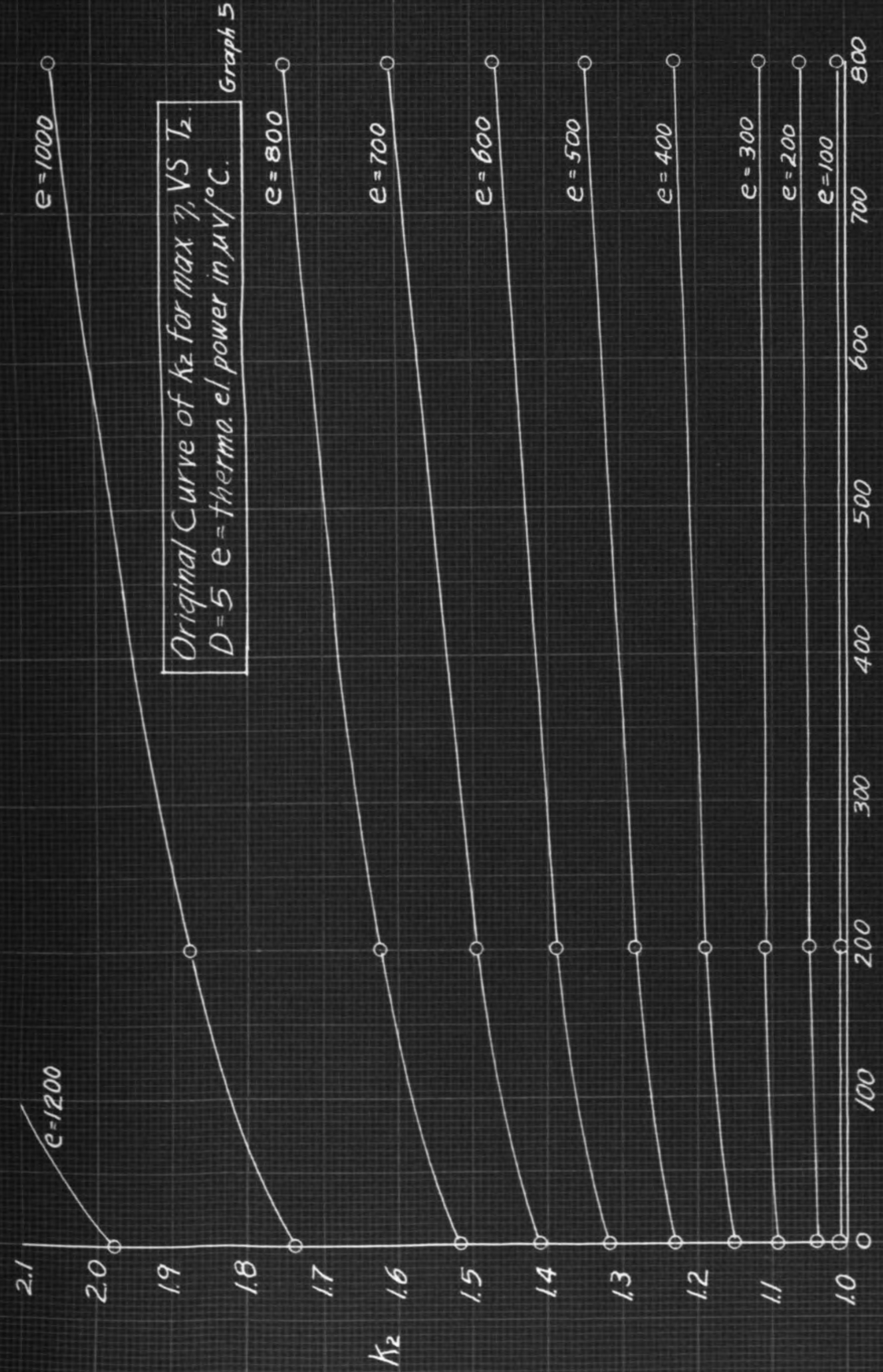
Graph 3



T_2 in degrees C. $T_1 = 0^{\circ}C$.



