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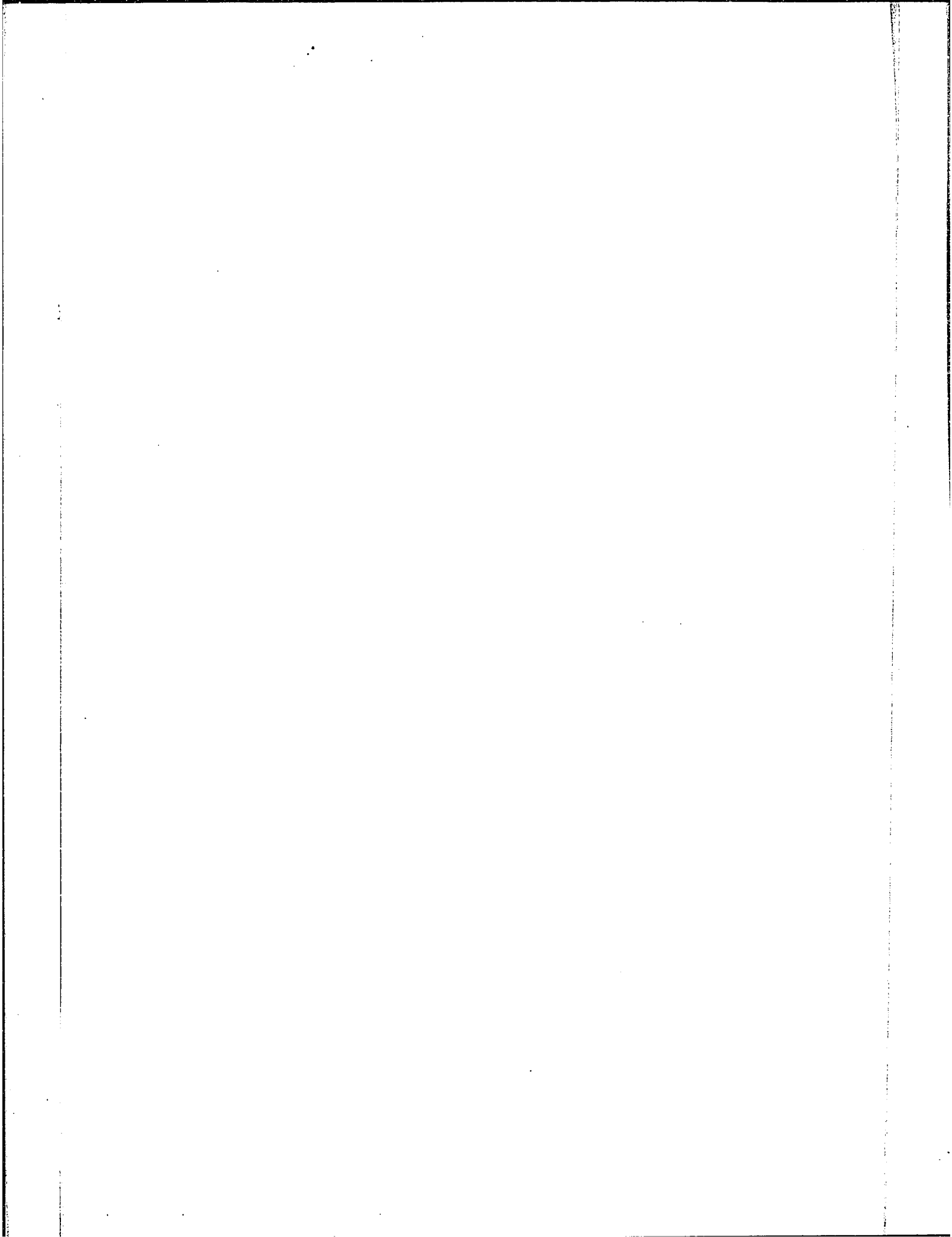
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EQUIVALENT CIRCUITS
of
THERMOELECTRIC COOLERS

by
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Master of Science in Electrical Engineering.

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CANADA



June 1963

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Supervisor

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I

ABSTRACT

Equivalent circuits are useful for simplified representation and deeper understanding of electrical devices. In this work a thermoelectric system is represented by equivalent circuits.

The first part of the work is introductory. It contains the definitions and derivations of the various thermoelectric effects.

A detailed description of the construction and the test results of an ideal thermoelectric cooler that had been built are given in the second part.

The derivation of the equivalent circuit of a thermoelectric system is given in the last part. It is based on a modified version of Onsager's Reciprocal Relations. The conditions under which the modified relations and the equivalent circuit hold are stated and explained. From the basic equivalent circuit ^{circuits} more are derived, these are two terminal-pair active networks of either the Π or T form.

A comparison of the results given in the last two parts and other comments conclude the work.

ACKNOWLEDGEMENT

It is with much pleasure that I acknowledge with gratitude the help and advice given to me by the members of the Electrical Engineering Department, in particular to Prof. G. S. Glinski for his supervision and guidance and to Mr. R. LeHenaff for his assistance in constructing the thermoelectric system. In addition I wish to thank Mr. E.L.R. Webb of the National Research Council for his advice and assistance in the initial stages of the project. Finally I would like to thank the National Research Council and the University of Ottawa for making this project possible, and the graduate students of the Electrical Engineering Department for their encouragement and helpful discussions throughout.

PREFACE*convenient*

Equivalent circuits are ~~handy~~ and familiar tools to the electrical engineer, on the other hand thermodynamic and thermoelectric processes are not, in general, so familiar. It was therefore considered useful to try and express the thermoelectric circuit by means of an equivalent network.

Originally it was intended to derive equivalent circuits to represent the dynamic behaviour of thermoelectric coolers (large signal analysis) but it was found at a very early stage that such a representation was impossible because of the nonlinearity of the equations and the number of variables involved.

The first chapter is introductory and most of Chapter Two was given for the sake of completeness. The derivation of ^{the} equations for the various thermoelectric effects and the behaviour of a thermoelectric cooler in the steady state are given in parts (a) and (b) of Chapter Two. Part (c) of the chapter gives the derivation of the generalized dynamic equations of a thermoelectric system. These equations indicate how complicated an equivalent circuit might be if based on ~~these equations~~.

The equations to be represented by an equivalent circuit are derived in Chapter Three. These equations are in their simplest form implying the largest amount of assumptions. The equations derived here are suitable for small signal analysis only. They are based on a modified version of Onsager's Reciprocal Relations. By lifting some of the restrictions ~~imposed~~ on the equations, one by one, the equations will become progressively more difficult and so does the equivalent circuit. It was felt ~~however~~ that work in this direction was beyond the scope of this thesis.

Chapter Five is an extension of Chapter Three. In it more equivalent circuits which are more practical were derived and described.

The construction and test results of an ideal thermoelectric cooler are discussed in Chapter Four and the first part of Chapter Six respectively.

The test results of the equivalent circuit are given in the second part of Chapter Six. Comments on the results and conclusions are given in

Chapter Seven.

This work may now be extended further to include, for example, temperature dependence of the various parameters. It may also be extended to cover cascaded systems or even cascaded systems made of materials with different figures of merit. These are just a few of the possible extensions to the treatment given here and are directly related to it.

IV

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CHAPTER 1: INTRODUCTION.

Thermoelectricity is the branch of science dealing with the interchange of heat and electrical energy. Any effect involved in that process and in that process only, is a thermoelectric effect. The field is over a century old and the literature is full of historical facts. * 1,2

In the last two decades the progress in the field has been rapid, (mainly) due to the development of semiconducting materials. Thermoelectricity has its use in many fields varying from space technology to home appliances. With the increase in use of thermoelectric effects it is felt that a certain method can be devised to ease the work of the designer. In this thesis an attempt is made to derive an equivalent circuit for a thermoelectric cooler. This means that the existing theory has to be modified slightly so as to yield itself to a representation in a form of a two terminal pair network.

In order to introduce the field of thermoelectricity a brief explanation of the various effects will be given.

THE SEEBECK EFFECT

If a circuit is made of two dissimilar metals or semiconductors A and B as shown in Figure 1.1a and the two junctions are kept at different temperatures then current will flow in the loop. If the circuit is broken in one of the materials then a voltage appears across these terminals (Figure 1.1b). This voltage is proportional to ΔT .

* Superscripts refer to bibliography list.

The Seebeck coefficient is defined as

$$\alpha(T) = \frac{\Delta V}{\Delta T} \quad (1-1)$$

where α = Seebeck coefficient

ΔV = voltage difference

ΔT = temperature difference between the junctions

The Seebeck coefficient depends on the choice of both materials and cannot be attributed to either material alone.

The drop in potential may be either positive or negative in the direction of the drop in temperature, depending on the choice of materials. This means that the sign as well as the magnitude is of importance. For convenience an absolute Seebeck coefficient is assigned to ^{each} ~~all~~ materials, so that when a circuit (or a thermocouple) is formed the total Seebeck coefficient will be the difference of the two absolute coefficients.

THE PELTIER EFFECT

When an electric current flows in a circuit of two dissimilar materials (conductors or semiconductors) then one junction will absorb heat from the surroundings at one junction and liberate it at the other junction. This is illustrated in figure (1-2). It was found that the rate of heat absorbed (or liberated) is directly proportional to the current flow hence:

$$P = \pi(T)I \quad (1-2)$$

where $\pi(T)$ = Peltier coefficient I = current flow

P = the power. Again the effect cannot be ascribed to either of the materials but is a property of the junction. An absolute coefficient for each material can be found.

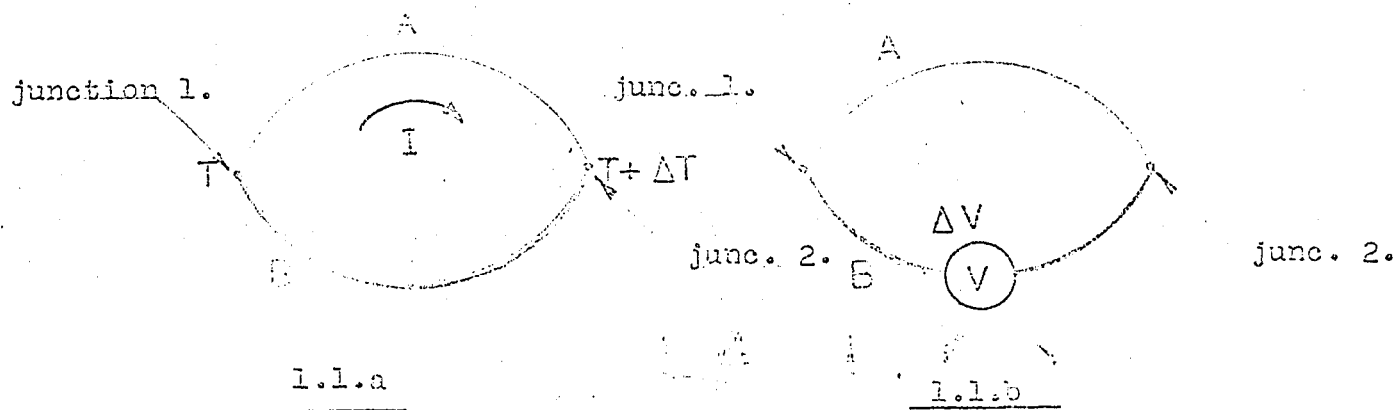


fig 1.1

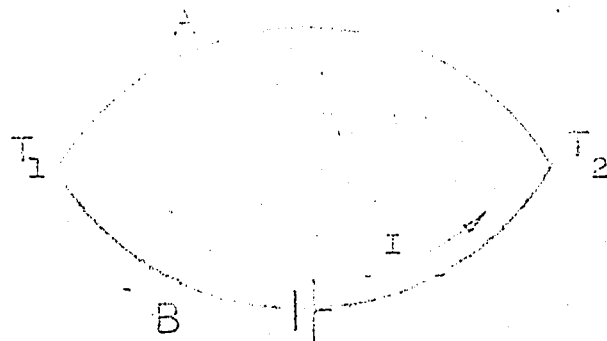


fig. 1.2

THE THOMSON EFFECT

Thomson (Lord Kelvin) realized that a relationship should exist between the Seebeck and Peltier effects. From thermodynamical arguments he derived the third relation (now known as the Thomson effect), which states that if in a current carrying conductor a temperature gradient exists then energy interchange between the surroundings and the conductor will take place. This effect is shown in figure (1-3). In this case the coefficient is ascribed to the material itself and not to the junction (it is also known as the homogeneous thermoelectric effect).

Hence the relation is

$$p = \tau(T) I \frac{dT}{dX} \quad (1-3)$$

i.e. the coefficient is calculated per unit length

P = Power absorbed or liberated

τ = Thomson coefficient

I = electric current

dT/dX = temperature gradient

Since the heat flow due to the Thomson effect depends upon the product of current and temperature gradient, and it is a second order effect and therefore is of secondary importance.

Thomson showed that the Peltier and Seebeck coefficients are related by the equation:

$$\pi(T) = \alpha(T)T \quad (1-4)$$

A DISCUSSION ON THE THERMOELECTRIC EFFECTS

The thermoelectric effects discussed above are reversible i.e. heat may be converted into electricity and vice versa. There are of course some irreversible thermoelectric effects. The most important is the Joule effect (commonly known as the resistance loss which occurs in all circuits with the exception of superconductors).

The Seebeck effect is utilized in thermoelectric generators. The most known is the thermocouple used for temperature measurements for the last 80 years or so.

The Peltier effect may be used for either cooling or heating but is used mainly for cooling, because heating effects can be produced more effectively by some other means. Therefore one may find in the literature reference to the Peltier cooler or Peltier cooling effect which are not strictly correct (since it neglects the heating effect).

The basic theory of thermoelectric refrigerators and generators was derived first by Altenkirch¹. He showed that for both applications, materials ~~were~~ with high thermoelectric coefficients, high electrical conductivity and low thermal conductivity were required. But it was quite a different matter knowing the favourable properties and obtaining materials embodying them. Up to the end of the second world war no real progress was made in the field of thermoelectricity. Only with the introduction of semiconductors the field was brought to life again. The pioneers in the field were the Russians, later on, the interest spread to the rest of the world. It ~~is~~ only then that the Peltier

was

effect could be used for thermoelectric cooling. The main reason for not using metallic junction in coolers was the low efficiency of the device, which was of the order of 0.3% but with semiconductors efficiencies of the order of 5% or better can be achieved and therefore commercial use can be made of the Peltier effect. Thermoelectric coolers are used today for spot cooling in electronics, laboratory instruments, air conditioning for submarines and other uses. The main advantage of a thermoelectric cooler is the absence of moving parts and hence low maintenance. The same applies to thermoelectric generators. The fact that there are no moving parts makes it possible to use them in remote places where frequent maintenance is impossible³.

Up to now ^{no} useful application has been found for the Thomson effect, but the effect must be taken into account when precise measurements are performed.

In order to measure the quality of the material for either a heat pump or a generator a figure of merit Z is defined

$$Z = \alpha^2 \frac{\sigma}{k} \quad (1-5)$$

where α = average Seebeck coefficient

σ = average electrical conductivity

k = average thermal conductivity

If it is assumed that α , σ and k are independent of temperature, then the average values are taken for the two legs shown in Fig. (1-4) i.e.

$$\alpha = \frac{\alpha_1 + \alpha_2}{2}$$

etc.

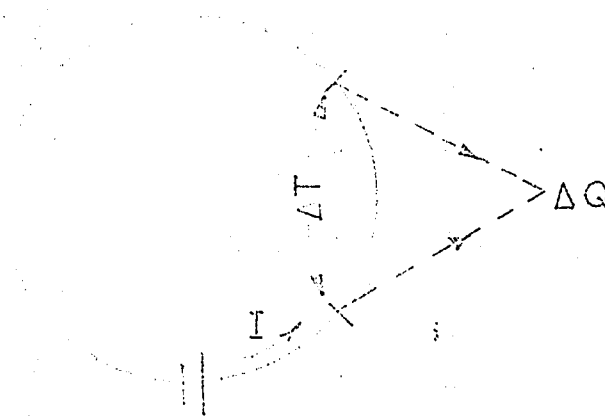


fig. 1.3

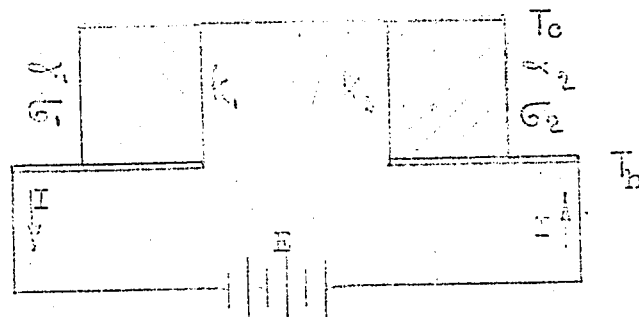


fig. 1.4

but if the values of the electrical conductivity, thermal conductivity and Seebeck coefficient are not independent of temperature and they are not, then the average value is taken also over a temperature range and then the value of Z is valid for this temperature range only (to a first approximation). This led to the materials being classified according to their working temperature range. A material suitable for a thermoelectric generator working at a temperature of 600°C . is not suitable for a refrigerator working at a temperature of -20°C . since the figure of merit changes considerably over such a temperature range.

A great deal of research is being done at the moment to increase the value of Z . It is worth mentioning that thermocouples having different values of Z may be cascaded in order to increase the overall efficiency of the system. Z has the dimensions of T^{-1} and it is sometimes known as Ioffe's coefficient since it was first used by A.F. Ioffe¹. This coefficient was derived experimentally and it was found that for metals it has ~~the~~ a value of about 0.1×10^{-3} per $^{\circ}\text{C}$., for semiconductor materials Z is of the order of 1×10^{-3} to 3.5×10^{-3} . Some manufactures claim a figure of merit of 4×10^{-3} and higher. With materials having a figure of merit of the order 5×10^{-3} and higher, commercial thermoelectric

refrigeration will be not only feasible but it will be able to compete with the compressor type refrigerator.

The exact analysis of thermoelectric systems is complicated because most of the parameters involved are temperature dependent, as a result many simplifications will be required in the following derivations in order to arrive at the required equivalent circuits.

CHAPTER 2: PHYSICAL BASIS OF THERMOELECTRICITY

a) THERMOELECTRIC PHENOMENA IN SEMICONDUCTORS

In this chapter a brief explanation of thermoelectric effects pertinent to the discussion is given. The equations governing these effects are derived as an extension of the P-N junction theory. This theory is given in greater detail elsewhere 1, 2, 4, 5, 6, 13.

Semiconductors in their pure state (intrinsic semiconductors) have a high resistance. It is only when impurity atoms are added that any appreciable conduction takes place. In thermoelectricity, the intermetallic compounds (also called III - V semiconductors for obvious reasons) e.g. Bismuth Telluride, Indium Antimonide etc. are mostly used because of their superior qualities, but these behave as though they belong to group IV of the periodic table. When impurity atoms from a group V metal, ^{are} introduced into an intrinsic semiconductor, one electron is left over after the four covalent bonds are satisfied. This leads to a "free" electrons for conduction and hence an "N" type semiconductor.

Similarly impurity atoms from group III of the periodic table lead to absence of electrons i.e. "holes" and hence a "P" type semiconductor. A hole may be regarded as a particle with an effective mass and effective velocity.

THE FERMI - DIRAC STATISTICS.

The semiconductors used in thermoelectricity are degenerate. (A degenerate semiconductor is one in which the concentration of current carriers in the conduction band

is so high that the distribution of energy cannot be approximated by classical statistics i.e. Maxwell - Boltzmann statistics). In order to determine the behaviour of the degenerate semiconductor the Fermi Statistics must be used.

The most important property is that both N and P type conduction is possible and a band gap exists in both types. The band gap is a band of energies that electrons cannot possess. The valence and conduction bands each represent a continuum of allowed energy levels, one level for each electron in the outer shell of each atom.

Figure (2-2) shows the band structure of thermoelectric semiconductors.

Note the narrow band of donor and acceptor levels which show a much greater density of impurities than for transistor semiconductors which are usually represented by single impurity levels.

At 0°K the energy states in the conduction band are empty. The valence band has one state for each electron and they are all occupied. Likewise the donor band is full of electrons and the acceptor band consists only of holes.

As the temperature rises electrons leave the donor band and enter the conduction band. This is the effect of heat on electron energy. Similarly in the P material electrons enter the acceptor level and holes appear in the valence band as a consequence. The probability that a state of energy (E) is occupied is given by the Fermi-Dirac Distribution Function

$$f(e) = \frac{1}{1 + e^{-(E - E_f)/kT}} \quad (2-1)$$

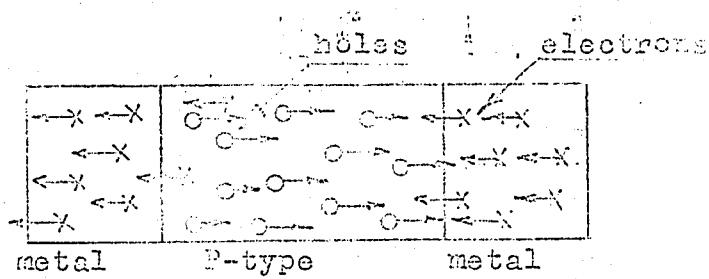
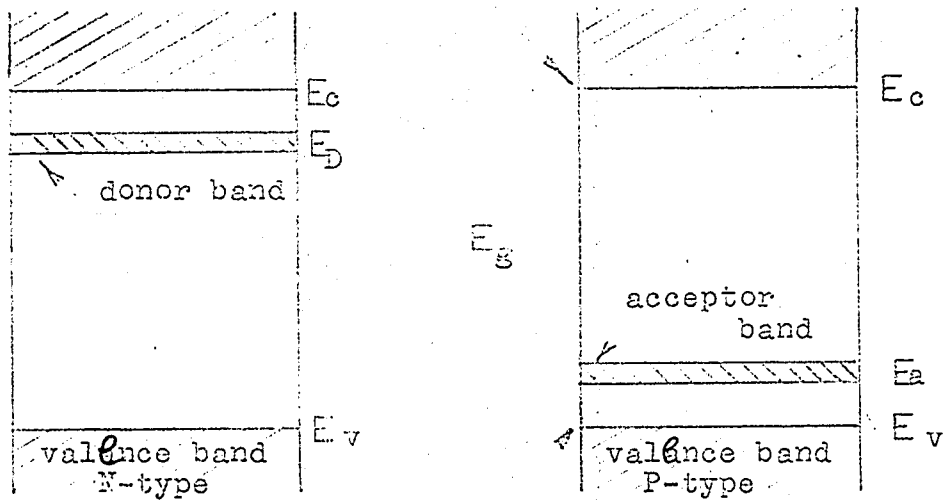


fig. 2.1

P-type conduction showing motion of holes in the semiconductor and electrons in the metal.

only electrons with energy E_c are conduction electrons



only holes with energy E_v are conduction holes

fig. 2.2

The value of $f(E)$, is the probability that a state with energy E is occupied . As shown in fig. (2-3) the curve is symmetrical on a semilog scale with most of the change from 1 to zero occurring within a few KT of the value where $f(E) = \frac{1}{2}$. This is known as the Fermi energy level. It can be seen that at low temperatures the change is abrupt becoming more gradual as T increases. The knowledge of the Fermi level enables us to plot the distribution of electron and holes at higher temperatures.

At low temperatures the Fermi level lies below the acceptor band for P type and above the donor band for the N type. The Fermi level drops as the temperature rises. This is explained by the increase in energy of mobile carriers. As the temperature rises, more low energy states (valence band) are emptied and high energy (conduction band) are occupied. Therefore the energy level having an occupation probability of $\frac{1}{2}$ is located at lower energy.

When a P-type material is joined ^{ed} to an N-type material a thermoelectric cell is formed. Although it is a P-N junction it does not possess the same properties as a P-N junction in the ordinary sense (i.e. diode). On the other hand some physical properties are the same, the most important are the formation of a transition region across the junction and the aligning of the Fermi Levels for the two types.

Bearing these properties in mind it is now possible to describe and derive the equations for the various thermoelectric effects.

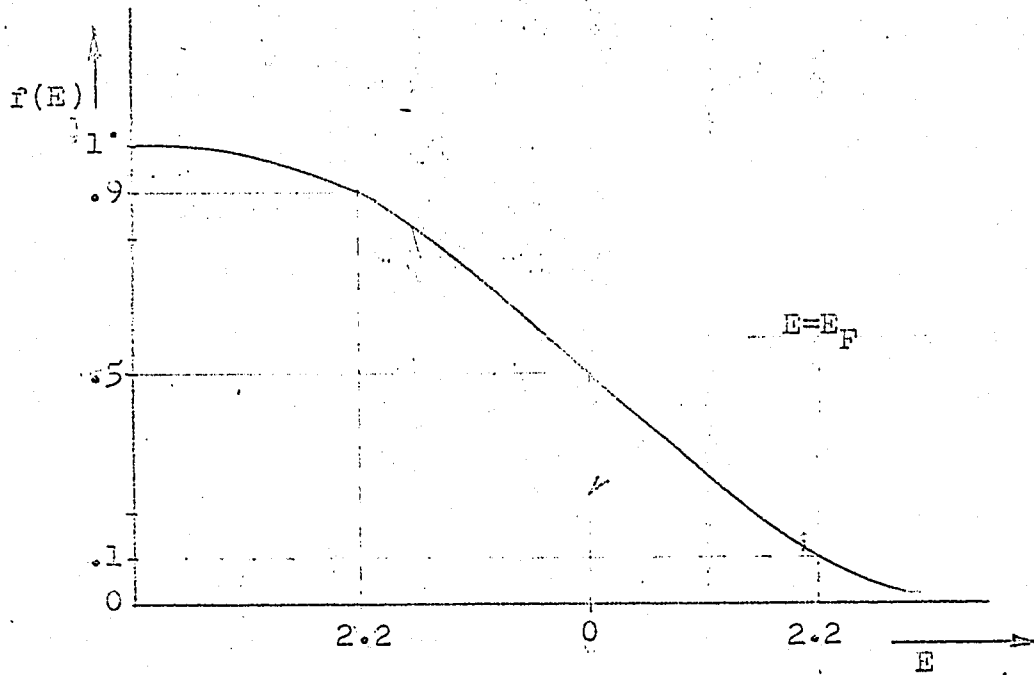


fig. 2.3

The Fermi-Dirac function

at high temps the material is essentially
intrinsic

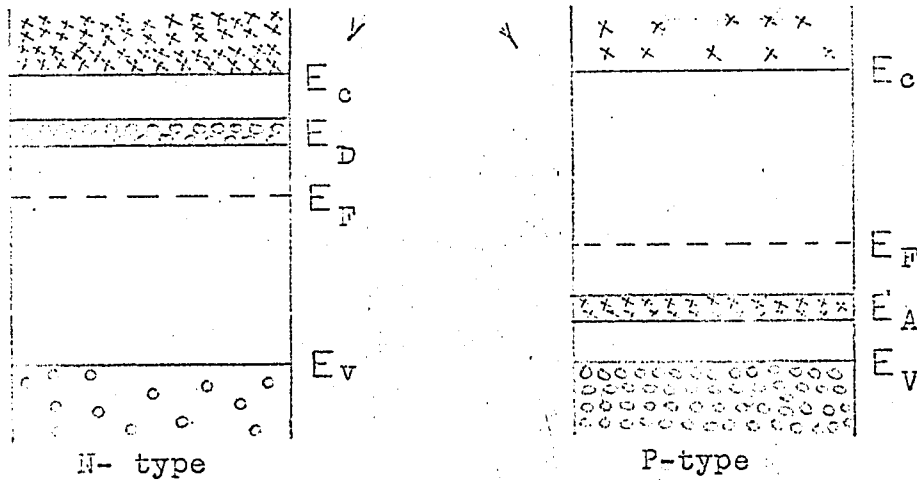


fig. 2.4

The Fermi levels lie below the donor band for the N-type
and above the acceptor band for the P-type

THE Peltier Effect.

Consider a P-N Thermoelectric cell to which a voltage source is connected and a certain current flows through the junction. As was said before Peltier cooling takes place at the junction by absorbing energy from the surroundings. The energy creates carriers (electron hole pairs E-H-P) in the transition region thus sustaining the current. The energy entering the junction is quantized each quantum being called a phonon. A calculation of the variation of phonon density with distance can be made. It is assumed that phonons of all energies, distributed according to the temperature, enter the crystal in the region of the junction. The phonon density is independent of time but will decay exponentially with distance. The probability of the phonons being absorbed depends on the density of the states of the same energy as the phonon.

The rate of absorption of heat is $\dot{Q}_x$ at a distance x from the junction. The value of $\dot{Q}_x$ is

$$\dot{Q}_x = \dot{Q}_0 e^{-x/L_D} \quad (2-2)$$

Where $\dot{Q}_0$ = heat flow rate from the source at the junction

L_D = diffusion length for phonons.

The graph describing equation (2-2) is given in figure (2-5).

