AN ELECTRICAL ANALOGUE

OF THE BERNOULLI EFFECT

By

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PREFACE

Michael Faraday and others thought of electricity as a fluid. This thesis describes a series of experiments that apply this concept. Since the problem contains both electrical and chemical theory it has been necessary to try to clearly present necessary information relating to the two fields.

Due to lack of complete experimental data it is too early to draw complete conclusions. However, the experiment has indicated the path of the investigation is in the correct direction.

The author wishes to express his appreciation to Mr. Robert E. Fearon, his former department head, for suggesting the problem and for his assistance in the various phases of the work. Thanks are also due to Dr. H. L. Jones for his constructive criticisms in the writing of this paper.

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CHAPTER I

ELECTRICAL AND CHEMICAL THEORY

The problem of making suitable measurements arises in many fields of science. If there is any possibility of making improvements or in expanding the accuracy of the present systems, it is most useful to persons engaged in scientific work.

This thesis is developed along both theoretical and experimental lines, and is an attempt to develop a new method of measuring certain chemical properties of solutions. There is a lack of information dealing directly with this work and therefore, most of the findings represent original work.

Basically, this "Electrical Bernoulli Effect", with which this thesis is concerned, is dependent upon two very important relationships that exist in nature. These are:

    (a)   That positive and negative ions in solutions do not necessarily carry the same fraction of the total current flowing.

    (b)   That positive and negative ions are affected differently by an orifice or reduction in mass-section area.

The second statement will be treated extensively in this thesis. The first relationship is well known and is covered thoroughly in reference material.

Before attempting to derive the relationships necessary for the study of pertinent phenomena, a review of existing knowledge in the various related fields is necessary.

If a beaker is filled with a solution containing hydrochloric acid, HCl, there will exist an equal number of positive hydrogen ions, H^+, and chlorine ions, Cl^-. The positive ions are called cations and the negative ones are anions. The process by which molecules in solution are separated into electrically charged ions is called electrical dissociation, while the solvent in which it occurs is called an ionizing solvent. The amount of this dissociation is a function of various factors such as normality of the solution, temperature, type of solution and solvent as well as others which are not necessary to this study. Into this solution of HCl are inserted two platinum electrodes which are separated from each other. These in turn are connected to a source of electromotive force. As a result hydrogen gas will be liberated at the cathode. By determining the amount of hydrogen liberated for a given amount of current, it is possible to arrive at a conclusion known as the Faraday's laws of electrolysis.[1] These laws may be stated as:

(a) The mass of any substance liberated is proportional to the amount of current flowing and the time during which it flows.

(b) The masses of different substances liberated by a given current in a given time are proportional to the chemical equivalents or combining weights of a substance. The term combining weight would be the ratio of atomic weight to the volume of the element.

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[1] H. J. Creighton, Principles of Electrochemistry, Vol. I, 1943, p. 15.

As is well known the charge of an electron or univalent ion is the same. Therefore, the charge of the ions which are to be studied will be 1.59×10^{-19} coulombs per ion.

It is a known fact there is a great similarity between gases and liquids in so far as some of the studies of diffusion are concerned. For instance in the study of osmosis, which deals with diffusion through a semipermeable membrane or partial obstruction, there is a great similarity. As an example, the osmotic pressure of a mole of solute in 1000 grams of water is approximately that of a mole of gas confined in one liter at room temperature.[2] In fact with suitable substitutions, the relation between pressure, volume and temperature is correct for the osmotic properties of solutions as well as gases. That is

$$PV = mR^{1}T$$

where P = Osmotic Pressure

               V = Volume of Solution

               m = Moles of solute

               R^{1} = Constant

               T = Temperature (absolute)

This theory will be utilized in this study which follows.

Certain terms will be necessary for the development of the required equations. The first term needed will be the concentration of ions, C, and will be defined in terms of units of 6.06×10^{23} ions per 22,400 cubic centimeters. The 6.06×10^{23} term is called

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[2] E. B. Millard, Physical Chemistry for Colleges, (1931), p. 168.

Avogadro's number and is a statement of the number of molecules in a mole or in a mass of substance equal numerically to its molecular weight. The number 22,400 cubic centimeters is a quantity representing the volume occupied by a gram mole of a gaseous substance under standard conditions of temperature and pressure, that is at 0 degrees centigrade and one atmosphere of pressure.

The density, D, of a substance is defined as the ratio of weight, w, to volume, V, or $D = w/V$. Therefore, for the problem at hand this definition may be changed to better suit the present problem and will be

$$D = \frac{CM}{V} \tag{1-1}$$

where D is the density in grams per cubic centimeter, C is the concentration as defined previously, M is the mass in grams and V is the volume in cubic centimeters. The numerical values may be substituted in the equation (1-1) which becomes

$$D = \frac{CM}{2.24 \times 10^4} = 4.46 \times 10^{-5} \text{ CM grams per cubic centimeter} \tag{1-2}$$

To obtain the charge density, ρ , which is the number of charges per unit volume, it is necessary to replace the mass, M, in equation (1-2) with the quantity, e, which is the total ionic charge of 6.06×10^{23} ions. Such a unit is consistent with M, which is the mass of 6.06×10^{23} ions. The relation for charge density is

$$\rho = \frac{Ce}{2.24 \times 10^4} = 4.46 \times 10^{-5} \text{ Ce coulombs per cubic centimeter} \tag{1-3}$$

To carry on this derivation it is necessary to derive the relation between current and the ionic velocity relation so that it may be used in later equations. The equation of current flow is given by[3]

$$A = \rho v \qquad (1\text{-}4)$$

where A = current density, amperes per square centimeter

ρ = charge density, coulombs per cubic centimeter

v = velocity, centimeter per second

Rewriting equation (1-4) and substituting equation (1-3) for charge density, ρ, gives

$$v = \frac{A}{Ce\ 4.46 \times 10^{-5}} \text{ centimeter per second}$$

$$(1\text{-}5)$$

This is then a relation which indicates that the velocity of the ions is proportional to the current density and inversely proportional to the concentration of the ions.

To continue the derivation it is necessary to obtain the electrical equivalent of Bernoulli's Theorem as shown in Figure 1.
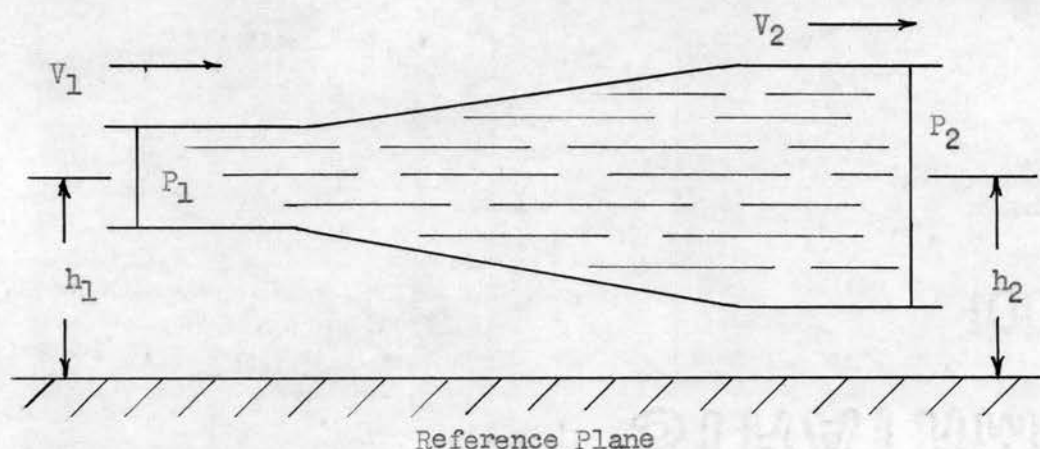

Reference Plane

Figure 1. Flow of Electrolyte through Restriction in Tube.

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[3]W. G. Dow, Fundamentals of Engineering Electronics, (1937), p. 97.

This theorem states the relation between energy levels as a fluid or electrolyte flows through a restriction or volume change. The equation of this relation is

$$P_1 + h_1 Dg_1 + 1/2\ DV_1{}^2 = P_2 + h_1 D_2 g_2 + 1/2\ DV_2{}^2$$

and if $h_1 = h_2$

$$P_1 - P_2 = 1/2\ DV_2{}^2 - DV_1{}^2$$

or $\quad P = 1/2\ D\ (V_2{}^2 - V_1{}^2)$ \hfill (1-6)

where P = pressure of liquid

h = height above reference plane

D = density of liquid (assume constant)

V = velocity of flow

The equation (1-6) is merely another way of stating the conservation of energy assuming no losses. Since the charge density, ρ , has been defined in equation (1-3) and velocity, V, defined in equation (1-5), a substitution may be made into equation (1-6) which then becomes

$$P = 1/2\ CMx4.46x10^{-5}\ \left(\frac{A}{Cex4.46x10^{-5}}\right)^2$$

$$= \frac{A^2\ M}{2\ Ce^2x4.46x10^{-5}} \qquad (1-7)$$

There may be a question regarding the substitution of the velocity equation (1-5) for the change in velocity relation in equation (1-6) however, the change in velocity will almost be the velocity at the restriction itself and therefore is a valid substitution although not entirely correct.