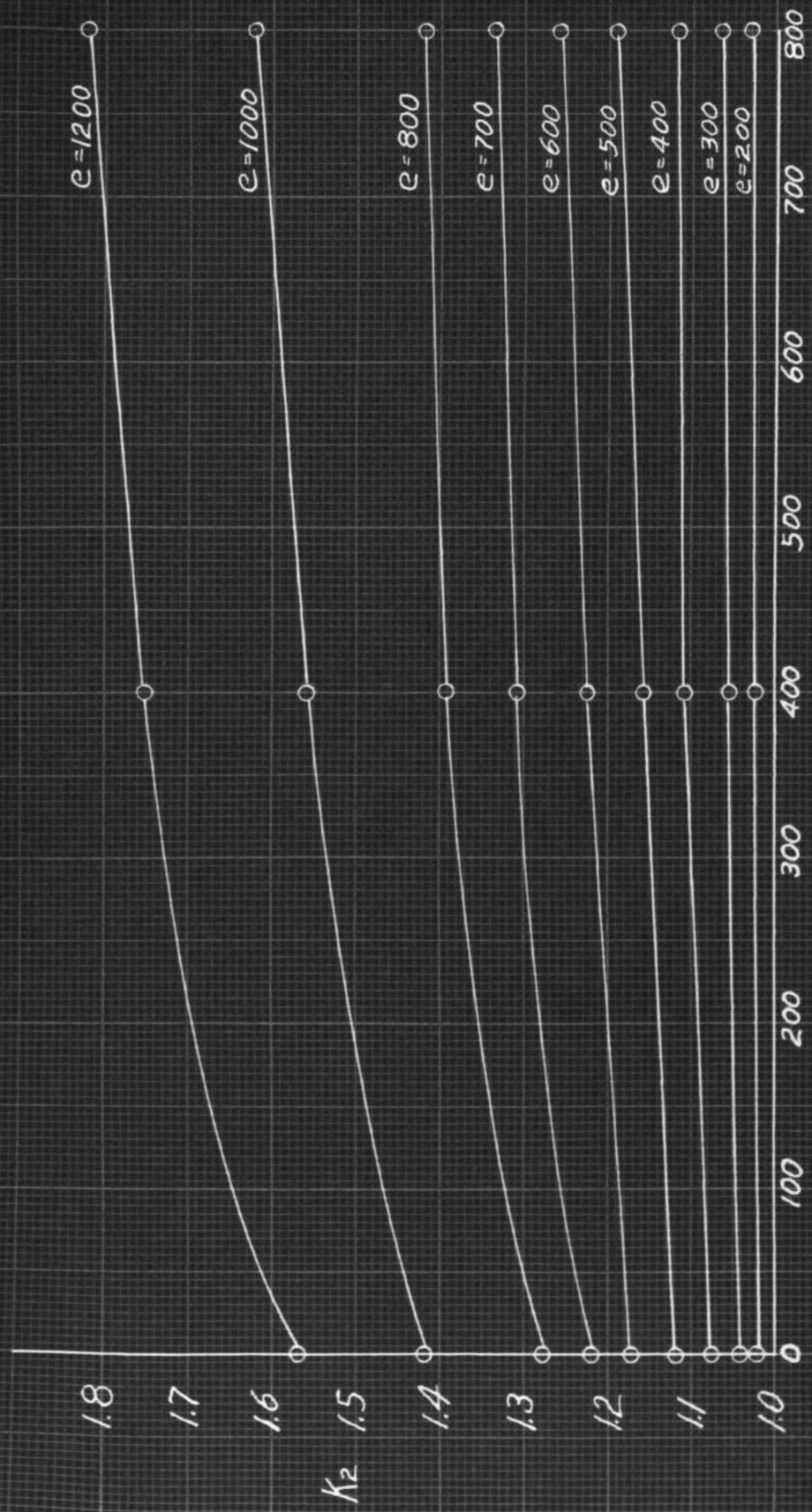
T_2 in degrees C. $T_1 = 0^\circ C$.



