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NATIONAL RESEARCH COUNCIL OF CANADA

ELECTRICAL ENGINEERING AND RADIO BRANCH

PRELIMINARY REPORT

ON

A PULSED MILLIVOLTMETER USED IN pH MEASUREMENT AND CONTROL

OTTAWA

AUGUST, 1946

maD

PRB-151

National Research Council of Canada
Electrical Engineering and Radio Branch

PRELIMINARY REPORT
ON
A PULSED MILLIVOLTMETER USED IN
pH MEASUREMENT AND CONTROL

by

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Officer-in-charge

Introductory pages - 2
Numbered pages - 12
Drawings - 4
Charts - 6

CONTENTS

NATIONAL RESEARCH COUNCIL OF CANADA

ELECTRICAL ENGINEERING AND RADIO BRANCH PRB-151

A PULSED MILLIVOLTMETER USED IN pH MEASUREMENT AND CONTROL
(Preliminary Report)

I. INTRODUCTION

The instrument described is, in effect, a portable high-input-impedance millivoltmeter with provision for controlling or correcting errors in the voltage being measured, provided such control can be effected by the operation of relays.

The specific purpose for which the instrument was developed is to measure and control the pH (Hydrogen-ion concentration) of a solution, using glass and calomel electrodes as the means of converting pH values to d.c. potentials, and using solenoid-operated valves to control the flow of acid or alkaline compensating solutions.

The inherent delay in the device permits it to follow, without undue "hunting", the relatively slow rates of pH variation produced by bacteriological fermentations, such as those yielding the polyhydric alcohols. The more rapid rates met in inorganic reactions could only be followed by reducing the time constant to a considerable extent.

II. PRINCIPLES INVOLVED

The instrument is essentially a null-point device; that is, it measures an unknown d.c. potential by comparing it with a known, controllable reference potential. When this controlled potential is made equal to the unknown potential, a null is indicated, the system is in balance and the measurement is achieved.

The method of observing the null (or equality of the two d.c. potentials) is to "chop" the difference potential, not in the familiar square-wave manner, but into pulses of relatively short duration compared to the recurrence period. Since the reference line or base line for these pulses is the controllable reference potential, the pulses will be positive-going or negative-going depending upon whether the unknown potential is more positive or more negative than the reference potential. Graphs in Chart 1 illustrate this principle. No pulses are produced when the two potentials are equal, and the system is said to be in balance.

The fact that the pulses have "sense" as well as amplitude, gives the system its control feature and enables it to distinguish between a solution which is too acid and a solution which is too alkaline.

III. USE OF THE INSTRUMENT IN THE LABORATORY

1. - For pH Measurement

The following steps should be observed in making a pH measurement:

1. Connect the glass and calomel electrodes to Plug 5 of the Amplifier Unit and, after flushing the calomel electrode slightly, place the electrode assembly in the solution to be measured. Turn the Power Switch (located on the Power Supply Unit) to "on" and the Coarse and Fine Millivolt Selector Knobs (on the Control Panel Unit) to "zero".

2. Wait a period of 3 minutes for the time delay to take effect. At the end of this time the Delay Relay will be heard to click.

3. Wait a further period of 1 minute for the Output Milliammeter (located behind a window on the Amplifier Unit) to settle down. This will, in general, show either a very low current, possibly zero, or a rather high current between 8 and 10 ma.

4. If the output current indication is low, turn the "+ Voltage -" knob to the negative side (-) and increase the Coarse Millivolt Selector one step at a time, observing the effect on the output current. The process should not be hurried as the time constant of the instrument is long and considerable time is required for the system to "settle" after each voltage change. When the coarse adjustment shows the effect of increasing the current, operate the Fine Millivolt Selector until the needle reads 3.8 milliamperes (halfway between the two red lines on the meter dial). Again, attempting to rush the balance merely produces overshooting and complicates the operation unduly.

Note:- If the output current indication had been higher than 3.8 ma. to start, the "+ voltage -" knob should have been turned to the positive side (+) and the same procedure carried out.

5. Before recording the final coarse and fine millivolt settings, check that the monitor meter (located on the Control Panel Unit) reads exactly full scale, that is, 100 microamperes. If it does not, adjust this current by means of one of the "Voltage Set" knobs in the lower corners of this panel.

6. Record the coarse and fine millivolt settings and add the two figures together. Consult a pH Conversion Chart (e.g. Chart 5) to obtain the pH of the solution.

7. To ensure the steadiest readings, the solution should be kept stirred constantly. Either a stirring-rod operated by an electric motor or a magnetic stirrer can be used without affecting either accuracy or stability of the system.

