

UNCONVENTIONAL ELECTRICAL POWER SOURCES

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ILLINOIS INSTITUTE OF TECHNOLOGY
OKLAHOMA A. & M. COLLEGE

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SEPTEMBER 1954

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是是我们的一个人,我们就是我们的一个人,我们就是我们的一个人,我们就是我们的一个人,我们就是我们的一个人,我们就是我们的一个人,我们就是他们的一个人,我们就是他 第一个人,我们就是我们的一个人,我们就是我们的一个人,我们就是我们的人,我们就是我们的人,我们就是我们的人,我们就是我们的人,我们就是我们的人,我们就是我们就是

FOREWORD

This report was prepared by Attie L. Betts and Paul A. McCollum of the School of Electrical Engineering. Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, on Air Force Contract No. AF 33(616)-2237. Project No. 6058. Electrical Generation Equipment. Task No. 60280. Study and Research Program on Unconventional Electrical Power Supplies. The work was administered under the direction of the Equipment Laboratory, Wright Air Development Center, with Dr. E. Naumann as project engineer.

A list of principal personnel associated with the project and indicating authorship of parts of the report is as follows:

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Dr. E. M. Hodnett - Chemist.

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The work performed in connection with this report represents the first year of activity of a proposed four year program of research.



ABSTRACT

The research covered by this report has been directed toward gaining information concerning the theoretical and practical limintations and capabilities of generating electrical power by means other than rotating machinery, conventional batteries, or radio active devices. Data and theory is presented on Workman-Reynolds Effect, Emission, Pyro-electricity, Thermopiles, Thermomagnetic Generators, Ion Exchange Memorane. Fuel Cells. Electrokinetic Transducer. Electrostatic devices, Oscillating Electromagnetic Industion, Piezbelectricity, Magnetostriction, and Photovoltaic Generators. A major portion of the fundings resulted from a library search. A limited amount of experimental and theoretical work was performed to verify and extend existing information. The thermoelectric effect, ion exchange membrane, oscillating electromagnetic induction, and fuel cells show promise of becoming valuable sources of electrical energy. The succeeding activity will be directed primarily toward extending available information on these power sources.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the excharge and stimulation of ideas.

FOR THE COMMANDER:

S. T. SMITH
Colonel, USAF
Chief, Equipment Laboratory

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INTRODUCTION

Many applications of electrical power could make use of so-called "unconventional sources." It would be advantageous to use these sources for various reasons, some of which are; waste products may be made to accomplish a useful purpose; weight and bulk might be conserved; or life and reliability might be increased for rugged environments. For example, high potential power sources for modern cathode-ray tubes quite frequently employ radio-frequency oscillators as intermediate generators of high voltage, low current power, since better personnel safety and a saving in weight is gained. In the case of the newly developed transistors, their utility would be broader if power sources commensurate with their size and weight were developed.

The intent of this project is not to develop final facts or to evolve a final design of a power supply. The intent is to determine where emphasis should be placed in a possible general development program of unconventional power sources. The method of approach utilized during this first year of effort has been to examine all available library sources for information on previous work and to add to the data thus obtained by laboratory tests and theoretical analysis insofar as time would permit. The completion of this task will involve the examination of possible sources to determine the parameters of operation through a literature search augmented by tests of laboratory models where practical. This examination will include the influence of modern engineering materials and processes on the design characteristics of the possible power supplies utilizing the various unconventional methods of generating power.

For purposes of defining the study, conventional electrical power supplies were considered to be those types, the use of which is common practice, and which consist either of primary and secondary batteries or of rotating dynamo-electric machinery (generators). Other types of electrical power supplies were considered unconventional for the purpose of the contracted study. Sources involving radioactive principles were excluded.

Insofar as possible and practical, it has been the aim to quantitatively evaluate the data obtained and to establish parameters, such as;

- (a) efficiency of power conversion.
- (b) required overall weight per power output and operating time.
- (c) required overall size per power output and operating time.
- (d) range of voltages and currents which can efficiently be provided.
- (e) life and reliability which can be expected.

Other aspects to be investigated, if applicable, were: methods of voltage control, means of paralleling, lubricants, audio and radio noise, effects of environment conditions, and any other special features of interest from an application standpoint.

It should be definitely emphasized that at this point in the study of unconventional electrical power supplies the information introduced on the preceding topics is by no means complete, but rather represents the results of the work during the first year of the contracted study. It is to be expected that much more investigation is necessary before any conclusive data can be presented.

Contrails

PART I

CONVERSION FROM HEAT ENERGY TO ELECTRICAL ENERGY

THE WORKMAN-REYNOLDS EFFECT

There are a number of papers that report the appearance of an electrical potential during the freezing of water. More recently, E. J. Workman and S. E. Reynolds? have investigated, in what appears to be the most extensive work to date, charge separation effects that occur during the freezing of aqueous solutions containing small amounts of inorganic impurities. They measured electrical potentials as great as 230 volts between the frozen and unfrozen portions of the solution. The polarities and magnitudes of the voltages are related to the natures of the solutes and to their concentrations, but they are independent of the freezing rate except to extreme values. The available current does, however, depend upon the freezing rate. J. Costa has observed the effect in liquid-solid transitions with naphthalene, and reports that the effect exists during sublimation processes. The most complete study presently available is that of Workman and Reynolds, hence, the remaining discussion will deal with the contents of that paper.

THEORY OF OPERATION The effect is ascribed to a process which selectively separates, ions at the ice solution interface. It was suggested previously by Errera4, that liquids whose molecules have permanent electrical dipoles pass through "colloidal" transition states upon freezing, and the combined electric dipoles of the colloidal particle may exceed that of the molecules comprising the particle. Workman and Reynolds have suggested that ions in solution are selectively absorbed in the crystal lattice in order to decrease the free potential energy of the system. Negative ions are preferentially absorbed in the crystal. However, the ammonium cation, NH1,, appears to be strongly absorbed. It is suggested that this ammonium cation absorption is due to its similiarity to the hydronium ion, H3O, which is the active ion in the formation of ice. The greatest effects were observed with dilute solutions of ammonium salts, and with dilute ammonium hydroxide solutions. Chemical evidence is presented in support of the charge-separation idea. The effect is also observed in solol7 solutions.

1 Chalmers, J. A. Atmospheric Electricity. Clarendon Press, London, 1949 Chapter XII.

Workman, E. J. and Reynolds, S. E. Electrical Phenomena Occuring During the Freezing of Dilute Aqueous Solutions and Their Possible Relationship to Thunderstorm Electricity. Physics Review. Vol. 78, 1950, pp. 254-259.

3. Costa, J. On the Thermo-Dielectric Effects. An Acad. Brasil. Cienc., Vol. 22, No. 3, 1950,pp. 235-348. Via Science Abstracts 54:1821. 1951.

4. Errera, J. The Colloidal State and Cohesion at the Time of Solidification. Trans. Faraday Soc. Vol. 24. 1928, p. 168.

5. Solol is the phenol ester of salicylic acid.

I-1

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CURRENT STATUS Apparently, no studies have been made to examine the effect as a possible source of power. The papers do not yield information from which exact calculations of the power potentialities can be made, but some rough estimates are possible. It should be said at the outset that no promise is seen for such a device as a practical means of producing power.

Maximum Efficiency

If one assumes that the energy effecting the ion separation comes from the transfer of thermal energy from the liquid phase at a temperature T₁ to the solid phase at a temperature T₂, one can then calculate a maximum theoretical efficiency for the process even though a change of state occurs, by the classical relation,

Efficiency =
$$\frac{T_1 - T_2}{T_1}$$

Selecting the maximum value possible for the aqueous solution, H_2O , for T_1 as $283^{\circ}K$ ($10^{\circ}C$), and the minimum value possible for T_2 as $243^{\circ}K$ ($-30^{\circ}C$), the maximum thermal efficiency is seen to be about 14%. There is reason to believe that this figure can be no greater, and that in practice it is usually smaller because high freezing rates reduce the potential produced by effecting a random orientation of ice crystals.

b. Actual Efficiency

Again it is desirable to pick data that will indicate the optimum experimental efficiency attained. The following data is selected from the Workman-Reynolds paper.

Freezing rate = 1 cc/min.
Current produced = 1 microampere.
Voltage produced = 230 volts, maximum.

The total energy transferred per second as heat is given by

 $Q = 1/60 \times 80 \times 1.18 = 5.6 \text{ joule/second}$

The total electrical energy generated is given by

 $P = 230 \times 10^{-6} \text{ watts} = 2.3 \times 10^{-4} \text{ watts}$

and the actual efficiency is given by

efficiency = $2.3 \times 10^{-14} \times 100/5.6 = 0.004$

or 0.004/0.14 = 0.03% of that theoretically possible.

The weight of approximately 90 pounds of solution would be required to produce a power output of one watt for a period of one minute.

d. Volume Per Unit Output

The device would have a volume of about 3 cubic feet per wattminute of energy produced.

e. Range of Voltages

The voltage of the device can be varied by using different solutions in the freezing chamber, or by the usual electrical divider networks.

f. Range of Currents

The reported current was one microampere. Presumably, one can increase the current by freezing over a large surface area. Nothing can be deduced about the noise level and life of the device.

PROJECTED STATUS It seems unlikely that a thermal process whose power cycle involves a change of state can ever have a reasonably high theoretical efficiency. It should be stated, however, that more research will be required in order to prove absolutely, that the device cannot be used used as a power source.

RECOMMENDATIONS On the basis of information presently available, it is recommended that a device for generating electrical power whose operation is based on the principle of a separation of charge during a change of phase, be regarded as impractical. This effect is secondary to the cooling process and therefore is not considered an efficient method of energy conversion.

THERMOMAGNETIC

A thermomagnetic generator is one that utilizes the change in magnetic permeability with temperature to produce an electromotive force. If a magnetic material is heated to the Curie point, it loses its magnetic properties. A magnetic circuit that contains an element that is alternately heated to the point where its relative permeability, #r, approaches unity, and then allowed to cool to such a point that the relative permeability increases, will have a varying flux, \$\phi\$, within the magnetic circuit, and any coil placed around a portion of this magnetic path will have an electromotive force induced in the coil that can provide power to an external circuit. The thermomagnetic generator is, by nature, a low-frequency alternating current source. The low-frequency is dictated by the heating and cooling cycle of the material in the magnetic circuit. The heating and cooling is controlled by valves or vanes to regulate the heat being applied. The schematic diagram of this type of generator is shown in Figure I-1

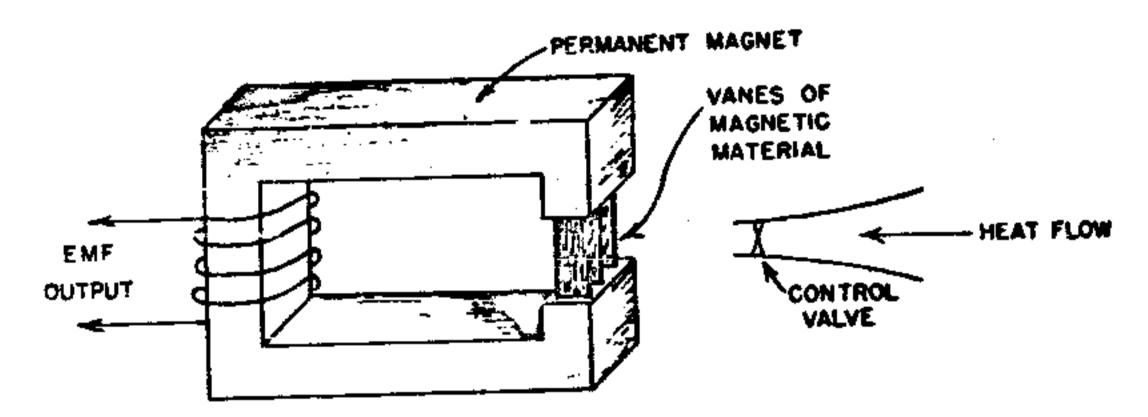


Figure I-1 . Elementary Thermomagnetic Generator

CURRENT STATUS Most of the work on this type of generating device was preformed in the period 1880-1890. The machines used were bulky and inefficient. A more modern work was performed by Erich Schwarzkopf in 1935 and is covered by U. S. Patent 2,016,000. There seems to be no available information on the efficiency of the generators described in the literature. The only indications concerning physical size indicates an active area of approximately 1/8 sq. ft/watt and a weight of 8 lb/watt.

PROJECTED STATUS The two obstacles to the development of this type of generating device are both related with thermal problems. The relatively slow heating and cooling cycle of the magnetic material limits the device to a low-frequency output of not more than a few cycles per second. The problem of thermal efficiency is the other major factor limiting the efficiency of operation. The available data is insufficient to establish any of the parameters with any degree of reliability at the present time. It is evident, however, that such a device would have a long life and low maintenance. The range of voltages

and currents is controlled by circuit design. Noise, both audio and radio-frequency, would be low. It is felt that the recent advances in engineering materials make the operation of a device of this type much more feasible as far as volume and weight are concerned, and the fact that waste heat could be utilized would be a definite advantage.

RECOMMENDATIONS The limitation of the output of the thermomagnetic generator to low frequencies is a decided disadvantage in its application as a power source. It is felt that the theoretical possibilities of this device should be studied, paying particular attention to any material or method increasing the rate at which a magnetic material can be heated or cooled through the Curie point.

Armour Research Foundation, Survey of Power Sources. Signal Corps Engineering Laboratories, Final Report, Contract No. W-36-039-sc-32132, May 1947, pp. 229-230.

PYRO-ELECTRICITY

Pyro-electricity is the name given the potential generated between two faces of an oriented crystal when this oriented crystal is subjected to heat either through a direct application of the heat or through electromagnetic radiation in the infrared spectrum. In order to evidence this phenomena the crystal must fall into one of the following catagories: polar, tripyramidal polar, tetartohedral, clinohidral, or triclinic asymmetric. These crystals must be oriented so that their axes of polarization correspond. When properly oriented, these crystals are reportedly capable of detecting temperature variation of the order of millionths of a degree centigrads.

The current flow given for this temperature measurement was in the order of 5 x 10⁻⁹ ampere. The crystal was reported to be able to follow frequency variation of heat application up to 1000 cycles per second.

Most of the experimentation on pyro-electricity has been confined to tournaline. Other crystal substances such as tartic acid, have been noted as having a stronger pyro-electric effect. Experimenters have had considerable difficulty in separating the potentials generated by the pyroelectric effect from those produced by crystal deformation and the thermoelectric effect present when the temperature gradient inside the crystal is not zero and impurities are present. When present, potentials caused by deformation and impurities are classed as "false pyro-electricity."

Among the patents utilizing the pyro-electric effect is one by Sivian covering the conversion from heat rays to electricity utilizing a heat transparent window in a hermetically sealed container to apply the heat waves to the crystal. A patent by Delano claims the transformation of heat energy to electrical energy using this phenomena.

No data was found that established the physical dimensions or weight of a generator utilizing pyro-electricity. In view of the limited current, 5 x 10" amperes, and the fact that most experimenters found that "false pyro-electricity" was usually stronger than pyro-electricity, this phenomena is not expected to require serious consideration as a source of electrical energy.

- 1 Cady, W. G. Electroelastic and Pyro-electric Phenomena, Proc. I.R.E. Vol. 18, No. 7 pp. 1247-1262, July, 1930.
- 2 Duhem, P. On a Theory of Pyroelectric Phenomena, Society Francaise de Physique, Paris 1889, pp. 59-66.
- 3 Ta, Yeou. Academic des science, Paris Vol. 207 part 2, pp. 1042-43.
- l, Sivian, L. J. U. S. Patent 2,299,260, October 20, 1942.
- 5 Delano, James K. U. S. Patent 2,317,523, April 27, 1943.

Contrails

RECOMMENDATIONS: The low power developed by pyro-electric crystals is such that this phenomena is not considered a desirable source of power at this time. It is recommended that no additional effort be expended in experimentation.

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EMISSION

Emission phenomena by which a measurable amount of power is generated includes:

I. Thermionic emission

II. Photoelectric emission

1. Photoemissive

2. Photoconductive

3. Photovoltaic

THERMIONIC EMISSION is a pure electron emission from solids which have been heated to incandescence by the application of an electrical or other heat source. As such, it can be considered the direct transmission of thermal energy into electrical energy. Electron emission as a function of temperature is expressed, according to Richardson¹, by

$$I = a T^{\frac{\kappa}{2}} \varepsilon^{-\frac{\kappa}{2}}$$

where I = emission per unit area in amperes
T = absolute temperature

a and b are constants, characteristic of the emitting surface. A body placed near the emitting body will collect the emitted electrons and become negatively charged with respect to the emitting body. Thus, connecting a load between the two will permit a current to flow and electric power will be derived. Data on the energy radiated as a function of the temperature have been summarized in the review by Lax and Pirani2, which contains complete references to the literature. Among the nure metals, the greatest emission is experienced with molybdenum and tungsten. At 2000°K, the values reported are in the order of 10 milliamperes/cm² for molybdenum and 1 milliamper/cm² for tungsten. The electron emissivity of tungsten can be greatly improved by the addition of 1 or 2 percent of thorium. The atoms diffuse to the surface of the filament where they form a mono-atomic layer, and the emission of such a filament at 2000°K is in the order of 3000 milliamperes/cm2. Further work with filaments coated with oxides of barium, calcium, strontium and others, has resulted in electron emissivities of 10,000 to 20,000 milliamperes/cm² at this temperature. However, their life would be very short at this high temperature and are thus operated commercially around 1100°K. The characteristics of such a filament are listed in Table I-1"and a comparison of commercially manufactured filaments with pure and thoriated tungsten is shown in Figure I-27. The emission in milliamperes/cm2 is plotted against the power input in watts/cm2. Efficiencies are also indicated at some points in milliamperes/watt. Comparable emission currents have been obtained from Richardson, O. W., The Emission of Electricity from Hot Bodies,

Longmans, Green and Company (1921).
Lax and Pirani, Handbuch der Physik, 21, 236-40.

Langmuir, I., and Rogers, W., Phys. Rev. 4,544 (1914).

Davisson, C., I.C.T. 6,53 (1929).

5 King, R. W., Bell System Tech. J., 2, no. 4 (1923).

oxide cathodes heated in a furnace, rather than electrically, and it is indicated that such a generator might be practical in an application a where there is a large amount of high temperature waste heat available.

RECOMMENDATIONS: It is felt that this process shows insufficient promise to warrant further activity other than checking current literature. Future developments may change this outlook, but current data does not predict this occurrence.

TABLE I-1
Characteristics of Western Electric Filaments

Temp:-	900°K	950 ⁰ K	1000°K	1050 ⁰ K	1100ok	
I _o (milliamps/cm ²)	20	45	90	170	310	
P _r (power radiated, watts/cm ²)	2.3	3.0	3•7	4.6	5.6	
Pe (power absorbed by emission. watts/cm ²)	0.02	0.045	0.09	0.17	0.31	
Efficiency (milliamps/watt) $I_0/(P_r + P_e)$	8.6	15.0	24	31	53	
Life (in thousands of hours)	(730)*	(170)*	20	20	7-4	

^{*}These figures are computed.

Kay, G. W. C., and Higgins, W. F., Proc. Roy. Soc. (London, Ser. A. 90, 430-34.