The work per unit volume associated with Δ P to transfer fluid ions in or out of the Δ P region is Δ P. This may be proven as follows:

$$\text{Work} = \text{Force x distance}$$

and $\quad$ Pressure $=$ Force /area

therefore, $\dfrac{\text{work}}{\text{area}} =$ Pressure x distance

or work/volume $= \Delta W = \Delta$ Pressure $\quad$ (1-8)

Also since the work done per unit charge is the definition of the volt, the following relation is true

$$E \text{ (volts)} = \frac{\text{work (joules)}}{\text{charge (coulombs)}} \qquad (1-9)$$

It would be helpful if this equation were defined differently so as to introduce the volume factor. It would then become

$$E \text{ (volts)} = \frac{\text{Work/volume}}{\text{charge/volume}} \qquad (1-10)$$

Therefore, equations (1-3) and (1-8) may be substituted and equation (1-10) becomes

$$E = \frac{\Delta P}{4.46 \times 10^{-5} \times Ce}$$

and from equation (1-7)

$$E = 1/2 \frac{A}{C^2 e^2} \times \frac{M}{e} \times \frac{1}{(4.46 \times 10^{-5})^3}$$

$$= 1/2 \left(\frac{A}{Ce}\right)^2 \times \frac{M}{e} \times \frac{1}{88.5 \times 10^{-15}} \times 10^{-7}$$

$$= 1/2 \left(\frac{A}{Ce}\right)^2 \times \frac{M}{e} \times 11.3 \times 10^{12} \times 10^{-7}$$

$$= 5.65 \times 10^5 \left(\frac{A}{Ce}\right)^2 \times \frac{M}{e} \text{ volts}$$

$$(1-11)$$

where $\quad$ M = mass of ions in grams

$\quad$ e = charge per 6.06×10^{23} ions in coulombs

$\quad$ A = amperes/sq. cm.

$\quad$ C = concentration in units of 6.06×10^{23} ions per 22.4 liters.

A study of the above relation yields some interesting relations. First the relation of M/e is often found in other physical problems except more commonly as e/M.

As a final check on this voltage equation it is important to see that the units are consistent throughout. One more definition is required to give a relation between mass and energy. This would be

$$\text{kinetic energy} = 1/2 \text{ Mass} \times (\text{velocity})^2$$

$$\text{or Mass} = 2 \times \frac{\text{kinetic energy}}{\text{velocity}}$$

where kinetic energy is in ergs and velocity is in cm/sec, therefore

$$\text{Mass} = 2 \frac{\text{ergs}}{(\text{cm/sec})^2} = \text{Constant} \times \text{ergs sec}^2 \text{cm}^{-2}$$

Rewriting equation (1-11) and omitting the constants yields

$$E = K' \times \left(\frac{A}{Ce}\right)^2 \times \frac{M}{e}$$

$$E = K' \frac{\text{coulombs} \times \text{sec}^{-2} \text{ cm}^{-4}}{\frac{\text{ions}^2}{(\text{cm}^3)^2}} \times \frac{\text{coulombs}^2}{\text{ions}^2} \times \frac{\text{mass}}{\text{coulombs}}$$

therefore

$$E = K' \frac{\text{ergs}}{\text{coulombs}}$$

Since $\frac{\text{ergs} \times 10^{-7}}{\text{coulombs}} = \frac{\text{joules}}{\text{coulombs}}$,

this relationship is recognized as the definition of the volt. Therefore the units are consistent throughout.

CHAPTER II

DESIGN AND CALCULATIONS

It is necessary to make some calculations before considerations of equipment design may be undertaken. Therefore in this chapter a study will be made of the chemistry and electrical theory that is involved.

In the study of ionized solutions it is necessary to know the amount of current carried by the positive and the negative ions. This term is known as the transference or transfer number and represents the fraction of the total current carried by each type of ion or the number of equivalents of each ion constituent transferred per faraday.[1] The faraday was defined in Chapter I. Since there exists both positive and negative ions in each electrolyte, it is to be expected there will be a transfer number for each ion. As was stated in the first chapter an important principle for the success of the experiment is that the anions and cations do not carry the same fraction of the total current per molecular weight. From data available in the various literature, transfer numbers for many electrolytes may be obtained. The requirements necessary are that the normality and temperature of the known solutions be available. The transference numbers are not greatly

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[1] E. B. Millard, Physical Chemistry for Colleges, (1931) p. 199

affected by temperature although there is some change. This is also true of concentration. Exact figures are available and will be used. The term "normality" is defined as "the number of equivalents of solute per liter of solution." This definition in turn requires clarification as to the meaning of equivalent weight. This is the weight in grams which will react with one gram atomic weight of a hydrogen ion. For instance the equivalent weight of hydrochloric acid is 1 mole; for sulfuric acid, 1/2 mole. From Table I, the transfer number for the positive ions of sodium chloride, NaCl, at 18° Centigrade and .01 normal solution is .396. The transfer number for the negative ion, Cl, will therefore be (1-.396) or .604.

TABLE I

Transfer Numbers of Cations at 18° Centigrade[2]

Electrolyte	.01 Normal
NaCl	.396
KCl	.496
LiCl	.332
HCl	.833
$AgNO_3$	.471

The transfer number for a positive ion, such as sodium, Na, is not the same in sodium chloride as it would be in a solution of sodium nitrate other conditions remaining the same. Therefore

[2] E. B. Millard, Physical Chemistry for Colleges, (1931), p. 201

each solution constitutes a new set of data and must be treated separately.

Another quantity requiring some explanation is the field strength in units of volts per centimeter of current path. Since the amount of current per sq. cm, A, is a function of the voltage applied to the circuit the quantity of volts per cm. is necessary for the calculations that follow. It does not make any theoretical difference how the field is produced. It will be done electromagnetically in this experiment.

Another quantity involved is the equivalent conductance in units of reciprocal ohms or $ohms^{-1}$. This is a term which defines a relation between electrical and chemical terminology. If Ohm's law is applied to conducting solutions or electrolytes it is necessary to introduce other definitions. As applied to solid conductors this law takes on the familiar form

$$I = E/R = E\lambda \qquad (2-1)$$

where I = amperes

R = ohm

$\lambda = ohms^{-1}$

The resistance, R, may be written in terms of the dimensions of the conductor, and the specific resistance, K, in ohms per centimeters. This is also the familiar

$$R = K \frac{length}{Area} \qquad (2-2)$$

where length is in centimeters

Area is in square centimeters.

The current will therefore be

$$I = \frac{E \times Area}{K \times length}$$

or $\frac{I}{Area} = A = \frac{E}{length} \times \lambda'$ (2-3)

where λ' is in $(ohm-cm)^{-1}$ and is the specific conductance or conductivity.

The required term is the equivalent conductance, and is available in the handbooks. It may be defined as the conductance which would be obtained between two parallel electrodes that are spaced one centimeter apart and having an area such that the volume of solution contains one mole or equivalent of solute between the plates.[3]

It follows that the specific conductance, λ' becomes

$$\lambda' = \frac{equivalent\ conductance}{\phi}$$
       (2-4)

where ϕ = the number of cubic centimeters which contain one equivalent of solute.

Therefore a .01 normal solution of hydrochloric acid which has an equivalent conductance of 369.3 at 18° C. would have a specific conductance of

$$\lambda' = \frac{369.3}{\frac{1000}{.01}} = .00369\ ohm^{-1} - cm^{-1}$$

Thus, there is enough information to derive the equation of the current per unit area or A.

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[3] H. J. Creighton, Principles of Electrochemistry, Vol. I, (1943), p. 68.

$$A \text{ in } \frac{\text{Amperes}}{\text{Sq. cm}} = \frac{\text{Normality}}{1000} \text{ x Equivalent Conductance}$$

$$\text{x Transfer Number x Field Strength}$$

$$(2\text{-}5)$$

A check of units shows

$$\frac{\text{Amperes}}{\text{Sq. cm}} = (\text{ohm} - \text{cm})^{-1} \text{ x Transfer Number x } \frac{\text{Volt}}{\text{cm}}$$

$$= \frac{\text{Volts}}{\text{ohms x cm}^2} = \frac{\text{Amperes}}{\text{Sq. cm}}$$

This follows because the transfer number is dimensionless.

For the positive ions or cations the equation (2-5) will become

$$A = \text{Specific Conductance x } \underset{(\text{positive})}{\text{Transfer Number}} \text{ x } \frac{\text{Field}}{\text{Strength}}$$

and for negative ions (cations)

$$A = \text{Specific Conductance x Field Strength x Transfer}$$

$$\text{numbers (negative)}$$

It is necessary to define the concentration, C, a little more in detail. In Chapter I this unit was defined in terms of 6.06×10^{23} ions per 22.4 liters of solution. Therefore if a .01 normal solution of univalent electrolyte is assumed, there would be .01 gram of hydrogen equivalent per liter of solution. However, in this particular case the definition was based on 22.4 liters instead of unity, and therefore, the concentration would be given as .01 x 22.4 or .224 $\frac{\text{grams}}{22.4 \text{ liter}}$.