8. Note that the green and red pilot lights (on the Control Panel Unit) are both extinguished when the balance condition is reached. For rough determinations, the balance point can be approximately reached simply by adjusting the millivolt selectors until both lights are extinguished, but for exactness, the amplifier output meter should be watched, as described above. The two red lines indicate approximately the points where one or other of the pilot lights comes on, and represents a tolerance of about ±4 millivolts or ± 0.08 pH. When the 3.8 ma. reading on the meter is used as the balance point, the tolerance to be expected is about ± 1 millivolt or ±0.02 pH, which is the limit of sensitivity of this unit.

2. For pH Control

A: Without the Aid of Buffer Solutions:

If the pH Conversion Chart for the particular set of electrodes is available (Chart 5 is only typical, and is not to be taken as applicable to every set of electrodes), the proper polarity (" + Voltage -"knob) may be set in and the proper millivolt settings on the coarse and fine selector knobs may be made immediately for the particular pH level desired. Then, after waiting for the system to settle down, the pilot lights will indicate whether the solution is too acid (pH too low) or too alkaline (pH too high). Solenoid-operated valves controlling acid or alkali or both, if properly connected to the output terminals of the Relay Unit, will then cause the correct compensating solution to flow into the bath until the pH is brought to the desired level, that which causes the system to balance, extinguishing the pilot lights and shutting off the valves. Any variation in the bath after this will result in unbalancing the system, lighting one or other of the pilot lights, turning on one or other of the solenoid valves and correcting the variation.

B: With the Aid of Buffer Solutions:

If the pH Conversion Chart is not available for the set of electrodes being used, it is advisable to prepare a test solution by means of buffer tablets for the particular pH level desired.

The system can then be balanced with the electrodes in this test solution (see I - For pH Measurement). Once the balance condition is determined, the settings for polarity (+ or -) and coarse and fine millivolt knobs should not be altered, and the electrodes should be transferred to the bath which is to be controlled. The solenoid valves, operating under the control of the system, will then bring the pH of the bath to the same level as that of the test solution.

It should be emphasized that, due to the long time-constant of the circuit and its sensitivity, it may take some time (several minutes) to settle after the shock resulting from the transfer of electrodes from one solution to the other. Over-shooting, or over-compensating effects, may at first occur, but after the first few minutes, the system will recover and take over control. After this it may be expected to maintain control of the pH within ± 0.02 if only one solenoid valve is required for control, or to within ± 0.08 if both solenoid valves are required.

Note:- In all applications of the instrument the monitor meter on the Control Panel should be kept at exactly full scale (100 μa.) by frequently adjusting the Voltage Set knobs. This maintains the calibration of the instrument.

IV. TECHNICAL FACTORS

Amplifier-Integrator Characteristic

The pulses produced by mechanical switching in the manner described under "Principles Involved" are applied to the input grid of a three-stage amplifier and thence to an integrating circuit which gives a d.c. voltage of the same polarity as the pulses, and almost directly proportional to the amplitude of the pulses (up to the point where the amplifier either saturates or cuts off).

Since this d.c. control potential is developed across a high-impedance load (20 megohms), a cathode-follower is used to operate sensitive relays (2 in parallel). The circuit is arranged so that at balance (pulse amplitude practically zero) one relay is energized and the other de-energized. A positive-going pulse of amplitude slightly greater than 2 millivolts increases the cathode voltage of this final stage and energizes the second relay, while a negative-going pulse of similar amplitude reduces the cathode voltage just enough to de-energize the first relay. This provides a two-way control where either acid or alkali correction might have to be applied to maintain a bath at constant pH. See Chart 2.

Sensitivity in pH Measurement

The slope of the Cathode-Current vs. Pulse Amplitude curve is determined by the overall gain of the pulse-amplifier, and this slope in cathode milliamps. per pulse millivolt is, in a sense, the sensitivity of the instrument, as far as measuring pH or millivolts is concerned. However, in practice, there is a limit to the reset accuracy of the "null point" (R, in Chart 2). This limit is set by the fact that switching transients and hum-input pickup have an exaggerated importance when the true error-pulse is very small (less than 1 millivolt). This has the effect of making R appear to wander up and down the curve by an amount corresponding to approximately 1 millivolt on the pulse axis. Thus, for the present circuit and input construction, the sensitivity of pH measurement is limited to about ±1 millivolt or ±0.02 pH and is more or less independent of the gain of the amplifier, provided the gain is sufficient to give good, but not violent, deflections from the null point when the pulse has an amptitude of a few millivolts.