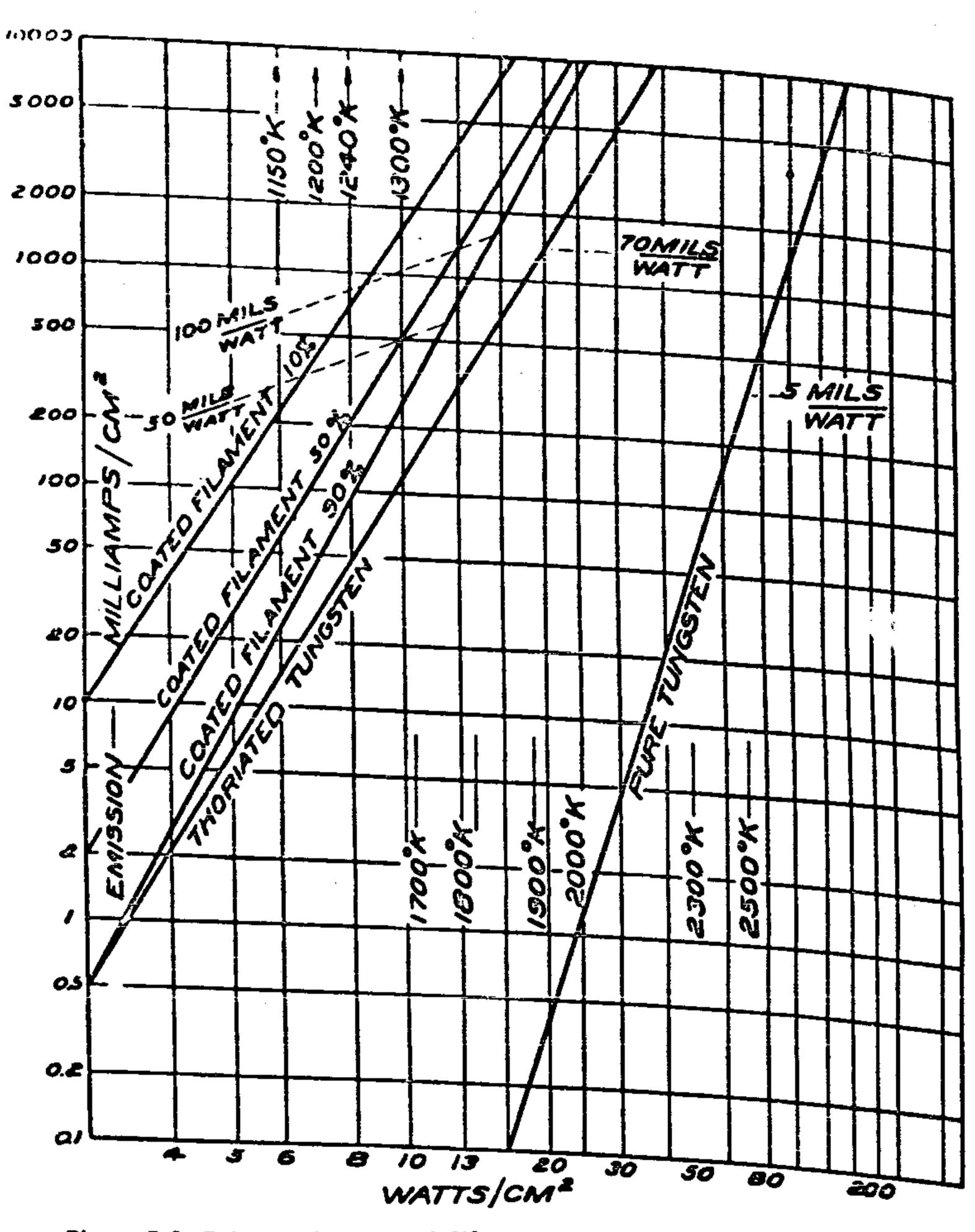


Figure I-2, Emission from coated filaments as a function of power input.

THERMOCOUPLES

The fact that a potential is produced when a junction of two dissimiliar materials is heated has long been known. The exact magnitude of this potential and the associated available current depends upon the individual materials, the methods used in preparing the materials, and the forming of the junction. The major portion of the work directed toward the use of thermoelectric generators as a source of electrical energy was preformed shortly after the invention of the incendescent lamp by Edison in 1879. The work was almost discontinued by about 1890 in favor of developing rotating machinery. In recent years, a renewed interest in thermoelectric generators has led to the development of the Marshall Generator, the research work of Telkes, a survey by Armour Institute, and materials development work by Franklin Institute4. Thermoelectric generators are characterized by low efficiency, small power output, great weight and volume per watt output, absence of commutation and moving parts, simplicity and ease of operation, adaptability to use of waste heat, and noiselessness. The efficiency of energy conversion claimed for current thermoelectric generators varies from 0.2% to 8.2%. This figure is limited primarily by thermal losses in the design.

Most of the material found in the literature is based on the efficiency of operation at maximum power output and not for maximum overall efficiency. For this reason, it is desirable to derive the general equations associated with overall efficiency.

The total electrical potential developed by a thermocouple is

where

E is expressed in volts.

Θ is thermoelectric power in volts per degree centigrade, ΔT is the temperature difference between the hot and cold junctions of the thermocouples.

The power output of the thermocouple is then

Power output =
$$\text{CIAT} - \text{I}^2 \left(\frac{\rho' \ell'}{\alpha'} + \frac{\rho' \ell''}{\alpha''} \right)$$
 watts,

Where I is the current in amperes

and
$$\left(\frac{\rho' \mathcal{L}'}{a'} + \frac{\rho' \mathcal{L}''}{a''}\right)$$
 is the internal resistance.

The heat input required to generate the CIAT electrical power would be

l Electrical World. Vol. 64 p. 385.

Telkes, Maria, U. S. Patent No. 2,229,482.

Armour Research Foundation, Survey of Power Sources. Signal Corps Engineering Laboratories, Final Report, Cont. No. W36-039-sc-32132, May 1947.

Franklin Institute, Development of Thermocouples for use on Thermoelectric Generators. Signal Corps Engineering Lab. Final Report Cont. No. W-36-039-sc-33654, Sept. 1950.

$$(eiat)\frac{Th}{\Delta T} = eith$$

Where T_h is the temperature of the hot junction in degrees Kelvin. The heat conduction losses, neglecting the Thompson Effect and assuming the walls to be perfect insulators, are

$$\Delta T \left(\frac{k a'}{L'} + \frac{k' a''}{L''} \right)$$

where k' k'' are the coefficients of heat conduction $\alpha' \alpha''$ are the areas of the two materials in sq. cm. $\ell' \ell''$ are the lengths of the two materials in cm.

The general efficiency can then be calculated from

efficiency =
$$\frac{\text{output}}{\text{input}} = \frac{\text{elat} - I^2(\frac{\rho L'}{\alpha'} + \frac{\rho L''}{\alpha''})}{\text{elth} + \Delta T(\frac{k'\alpha'}{L'} + \frac{k'\alpha'}{L'})}$$

This shows the effect of the various parameters on the efficiency, including the fact that the electrical and thermal conductivities of the elements themselves affect the overall efficiency of the thermopile generator.

An important characteristic of such a device is the maximum efficiency that can be expected under specific conditions. To determine this maximum efficiency it is first necessary to differentiate the equation for efficiency with respect to the current output.

$$\frac{d\varepsilon}{dI} = \frac{\left[e_{IT_h} + \Delta T\left(\frac{k\alpha}{L'} + \frac{k\alpha}{L''}\right)\right]\left[e_{\Delta T} - 2I\left(\frac{k'\alpha}{L'} + \frac{k'\alpha''}{L''}\right)\right] - \left[e_{I\Delta T} - I^2\left(\frac{k'\alpha}{L'} + \frac{k'\alpha''}{L''}\right)\right]e_{T_h}}{\left[e_{IT_h} + \Delta T\left(\frac{k'\alpha'}{L''} + \frac{k'\alpha''}{L''}\right)\right]^2}$$

Setting this equation equal to zero and solving for the current occurring at maximum efficiency yields

$$I_{\frac{MAX}{EFF.}} = \frac{\Delta T \left(\frac{k'a'}{\ell'} + \frac{k'a'}{\ell''} \right)}{e T_h} \left(\sqrt{1 + \frac{e^2 T_h}{\left(\frac{\ell'\ell'}{a'} + \frac{\ell'\ell'}{a''} \right) \left(\frac{k'a'}{\ell'} + \frac{k'a'}{\ell''} \right)}} - 1 \right)$$

Substituting this value of current into the general equation for efficiency gives an expression for maximum efficiency of

$$\mathcal{E}_{MAX} = \frac{\Delta T}{T_{h}} \left[1 + \frac{2\left(\frac{\rho' \mathcal{L}'}{\alpha'} + \frac{\rho' \mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}'}\right)}{e^{2} T_{h}} - \frac{2\left\{ 1 + \left(\frac{\rho' \mathcal{L}'}{\alpha'} + \frac{\rho' \mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\rho'\mathcal{L}''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\mu'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\mu'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\mu'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\mu'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{\mu'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}'} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{k'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}''} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{k'\alpha''}{\alpha''}\right) \left(\frac{k'\alpha'}{\mathcal{L}''} + \frac{k'\alpha''}{\mathcal{L}''}\right) - \frac{2\left\{ 1 + \left(\frac{\rho'\mathcal{L}'}{\alpha'} + \frac{k'\alpha''}{\alpha''}\right) - \frac{2\left(\frac{\alpha'}{\alpha''} + \frac{k'\alpha''}{\alpha''}\right) - \frac{2\left(\frac{\alpha'}{\alpha'} + \frac{k'$$

This is the general equation for maximum efficiency. It can be simplified by imposing the following definitions and conditions.

$$a' = a'' = a$$
 $l' = l'' = l$

$$\frac{\rho' + \rho''}{2} = \bar{\rho}$$
 so $2\bar{\rho} = \rho' + \rho''$

$$\frac{k + k}{2} = \bar{k}$$
 so $2\bar{k} = k' + k''$

and $A = \frac{e^2 T_h}{4 \bar{\rho} \bar{k}}$. Then the current for maximum efficiency

becomes $I_{\text{AAX}} = \frac{e\Delta \tau (92)}{2A\overline{\rho}} \left[\sqrt{1+A} - 1 \right]$

and the maximum efficiency equation is

$$E_{MAX} = \frac{\Delta T}{T_{N}} \left[1 + \frac{2}{A} - \frac{2}{\sqrt{1+A}} (1 + \frac{1}{A}) \right]$$

In some applications the operation of thermocouples at maximum power output is of primary interest. To determine the conditions existing at maximum power output equation is differentiated with respect to I

$$\frac{dR}{dI} = e\Delta T + 2I\left(\frac{P'L'}{a'} + \frac{P''L''}{a'''}\right)$$

With this equation equated to zero, the current corresponding to maximum power output becomes

$$I_{\text{power}} = \frac{e\Delta T}{2\left(\frac{p'l'}{a'} + \frac{p'l'}{a'}\right)}$$

amperes,

which shows the maximum power output to be

$$\frac{e^2 \Delta T^2}{4 \left(\frac{\rho' \ell'}{a'} + \frac{\rho' \ell'}{a''} \right)}$$

watts.

The efficiency at maximum power would then be

$$\mathcal{E}_{MP} = \mathcal{L} e^{2} \Delta T \left[\frac{1}{e^{2} T_{h} + 2 \left(\frac{P' L'}{\alpha'} + \frac{P' L'}{\alpha'} \right) \left(\frac{k' \alpha'}{L'} + \frac{k' \alpha''}{L''} \right) \right]$$

or if expressed in terms of the parameter "A".

$$\mathcal{E}_{MP} = \frac{\Delta T}{2 T h} \left[\frac{1}{1 + \frac{2}{\lambda}} \right]$$

CURRENT STATUS: The library search for the thermoelectric powers and associated characteristics of materials proved to be unsatisfactory due to lack of information concerning the conditions surrounding the experiments and the degree and type of impurities present in the samples tested. The curves shown in Figure I-3 have been computed in order to more readily determine the characteristics a material must have if it is to be a satisfactory source of electrical energy. The ordinate of these curves is the difference in thermoelectric powers of the materials in microvolts per degree centigrade. The abscissa is in theoretical overall maximum efficiency. The individual curves are for different values of PL. The form factor assumes that the two materials have the same physical dimensions. This curve can be used either to determine the P
ot E product required to produce a certain maximum efficiency for a given thermoelectric power, or the thermoelectric power required to produce a certain maximum efficiency if the Product is known, or to determine the maximum efficiency if the thermoelectric power and P & product are known. Curves of this nature can be plotted for a variety of temperatures. In using the curves, it is necessary that the values for thermoelectric power, P, and & correspond to the temperature used in plotting the curve since each of these parameters is a function of temperature.

RECOMMENDATIONS: It is felt that the best advantage can be gained by tabulating the related parameters of the various materials that might be used as elements in a thermopile generator. Particular emphasis should be placed on finding materials with a low PAE product and a high thermoelectric power. It is also felt that information on contact potentials and Fermi energy levels should also be tabulated for possible correlation with a view toward predicting the effects of impurities on the thermoelectric phenomenon. A laboratory test set-up for experimentation is needed to correlate data and theory and for verification purposes. It is felt that the success of thermopiles as converters of energy from heat to electricity is strictly dependent upon finding materials having a favorable combination of physical properties.

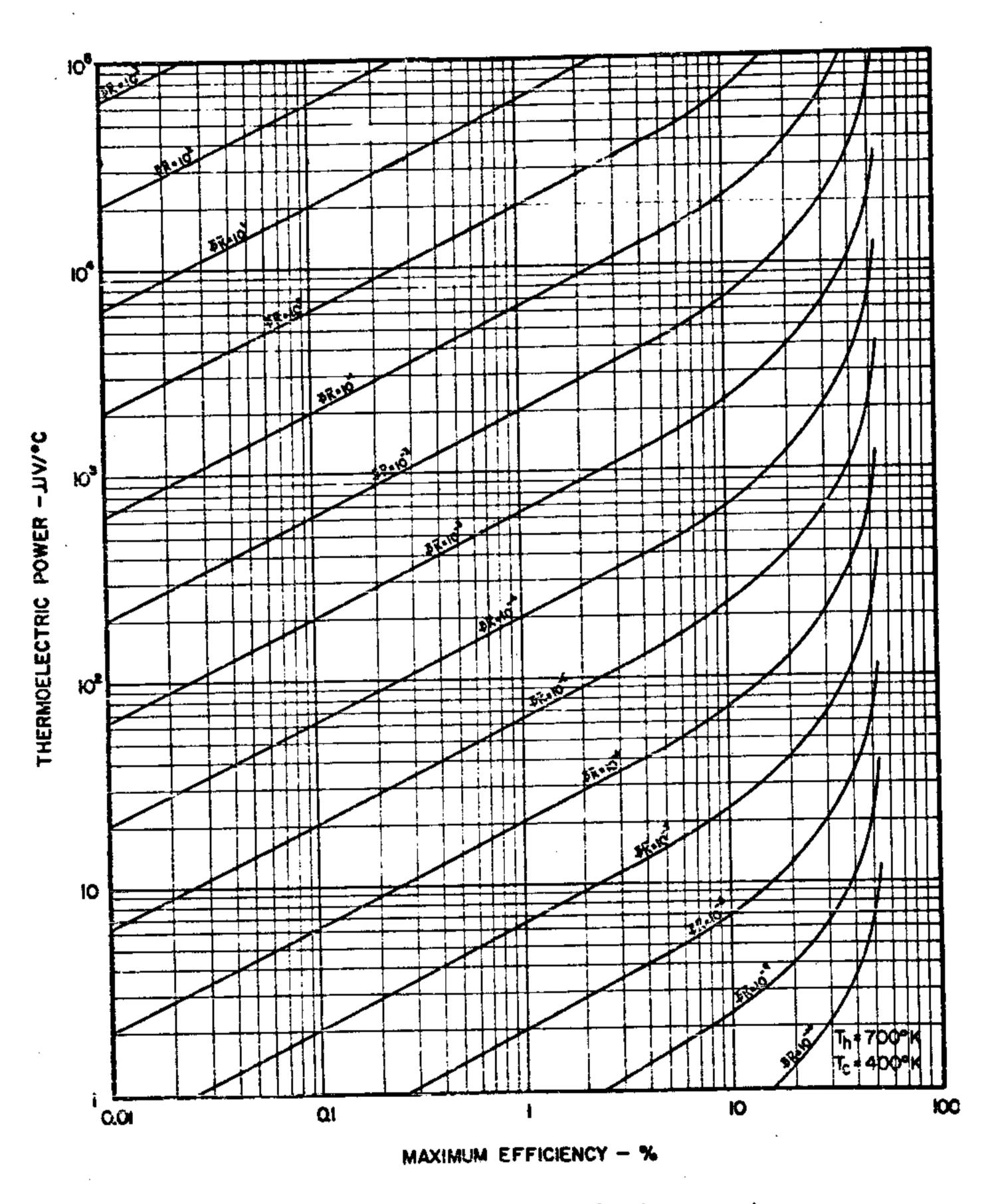


Figure I-3 Relation between parameters of a thermocouple.

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TABLE I-2
INFORMATION SOURCES

Information Source	Watts Output	Cu ft. Per wait	Lbs. Per watt	Page No. in Armour Report	
Electrical Review Volume. 22. March 1886. p. 332	120	0.100	5.00	118	
Electronics Volume 19. May 1946 pp. 196-202	5	0.065	2.25	127	
Electrical Engineer Vol. 19. May 1895 pp. 383-385	275	0.0067	2.90	121	
Electrical World Vol. 29. May 1897 p. 630	10.4	0.0141	1.92	134	
Electrical World Vol. 64. August 1914. p. 385	933	0.027	4.28	136	
U. S. Patent 1,618,744	5	0.200	3 00	153	
U. S. Patent 1,667,142	18	0.055	2.78	154	

PART II

CONVERSION FROM CHEMICAL ENERGY TO ELECTRICAL ENERGY

ION PERMEABLE MEMERANES

THEORY OF OPERATION

Even before the turn of the century, it was known that in Diological processes some membranes permit the passage of ions of only one sign. The fact that such membranes would be useful in studying natural phenomena and synthetic processes was recognized, and some investigators fabricated artificial membranes which were selective to ions of one sign; several different materials were used, including cellulose and collodion. These membranes could be treated potentiometrically when separating solutions of different activities, but they had the common characteristic of offering high resistance to current flow. Continued research with membranes coupled with the development of efficient granular ion exchange resins and tough organic polymers supplied the information needed to fabricate very durable membranes of high electrical conductivity.

The membranes to be used in this project are commercially available Amberplex C-1 cation permeable membrane and Amberplex A-1 anion permeable membrane manufactured by Rohm and Haas Company, Philadelphia. If other commercially available membranes more suited to the purpose are found in the future, they too will be employed. Amberplex membranes possess excellent mechanical durability; below 95°C they are highly resistant to concentrated solutions of acids, bases and salts and to most common organic solvents; their conductivity is comparable to 0.01 --0.1 normal aqueous solutions of strong electrolytes, which permits passage of enough electrons and ions to be of practical value. The membranes are similar to granular ion exchange resins except that the former are in sheet form. The structure of the membranes is a three-dimensional network of an insoluble organic polymer. Their reactivity comes from active groups bound into the polymer. These groups are free to ionize and take part in ordinary ion-exchange reactions. Cation permeable membranes have reactive acidic groups which ionize to leave negative charges attached to the polymer; anion permeable membranes have basic groups which ionize, leaving positive charges on the polymer. In the interstices of the polymer there is water; cation permeable membranes are capable of exchanging any cations which may be in this interstitial water. It is evident that the mechanism of electrical conductivity is similiar to that in aqueous solutions of electrolytes, i. e., by mobile ions. Random passages exist through the membranes, and in the ideal case the passages are just wide enough to permit ions to pass through

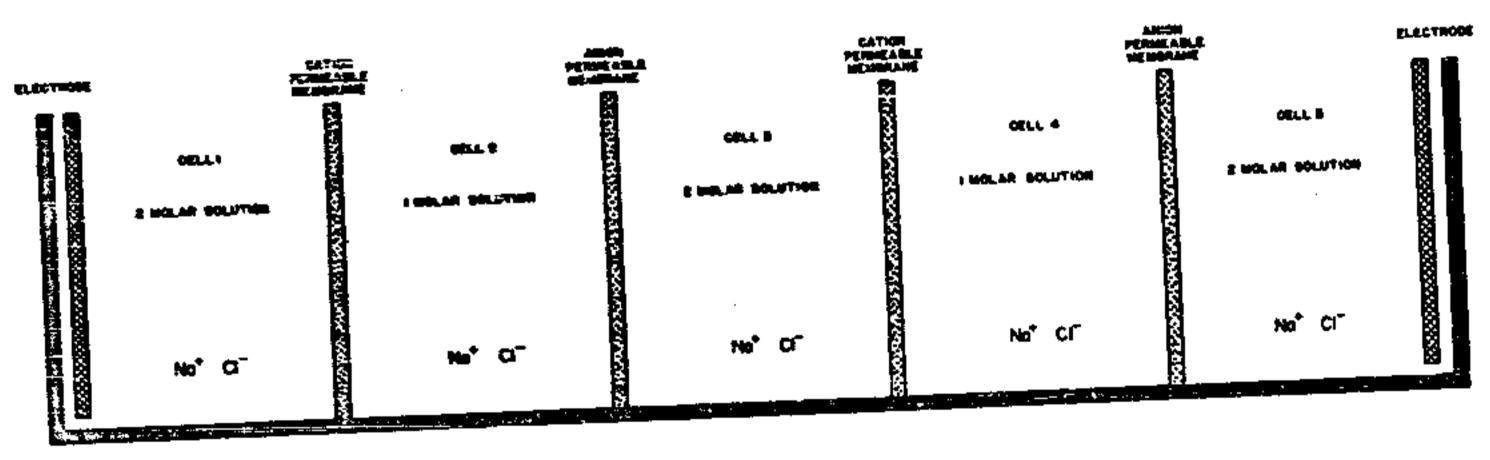
Meyer, K. H. and Sievers, J. F. Helv. Chim Acta. Vol. 19, 1936, pp. 649, 665, 963.

² Sollmer, K. J. Electrochem Soc. Vol. 97, 1950 p. 139C.