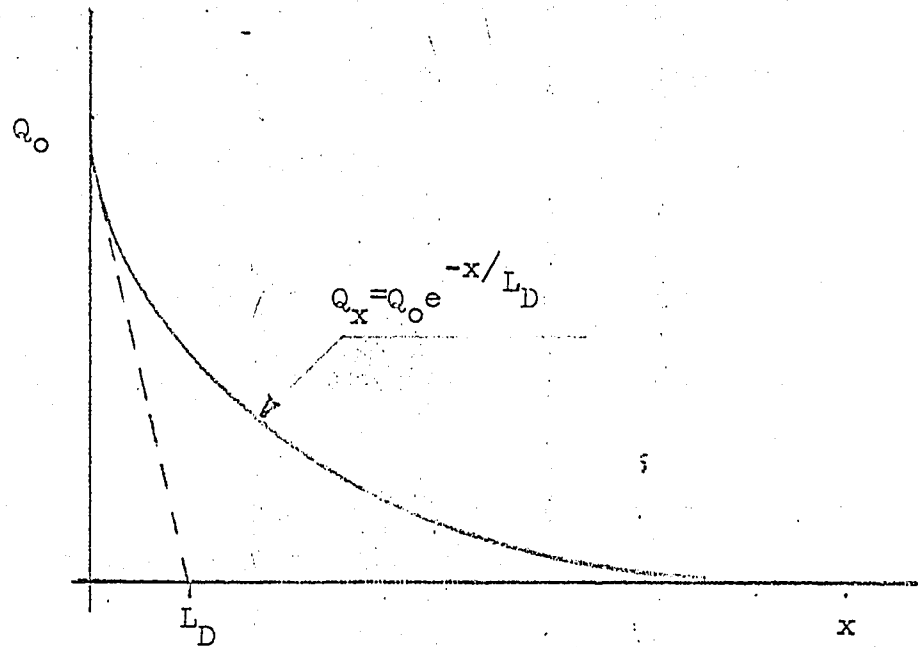


fig.(2-5)

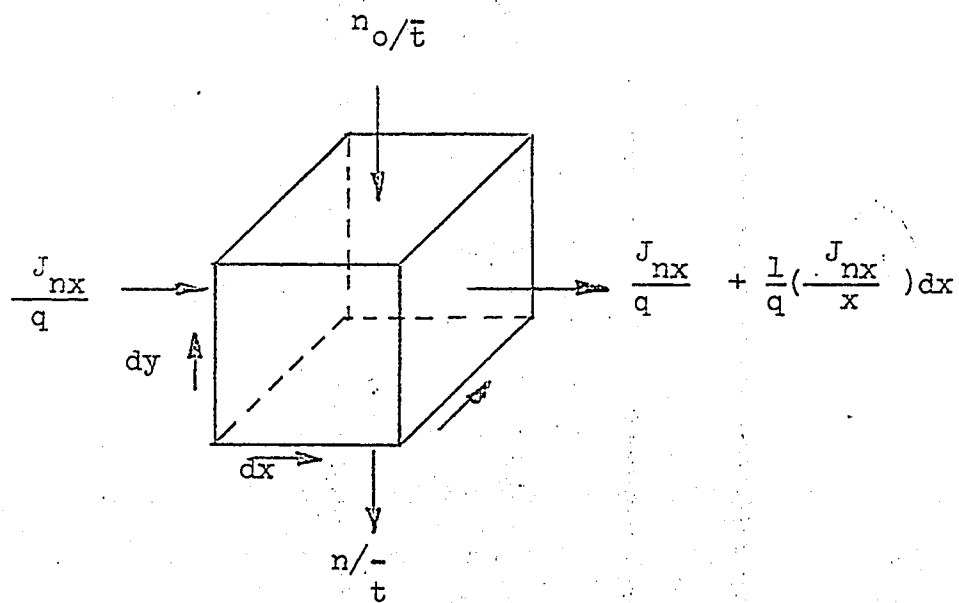


fig.(2-6)

The ^{is} heat rate removed from the cooled region is equal to the product of the net E.H.P. generation rate and the average energy absorbed per event. If $\bar{t}$ is the average recombination time

$$d \dot{Q}_x = \left(\frac{n_o}{\bar{t}} - \frac{n}{\bar{t}} \right) dx E'_g \quad (2-3)$$

where $d \dot{Q}_x$ = rate of heat absorbed in a volume dx long

$$\frac{n_o}{\bar{t}} dx = \# \text{ of electrons generated/sec/unit vol.}$$

$$n dx / \bar{t} = \# \text{ of electrons recombined/sec/unit vol.}$$

$$E'_g = \text{average energy absorbed/event}$$

The decay in space of a particular group of electrons is

$$n(x) = n_o(x) e^{-x/L_P} \quad (2-4)$$

where L_P - diffusion length for electrons in the P region.

hence $n_o/\bar{t}$ and $n/\bar{t}$ are the generation and recombination rates

are also functions of x .

$$\frac{d}{dx} \left(\frac{n(x)}{\bar{t}} \right) = \frac{n_o(x)}{\bar{t}} e^{-x/L_P} = - \frac{n(x)}{\bar{t}} \quad (2-5)$$

(E'_g is the average energy needed to create a pair). The number of thermal electrons in the conduction plus acceptor bands is exactly matched by the holes in the valence plus donor bands. At any instant of time

$$n + N_a = p + N_d \quad (2-6)$$

where N_a and N_d are the impurity densities of acceptors and donors, in the P & N regions respectively. This equation assumes complete activation of the impurity bands.

The net current density out of a unit cube of material figure (2-6) in the transition region must balance with the net charge formation rate.

$$\frac{J_{nx}}{q} + \frac{n_o(x) dx}{\bar{\tau}} = \frac{1}{q} (J_{nx} + \frac{\partial J_{nx}}{\partial x} dx) + \frac{n(x)}{\bar{\tau}} dx \quad (2-7)$$

where J_{nx} is the electron current density.

A similar expression can be written for J_{px}

Hence
$$\frac{dJ_{nx}}{dx} = \frac{q}{\bar{\tau}} [n_o(x) - n(x)]$$

but
$$J_{nx} = q D_n \left(\frac{dn(x)}{dx} \right)$$

$$\therefore q D_n \frac{d^2 n(x)}{dx^2} = \frac{q}{\bar{\tau}} [n_o(x) - n(x)] \quad (2-8)$$

From equation (2-3)

$$[n_o(x) - n(x)] = \frac{\bar{\tau}}{E_g'} \left(\frac{d\dot{Q}_x}{dx} \right)$$

Hence
$$q D_n \left(\frac{d^2 n}{dx^2} \right) = \frac{q}{\bar{\tau}} \left(\frac{\bar{\tau}}{E_g'} \right) \left(\frac{d\dot{Q}_x}{dx} \right) = \frac{1}{E_g'} \left(\frac{-\dot{Q}_o}{L_D} \right) e^{-x/L_D} \quad (2-9)$$

$$\therefore \frac{d^2 n}{dx^2} = \left(\frac{-\dot{Q}_o}{D_n E_g' L_D} \right) e^{-x/L_D}$$

integrating

$$\frac{dn}{dx} = \left(\frac{\dot{Q}_o}{D_n E_g'} \right) e^{-x/L_D} + C_1$$

When $x = \infty \quad \frac{dn}{dx} = 0 \quad \therefore C_1 = 0$

Integrating again

$$n(x) = \left(\frac{-\dot{Q}_0 L_D}{D_n E_g} \right) e^{-x/L_D} + C_2$$

When $x=0 \quad n(\infty) = n_p$ i.e. the equilibrium minority carrier density

Hence $n = n_p - n_{p0} e^{-x/L_D} \quad (2-12)$

Where $n_{p0} = \frac{\dot{Q}_0 L_D}{D_n E_g} = \text{minority carrier density at } x=0$

But whatever the shape of the function $n(x)$ it is zero at $x=0$
i.e. $n_{p0} = n_p$

Finally $n = \frac{\dot{Q}_0 L_D}{D_n E_g} (1 - e^{-x/L_D}) \quad (2-13)$

Hence the electron current I_{gm} due to thermal E.H.P. production is

$$I_{gm} = q D_n \left(\frac{dn}{dx} \right) = q D_n \left(\frac{\dot{Q}_0}{D_n E_g} \right) e^{-x/L_D} \quad (2-14)$$

at

$$x=0 \quad I_{gm} = I$$

$$\therefore I = \frac{q \dot{Q}_0}{E_g}$$

Thus we arrive at an expression for the Peltier coefficient

$$\underline{\underline{\pi_{mp} = \frac{\dot{Q}_0}{I} = \frac{E_g}{q}}} \quad (2-15)$$

An examination of this equation reveals the properties needed for a good Peltier cooler. The average energy absorbed per event when a phonon creates an E.H.P. is a function of the energy distribution. A degenerate semiconductor will have a plentiful supply of electrons in the donor band or holes in the acceptor band. Low energy phonons are absorbed by extrinsic semiconductors while it takes high energy phonons to create pairs in intrinsic semiconductors. The optimum doping intensities place thermoelectric materials between the intrinsic and extrinsic condition. It appears from the above analysis what is needed is a state distribution function that exactly matches the continuous phonon energy distribution function for a given temperature.

THE THOMSON EFFECT

The Thomson effect is a reversible transformation gradient of electrical energy and heat due to a finite temperature in any single material. The heat is transferred at a rate proportional to the current and temperature gradient. The physical process is the change in energy content of the carriers with temperature. The heat is absorbed at a rate

$$d\dot{Q}_{Thm} = \tau I \left(\frac{dT}{dx} \right) dx \quad (2-16)$$

where τ = Thomson coefficient

In the N leg the electrons move in a direction of positive temperature gradient and against the direction of positive current. The electrons move from a region rich in electrons to one deficient in electrons. This is due to the thermal diffusion of carriers away from the hot end. Hence there is a drop in potential energy for the carrier as it moves away from the region of dense charge.

A corresponding action takes place in the P type. When holes flow to a region of higher temperature, heat is absorbed and hole density decreases.

The current is negative in the N material and positive in the P material, while dT/dx is positive in both. Since heat is absorbed in both legs, it is clear that N is negative and P is positive. In terms of band structure of extrinsic semiconductors the above model can be described as a shift in energy level occupation with temperature. The Fermi Dirac distribution of electrons and holes accounts for the occupation of higher energy states by electrons above E_c and lower energy states for holes below E_v as temperature rises.

The total thermoelectric effect includes generation of irreversible Joulean heat I^2R .

Hence

$$\dot{Q}_{Total} = (\tau I \Delta T + I^2 R) \quad (2-17)$$

THE SEEBECK EFFECT

The thermoelectric cooler is driven by an external voltage source of voltage E , Kirchoff's law requires E to be balanced by internal voltages. These voltages are the IR drop and the thermoelectric or Seebeck voltage E_s . The thermoelectric voltage is itself the sum of four e.m.f.'s, associated with the Peltier and Thomson effects. The useful cooling power is $E_s I$.

The sum of the Peltier and Thomson energy conversion rates is

$$\dot{Q} = \pi_p I + I \int_{T_c}^{T_h} \tau dT = E_s I \quad (2-18)$$

if $\dot{Q}$ is expressed as Joules/sec it is clear that the terms on the R.H.S. of equation (2-18) ^{have} take units "volts times amperes".

$$\text{Thus } \pi_{np} = E_p$$

$$\& \int_{T_c}^{T_h} \tau dT = E_T \quad \text{where}$$

E_p & E_T are Peltier and Thomson voltages respectively.

The Seebeck voltage $E_s = E_p + E_T$. The proportionality between E_s & ΔT can be written as

$$E_s = \alpha \Delta T \quad (2-19)$$

where α , the Seebeck coefficient, is the rate the thermal e.m.f. changes with temperature in a given system. The two materials involved, their two junctions and the two bulk effects (E_p & E_T) make up the Seebeck coefficient, α is not independent of temperature and this led Lord Kelvin to develop the thermodynamic foundation of thermoelectric effects.

In general the power source is not connected at the hot junction. Hence the general case shown in figure (2-7). Subtracting the circuit IR drop from the applied voltage E , E_s just sustains the internal potentials. It should be pointed out that the internal potentials oppose each other in pairs. Thus the net Seebeck voltage is the sum of the difference between two Peltier voltages and the difference between two Thomson voltages

$$E - IR = (E_{p_c} - E_{p_h}) + (E_{T_p} - E_{T_n}) \quad (2-20)$$

The voltage E_s developed around a thermoelectric circuit is due to two temperature effects in each leg; (1) A shift in Fermi level downward at the hot end due to greater occupancy of conduction band state and (2) the potential gradient established by the redistribution of charge. The net potential drop in volts is

$$E_s = \frac{1}{q} \left[(E_c - E_f)_c + \phi_{sc} \right] - \frac{1}{q} \left[(E_c - E_f)_h + \phi_{sh} \right] \quad (2-21)$$

Where $(E_c - E_f)$ = the conduction band separation from the Fermi level.

ϕ_s = Electrostatic potential of the conduction band edge due to thermal diffusion. The contribution of the metal ends is negligible

By definition $\alpha_n = \frac{dE_s}{dT}$, thus

$$\alpha_n = \frac{1}{q} \left[\frac{+d(E_c - E_f)}{dT} + \frac{d\phi_s}{dT} \right] \quad (2-22)$$

The band gap width and doping levels determine the first term, which is the Fermi contribution to thermoelectric effect. The change in ϕ_s is due to the Thomson specific heat of electron gas.

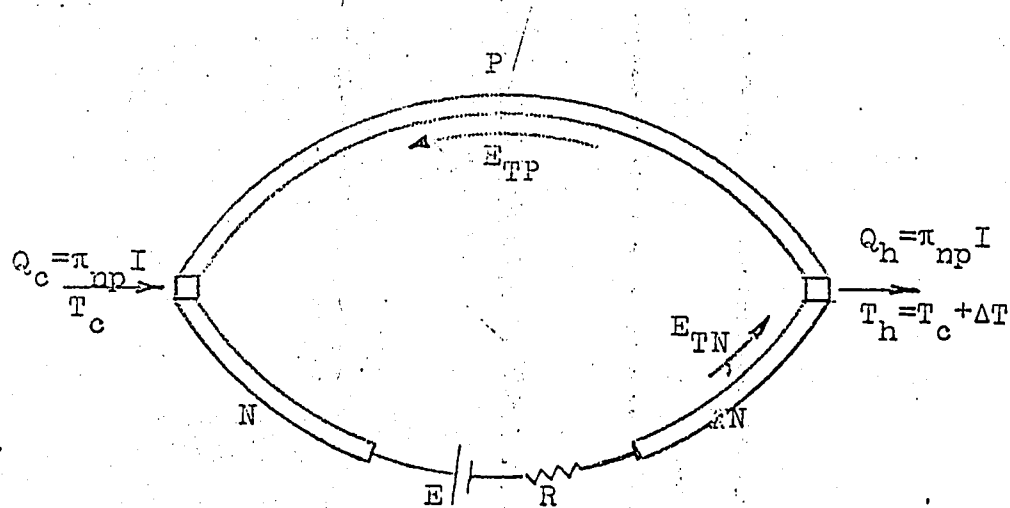


fig. 2.7

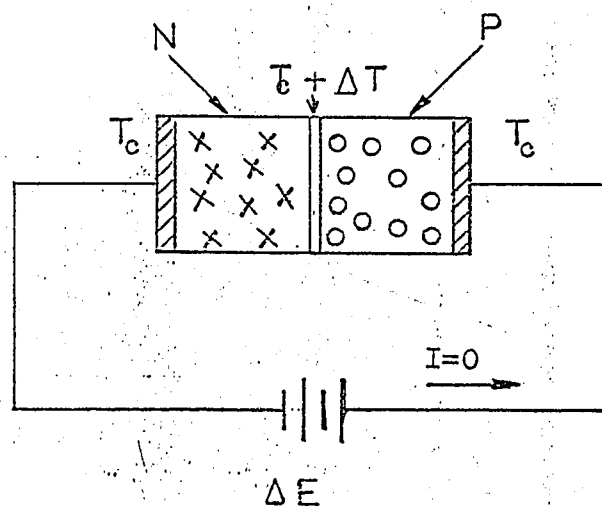


fig. 2.8

A P-N junction with a thermal gradient in each material and with zero current

Figures (2-8) and (2-9) show graphically the effect of temperature gradient on a P-N junction. Figure (2-8) shows the diffusion of carriers to the cooler end of each leg, similar to condensation of a vapor on cooling. In figure (2-9) it is seen that the conduction band edge drops as the temperature increases for N type material and the valence band edge rises as temperature increases for P type material. The Fermi level coincide across the hot junction so that the Seebeck voltage is

$$\phi_n + \phi_p = qE_s \quad (2-23)$$

Having defined α_n for the N type semiconductor and recognizing the existence of the corresponding α_p we have

$$\begin{aligned} \phi_p &= q\alpha_p \int_{T_c}^{T_c+\Delta T} dT \\ \phi_n &= -q\alpha_n \int_{T_c}^{T_c+\Delta T} dT \end{aligned} \quad (2-24)$$

as the changes in potential energy from the cold to the hot end. We now add these energies to obtain

$$\alpha_{pn} = \alpha_p - \alpha_n = \frac{\Delta E_s}{\Delta T}$$

$$\text{Hence } E_s = \int_{T_c}^{T_c+\Delta T} \alpha_{pn} dT \quad (2-25)$$

by substitution in (2-18) and (2-19) we get

$$\int_{T_c}^{T_c+\Delta T} \alpha_{pn} dT = \Pi_{pn} + \int_{T_c}^{T_c+\Delta T} (T_p - T_n) dT \quad (2-26)$$

differentiating we get

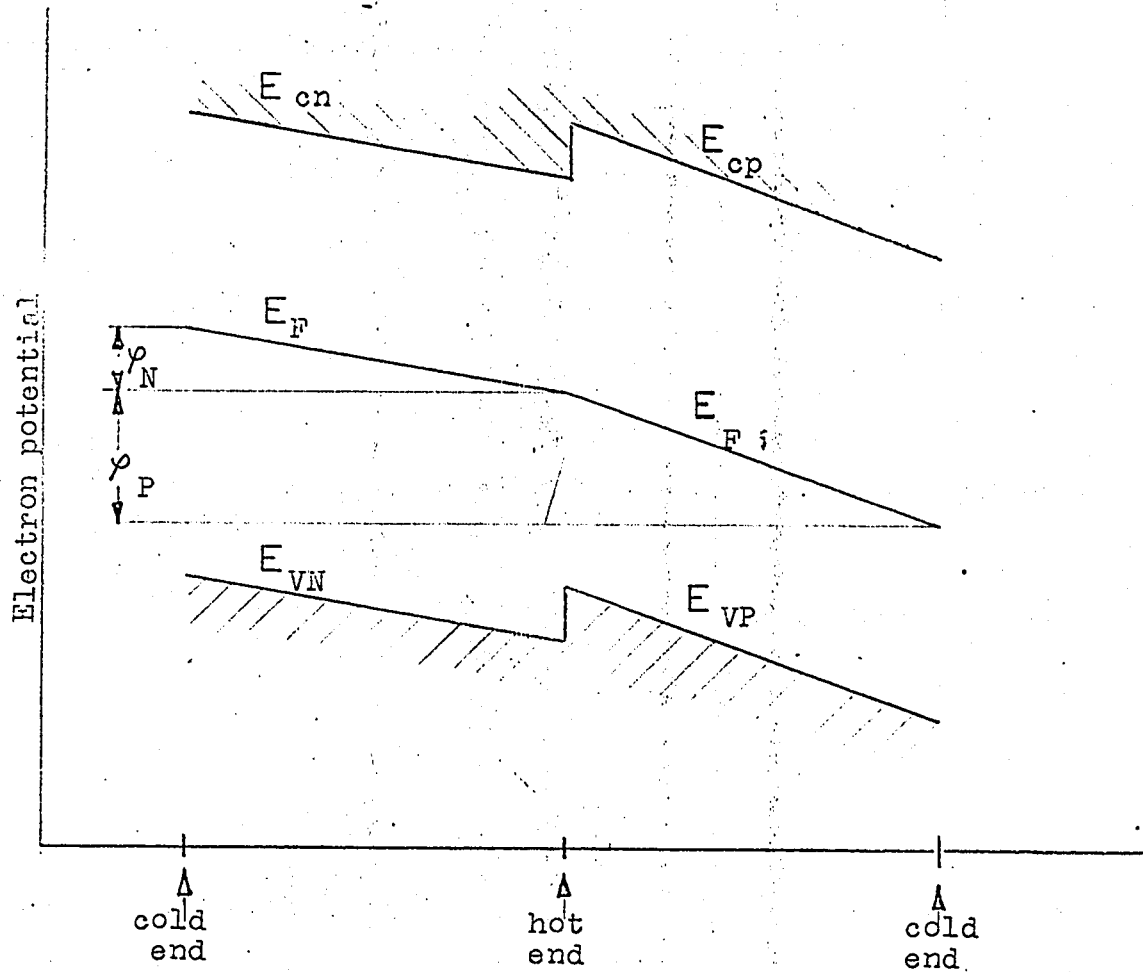


fig. 2.9

Energy level diagram showing the drop in conduction band edge in the same direction as the temperature gradient for N-type material and in the opposite direction for P-type material.

$$\alpha_{pn} = \frac{\pi_{pm}}{\Delta T} + (\tau_p - \tau_n) \quad (2-27)$$

$$\text{or } \frac{\Delta E_s}{\Delta T} = \frac{\pi_{pn}}{\Delta T} + (\tau_p - \tau_n) \quad (2-28)$$

More relations will be derived in later sections.

b) THEORY OF THERMOELECTRIC COOLING

A very important feature of thermoelectric cooling (or generation) is the independence of the efficiency of the unit on its capacity. Hence it can be derived using the parameters of only the heat pump.

With the same notation as before and where A_n & A_p are the cross sectional areas of the N & P type materials we get the following relations:

The heat pumped from the cold to the hot junction by the Peltier effect is

$$\begin{aligned} Q_o &= \pi_{np} I \\ &= \alpha_{np} T_c I = (\alpha_n - \alpha_p) T_c I \end{aligned}$$

An amount of heat $K\Delta T$ leaks back from the hot to the cold junction where

$$K = \frac{A_p K_p}{l_p} + \frac{A_n K_n}{l_n} \quad (2-29)$$

Assuming $A_n = A_p = A$ & $l_n = l_p = l$

$$\text{then } K = K_n + K_p \quad (2-29a)$$

Due to the passage of current in the thermocell* a certain amount of power is lost by heating. It can be shown that irrespective of the value

* A thermocell is a single thermoelectric couple used for heat pumping. This name has been used for the last five years.

of the temperature gradient, the Joule heat is equally divided between the hot and cold junctions. Hence the amount of heat due to the Joule effect at the cold junction is

$$Q_j = \frac{1}{2} I^2 R \quad (2-30)$$

Where $R = \frac{\rho_n l_n}{A_n} + \frac{\rho_p l_p}{A_p}$

Since $A_n = A_p = A$ $l_n = l_p = l$ and $\rho = \text{resistivity}$

$$R = \frac{l}{A} (n + p) = R_n + R_p \quad (2-30a)$$

Under steady state conditions i.e., the temperature of the hot and cold junctions are T_h & T_c respectively the heat absorbed from the surroundings plus the heat flowing along the arms are equal to the heat removed by the Peltier effect, the heat flowing along the arms consists of the Joulean heat and the heat due to thermal conduction.

Therefore the net heat removed from the cold junction is

$$Q_c = Q_o - K T - Q_j$$

$$Q_c = \Pi_p I - K(T_h - T_c) - \frac{1}{2} I^2 R \quad (2-31)$$

or $Q_c = \alpha T_c I - K(T_h - T_c) - \frac{1}{2} I^2 R \quad (2-31a)$

The power supplied to the thermocell consists of two parts; the Joulean heat loss and the pumping power. Therefore, the power supplied P is given by

$$P = \alpha_{pn} (T_h - T_c) I + I^2 R \quad \text{dividing by } I \quad (2-32)$$

$$V = \alpha_{pn} (T_h - T_c) + IR \quad (2-32a)$$

The coefficient of performance is defined as

$$\eta = \frac{Q_c}{P} \quad (2-33)$$

namely
$$\eta = \frac{\alpha_{pn} I T_c - K(T_h - T_c) - \frac{1}{2} I^2 R}{\alpha_{pn} (T_h - T_c) I + I^2 R} \quad (2-34)$$

For a given thermocell and for fixed hot and cold junction temperatures the coefficient of performance is a function of the current I , the thermal conductance K and of the resistance R . But R & K are not independent; they are related by the figure of merit Z . For a given cooling capacity the ratio Q/A should go up with electrical and thermal conductivities. The best conditions to minimize the effect of Joule heating and thermal conductance are taken. It can be shown that η reaches a maximum value when physical properties of the cell obey the ratio;

$$\frac{l_p A_p}{l_n A_n} = \left(\frac{K_p \sigma_p}{K_n \sigma_n} \right)^{1/2} \quad (2-35)$$

Where σ_p and σ_n are the specific resistivities of the P&N semiconductors.

From equation (2-31) we get

$$T_h - T_c = \frac{\pi I - \frac{1}{2} I^2 R - Q_c}{K}$$

$$\frac{\partial (T_h - T_c)}{\partial I} = \frac{\pi - IR}{K} = 0 \quad \text{Hence } I = \frac{\pi}{R}$$

$$\therefore (T_h - T_c)_{\max} = \frac{\frac{\pi^2}{R} - \frac{1}{2} \frac{\pi^2}{R} - Q_c}{K} = \frac{1}{2} \frac{\pi^2}{RK} - \frac{Q_c}{K} \quad (2-36)$$

if $Q_c = 0$ i.e. no load conditions

$$\Delta T = (T_h - T_c) = \frac{\pi^2}{2RK} \quad (2-37)$$

but $\pi = \alpha T$ from (2-27)

$$\text{hence } \Delta T = \frac{\alpha_{pn}^2 T_c^2}{2RK} = \frac{1}{2} Z (T_c^2) \quad (2-37a)$$

$$\text{where } Z = \frac{\alpha_{pn}^2}{RK} = \text{figure of merit}$$

differentiating equation (2-34) we get

$$\frac{dh}{dI} = \frac{\alpha [T_c(T_h - T_c)I + I^2 R] (\alpha T_c - IR) - [\alpha I T_c - K(T_h - T_c) - I^2 R] \times [(T_h T_c) + 2IR]}{(T_h - T_c)I + I^2 R} = 0$$

$$\text{hence } \alpha^2 T_c (T_h - T_c) I - \alpha I (T_h - T_c) R + I^2 R \alpha T_c - I^3 R^2 - [\alpha I (T_h - T_c) + 2\alpha I^2 R T_c - \frac{1}{2} I^2 R \times \\ \times \alpha (T_h - T_c) - I^3 R^2 - K \alpha (T_h - T_c) - 2KIR(T_h - T_c)] = 0$$

$$I = \frac{2KR(T_h - T_c) \pm \sqrt{(4K^2 R^2 (T_h - T_c)^2 + 2K\alpha^2 (T_h - T_c)^2 R(T_h + T_c))}}{\alpha R(T_h + T_c)}$$

$$I = \frac{2KR(T_h - T_c)}{R(T_h + T_c)} \frac{1 \pm \sqrt{1 + Z(T_h + T_c)}}{Z} = \frac{2\alpha}{ZR} \frac{T_h - T_c}{T_h + T_c} \left[1 + \sqrt{1 + Z(T_h + T_c)} \right]$$

$$I = \frac{2}{ZR} \frac{T_h - T_c}{T_h + T_c} \frac{(1 + \sqrt{1 + Z(T_h + T_c)}) (1 - \sqrt{1 + Z(T_h + T_c)})}{(1 - \sqrt{1 + Z(T_h + T_c)})} = \frac{2(T_h - T_c)}{Z(T_h + T_c)} \frac{1 - 1 - \frac{1}{2} Z(T_h + T_c)}{(1 - \sqrt{1 + Z(T_h + T_c)})}$$

Finally we get

$$I = \frac{\alpha_{pn} \Delta T}{(\sqrt{1 + \frac{1}{2} Z(T_h + T_c)} - 1)R} \quad (2-39)$$

Substituting the value of I in equation (2-34) and letting

$$A = \sqrt{1 + \frac{1}{2} Z(T_h + T_c)} \text{ we get}$$

$$\eta = \frac{\frac{(T_h - T_c)T_c}{(A - 1)R} - \frac{1}{2} \frac{(T_h - T_c)R^2}{(A - 1)R} - \frac{K(T_h - T_c)}{1}}{\frac{\alpha (T_h - T_c)}{(A - 1)R} \times \frac{\alpha (T_h - T_c) A}{(A - 1)}}$$

$$= \frac{T_c}{T_h - T_c} \times \frac{A - 1 - \frac{1}{2} \frac{T_h}{T_c} + \frac{1}{2} - \frac{1}{2} \frac{T_h}{T_c} - \frac{1}{2} \frac{T_h}{T_c} - \frac{1}{2} - \frac{1}{2} \frac{T_h}{T_c} + 2}{A}$$

$$= \frac{T_c}{T_h - T_c} \times \frac{\frac{2}{Z T_c} (A - 1) + (A - 1) - \frac{T_h}{T_c}}{A}$$

$$= \frac{T_c}{T_h - T_c} \times \frac{\left(\frac{2}{Z T_c} + 1 \right) \times (A - 1) - \frac{T_h}{T_c}}{A} \times \frac{A + 1}{A + 1}$$

$$= \frac{T_c}{T_h - T_c} \times \frac{\frac{T_h}{T_c} + 1 + \frac{1}{2} Z (T_h + T_c) - \frac{T_h}{T_c} A - \frac{T_h}{T_c}}{A(A + 1)}$$