This completes the information necessary for the solution of equation (1-11) for the voltage. From Table I, the transfer numbers

for LiCl at 18° C. are .332 for the cation and .668 for the anion. If the field strength is taken as 1000 volts per cm, the equivalent conductances are shown in Table II. For lithium chloride, LiCl, the value is 92 ohm^{-1} – cm^{-1}. The current per unit area

TABLE II
Equivalent Conductance of Aqueous
Solutions at 18° Centigrade[4]

Electrolyte	.01 Normal
NaCl	102
KCl	122.4
LiCl	92.0
HCl	368.1
Ag NO$_3$	107.8
HNO$_3$	365.0
KNO$_3$	118.1

for the positive ions will be

$$A = \frac{.01}{1000} \times 92 \times .332 \times 1000 = .306 \text{ amperes/sq cm}$$

$$E = 5.65 \times 10^5 \times \left(\frac{.306}{.224 \times 9.64 \times 10^4} \right)^2 \times \frac{3}{9.64 \times 10^4}$$

$$= 5.65 \times 10^5 \times (.0202) \times 10^{-8} \times .312 \times 10^{-4}$$

$$= .0356 \times 10^{-7} \text{ volts}$$

For the Cl ion the value of A will be

$$A = \frac{.01}{1000} \times 92 \times .668 \times 1000 = .615 \text{ amp/sq cm}$$

[4] E. B. Millard, *Physical Chemistry for Colleges* (1931), p. 192

$$E = 5.65 \times 10^5 x \left(\frac{.615}{.224 \times 9.64 \times 10^4} \right)^2 x \frac{35.5}{9.64 \times 10^{+4}}$$

$$= 5.65 \times 10^5 x .081 \times 10^{-8} \times 3.68 \, 10^{-4}$$

$$= 1.68 \times 10^{-7} \text{ volts}$$

The voltage difference between the ions will be

$$E_{difference} = E_+ - E_- = (.0356 - 1.68) \, 10^{-7}$$

$$= -1.64 \times 10^{-7} \text{ volts}$$

These calculations may be obtained in a similar manner for other electrolytes and the results obtained are shown in Table III.

TABLE III

Calculations of Voltage, $E_{Diff.}$, Due to Bernoulli Effect, 18° Centigrade.

Electrolyte	E, due to Cations	E, due to Anions	Difference, $E_{Diff.}$
LiCl	$.0356 \times 10^{-7}$ volts	1.68×10^{-7} volts	-1.64×10^{-7} volts
HCl	$.120 \times 10^{-7}$ volts	1.7×10^{-7} volts	$.05 \times 10^{-7}$ volts
NaCl	0.48×10^{-7} volts	1.55×10^{-7} volts	1.07×10^{-7} volts
$AgNO_3$	3.2×10^{-7} volts	2.42×10^{-7} volts	1.18×10^{-7} volts

It can be concluded from the preceding calculations that the measurements will be difficult to obtain. Therefore it is necessary that calculations should be made to determine the possible limitations that may be placed upon the ultimate level of measurement.

In the experimental procedure it is necessary to amplify the required signal to such an extent that thermal noise becomes an important factor. This thermal agitation occurs in the first amplifier stage and is due to the random motion of the free electrons in the associated conductors. As a result small potentials are produced across the terminals of the input tube. Although there are other noise types, that due to thermal agitation sets the limit to the smallest voltage that can be amplified without being lost in the noise background.[5] In actual amplifiers this factor may not be the largest of the noise sources, but does establish the lowest level of measurement.

The equation for the thermal agitation is expressed as[6]

$$E^2 = 4k \, TR \, (f_2 - f_1)$$

where k = Boltzmann's constant = 1.374×10^{-23} joule per degree Kelvin

T = absolute temperature, degrees Kelvin

R = resistance component of impedance where noise is generated

E = effective value of voltage lying between frequencies f_1 and f_2.

If an input resistance of 10000 ohms is assumed and a frequency band-width of 30 cps at room temperature, 300 degrees Kelvin, the resulting noise voltage will be

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[5] F. E. Terman, Radio Engineers Handbook, (1943) p. 477

[6] Ibid, p. 477

$$E^2 = 4 \times 1.374 \times 10^{-23} \times 300 \times 10000 \times 30$$

$$= 49.5 \times 10^{-16}$$

$$\text{or} \quad E = 7.05 \times 10^{-8} \text{ volts}$$

This noise level is below the calculated signal levels and should not limit or interfere with the measurements. A further reduction is theoretically possible by increasing the time for a given measurement.

The 10,000 ohm input resistance has been assumed because it is approximately the resistance of the solutions being used. Calculations will be based on an assumed solution of .01 normal hydrochloric acid which has an equivalent conduction of 369.3 ohms^{-1}. The specific conductance will then be .00369 ohm-cm^{-1} and the specific resistance will be

$$k = \frac{1}{.00369} = 271 \text{ ohm-cm}$$

If the cell containing the solution has a cross section area of 0.2 sq. cm. and a path length of 8.0 centimeters the resistance will be

$$R = 271 \times \frac{8}{.2}$$

$$= 10,840 \text{ ohms}$$

If it is found possible to increase the input resistance because of a better than expected signal to noise ratio, then there will result a subsequent decrease in loading effect upon the amplifier input circuit.

CHAPTER III

DESCRIPTION OF APPARATUS

It was necessary to design suitable apparatus for the special type of measurements proposed.

Two basic units of apparatus were required for the investigation. These consisted of the transmitting and receiving sections, which involve the following units:

A. Transmitting Section

    (a) Oscillator

    (b) Modulator

    (c) Power Supply

    (d) Measuring Cell

B. Receiving Section

    (e) Pick-up Electrodes

    (f) Pre-Amplifier

    (g) Oscilloscope

The complete assembly is shown in the block diagram of Figure 2.

The requirements for the apparatus were quite extensive and time consuming since very little of the equipment was immediately available. The determining factors in the design of the apparatus depended on the size of the coil and the electrolytic cell. These items will be given precedence in the following discussion in
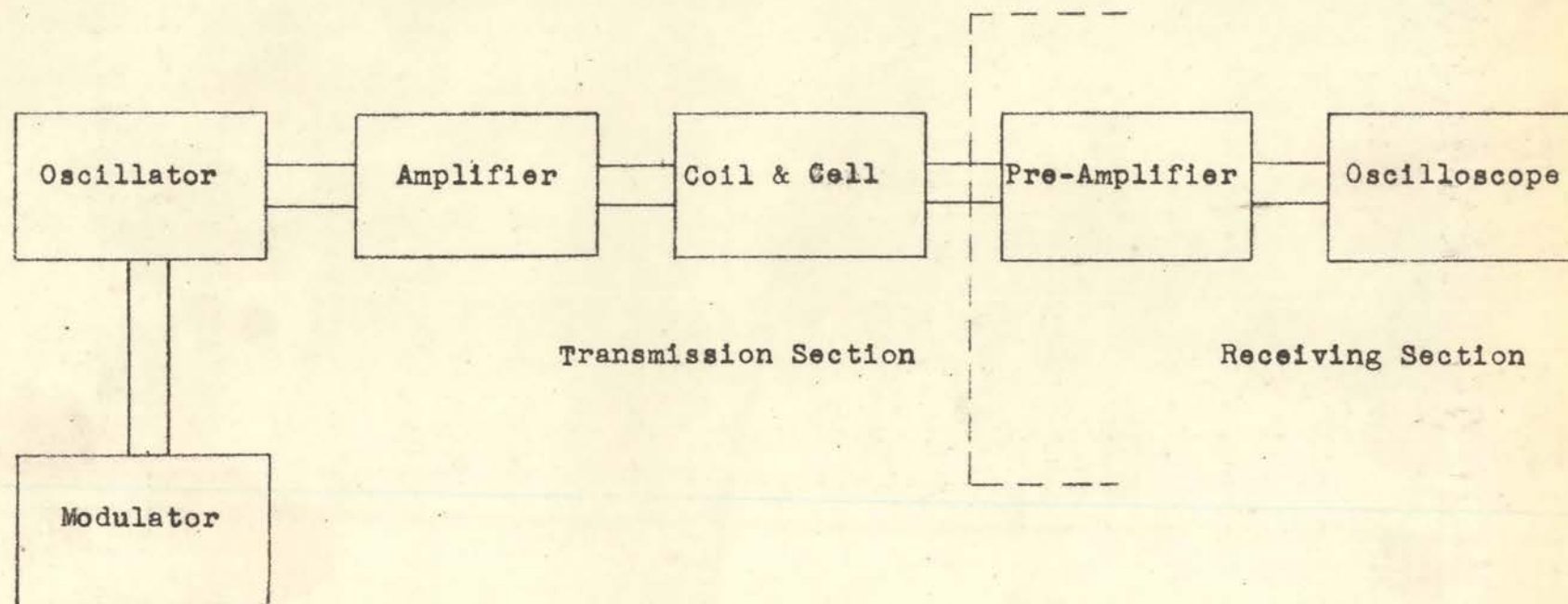
Figure 2. Block Diagram of Apparatus

order that a number of the important design factors may be determined. In order to keep the amplitude distortion of the cell as small as possible it was necessary to omit iron from the circuit between the coil and cell. This made it necessary to employ an air-core coupling. It was decided to base all design on a frequency of one megacycle per second. This happens to be a convenient frequency from the standpoint of design information and is easy to obtain.

The cell for the solution was made of polystyrene because of the excellent chemical resistance of that material to the various electrolytes that were to be used. A diameter of 2 inches was chosen because of the availability of tubing and rod material. Two electrolytic cells were built in order to provide a check for experimental accuracy. One of these was made with a built-in obstruction, whereas in the other this obstruction was omitted. This allowed for quick interchange of the cells so as to eliminate any question concerning the accuracy of the measurements that were obtained. The cell with the orifice is shown in Figure 3. It may be seen there is a slot parallel to the face of both cells. This was included because of the requirement of inserting a probe near the location of the obstruction.