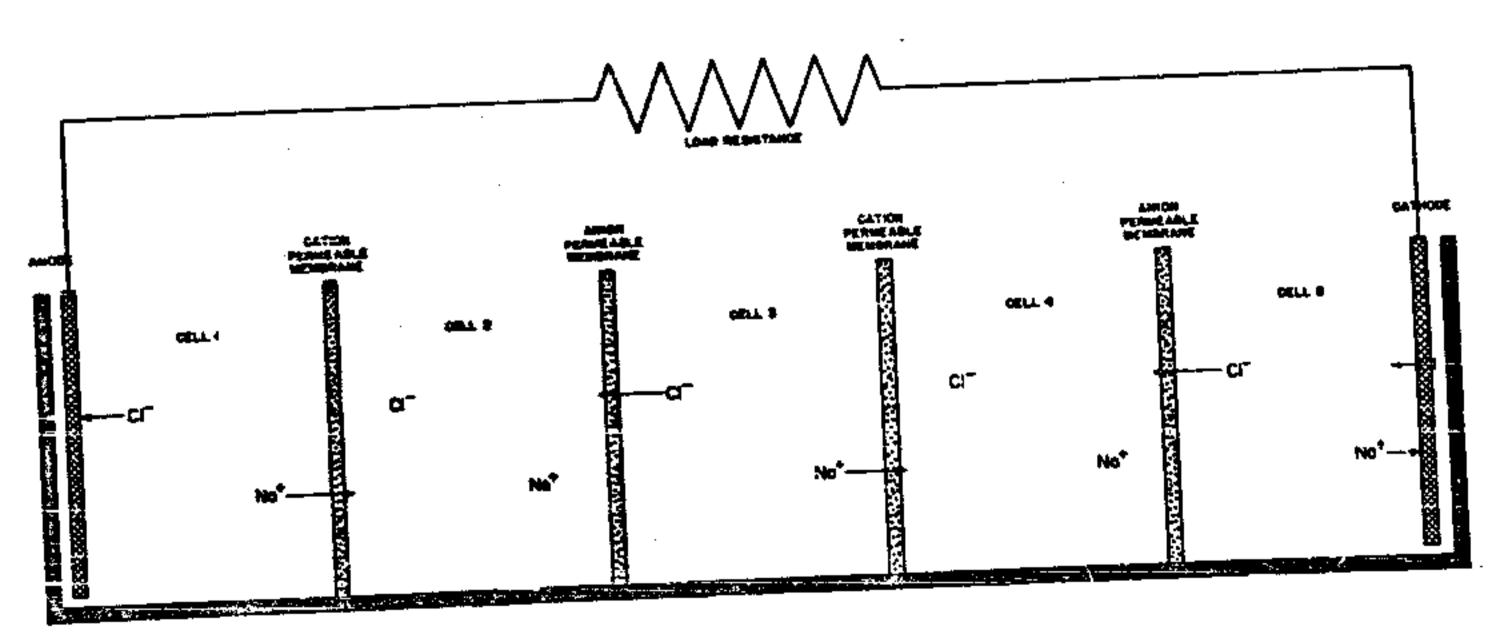
Juda, W. Rosenberg, N. W., Marinsky, J. A. and Kaspar, A. A. J.A.C.S. Vol. 74. 1952. p. 3736.

^{4.} Winger, A. G., Bodamer, G. W., Kumin, R. J. Electrochem Soc. Volume 100. 1953. p. 178.

only by displacing some of the ions on the groups lining the passages. The selective permeability or permselectivity of a membrane is the preferential transfer by the membrane of ions of a given sign. The permselectivity of the membrane approaches the ideal case in dilute solutions, i.e., about 98% from approximately 0.03 molar solutions. As the concentrations of the surrounding solutions increase, the permselectivity decreases. This means that an increasing fraction of the current is carried by ions of the same sign as the attached charges in the membrane. It seems necessary to use solutions of greater concentration that 0.03 molar in a battery in order for it to have the low internal resistance which permits satisfactory current withdrawal. The internal resistance which permits satisfactory current withdrawal. The permselectivity of a membrane separating 1 molar and 2 molar solutions is about 65%. The 1 molar and 2 molar solutions have high conductance, and the 65% permselectivity indicates theoretical ampere efficiency of 65%. These values may be suitable for a battery.



(a) Charged Battery.



(b) Operation Curing Discharge.

Figure II-1. Battery operation using NaCl as electrolyte WADC TR 54-409

The proposed battery is essentially a series of concentration cells with transference. A potential occurs across each membrane because of difference in concentrations of the two solutions which the membrane separates. Electrodes from these cells need be reversible to only one ion. After consideration of several reversible electrodes, the silversilver chloride electrode and the calomel electrode, which are reversible to chloride ion, were chosen as suitable for this work. Therefore, the electrolyte may be any which contains chloride ion. The sodium ions diffuse through the cation permeable membranes from higher to lower concentration. Chloride ions diffuse through the anion permeable membranes causes the left sides of the cation permeable membranes to become positive with respect to the right sides, and the right sides of the anion permeable membranes to become negative with respect to the left sides. The total effect is, that the left sides of all the membranes become positive with respect to the right sides. Of course, the solutions in all cells must remain electrically neutral. This neutrality is maintained by diffusion of equal numbers of sodium and chloride ions into cells 2 and 4 from cells 1, 3 and 5; as sodium ions leave cell 1, chloride ions are removed from solution by chloride ions from the cathode. The operation continues until the solutions in all cells are of equal concentration.

The battery can be recharged as in an ordinary storage battery, or it can be recharged by removing the spent solutions and replacing them with new solutions. If the latter procedure is followed, the more concentrated solutions are put into the cells formerly occupied by less concentrated solutions, and vice versa, i. e., the more concentrated solutions are put into cells 2 and 4, and the less concentrated solutions are put into cells 1, 3 and 5. This method is used because during the previous discharge the anode in cell 1 gained chloride ions while the electrode in cell 5 lost the same number of chloride ions. So, when the battery is discharged again, the polarity of the cell should be reversed to prevent the electrode in cell 5 from becoming short of chloride ions. The method just given should prevent either electrode from becoming spent.

MEMBRANE FOTENTIAL Expressions have been derived for the potential across a membrane. 1,2,3 For perfectly permselective membranes separating dilute solutions, the potential is given by the Nernst Potential expression

$$E = \frac{RT}{nF} \cdot \ln\left(\frac{a_2}{a_1}\right) \tag{1}$$

where

Servery of

R = the gas constant T = absolute temperature

F = Faraday

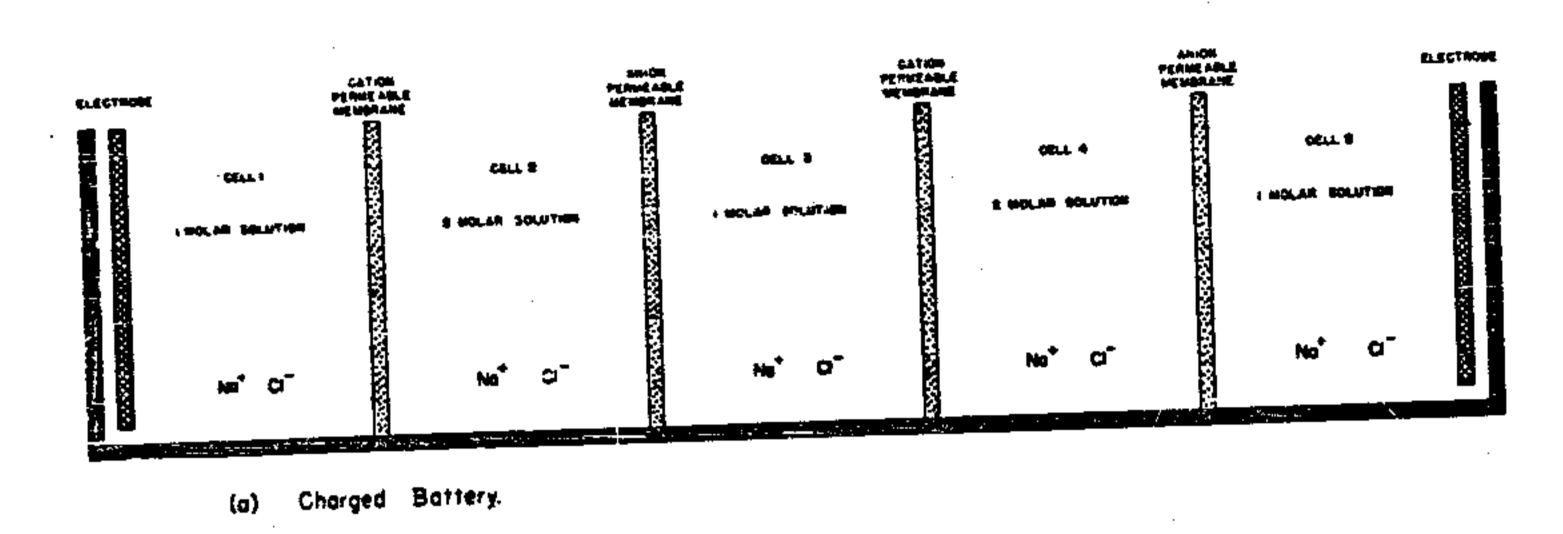
 a_1 and a_2 = activities of the solutions.

Meyer, K. H. and Sievers, J. F. loc.cit.

Teorell, T. Proc. Nat'l Acad. Sci.U.S. Vol. 21, 1935,p. 152.

Rohm and Haas Co. Amberplex Ion Permeable Membranes. Phil.1952,p. 32.

II-3



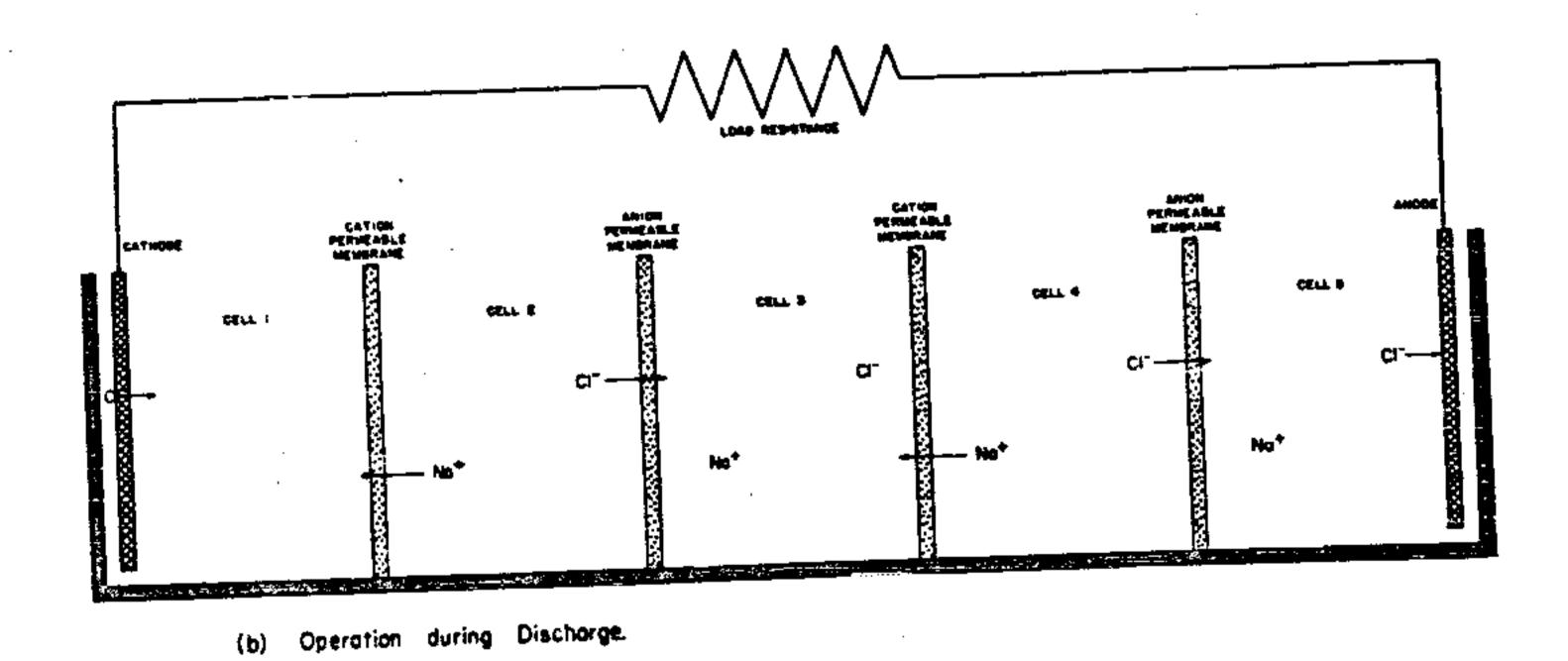


Figure II-2. Battery recharged by replacing Solutions

ADO IR 54-409

For a membrane separating solutions which have large concentrations of ions compared to the fixed ion concentration of the membrane (and at present this seems to be the necessary condition to give a battery minimum internal resistance), the potential is the diffusion potential between two electrolytes;

$$E = (t^{+} - t^{-}) \frac{RT}{nF} - \ln(\frac{a_2}{a_1})$$
 (2)

where

t and t are the average transport numbers of cation and anion, respectively, in the solutions.

The electrodes in contact with solution do not contribute to the total E because they are both of the same type; the effect of each is cancelled by the other. The resistance of the electrodes are not known, so it is impossible to approximate the internal resistance of the battery; the resistance must be obtained by experiment.

CURRENT STATUS Preparations are being made for laboratory evaluation of the battery.

PROJECTED STATUS By using equation (2) in the Theory of Operation, it is possible to calculate the approximate voltage per membrane in a battery. This is done for sodium chloride solution. It was impossible to find in the available literature all the values for equation (2) at the desired temperature, 25°C, so the calculation was made by using some approximations. The membrane separates solutions of 1 molar and 2 molar; the average of these is 1.5 molar; therefore, values of t and t at 1.5 molar should be used. These values were not found in the available literature, but they were found for 1.2 molar solutions at 25°C. Since the change in transport numbers for a small change in concentration is not critical to this case, the values of 1.2 molar solution were used. The molar activities at 25°C were obtained by converting the corresponding molal activities², using the densities of 1 and 2 molal solutions. These densities were interpolated from the values given for 20° and 30°C. At 25°C then, per cell,

$$E = (t^{+} - t^{-}) \frac{RT}{\eta E} \cdot ln(\frac{\alpha_{z}}{\alpha_{i}})$$

$$= (0.383 - 0.617) \cdot \frac{(8.314)(298)}{96,500} (2.303) log_{(2)}(0.669)$$

= 4.4 millivolts.

Washburn and Millard, J.A.C.S. Volume 37. 1915 p. 694.
Robinson and Harned. Chem. Rev. Volume 28. 1941, p. 419.

RECOMMENDATIONS The possibility that concentration cells which utilize ion permeable membranes may be useful as a source of power is worthy of investigation. Voltage can be increased by, (a) increase in temperature, (b) use of an electrolyte with greater activity and/or greater difference between transport numbers, and (c) using many membranes in the same battery.

H-6

FUEL CELLS

For many years, investigators have been attracted to the problem of converting the energy of fuels directly to electrical energy without passing through the intermediate thermal and mechanical stages. Interest in the problem has remained active. Much of the early work was concerned with the direct use of some solid fuel, usually carbon. In this case, the chemical reaction and its accompanying free energy change can be written thus:

To obtain the energy of this reaction by the electrochemical reaction of carbon and oxygen, these elements must function as the electrodes in a cell and each must acquire a charge, either by sending ions into the electrolyte or by the discharge of ions from the electrolyte. In the first case, positive carbon ions migrate into the electrolyte leaving the carbon electrode negatively charged, or anodic. The oxygen likewise must release negative ions to the electrolyte leaving the electrode positive or cathodic. Unfortunately, however, carbon and oxygen ionize in this manner only under special conditions, if at all. The second process, the discharge of ions from the electrolyte does occur though slowly. This type of fuel cell had much appeal to the early investigators because of its direct approach. These cells are evident in the literature in many variations; operating either at ordinary temperatures with aqueous electrolytes, or at elevated temperatures using fused electrolytes or aqueous electrolytes under pressure. Platinum, iron, nickel, silver, copper, and oxides were employed as cathode materials, but the potentials of the electrodes were never studied independently to determine whether low reactivity at the carbon or at the oxygen electrode was the limiting factor. Some early cells of this type were reported to operate with over 80% of the theoretical efficiency, and up to one ampere per cubic inch of volume at one volt potential. None of the other papers report so great an output per unit volume as this, hough another cell reportedly delivered 470 watts per cubic meter. 4 Many report voltages on the order of 0.8 to 1.2.

Because of the sluggish kinetic behavior of carbon as a solid anode, investigation of this "direct" type of cell has, in recent years, been abandoned for the more promising "indirect" type. These "indirect" cells

¹ E. Baur and J. Tobler, Z. Elektrochem., 39, 169-80 (1933).

Anon, Z. Elektrochem., L, 129-136, 165-171 (1897).

Jacques, W. W., Harpers Magazine, 94, 144-50 (1896-7).

Baur, E. Treadwell, W. D., and Trumpler, G., Z. Elektrochem., 27

are those which operate by use of the gaseous reaction products of carbon and oxygen. They offer three distinct advantages over the type previously discussed, namely; (1) improved kinetic behavior, (2) no accumulation of inorganic impurities such as are present in the ash of solid commercial fuels, and (3) by proper design they can be made continuously regenerative and serve as a constant source of power without need of renewing electrodes, recharging, or other shut-down. One consideration must be kept in mind when choosing the reaction by which the reaction product is made. It must be one in which a significant amount of free energy change takes place in the cell for high efficiency. If, for instance, the cell were to operate on carbon monoxide, the reaction would be, $CO + \frac{1}{2}O_2 \rightarrow CO_2$, and free energy change at 25°C, would be -61,750 calories. Thus, even at 100 percent operating efficiency, only 65.5% of the energy in the original carbon could be recovered. In a cell which operates on 50_9 in this manner, $50_9 + \frac{1}{2}0_2 - 50_3$ being reduced again to sulfur dioxide by carbon to maintain the operation only 34.5% of the original energy in the carbon can be recovered as electrical energy. A more promising possibility, from the thermodynamic standpoint, is a cell operating on "water gas" by the equation; $CO + H_2 + O_2 \rightarrow CO_2 + H_2O$, for which the free energy change is -116,000 calories at room temperature. This is the fuel used by some of the more recently patented cells, one of which will be described later. The earliest cells, operating on gaseous reaction products, used two electrodes of spongy, porous, or perforated platinum saturated with hydrogen for the anode, and oxygen for the cathode. Many patents exist on the early designs. The cell of Mond and Langer used perforated platinum sheets covered with platinum black to increase reactivity, produced from 1.45 to 1.82 watts per 700 sq. centimeters of active surface. Currents of 2. to 2.5 amperes at 0.73 volts could be drawn from this cell. Others studied showed the effect of pressure on the capacity of hydrogen electrodes of spongy platinum, gold and palladium. At 580 atmospheres, the capacity of spongy platinum was estimated to be 56 ampere hours per kilogram. Only this year, encouraging results have been reported from a hydrogenoxygen cell using gintered porous nickel electrodes operating at 240° F and 800 lb./sq.in. Open circuit voltage was 1.05, dropping to 0.9 volt at a current density of 151 amp/sq.ft., and 0.6 volts at 1000 ampere per square foot output.

Attempts to utilize carbon monoxide in cells at room temperature have all failed, and a large number of cells have been proposed to operate in the 500 to 1,000°C range to increase the electromotive activation of not only carbon monoxide but hydrogen as well. Various

WADC: TR Sh-h09

Mond, L., and Langer, C., Proc. Roy. Soc. (Lendon), 46, 296-308(1889)
 Cailletet, L., and Collardeau, E., Compt. Rend., 119,830-4 (1894).

³ Bacon, F. T., BEAMA J. 61, 6-12 (1954); CA 48:5678 (1954).

Contrails

9

reports on the success of these cells run from 0.2 to 1.0 amp/sq decimeter for the current density.

Since the time of the earliest cells, it has been established that at ordinary pressures, activation takes place only at dry solid surfaces he cause of the general tendency of liquids to displace absorbed gases from the activation surface. Many devices have been proposed to avoid this difficulty with varying degrees of success. Schwid's Diffusiongaselektrode, where the gas is introduced from the inside of a porcus electrode with sufficient pressure to prevent entrance of the electrolyte, proved successful for a time with considerable improvement in current output, but it would finally wet and become inactive. Electrode coatings of gelatinous materials, paraffin, resins, and laquers, were all tried in order to allow gas flow in one direction without return flow of the electrolyte. One recent and promising solution to this dilemma comes from Baur and his coworkers. 2,3 He proposed a cell operating at high temperatures with a solid electrolyte. One such cell is pictured in Figure II-3, the operating characteristics of five cells in series in Figure 11-4. This type of cell and its electrolyte are the subject of several patents, some of which claim efficiencies of 60 to 75%4. The operating temperature is from 1200 to 1850°F, and the output was reported to be as high as 10 watts per liter of volume on the original cell but only 0.77 watt per liter on a large model.

The electrode tubes have a wall thickness of 1 mm and present a resistance of 2 ohms per 20 square centimeters of conducting area at the operating temperature. This electrolyte is composed of a mixture of WO3, CeO2, plastic clay and oxides of heavy metals, such as Mn, Cr, Fe, Ni, and Co. The quantity of these metal oxides should be kept low. The reactions which occur at the electrodes to produce current can be represented:

Positive electrode (cathode).