Substituting back
for A we

finally get $\eta = \frac{T_c}{T_h - T_c} \times \frac{\sqrt{1 + \frac{1}{2} Z (T_h + T_c)} - \frac{T_h}{T_c}}{\sqrt{1 + \frac{1}{2} Z (T_h + T_c)} + 1}$

hence $\eta = \frac{T_c}{T_h - T_c} \times \frac{\sqrt{1 + \frac{1}{2} Z (T_h + T_c)} - \frac{T_h}{T_c}}{\sqrt{1 + \frac{1}{2} Z (T_h + T_c)} + 1} \quad (2-40)$

It can be seen from equations (2-37a) and (2-40) that under steady state conditions for a fixed value of T_c and T_h both the co-efficient of performance and the maximum temperature drop depend on the value of the figure of merit Z and when $Z \rightarrow \infty$ the coefficient of performance becomes that of the Carnot cycle for an ideal thermodynamic machine i.e.

$$\eta_c = \frac{T_c}{T_h - T_c} \quad (2-41)$$

In the above derivation the following assumptions were made:

- 1) The electrical and thermal conductivities are independent of temperature;
- 2) The thermoelement consists of homogeneous material;
- 3) The electrical resistance, thermal resistance and specific heat of the connecting straps are small and therefore neglected;
- 4) The temperature gradient from hot to cold junction is linear;
- 5) The heat and current flow are one dimensional;
- 6) The Thomson coefficient is negligible;
- 7) Heat transferred by convection and radiation from hot to cold junction through the legs is negligible;
- 8) Only single stage with one thermoelectric element is considered;
- 9) The analysis applies to steady state conditions only;

The above restrictions limit the application of the various equations therefore general equations for dynamic conditions will be derived next.

c) DYNAMIC RESPONSE OF A THERMOELECTRIC COOLER

In order to describe completely the system depicted in figure (2-10), three pairs of equations are required:

- 1) Each junction at any instant of time must have its energy under balance. The amount of heat removed from the load is equal to the difference between the amount of heat pumped by the Peltier effect and the heat reaching the cold junction by thermal conduction

$$\dot{Q}_c = \alpha_{(PM)_c} T_c I(t) - K_m A_m \left. \frac{\partial T_m}{\partial x} \right|_{x=0} - K_p A_p \left. \frac{\partial T_p}{\partial x} \right|_{x=0} \quad (2-42)$$

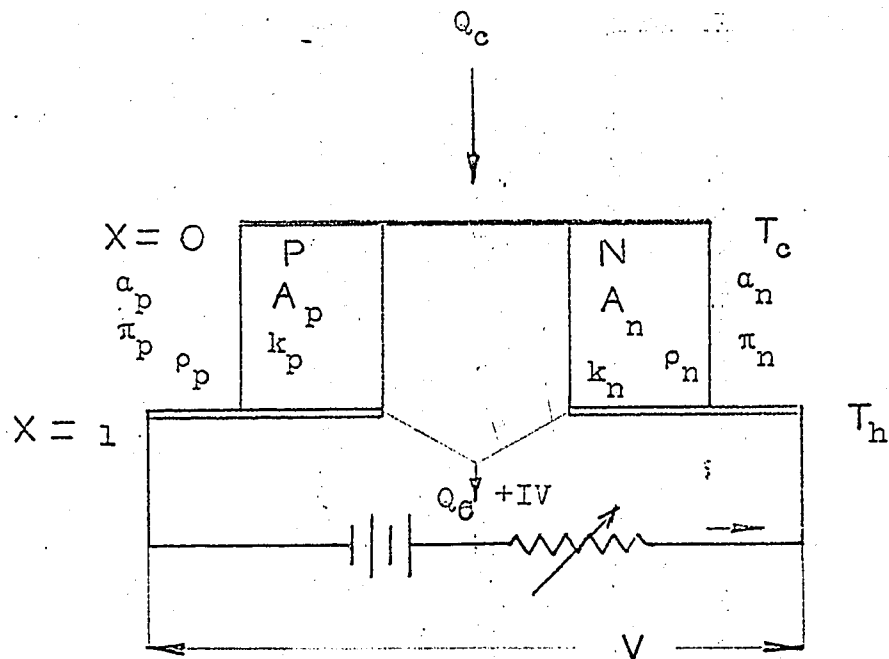


fig. 2.10

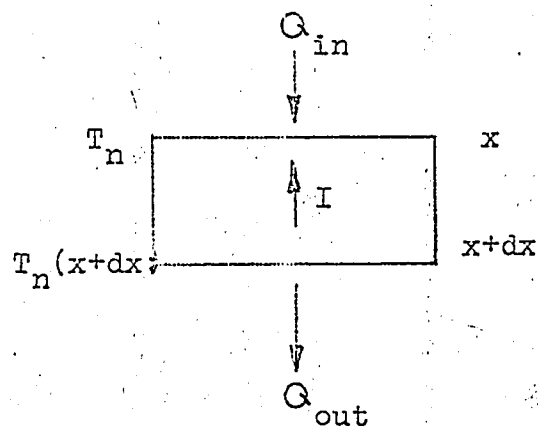


fig. 2.11

An element of length dx in the N leg

and the amount of heat removed from the hot junction by the surroundings (or another coolant) is the difference between the heat brought to the hot junction by the Peltier effect and the heat conducted back to the cold junction

$$-\dot{Q}_h = -\alpha_{(Pn)} T_h I(t) + k_n A_n \left. \frac{\partial T_n}{\partial x} \right|_{x=L} + k_p A_p \left. \frac{\partial T_p}{\partial x} \right|_{x=L} \quad (2-43)$$

2) The rate at which the energy of the system is decreased is given by

$$\dot{Q}_h - \dot{Q}_c + V I(t) + \frac{dW}{dt} = 0 \quad (2-44)$$

where W is the energy accounted for by the specific heat of the P&N legs and is given by

$$W(t) = A_n \int_0^L C_n T_n(x,t) dx + A_p \int_0^L C_p T_p(x,t) dx \quad (2-45)$$

3) In order to determine the temperature distribution in the two legs of the thermocell consider an element of length dx in one of the legs, say the leg of N type material, and let the element be at a distance x from the cold junction. Let the power and current flow be as shown in figure (2-11).

The Law of Conservation of Energy requires that

$$\dot{Q}_{in} - \dot{Q}_{out} = \dot{Q}_j + \dot{Q}_c - \dot{Q}_s \quad (2-46)$$

where $\dot{Q}_j$, $\dot{Q}_\tau$ & $\dot{Q}_s$ are the Joulean heat, the Thomson heat and the decrease in stored energy respectively

$$\dot{Q}_{in} = K_n A_n \left. \frac{\partial T_n}{\partial x} \right|_x$$

$$\dot{Q}_{out} = K_n A_n \left. \frac{\partial T_n}{\partial x} \right|_{x+\Delta x}$$

The Joulean heat is given by

$$\dot{Q}_j = I^2 \rho_n \frac{\Delta x}{A_n} ,$$

$$\dot{Q}_\tau = I \tau_n \frac{\partial T_n}{\partial x} \Delta x$$

gives the Thomson heat

$$\text{and } \dot{Q}_s = C_n A_n \frac{\partial T_n}{\partial t} \Delta x + C_p A_p \frac{\partial T_p}{\partial t} \Delta x \quad \text{gives the decrease}$$

in stored energy. Substituting these values in equation (2-46) yields

$$K_n A_n \left(\frac{\partial T_n}{\partial x} \right) \Delta x - I^2 \rho_n \frac{\Delta x}{A_n} - I \tau_n \frac{\partial T_n}{\partial x} \Delta x + C_n A_n \frac{\partial T_n}{\partial t} \Delta x = 0 \quad (2-47)$$

In the p leg the equation will have the same form; the only difference is in the direction of current flow. Hence for the P leg we get:

$$K_p A_p \frac{\partial T_p}{\partial x} \Delta x - I^2 \rho_p \frac{\Delta x}{A_p} + I \tau_p \frac{\partial T_p}{\partial x} \Delta x + C_p A_p \frac{\partial T_p}{\partial t} \Delta x = 0 \quad (2-48)$$

Integrating equations (2-47) and (2-48) with respect to x we get

$$K_n A_n \frac{\partial T_n}{\partial x} \Big|_{x=l} - K_n A_n \frac{\partial T_n}{\partial x} \Big|_{x=0} - I^2 \int_0^l \frac{\rho_n}{A_n} dx - I \int_0^l \tau_n \frac{\partial T_n}{\partial x} dx + C_n \int_0^l A_n \frac{\partial T_n}{\partial t} dx = 0 \quad (2-49)$$

and

$$K_p A_p \frac{\partial T_p}{\partial x} \Big|_{x=l} - K_p A_p \frac{\partial T_p}{\partial x} \Big|_{x=0} - I^2 \int_0^l \frac{\rho_p}{A_p} dx + I \int_0^l \tau_p \frac{\partial T_p}{\partial x} dx + C_p \int_0^l A_p \frac{\partial T_p}{\partial t} dx = 0 \quad (2-50)$$

hence

$$\begin{aligned} \dot{Q}_h = & -\alpha_{pn} T_h + K_n A_n \frac{\partial T_n}{\partial x} \Big|_{x=0} + K_p A_p \frac{\partial T_p}{\partial x} \Big|_{x=0} + I^2 \left[\int_0^l \frac{\rho_n}{A_n} dx + \right. \\ & \left. + \int_0^l \frac{\rho_p}{A_p} dx \right] + I \int_{T_c}^{T_h} \tau_n dT - I \int_{T_c}^{T_h} \tau_p dT - \\ & - \frac{\partial}{\partial t} \left[C_n A_n \int_0^l T_n dx + C_p A_p \int_0^l T_p dx \right] \end{aligned} \quad (2-51)$$

Now substituting equations (2-42) and (2-51) in equation (2-44) we get after simplification

$$V = \left[\alpha_{(pn)_h} T_h - \alpha_{(pn)_c} T_c \right] - \int_{T_c}^{T_h} (\tau_n - \tau_p) dT - I \left(\int_0^l \frac{\rho_n}{A_n} dx - \int_0^l \frac{\rho_p}{A_p} dx \right) \quad (2-52)$$

If equation (2-52) is reduced to steady state conditions we will obtain equation (2-32a) again.

Equations (2-42), (2-43), (2-49) and (2-52) describe a thermoelectric refrigerator under all conditions.

In the above derivation a number of assumptions were again made;

- 1) The thermal and electrical conductivities are independent of temperature;
- 2) The Seebeck and Thomson coefficients and the specific heat are also independent of temperature;
- 3) The thermoelements are made of homogenous material.

Without these restrictions the equations obtained would have nonlinear coefficients and hence would make them impossible to handle. The above equations are very useful for investigating the behaviour of the system. Under dynamic conditions the analysis can be broken into large signal and small signal analysis, a detailed treatment of that nature is given in reference (7). The equations above have product type nonlinearities of current and temperature gradient and terms involving I^2 hence the time dependence of current is difficult to determine.

d) THERMODYNAMICS OF THERMOELECTRIC COOLERS.

In 1854 Lord Kelvin proposed a "quasi-thermodynamic" method of analysis for the thermoelectric effects. Although Kelvin himself pointed out that the method was not completely justifiable, experiments confirmed the results obtained. This theory was applied successfully in a number of cases ⁸ and others. In 1931 Onsager revised the problem and proved a general set of reciprocal relations treating the symmetry in the mutual interference of two or more irreversible processes occurring simultaneously in a system, and pointed out that the whole class of results obtained by Kelvin follows from the reciprocal relations.

Onsager's Reciprocal Relations became the main tool for treating systems involving more than one phenomenon. The thermoelectric effects were treated again using these relations by de Groot¹⁰, Domenicali¹¹, Callen¹² and others. Callen's and Domenicali's treatments are the most extensive and the treatment here will follow them in a sort of fusion.

In general a set of irreversible processes which has measurable parameters β_{ij} , say, can be expressed in the form;

$$\frac{\partial \beta}{\partial t} i = \sum_{ij} L_{ij} \sigma_{ij} \quad \text{where} \quad \sigma_j = \frac{\delta S}{\delta \beta_j} \quad (2-53)$$

where s is the entropy.

This is assuming that the macroscopic laws (Ohms law etc) can be expressed in a linear form. The σ_j are a measure of the deviation of entropy from its equilibrium state, since at equilibrium σ_j is zero (because s is a maximum at equilibrium). The kinetic coefficients "L"'s are functions of the state of the system depending on parameters such as temperature composition etc.. The quantity L_{ij} is a measure of the interference of the j^{th} process on the i^{th} .

Onsager's theorem states that $L_{ij} = L_{ji}$. This theorem simplifies the work and enables the coefficients to be determined. In order to simplify the work further the rate of production of entropy will be considered instead of the entropy itself (it is more difficult to find the connection between the entropy and the variable α_j). Therefore we get from a Taylor expansion

$$\delta S = \sum_j \left(\frac{\delta S}{\delta \beta_j} \right) \delta \beta_j = \sum_j \sigma_j \delta \beta_j \quad (2-54)$$

Therefore the rate of production of entropy is given by;

$$\frac{dS}{dt} = \sum_j \sigma_j \left(\frac{\partial \beta_j}{\partial t} \right) \quad \text{or} \quad \dot{S} = \sum_j \sigma_j \dot{\beta}_j \quad (2-55)$$

These equations can now be applied to a thermodynamic process where the mutual interactions are between heat and electric current flows. If the particle current density is J , the entropy s and energy density W then the divergence of each is the rate of change per unit volume of the corresponding variables, also we get the heat current density (Q) to be

$$Q = Ts \quad (2-56)$$

For a steady state process

$$\nabla \cdot W = 0 \quad (2-57)$$

$$\nabla \cdot J = 0 \quad (2-58)$$

$$\nabla \cdot S = \dot{S} \quad (2-59)$$

($\dot{S}$ = rate of production of entropy per unit volume)

The value of $\dot{S}$ has now to be determined.

$$Ts = W - VJ \quad (2-60)$$

where V = electrical potential. Strictly speaking the electrochemical potential μ must be used but $\mu = \mu_c + \mu_e$ where μ_c is the chemical potential and μ_e the electrical potential. For metals or semi-conductors μ_c is negligible and μ_e is V . Using (2-56) equation (2-60) becomes

$$Q = W - VJ \quad (2-61)$$

Hence under steady state conditions

$$\nabla \cdot Q = -\nabla V \cdot J \quad (2-62)$$

i.e. the rate of increase in heat current is equal to the rate of decrease in the potential energy current.

Hence

$$\dot{S} = \nabla \cdot S = \nabla \cdot \frac{1}{T} W - \nabla \cdot \frac{V}{T} J = \nabla \cdot \frac{1}{T} Q - \frac{1}{T} \nabla V \cdot J$$

using (2-62)

$$\dot{S} = \nabla \cdot \frac{1}{T} Q + \frac{1}{T} \nabla \cdot Q \quad (2-63)$$

Now it is possible to write a set of simultaneous equations where the currents are J and Q , the corresponding forces $\frac{1}{T} \nabla V$ and $\nabla \frac{1}{T}$

$$\left. \begin{aligned} -J &= L_{11} \frac{1}{T} \nabla V + L_{12} \nabla \frac{1}{T} \\ Q &= L_{21} \frac{1}{T} \nabla V + L_{22} \nabla \frac{1}{T} \end{aligned} \right\} \quad (2-64)$$

Callen had shown that the "L" coefficient in the above two equations have the following values

$$\begin{aligned} L_{11} &= \frac{T}{e^2} \sigma \\ L_{12} = L_{21} &= - \frac{T^2}{e^2} \alpha \\ L_{22} &= \frac{T^2}{e^2} \sigma \alpha^2 + T^2 k \end{aligned} \quad (2-65)$$

Where: σ is the electric conductivity which is defined in this case as the electric current density (eJ) per unit electric gradient, k is the thermal conductivity (the ratio of heat current to a unit temperature gradient) and e is the electronic charge.

Since these quantities are not easily measured these equations are more of a theoretical value than a practical. A more useful set will be derived later on.

CHAPTER III

EQUIVALENT CIRCUITS OF THERMOELECTRIC COOLERS

In the last part of chapter two the general thermodynamic equations of a thermoelectric system were derived and, as was stated, these equations (pair 2-54) do not yield themselves to a representation by an equivalent circuit because not all the parameters are easily measured. In this chapter ^{TWO} a pair of equations that are representable by an equivalent circuit are derived. It is obvious that these equations are not as general as (2-54) but ~~are~~ nevertheless useful. In addition to the assumptions made in chapter two, some more will be made here in order to facilitate the derivation of the required equations. These equations will then be represented by equivalent circuits. One of the most convenient forms of an equivalent circuit is the two terminal-pair network, it is widely used in transistor and amplifier work and therefore will be used here.

Consider the two terminal pair network shown in figure (3-1) where v_1 , i_1 and v_2 , i_2 are the input and output voltages and currents respectively, the relations between them can be written as follows:

$$\left. \begin{aligned} i_1 &= f_1(v_1; v_2) \\ i_2 &= f_2(v_1; v_2) \end{aligned} \right\} \quad (3-1)$$

differentiating

$$di_1 = \left(\frac{\partial f_1}{\partial v_1} \right) dv_1 + \left(\frac{\partial f_1}{\partial v_2} \right) dv_2 \quad (3-2)$$

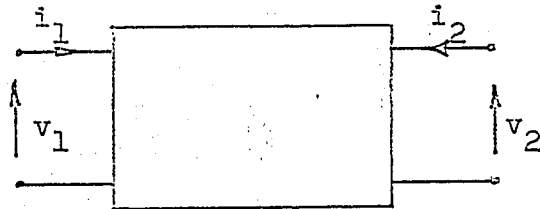


fig. 3.1

A general two terminal-pair network

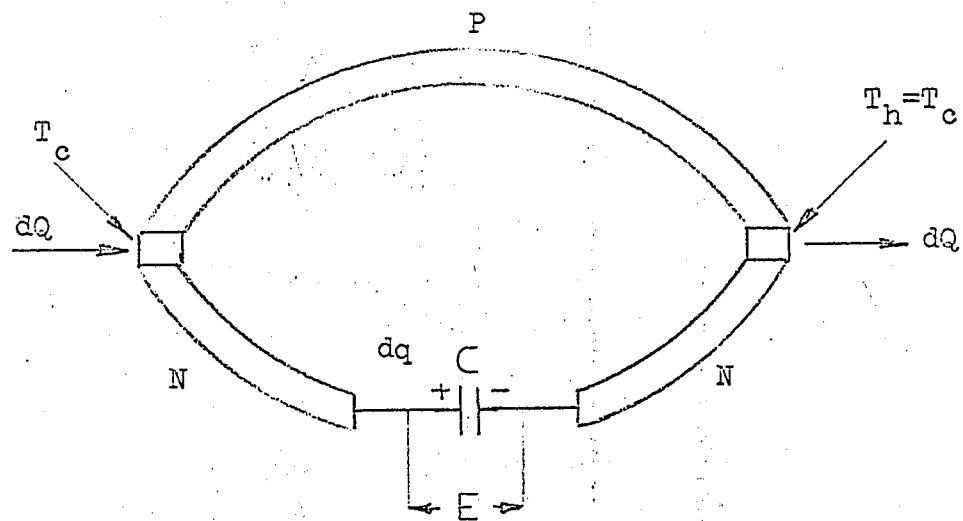


fig. 3.2

$$di_2 = \left(\frac{\partial f_2}{\partial v_1} \right) dv_1 + \left(\frac{\partial f_2}{\partial v_2} \right) dv_2 \quad (3-3)$$

If only small signals are considered equations (3-2) and (3-3) may be written

$$i_1 = \left(\frac{\partial f_1}{\partial v_1} \right) v_1 + \left(\frac{\partial f_1}{\partial v_2} \right) v_2 \quad (3-4)$$

$$i_2 = \left(\frac{\partial f_2}{\partial v_1} \right) v_1 + \left(\frac{\partial f_2}{\partial v_2} \right) v_2 \quad (3-5)$$

Replacing the $\frac{\partial f}{\partial v}$ terms by some kinetic coefficients the equations become

$$i_1 = y_{11} \times v_1 + y_{12} \times v_2 \quad (3-6)$$

$$i_2 = y_{21} \times v_1 + y_{22} \times v_2 \quad (3-7)$$

(Note the y terms here are active coefficients and should not be confused with the passive ones). Equations (3-6) and (3-7) are completely general and hold for any active two terminal pair network. Hence, if a thermoelectric circuit is to be represented in a form of a two terminal pair network, then the equations representing the thermoelectric circuit must be of the form of equations (3-6) and (3-7). These equations will be derived now.

From the First Law of Thermodynamics the total change in energy is zero.

$$\Delta U = \Delta Q - \Delta W = 0 \quad (3-8)$$

where U = total energy

Q = energy absorbed

W = energy expended

The energy supplied by the battery is EI per second or Eq per unit charge and the reversible portion is $E_s I$, where E_s as before is the Seebeck voltage.

From Onsager Reciprocal Relations it is known that in a system where more than one energy mechanism exist, there must be some cross-coupling terms. A pair of simultaneous linear equations similar to pair (2-64) can now be written in terms of flow functions (heat flow and current flow) and driving forces (voltage gradient, temperature gradient).

$$I = M_{11} \nabla V + M_{12} \nabla T \quad (3-9)$$

$$Q = M_{21} \nabla V + M_{22} \nabla T \quad (3-10)$$

Again these equations are general, but they must satisfy equations (3-6) and (3-7) and (2-53). If in equation (2-53) $\beta_1, \beta_2, \beta_3, \dots, \beta_n$ are the variables in the system under equilibrium with entropy S then for non equilibrium the variables will be $\beta_1 + \Delta\beta_1, \beta_2 + \Delta\beta_2$, etc. Since under equilibrium conditions the entropy S is maximum, the resulting change in entropy will be negative and of magnitude ΔS . This really means that the signal components of the variables are small changes about an operating point from the entropy and other variables.

Conceptually entropy is a ratio of energy change to driving potential. An electric analog is the ratio of energy change to voltage which has the unit of charge displacement.

For a reversible system

$$\Delta S_{rev} = \frac{\Delta Q}{T} = 0 \quad (3-11)$$

but for an irreversible system

$$\Delta S_{irrev} = \left| \frac{\Delta Q_1}{T} + \frac{\Delta W_1}{T} \right| > 0 \quad (3-12)$$

In equation (3-12) ΔQ_1 = energy transported and ΔW_1 = energy dissipated.

If figure (2-7) is modified slightly and the battery is replaced by a capacitor C as shown in figure (3-2), then when a small amount of charge dq is allowed to leave the capacitor in such a way that the voltage E remains unchanged (i.e. ΔE is very small) the total entropy change is:

$$dS = dS_{T_c} + dS_{T_c + \Delta T} + dS_{cap} \quad (3-13)$$

Where ΔS_{T_c} and $\Delta S_{T_c + \Delta T}$ are the changes in entropy at the cold and hot junctions respectively and ΔS_{cap} is the change in entropy of the capacitor. Using the convention that energy entering the thermoelectric arms is negative and the energy leaving them is positive, equation (3-13) can be written

$$\begin{aligned} dS &= - \frac{dQ}{T_c} + \frac{dQ}{T_c + \Delta T} - \frac{dq \Delta E}{T_c} \quad (3-14) \\ &= \frac{-dQ(T_c + \Delta T) + dQ T_c}{T_c(T_c + \Delta T)} - \frac{dq \Delta E}{T_c} \end{aligned}$$

for small ΔT

$$dS \approx - \frac{dQ \Delta T}{T_c^2} - \frac{dq \Delta E}{T_c} \quad (3-15)$$

differentiating with respect to time

$$\dot{S} = - \dot{Q} \frac{\Delta T}{T_c^2} - \dot{Q} \left(\frac{\Delta T}{T_c^2} \right) - \frac{I \Delta E}{T_c} \quad (3-16)$$

In equation (3-16) the second term is negligible and the third term is differentiated with respect to time for the charge dq only (since ΔE is very small). Rewriting equation (3-16) in a more useful form by allowing the small changes to ^{be} the total changes in the system we get:

$$\dot{S} = - \dot{Q} \left(\frac{\Delta T}{T_c^2} \right) - I \left(\frac{\Delta E}{T_c} \right) \quad (3-17)$$

Equation (3-17) states that the rate of change of entropy is the sum of the product of the two entropy flows by their respective driving functions. The first term is thermal and the second electrical. These relations can satisfy if in equation (2-53)

$$\frac{\partial \beta_1}{\partial t} = \frac{dq}{dt} = I \quad (3-18)$$

$$\gamma_1 = \frac{\partial S}{\partial \beta_1} = \frac{\partial S}{\partial q} \quad (3-19)$$

$$\frac{\partial \beta_2}{\partial t} = \frac{dQ}{dt} = \dot{Q} \quad (3-20)$$

$$\text{and } \frac{\partial S}{\partial \beta_2} = - \frac{\Delta T}{T_c} \quad (3-21)$$

If in equation (3-17) $\dot{Q} = 0$ then

$$dS = \Delta E \quad (3-22)$$

Now Onsager's Reciprocal Equations can be written slightly different from equations (3-9) and (3-10), i.e.

$$I = -L_{11} \left(\frac{\Delta E}{T_c} \right) - L_{12} \left(\frac{\Delta T}{T_c^2} \right) \quad (3-23)$$

$$Q = -L_{12} \left(\frac{\Delta E}{T_c} \right) - L_{22} \left(\frac{\Delta T}{T_c^2} \right) \quad (3-24)$$

As the Reciprocal Relations demand $L_{12} = L_{21}$. By setting all potentials or the driving forces to zero but one, the value of the coefficients may be determined. With $\Delta T = 0$ in equation (3-23) we get

$$I = -L_{11} \left(\frac{\Delta E}{T_c} \right) \quad \text{or} \quad \frac{I}{\Delta E} = -\frac{L_{11}}{T_c} = G = \text{electrical conductance at constant temperature} \quad (3-25)$$

If now $I = 0$ then

$$\frac{\Delta E}{T_c} = -\frac{L_{12}}{L_{11}} \left(\frac{\Delta T}{T_c^2} \right) \quad (3-26)$$

substituting (3-26) in (3-24) we get.

$$\dot{Q} = \frac{L_{21} L_{12} - L_{11} L_{22}}{L_{11} T_c^2} \Delta T \quad (3-27)$$

from the nature of this equation the obvious relation is obtained.

$$K = \frac{L_{21} L_{12} - L_{11} L_{22}}{L_{11} T_c^2} \quad (3-28)$$

Where K is the thermal conductivity. Substituting equation (3-25) in (3-24) we get;

$$\dot{Q} = -L_{21} \left(\frac{\Delta E}{T_c} \right) = -L_{21} \left(\frac{I}{-L_{11}} \right) = \left(\frac{L_{21}}{L_{11}} \right) I \quad (3-29)$$

and since $\dot{Q} = (\pi I)$ by definition, it follows that

$$L_{21} = \pi \quad (3-30)$$

Going back to equation (3-26) again

$$\frac{\Delta E}{T_c} = - \frac{L_{12}}{L_{11}} \frac{\Delta T}{T_c^2}$$

$$\frac{\Delta E}{\Delta T} = - \frac{L_{12}}{L_{11} T_c} \quad (3-31)$$

but $\frac{\Delta E}{\Delta T}$ is ^{the} Seebeck coefficient, by definition,
therefore, $\alpha = \frac{-L_{12}}{L_{11} T_c}$

Since $L_{12} = L_{21}$ it follows from (3-30) and (3-32) that:

$$\alpha = \frac{\Pi}{T_c} \quad (3-33)$$

Another important result follows from the consideration of conservation of energy. In figure (3-2) follow the charge dq around the loop. It can be seen then that the Thomson heat is

$$dQ_T = -(\tau_p - \tau_m) dq \Delta T \quad (3-34)$$

where τ_p and τ_m are the Thomson coefficients of the P and N materials.

The heat rejected by the Peltier effect is

$$dQ = \Delta \Pi dq \quad (3-35)$$

where $\Delta \Pi$ is the change in Π due to ΔT .

The energy given by the condenser is $dq \Delta E$ (assuming as before that ΔE is very small i.e. E constant, which is true for an ideal battery).

Hence the total change in energy is

$$-(\tau_p - \tau_m) dq \Delta T + \Delta \Pi dq + dq \Delta E = 0 \quad (3-36)$$

or

$$(\tau_p - \tau_m) = \frac{\Delta E}{\Delta T} + \frac{\Delta \pi}{\Delta T}$$

Using (3-31) and (3-33) we get

$$\tau_p - \tau_m = -\frac{\pi}{T_c} + \frac{\Delta \pi}{\Delta T} = \frac{-\pi \Delta T + T_c \Delta \pi}{T_c \Delta T}$$

or

$$\frac{\tau_p - \tau_m}{T_c} = \frac{-\pi \Delta T + T_c \Delta \pi}{T_c^2 \Delta T} = \frac{-\pi + T_c \frac{\Delta \pi}{\Delta T}}{T_c}$$

$$\frac{\tau_p - \tau_m}{T_c} = -\frac{d\alpha_{em}}{dT} \quad (3-37)$$

This equation (3-37) indicates that the variation of thermoelectric power with temperature determines the Thomson coefficient.