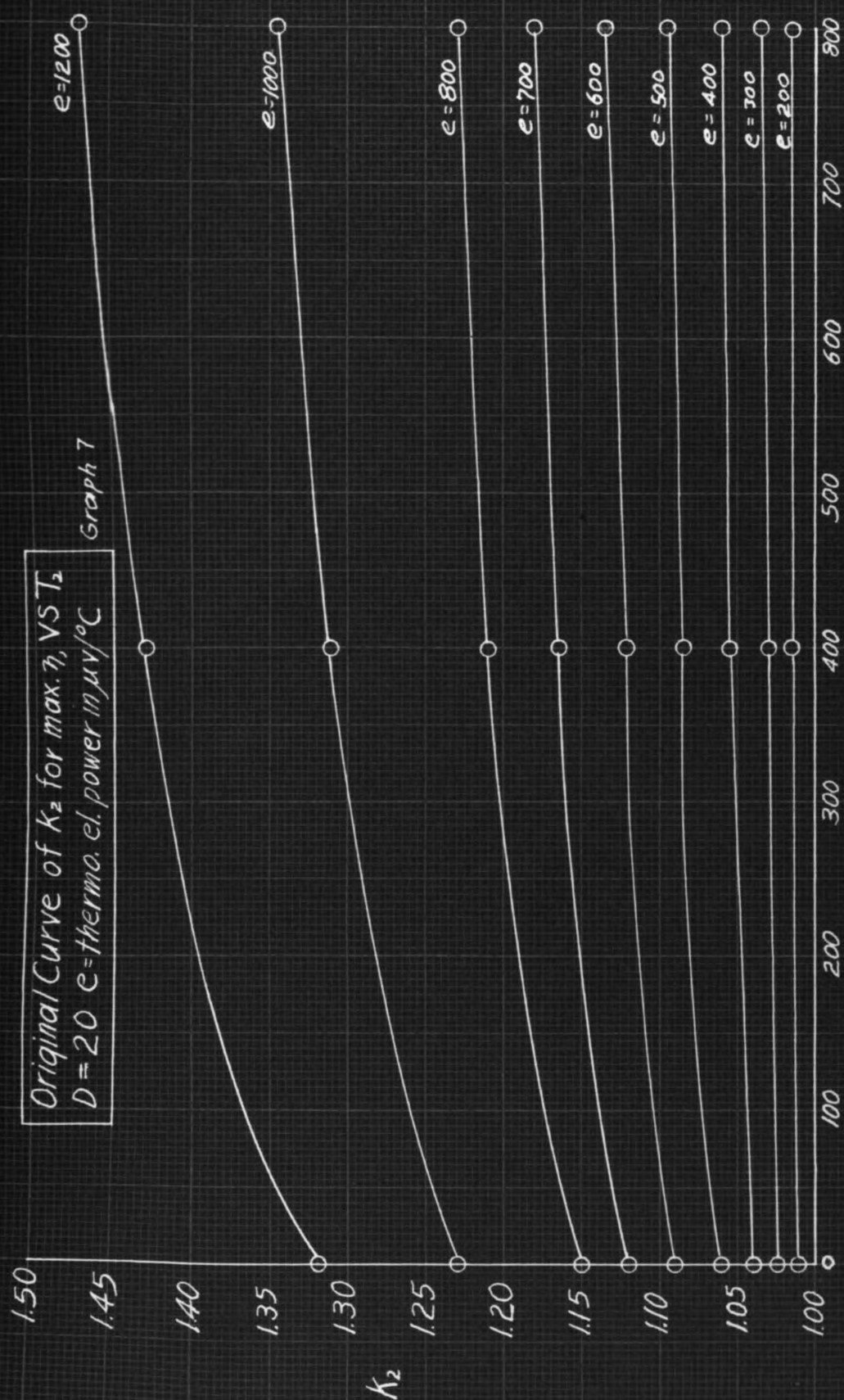


Original Curve of k_2 for max. η VS T
 $D=10$ e = thermo. el. power in $\mu V/^\circ C$