The design of the coil was dependent upon the frequency selected and the diameter of the electrolytic cell. The Q of a single layer coil at radio frequencies depends upon several factors. In general, however, with a given inductance and coil diameter, the Q is a maximum when the ratio of length to diameter
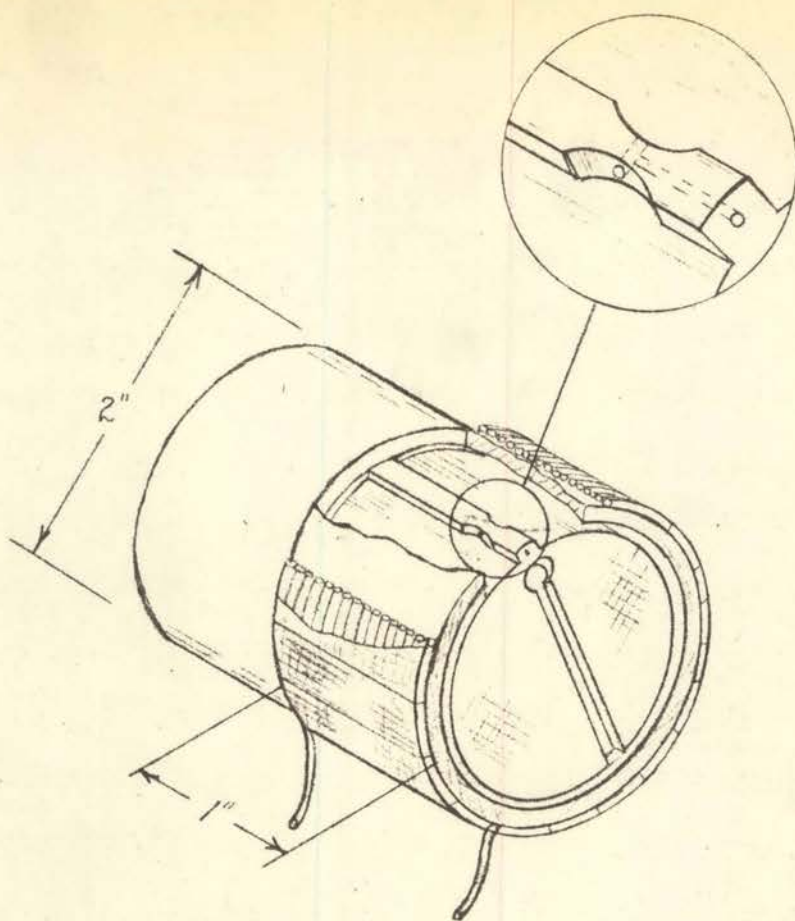
Figure 3. Illustration of Solution Cell and Coil

is of the order of 1/2 to 1. Furthermore with all factors fixed
except the size of the wire, the highest Q is obtained with a
wire size somewhat smaller than the largest that can be placed
in the available space. For a coil of 2 inches in diameter the
maximum length would be about 1 inch. By a cut and try process
a number 17 single Formvar wire was used for the required 14
turns. By the use of a radio frequency Q meter, it was found that
the coil had a Q of 155 at 1 megacycle per second. It also had
an inductance of 13.2×10^{-6} henries, a d-c resistance of .07
ohms and an a-c resistance of Rac = $\frac{WL}{Q}$ or .535 ohms. The capacity
required for tuning was found to be .00192 microfarads. The
inductance value was quite satisfactory because at the operating
frequency, the impedance of the input circuit matched the load
impedance of the vacuum tube. The coil shape may be seen in
Figure 3. The coil diameter was actually somewhat greater than 2
inches; however, it was made as close to this value as possible so
as to insure close coupling to the solution cell.

To obtain some idea of the magnitude of the induced voltage
in the cell it is necessary to make a few additional calculations.
Since the coil has 14 turns and the cell may be considered as a
one turn device, it is only necessary to determine the mutual coupling
that exists between the two elements. From these relationships the
voltage induced into the secondary may be calculated.

The mutual inductance between two single layer concentric
solenoids is given by Terman[1] as

$$M = .0501 \frac{a^2 n_1 n_2}{g} \left[1 + \frac{s^2 a^2}{8g^4} \left(3 - 4 \frac{l^2}{a^2} \right) \right] \text{microhenries} \quad (3\text{-}1)$$

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[1] F. E. Terman, Radio Engineers Handbook, 1943, p. 71.

This relation is correct if the outer coil is longer than the inner one. In this equation, the symbols have the significance shown in Figure 4. In this figure the outside coil represents the driving
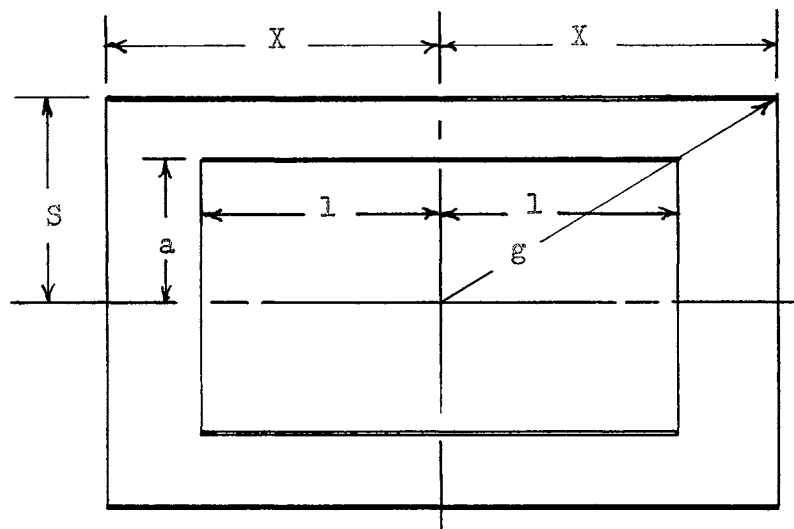

Figure 4. Coaxial Coils with Outer Coil the Longer coil while the inner coil consists of the solution cell with its electrolyte.

The cell and coil have the following dimensions.

$$x = .5 \text{ inch} \qquad a = .922 \text{ inch}$$

$$s = 1 \text{ inch} \qquad n_1 = 14 \text{ turns}$$

$$1 = .438 \text{ inch} \qquad n_2 = 1 \text{ turn}$$

and $\quad g = \sqrt{1^2 + .5^2} = 1.125$

from equation (3-1)

$$M = \frac{.0501 x .922^2 x 14 x 1}{1.125} \left[1 + \frac{1^2 x .922^2}{8 x 1.125^4} \left(3-4 \frac{.438^2}{.922^2} \right) \right]$$

$$= .53 \left[1 + .0668 (3 - .903) \right] = .53 (1 + .14) = .605 \text{ mh}$$

This relation is subject to considerable error especially at radio

frequencies. However, it does give a starting point for the calculations which follow. It should be noted that the low value for the mutual inductance made it necessary to change a frequency that was correspondingly high. One megacycle was selected as about optimum.

The problem of inductively coupled circuits has been treated in detail by Terman[2] and will be used in the following calculations. There is one simplification made which will not effect the accuracy of the work, but does cut down on the amount of labor involved in the calculations. This, is the fact that self-inductance of the single turn coil, represented by the electrolytic cell, is very low and may be neglected.

The fundamental circuit is shown in Figure 5. A primary voltage of $-\mu\, e_g$ is shown, where μ and e_g represent respectively the amplification factor and grid voltage of the vacuum tube. The resistance R_p is the plate resistance of the tube; C_p is the capacity required to tune the coil and is $.00192\ \mu$ f; L_p is the inductance of the coil and is 13.2×10^{-6} henries; M is the mutual inductance previously calculated to be $.605$ microhenries; L_s is the secondary or cell inductance which is to be neglected and r_s is the cells resistance of the electrolytic cell, and is approximately 10,000 ohms. As previously stated this value varies with the solution employed and therefore only represents one particular case.

A 6V6 type vacuum tube is satisfactory because it has sufficient driving power and a relatively low plate resistance. The plate