From equations (3-17), (3-23) and (3-24) another important relation can be derived. From (3-23)

$$L_{11} \frac{\Delta E}{T_c} = -I - L_{12} \left(\frac{\Delta T}{T_c^2} \right)$$

$$\text{or} \quad \frac{\Delta E}{T_c} = -I \left(\frac{1}{L_{11}} \right) - \left(\frac{L_{12}}{L_{11}} \right) \left(\frac{\Delta T}{T_c^2} \right) \quad (3-38)$$

substituting (3-38) in (3-24)

$$\dot{Q} = -L_{12} \left[-I \left(\frac{1}{L_{11}} \right) - \left(\frac{L_{12}}{L_{11}} \right) \left(\frac{\Delta T}{T_c^2} \right) \right] \quad (3-39)$$

now using (3-39) and (3-38) in (3-12) we get

$$= \left\{ -L_{21} \left[-I \left(\frac{1}{L_{11}} \right) - \left(\frac{L_{12}}{L_{11}} \right) \left(\frac{\Delta T}{T_c^2} \right) \right] - L_{22} \left(\frac{\Delta T}{T_c^2} \right) \right\} \frac{\Delta T}{T_c^2}$$

$$- I \left[-I \left(\frac{1}{L_{11}} \right) - \left(\frac{L_{12}}{L_{11}} \right) \frac{\Delta T}{T_c^2} \right]$$

rearranging the terms and simplifying

$$\dot{S} = \frac{I^2}{L_{11}} + \frac{L_{22}L_{11} - L_{12}L_{21}}{L_{11}} \left(\frac{\Delta T}{T_c^2} \right)^2 + I \frac{L_{12} - L_{21}}{L_{11}} \left(\frac{\Delta T}{T_c^2} \right)^2 \quad (3-40)$$

In equation (3-40) it is easily seen that the first term I^2/L_{11} is the Joule heat, the second term $(L_{22}L_{11} - L_{12}L_{21}) \times \left(\frac{1}{L_{11}} \right) \left(\frac{\Delta T}{T_c^2} \right)^2$ is the conduction heat and the third term is the reversible heat since $L_{12} = L_{21}$.

Until now the values of the different effects were determined in terms of the "L" coefficients it is now necessary to express the "L"'s in terms of the known coefficients. In order to do it we assume that the gap in which the condenser seats is very small and that it can be depicted as shown in figure (3-3). The value of G found in (3-25) has the dimensions of current density per volt, therefore, the total resistance R is given by

$$R = \frac{1}{G} = \frac{l_n}{G_n A_n} + \frac{l_p}{G_p A_p} \quad (3-41)$$

Where l_p, l_n, G_p, G_n, A_p and A_n are the lengths, specific conductances and cross sectional areas of the P and N materials respectively. Using the mobility equation⁴ for each material and assume $A_n = A_p = A$

$$\frac{1}{G} = \frac{l_n}{Aq\mu_n n} + \frac{l_p}{Aq\mu_p p} \quad (3-42)$$

Where μ_n, μ_p, n and p are the mobilities and carrier concentrations for the N and P materials respectively.

$$\therefore G = \frac{qA \mu_p m_p}{n \mu_n l_p + p \mu_p l_m} = \frac{-L_{11}}{T_c} \quad (3-43)$$

Now using in equation (3-43) Einstein's Relation which states $\frac{\mu}{D} = \frac{q}{K T}$

Where D is the diffusion and K Boltzmann's constant, we get

$$-\frac{L_{11}}{T_c} = \frac{qA \frac{q D_n m}{K T_c} \times \frac{q D_p p}{K T_c}}{\frac{n q D_n l_p}{K T_c} + \frac{p q D_p l_m}{K T_c}}$$

and dividing numerator and denominator by

$$\frac{n D_n p D_p}{K T_c} \text{ gives}$$

$$\frac{-L_{11}}{T_c} = \frac{A q^2}{\left(\frac{l_p}{n D_p} + \frac{l_m}{m D_m} \right) K T_c}$$

$$\text{or } L_{11} = \frac{-q^2/K}{\frac{l_p}{n D_p} + \frac{l_m}{m D_m}} \text{ per unit area} \quad (3-44)$$

From (2-15) and (3-30)

$$\pi = \frac{Eg}{q} = \frac{L_{21}}{L_{11}}$$

therefore

$$L_{21} = L_{11} \left(\frac{Eg}{q} \right) = - \frac{\left(\frac{Eg}{q} \right) \left(\frac{q^2}{K} \right)}{\frac{l_p}{n D_p} + \frac{l_m}{m D_m}} = L_{12} \quad (3-45)$$

From (3-28)

$$L_{22} = \frac{L_{11} K T_c^2 + L_{21} L_{12}}{L_{11}}$$

$$\text{or } L_{22} = \frac{L_{12}^2}{L_{11}} - K T_c^2 \quad (3-46)$$

$$\text{but } \left(\frac{L_{12}}{L_{11}} \right)^2 = \pi^2$$

$$\text{therefore } L_{22} = \pi^2 L_{11} - K T_c^2$$

Finally

$$L_{22} = \left(\frac{Eg}{q} \right)^2 \left(\frac{-q^2/K}{\frac{l_p}{nD_p} + \frac{l_n}{mD_n}} \right) - K T_c^2$$

The heat, unlike the current, flows back from the hot to the cold junction in parallel paths hence

$$K = K_n + K_p = \frac{k_n}{l_n} + \frac{k_p}{l_p}$$

Where k_n and k_p are the specific thermal conductivities of the N and P materials respectively.

The thermoelectric power is given by

$$\alpha = \frac{\pi}{T_c} = \frac{-L_{21}}{L_{11} T_c} = \frac{Eg}{K T_c} \quad \text{as before}$$

but from equations (3-43) and (3-44) G is given by

$$G = \frac{q^2/K T_c}{\frac{l_p}{nD_p} + \frac{l_n}{mD_n}} \quad (3-48)$$

Now equations (3-23) and (3-24) can be written

$$I = G \Delta E + G \pi \frac{\Delta T}{T_c} \quad (3-49)$$

$$\dot{Q} = G \pi \Delta E + \left(\pi^2 G T_c + K T_c \right) \frac{\Delta T}{T_c} \quad (3-50)$$

i.e. the L's are expressed in terms of physical parameters that are either known or can be determined. Note that the electric potential difference is ΔE whereas the thermal potential difference is $\Delta T/T_c$. The last two equations are useful for problems where T_c is constant and one wants to determine ΔT and $\dot{Q}$ as a function of I and E , e.g. thermoelectric cooler.

Having derived a set of reciprocal relations in terms of measurable parameters they can now be represented in a form of an equivalent circuit. In order to ease the derivation, figure (3-2) can be distorted slightly as shown in figure (3-4).

In figure (3-5) the equivalent circuit of equations (3-49) and (3-50) is shown.

From the equations and figure (3-5) it follows that

- G = input electrical conductance with $\Delta T = 0$
- $(\pi^2 G + KT)$ = output thermal conductance with $\Delta E = 0$
- G = short-circuit Peltier transfer admittance.

The above equations were written in the form of

$[I] = [Y][E]$ i.e. "admittance" equations. Obviously they can be written in terms of the "impedance" parameters, $[E] = [X][I]$ rewriting equations (3-49) and (3-50) in a matrix form

$$\begin{bmatrix} I \\ \dot{Q} \end{bmatrix} = \begin{bmatrix} G & \pi G \\ G\pi & \pi^2 G + kT_c \end{bmatrix} \times \begin{bmatrix} \Delta E \\ \frac{\Delta T}{T_c} \end{bmatrix}$$

inverting the admittance matrix the result is;

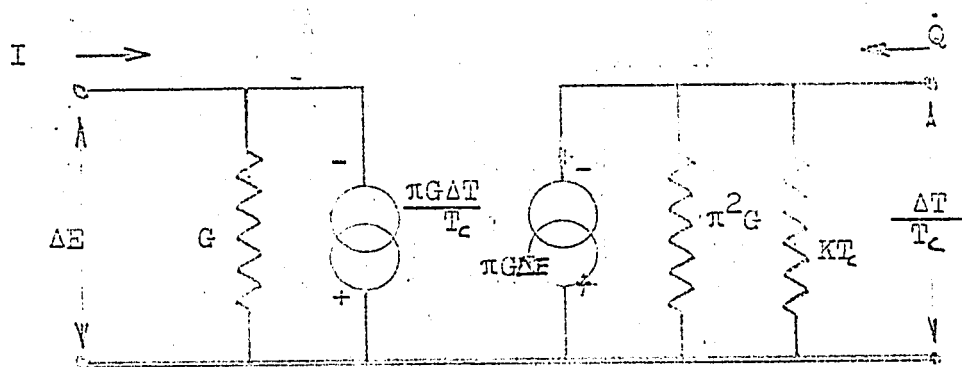


fig. 3.5

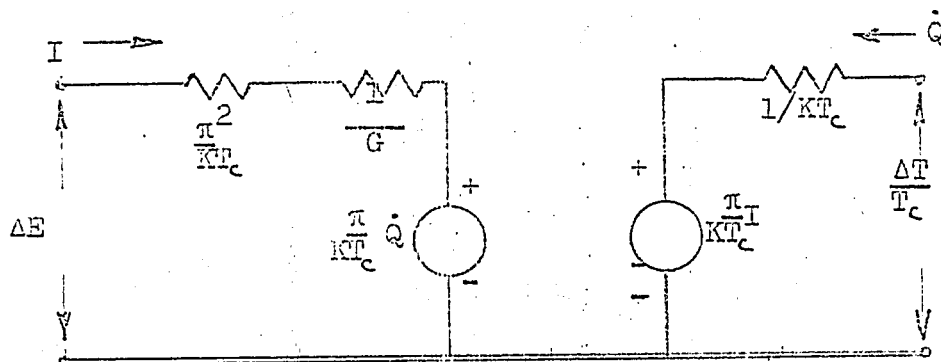


fig. 3.6

$$y^{-1} = \frac{\begin{vmatrix} G\pi^2 + kT_c & -\pi G \\ \pi G & G \end{vmatrix}}{\Delta}$$

where Δ = determinant of the admittance matrix

$$\text{and } \Delta = G^2\pi^2 + GkT_c - G^2\pi^2 = GkT_c$$

$$\therefore \begin{vmatrix} \frac{\pi^2}{kT_c} + \frac{1}{G} & -\frac{\pi}{kT_c} \\ -\frac{\pi}{kT_c} & \frac{1}{kT_c} \end{vmatrix}$$

finally

$$\begin{vmatrix} E \\ \frac{\Delta T}{T_c} \end{vmatrix} = \begin{vmatrix} \frac{\pi^2}{kT_c} + \frac{1}{G} & -\frac{\pi}{kT_c} \\ -\frac{\pi}{kT_c} & \frac{1}{kT_c} \end{vmatrix} \begin{vmatrix} I \\ \dot{Q} \end{vmatrix}$$

or in equation form

$$E = I \left(\frac{\pi^2}{kT_c} + \frac{1}{G} \right) - \left(\frac{\pi}{kT_c} \right) \dot{Q} \quad (3-51)$$

$$\frac{\Delta T}{T_c} = \left(\frac{-\pi}{kT_c} \right) I + \left(\frac{1}{kT_c} \right) \dot{Q} \quad (3-52)$$

Equations (3-51) and (3-52) are represented by an equivalent circuit in figure (3-6)

From equations (3-51) (3-52) and figure (3-6) $\left(\frac{\pi^2}{kT_c} + \frac{1}{G} \right)$ is the input electrical impedance with output open circuited

$\frac{1}{kT_c}$ is the output thermal impedance with the input open circuited and $\frac{\pi}{kT_c}$ = Peltier transfer impedance on open circuit.

The above derivation was for an ideal system to which the same restrictions as in chapter two apply, namely:

- 1) all parameters are independent of temperature
- 2) heat sources and sinks are ideal
- 3) all electric sources are ideal
- 4) both heat and electricity flow through the lattice only and in one plane.
- 5) The metal conductor between the P and N legs has no electrical resistance or thermal conductance and it does not affect the value of any thermoelectric coefficient.
- 6) The Joulean heat is divided equally between the junctions.

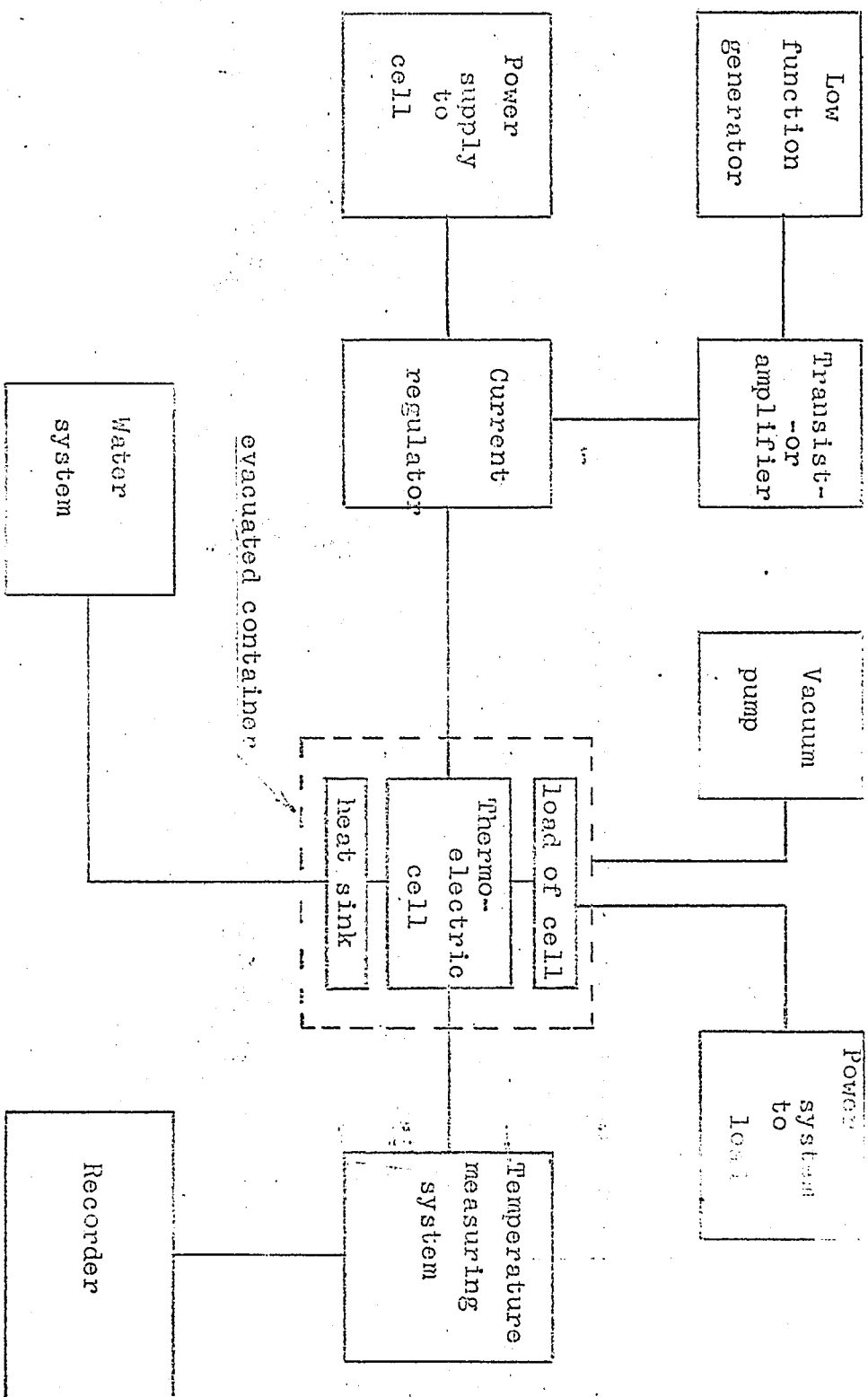
These restrictions make the system ideal. In reality an approximation is required. Therefore, the system to be considered for representation by an equivalent circuit will be an ideal system but modifications will be made to allow for changes that depart from ideal conditions e.g. resistance temperature dependence, etc.

CHAPTER 4: EXPERIMENTAL THERMOELECTRIC CIRCUIT.

a) SET UP

The experimental set up of the thermoelectric system is as indicated by the block diagram in fig. (4-1).

The thermoelectric element is made of Bi_2Te_3 alloys and manufactured by Ohio Semiconductors. It consists of a single pair of P-N legs that are joined at one end by a single copper strap. At their other end each leg is attached to a large copper strap that acts both as a heat sink and current lead. The thermocell is shown in fig. (4-2). Some of the important features of the cell are; very low ohmic resistance (of the order $.0025\Omega$), a good figure of merit ($1.6 \times 10^{-3}/^\circ\text{C}$) and low thermal conductivity ($5 \times 10^{-2} \text{ w}/^\circ\text{C}$). The main disadvantages of the thermocell are poor mechanical strength and lack of electrical insulation. In order to maintain good thermal contact between the load and the cold junction of the thermocell a thin layer of varnish was placed on the cold junction to insulate electrically from the load and a thin layer of silicon grease was used to ensure good thermal contact between the cold junction and the load. In order to maintain a good thermal contact and good electrical insulation between the hot junction (large copper straps) and the heat sink, the heat sink was made of aluminum which was anodized (see appendix for anodizing procedure), thus giving an effective thin layer of electrical insulation. Because the layer of anodic coating is only few molecules thick it does not affect the thermal conductivity of the aluminum. Again a thin layer of silicon grease was used to ensure a good thermal connection between the surfaces in contact of the hot junction and the aluminum heat sink.



Block diagram of the complete thermoelectric system

Fig. (4-1)

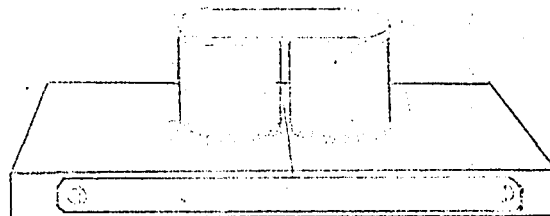


Fig. (4-2)

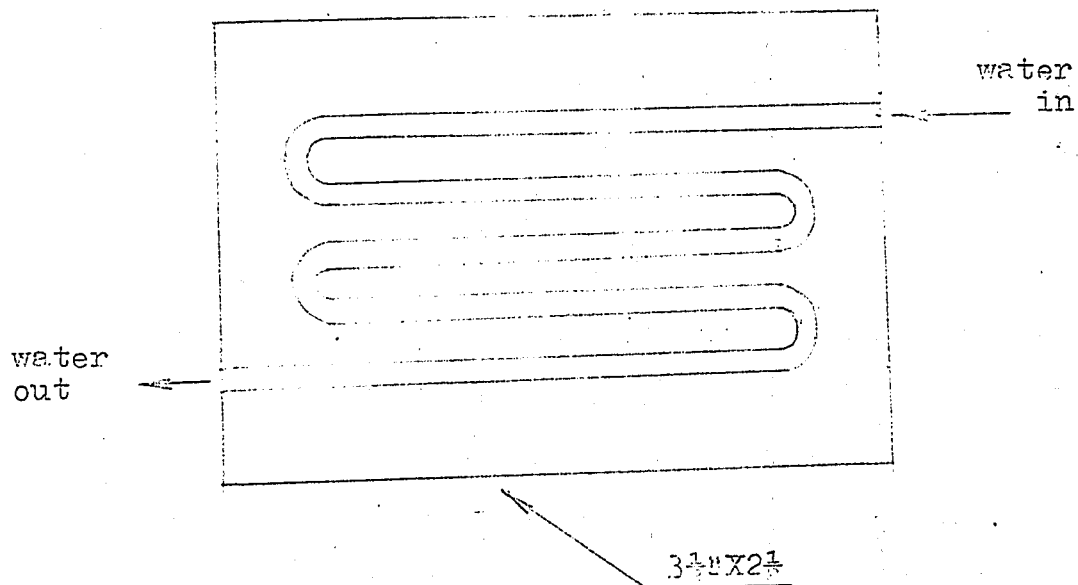
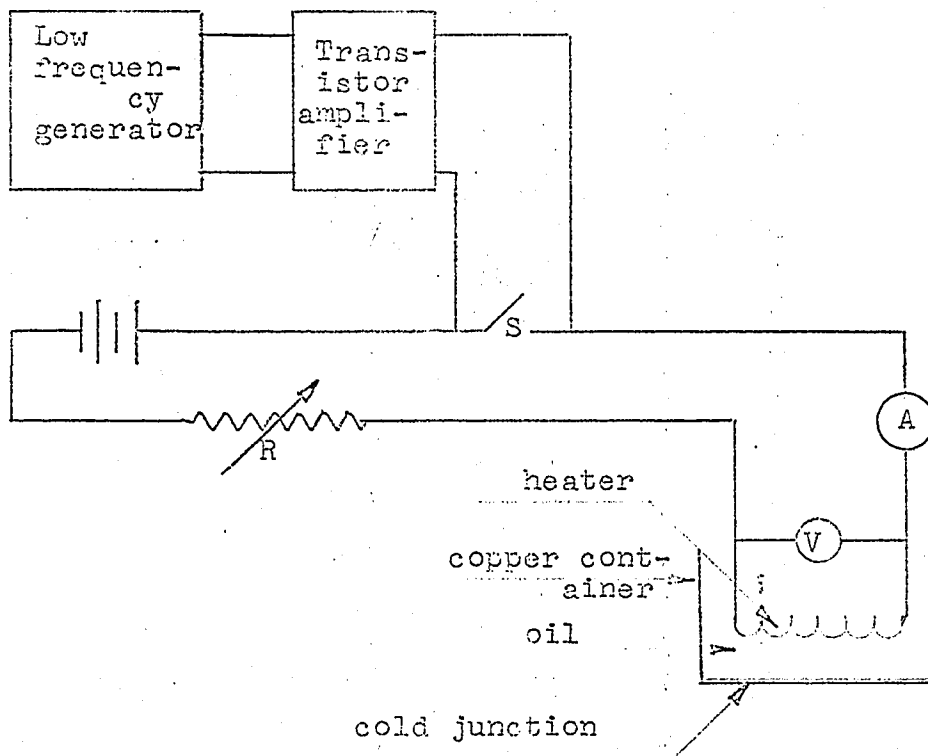


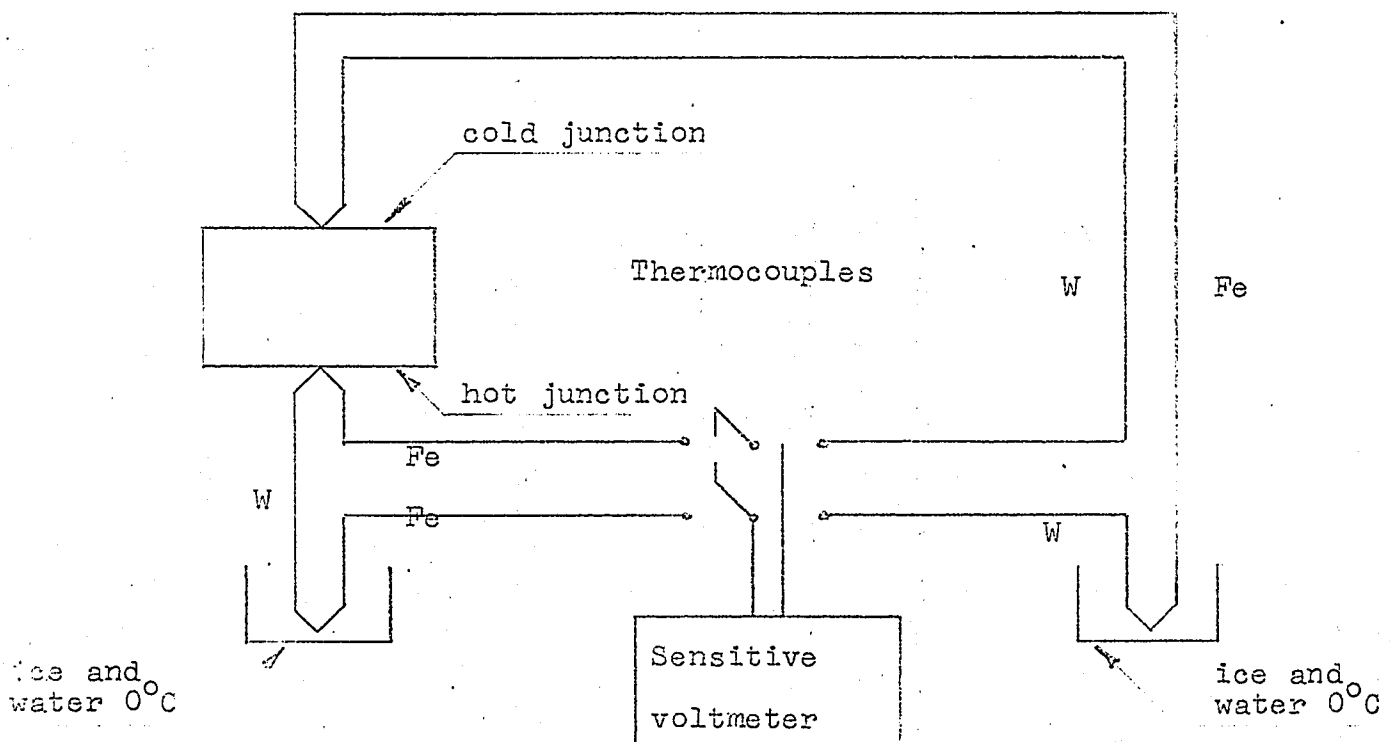
Fig. (4-3)

The heat sink itself has a water passage machined through it in such a way that the surface area under which the water passes is as large as the copper straps of the thermocell itself. The heat sink is shown in fig. (4-3).

The heat sink was mounted on a steel base. Through the base all electrical connections were made, by using epoxy resin as electrical insulation. Great care ensured air tight connections. The connections for water inlet and outlet were also made air tight with respect to the volume around the thermocell. A pressure rubber hose connects a half inch outlet in the steel base and the vacuum pump. A special seat for a bell jar was machined and grounded on the base and again the surfaces in contact are made air tight by using silicon grease between them. The bell jar covers the thermocell, its load, and the heat sink. The space under the bell jar is evacuated to a pressure of approximately two hundred microns. At this pressure the mean free path of air is of the same order as the container, therefore the heat transported by convection is negligible. For similar reasons the heat transferred by conduction is also negligible (for a justification, and a discussion of the last 2 statements see "High Vacuum Techniques" by Yarwood and "Scientific Foundations of Vacuum Techniques" by Dushman and Lafferty, or one of the many other books dealing with the same topic). The thermal conductivity of air does not vary linearly with pressure but it remains very nearly constant from 760 mm Hg to about 8 mm Hg and only below that the fall in thermal conductivity with pressure is sharp. It is therefore important to keep the pressure under the bell jar very low. By means of a vacuum pump (Welch pump model 1403H) the pressure is kept at about two hundred microns. Therefore the heat conducted or convected from the surroundings to the thermocell is neglected. The amount of heat absorbed by radiation



Schematic diagram for the loading system of the cold junction
fig. (4-4)



Temperature measuring system
fig. (4-5)

is also small due to the relatively small temperature difference involved. If the temperature difference is greater than 150°C the heat absorbed must be taken into account. It is assumed therefore that the heat from the load is being transferred to the cold junction and then through the P and N legs to the hot junction and eventually to the heat sink, in one plane (the plane of the junctions).