Graph 6



T_2 in degrees C. $T_1 = 0^\circ C.$

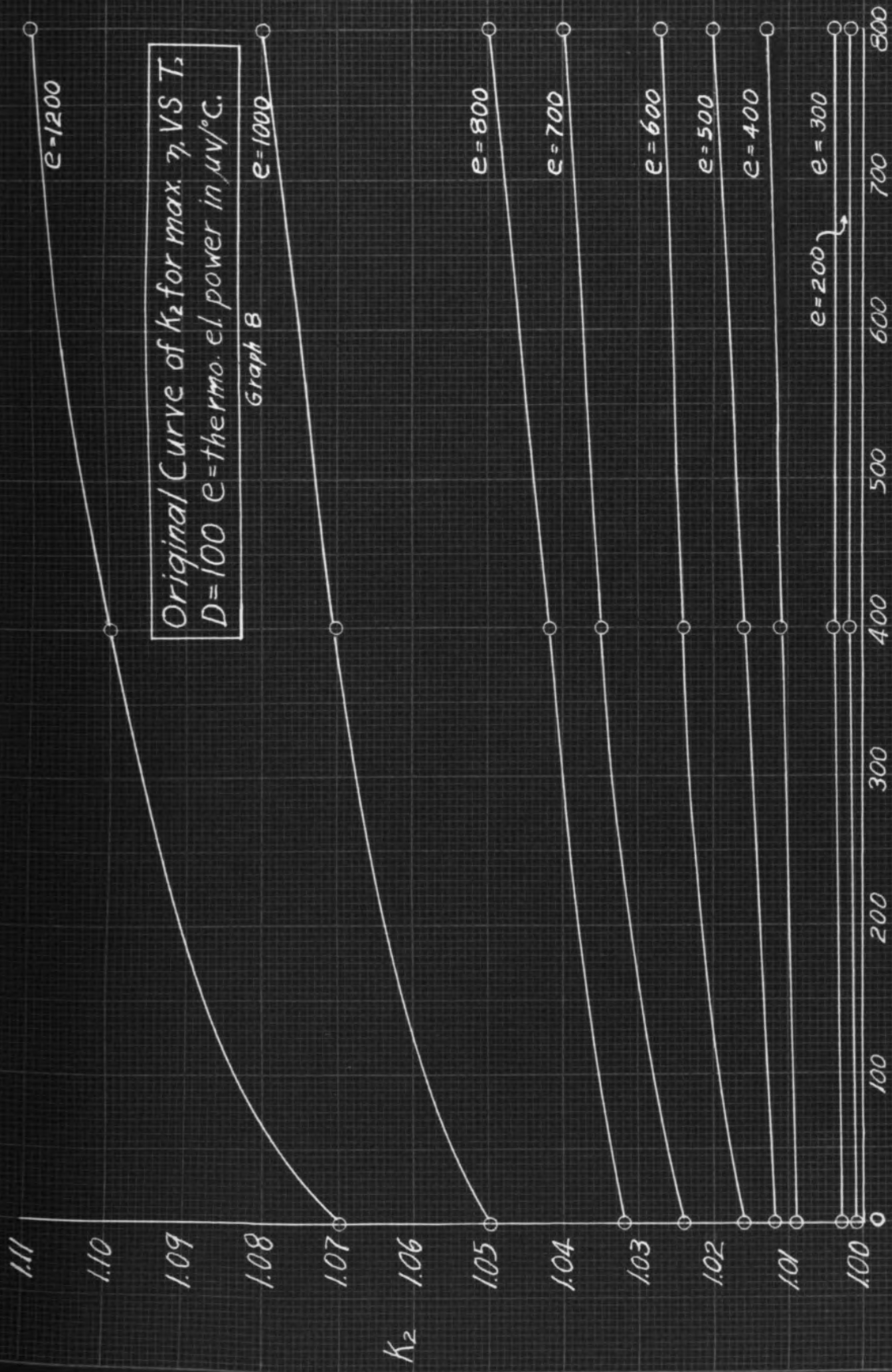


Original Curve of k_2 for max. η , VS T_2
 $D = 20$ e=thermo. el. power in $\mu\text{V}/^\circ\text{C}$

Graph 7

T_2 in degrees C. $T_1 = 0^\circ\text{C}$.