Negative electrode (anode).

$$Fe + 0^2 \longrightarrow FeO + 2e$$

1 Schmid, A., Jelv. Chi. Acta. 7, 370-3 (1942).
2 Baur, E., and Preis, H., Z. Elektrochem., 43, 727-32 (1937).

Baur, E., and Preis, H. Ibid. 44, 695-8 (1938).

Gorin, E., U. S. Pat. 2,581,650 (1952).

Baur, E., Ger. Pat. 713,570 (1941).

Contrails

And the regeneration reactions which go on at the same time are:

Positive electrode (cathode).

Negative electrode (anode).

The reaction at the cathode or air electrode, has always been a point of concern to workers in this field, and it is generally thought that the most serious difficulties in the achievement of a successful fuel cell are encountered at the oxygen electrode. This is because gaseous oxygen establishes its potential sluggishly at best on inert electrodes at ordinary temperatures and polarizes at once if there is any appreciable current drain.

Fuel cells operating on dissolved reaction products and on solid reaction products of carbon have many examples in the literature, but they are usually quite involved and almost without exception of very low efficiency.

The cell described here differs from the thermal battery type cell in that this cell can operate continuously and utilizes the ionized gases of combustion reacting with a solid electrolyte instead of the combustion of the electrolyte.

RECOMMENDATIONS It is felt that the data on this process indicates sufficient promise to make a continued investigation practical. The construction of a laboratory model should yield some of the data required to formulate better conclusions pertaining to the capabilities of the process. It is recommended that further activity be directed toward examining the capabilities of the fuel cell phenomena as a possible source of electrical power.

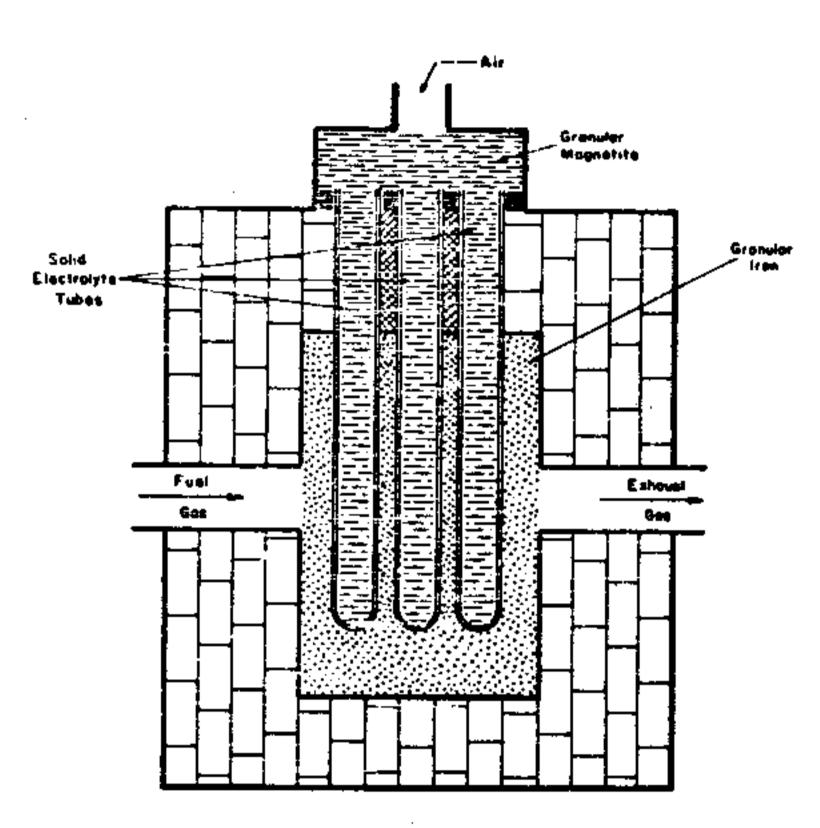


Figure II-3 Bour's cell with solid electrolyte.

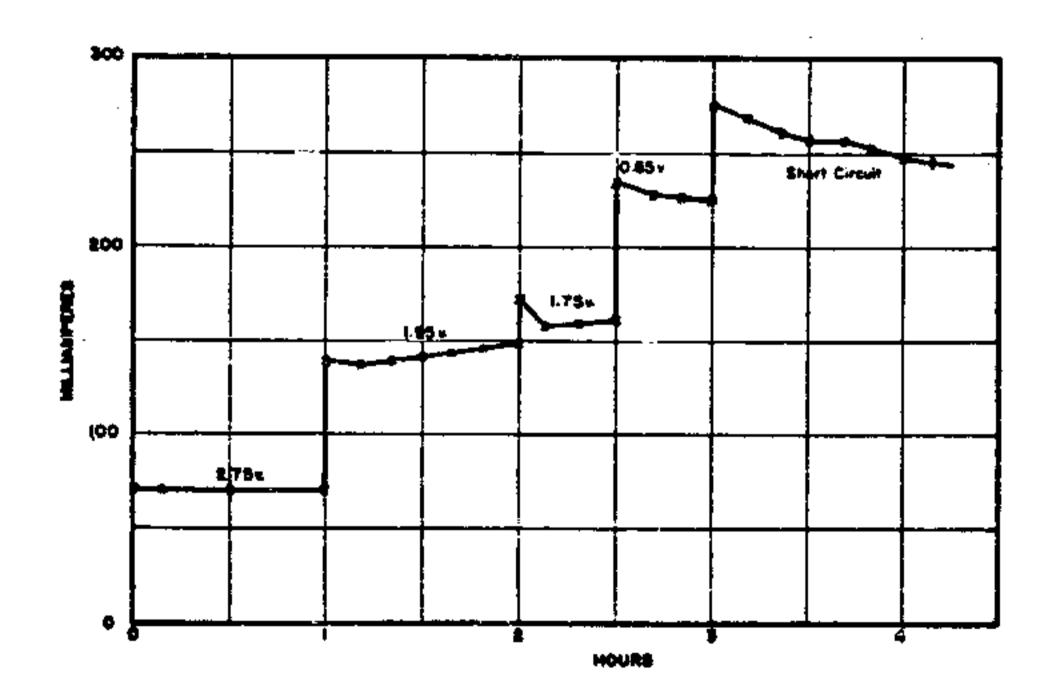


Figure II—4 Characteristics of solid-electrolytic cell under load.²

Baur, E., and Preis, H. Elektrochem., 44, 695-8 (1938).
 Baur, E., and Preis, H. Ibid., 43, 727-32 (1937).

PART III

CONVERSION FROM MECHANICAL ENERGY TO ELECTRICAL ENERGY

OSCILLATING ELECTROMAGNETIC INDUCTION

The fundamental principle of operation for the generation of power by oscillating electromagnetic induction is that of varying the magnetic flux lines linking a coil. This variation in flux linkages may be accomplished by either moving the coil in a magnetic field as shown schematically in Figure III-1, or by varying the reluctance of a magnetic circuit containing the coil as shown in Figure III-2. Two devices in common usage that utilize oscillating electromagnetic induction for the conversion from mechanical energy to electrical energy are the reluctance phonograph pickup and the sound powered in Figure III-1.

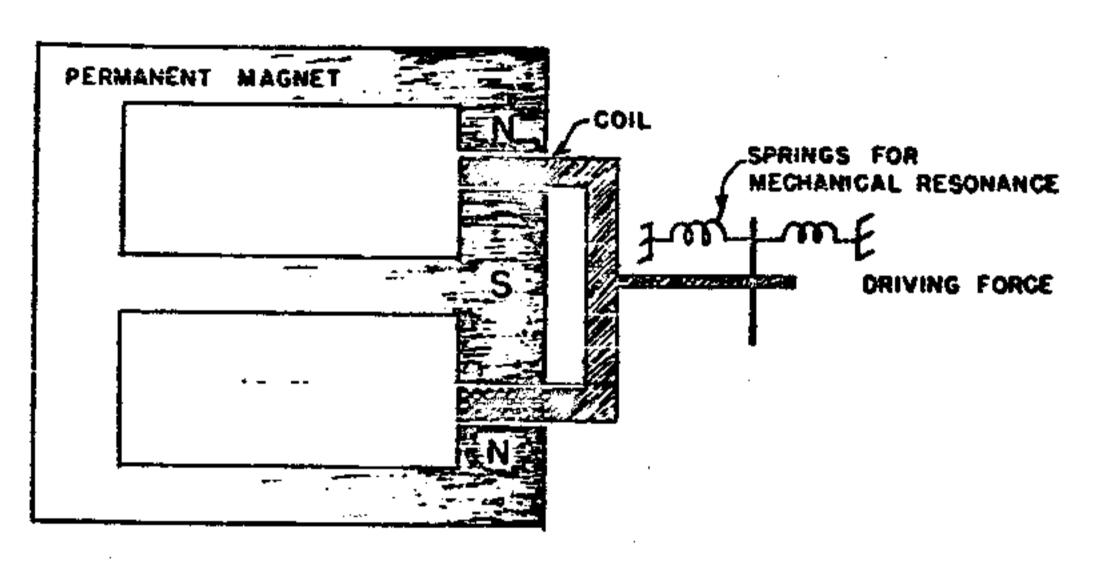


Figure III-1 Moving Coil Oscillating Electromagnetic Induction

where

G = BlA

e is expressed in volts

B is in Webers per square meter

 $\bar{\boldsymbol{\ell}}$ is in meters

y is in meters per second.

If, for example, B is 0.5 Webers/sq. meter, $\mathcal L$ is 30 meters, and ν is 1sin ω t then

 $ext{C} = (0.5)(30)(1 \sin \omega t) = 15 \sin \omega t$.

Thus for a current of 1 ampere the power could be about 10 watts/coil. The electrical losses are I'R and the mechanical losses would be the friction and windage of the coil assembly. The amount of driving power required can be reduced by using mechanical springs to resonate with the mass of the coil assembly at the desired operating frequency. The

III-1

inherent characteristics of such an assembly will limit the frequency of operation to low values.

The device shown in Figure III-2 will

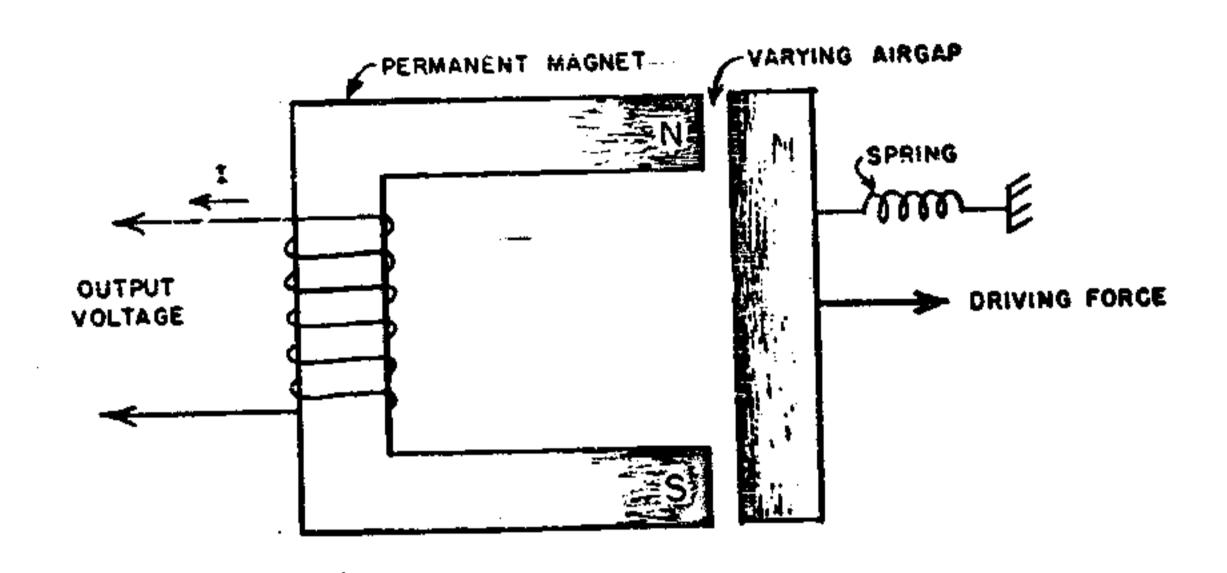


Figure III-2 Variable Reluctance Oscillating Electromagnetic Induction

have a voltage generated that is $e = n \frac{d\phi}{dt}$ where e is in voltage generated that is $e = n \frac{d\phi}{dt}$ is the rate of change of where e is in volts, 7.5 x 10^{-2} webers/second, then $e^{2} = (200)(7.5)(10^{-2}) = 15$ volts/coil, or if obtained by simple harmonic motion, the power output for a current of 1 ampere would be of the order of 10 watts. The electrical losses for a generator of this type would include hysteresis and eddy current losses due to changing flux densities as well as I'R losses in the coil itself. The mechanical losses are again dependent upon the windage and friction of the moving element. The load coupling is accomplished through the variation in flux density and the resultant variation in pull on the oscillating element. This element has an advantage over the oscillating coil in that a greater number of turns may be used without adding mass to the moving element. The disadvantage with respect to the moving coil, is that the varying flux density introduces magnetic losses and also results in a larger harmonic content in the output voltage.

The mechanical considerations make oscillating electromagnetic induction inherently a low frequency device. The output per unit weight and volume should compare favorably with rotating machinery of the same frequency. Conversion efficiency should be in the order of 90%.

RECOMMENDATIONS: The general theoretical characteristics on this type of generating device show a favorable outlook for power generation capabilities. The lack of information concerning performance indicates a desirability of constructing a laboratory model for testing purposes.

III-2

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ELECTROSTATICS

In this investigation, the literature has been searched and a follow-up made of all sources of references in order to determine and to analyze previous work done along this line. Although the static generators have been largely replaced by batteries and magnetic generators as sources of power, they still have a place in the production of high potentials where little power or current is needed. Especially in the study of nuclear physics and the disruption of the nucleus of the atom they excell other types.

In form, the static machines vary from the ordinary ebonite rod that is stroked with fur or flannel, and the glass rod stroked with silk, to the ebonite plate with proof plane for removing charges and the static generator used for simple demonstrations in the physics lectures, in which the charge is carried from the rotating plates by points and stored in Leyden jar condensers. In the last thirty years, considerable effort and time have been spent in developing very high voltage generators for use in atomic nuclear work. The Cockroft Walton generator was the fore-runner of the Van de Graaff high voltage generator.

Massachusetts Institute of Technology has developed four of the Van de Graaff generators ranging in potential from 80,000 volts to 10,000,000 volts. The limitation on the voltage that can be generated is a function of the insulation of the surrounding materials. Much study has been made and is still being made to improve the insulation and raise its "breakdown" potential.

The static generator has advantages over other types of generators in that it is possible:

(a) to obtain strictly homogeneous beams,

(b) to focus them accurately into tubes,

(c) to eliminate stray radiation as from vacuum tubas,

(d) to use scurces to full capacity.

The power delivered by static generators is usually in the order of a few hundred milliwatts due to the low current which is in the range of 10-9 amperes.

Most electrostatic machines with sizeable output are large and bulky and cannot be moved from place to place easily.

As a summary, it can be stated that electrostatic generators

(a) have low efficiency of power conversion,(b) have large weight per unit power output,

(c) are large and bulky,

(d) have a range of voltage from a few thousand volts to ten million volts, but currents from 10-12 to 10-9 amperes,

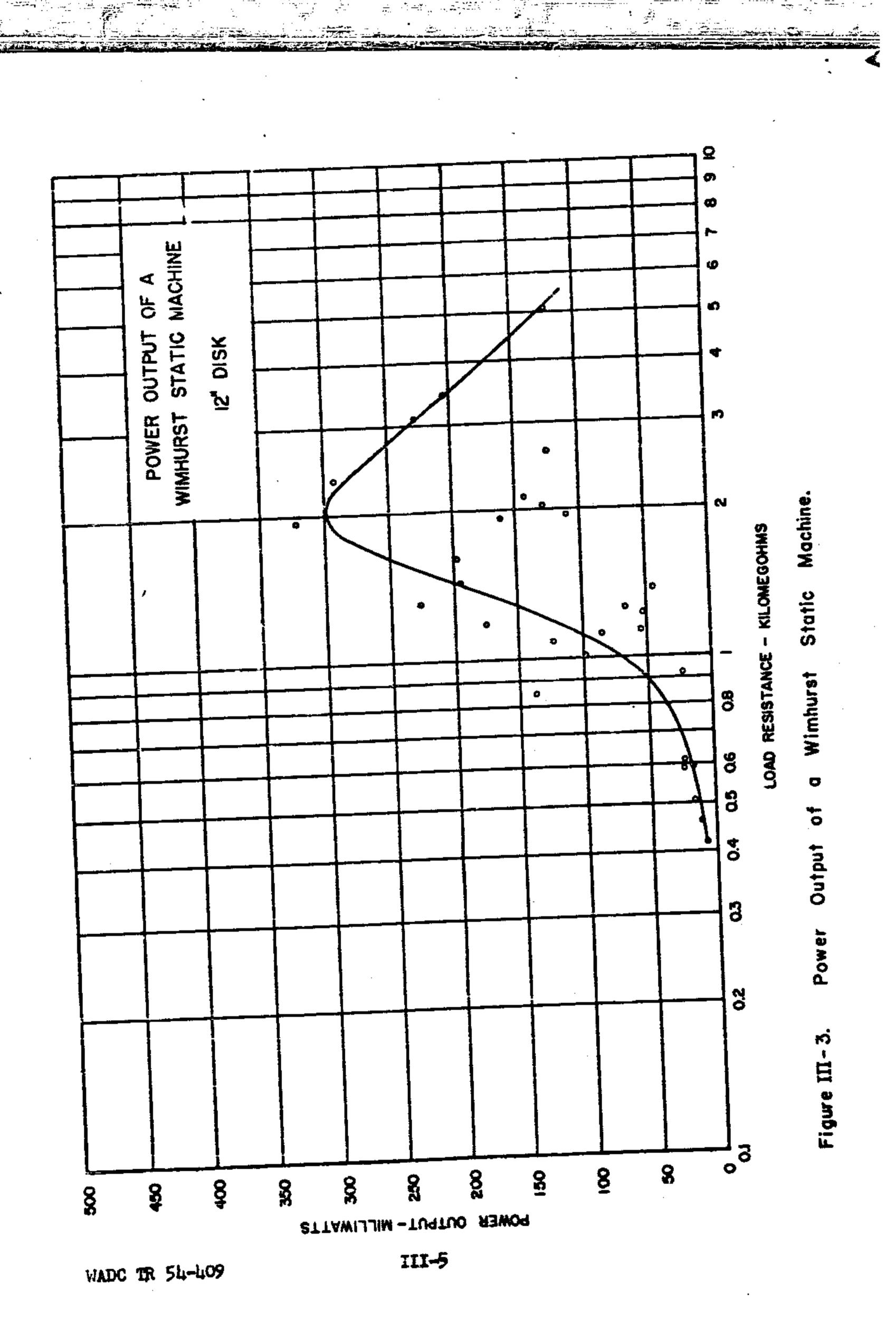
(e) have long life and are fairly reliable if protected from weather changes,

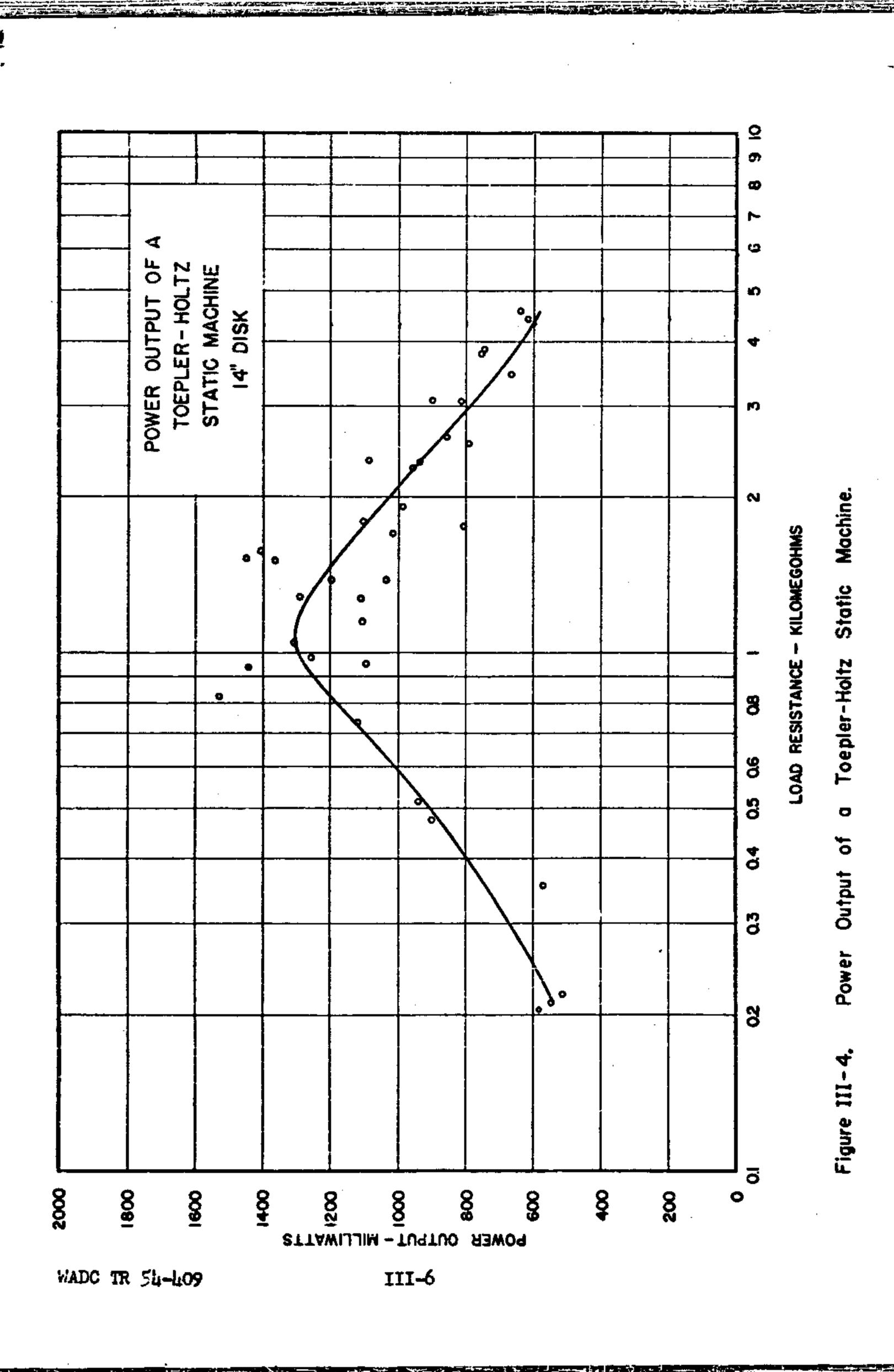
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(f) are rather cheap in construction.