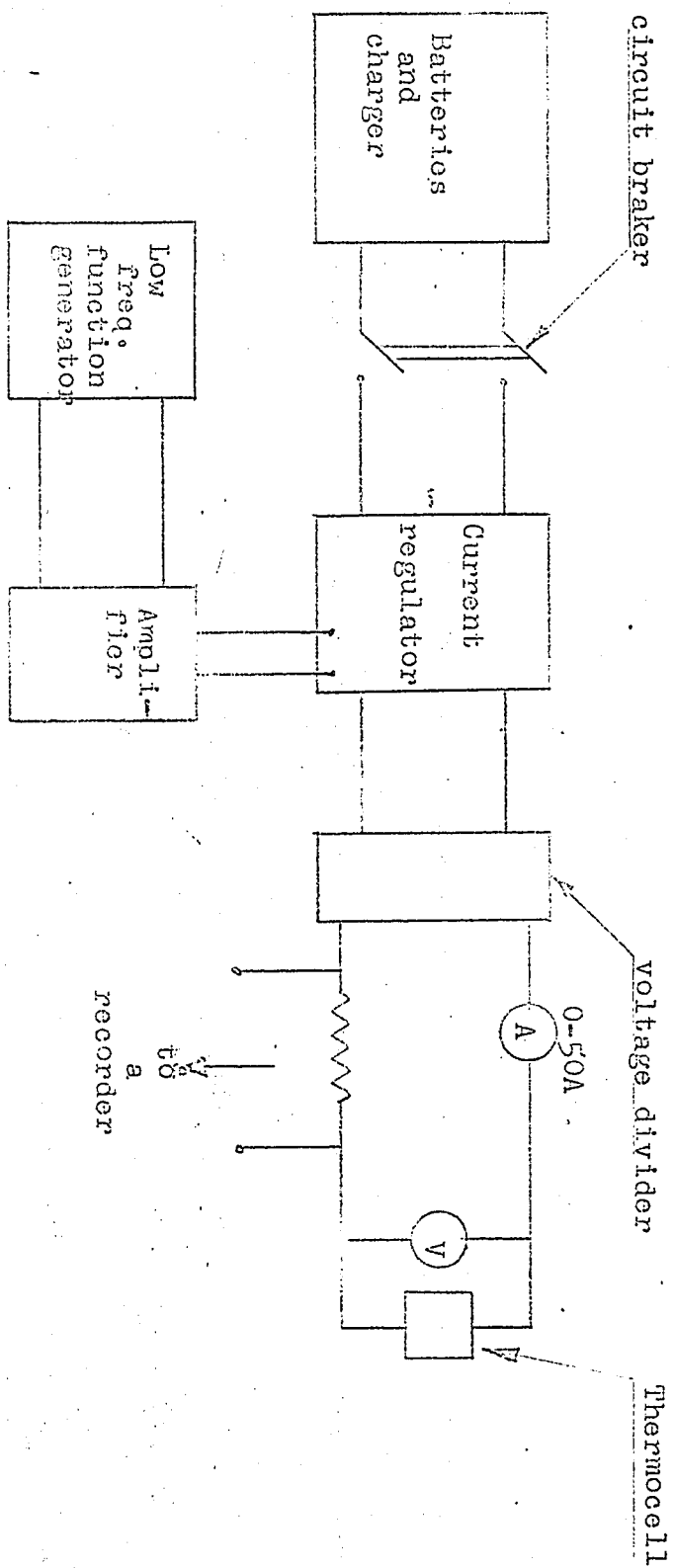
The loading arrangement consists of a rectangular copper container filled with oil (of specific heat .48 and vapor pressure better than .001 micron at 50°C), a heater, a power supply and provisions for applying transients. The arrangement is shown schematically in fig.(4-4) and is self explanatory. It is though, worth mentioning that 3 types of transients may be investigated, if necessary, as the wave-forms available from the signal generator used are sinusoidal, triangular and square waves, most useful are the sinusoidal and the square waves. The useful frequency range is from two cycles per minute and lower, down to about one cycle per five minutes (this low frequency can be obtained from the signal generator used).

The temperatures of the hot and cold junctions is measured by means of iron constantan thermocouples. The reference point is 0°C obtained from melting ice (for higher accuracies, ice made from distilled water must be used). The arrangement is shown schematically in figure (4-5) again the arrangement is self explanatory.

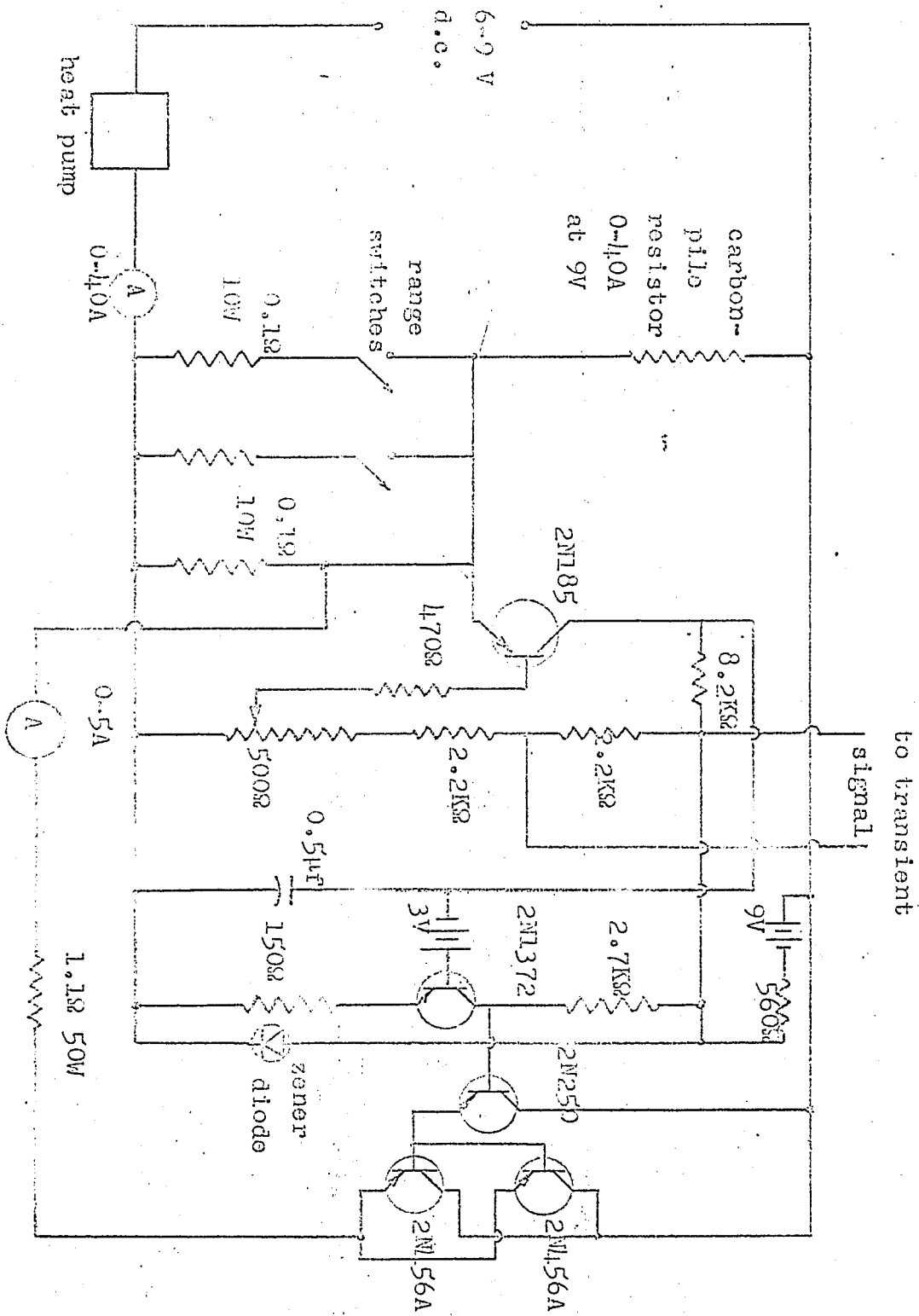
The voltmeter readings were converted to $^{\circ}\text{C}$ by means of reference tables for thermocouples (N.B.S. circular 561). It is worth noting that if a continuous record of temperatures is necessary then the output of the sensitive voltmeter may be connected to a strip chart recorder.

The power supply system consists of two 6V large capacity batteries, a circuit breaker, a current regulator and a voltage divider. The arrangement is shown in fig. (4-6). As can be seen from the figure, controlled transients can be applied to the supply current. The circuit diagram of the current regulator is shown separately in fig. (4-7). The maximum deviation of current it can regulate is four amperes, if the current deviation is greater than that regulation is lost and correction must be made manually. The main disadvantage of using batteries is that their effective period of operation is relatively short. This period can be extended considerably by connecting the battery charger in parallel with the batteries and keeping the voltage constant at 6V. The current regulator takes care of the ripple produced by the charger at the output terminals (the reason for not using the battery charger alone as a power supply is that it is not capable of delivering the amount of current required which is in some cases over 30A). The ripple reaching the terminals of the thermocell should not exceed 8% of the d.c. value. It is important to bear in mind that the ripple will contribute to the Joulean heat but will not pump heat at all, therefore it should be kept at a minimum. It is obvious that the ripple reduces the overall efficiency of the system.

Another factor that affects the efficiency of the thermocell is the temperature of the hot junction. It can be seen from equation (2-40) that the first part of the expression $\frac{T_c}{T_h - T_c}$ which is the efficiency of a Carnot cycle and as T_h falls the efficiency of the cycle increases for a given T_c . Therefore the heat sink is water cooled. In order to be able to control (to a certain extent only) the temperature of the hot junction the flow of water is controlled by a needle valve. In



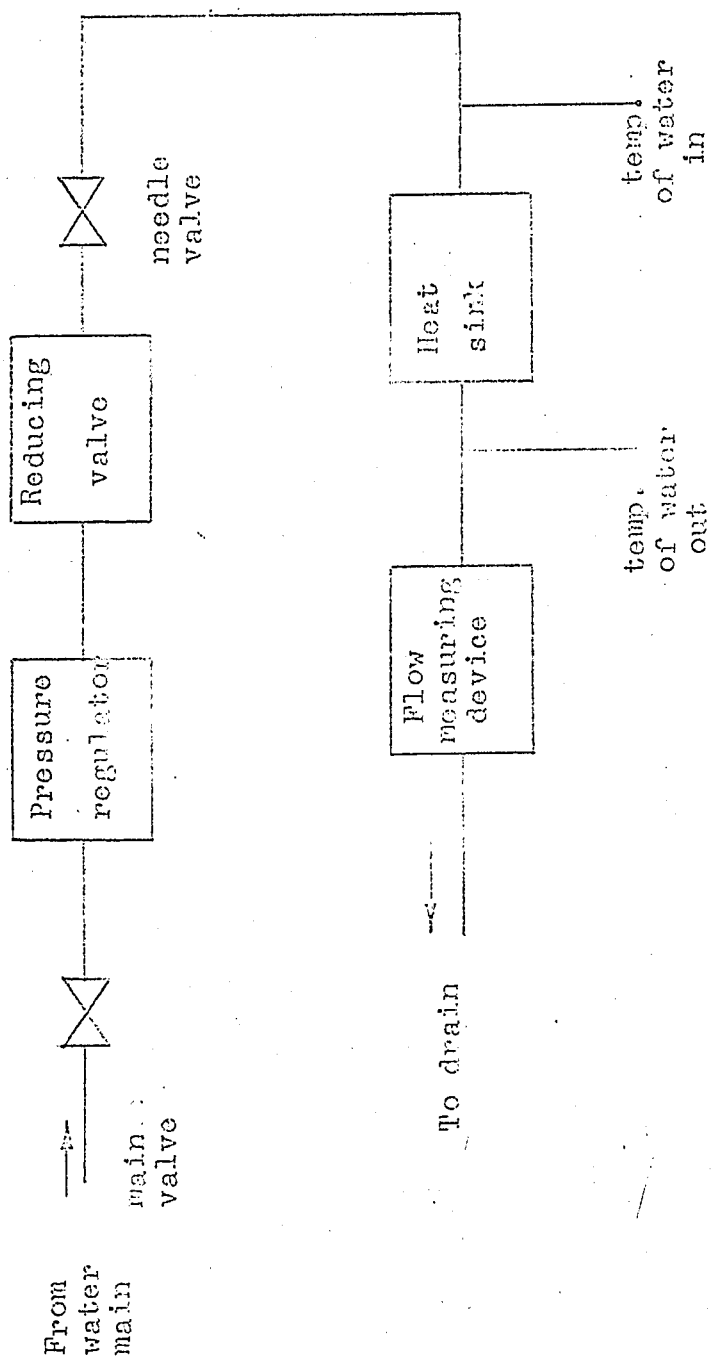
Power supply system with arrangement for current transients
 fig. (4-6)



Schematic diagram of current regulator.
(taken from ref. 7)

preliminary experiments it was found that the water pressure of the supply varied at random with time, hence manual control was impossible. To overcome this a reducing valve with a pressure regulator ~~was~~ connected in the water line thus keeping the pressure and flow constant at any desirable value. The water system is shown in figure (4-8).

It is felt that an explanation as to why all the above precautions were taken is necessary. It is best explained by considering an ordinary (even domestic) thermoelectric refrigerator under normal operation. If the hot junction is air cooled, then the heat given to the surroundings may raise the ambient temperature in the vicinity of the refrigerator. Since heat conducted through the walls depends on the ambient temperature any increase in it will also increase the heat conducted back in. Every time the door is opened heat will go into the cooled compartment and the amount going in will depend on many factors such as, ambient temperature, length of time the door is left open, how wide it is open etc. Variations in the power supply, humidity and other variables may also affect the operation. Since the performance of such a model is unpredictable and impossible to analyze mathematically, the system has to be "idealized" somewhat so that it will yield itself to mathematical representation. The various processes that take place simultaneously in a real system can be simulated and controlled on the ideal system built, for example the opening of a door can be represented by a square wave transient input to the load system and the response of the system can be determined. In this manner the effect of most other phenomena taking place may be investigated.



Water control system

fig. (11-8).

CHAPTER 5: EQUIVALENT CIRCUITS - SET-UP.

The first part of this chapter is in a way an extension of Chapter 3 because more equivalent circuits will be derived in it. In the second part the experimental set-up will be described.

a) Some more equivalent circuits

Consider again the admittance and impedance equations derived in Chapter 3, namely

$$I = G \Delta E + G \pi \frac{\Delta T}{\epsilon} \quad (3-49)$$

$$\dot{Q} = G \pi \Delta E + (\pi^2 G + K \epsilon) \frac{\Delta T}{\epsilon} \quad (3-50)$$

and

$$\Delta E = \left(\frac{\pi}{K \epsilon} + \frac{1}{G} \right) I - \frac{\pi}{K \epsilon} \dot{Q} \quad (3-51)$$

$$\frac{\Delta T}{\epsilon} = - \frac{\pi}{K \epsilon} I + \frac{1}{K \epsilon} \dot{Q} \quad (3-52)$$

The equivalent circuits for these two pairs of equations were given in figures (3-5) and (3-6) for the first and second pairs respectively. These equivalent circuits are known as two-generators equivalent circuits and sometimes they are not convenient to use. Hence equivalent circuits employing one generator only will be derived.

Any two terminal pair network can be represented by:

$$E_1 = Z_{11} I_1 + Z_{12} I_2 \quad (5-1)$$

$$E_2 = Z_{21} I_1 + Z_{22} I_2 \quad (5-2)$$

where

$$Z_{11} = \frac{E_1}{I_1} = \text{input impedance with output open i.e. } I_2 = 0$$

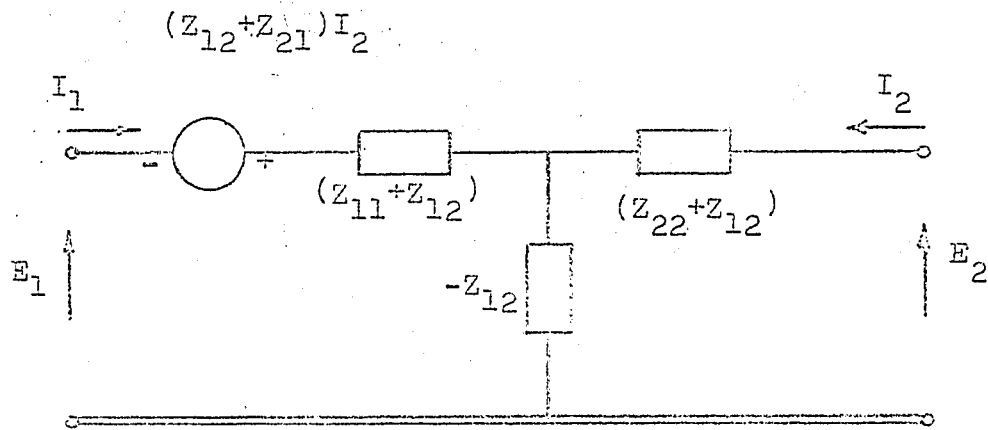


fig.(5-1)

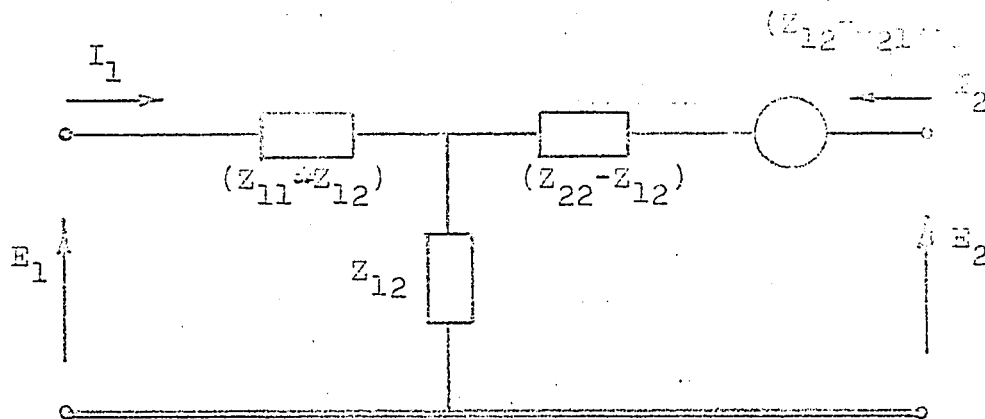


fig.(5-2)

$$Z_{12} = \frac{E_1}{I_2} = \text{transfer impedance with input open i.e. } I_1 = 0$$

$$Z_{21} = \frac{E_2}{I_1} = \text{transfer impedance with output open i.e. } I_2 = 0$$

$$Z_{22} = \frac{E_2}{I_2} = \text{output impedance with input open i.e. } I_1 = 0.$$

Knowing that Z_{12} is the mutual impedance and using the same convention for currents and voltages as in Chapter 3 equations (5-1) and (5-2) can be rewritten as

$$E_1 = Z_{11}I_1 - Z_{21}I_2 + (Z_{12}+Z_{21})I_1 \quad (5-3)$$

$$E_2 = Z_{21}I_1 + Z_{22}I_2 \quad (5-4)$$

The equivalent circuit for these equations is given in figure (5-1).

Alternatively equations (5-1) and (5-2) can be written

$$E_1 = Z_{11}I_1 + Z_{12}I_2 \quad (5-5)$$

$$E_2 = -Z_{12}I_1 + Z_{22}I_2 + (Z_{12}+Z_{21})I_1 \quad (5-6)$$

The equivalent circuit for the last two equations is given in figure (5-2). The only difference between figures (5-1) and (5-2) is the position of the voltage generator in the arms of the T. Since this generator is to indicate the coupling of the input and output, the generator in the input terminals will depend on the output current and the generator connected at the output terminals will be a function of the input current.

Sometimes it is more convenient to have a "hybrid" set giving say I_1 and E_2 then again from (5-1) and (5-2)

$$I_1 = \frac{E}{Z_{11}} - \frac{Z_{12}}{Z_{11}} I_2 \quad (5-7)$$

$$E_2 = \frac{Z_{21}}{Z_{11}} E_1 - \frac{Z_{12}}{Z_{11}} Z_{21} I_2 + Z_{22} I_2 \quad (5-8)$$

Using the same method as before (5-8) becomes

$$E_2 = -\frac{Z_{12}}{Z_{11}} E_1 - \frac{Z_{12}}{Z_{11}} Z_{21} I_2 + Z_{22} I_2 + \frac{Z_{12} + Z_{21}}{Z_{11}} E_1 \quad (5-9)$$

The equivalent circuit for equations (5-7) and (5-9) is given in figure (5-3). Since the elements of figure (5-3) are relatively more complicated this type of network will not be pursued further.

Applying the above technique to equations (3-51) and (3-52) we get;

$$\Delta F = \left(\frac{\pi}{kT_c} + \frac{1}{G} \right) I + \frac{\pi}{kT_c} \dot{Q} - \frac{\pi}{kT_c} \dot{Q} \quad (5-10)$$

$$\frac{\Delta T}{T_c} = -\frac{\pi}{kT_c} I + \frac{1}{kT_c} \dot{Q} \quad (5-11)$$

The equivalent circuit for equations (5-10) and (5-11) is given in figure (5-4). Since the value of π is always smaller than unity all the values in figure (5-4) are positive.

In order to have the generator on the output side equations (3-51) and (3-52) must be written as follows;

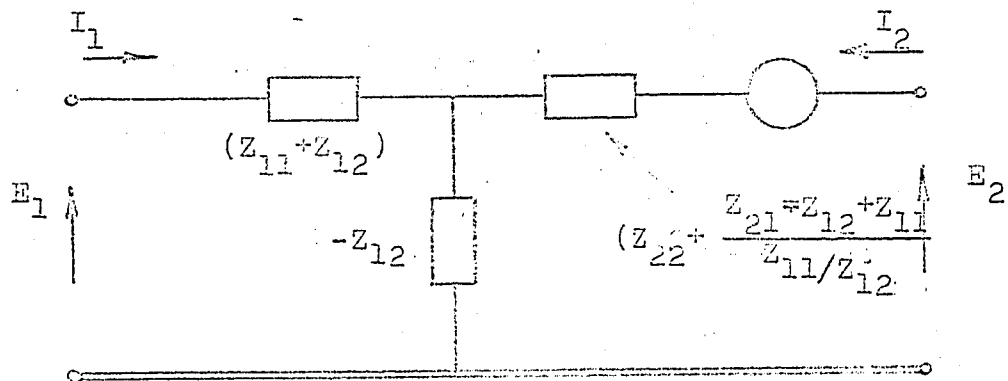


fig.(5-3)

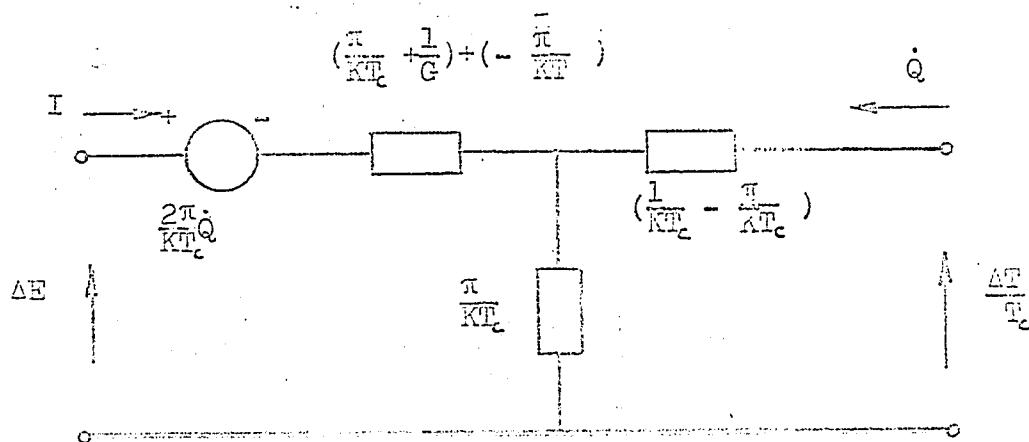


fig.(5-4)

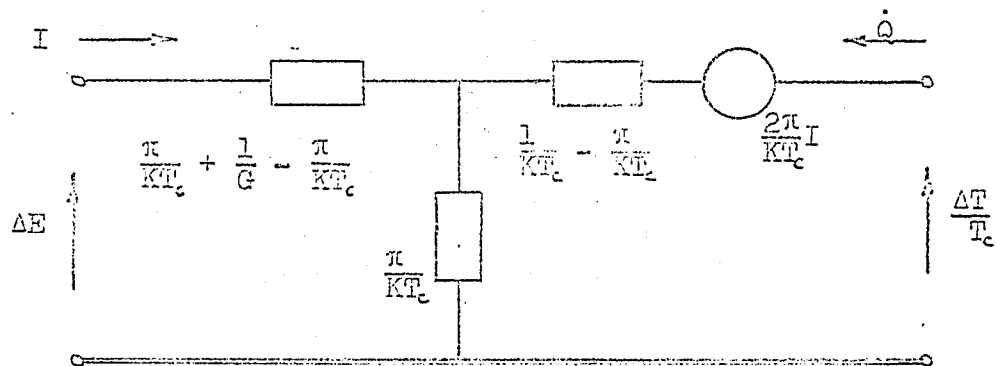


fig. (5-5)

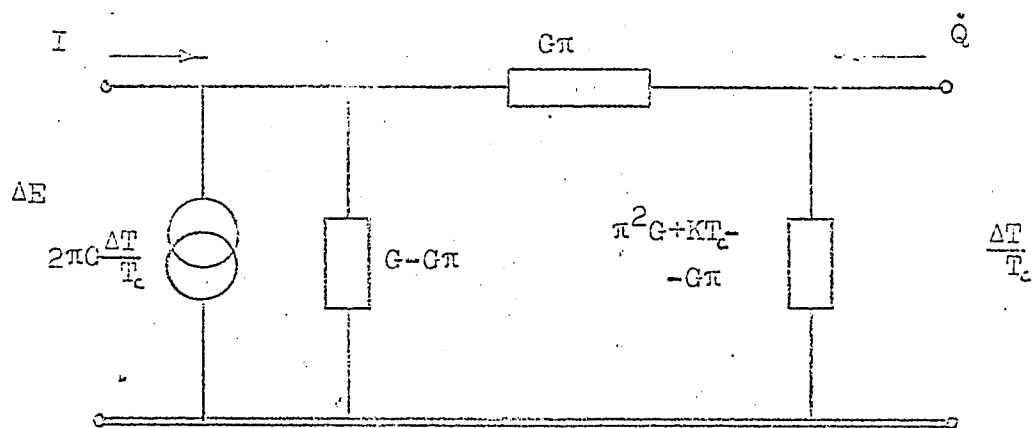


fig. (5-6)

$$\Delta E = \left(\frac{\pi}{kT_c} + \frac{1}{G} \right) I - \frac{\pi}{kT_c} \dot{Q} \quad (5-12)$$

$$\frac{\Delta T}{T} = \frac{\pi}{kT_c} I + \frac{1}{kT_c} \dot{Q} - \frac{2\pi}{kT_c} I \quad (5-13)$$

and the equivalent circuit is given in figure (5-5). The passive part of figure (5-5) is identical with the passive part of figure (5-4) which is to be expected.

In a similar ^{fashion} ~~position~~ starting with the general equations

$$I_1 = y_{11}E_1 + y_{12}E_2$$

$$I_2 = y_{21}E_1 + y_{22}E_2$$

equivalent circuits of the π form having current generators can be derived. This will be done directly for equations (3-49) and (3-50) without deriving the general cases.

In order to have the current generator on the input side, equations (3-49) and (3-50) are written as follows:

$$I = G\Delta E - G\pi \frac{\Delta T}{T_c} + 2G\pi \frac{\Delta T}{T_c} \quad (5-14)$$

$$\dot{Q} = -G\pi\Delta E + (\pi^2 G + kT_c) \frac{\Delta T}{T_c} + 2\pi G\Delta E \quad (5-15)$$

The equivalent circuit for these equations is given in figure (5-6). If it is desired to have the current generator on the output side equation (3-49) and (3-50) become

$$I = G\Delta E + G\pi \frac{\Delta T}{T_c} \quad (5-16)$$

$$\dot{Q} = -6\pi\Delta E + (\pi^2 G + K T_c) \frac{\Delta T}{T_c} + 2\pi G \Delta E \quad (5-17)$$

and the equivalent circuit is given in figure (5-7)

By close inspection of the last four equivalent circuits it can be seen that the passive elements are not of the same type but they are a mixture of electrical and thermal units. This is easily overcome by using scale factors when constructing a practical circuit. The technique used above can be extended to other types of equivalent circuits¹⁴.

b) Experimental Set-Up

Not all the equivalent circuits described in Chapter Three and the first part of this Chapter were actually breadboarded and tried, but some were. The set up is fairly similar, therefore only two equivalent circuits will be described in detail, they are the ones corresponding to figures (5-5) and (5-7). The circuit corresponding to figure (5-5) will be called "T equivalent circuit" and the second "Π equivalent circuit," the names were chosen for obvious reasons.