Sensitivity in pH Control

The sensitivity of control, as distinct from the sensitivity of measurement described above, hinges on the accuracy of relay adjustment rather than the reset accuracy of the null point. Since both relays operate at points somewhat removed from the balance-point R, the effect of input transients is largely swamped out and the reset accuracy of these points appears to be much greater than that of the null point. Thus, once the relays are adjusted, they tend to operate at very nearly the same point on the curve every time.

The adjustment of the sensitive relays to operate at the desired points on the curve is quite difficult, due to the proximity of the pull-in and drop-out points, resulting in rather small gaps between contacts. For this reason it is desirable to have the slope of the curve as steep as possible, without being so steep as to produce unnecessarily rapid and uncontrollable responses to off-balance conditions. A slope of 0.23 milliamps. per millivolt (with 2500 ohms in the cathode) seems to be about right for most purposes.

In controlling a bath which is constantly producing either acid or alkali, only one relay is used and the control operates over the spread PQ or ST. This gives quite close control (about ±1 millivolt or ±0.02 pH). This tolerance becomes slightly larger when the rate of change of pH increases, as there is some lag in the system and a certain amount of overshooting takes place. This, however, is usually of no consequence.

In the case where the pH varies in a quite random manner and both sides of the control system must be used, the sensitivity of control is determined by the spread PT, again with some overshoot when the rate is violent. This double control is rarely used, but is capable of tolerances of ±4 millivolts and ±0.08 pH none the less.

Range of the Instrument

The present instrument covers a range of -140 millivolts to +140 millivolts. Using Beckman Electrodes this corresponds to a range of pH5 to pH10 (see Chart 5 for typical Conversion Graphs pH to Voltage for the Beckman and other electrodes).

V. DESCRIPTION OF CIRCUIT AND SCHEMATIC DIAGRAMS

Functional Diagram and Circuit of Relay Unit (Drawing 1):

The drawing shows a block diagram of the whole system, with interconnecting cables between the units.

The output (Plug 4) of the Control Panel Unit is a d.c. reference potential which lies in the range -140 to +140 millivolts, continuously variable and voltage-regulated.

The Amplifier-Integrator Unit compares this d.c. reference potential with the d.c. potential from the bath electrodes (Plug 5) by the chopping method described above. The circuit is so arranged that a positive error pulse into the amplifier causes the red light to go on, indicating that the bath is too acid (pH low) and that alkali is flowing into the bath to restore the balance. If the error pulse is negative, the green light is on, indicating a bath more alkaline than desired (pH high) and that acid is flowing into it to restore the balance.

It can be seen from the above that the pH level at which the bath is maintained by the control system will depend upon the setting of the d.c. reference potential, since the circuit operates to bring the bath potential and the reference potential to a balance and this is done by changing the pH of the bath.

The Relay Unit contains two buffer relays and a delay relay. The buffers are operated by the two sensitive relays in the Amplifier-Integrator unit and will control solenoid valves for acid or alkali addition which consume up to 660 volt-amperes. The delay relay is in series with the acid solenoid valve circuit and operates from a 115-volt line which comes on three minutes after the main power line is switched on. This delay ensures that the rest of the circuit has a chance to warm up and the long time-constant circuit has a chance to charge up before the acid control takes effect. These problems do not arise in the alkali control circuit, so that a similar delay relay is not needed here.

Circuit of Power Supply Unit (Drawing 2):

The power supply produces +300 volts for use in the amplifier circuit and control panel; -250 volts for use in the control panel; 6.3 volts a-c floating; 6.3 volts a-c grounded on one side; 115-volts a-c delayed 3 minutes. In addition to the above there is a set of relay contacts delayed three minutes which controls the plate supply to V3, the output stage of the Amplifier-Integrator circuit.

Circuit of Amplifier-Integrator Unit (Drawing 3):

The Amplifier Integrator and the sensitive relays are included in this circuit.

The microswitch pulsing chopper at the input to V1 is operated mechanically by a telephone relay, actuated about once every two seconds by the Relaxation Oscillator V8 (an 884 thyratron). The two condensers (0.05 and 0.001 microfarads), which represent the only load on the bath electrode circuit, must be high-quality mica condensers. Thus, provided there is no grid current, the input impedance is many times greater than the impedance of the electrodes (the glass electrode alone may have an impedance varying from 50 to 500 megohms depending on temperature while the calomel-electrode has an impedance in the range 10,000 to 20,000 ohms). Thus the loading effect on the bath circuit should be quite negligible.