In connection with this investigation a method of measuring the power output of static machines was worked out. This consisted of measuring the potential output directly with a high resistance voltmeter such as a Hewlitt Packard 410A with a high voltage probe. The load current was measured with a sensitive current galvanometer. From these measurements the load resistance and power dissipated were computed. Load resistance was obtained by coating a dielectric dowel with carbon. Humidity, of course, had a great effect on machine operation, and is presumably the cause of scattered data points on the graphs of Figures III—) and III—4.

RECOMMENDATIONS The data obtained from literature and experiment does not indicate much promise for the electrostatic devices as generators of electrical power. For this reason, it is recommended that the effort directed toward electrostatic generators be limited to the study of recent literature for possible new developments of interest.





PIEZO-ELECTRICITY

The discovery of the piezo-electric effect in certain crystalline substances was credited to Pierre Curie and his associates, though the effect was first discovered by Haüy in 1782. A number of dielectric crystalline materials, if subjected to properly oriented strain, develop electric polarization. The magnitude of this polarization potential is roughly proportional to the applied strain. The inverse of this process is notably important in certain applications and is known as electrostriction. The piezo-electric effect is closely related to the phenomena of pyro-electricity also, and is considered an indirect effect of thermal expansion or contraction of the crystal.

The most commonly used crystals displaying this effect are quartz, tourmaline and Rochelle Salt. The crystal structure must not possess a center of symmetry if it is to display piezoelectric effects. The conventional piezoelectric device consists of one or more plates cut from a crystal with electrodes attached to the plate faces. Quartz is especially suitable at rather high frequencies and displays a marked natural resonance characteristic in this range.

Quartz has a tendency to fracture at pressures in the neighborhood of 1000 atmospheres, and the potential difference developed by applied stresses is relatively low.

Rochelle salt crystals, on the other hand, develop considerably higher piezo-electric potentials under stress, and have a lower natural resonance. This makes their application in low frequency systems desirable. While the piezo-electric potential of Rochelle salt (Sodium Potassium Tartrate) are roughly proportional to the applied stress, the potential is dependent to some extent on ambient conditions and individual crystal characteristics. Thus, such factors as temperature, humidity, polarization, specimen variations, hysteresis and saturation must be considered when calculating crystal sensitivity.

Most Rochelle Salt transducers utilize a "bi-morph" principle 3,4. This method consists of cementing together two crystal plates arranged in opposition, and having electrodes cemented to the exterior opposite faces of the plates. As a direct result of this construction, the unit displays a very high equivalent internal impedance which limits the

Physical Review 17:475, 1921; 19:478, 1922; 20:639, 1922; 21:348, 1923; 24:560, 1924; 35:269, 1930.

Design of Crystal Vibrating Systems, William Fry, I. Taylor, B. Henvis (Naval Research Lab) Dover Publishers.

³ Institute of Radio Engineers 19:2022, 1931.

⁴ Electronics p. 116, May 1932.

application of the device to load circuits of correspondingly high impedance if advantage is taken of the full value of the piezo-electric potential over a band of frequencies.

Some improvement has been made in this respect, however, since it has been found that an extremely thin gold foil electrode will bond itself to the crystal surface. Using this technique, the plate may be cut much thinner than conventional construction requires and a very high capacitance results. The capacity may be evaluated according to

 $C = 0.0088 \frac{KA}{d}$

where

K is dielectric constant

A is area in sq. cm.

d is thickness in cm.

By mounting this crystal in a "monobar" mechanical system, further advantage may be taken of the actuating force, thus developing a higher piezo-electric potential under load conditions and raising the natural resonant frequency to the extreme supersonic range.

All crystals display resonance at some frequency. Thus the equivalent electrical network representing the crystal impedance may be shown as inductance, capacitance, and resistance, interconnected. The equivalent electro-mechanical resistance component dissipates very little energy at the frequency of resonance, hence the electrical equivalent circuit displays a very high Q (X for a series connection) and rather high mechanical to electrical conversion efficiency. As an electrostriction device, the conversion efficiency of the tweeter type of loud speaker is approximately 68%.

As a generator, if the crystal is operated at its resonant frequency and the equivalent electrical capacity is tuned out with a suitable inductance, the efficiency of conversion may be raised to 90%, and the amount of power developed per square centimeter of area may approach as much as 10 watts. Such generating devices require a vibrating drive mechanism and operate in the range from 10,000 to 100,000 cycles per second.

Obviously, with the crystal operating at its natural series resonant frequency, the internal impedance of the device will be quite low so that the piezo-electric potential will remain reasonably constant under varying load conditions.

Certain of the Barium Titanate crystals recently introduced will display extremely high dielectric characteristics, and since they are much more stable that Rochelle Salt with respect to high temperature and

1 Electronics, Vol. 16, April 1943, p. 88.

III-8

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Contrails

humidity effects, they may prove advantageous as a piezo-electric source of power.

RECOMMENDATIONS It is felt that the implications of new materials indicate a need to continue the investigation of the piezo-electric phenomena as a possible source of electric power.

III-9

MAGNETOSTRICTION

The magnetostrictive effect is apparent in two forms; the conversion of electrical energy to mechanical energy when a magnetostrictive material elongates or contracts upon being placed in a magnetic field, or mechanical energy is converted to electrical energy in the opposite manner by compressing or stretching magnetized material to produce an emf in an adjacent coil. Up to the present, neither of these forms have been investigated for the purpose of generating electrical power, though the former has had considerable application in producing acoustic power.

Some of the various ways in which magnetostriction transducers or generators can have their components arranged are pictured by Osborn. All of these consist of driving coils surrounding, in some manner, a magnetostrictive core. To produce accustic power, an alternating current is passed through the driving coils. This produces an alternating flux in the core which changes its dimensions, so that if the whole transducer were immersed in some fluid, it would send out acoustic waves. On the other hand, mechanical energy is transformed into electrical energy by strain of the core due to pressure waves. This produces a change of core flux which in turn induces a voltage in the driving coil.

Calculations made on the basis of laboratory measurements show that a carefully mounted transducer with proper loading exhibits well over 90% efficiency of conversion from electrical to mechanical energy. However, in practice, when mounted into an actual housing and mechanically loaded, its efficiency falls off to approximately 70%. No figures are available for the reverse phenomena.

The two materials most extensively used for transducer cores are nickel and permalloy (45% nickel - 55% iron). A comparison of their magnetostrictive effects is shown in Figure III 52, in which the solid lines show measurements of the changes in length divided by length as a function of the magnetic flux density B in gauss. The dotted lines show the strain plotted as a function of field strength H.

RECOMMENDATIONS It is not deemed advisable to perform experimentation on this device without a more adequate theoretical analysis of the operating characteristics. Since other processes show more promise, it is felt that extensive effort on magnetostriction should be deferred at this time but that literature sources should be examined for new developments.

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Osborn, J. A. Elec. Engr., 57. No. 1, 571-8 (1948).

Mason, W. P., Electromechanical Transducers and Wave Filters, 2nd

ed., p.216, D. Van Nosirand Co., Inc., New York, 1948.

McKeehan, L. W., and Cioffi, P.P. Phys. Rev., 28 No. 1,146 (1946).

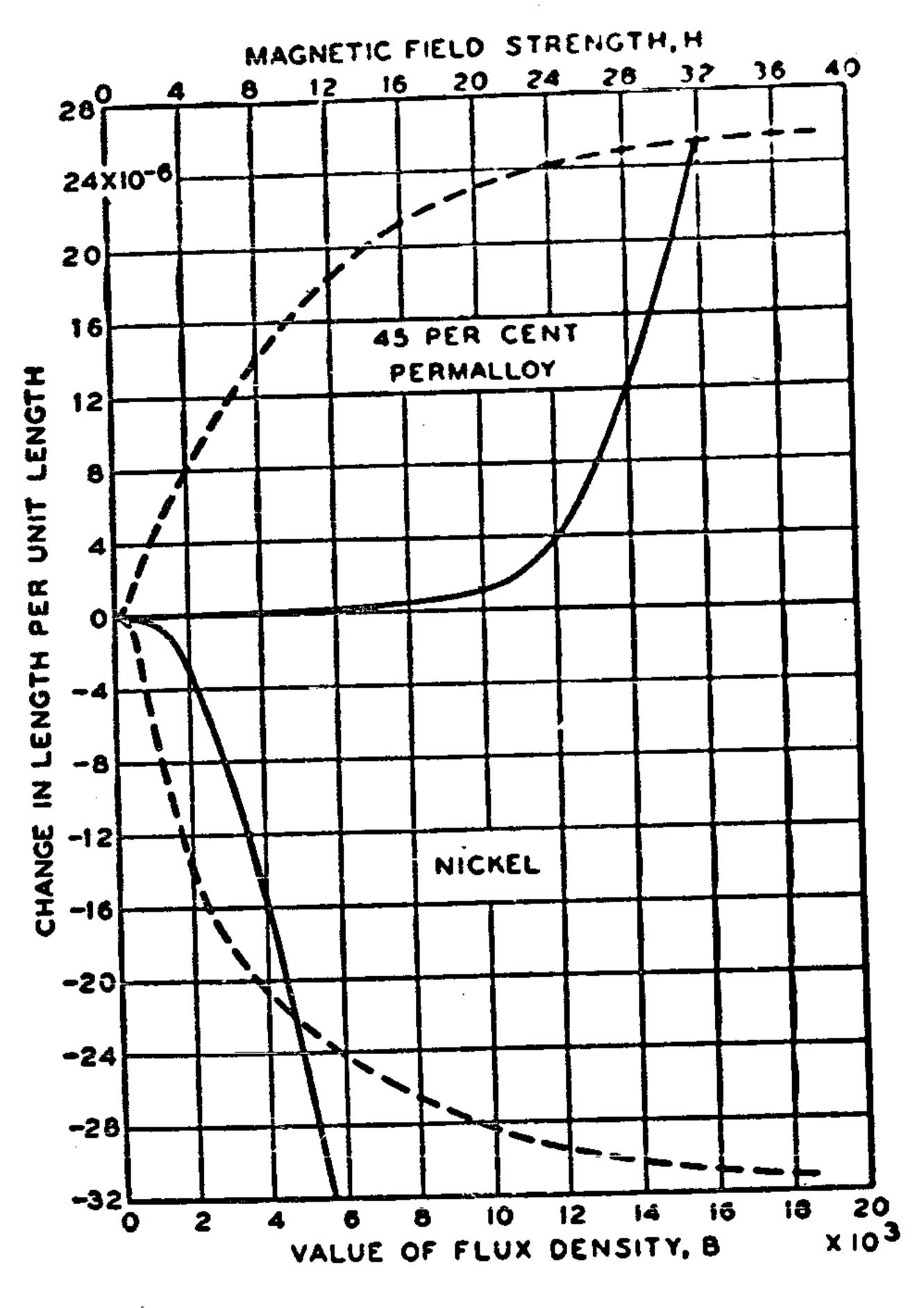


Figure III-5 Engnetostrictive Effect in Nickel and 45 % Permalloy.

III-11

ELECTROKINETIC TRANSDUCERS

Work with electrokinetic transducers started at Oklahoma A & M College in November, 1948, following the appearance of an article in "The Review of Scientific Instruments," Volume 19, Number 10. This article by Milton Williams, Humble Oil and Refining Company, Houston, Texas, can be condensed as follows: A description is given of a transducer which be condensed as follows: A description is given of a transducer which utilizes, for the transformation of sonic to electric energy, the electrotic potential developed by the movement of a fluid through a porcus kinetic potential developed by the movement of a fluid through a porcus solid. The construction and calibration of the transducer are discussed, and results of measurements of the pressure fluctuations in an oil pipe and results of measurements of the pressure fluctuations in an oil pipe line are presented. After making several experimental models, a design suitable for use as a pressure measuring device was perfected.

A similar device built at Oklahoma A & M College was found to operate very well in some respect, but discrepancies were noted between Mr. Williams's proposed method of operation and what was observed under working conditions. In the first place, the transducers are not capable of determining static pressure, i. e., it is necessary to have a change in pressure in order to have power output. This led to the insertion of a pressure in order to have power output. This led to the insertion of a SE-4 strain gage pickup and an electrokinetic transducer at the same point in a pipe line. Observation of the traces on the same time axis from oscillograph records showed that the EK transducer was recording a flow indication and not static pressure. This was further verified by observing that when a pressure wave varying sinusoidally was generated in the pipe line, the traces from the EK transducer was recording the sine wave as a cosine wave. This fact, together with difficulties of calibration, led to the discontinuance of this instrument as a pressure pickup.

Several observations made while using the EK transducer as a pressure pickup, and since that time, led the project personnel to suggest further investigation as a power producing device. As a pickup, having a diaphragm 1/16 inch thick, it was found that pressure variations in the order of 1/2 pound per square inch were detectable, and that a pressure variation of 20 pounds per square inch would give an output of 160 to variation of 20 pounds per square inch would give an output of 160 to variation of 20 pounds per square inch would give an adiaphragm 4 to 5 by the Beta Corporation, Richmond 26, Virginia, using a diaphragm 4 to 5 times as large, gives data showing an output of 325 m.v. per pound per square inch. If this instrument were subjected to a 50 psi pressure variation, one could expect some 16.250 volts output at the frequency of the pressure variation.

Mr. Claude E. Cooke, graduate student at the University of Texas, while working with porous plugs and observing the voltages due to sinusoidal pressure variations, gave a report at the 195h Austin meeting of The American Physical Society. Mr. Cooke, using a plug la in diameter and la long, obtained outputs as high as 300 volts (r.m.s.) from pressure and la long, obtained outputs as high as 300 volts (r.m.s.) (0.1448 lbs/in²) variations in the order of 10,000 dynes per Cm² (r.m.s.) (0.1448 lbs/in²)

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The work done at Oklahoma A & M College and by Mr. Williams has been concerned only with potential generation. The internal impedance of the EK transducer, using pyrex glass and distilled water, was seemingly between 90 and 100 thousand ohms. Impedances necessary to give maximum potential output would not be the proper match for maximum power output. Mr. Cooke arrived at the following equations relating E, I, V, and P:

$$I = C_{11}E + C_{12}P$$

 $V = C_{21}E + C_{22}P$

where I and V are electric current and volume flow rate, and E and P are the electric potential difference and the pressure difference across a porous medium. The constants C_{11} , C_{12} , C_{21} , and C_{22} , are constants from electrokinetic phenomena. $C_{11} = I/E$, $C_{22} = V/P$, $C_{12} = C_{21} = 0.056$ to 0.060 at 20 cps for pyrex glass and water. Mr. Cooke, while adhering to the streaming potential theory, found that the output in volts from the cells decreased at some high frequency. However, the finer the porosity of the plugs, the higher the frequency before the potential approached zero.

At Oklahoma A & M College³, using fine porosity discs, these transducers have been driven to as high as 100 K.C.; in fact, a solid thin pyrex diaphragm has been substituted for the porous disc and appreciable output still observed. This has prompted the questioning of the validity of the assumption that flow is actually taking place through the porous medium when the frequency becomes high. Without final verification, it is proposed that the output is some function of a pressure wave as it traverses the combination of electrodes and porous disc. In fact, a statement of the proposed method action can be summed up as follows:

From Creighton and Koehlers Electro-Chemistry, it is found that when two heterogeneous substances are brought into contact, the one having the higher dielectric constant will, in general, assume a positive charge with respect to the other, this being accounted for by the shape of the potential boxes between the electrodes, diaphragm and electrolyte. In the case of the transducer, there are two metallic electrodes inside a glass tube with a fritted disc between them. When filled with water, the higher dielectric constant of the water with respect to the pyrex glass, causes the water to assume a positive charge. The potential boxes

Norton, J. R. A Theoretical Study of the Electrokinetic Transducer, A Master's Thesis, Oklahoma A & M College, 1951.

Cooke, Claude E. Electrokinetic Transducer, A doctorial dissertation
The University of Texas, 1954.

Norton, J. R. "Test Data on Electrokinetic Transducer" unpublished data from experimental tests, Oklahoma A & M College, 1952.

Creighton, H. Germain, "Principle and Application of Electrochemistry"
Volume 1, McGraw-Hill, p. 114.

between the electrodes and water, and the water and the fritted disc, cause an abundance of positive ions whose mobilities are in excess of the ordinary positive ion mobility because of the influence of the potential system.

The theory of transducer operation as proposed by Professor Nortonia as follows:

"In a system consisting of metallic electrodes contained in a glass tube filled with water, the electrodes and the water present to the positive ions from the metal and glass overlapping potential boxes whose effect is the lowering of the potential barrier allowing mutual transition of ions until a condition by mechanical agitation, or variable pressure, results in an excess of positive ions in one potential box which gives rise to a potential difference between the electrode and the water. The superposition of the fritted disc between the electrodes is somewhat similar to the heating of the filament of a vacuum tube. This disc becomes a source of a concentration of positive ions which presents a field to the water electrode potential boxes such as to cause a further lowering of the potential boundary and hence a greater mobility for ionic transmission." It has been found that by the use of this potential box theory, all of the observed phenomena can be explained. It has not been attempted to determine the size and shape of the potential boxes, without which it is impossible to determine quantitatively what the output should be.

DESCRIPTION OF APPARATUS

The transducer used in these tests was constructed in the Research Apparatus Development Laboratory and consisted of a 50 mm course porosity fritted disc inserted in a 55 mm glass tube. Two tungsten electrodes were welded into the glass tube and brazed to two copper screens in contact with each side of the fritted disc. The 50 mm tube was fitted with a rubber stopper having a short length of approximately 6 mm glass tubing inserted therein. By use of a short hose connection, this apparatus was subjected to variable pressure obtained from a cylinder and piston as shown in the accompanying photograph of Figure III-6. There are no valves in the cylinder and piston combination, so the pressure wave is free to travel from the piston face into the transducer, being affected only be the impedances of the various materials and changing cross sections. (See sketch of Figure III-7).

RESULTS OF TEST

Setting the piston travel for 0.25", the data represented by the curves on Figure III-8 was obtained by varying the load resistance with the valve between the cylinder and auxiliary supply being closed.

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In order to determine the pressure variation applied to the transducer, a pressure pickup was inserted between the cylinder and the transducer. The voltage applied to the pickup was sufficient to produce 0.1" deflection of the oscilloscope beam for 5#/sq.in.pressure variation. The curves of Figure III-9 represent the data obtained from this setup. From the graphs, it is evident that the omission of the separating diaphragm, used in the pressure pickups, allows considerable resonant conditions to exist. At 10 and 30 cps, identical power outputs were obtained with a pressure ratio of 10 to 1. Acoustical resonance existed in the $21\frac{1}{2}$ to 22 cps range as is evident from the pressure increase of 2 to 1. It is interesting to note that the internal impedance of this unit was approximately 40,000 chas which corresponds very closely with the measured D. C. resistance. Previous cells have usually had a D. C. resistance in the range from 80,000 to 100,000 ohms. An attempt to deoxidize the copper screen electrodes is believed to have contaminated the porous disc since a reading no higher than 45,000 ohms of D. C. resistance was ever obtained.

Efficiency - at resonant conditions of 212 cps and 8 psi pressure variation.