I. THE T EQUIVALENT CIRCUIT

Consider figures (5-2) and (5-5) simultaneously and compare values, i.e.

$$Z_{11} - Z_{12} = \frac{\pi}{K T_c} + \frac{1}{G} - \frac{\pi}{K T_c} = \frac{1}{G} \quad \text{in the input branch}$$

$$Z_{12} = \frac{\pi}{K T_c} \quad \text{in the mutual branch}$$

$$Z_{22} - Z_{12} = \frac{1}{K T_c} - \frac{\pi}{K T_c} \quad \text{in the output branch}$$

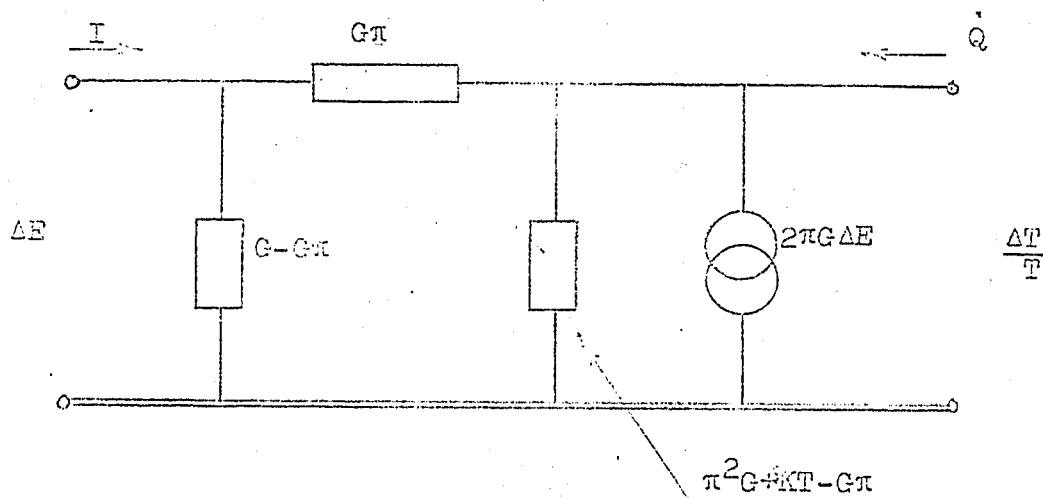


fig. (5-7)

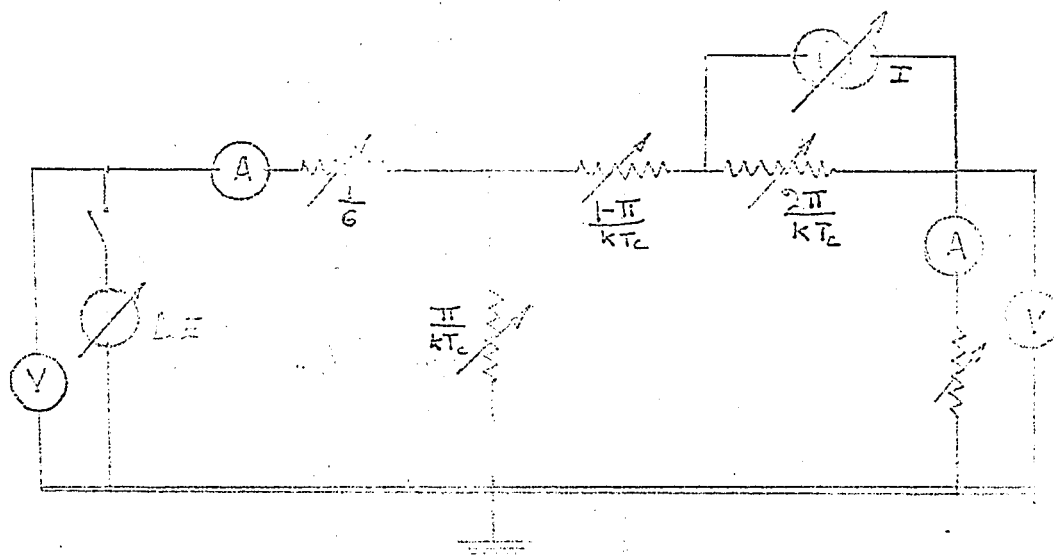


fig. (5-8)

and the value of the generator is $(Z_{12} + Z_{21}) I_1 = \frac{2T}{KT_c} I_1$

An inspection reveals that most values are temperature dependent, this means that either an experiment at constant temperature must be carried or a continuous change of variables is necessary if T_c changes. The experimental set up is the same whether T_c changes or not. The circuit is connected as shown in figure (5-8). The variable resistors used were decade boxes (General Radio) and rheostats (Jagabi). ^{Regulated} The power supplies were used ~~were regulated~~. The circuit is simple and straightforward. The procedures, results and limitations will be discussed later.

II. THE T EQUIVALENT CIRCUIT

From figure (5-7) the conductance of the input branch is $G(1-T)$, the conductance between the input and output nodes is $G(1-T)$ and that of the output branch is $GT(T-1) + KT$. In this case, as in the former, the internal generator of the equivalent circuit is connected across the output branch, the circuit is connected as shown in figure (5-9).

The main reason for choosing the above circuits with the internal generators connected on the output side is that the quantities of interest are heat flow and temperature, therefore they are taken as output quantities. Since the internal generator is the coupling term, the generator in the input branch, as in figure (5-6), is a function of $\Delta T/T_c$ and therefore cannot be used. But if $\Delta T/T_c$ and $\dot{Q}$ were known and the values of ΔT and I were the unknowns then the circuit corresponding to figure (5-6) would have been used.

The circuit is connected as shown in figure (5-9). Again it is simple and self-explanatory. The procedure involved is more complicated than what it might seem at first, it will be discussed later on.

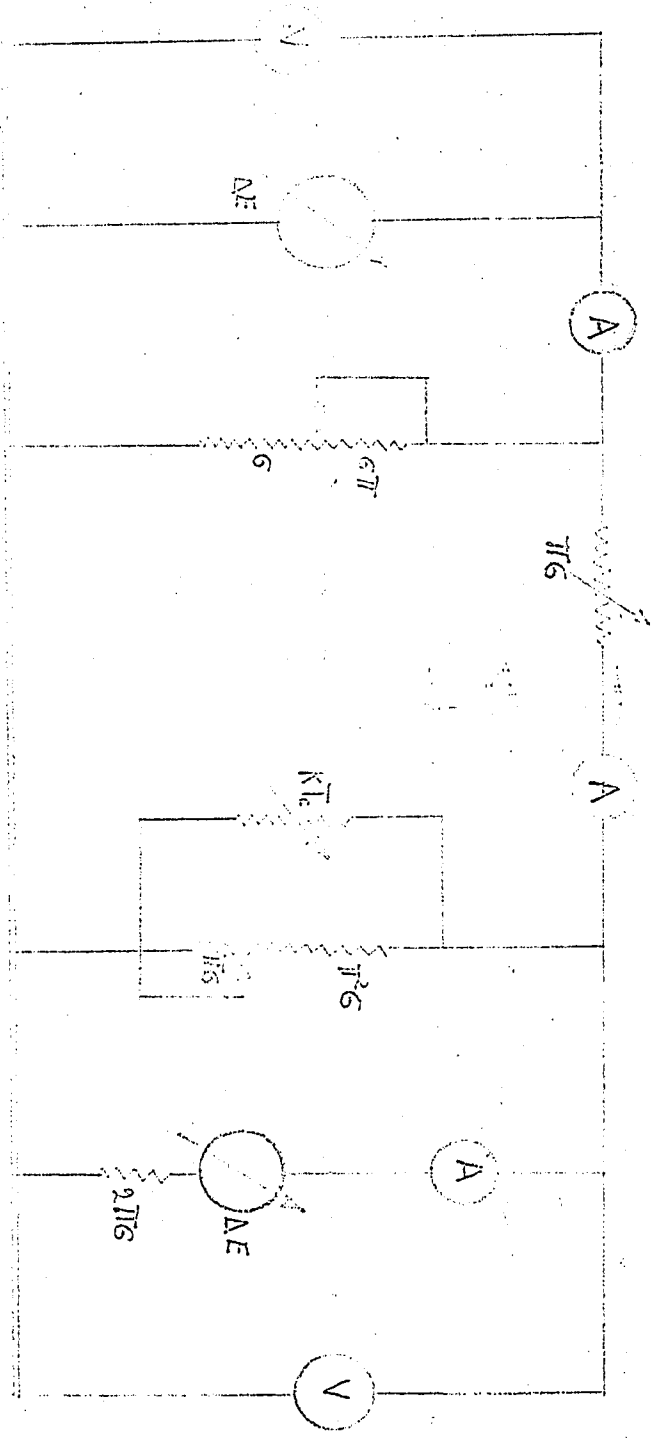


Fig. (5-9)

CHAPTER 6: EXPERIMENTAL PROCEDURE AND RESULTS.

a) THERMOELECTRIC SYSTEM

I No-Load Tests and Results

A number of interesting tests were carried out under no-load conditions.

In order to determine the minimum temperature that the cold junction can reach the circuit was connected up as shown by the block diagram in fig. (6-1).

The following procedure was found to be the best and in that ~~this~~ order.

With the bell jar in place the space around the thermocell was evacuated for about 20 minutes. In the meantime the flow of water to the heat sink was turned on and adjusted to about 600 cubic centimetres per minutes (it was found that any increase of water flow above 600 c.c./min. did not reduce further the temperature of the hot junction). The power supply was then switched on and the current increased in steps until a maximum temperature drop was achieved. The response time of the thermocell on no load is relatively short (it is about 30 seconds as compared to 360 seconds on load), but it must be ascertained that the temperature reached a steady state value before a further increase in current. This was done by observing constantly the temperature and by allowing a large enough time interval between incremental changes of current. The experiment was repeated for different flow quantities of water through the heat sink. The results are shown in figures (6-2), (6-3) and (6-4).

II Load Tests

The circuit is shown in fig (6-5) and the procedure is similar to the one given above. The main difference is in the time required for

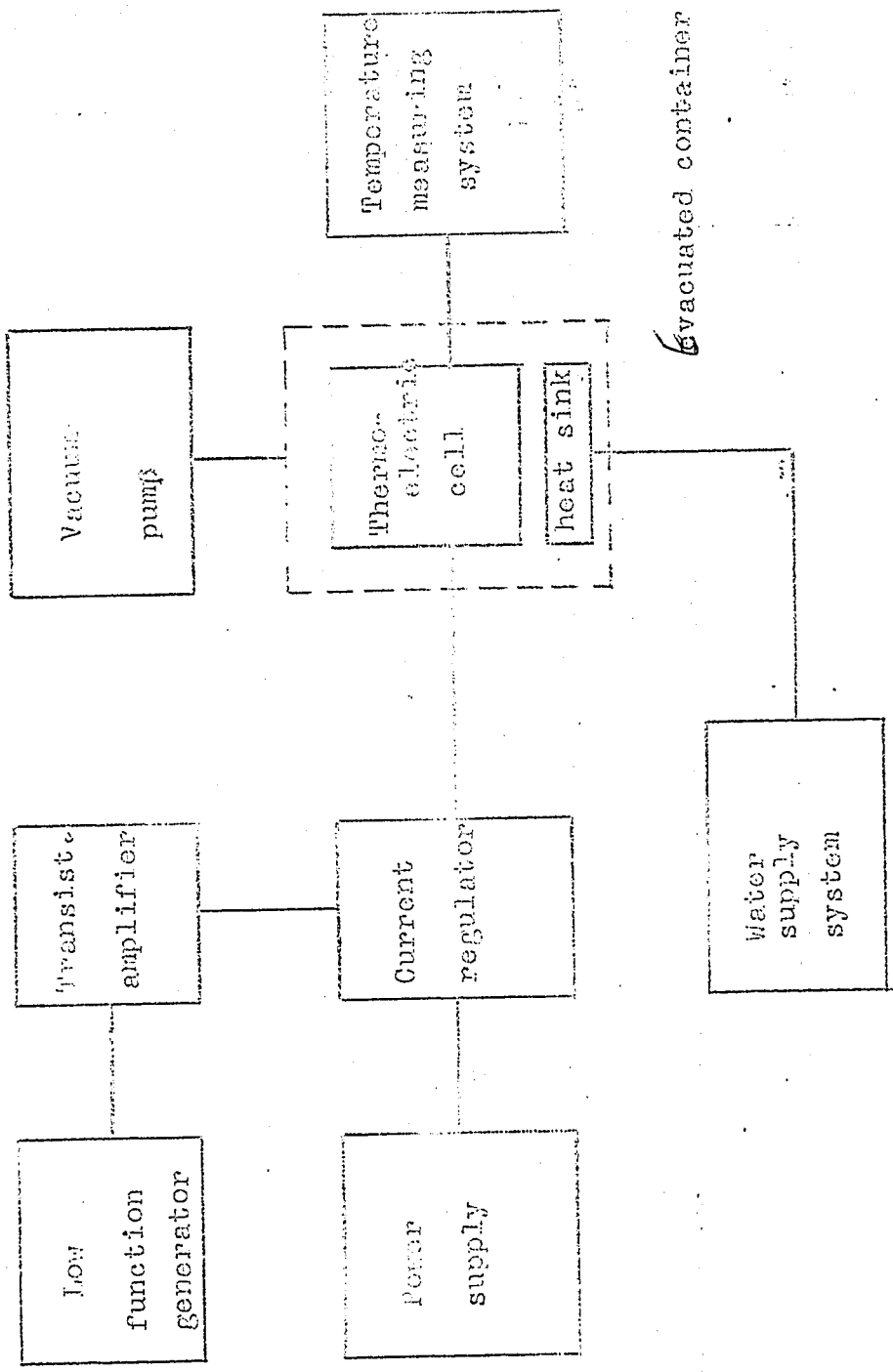
the cold junction to reach a steady temperature.

The time to reach a steady temperature under load conditions will depend on the heat capacity of the load. For the load used in the test the time required was about 6 minutes. Therefore the time interval between different values of current was usually 3 minutes. The results of these tests for different water flows through the heat sink are given in figures (6-6), (6-7) and (6-8). As can be seen from the results the temperatures of both the cold and hot junctions are higher than the temperature under no load conditions. Figure (6-9) shows the maximum temperature difference achieved under different loads.

III Transient Tests

Two different kinds of tests to determine the transient response of the system were performed; 1) Temperature response to transients applied to the current supply of the thermocell and 2) Temperature response to a sudden change in the load of the cold junction.

In the first case the system was allowed to reach a steady state for a certain supply current I and then a current pulse, which was either positive or negative with respect to the supply, was applied. The duration and magnitude of the pulse depended mainly on the load of the system. The larger the load the longer the transient had to be; this is due to the heat capacity of the load. Since the load was made of a copper container with oil in it, the capacity of the load was constant, whereas the load itself depended on the power supplied to the heater immersed in the load (see description of loading system in chapter 4). The transient test was repeated for different loads, the results are shown in figures (6-10) and (6-11). For the sake of comparison all transient tests were made for the same steady state value of current namely 15 amps with a step current of 5 amps.



Block diagram of connections for no-load tests

fig. (6-1)

A plot of the cold junction temperature vs.
applied current for different water flows under no load.

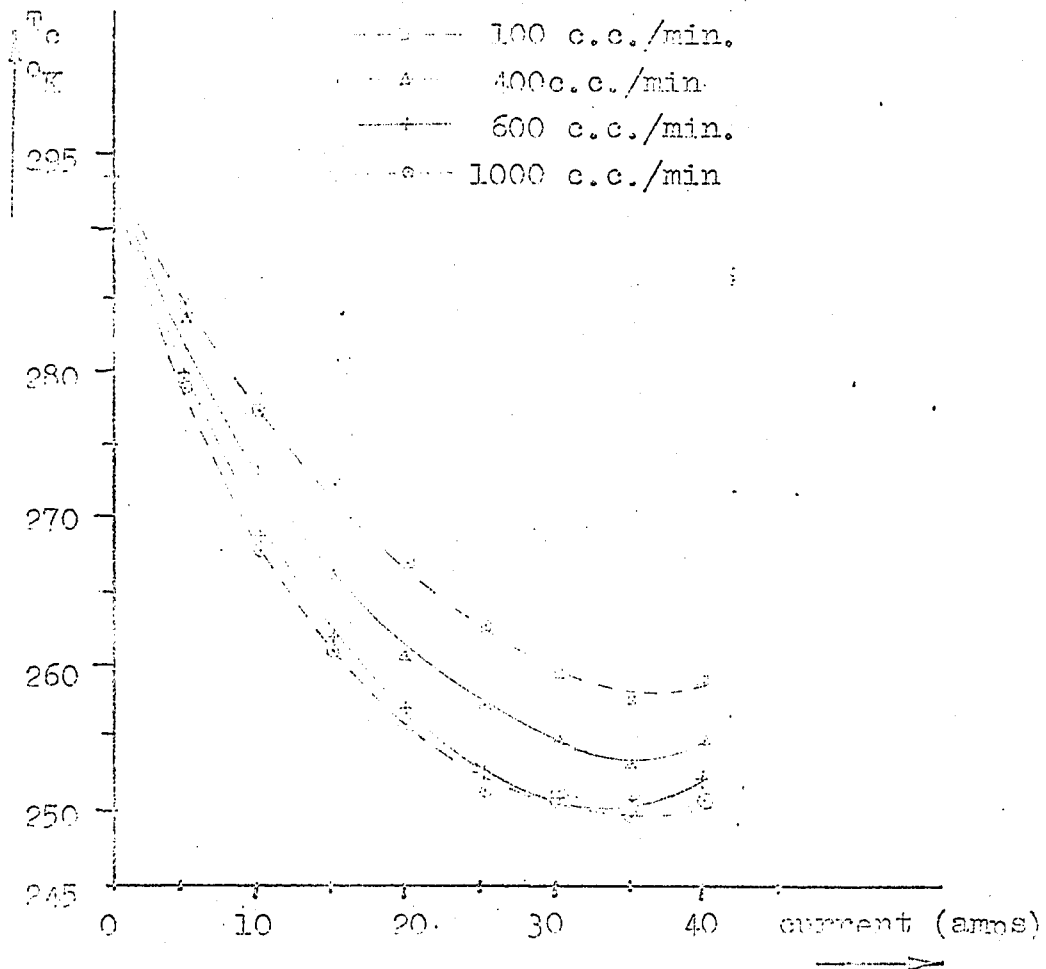
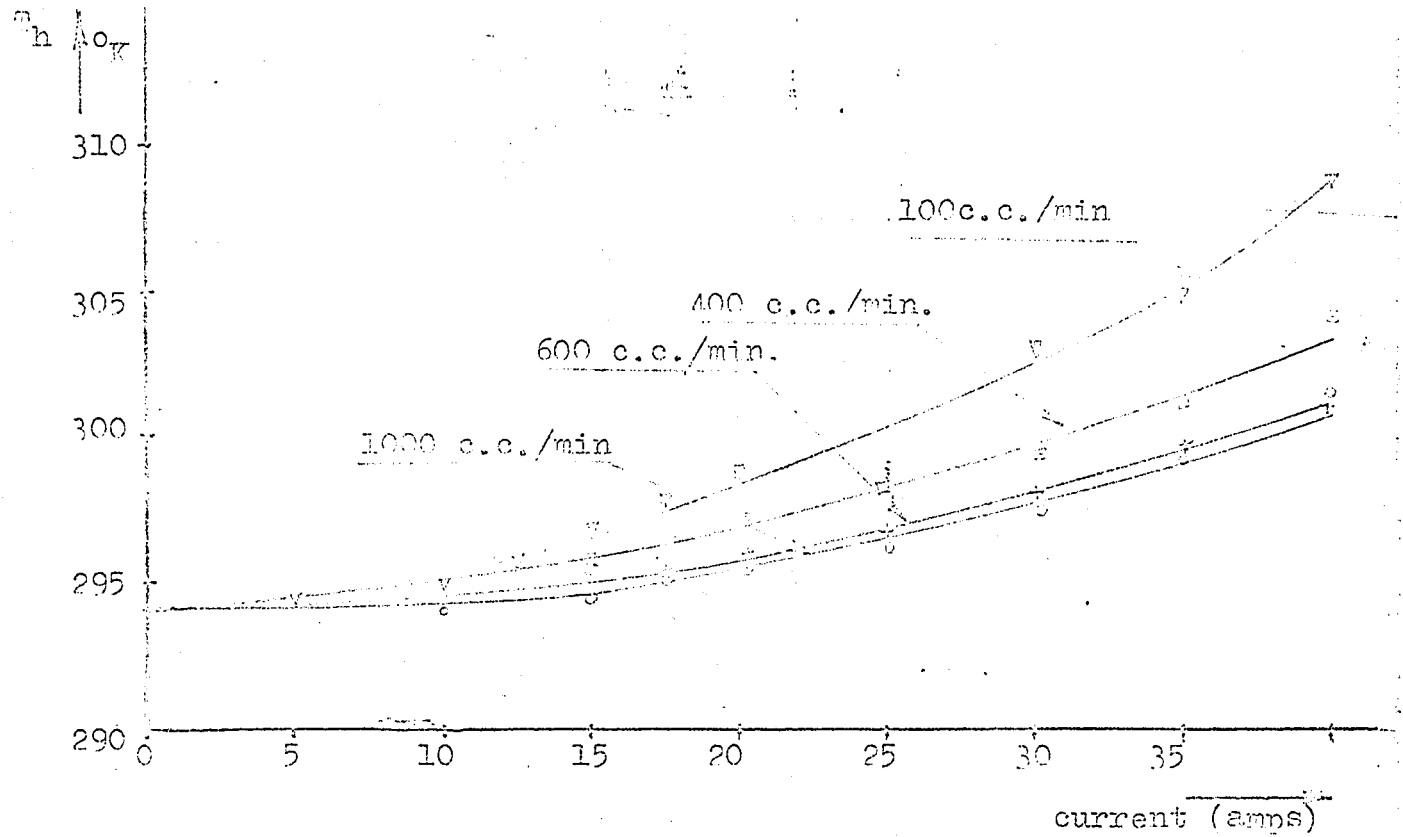


Fig. (6-2)



A plot of the hot junction temperature vs. applied current for different water flows under no load.

Fig. (6-3)

A plot of temperature difference vs. applied current for different water flows under no load .

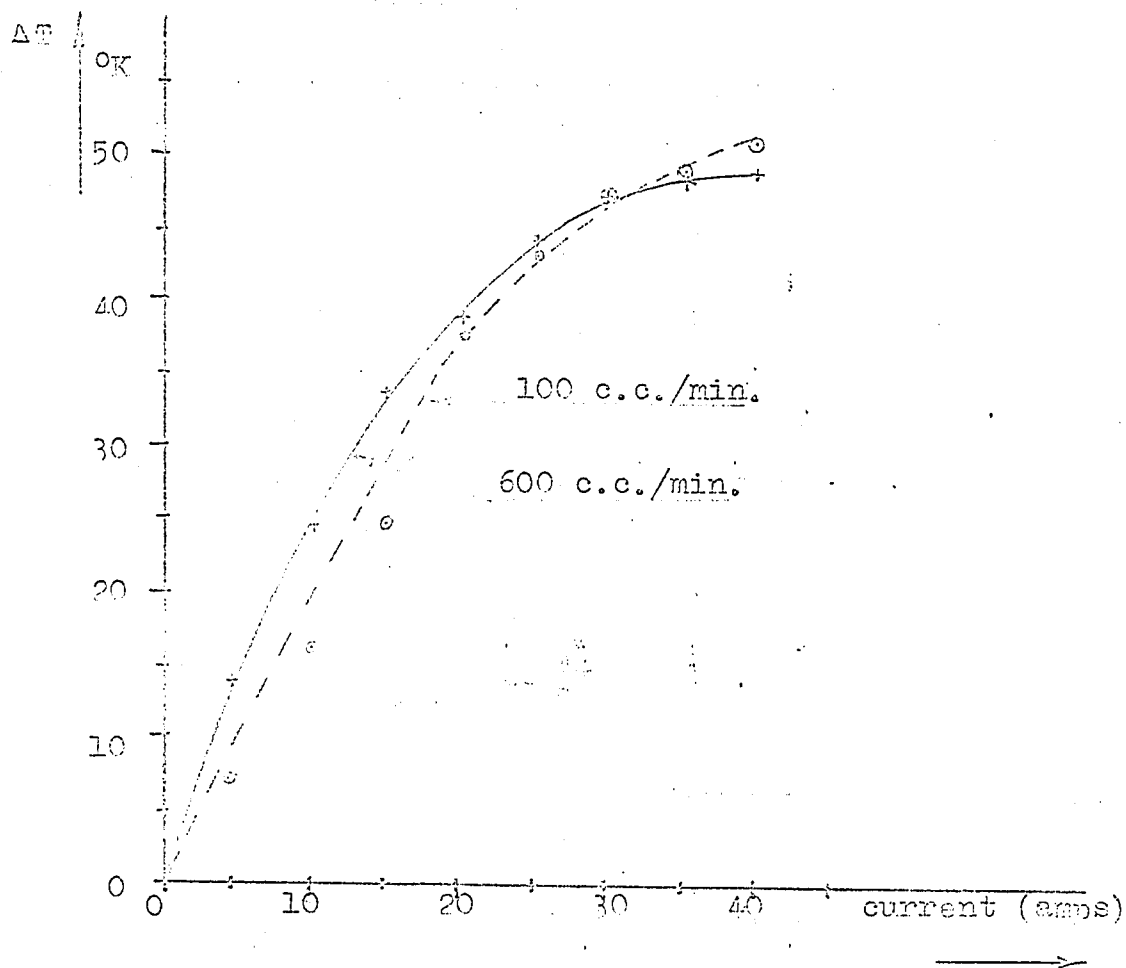


Fig. (6-4)

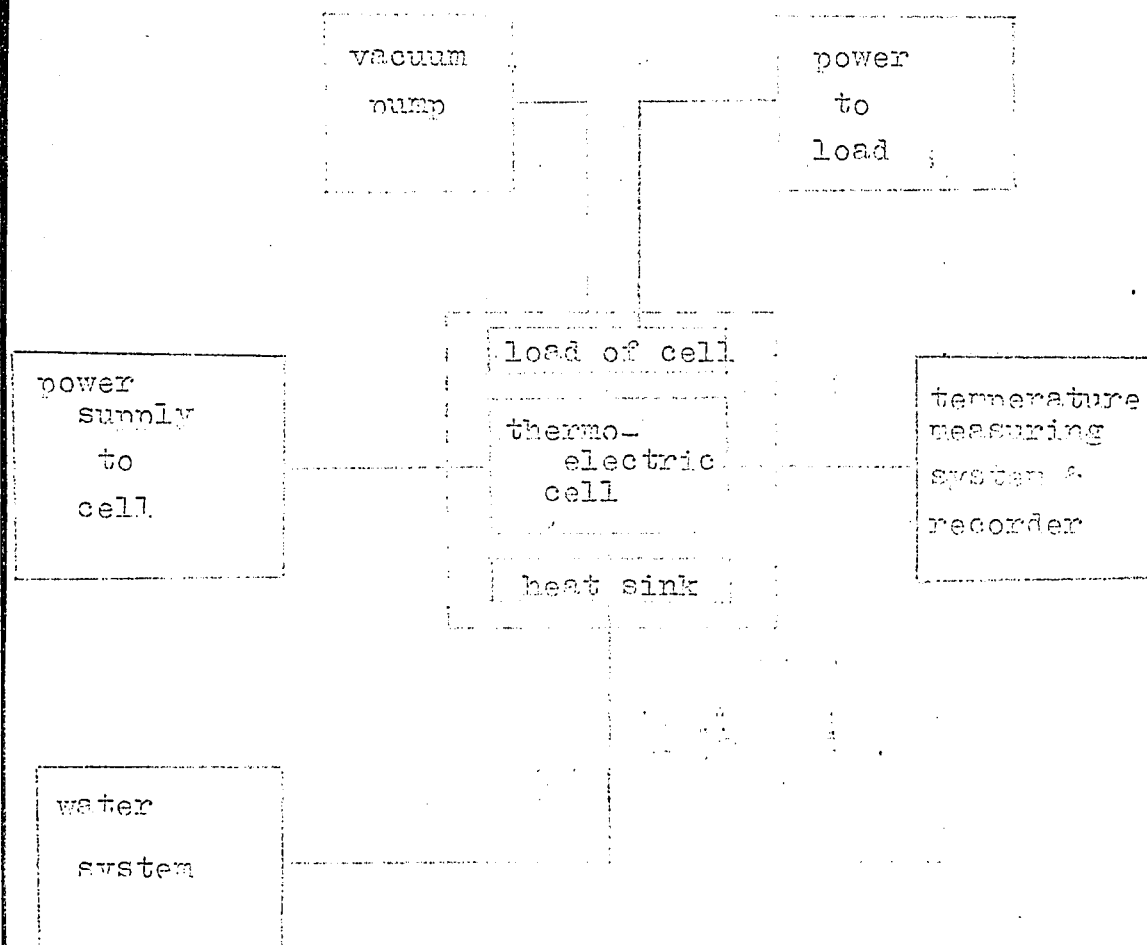


Fig. (6-5)

A plot of cold junction temperature vs. current for a constant load of 1 watt and different water flows.

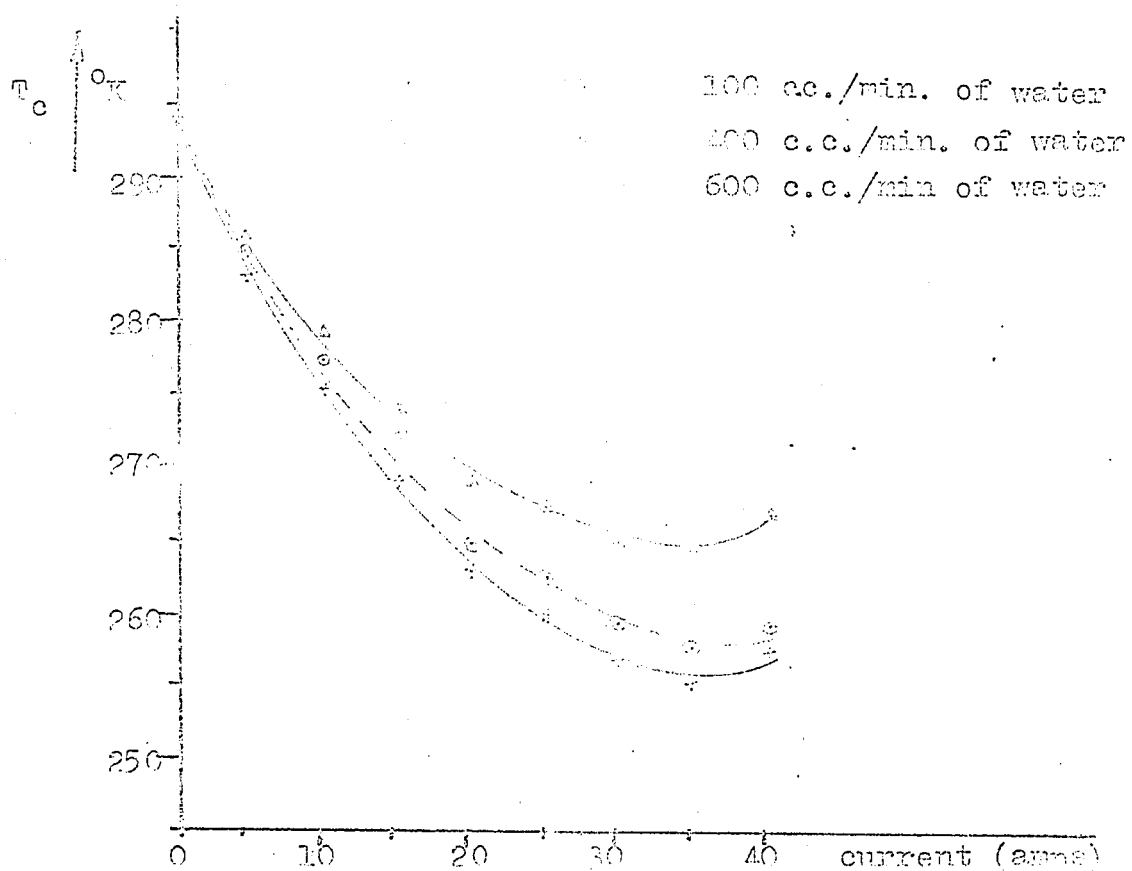


Fig. (6-6)

A plot of the hot junction temperature vs. current for a constant load of 1 watt and different water flows.