[2] F. E. Terman, Radio Engineers Handbook, 1943, pp. 148-150.
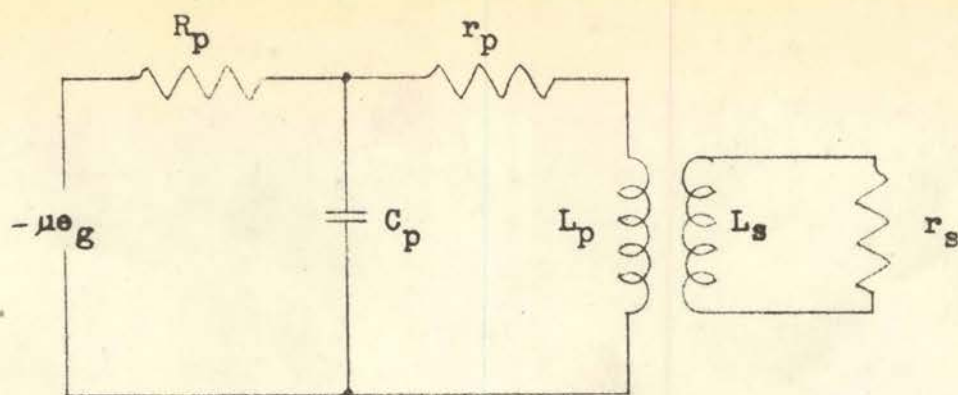
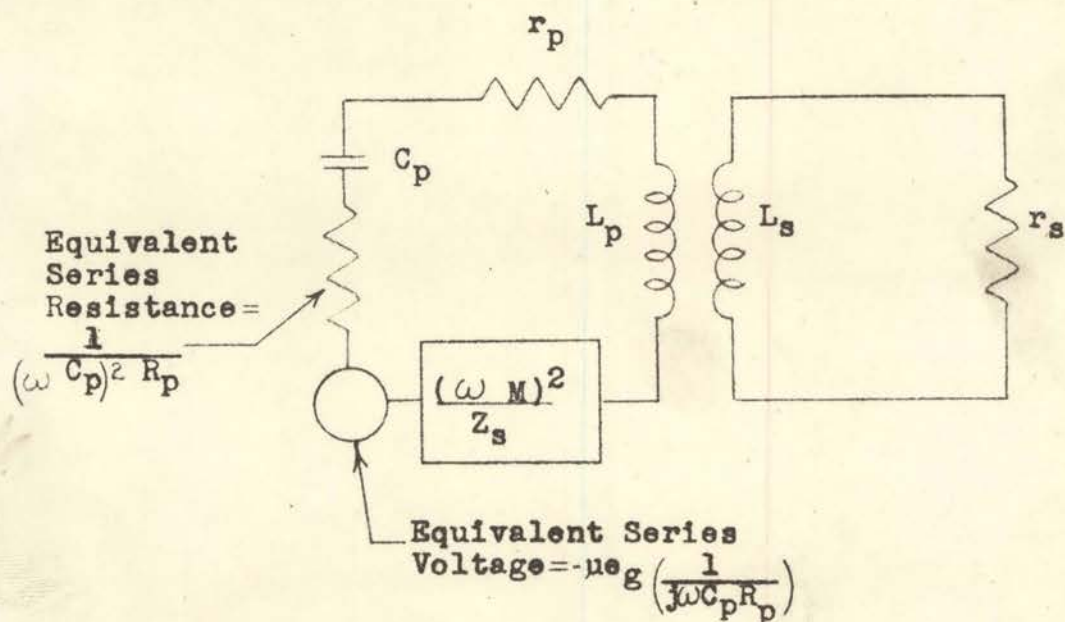Figure 5. Equivalent Circuit for Coil Coupled
to Solution Cell.

Figure 6. Simplified Circuit Showing Reduction
Of Parallel Tuned Circuit to a Series
Arrangement.

resistance if 50,000 ohms, the transconductance, G_m , is 4000 micromhos and the required driving voltage is only 10 volts r.m.s.

The circuit shown in Figure 5 may be simplified by the use of Thevenin's theorem to a simple series arrangement[3] as shown in Figure 6. All symbols have been previously defined. The only qualification to be made is that the resistance of the vacuum tube is much greater than $1/WC_p$. The equivalent series resistance will be

$$\text{Eq. Res} = \frac{\frac{1}{(WC_p)^2}}{R_p} = \frac{\frac{1}{(2\pi 10^6 \times .00192 \times 10^{-6})^2}}{50,000}$$

$$= \frac{\frac{1}{142 \times 10^{-6}}}{50,000} = \frac{1}{7.1} = .141 \text{ ohm}$$

(3-2)

The equivalent series voltage will be

$$\text{Eq. Voltage} = \frac{E \; 1/jWC_p}{R} = \frac{10 \times 50,000 \times 4000 \; 10^{-6} \; 1}{\frac{j \; 2\pi 10^6 \times .00192 \times 10^{-6}}{50,000}}$$

$$= \frac{40000 \times 10^{-6}}{j \cdot 0121} = -j \; 3.31 \text{ volts}$$

(3-3)

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[3]F. E. Terman, Radio Engineers Handbook, 1943, p. 162.

Since the effect of the secondary current is to couple an
impedance into the primary, this quantity will need to be cal-
culated. The coupled impedance will be

$$\frac{\overline{\omega M}^2}{Z_s} = \frac{2\pi \times 10^6 \times .605 \times 10^{-6}}{10,000} = 14.4 \times 10^{-4} \text{ ohms}$$

This value is small compared to the other quantities and therefore
may be neglected. The current that will flow in the primary
circuit will therefore be

$$I_p = \frac{\text{Equivalent Series Voltage}}{\text{Total Series Impedance}}$$

$$= \frac{3.31}{.141 + .535 + j\,(2 \times \pi 10^6 \times 13 \times 10^{-6} - \frac{10^6}{2\pi 10^6} \times .00192)}$$

$$= \frac{3.31}{.676} = 4.9 \text{ amperes}$$

The voltage induced in the secondary is therefore

$$E_s = -j\omega M I_p$$

$$= -j\,2\pi 10^6 \times .605 \times 4.9 \times 10^{-6}$$

$$= -j\,18.7 \text{ volts}$$

Since the cell has an equivalent length of path that is approximately
1.844 inches or 5.8 inches, then the field strength in volts per
cm is $\frac{18.7}{5.8 \times 2.54}$ or 1.22 volts/cm.

From this calculation the question may be raised as to the
reason for the earlier assumption that set the field strength at
1000 volts per cm. The answer to this question is rather complex
and involves potential theory. Without becoming too involved it
may be said that the potential drop will be almost entirely across

the obstruction or orifice in the cell. In other words this cell may be thought of as a conductor in series with a large resistance. Consequently any voltage that appears in the circuit would consist almost entirely of the drop across the resistance. Since the polystyrene restrictor is only about .026 centimeters in path length, the peak field strength could be

$$\frac{18.7 \times 1.414}{.026} = 1000 \text{ volts/cm.}$$

The process of designing and constructing the oscillator was a relatively simple matter. A Hartley circuit was used because of its simplicity and relatively good frequency stability. A crystal controlled oscillator could have been used if additional frequency stability had been required. As shown in Figure 7, the coil, L, was wound on a 1-1/4 inch bakelite form. The cathode tap was located 14 turns from the ground connection. There was a total of 100 turns of #24 Formvar wire on the coil. The rest of the circuit was conventional except for perhaps the choice of circuit values in the plate section. The oscillator had more output than required and so there was some deliberate attenuation introduced to eliminate any tendency to over-drive the final stage.

The type of the measurement involved is quite critical. From equation (1-11) it can be seen that the measured voltage varies as the square of the current per sq. cm. Therefore if a modulated voltage is induced into the cell, the non-linear relation between voltage and current should produce a demodulation term. More specifically it follows that if the one megacycle per second
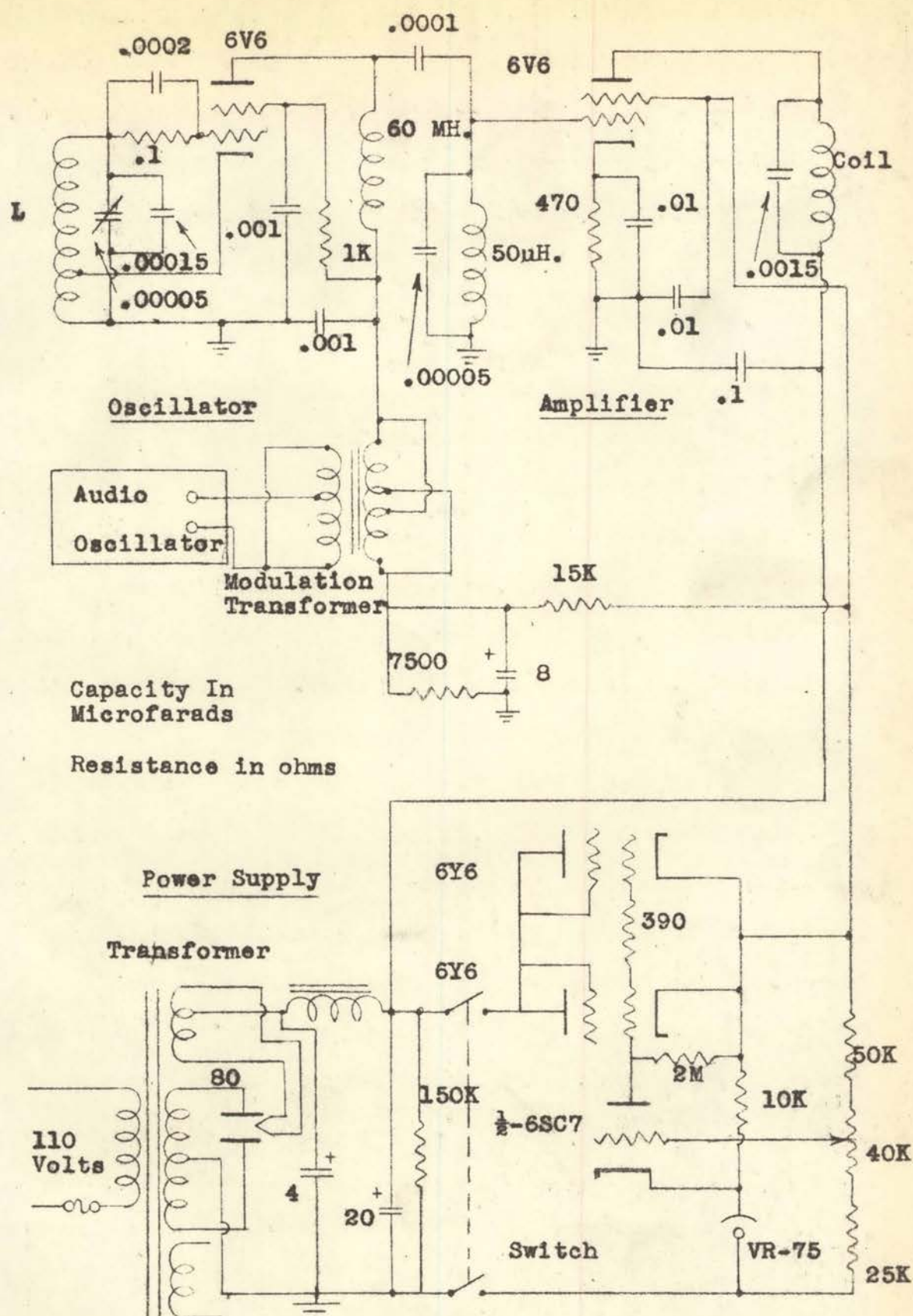
Figure 7. Schematic of Transmitting Section.

frequency is amplitude modulated by a one kilocycle per sec. voltage, and introduced into a non-linear circuit, the 1 kilocycle per sec. frequency will appear as one of the products of modulation.