 $W = \frac{PAV}{2}$

W = Power ft lbs/sec

P = Pressure variation

A = Area

y = Velocity of Fluid

Since the piston producing the pressure variation was 1/2" in diameter, and the fritted disc was approximately 2 inches in diameter, the velocity must be corrected as follows:

then with a stroke of 0.25 inches

$$W = \frac{PAS}{32}$$
= (8) (1) (\frac{0.25}{12})(\frac{2 \ 21.5}{32})

= 2.21 ft lbs/sec

= 2.99 watts

The electrical power output was 0.00532×10^{-3} watts, then the efficiency

Efficiency =
$$\frac{5.32}{2.99}$$
 x 10^{-l₁} = 1.78 x 10^{-l₁}%

Waller, E. J. A Theoretical Study of Impedance Matching as Applied to Surge Suppression Instruments in Hydraulic Systems. A Master's Thesis, Oklahoma A & M College, 1951.

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Additional properties and characteristics:

Estimated weight per watt output = 2.82 x 10⁵ lbs at given efficiency, Voltage range 0 to 1 volt - at lower frequency and higher pressure, can obtain 5 to 6 volts output, Current range 0 to 0.013 x 10-3 amp., Life unlimited so long as electrolyte is uncontaminated.

DISCUSSION OF RESULTS

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It is evident that the cell used in these tests was of poor quality. By the use of platinum electrodes, the corrosion difficulty would have been eliminated - this would have altered the internal impedance and hence markedly affected the shape of the power curve. It is known that higher frequency response can be obtained by the use of a finer porosity disc. Experimentation with varied thickness of disc has not been conducted, but the work of Cooke indicates that higher potentials may be gained by the use of a thicker disc.

The work completed as a part of the present study was intended as a guide for possible future exploration as an electrical power generating device. Although the tests were not performed under the best of conditions, they do indicate that some marked changes in performance are prerequisite to the construction of any efficient energy conversion device utilizing this principle.

RECOMMENDATIONS

At some later date, a more thorough study could be made to determine the effects of such parameters as thickness and area variations of the porous membrane, the porosity of the membrane, materials given satisfactory operation as membranes, composition and concentration of the material comprising the boundary with the membrane, volume and shape of the container, types, materials and shapes of the electrodes, methods of coupling the driving force to the device and resonance phenomena. Since the electrical force, or potential, is apparently a function of total flow, or pressure, and the motion or available load current a function of velocity of the flow, i. e., the derivative of the pressure. it would appear advantageous to correlate data and materials of this device with known dielectric theory.

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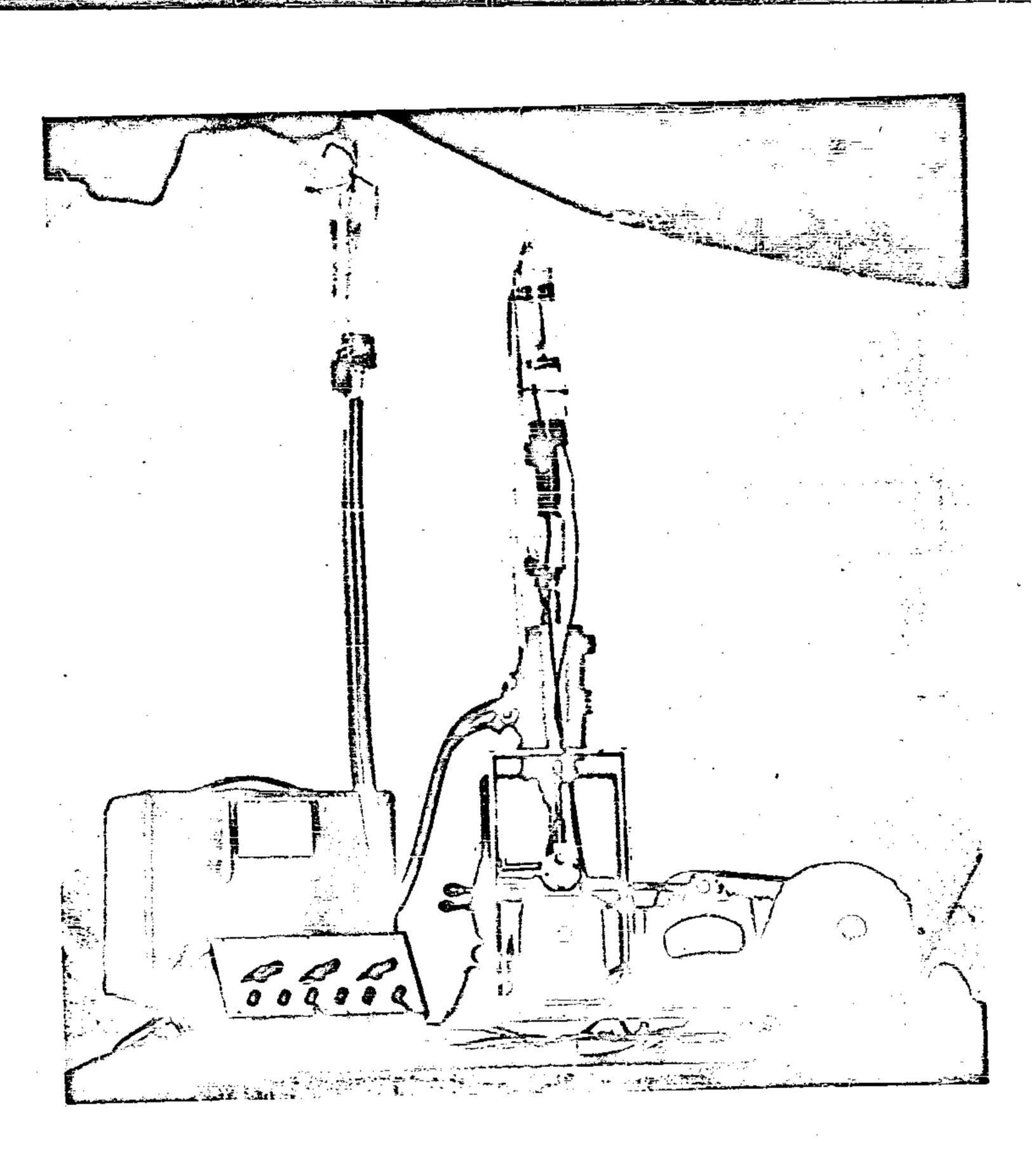
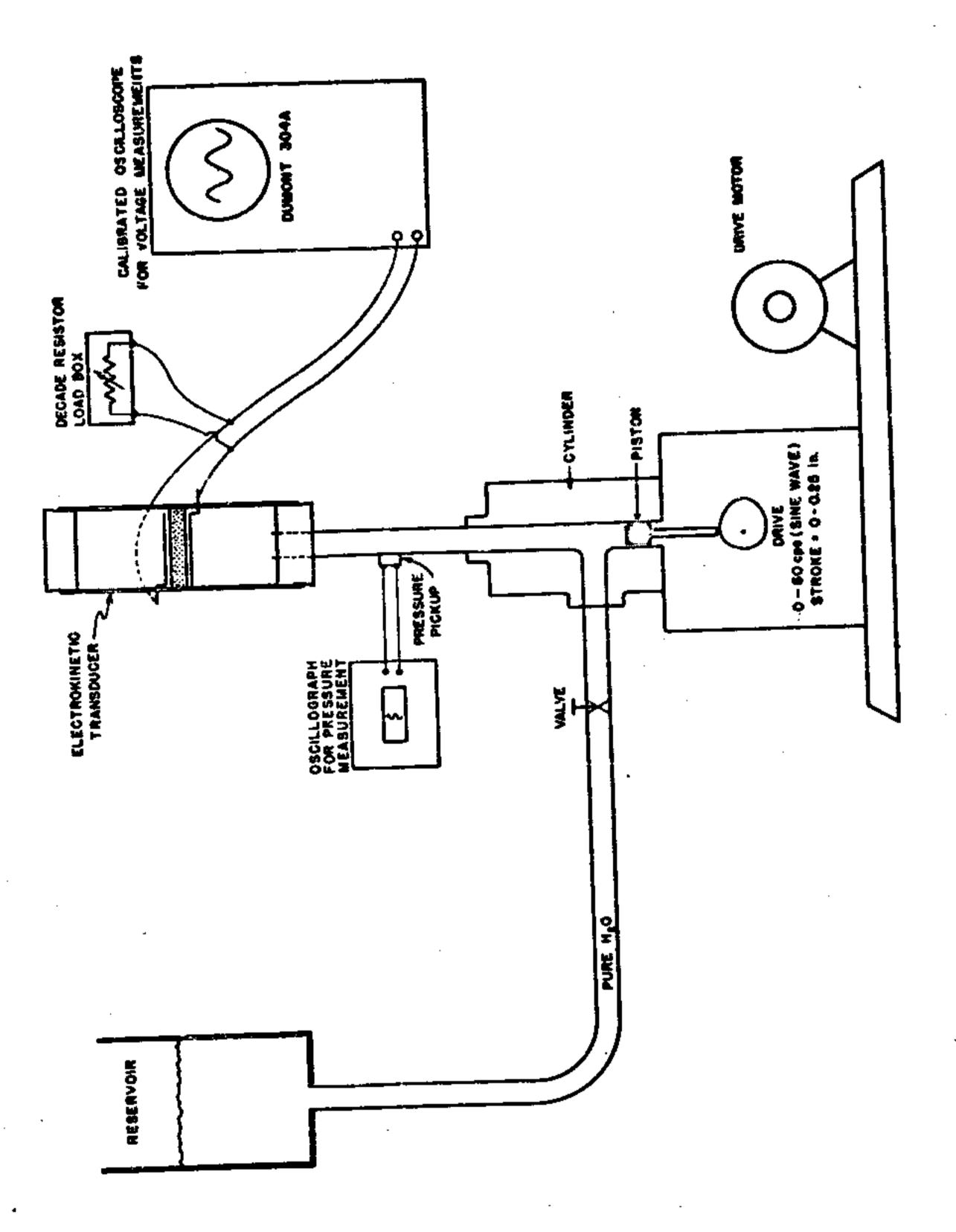


Figure III-6 Experimental Setup on the Electrokinetic Transducer.

III-17

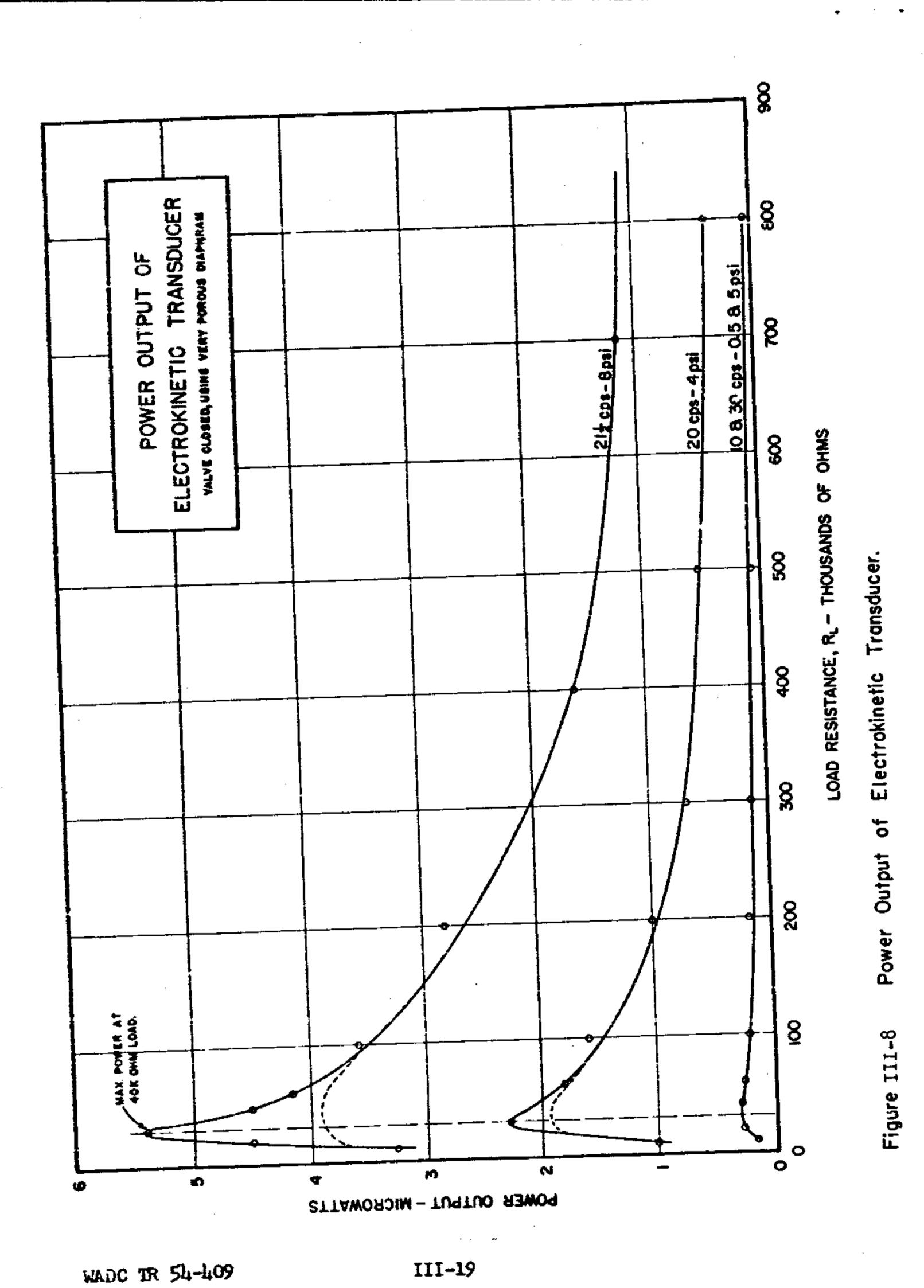


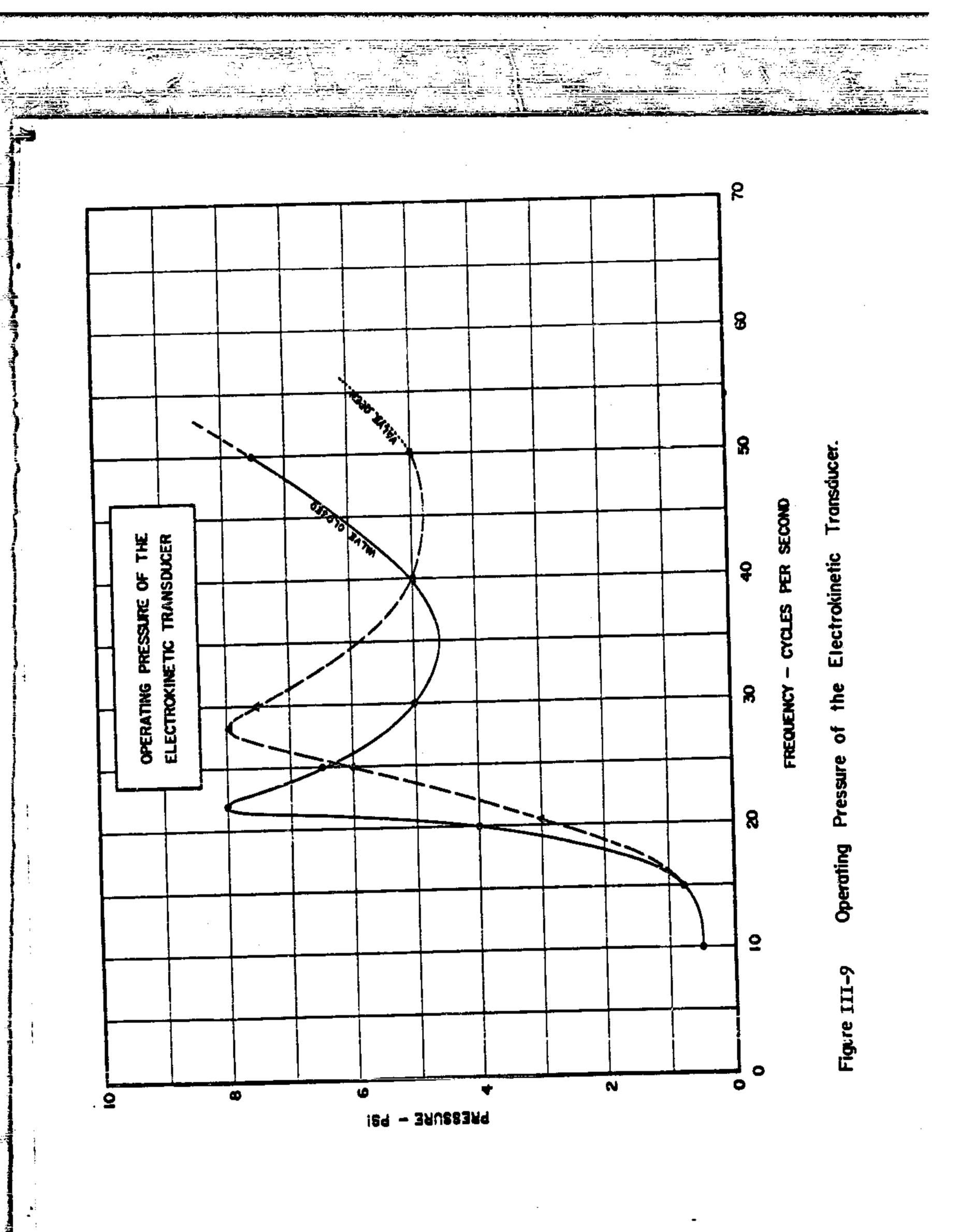
Test Setup for the Electrokinetic Transducer.

Figure

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PART IV

CONVERSION FROM SOLAR ENERGY TO ELECTRICAL ENERGY

PHOTOVOLTAIC

When radiant light energy strikes certain light-sensitive surfaces or materials, a potential disturbance occurs which can be utilized to deliver electric power to an external circuit.

This self generating characteristic occurs in several metallic films and in certain electrolytes. The effect was described by E. Becquerel and may be applied to several types of cells.

When using pure metal electrodes in the cell, the self-generating characteristic is rather insignificant, but if the illuminated electrode is coated with a semiconductor (which also has rectifying properties) such as copper exide, silver bolide, thallium, exysulphide, or selenium, the cell will have an open circuit voltage of the order of 0.1 volt and a current sensitivity (short circuit) of 150 micro amps/lumen.

Certain electrolytes such as solutions of uranous acid also display this self generating characteristic. No commercial applications of this type of cell have yet been found.

These cells show decidedeffects of fatigue at the electrode surface. There are two explanations of this effect, both of which seem to be in-adequates

1. The primary process is the photoelectric emission of electrons from the electrode into the electrolyte.

2. Light initiates a photo chemical reaction changing the surface character of the illuminated electrode.

The iron selenium cell is one of the more common barrier layer cells. An iron base is coated with a layer of iron selenide which is in turn covered with a transparent film of conducting lacquer. The cell operates due to the difference between the forward and reverse flow characteristics.

The voltage generated is of the order of 0.2 volt in bright light, but is non-linear with respect to light intensity. Current of a few milliamperes may flow from large cells. When the external circuit is properly designed, current flow may be made directly proportional to light intensity striking the cell. The cell has a low internal impedance (high internal capacity) and fails to follow sudden changes due to light modulation.

These cells are quite sensitive to temperature, losing all sensitivity above 55°C. While the generated voltage and internal resistance of the

- E. Becquerel "On Electric Effects Under the influence of Sclar Radiation" Compt. Rend. vol. 9, p. 561, 1839.
- 2 Case, Phys. Rev. 15, pp. 289, 1920.

cells are temperature functions below 55°C, short circuit current is essentially independent of temperature.

These cells may be connected in series or in parallel for multiplying voltage or current capacity.

Other types of cells which display self generating characteristics when light impinges are:

1. Cells using fluorescent electrolytes which produce open circuit voltages of the order of 0.25 volt and have a linear current response.

2. Illuminated crystals of molybdenite produce potentials of a few microvolts.

BELL SOLAR BATTERY
This cell has just recently been announced by the Bell Laboratories and while available information is quite limited, several pertinent characteristics of the cell have been made available. This cell which converts light energy into electrical energy consists of a silicon block having controlled impurities introduced at the light sensitive surface. Power is taken from the cell through connections to the block and from the surface layer. The cell has a theoretical conversion efficiency of 22%, but the present practical efficiency is 6%.

Full sunlight exposure gives a current flow of approximately 2h milliamps/square centimeter of surface at 0.5 volt or a power sensitivity of about 50 watts/square yard of exposed surface. To avoid any confusion that might arise due to nomenclature, it is deemed desirable to distinguish between the "Solar Battery" and phototransistors. The "Solar Battery" is a photovoltaic device that converts radiant energy into electrical energy. The phototransistor is not a source of power but is a device utilizing the radiant energy to control the connected power.

RECOMMENDATIONS The new developments in the field of photovoltaic devices show favorable promise as sources of electrical power. It is felt that progress of present activities should be closely followed to determine possible future work in this field.