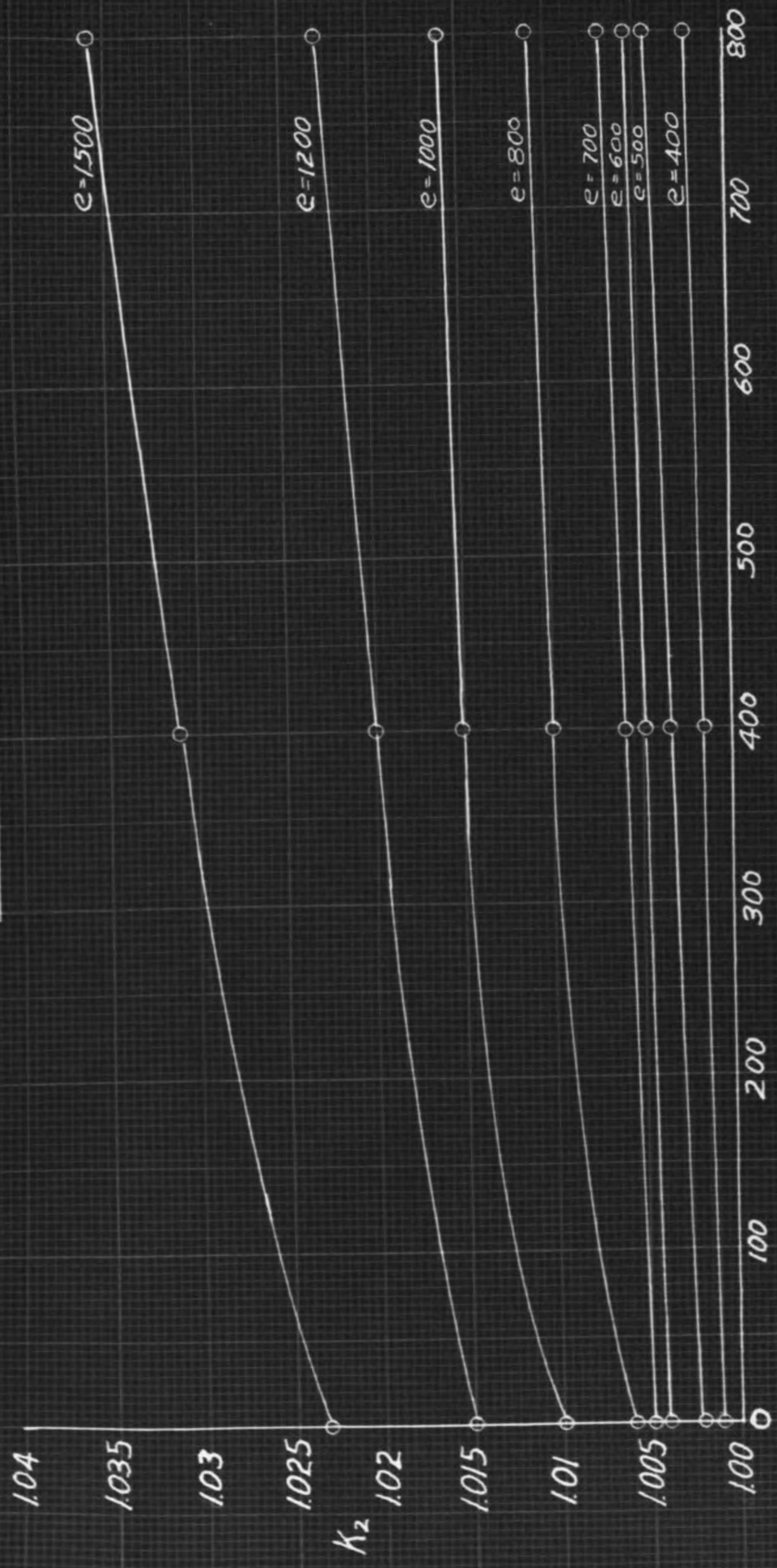




T_2 in degrees C. $T_1=0^\circ C$.

Original Curve of k_2 for max. η , VS T_2
 $D = 500$ e=thermo. el. power in $\mu V/^\circ C$.