If the equation for the simple amplitude modulation as written[4]

$$i = I_m (1 + m \sin 2\pi f_s t) \cos 2\pi ft,$$
(3-3)

expansion will result in

$$i = I_o \sin 2\pi ft + \frac{mE_o}{2} \cos 2\pi (f-f_s) t$$

$$- \frac{mE_o}{2} \cos 2\pi f (f + f_s) t$$
(3-4)

where i = instantaneous current

m = modulation factor

f = frequency of carrier

f_s = modulation frequency

I_o = average amplitude of the wave

If the equation of (1-11) is written as

$$E \text{ varies } (A)^2$$
(3-5)

and equation (3-4) is substituted in this relation, and squared, there will be produced many new frequencies. One kilocycle per second will be one of the frequencies obtained. Actually there are some other frequencies such as 2 kilocycles per sec.

From the preceding discussion it follows that it is necessary to either modulate the oscillator stage or a buffer stage. Since

[4]W. L. Everitt, Communication Engineering, (1937), p. 382

the operation of the circuits involved, except the oscillator, were operated Class A it was decided to plate and screen modulate the oscillator itself. The only objection to this procedure is that a frequency modulation term is produced.[5] However, there is not a great deal of objection to this. The choice of plate and screen grid modulation rather than some other means was due to the excellent response of this system.

The circuit is shown in shown in Figure 7. It may be seen that the modulating voltage is applied to both plate and screen grid. This is necessary because of the shielding action of grid number 2 of the 6V6. A study of the figure shows the audio frequency voltage of one kilocycle per second has been coupled into the radio frequency oscillator by means of a modulation transformer. This transformer serves the dual purpose of matching the circuits properly and keeping the direct current of the 6V6 out of the output of the audio oscillator. In order to obtain maximum useful signal it was necessary to modulate at one hundred percent. This required that the audio oscillator have sufficient voltage to drive the plate and screen combination from approximately zero to twice the value of the plate and screen supply voltage. This circuit produced a carrier with a value of 12 volts r.m.s. which was modulated 100% by the one kilocycle signal.

The final amplifier stage that drives the coil was operated Class A so as to insure low distortion in the plate circuit. The 6V6 tube, as previously stated, was utilized in this stage because

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[5]F. E. Terman, Radio Engineers Handbook, (1943), p. 550

of its ability to handle a relatively large driving voltage as
well as for a favorable value of its transconductance.

The voltage across the output coil was found to be 140 r.m.s.
volts at one megacycle per sec.

The receiving section is not particularly complicated
except for the arrangement of the pickup electrodes. These
electrodes consist of #32 platinum wire immersed in the electro-
lytic solution at two sets of points. These positions are at
the largest and the smallest potential points in the solution.
These points are located respectively at the orifice and at a
location diametrically opposite to this point. The wires are
brought out in parallel and across the top of the cell so as to
nullify any possible induced current. Platinum was chosen because
of its relative inertness to corrosion by the various electrolytes
that were used. Other materials could have served the purpose
but for the possibility of deterioration during the experiment.

The electrodes were connected to a pre-amplifier through
an input transformer. The amplifier, which is conventional in
its design is shown in Figure 8. A 1000 cycle per second tuned
band-pass filter has been placed in the grid circuit of the final
stage to reject the harmonics and to narrow the overall frequency
response. This resulted in a better signal to noise ratio. The
circuit, exclusive of the transformer, has a gain of approximately
95 decibels. There is about 9.5 decibel additional gain from
the transformer. This results in a total gain of approximately
105 decibels overall. At 2000 cycle per second and at 500 cycles
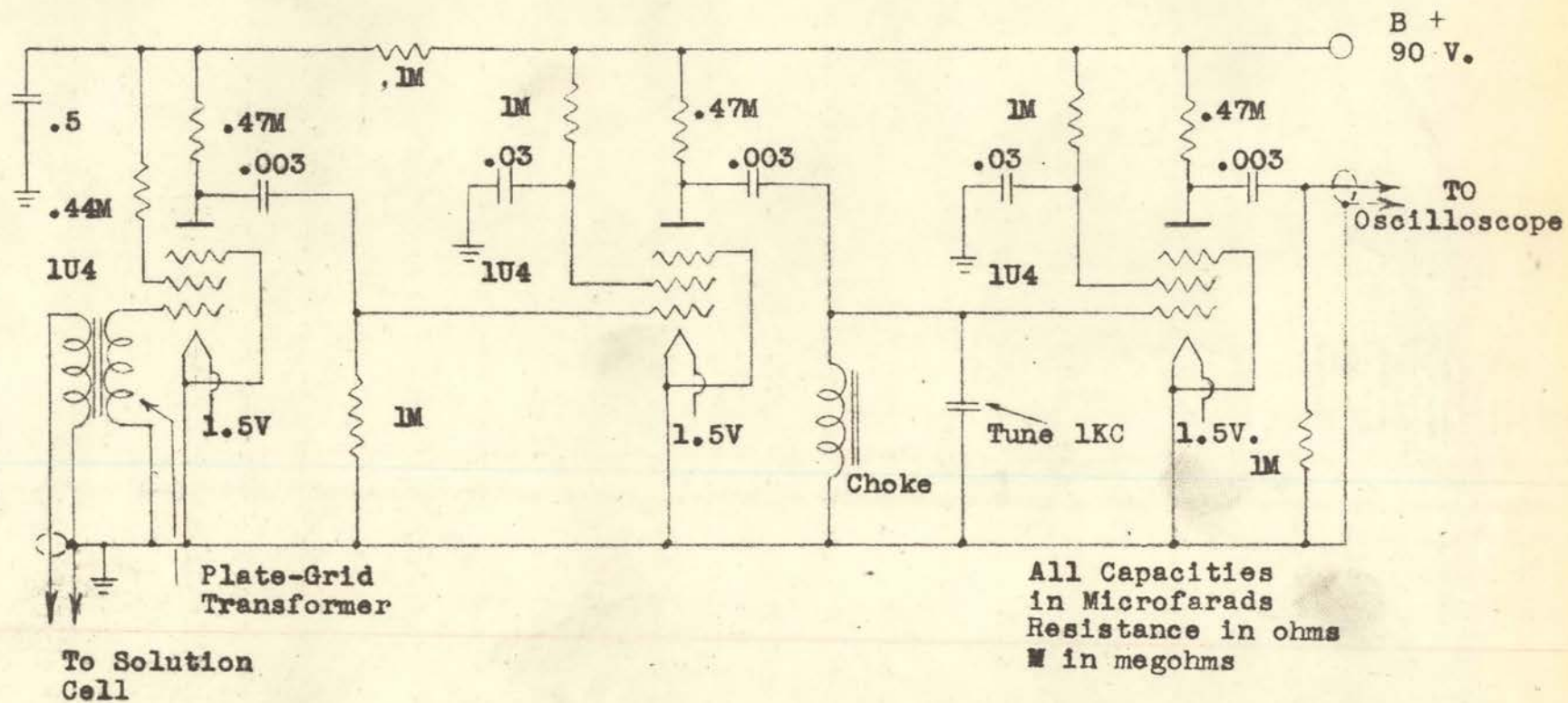per second the gain of the amplifier is down approximately 20

Figure 8. Schematic of Receiving Section

decibels. When this amplifier was used in conjunction with the oscilloscope there was more than enough gain to observe the smallest available signals. The oscilloscope has a maximum vertical sensitivity of 30 millivolts per inch, peak to peak. This results in a gain ratio on the 3 volt scale of

$$\frac{3}{.03} = 100 \text{ to } 1$$

which is equivalent to 40 decibels.

CHAPTER IV

RESULTS AND CONCLUSIONS

A preliminary check was made of the apparatus before any actual measurements were attempted. This check consisted of the adjustment of the radio frequency oscillator to the one megacycle per second frequency and the tuning of the output coil for maximum output. In order to observe any spurious signals the probes were inserted into the empty cell and the results observed visually on the oscilloscope. The observed spurious signals were eliminated by additional shielding.

In this experiment two parameters were investigated, one being the kind of electrolyte employed, the other the concentration or strength of electrolyte. Acids and alkalies were not employed because of their corrosive properties.

The first tests were made using an 0.1 normal solution of sodium chloride. This salt was readily available in pure form and was satisfactory for the purpose. In order to determine the nature of the second order effect, the demodulated output voltage was measured for an increasing series of values of the input voltage. The results were consistent for values of output voltage that were above the thermal noise level of the amplifier of the receiver. The results are shown in Table IV for a 0.1 normal solution of sodium chloride.