1 Coblentz and Hughes, Phys. Rev. 29, 365 (A), 1927

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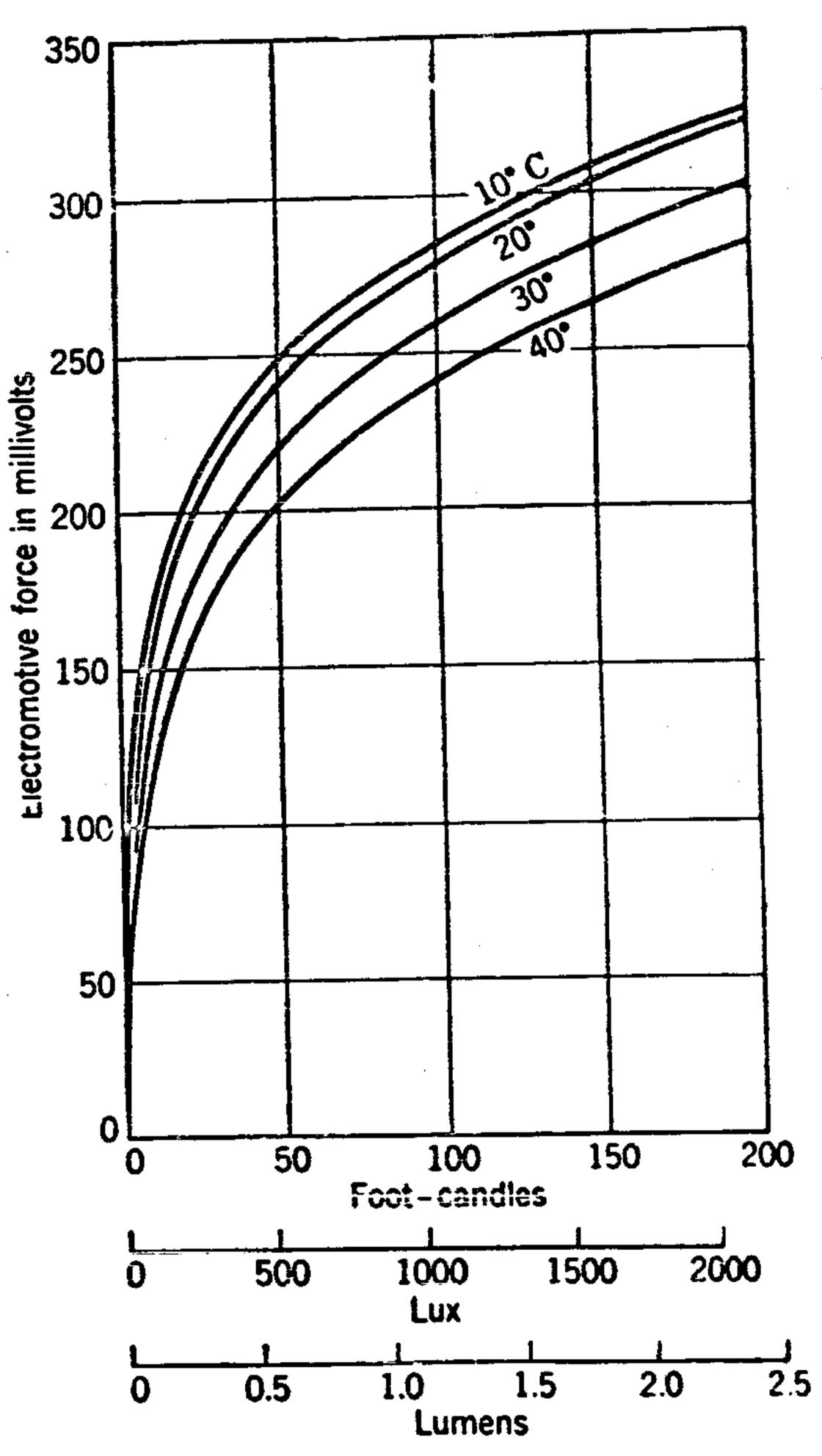


Figure IV-1. Open-Circuit Potential of a Jelenium Cell as a Function of Illumination and Temperature.

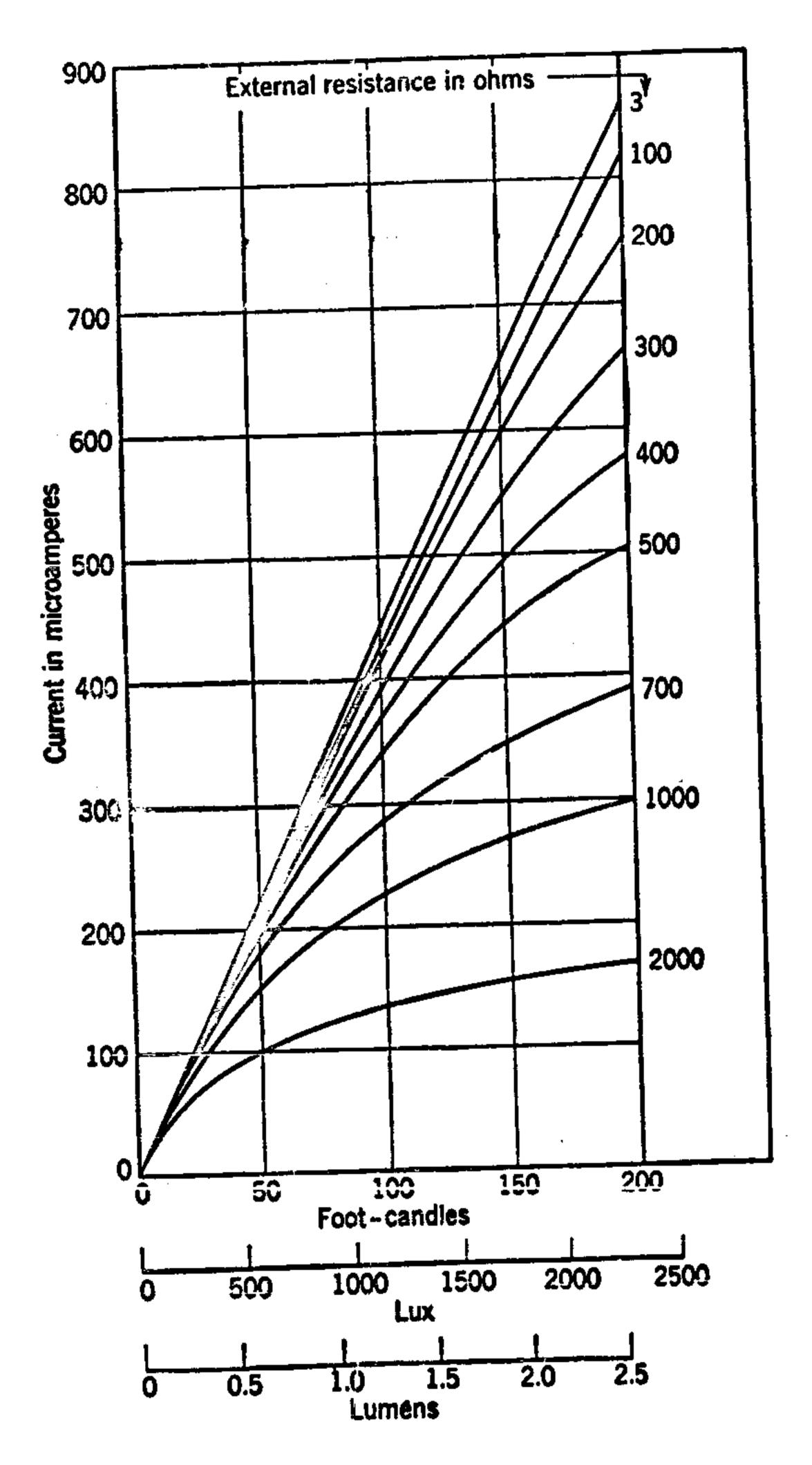


Figure IV-2 Photocurrent Characteristics of Selenium Barrier-Layer Cells.

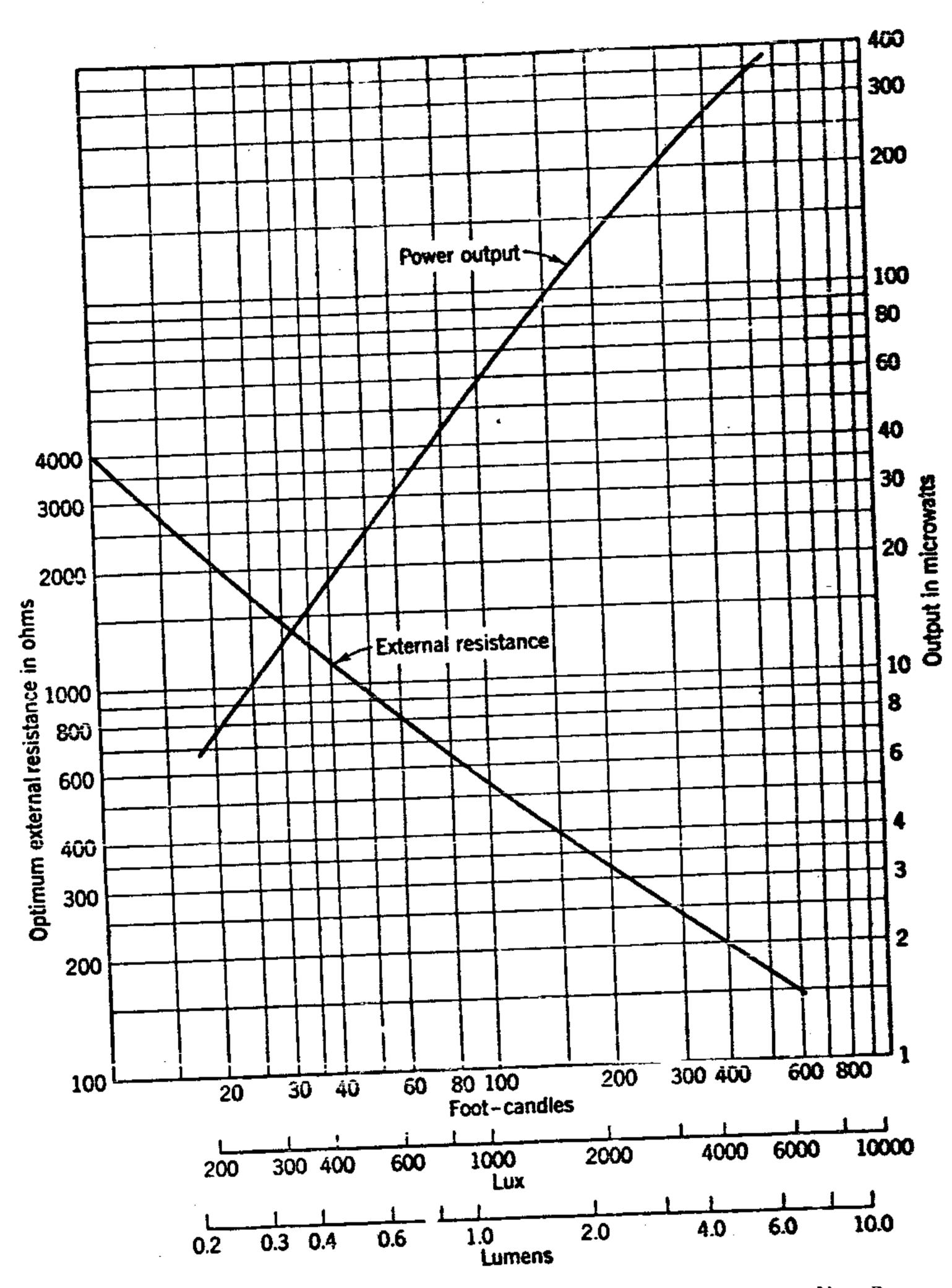


Figure IV-3 Variation of Optimum Load Resistance and Corresponding Power Cutput with Illumination for Solenium Barrier-Layer Cells.

Contrails

PART V

SUMMARY AND CONCLUSIONS

The activities of the first year of research were not sufficient to exhaust any of the phenomena but does indicate that some areas show more promise than do others. Some of the engineering parameters could not be established with any degree of precision. The values that could be determined are tabulated in Table V-1. It should be pointed out that the values shown are subject to modification as the research progresses.

The data indicates that primary emphasis should be placed on determining the capabilities of the ion selective membrane, the fuel cell, thermopiles, and oscillating electromagnetic induction and secondary emphasis on the thermomagnetic generator, the piezo-electric, and photo-voltaic effects. It is recommended, also, that a continuous reevaluation be undertaken to establish the influence of modern materials on the performance of all unconventional power generating phenomena.

PICEFORMANCE SUMMARY TABLE V-1

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					F. 1		
Phen amenu	Theoretical Efficiency	Measured Efficiency	Weight per KW	Volume per KW	Volts	Current	Other
Ion Selective	65%				4.4 millia-		
Fuel Cells		60-754(1)				1000 smps/ sq. ft.	600 watts/ 89. ft.
Workman-Reynolds Rffect	14%	9,000.0	90,000 1bs.	3000 cu.	230		
Thermomagne':1c			8,000 lbs.				1.8 sq.ft/ watts
Thermopile	56.64	8.75%(2)	4,000 1bg	3)25 cu.ft.	31 volts(3)	30	(
Pyro-electricity						5 x 10 ⁻⁹	
Entestoa						10ms/cm ²	
Oscillating Electro magnetic Induction							
Electrostatics	%				10 x 100 Volts	10 ⁻⁹ emps	
Zlectrokine:1c Transducer		1.78 × 10-4	82.82 x 10 ⁸	1.88 x 10	8	13 m a	
Piezo-electicity	\$ 06						10 vetts/
Magnetostrintion							
Photovolta1::	22¢(¼)	(η) ⁹ /9		15	•		

. .. Elektrochem., 4, 129-136,165-171
. Engr. Vol. 19, pp 383-385
. Norld, Vol. 64, pp 385
. Liboratories, Publicity releases, Su Anon, Elec. Elec. Bell I

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releases, Summer,

BIBLICGRAPHY

General

ATER, Journal of, p. 77, Conference on Energy Sources

1. Electromagnetic 2. Thermoelectric 3. Electrostatic

4. Piezoelectric 5. Contact Electricity 6. Emission Phenomena

7. Pyroelectric 8. Magnetostrictive 9. Earth Potential

10. Electrochemical

Worken-Reynolds Effect

- Conn., R. and Devin, O. "Raindrop Charge and Electric Field in Active Thunderstorms". Jour. Met. Vol. 10, pp. 279-284; Aug. 1953

 Measurements on over 7000 drops are reported; and the average charge was 0.022 esu for positively charged drops and 0.031 esu for negatively charged drops.
- Schaefer, V. J. "A Confirmation of the Workman-Reynolds Effect". SA 4947, Vol. 53, 1950 Letters in Phys. Rev. 77, 721 (Mar. 1, 1950) The electrical potential acquired by dilute of salts in the process of freezing was studied in an apparatus similar to that used by Workman-Reynolds.
- Schaefer, Vincent J. "A Confirmation of Workman-Reymolds Effect" Phys. Rev. 77. 721 (1950) Sea water and several inorganic salts used.

Ion Membrane

- Beutner, R. and Barnes, T. C. "Two Schools of Thought in Electrophysiological Theory" Euclides 10, 293-301 (1950) (in English)
 The well-established theory basing bioelectricity upon selective ion permability of membranes is considered invalid. Instead, bicelectric phenomena are explained on the basis of static e.m.f.'s induced in cell membranes by selective absorption of ions in the membrane surfaces.
- Crane, E. E. Bioelectric Potentials, their Maintenance and Function"
 Progress in Biophysics and Biophysic Chem. I, 85-136 (1950)
- Grundfest, H. "Mechanism and Properties of Bioelectric Potentials" Modern Trends Physiol. and Biochem. 1952, 1953-228. General Theory.
- Lorenz. Phillip B. "The Phenomenology of Electrocemosis and Streaming Potentials" J. Phys. Chem. 56, 775-8 (1952) Chem. Abs. Vol. 46, 1952, A mathematical treatment of electrokinetic processes.
- Hagasava, M. "Theory of the Membrane Potential Across Films of Organic PolymersII." J. Chem. Soc. Japan, Pure Chem. Sect. 70, 45-7 (1949) CA 45, 4115 c(1951)
- Magasawa, Mitsuw. "Theory of the Membrane Potential Across Films of Organic Polymers. I." Criticism of the theory of Meyer-Teorell.

 J. Chem. Soc. Japan, Pure Chem. Sect. 70, 4-7 (1949) CA 45,2744(1951)
- Magasawa, M. "Theoretical Equation of Membrane Potential" J. Chem. Soc. Japan Pure Chem. 70, 160-3 (1949) CA 75, 4115.

Neihof, R. and Sollner, K. J. Phys. and Colloid Chem. 54, 1957-76 (1950) CA 44, 1802 g (1950) A quantitative electrochemical theory of the electrolyte permeability of mosaic membranes composed of selectively anion-permeable and selectively cation-permeable parts and its experimental verification. I. An outline of the theory and its quantitative test in model systems with auxiliary electrodes.

Fuel Cell

- Gariss, Everett (to Pittsburg Consolidation Coal Co.) "Converting Carbon to Electrical Energy" CA 46:2934e (1952) U.S. Patent 2,581,650 Jan.8, 1952.
- Howard, H. C. "Chemistry of Coal Application" CA39:31435, pp. 1568-85, 1945 M. Y. J. Wiley & Sons Inc. Review with extensive references on the direct generation of electricity from coal to gas.
- Schwabe, K. Papier Fabr. 39, pp. 129-32, (1941) Electromotive combustion cell oxidizing sulfite waste liquor to produce electric energy.

Thermopile

- Bridgman, "Thermo-Electric Force Under Pressure" Proc. Am. Acad. Arts.Sci. vol. 53 (1918) p. 269. Pressure exerted upon a thermojunction causes an increase in emf from two to five times the original value.
- Rust, A. "Thermo-Electricity Theoretically and Practically Considered" Elec.
 World Vol. 14 (1889) pp. 52, 69 and 90. An illustrated series of
 articles discussed the theory of thermoelectric couples and describes
 many experimental thermocouples. A thermoelectric generator (Magnopile)
 comprising 6000 elements generates 96 volts.
- Kohler, "Thermojunctions" Philips Tech. Rev. Vol. 3, (1938) p. 165. The construction and action of junctions are discussed. Various design formulae are classified.
- Gore, G. "On the Peltier Effect at Different Temperatures." Phil. Mag. Ser. 5, vol. 21, (1886) p. 359 The magnitude of the Peltier effect is a function of a temperature of such combinations of metals as antimony and silver.
- Asher, "Improvements of Thermo-Electric Batteries" Elec. World vol. 28 (1896)

 pp. 229 and 535. Losses occurring in thermocouples are discussed.

 Historical data is given and several heat-saving improvements are suggested.
- "Gulcher's Thermo-Battery" Miec. World vol. 15 (1890) p. 92. Fifty thermocouples of nickel and an antimony alloy are mounted on a slate slab. Gas flames and cooling fans maintain the temperature gradient. The device delivers 8.58 watts at 4 volts while consuming 9 cubic feet of gas per hour.
- "The Comparative Efficiencies of Dynamos and Thermopiles" Elec. World vol. 17 (1891)
 p. 100. For a given amount of electrical output a good thermopile requires three times as much gas as a dynamo driven by a gas engine.
- "International Critical Tables of Mamerical Data, Physics, Chemistry, and Technology"

 Vol. 6, pp. 214 ff; (1926-1933) New York: McGrew-Hill Book Co. The

 Tables include thermoelectric data on various substances.

- "Temperature: Its Measurement and Control in Science and Industry"

 pp. 1227 ff; Hew York; Reinhold Publ. Corp. (1941)

 The reference book gives various quantitative data on the thermoelectric properties of pure metals and alloys used in temperature
 measuring thermocouples.
- Abeles, F. "Increased Electrical Resistance and Thermoelectric Power Due To Iacunae in Metals" Coupt. Rend. Acad. Sci. (Paris) vol. 237, pp. 796-798, October, 13, 1953. The changes of resistances and thermoelectric power due to lattice defects are evaluated in terms of electron moments and impurity concentrations, using a simple model according to which the metal consists of an electron gas obeying Fermi-Dirac statistics.
- Asher, "Electricity and Power Direct from Heat" Sci. Ager. Vol. 86 (1902)
 The advisability of erecting large solar thermoelectric batteries
 is discussed.
- Athearn, "Thermo Piles for Telegraph Furposes" Teleg. Age. (1897).