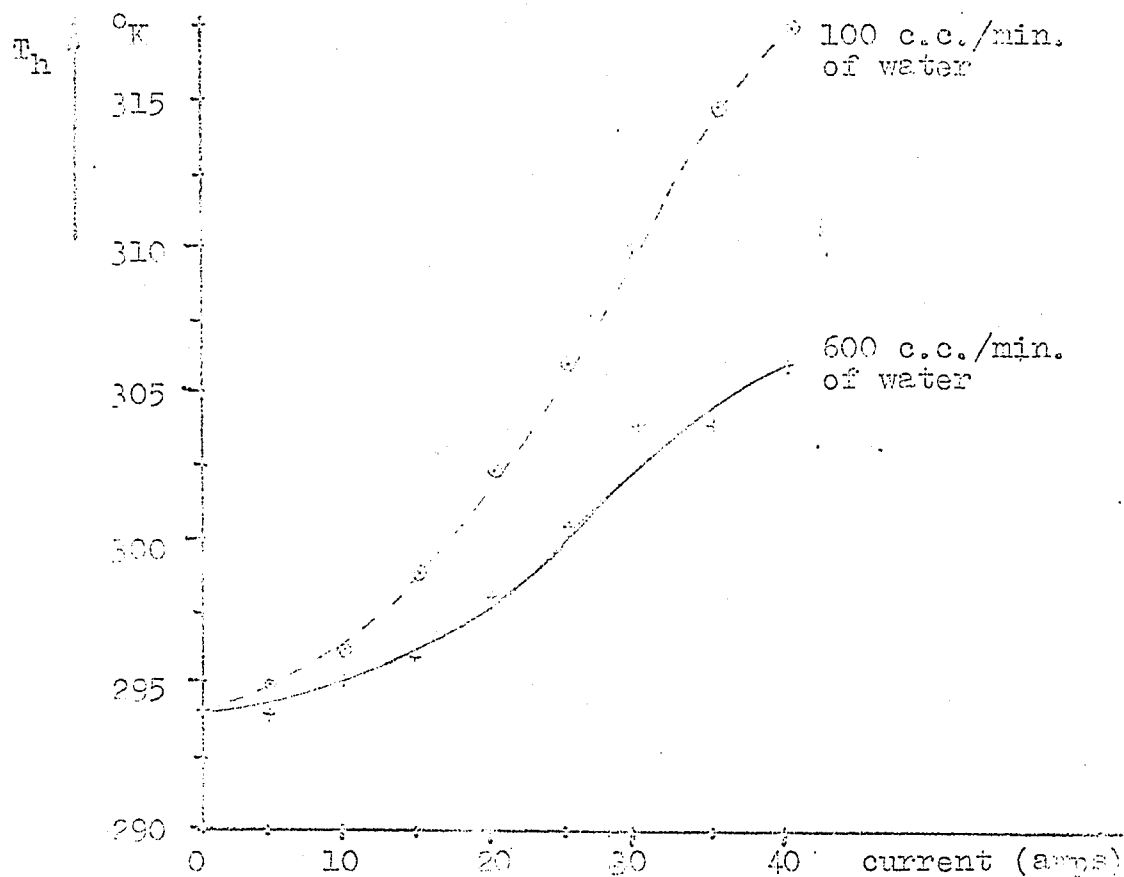


Fig. (6-7)

A plot of temperature difference vs. current for a constant load of 1 watt and different water flows.

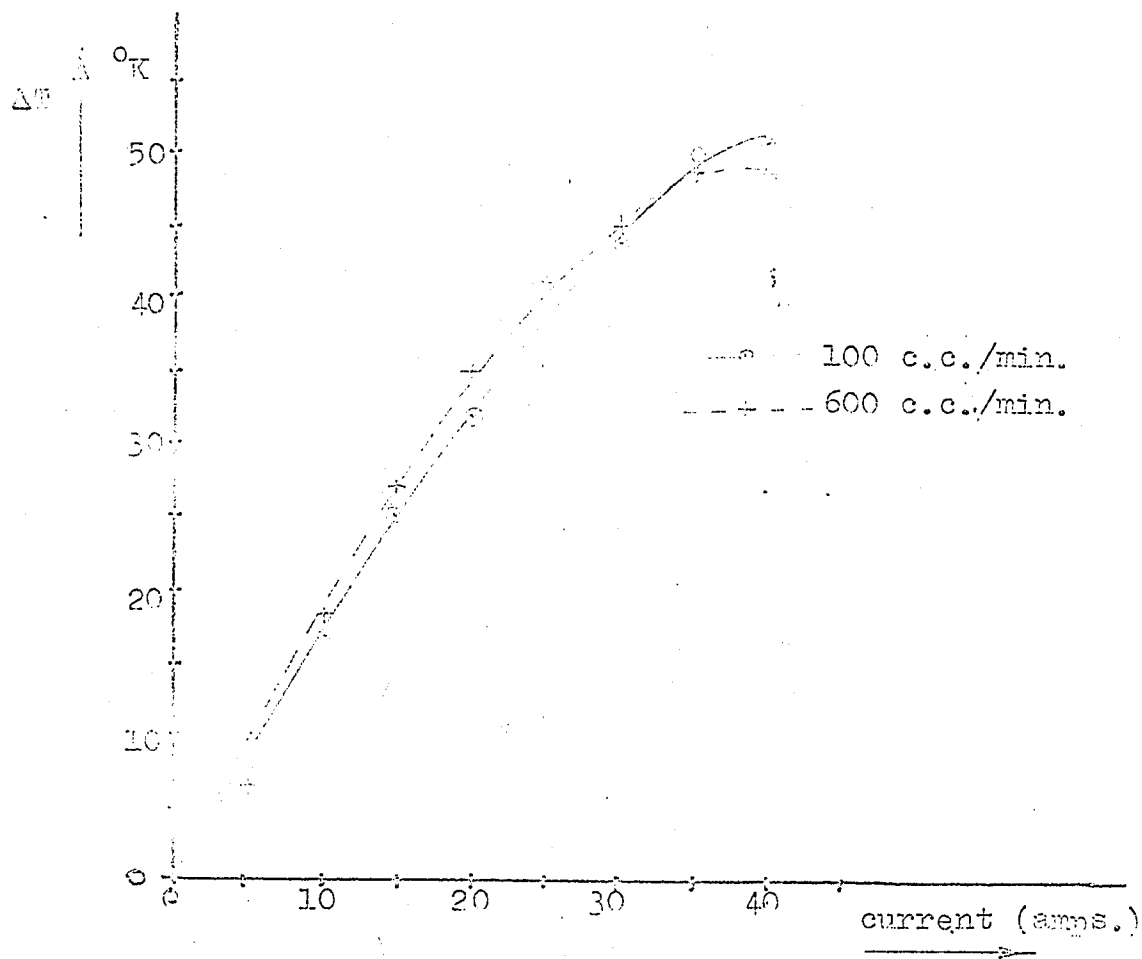


Fig. (6-8)

A plot of maximum temperature difference vs.
load at a constant water flow of 600 c.c./min.

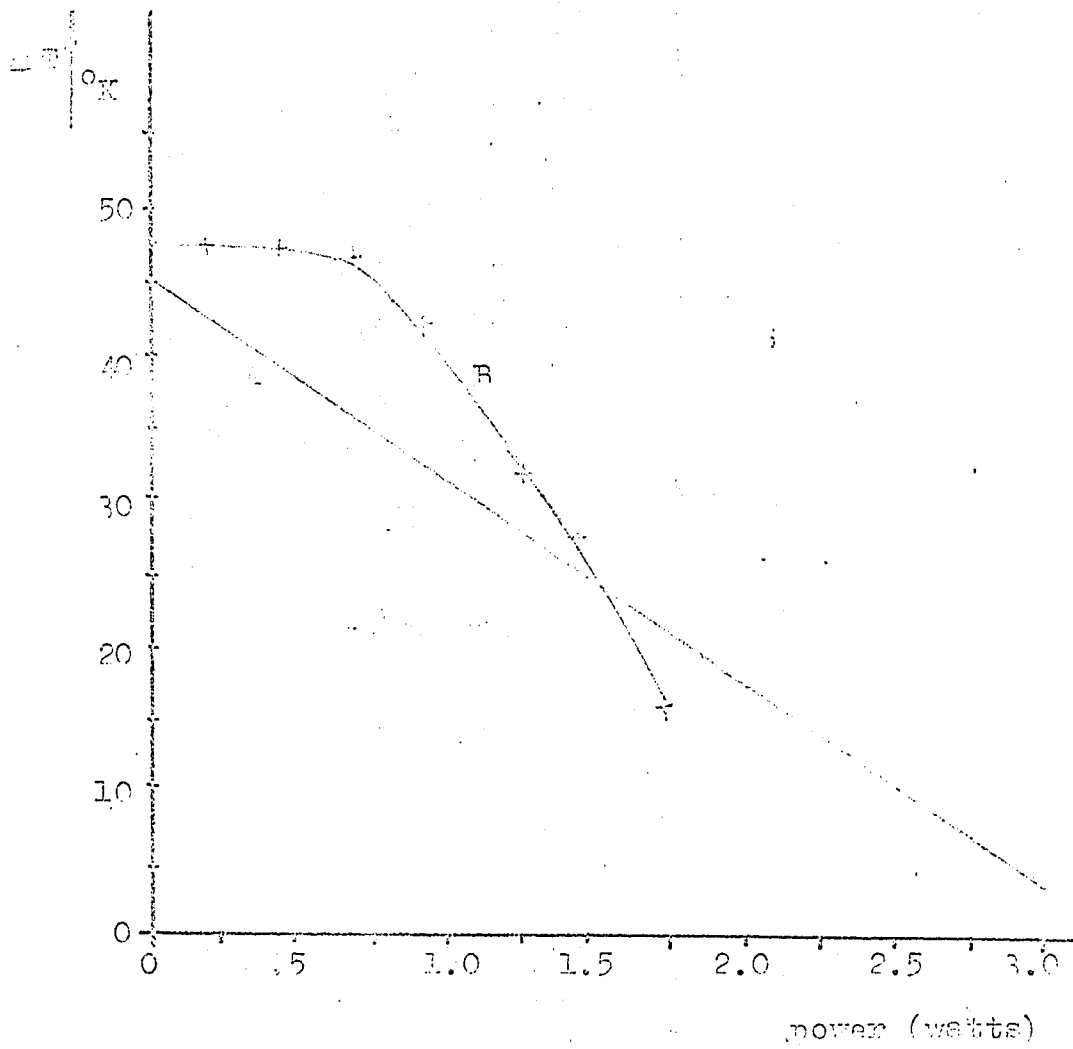


Fig. (6-9)

A - The theoretical curve for constant current of 30A
and constant T_h

B - Measured curve where the current and hot junction
temp. T_h vary.

Response to a step change in the supply current, the step being from 15 to 10 amperes.

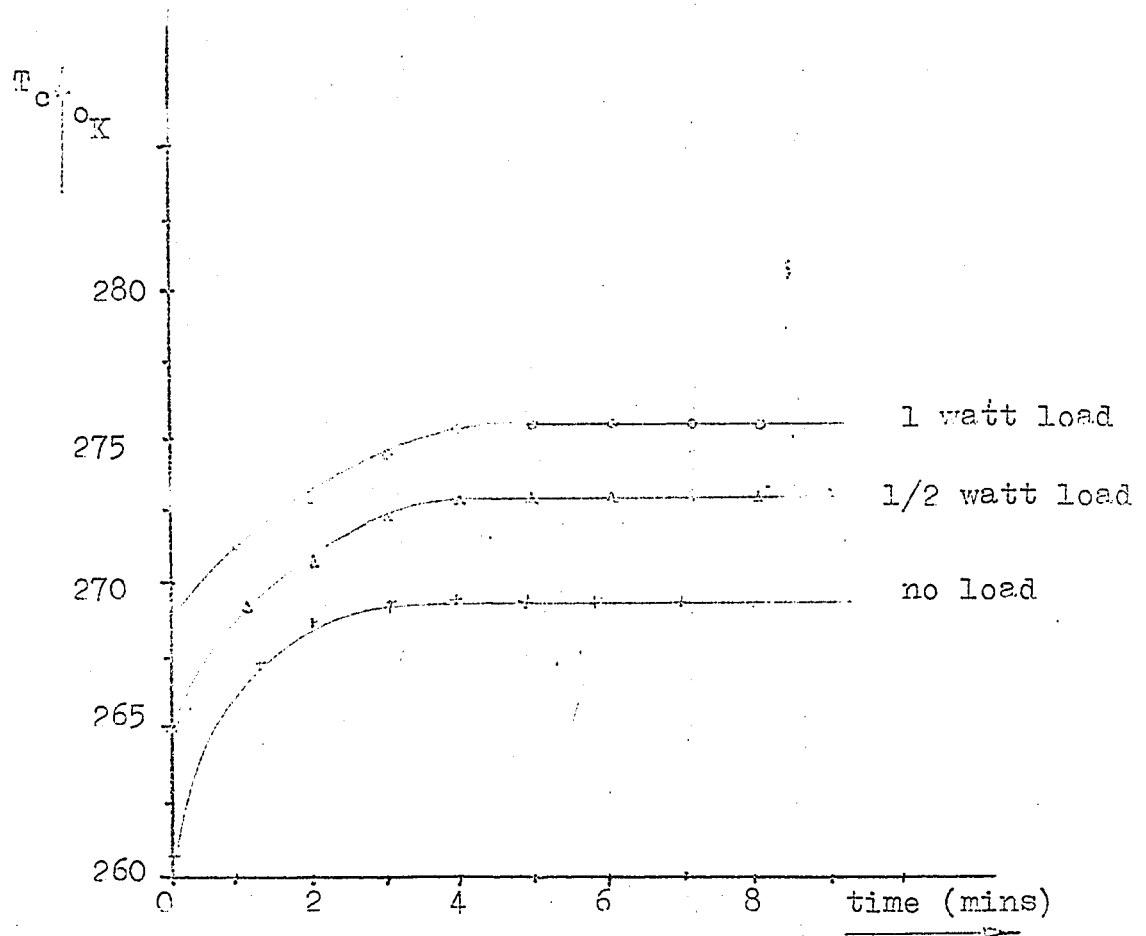


Fig. (6-10)

Response to a step change in the supply current, the step being from 15 to 20 amperes.

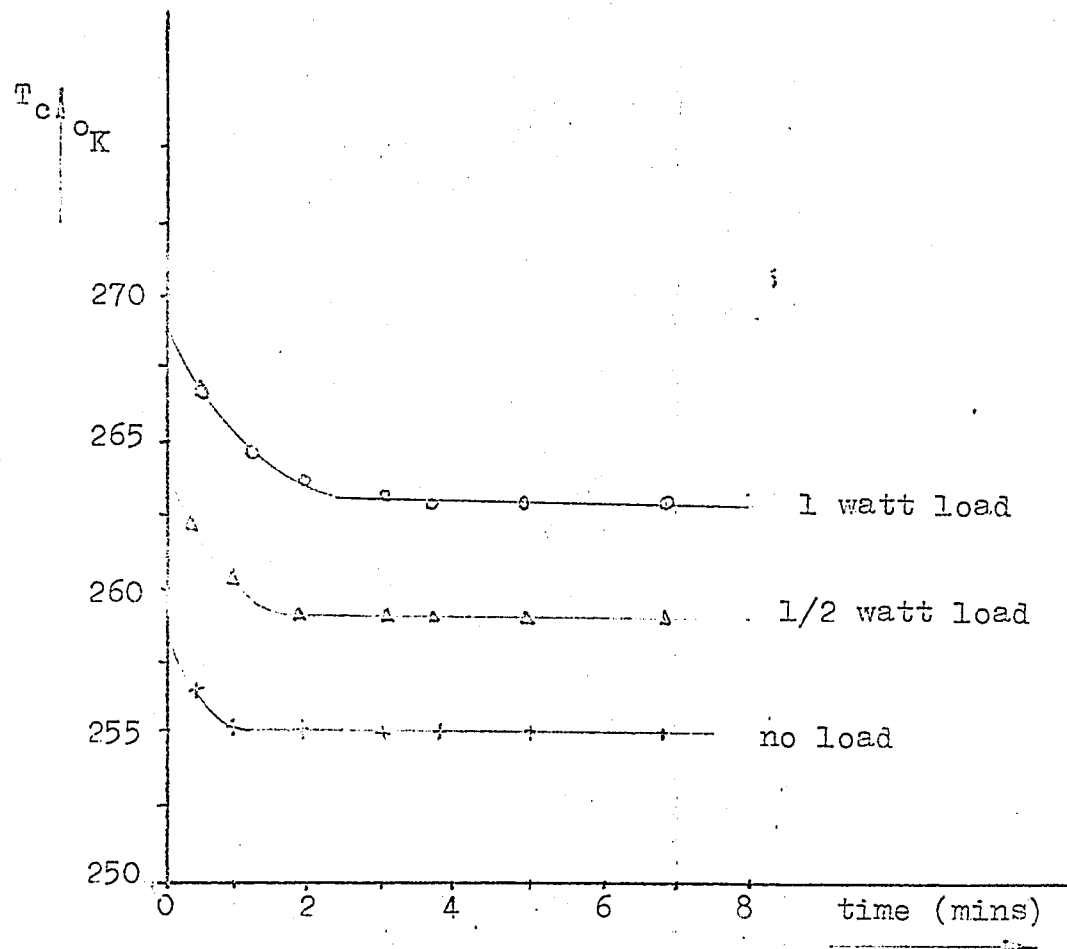


Fig. (6-11)

Response to a step change in load at a steady current of 15 amperes (the step being 1/4 w. in magnitude)

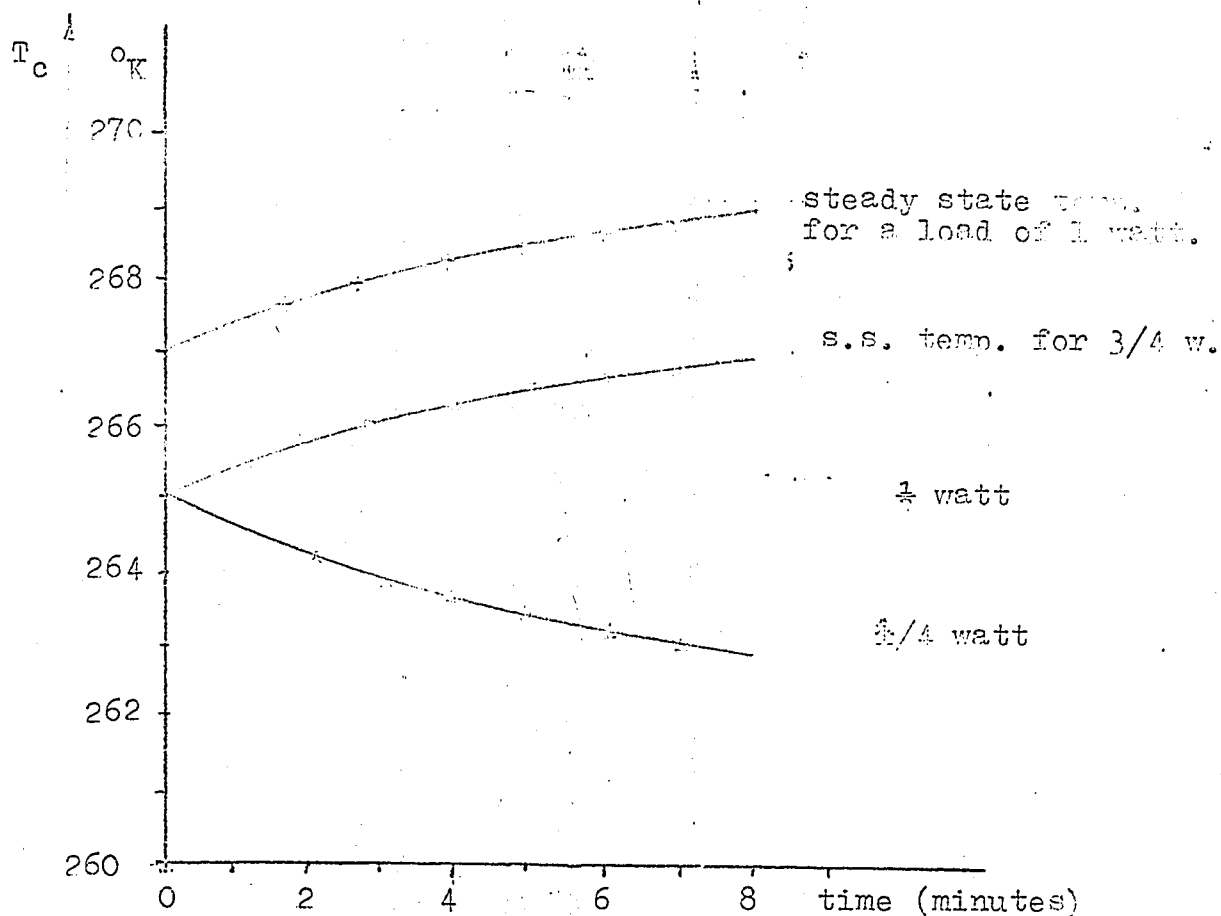
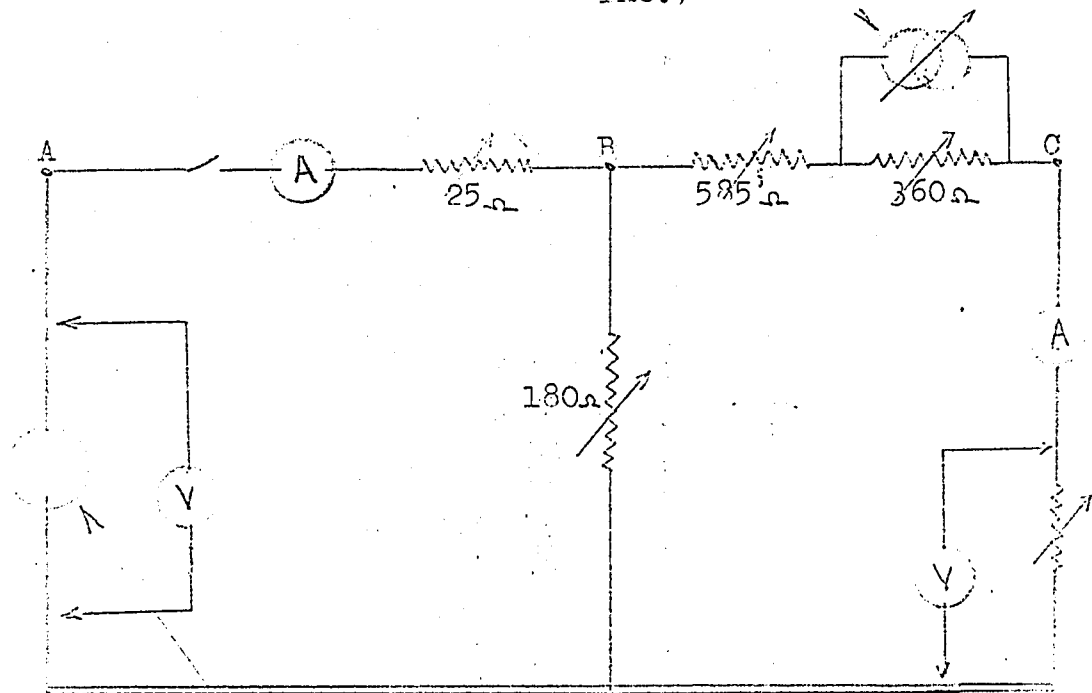


Fig. (6-12)

As might be expected the response time is the same for all changes, this is due to the thermal capacity of the load (which remains constant).

constant current generator
(Electronic Measurements
Inc.)



Harrison Labs.
power supply

Fig. (6-13)

In the second case the procedure was similar. The system was allowed to reach a steady temperature and then the load was either reduced or increased by changing the current supplied to the immersed heater. The results are shown in figure (6-12).

A discussion of the results given in this section will be carried out later.

b) EQUIVALENT CIRCUITS - PROCEDURE AND RESULTS

I) T Equivalent Circuit

Before setting up the circuit the values of all elements must be worked out with their appropriate scaling factor. From the manufacturer's data all the required information can be calculated. This is best illustrated by an example. Since it was assumed that all parameters are independent of temperature, their average value was taken over the range 250-350°K. It was found that in this range

$$R = .0025 \Omega$$

$$K = .0065 \text{ w/}^\circ\text{C}$$

$$\text{and } \pi = .025 \text{ V}$$

Assuming that $T_c = 255^\circ\text{K}$ and $\dot{Q} = 1 \text{ W}$ and using a factor of 10000 for the resistances, the various quantities can be calculated

$$\frac{\pi}{KT_c} = 180 \Omega$$

$$\frac{1-\pi}{KT_c} = 585 \Omega$$

$$\frac{2\pi}{KT_c} = 360 \Omega$$

The voltage source in the output branch depends on the input current, therefore it was made of the current generator in parallel with $2\pi/KT_c$. From the above it follows that the scaling factor for current is 1/1000, if the voltage is scaled by a factor of 10. Suppose the current is 30A, i.e. 30 mA is the equivalent. Then the procedure is as follows: increase the input supply voltage from zero to give 30 mA output current, adjust

Plots of power removed from cold junction
vs. supply current, for two values of cold junction
temperature,

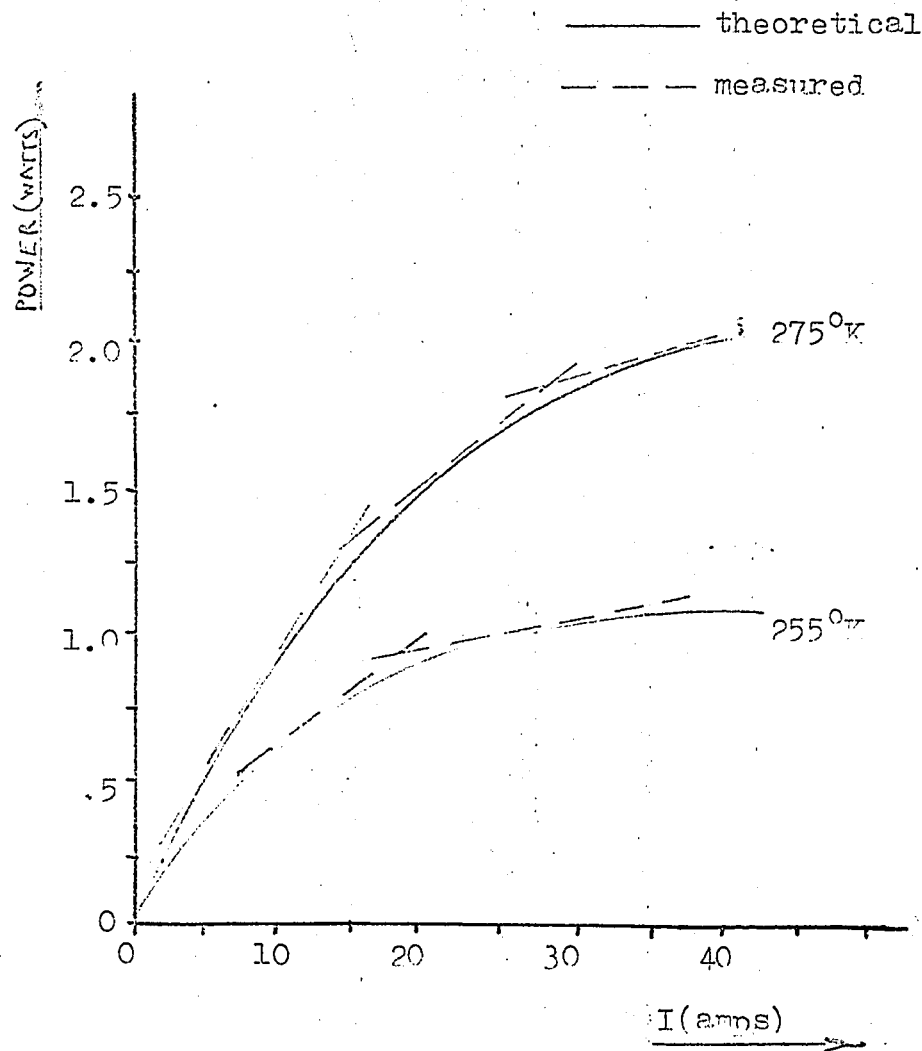


Fig. (6-14)

Plots of required supply current vs.
temperature difference for various values of cold
junction temperature.