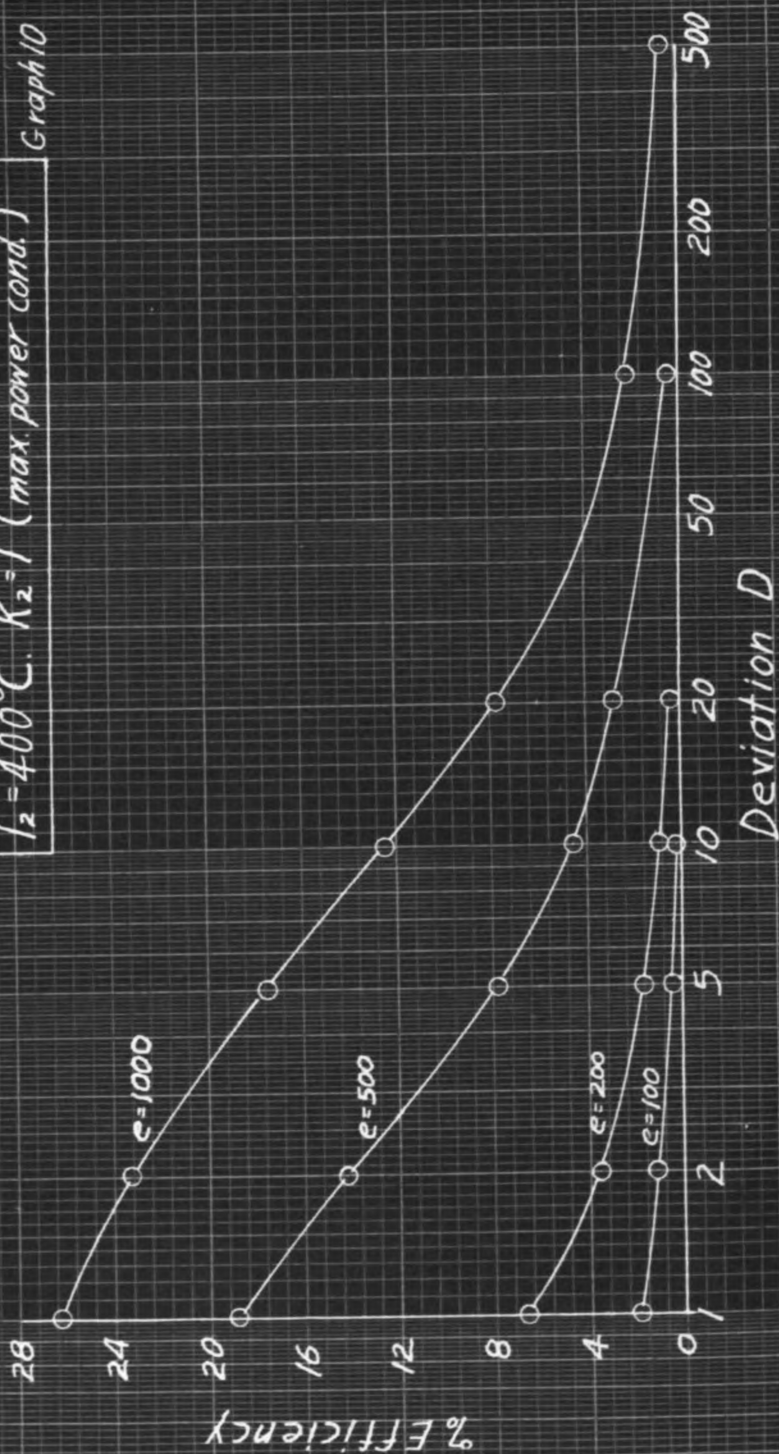
Graph 9



T_2 in degrees C. $T_1 = 0^\circ C.$

Efficiency vs Deviation $e =$
thermo. el. power in $\mu\text{W}/^\circ\text{C}$. $T_1 = 0^\circ\text{C}$
 $T_2 = 400^\circ\text{C}$. $K_2 = 1$ (max. power cond.)