 A thermoelectric generator comprising elements which are poured in a mold can charge two storage batteries at a rate of two amperes.
- Bate, J. A. "Electric and Metallic Properties of Metals and Alloys" Ref.
 Austrialiaian Engr. 45, Jan. 1952, 79-89, Factors affecting thermoelectric effort.
- Betz, G. "E. Raub's New Thermo-Electric Esttery" Elec. Rev. Vol. 22, (1888)
 p. 332. Three different models of the Raub generator are described.
 Their output ranges from 25 watts for the smallest to about 68 watts for the largest. Each model has an emf of 3 volts. Each generator comprises a vertical cylinder with a gas burner at the bottom.
- Bidsell, "Thermal Electromotive Forces in Crides" Phys. Rev. Ser. 2, vol. 3 (1914) p. 204. Thermocouples of tin, iron, chromium, tungeten, cadmium, zinc, lead and their oxides yield electromotive forces as high as 1.5 volts with a temperature difference of 800.
- Burns, G. Preston. "Efficiency of the Thermoelectric Process" Phys. Rev. 78, 327 (1951) CA 45, 6053a (1951)
- Coblentz, W. W. "Various Modifications of Thermopiles Enving a Continuous Absorbing Surface" Bull. Bur. Standards, vol. 11 (1915) pp. 131-181. The construction and efficiency of thermopiles is discussed in detail. The maximum efficiency of a thermopile is calculated to be 12 per cent.
- Dickerson, E. H. "Apparatus for Heating Thermopiles" U. S. Pat. 563,262, July 7, 1896. The generator comprises a series of thermocouples each of which is shaped into his inverted "U" with the horizontal portion protruding through the heating compartment which is fitted with a gas burner. Fuel gas and air are fed to the burner through tubes which are spirally around the chimmer. Hence the fuel is preheated before communities.
- Eaten Nfg. Company Catalog. "Thermoelectric Generator" July, 1946. A portable, herosene burning generator is described. It is designed to replace batteries in the operation of radio sets where central station power is not available. The fuel burns at the rate of one quart in 6 to 8 hours.

- Findley, H J. "Heating Apparatus" Nov. 7, 1944, A pressure-fed burning space heater incorporates a thermoelectric generator supply the blower motor and fuel pump. Uniform heating of junctions is claimed. An impeller is used to provide a large temperature differential between hot and cold junctions.
- Flock, E., Olsen, L. O., Freeze, P. D. "The Use of Thermocouples in Streaming Exhaust Gas" Third Symposium on Combustion and Flame and Explosion Phenomena. J. O. Herschfelder and Bernard Lewis, pp. 655-662.

 Factors involved in measurement of temperature.
- Geiling, L. "Use of Thermoelements in Space" Weltraumfahrt No. 3, 59-60 (1951) CA 45, 7874 e (1951) With elements of 90 Bi-10 Sb and 75 Sb-25Cd under the influence of solar radiation in space it is possible to generate 2.5 watts/m. of exposed material. This corresponds to 140 kg. of element material per k. w.
- Gottscho, L., "Thermo-Electric Pile" U.S. Pat. 650,062, May 22, 1900. The elements of the generator are bismuth and antimony. A star shaped arrangement of wires join the hot and cold junctions.
- Morgan, F. Haydn, Danforth, W. E. "Thermocouples of Refrectory Metals, W-Ta Thermoelectric Power to 3000° W-Mo to 2600° ect." J. Appl. Phys. 21, 112 (1950).
- Hermann, Otto, "Thermoelectric Element" U. S. Pat. 1,572,117, Feb. 9, 1926

 A negative element of Hi (81%)-Mo (17%) -V (2%) and a positive element of Hi (40%)-Cu (60%) generate a high emf. The resistivity of the thermocouple is low.
- Entchins, C. C. "Thermo-Electric Heights of Antimony and Bismuth Alloys"

 Am. J. Sci. Vol. 148 (1894) p. 226. Experiments are made to determine which combination of these alloys produce the highest emf.
- Jackson, R. "Mew Mothods of Gas Temperature Measurement" Bul. Brit. Coal Utilization Research Soc. 15, 245-56 (1951) ref. CA 44:5566b A review covering thermocourles at high temperatures etc.,70 references.
- Jackson, R. "The Measurement of Gas Temperature by Thermocouples"
 Bul. Brit. Coel Utilization Research Assoc. 14, 33-9 (1950)
 A review of covering plain thermocouples, etc. 30 references.
- Keinath, G. "Thermoelements" Arch. Tech. Messen, Vol. 2, (1933) p. T10-T11.
 Various thermocouples are discussed. A bibliography is appended.
- Keinath, G. "Thermoelements" Arch. Tech. Messen, Vol. 2, (1932) p. T156.

 The thermoelectromotive force of various thermocouples is tabulated.

 A bibliography is appended.
- Mersten, H. and Schaffert, R. "Construction of Thermo-Elements by Electrode-Position" Rev. Sci. Instruments vol. 3 (1932) pp. 189-195.

 Methods of constructing electroplated thermocouples are discussed.
- Landdes, J. J. Phys. Rev. 74, 479-88 (Aug. 15, 1948) Measure of Thompson Coefficients for metals at high temperature and of the Peltier coefficients for solid liquid interfaces of metals.

 \mathcal{L}^{j}

- Wol. 19 (1946), No. 5 pp. 196-202. The generator comprising 168 couples of Chromel P. and Constantan was developed by the Signal couples Engineering Laboratories. It burns 80- or 100- octans gasoline and produces 5 watts when operating at a temp. gradient of about 6000. The efficiency is approximately 0.2per cent and the weight is 2.25 pounds per watt output. Ten-and twenty-watt sizes also were built.
- Logwood, C. V. "Thermal-Generator" U. S. Fat. 1,585,159, May 18, 1926
 A cylindrical thermopile has elements of copel and chromel. It is designed for use with radio receivers and is heated by a centrally located induction coil.
- Milnes, H. R. "Thermal Generation of Electric Current" U. S. Pat. 2,215,332, Sept. 17, 1940. A novel thermocouple and a generator employing it are described. The positive element is Cu(?0%), Ag (24%), Cu0 (6%) and the negative Ag (6%), Cu(33%). Both elements are cylindrical and the negative Ag (6%), Cu(33%). Both elements are cylindrical disks 1/8 inch thick held within a ceramic tube and separated by a nickel rod. Operating temperatures are 300-400 C at the hot junction and 100 C at the cold.
- Milnes, H. R. "Thermo-Electric Elements and Method of Making the Same" U. S. Pat. 2,232,960, Feb. 25, 1941.
- Reed, C. J. "Thermo-Electric Batteries" Elec. World Vol. 29 (1897) p. 565.
 Various types of thermoelectric generators are summarized.
- Rosser, "Thermoelectric Thermometry" J. Appl. Phys. Vol. 11 (1940) pp. 388-407, Fundamental laws and theories of thermoelectric phenomena and their historical development and application to temperature measurement are considered in detail. Fractical thermoelectric thermometry is discussed.
- Shenker, H., Lauritzen, J. I., Jr., Corruscini, R. J., Reference Tables for Thermocouples. U. S. Matl. Bur. Standards, Circ 508, p. 71, (1951) CA 45, 6476 h. (1951)
- Sondheimen, E. H. "The theory of the Thermoelectric Power of Metals" Proc. Comb. Phil. Soc. 43 part 4, 571-5 (1947). Formula reduces at high and low temps to the correct lat. order expression for thermo-electric power.
- Sparrow, H. T. and Wilson, J. M. Thermocouple, U. S. Pat. 2,378,804, June 19, 1945, A simple and inexpensive method of constructing thermocouples is described.
- Troy, W. C., and Steven, G. "Thermocouple" U. S. Patent 2,588,998, March 11, 1952, Tungsten and iridium thermocouple used up to 2100°C.
- White, W. C. "Some Experiments with Peltier Effect" Elec. Engr. M. Y. 70, 589-91. The possibility of using peltier effect in a thermoelectric power generator. A couple of Bi-Sb and a Bi-Sn alloy was used with a cooling effect of 10°C. Efficiency was low. Conclusion: There was no chance of developing any sort of generator or refrigerator.

Approved for Public Release

- While, Herbert H. "Volta Potentials of Copper Nickel Alloy and Several Metals in Air" J. of Applied Phys. Vol. 22, No. 12, (Dec. 1951)

 Volta potentials of various metals approximately parallel the emf. series.

 Metals abraded wat are more noble than when abraded dry, the transition metals change an average of .28 volt compared with .07 volt for non-transition metals. Commercial nickel-copper alloys above 50% nickel age more rapidly than laboratory alloys.

 Ref. S. Langmuir, Phys. Rev. 2, 402-450 (1913) WA Zisman, Rev. Sci. Inst. 3, 367 (1932) W. A. Zismann and H. G. Yamin, Phy. 4, 7 (1933).
- Wilson, Harold A., PhD, Prof. of Physics Rice Inst. "Thermoelectricity"
 Vol. 8, page 207a, If a circuit is made by joining the ends of 2 wires
 of different metals, it is found that if one of the junctions is kept
 at a temperature higher than the other, a current flows round the
 circuit. The currents so obtained are called thermoelectric currents.
 A good thermodynamical theory, by Lord Keivin is given.

Electrokinetic and Streaming Potential

- Schmid, G. and Schwarg, H. "Electrochemistry of Fine-Pore Capillary Systems IV. Dialysis Potentials" Z. Elektrochem. 55, 684-9 (1951)

 Apparatus and theory.
- Schmid, G. "Electrochemistry of Fine-Pore Capillary Systems II. Electrocsmosis" Z. Elektrochem. 55, 229-37 (1951).
- Schmid, G. and Schwarg, H. "Electrochemistry of Fine-Pore Capillary Systems. V. Streaming Potentials; Donan Hindrance of Electrolyte Transfer by Streaming" Z. Elektrochem. 56, 35-44 (1952).

 Apparatus and theory.
- Schmid, G. "Electrochemistry of Find-Pore Capillary Systems I (Summary)" Z Elektrochem. 54, 424-30 (1950).
- Grahame, D. C. "Riectrical Double Layer & the Theory of Electrocapillarity" Chem. Reviews 41, 441-50 (Dec., 1947) A review with bibliography.
- Kruyt, H. R. "Streaming Potentials" Kolloid Z 22, 81 (1918).
- Eversole, W. G. and Boardman, W. W., "A measurement of the Magnitude of the el' kinetic Current in Liquid Flow Thru a Single Capillary. A Formula is developed" Proc. Iowa Acad. Sci. 49, 334 (1942)
- Zhuhou, I. I. and Fridvikhaberg, D. A. "The Electrokinetic Potential. 0.001. H. ECL thru Colloidion Membranes and Ceramic Membranes." Kolloid Zhur, 12, 25 (1950) Electrokinetic characteristics of capillary systems III.
- Meal, S. M. Trans. Faraday Soc. 42, 473-8 (1946) Development of a theory of electric current from streaming potentials through porous plugs an equation is developed.
- Samartsev, A. G. and Ostroumov, V. V. "Streaming Potentials in Fine-Pore Quartz Membranes" Kolloid Zhur, 12, 136-145 (1950) CA 44, 5679 1, (1950).

- Palitzoch, S. "Boundary Surfaces of Callelose Fibers and Their Electrokametic Potentials" Tids. Textiltek, 2, 165-177 (1951) CA 45, 10576 h (1951) A review with 99 references.
- Fischer, C. and Muller, F. H. Mahnwissen Schaften 30, 604 (1942) Electric current from diffusion of H₂O through organic foils or membranes.

 Maximum current is of the order 10-14 amps.
- Author Unknown. CA 38: 5962 101, 43 (1942) Electric current from diffusion of H₂0 thru a dielectric material on the order of 10⁻⁴ amp. Mechanism is unexplained.
- Vogutskii, S. S. and Panich, B. M. and Kal'Tanova, K. A. "The Electrokinstic Potential of Melamin Resin Particles in Aqueous Solutions" Kelloid Zhur, 13, 242-8 (1951) CA 15, 9997 c (1951)
- Ostroumov, V. V. "Electrokinatic Potential in Fine-Porous Membranes" Kolloid
 Zhur 13, 371-8 (1951) Streaming Potentials.
- Magasawa, M. "Theory of Streaming Potentials" J. Chem. Soc. Japan Pure Chem. Sect. 72, 547-50 (1952) Chem. Abs. vol. 46, 1952.
- Camp, L. "Broad-Band Directional Barium Titanate Transducers" Jour. Acous. Soc. Amer., vol. 25, pp. 297-301 March, 1953. Transducers suitable for underwater operation, and having desired directional characteristics, are constructed from arrays of short thinwalled BaTiO2 tubes in a fluid medium.
- Maxur, P. and Overbeek, J. Th. G. "Electrocomosic and Streaming Potentials in Diaphragms II, Quantitative Relation between electrokinetic Effects" Rec. Trav. Chim. 70, 83-91 (1951) (In English) CA 45, 4997 h (1951)
- Sel'tser, G. I. "Theory of Streaming Potential in Marrow Capillaries" Kolloid Zhur 13, 273-82 (1951) CA 45, 9997 b (1951).

Electrostatic

- Trump and Van de Graff, "A Compact Pressure-Insulated Electrostatic X-Ray
 Generator" Phys. Rev. Vol. 55, 1160-5 (June, 1939) At air pressures
 of 11 atmospheres absolute 1250 Ey X-Rays are obtained with currents
 of over one milliamperes supplied by the single 14 inch belt. With
 gas the voltage and current can be obtained at 1/3 the pressure required
 by air. Construction complicated.
- Roudaut, John "Friction Compretor" U. S. Pat. 2,577,542, December 4, 1951.
- Bound, H. Staub, H. H. and Winkler, H. "High-Pressure Electrostatic Generator of the University of Zurich" Hely. Phys. Acta. 24, 632-3 (1951)

 Lauritson type 450 ky at atmos. pressure, 1.8 mr. at 10 atmos.
- Vandegraff, K. T. Compton & Van Celta, "The Electrostatic Production of High Voltage for Muclear Investigation" Phys. Rev. Vol. 43, (Feb. 1, 1953) The disruption of atomic nuclei may be achieved by generation of current of very high voltage. Electrostatic generators are free from ripling effect of high voltage or the inherent defect of A. C. voltage and also have the simplicity of construction.

Approved for Public Release

- Coolidge, John E. and Schulz, George "Static Electrification of Dust Particles on Dispersion into a Cloud" J. Applied Phys. 22, 103 (1951).
- Gross, B. "Static Charges on Dielectrics" Brit. J. Applied Phys. 1, 159-67, (1950).
- Harper, W. R. "The Volta Effect as a Cause of Static Electrification" Proc. Roy. Soc. A. 205, 83-103 (1951) Apparently good source of material on Tribo-Electrification (rubbing). Theoretical.
- Van Rossem, A. "Light Phenomena on Elongating Vulcanized Rubbers" Proc. 2nd
 Rubber Technol. Congr. (London) 1948, 345-50. The apparent relation
 between luminescence and reinforcement leads to the conclusion that
 during stretching and adhesion between rubber and the filler particles
 in broken electric charges are set up on the extremely large surfaces,
 and these result in discharges into the surrounding vacuole because
 there is such a tremendous number of these discharges there is a visible
 light phenomena.
- Wilmhurst-Beama, "Power From Hot Water Springs" Elec. Engr. Abs. 60, 42-7.

 Electric power in Belgian Congo tin mine is obtained by utilizing the difference in temperature between water at 200°F obtained from a spring and cold water from natural drainage.
- Tournier, M. "The Physical Properties of Crystals and Their Symmetry" Cah.

 Phys. No. hip. pp. hh-73; July 1953. Certain properties of crystals can
 be predicted from the elements of symmetry in the cause and effect
 relations of the phenomena associated with them. Tensor and Matrix
 methods are used to express the pyroelectric, dielectric, piezoelectric
 and elastic processes. Various crystalline systems are explained,
 and an indication is given of the properties to be expected of them
 according to this analysis.
- Downing, H. L. "Some Notes on the Properties and Manufacture of Piezoelectric Quartz crystals" Proc. IRE (Australia) Vol. 14, pp. 241-48 Oct. 1953. The frequency stability, temperature coefficient and activity of quartz resonantors are discussed, and the relation between these properties and the oscillating frequency of a circuit including the crystal is examined. The performance of some typical units is shown graphically.
- Cady, W. G. "Nature and Use of Piezoelectricity" AIEE Journal Fages 758-762.
- Dunn, S. C. "Voltage Measurements on Rochelle Salt Under Compression Flood" Arch. Tech. Messen issue 200, 197-8 Sept. 1952 in German phys. Abs.
- Cady, W. G. "Nature and Use of Piazoelectricity" AIEE Journal P. 758-762.

 If stress T. produces polarization in certain directions then electric field will give rise to same effect. It differs from electrostriction. See Voigt "Lehrbuch der Kristallphysic" page 761.
- Srivastova, K. G. " A New and Quick Method for Detection of Piezo-electricity and Measurement of the Peizo-electric Constants" Indian J. Phys. 25m 33-4 (1951).
- Parsons, P. L. Bechmann, R. "Piezoelectric Behavior of Partially Plated Square Plates Vibrating in Contour Modes" From. Phys. Spc. Lond. B. 64, 706-12 (1951).

8-IV

Approved for Public Release

7

- Bardson, J. and Shockley, W. "Deformation Potentials and Moloilities in Non-polar Crystals" Phys. Rev. <u>80</u>, 72-80 (1950) It appears theoretical.
- Bechmann, R. "The Linear Piezoelectric Equations of State" Brit. Jour. Appl. Phys. vol. 4, pp. 210-212 July1953. The different forms of the equation of state obtained from various combinations of stress, strain, electric field, electric displacement and polarization are given in tabular form.
- Dunn, S. C. "Voltage Measurements on Rochelli Salts Under Compression Load" Arch.
 Tech. Measer Issue 200 197-8 Sept. 1952 in German.
- Parthasarathy, S., Pancholy, M., and Chhapgar, A. F., Ann. Phys. Lpz. Vol. 12, pp. 1-7; April 16, 1953 in english. The results reported in Jour. Sci. Industr. Res. 1944 were confirmed by observing the diffraction patterns of the oscillating quartz.
- Wooster, W. A. "Physical Properties and Atomic Arrangements in Crystals"

 Rep. Frogr. Phys. Vol. 16, pp. 62-82; 1953, A survey is made of the relation between the structure of crystals and their magnetic, optical, piezoelectric and elastic properties. Recent work on paramagnetic resonance absorption at high frequencies is discussed in connection with the spinels. The spontaneous electric polarization of Rochelle salt and KH_POh is attributed to co-operative movements of hydrogen ions.

Photovoltaic

- Buckingham, M. J. and Makinson, R. E. B. "The Second Order Photoelectric Effect at a Metal Surface" Proc. Phys. Soc. Lord. A 64, 135-9 (1951) A 18 (600) 478.
- Becker, M. and Fan, H. Y. "Photogoltaic Effect of P-E Junctions in Germanium"
 Letters in Phys. Rev. 78, 3-1-2 (May 1, 1950).
- Blocher and Carrett, James Chem. Soc. 69, 1594-8 (July, 1947). The photo-voltaic effect, the special sensitivities of Cadmium, Zinc, and Silver electrodes; the effect of ph and oxygen.
- Copeland, et al. "The Photovoltaic Effect" Chem. Review 31, 177-227 (Aug. 42)
 A review with bibliography.
- Ichovic, K. "The Photo-Voltaic Effect" Phys. Rev. 74,463-71 (Aug. 15, 1948)
 The Schottky-Mott Theory of the barren layer sectification is extended to the light absorped in the barrier layer.
- Tavin and White. "The Photovoltaic Behavior of Organic Sybstances in Solution" J. Chem. Phys. 18, 417-26. Comparison or photovoltaic behavior and fluoriscent properties.
- Handrat, G. "A New Contribution to the Theory of Photo-Electric Cells of the Earler Layer Type" Istenbul Univ. Fen. Fak. Mec. 12, 127-50 (Apr. 1947) in French. In SE and Copper Oxide photovoltaic cells the electronic emission originated in the semi-conduction.
- Phillips, Mayor C. E. S., Lecturer in Padiology at University College, London "Selenium Cells" Vol. 20, p. 303a. Three pages on construction, theory of operation, and practical applications of selenium cells.

VI-9

Approved for Public Release

Reission

Champeir, Robert, "Transformation of Heat into Electric Energy in Thermionic phenomena" Le Vide 6, 936-40 (1951) CA 45, 551 f. (1951)

Pyroolectric

- Brown, Aktiengesellschaft, Ecveri and Cic "Heat Engine Generating Station of High Capacity Operated with Fuel Cas from Solid Combustibles" Germ. Pat. 804,625, April 26, 1951 (Cl. 46f, 370).
- Wilson, Harold A. PhD, Prof. of Phys. Rice Inst., "Pyroelectricity"
 Vol. 8, p. 204a, The charge occurring on crystals such as tourmaline
 when heated in ashes with water, etc, Canton showed that the charges
 are produced by temperature changes. Lord Kelvin (1860) worked out the
 presently accepted theory. From his work Voigt found that the polarization
 "P" for tournaline at 24°C is 33.4 E.S.C. and changes 1.2 E.S.U.
 per degree temperature rise. Found another reference to same phenomena
 by Aepimus, Franz U. T. Published in Memoires de l'Academic Royale Dec.
 Science, Berlin Vol. 12-P'105, 1756 and abstracted in "Source Book in
 Physics, William Francis Magilo-First Edition McGraw Hill, 1935.
- Author Unknown, "Electrical Properties of Ceramics as Influenced by Temperature" Trans. of AIEE, 48, 734-41 (Sept. 29) Resistance.