TABLE IV

Second Order Effect for 0.1 Normal Solution, NaCl

Input Voltage (Volts)	Output Voltage (Microvolts)
23.4	3.5
27.6	4.2
29.9	5.3
36.1	6.0
44.6	8.9
49.0	10.1

Two additional sets of data were obtained for 0.25 and 0.50 normal solutions. The results of these runs are set forth in Table V and Table VI respectively.

TABLE V

Second Order Effect for 0.25 Normal Solution, NaCl

Input Voltage (Volts)	Output Voltage (Microvolts)
19.1	3.5
23.4	4.2
25.4	4.6
27.6	4.6
31.8	5.9
38.2	7.1
44.5	8.7

TABLE VI

Second Order Effect for 0.5 Normal Solution, NaCl

Input Voltage (Volts)	Output Voltage (Microvolts)
20.2	3.0
23.4	4.2
29.8	5.3
36.2	6.5
38.3	7.1
42.5	7.8

The data from these tables are shown in graphical form in Figure 9. These curves indicate that a change in the strength of the solution does not effect the voltage of the orifice. The reason for this is that an increase or decrease in solution strength only serves to change the current density and the concentration of the ions. Consequently the two effects cancel each other since they are equal and opposite.

Tests were also made for 0.1 and 0.2 normal solutions of sodium bromide. The results for these are shown in Table VII and Table VIII respectively.
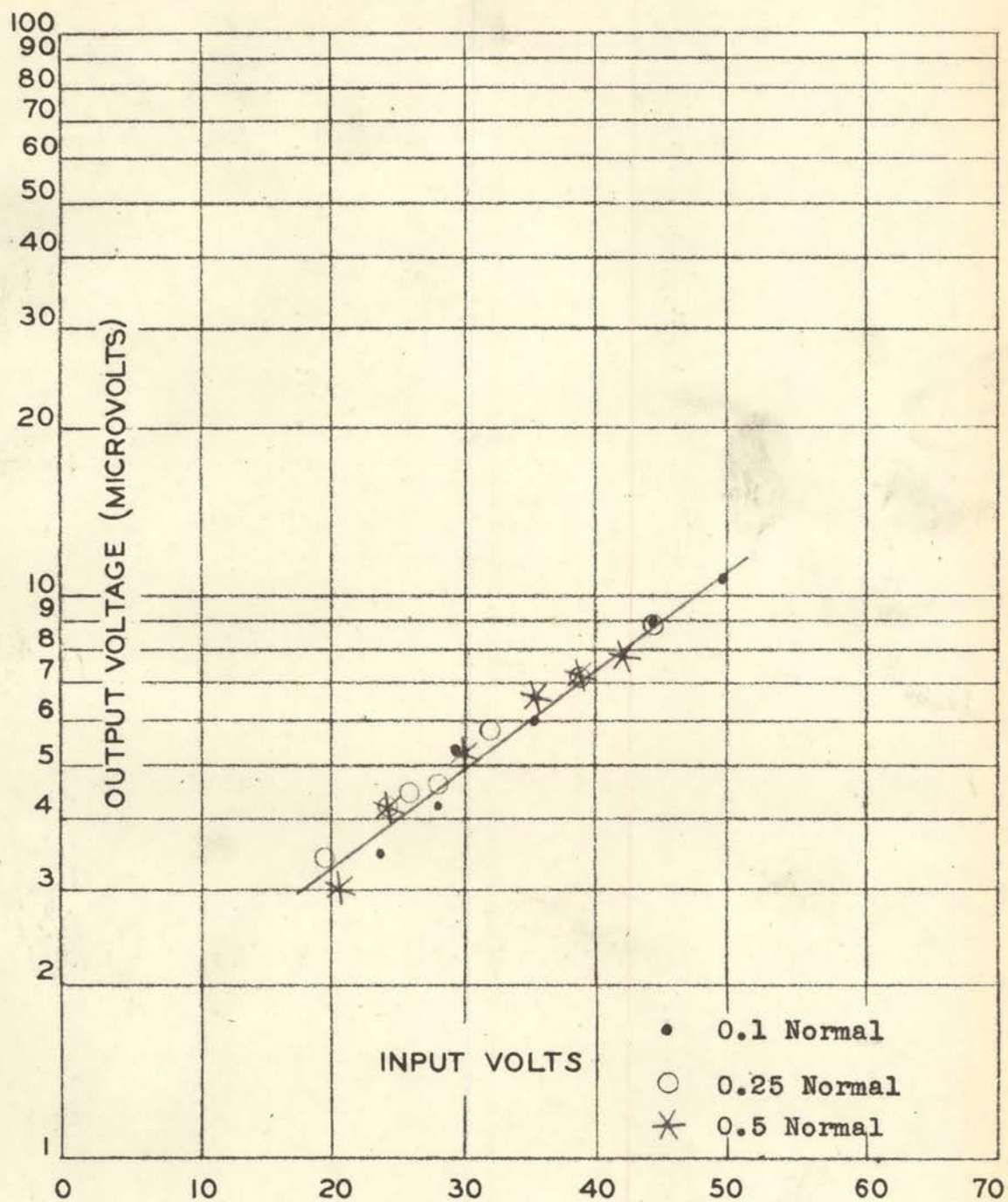
Figure 9. Second Order Effect for Sodium Chloride.

TABLE VII

Second Order Effect for 0.1 Normal Solution, NaBr

Input Voltage (Volts)	Output Voltage (Microvolts)
19.1	4.2
23.4	5.3
27.6	7.1
32.9	8.3
38.2	9.2
70	41.0

TABLE VIII

Second Order Effect for 0.2 Normal Solution, NaBr.

Input Voltage (Volts)	Output Voltage (Microvolts)
21.2	5.3
25.5	5.9
29.7	6.5
34	8.3
42.5	10.6
53.2	18.9
69	35.4

These results are shown graphically in Figure 10. It will be noted that there is a very close agreement between the two sets of data as would be expected.
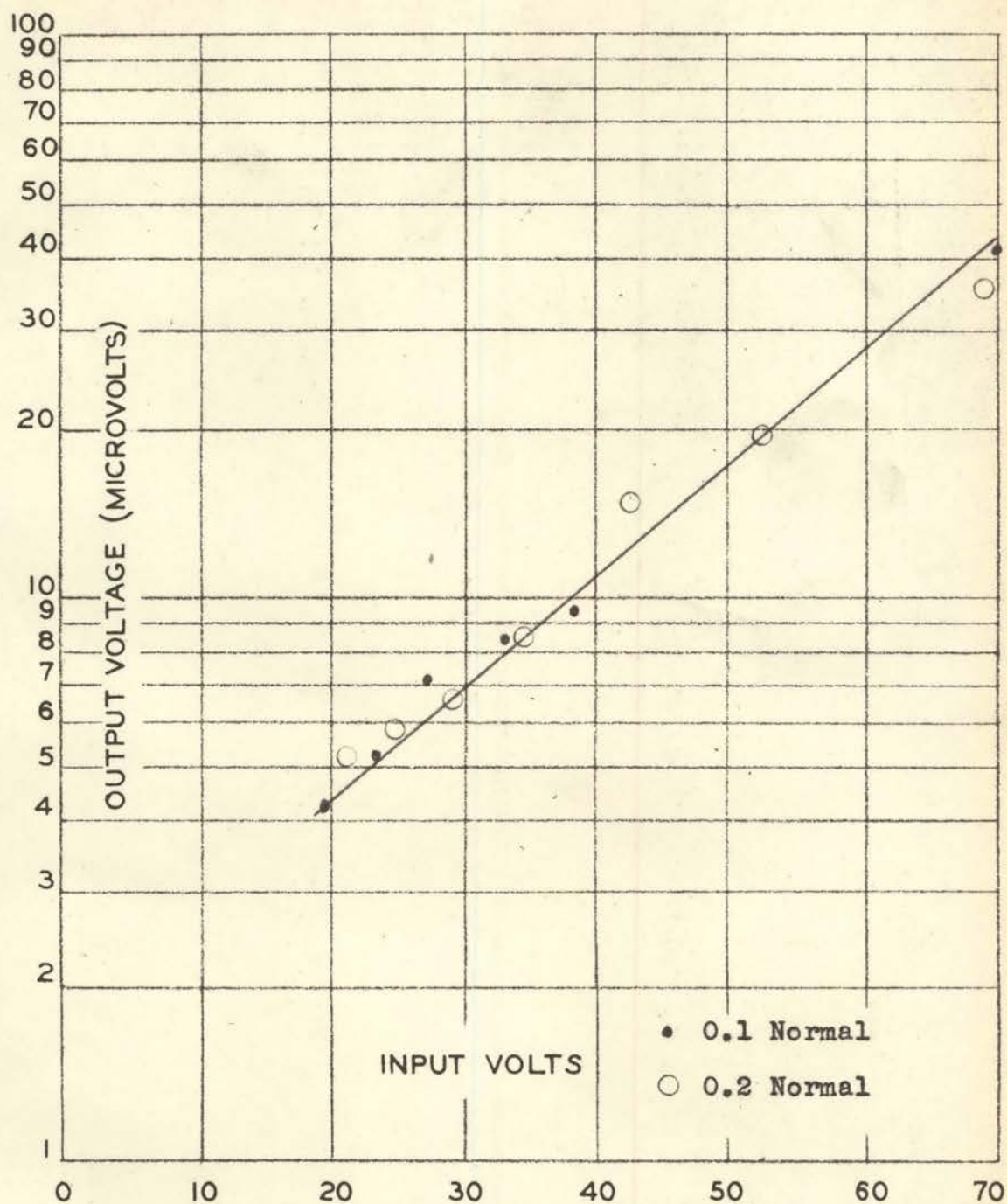
Figure 10. Second Order Effect for Sodium Bromide.