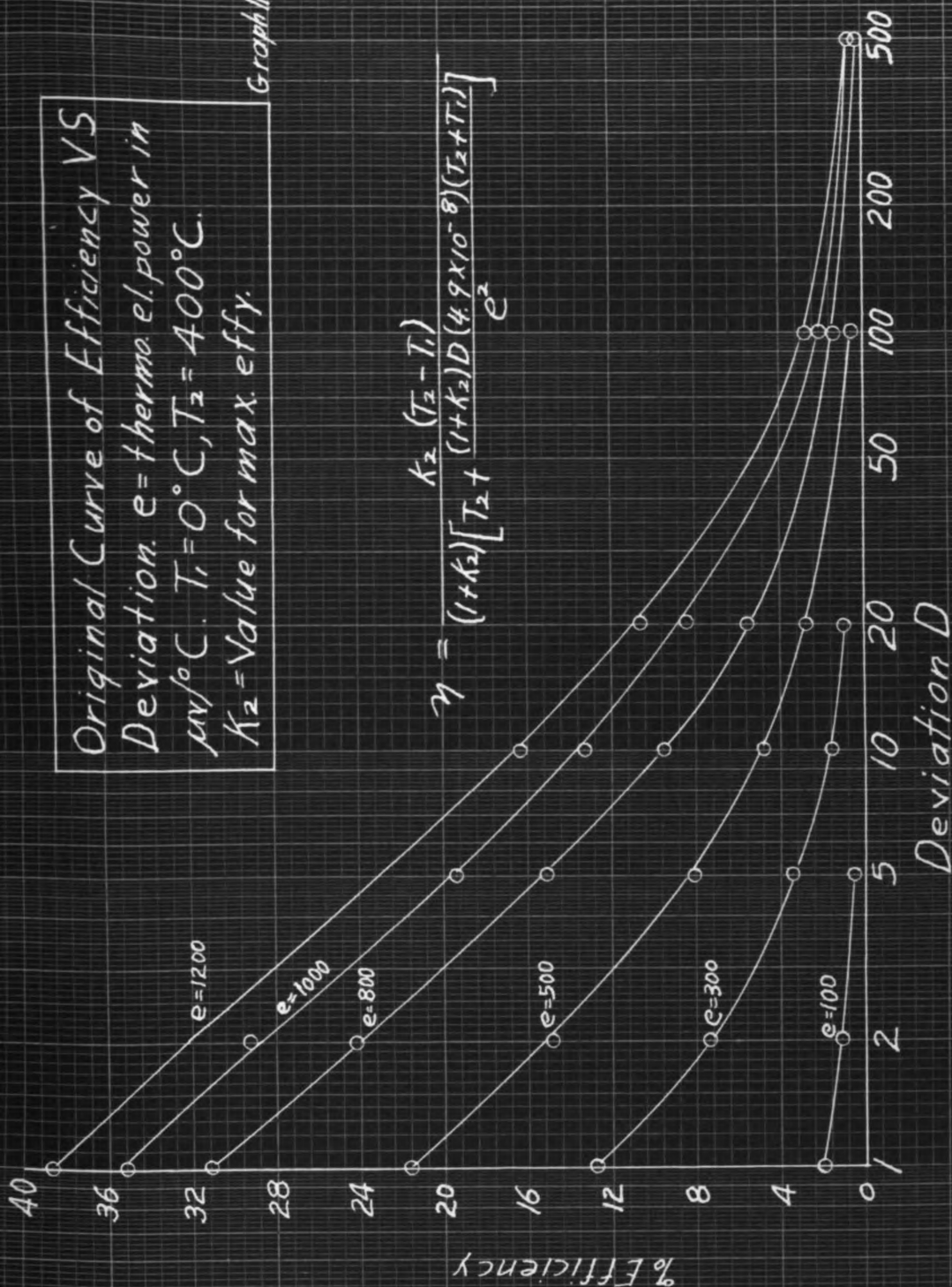
Graph 10



Original Curve of Efficiency VS
Deviation. $e = \text{thermo el. power in}$
 mV°C . $T_1 = 0^\circ\text{C}$, $T_2 = 400^\circ\text{C}$.
 $K_2 = \text{Value for max. effy.}$

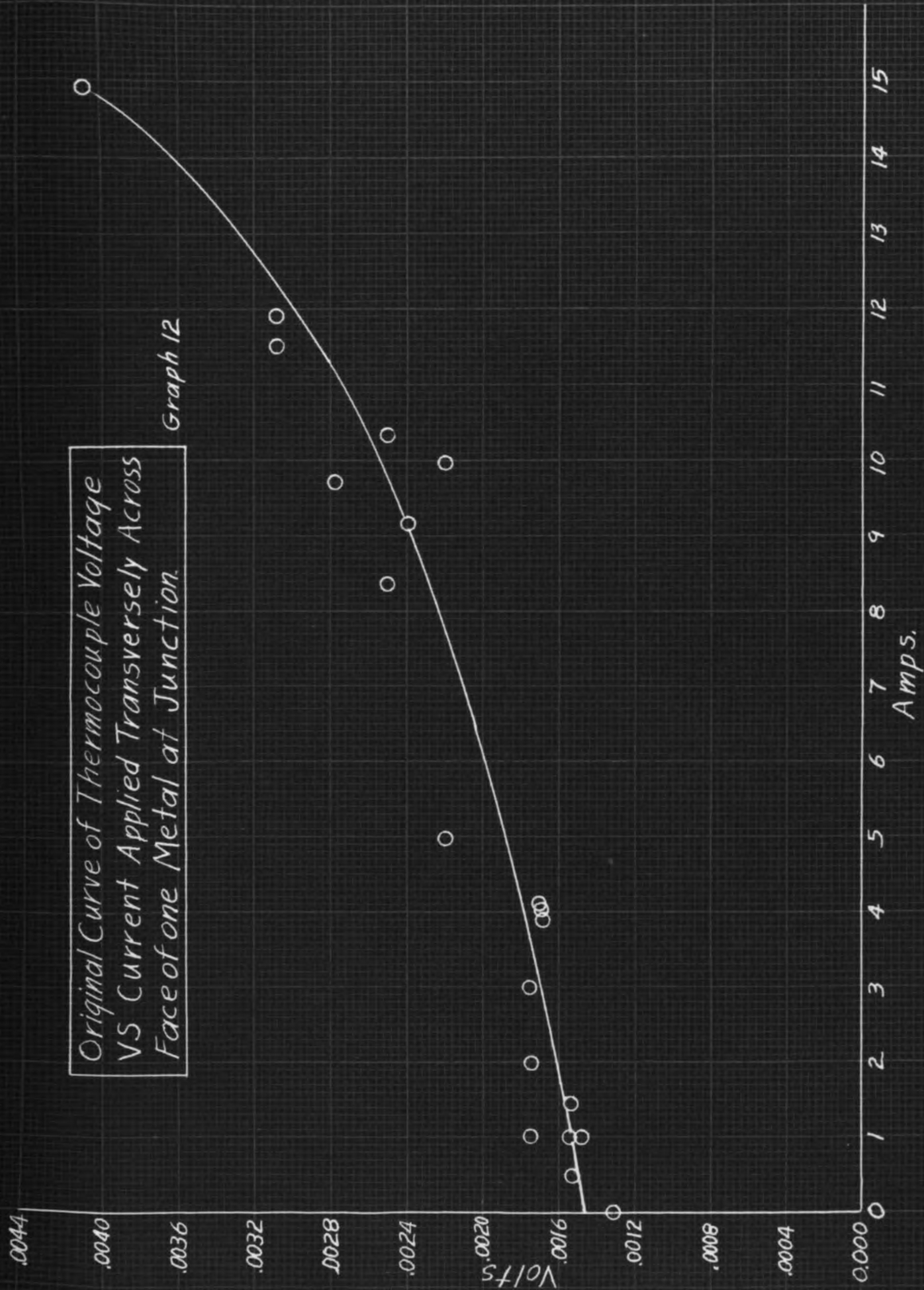
Graph //

$$\eta = \frac{K_2 (T_2 - T_1)}{(1 + K_2) \left[T_2 + \frac{(4.9 \times 10^{-8}) (T_2 + T_1)}{e^2} \right]}$$