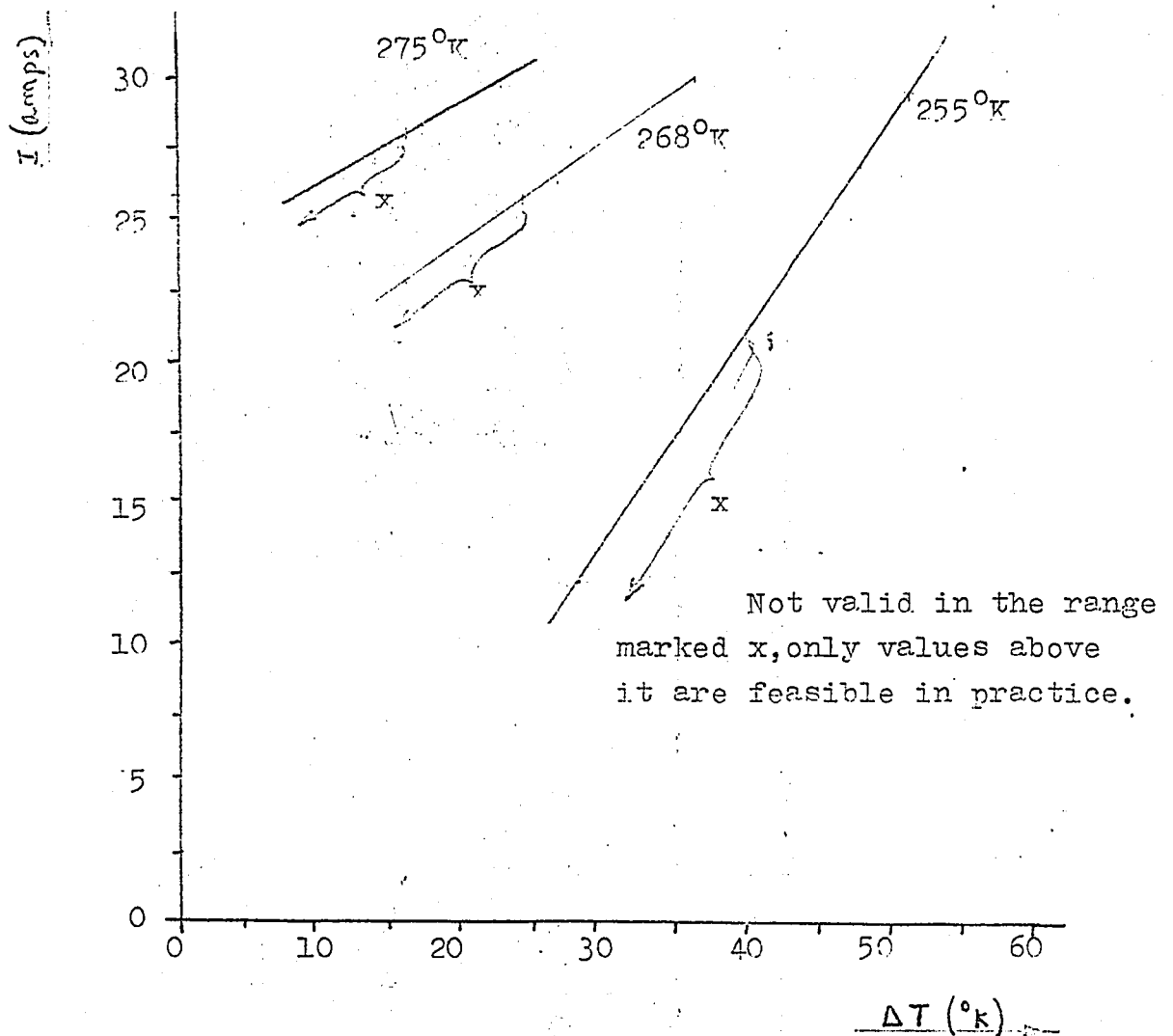


Fig. (6-15)

the current generator to give the same current. It will be necessary to readjust the input value and maybe that of the current generator too. The voltages at points A, B and C shown in figure (6-13) and the different voltages can now be read and they are 6.83V at A, 6.18 at B and 5.34 at C. The voltage at C is of interest and it gives a ΔT of 53.4°C. It may be pointed out here that from the above description the procedure seems easy. In fact it is unnecessary to build a model because it is easier to calculate the values directly from the equivalent circuit then to determine the values from a model. The results are shown in figures (6-14) and (6-15).

II) π Equivalent Circuit

Using the same values for R, K, π and T_c as before, the values for the π network are :

$$G(1-\pi) = 390 \Omega$$

$$G\pi = 10 \Omega^{-1}$$

$$G\pi^2 + kT - G\pi = 11.41 \Omega^{-1}$$

$$2\pi G = 20 \Omega^{-1}$$

The balancing procedure for this arrangement was more complicated and did not give satisfactory results. Hence the values were calculated and plotted, as shown in figures (6-16) and (6-17).

Plots of power removed from cold junction
vs. current, for two values of cold junction temp.

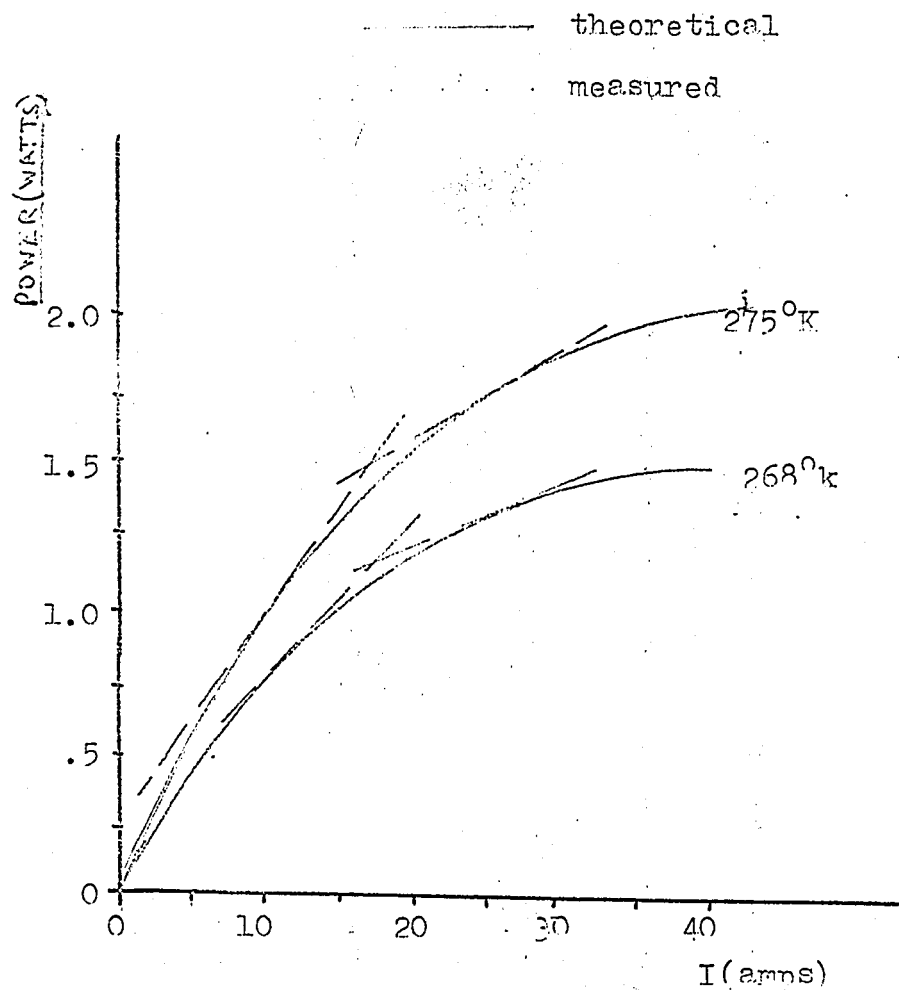


Fig. (6-16)

Plots of required supply current vs.
temperature difference for various values of cold
junction temperature.

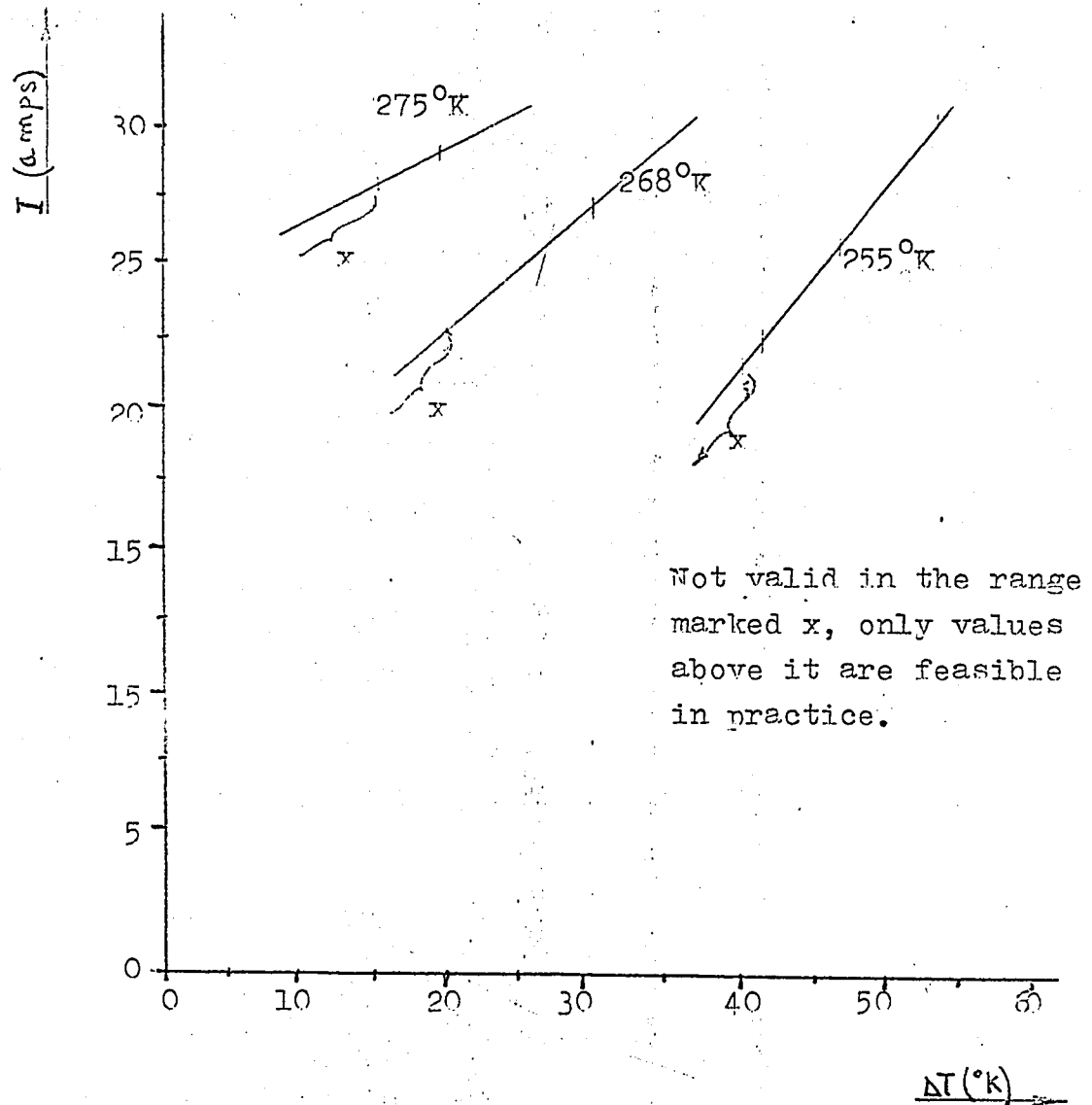


Fig. (6-17)

CHAPTER 7: COMMENTS AND CONCLUSIONS:

The comments will be divided into two parts, the first will deal with the thermoelectric system and the second with the equivalent circuit.

In general the performance of the thermoelectric system was very good, only at high currents the temperature went up a little; this indicates that the heat sink was not ideal. Under the conditions of the experiment the results, where it was possible to compare, were better than the manufacturer's specifications. As can be seen in figure (6-3) the temperature of the hot junction does not increase uniformly with the decrease in flow of cooling water. It was found that for water flows less than 100 c.c./min. the increase in temperature was even greater; this in turn increased the temperature of the cold junction (due mainly to heat conducted back from the hot to the cold junction). Because of this increase in temperature of the hot junction at high currents, the curve of ΔT vs. I , for a flow of 100 c.c./min. crosses that for a flow of 600 c.c./min. in figure (6-4). It might be misleading to think that the minimum temperature reached is lower, the larger temperature difference is due to the increase in temperature of ^{the} hot junction so giving a larger ΔT , the same comment applies to figure (6-8). The system performs best for loads up to 1 watt -- this can be seen in figure (6-9). The efficiency for high currents falls off rapidly due to the increase in Joulean heat and thermal conductance. Figures (6-10), (6-11) and (6-12) show that the time constant of the system is very long. The system can therefore be used as an analog to systems having large capacities, as suggested elsewhere¹⁵.

The equations and equivalent circuits derived in Chapter Three are useful, as was said at the outset, for small variations. It is not really necessary to build an analog circuit to these equations, it is easier to calculate, because in order to set up the equivalent circuit on the bench many calculations have to be performed. In practice the temperature of the hot junction is fixed and that of the cold junction T_c is the variable, but because of the nature of the derivation, T_c came out to be the fixed value (i.e. the independent variable) this reduces somewhat the usefulness of the equations. It was found impossible to derive equations with T_h fixed. The equations were derived for a single junction (or cell), so were the equivalent circuits. If a thermoelectric module is used then depending on the number of cells in it, the equations and equivalent circuits can be easily modified. For example, if a module has n cells in it then the resistance R in the desired equations becomes nR and the thermal conductance K becomes K/n and so on.

It might seem that the results are not related, but a close inspection reveals that they are. Since the equations are linear the results are straight lines but because these equations hold for small variations only the results are valid only in the marked ranges. As might be expected the higher the cold junction temperature the larger is the amount of heat the cell is capable of pumping out of the cold junction, for a given current. This is indicated in figures (6-14) and (6-16). Figures (6-15) and (6-17) give the possible range for the hot junction temperatures for fixed cold junction temperatures. The ranges marked x in figures (6-15) and (6-17) are not valid because they give hot junction temperatures below ambient and therefore impossible to achieve in practice.

If a more general pair of equations is required then the associated equivalent circuit will be more complicated. The derivation of a completely general set of equations will have to be based on the dynamic equations derived by Gray⁷ who points out that this is indeed difficult if at all possible.

On the other hand it is possible to extend the range of the equations derived in Chapter Three by allowing the resistance and thermal conductance to be linear function of temperature; this may result in a non linear equivalent circuit. The complexity of the derived equations can ~~now~~ be increased now, the complexity of any other equation will depend on the number of assumptions made.

The derived equation may be used to either check a design or for calculation of small variations about a point.

APPENDIX I

Anodizing Procedure

The aluminum plate to be anodized must be thoroughly cleaned. After cleaning, the plate must be immersed for ten seconds in a solution of Caustic Soda (NaOH), at a temperature of 150°F. The strength of the solution is 40 gms NaOH per litre of water. Then it must be immersed for 20 seconds in boiling water and washed afterwards with cold water. The aluminum plate is now ready for anodizing.

The anodizing solution is made from water and Sulfuric Acid (H_2SO_4 of specific gravity 1.84 gms/cc), the strength of the solution being 200 gms/litre. Six litres of solution are required for every square foot of anode surface. The surface area of the cathode must be at least twice as large as that of the anode. The cathode is made of lead and it must be thoroughly cleaned before use. The anode is, of course, the aluminum plate to be anodized. The leads to both electrodes must be made from aluminum (only the section that is immersed). The distance between the electrodes must be such that the voltage between them will be not less than 10 Volts and a current density of 15 amps/ft² ^{of} ~~per~~ anode area must be maintained. The longer the plating time the thicker is the coating. It was found that if the plating is maintained for an hour a good insulating coat is produced.

After anodizing the surface must be hardened, this is done by placing the coated plate for 10 minutes in boiling water.

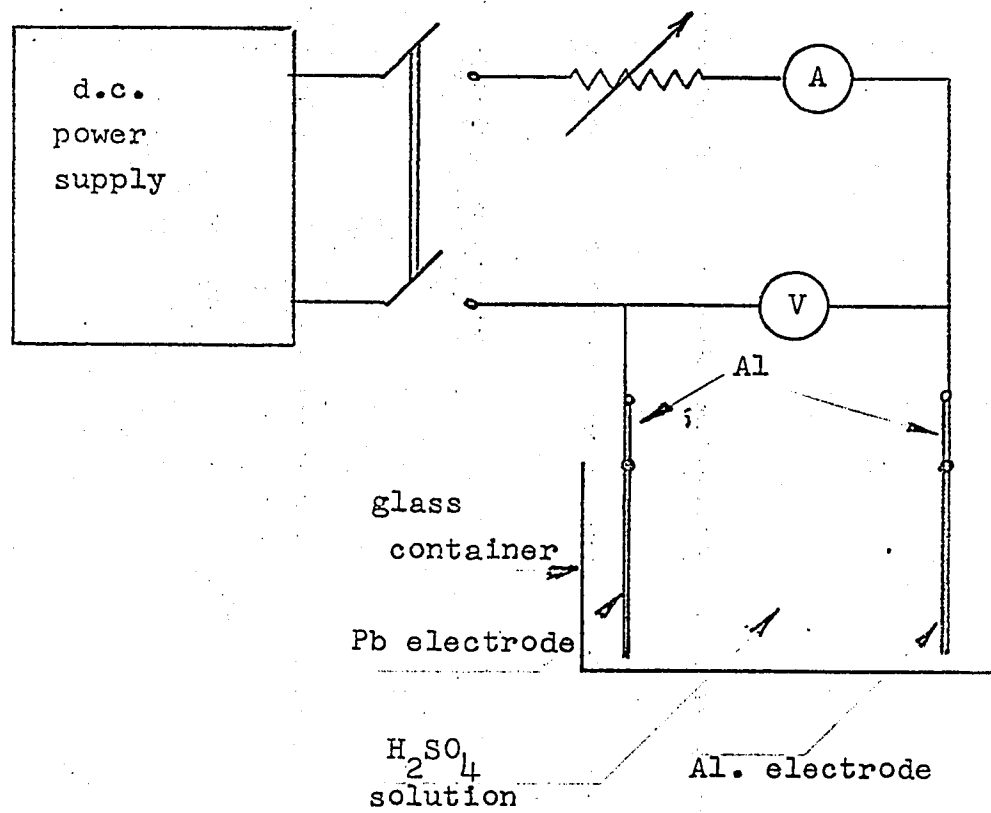


fig.(A-1)

This completes the anodizing process. The circuit diagram is given in figure (A-1).

Any further information may be obtained from;

- 1) Handbook of Industrial Electroplating by Olard E.A. and Smith E.B. Iliffe and Sons London 1948.
- 2) Handbook of practical electroplating by Rodgers T.M. The MacMillan Comp. 1959.
- 3) Electroplating - Field S. and Weill A.D. Pitman London, 1946.
- 4) Principles of electroplating and electroforming by Bleem W. and Hogaboom G.B. - McGraw Hill 1949.

APPENDIX II

Some photographs of the equipment used are given here.

Figure (II-1) shows the entire set up.

Figure (II-2) shows the steel base, the heat sink, the mounting arrangement for the thermocell and its load. The thermocell is hidden by the load.

Figure (II-3) is the same as fig. 2 with the bell jar in place.

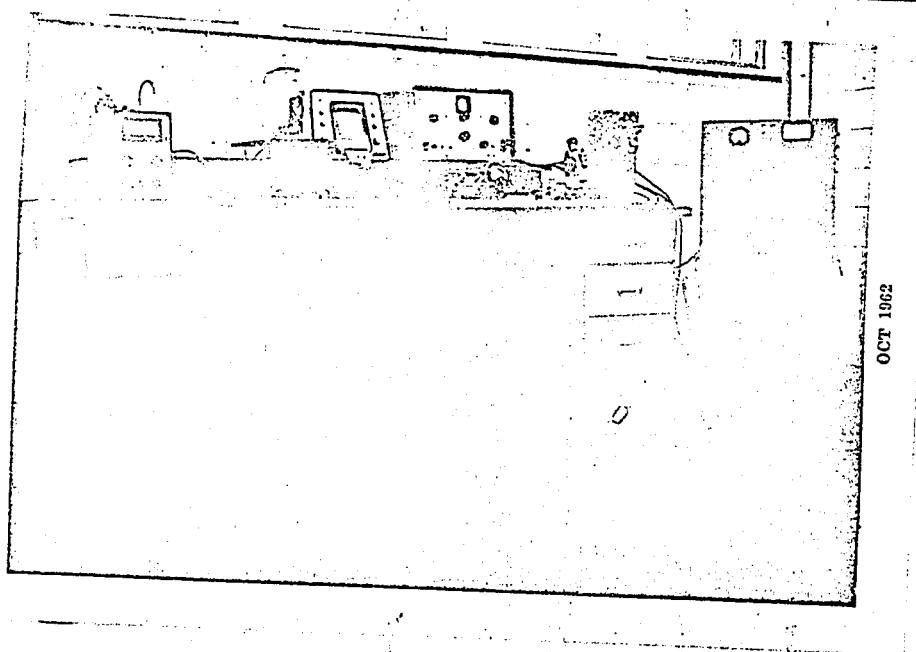
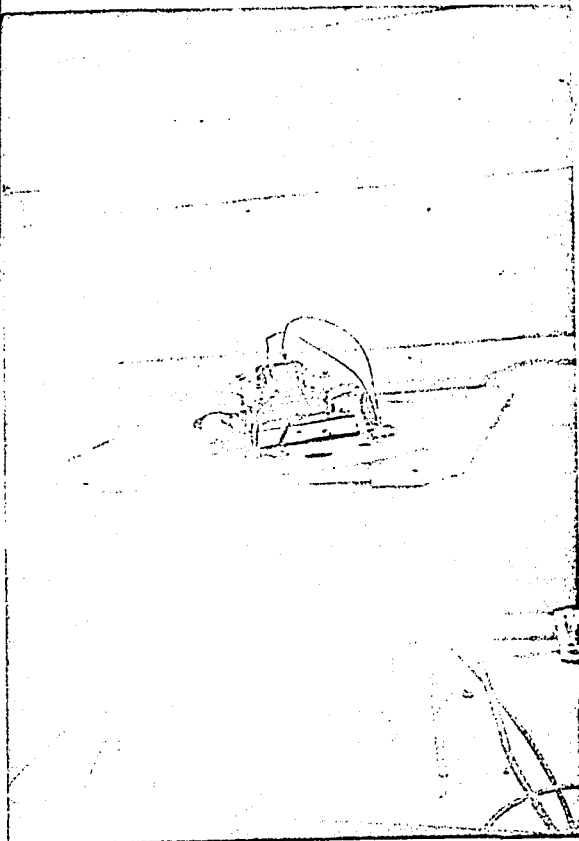


figure (II-1)



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figure (II-2)

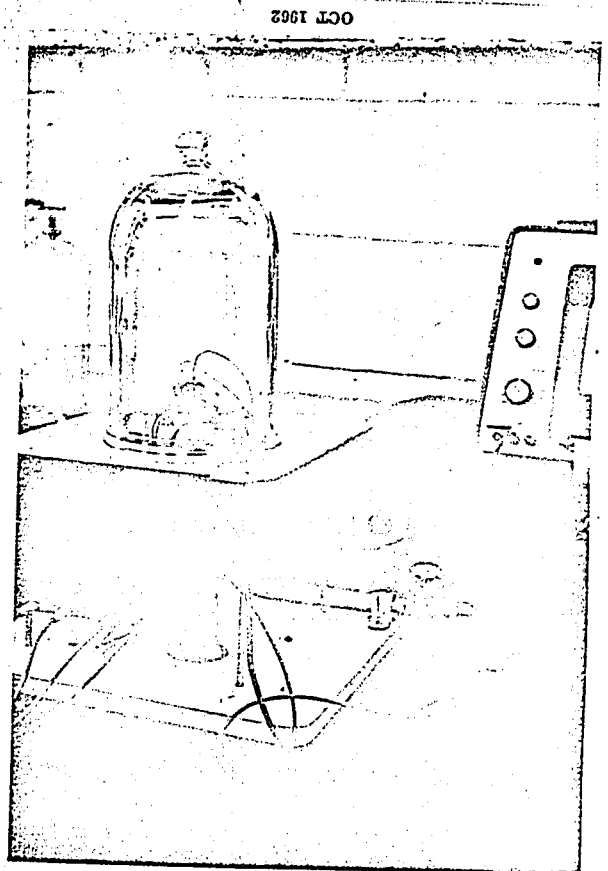


figure (II-3)

LIST OF REFERENCES

- 1) Ioffe A.F. "Semiconductor Thermoelements and Thermoelectric Cooling"
Infosearch, London 1957.
- 2) Goldsmid H.J. "Applications of Thermoelectricity"
Methuen's Monographs London.
- 3) Carry T.M. "Design of a 100W Thermoelectric Generator"
Electrical Engineering Vol. 79 P-482 June 1960.
- 4) Heikes R.R. and Ure R.W. "Thermoelectricity Science and Engineering"
Interscience N.Y. 1961.
- 5) MacDonald D.K.C. "Thermoelectricity an Introduction to the Principles of"
J. Wiley N.Y. 1961.
- 6) Cadoff I.B. and Miller E. "Thermoelectric Materials and Devices"
Reinhold Publishing Co. N.Y. 1960.
- 7) Gray P.E. "The Dynamic Behaviour of Thermoelectric Devices"
Technology Press 1960.
- 8) Bridgeman P.W. "Thermodynamics of Thermoelectric Phenomena in Metals"
- 9) Onsager L. "Reciprocal Relations in irreversible processes"
Phys. Rev. Volume 37 Feb. 15 1931 P(405-426).
- 10) De Groot J.R. "Thermodynamics of Irreversible Processes"
Interscience N.Y. 1950.
- 11) Domenicalli "Irreversible Thermodynamics of Thermoelectricity"
"Review of Modern Physics" Vol 26 No 2 Apr 1954
P-237.
- 12) Callen H.B. "The Application of Onsager's Reciprocal Relations to thermoelectric Thermomagnetic and Galvanomagnetic effects"
Physical Review vol 73 No 11 June 1 1948.

- 13) Voldes L.B. "The Physical Theory of Transistors"
McGraw Hill 1961.
- 14) Peterson L.C. "Equivalent Circuits of Linear Active 4
Terminal Networks"
Bell Sys. Tech. Jour. Vol 27 No 4 1948 P-593.
- 15) Webb E.L.R. "Equivalent Circuit for a Thermoelectric Converter"
RROC. I.R.E. Vol. 49, May 1961.

Among the many other sources consulted the following were found most useful but no particular reference to them was given in the text.

- 1) Alfonso N. &
Milnes A.G. "Transient response and ripple effects in thermo-
electric cooling"
Electrical Engineering Vol. 79 June 1960
- 2) Angello S.J. "Recent Progress in thermoelectricity"
Electrical Engineering Vol. 79 May 1960
- 3) Arai T.T. &
Madigan J.R. "Response of thermocouple circuits to non steady
currents"
J.A.P. Vol. 32 Apr 1961 #4.
- 4) Benedicts R.P. "Thermoelectric effects"
Electrical Manufacturing Vol. 65 #2 1960
- 5) Goldsmid H.J. &
Douglas R.W. "The use of semiconductors in thermoelectric
refrigeration"
Brit. J.A.P. Nov. 1954 p-386.
- 6) Giacolleto L.J. "Terminology and equations for linear active four
terminal networks including transistors"
RCA Review Vol. 14 #1 1953
- 7) Gray P.E. "The effect of source and sink thermal resistance
on thermoelectric performance"
Trans. AIEE Paper 60-18 Oct. 1959.

- 8) Groves G.M. "Properties of a thermoelectric cell"
J.A.P. Vol. 29 p-1611 Nov. 1958.
- 9) Hartsaw W.D. "The Peltier Effect"
Refrigerating Engineering, 31 Sept. 1958.
- 10) Heinicke J.B. "Thermoelectric Refrigeration"
Refrigerating Engineering, Feb. 1959.
- 11) Jaumat F.E. "Thermoelectric Effects"
Proc. IRE Vol. 46 #3 1958, p-538
- 12) Kaye J. & Welsh J.A. "Direct conversion of heat to electricity"
J. Wiley & Sons 1960.
- 13) Kittel C. "Introduction to solid-state physics"
J. Wiley & Sons 1956.
- 14) Lackey R.S. & Wright W.L. "Thermoelectric Refrigeration and its applications"
Electro-Technology Jan. 1961.
- 15) Rittner E.S. "On the theory of the Peltier heat pump"
JAP Vol 30 #5 1959.

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