It will be seen that a small pulse at the input of V1 will be amplified and appear as a pulse of similar polarity at the first cathode of the 6SN7 (V3). This pulse, passing to the integrator diode V4, is converted to a dc potential of about the same magnitude as the pulse and of the same polarity. The d.c. potential is taken off at the midpoint of the integrator load (10 meg, 1 meg, 10 meg) and applied to the grid of a cathode-follower 6SN7 (V3), where it determines the cathode current and therefore the operation of the two parallel sensitive relays L2 and L3.

The sensitive relays are adjusted so that when the integrator output is zero one relay is energized (L2, acid controlling) and its contacts are open, while the other relay is de-energized (L3, alkali controlling) and its contacts are also open. Thus the appearance of a pulse will cause the integrator to produce either a positive or a negative d.c. potential which will increase or decrease the relay currents and either energize L3 or de-energize L2, thus closing one or other of the control lines for acid or alkali. Note that the acid-controlling contacts are closed when the power is first turned on and remain that way until the circuit becomes stable. To prevent the flow of acid during this warm-up period, the acid solenoid-valve circuit is kept open by the 3-minute delay relay mentioned above.

Circuit of Control Panel (Drawing 4):

The output at Plug 4 is determined by the settings of the Coarse Voltage Control (7-position switch) and the Fine Voltage Control (200-ohm potentiometer) and falls in the range from zero to 140 millivolts, developed across a resistance of from zero to 1400 ohms. The metering switch (+ Voltage -) serves to reverse the polarity of this voltage and to connect the 100-microamp meter so that it always measures the series current in the voltage-dividing circuit. The 3000-ohm potentiometers (Voltage Adjust) provide sufficient control that the current in this voltage divider can always be made exactly 100 microamps in spite of normal small variations in the output of the V-R tubes. Calibration of the instrument is affected by the accuracy and stability of the voltage-divider components. 1% accuracy in the output voltage can only be maintained if 1% accuracy in each component is guaranteed (see Calibration curve in Chart 3).

The red and green pilot lights are operated by the sensitive relays in the Amplifier-Integrator unit, and their operation is described above.

VI CHARTS

Chart 1: Principle of Operation

As referred to in the text, this chart shows the formation of pulses from the d.c. error voltage.

Chart 2: Amplifier-Integrator Characteristic

Described in the text, this chart shows a typical characteristic of cathode-current output versus pulse-voltage input.

Chart 3: Calibration as a Millivoltmeter

The curve shows that the scale marking is consistently high, the error being about 2.5% in the range 0-110 millivolts. The calibration curve is dependably linear up to 110 millivolts. Above this, the slope increases somewhat, so that the error increases to about 7% at the extreme range.

The cause of this calibration error is probably in the selection of the 200-ohm resistors which make up the voltage-dividing switch circuit. These resistors appear to be consistently 2.5% low in the 0-110 mv range and about 20% low from 110 to 140 mv. The error could be compensated for in the 0-110 mv range by increasing the current through the voltage-divider by 2.5%.

This calibration curve represents the average of seven curves, taken over a three and one-half day period. A standard potentiometer circuit and Weston Standard Cell were used as the calibration reference potential.

Chart 4: Stability

The stability of calibration over a 3½-day period is shown in this chart. Departure from the mean calibration curve is plotted against the dial reading for seven sets of readings. The maximum departure of any one point was 0.9 millivolts, which appears to be about the limit of variation due to inherent instability under normal operating conditions. This is the equivalent of about 0.02 pH for the Glass and Calomel electrodes.

The estimated visual resetting accuracy of the instrument at the balance point is ±0.1 millivolt, which is so small that the 0.9 mv. figure can be said to be inherent in the circuit and not in the manual operation of the instrument.

Hum pickup, contact potentials in the microswitch and tube noise at the input to the amplifier are probably the chief sources of instability, and it is conceivable that these could be further reduced, if necessary.

Chart 5: Conversion from pH to Voltage

It is well known that the calibration of each set of electrodes differs slightly from that of other sets, so that, if great accuracy is desired, a separate calibration for each pair of electrodes should be made.

This chart shows, in curve A, a typical calibration for the Beckman Standard Glass Electrode and Standard Calomel Electrode, using a set of Coleman Buffer Solutions, the curve being corrected for 30°C.

Superimposed on the same chart are calibration curves for three Leeds & Northrup electrode pairs, also corrected for 30°C. These curves are included merely for comparison and were copied from L & N Booklet STD 21074 (Standard Conversion Tables - Voltage to pH). The electrodes themselves were not available for test.

Note: Polarity of voltage shown in the L & N Tables is opposite in sense to that shown in Chart 5. This is due to the fact that in the L & N instruments the glass electrode is grounded, whereas in this instrument the calomel electrode is grounded.