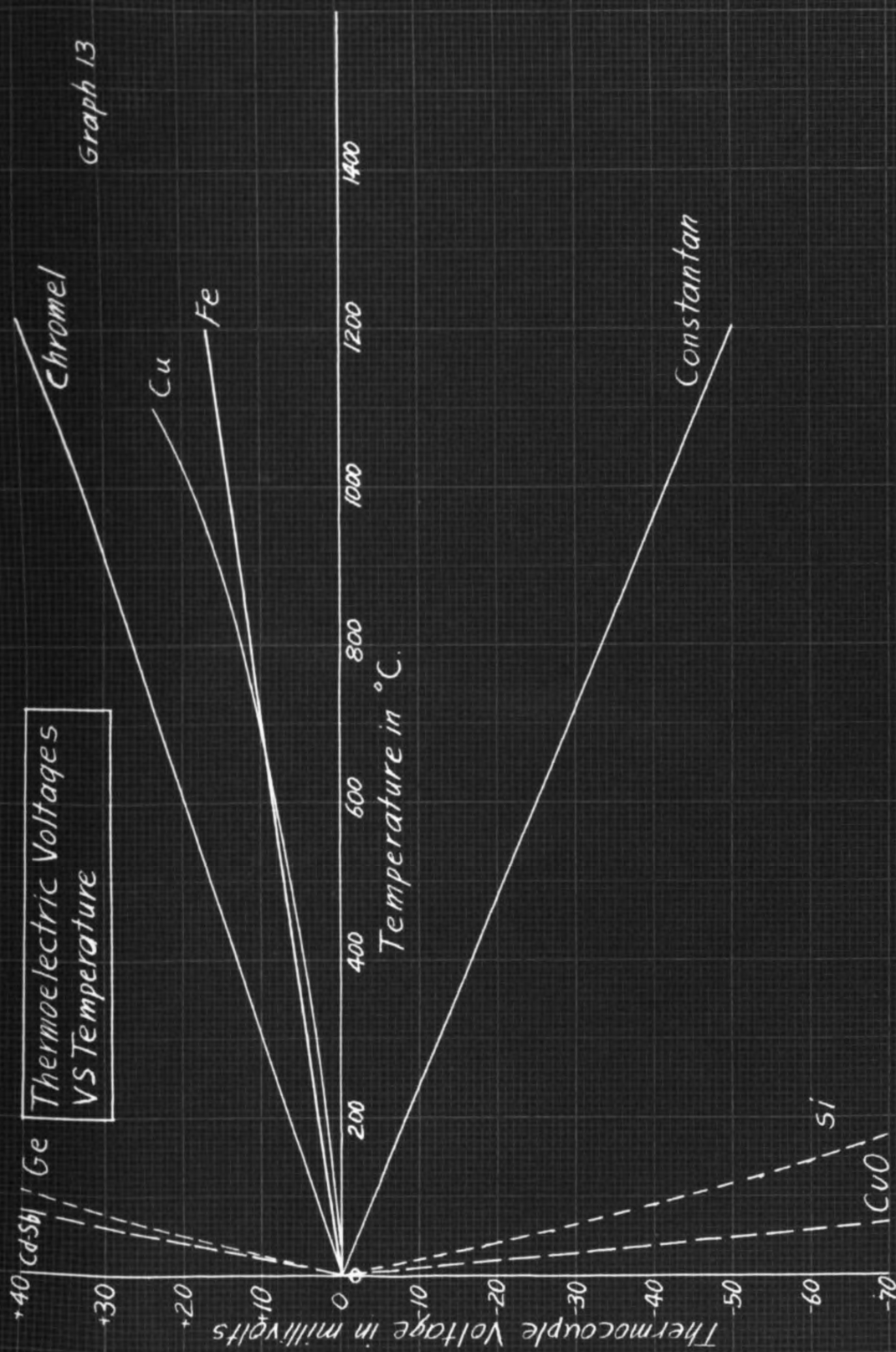


Original Curve of Thermocouple Voltage
VS Current Applied Transversely Across
Face of one Metal at Junction.

Graph 12



Graph 13



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2,397,756	Schwarz
575,027	(British) Westinghouse Elec. Inter. Co.
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