Potassium chloride was selected as the third electrolyte to be tested. In this case solutions of 0.1 and 0.2 normal were employed. The results of these measurements are shown in Table IX and Table X respectively.

TABLE IX

Second Order Effect for 0.1 Normal Solution, KCl

Input Voltage (Volts)	Output Voltage (Microvolts)
17	4.8
25.4	7.1
36.2	11.8
51	29.6
68	47.5

TABLE X

Second Order Effect for 0.2 Normal Solution, KCl

Input Voltage (Volts)	Output Voltage (Microvolts)
19.1	4.2
21.2	5.3
31.8	8.3
42.5	13.6
55.3	29.6
66.0	41.5

The data from these tables are shown graphically in Figure 11. The results are very similar.
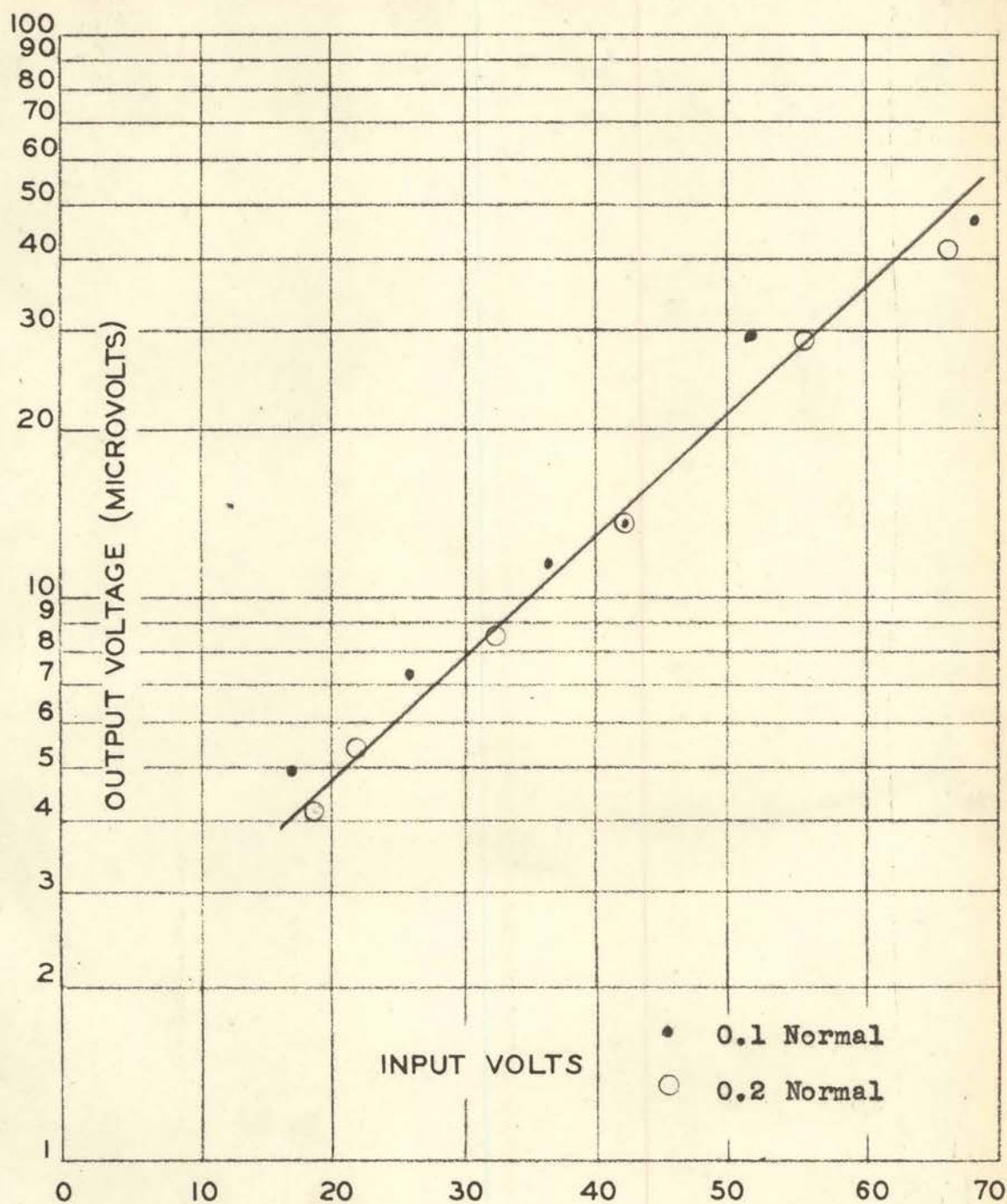
Figure 11.   Second Order Effect for Potassium Chloride.

The data for the 0.1 normal solutions of sodium chloride, sodium bromide, and potassium chloride are shown in Figure 12. The curves for sodium bromide and potassium chloride are almost the same. This indicates that the two substances have nearly identical properties.

These results substantiate the theory that postulates the existence of the second order voltage.

For all types and concentration of solutions that have been investigated, it was found that the output voltage was directly proportional to the square of the applied voltage. It should be noted that the results obtained in this investigation represent a new discovery. It is suggested that effect might be called the "Fearon Effect", after R. E. Fearon who conceived the original idea and predicated the experimental arrangements.
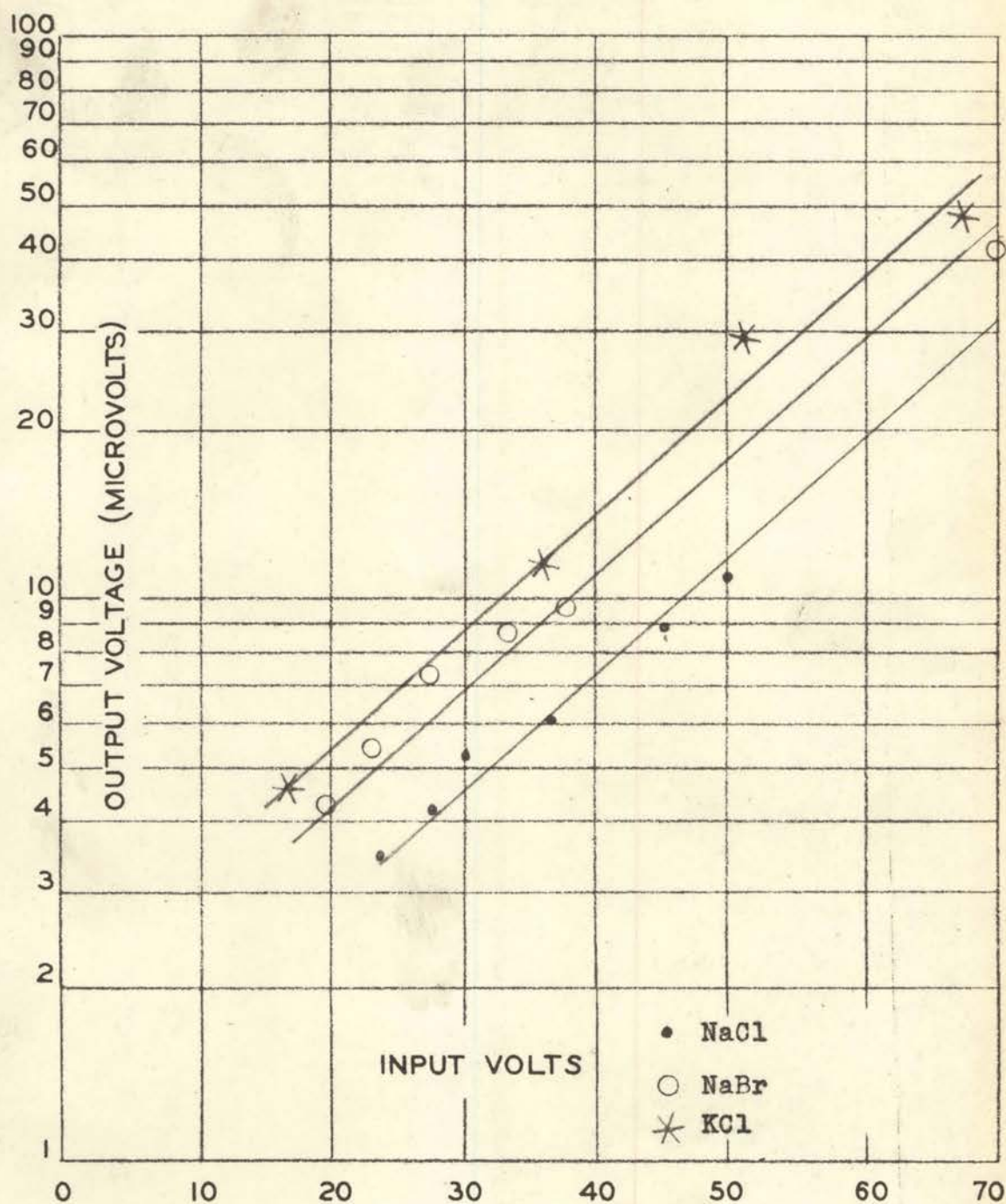
Figure 12.   Second Order Effect for 0.1 Normal Solution

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