Chart 6: Temperature Characteristic of Typical Electrodes

The chart shows four curves of Millivolts against Degrees Centigrade, taken for a typical pair of Beckman Electrodes (Glass and Saturated Calomel) for pH of 5.0, 6.1, 7.2 and 8.1.

In general, for a given pair of electrodes, the slope of the temperature characteristics will be different for each value of pH. For the Beckman Glass and Calomel Electrodes, the characteristics become somewhat steeper as the pH increases.

For comparison, a set of curves for the L & N Glass and Saturated Calomel Electrodes are included for the same values of pH.

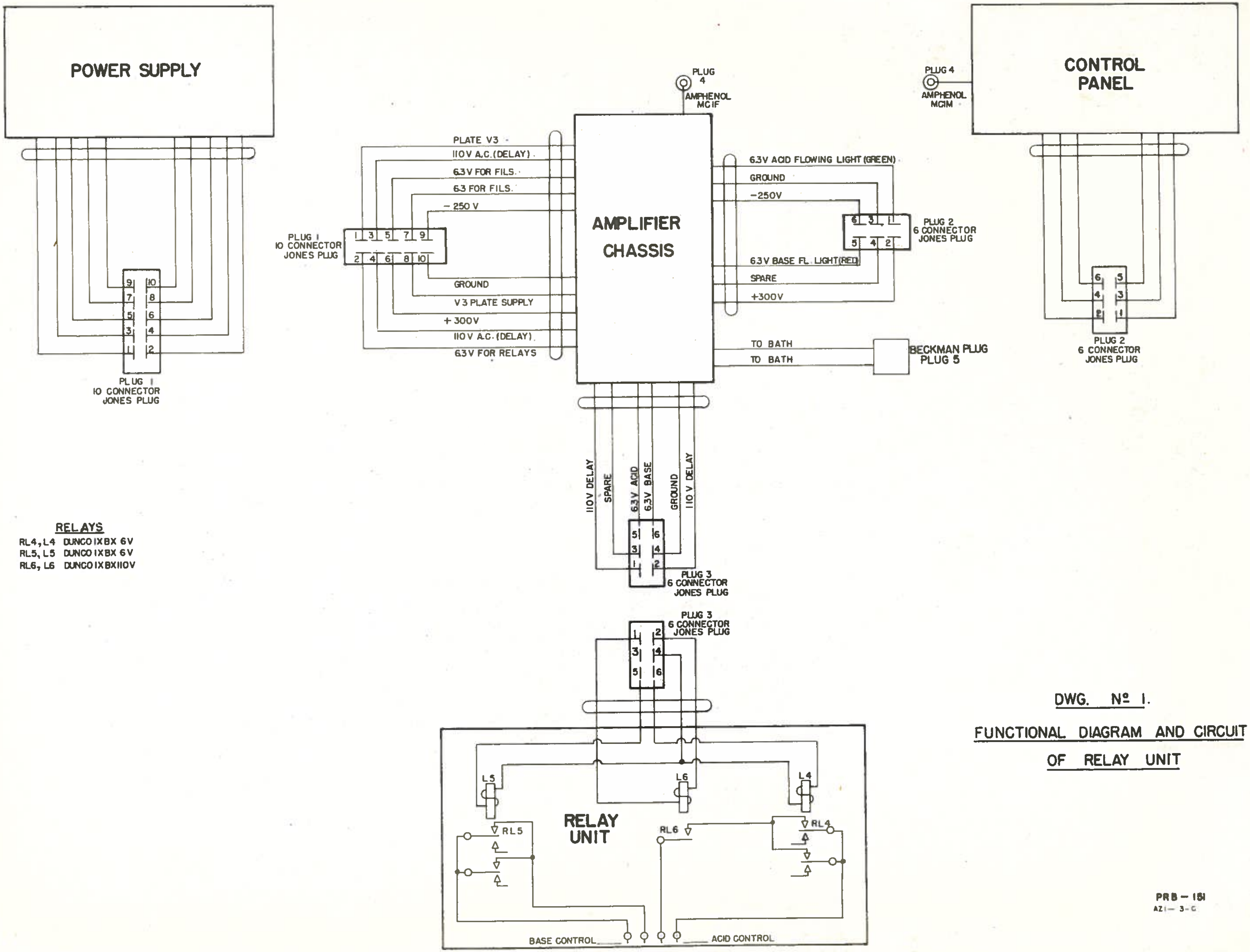
It is not to be concluded from these curves that the slope of the temperature characteristic is always negative. On the contrary, the slope may be positive, negative or zero, depending on the types of electrodes used and the pH range under investigation.

It should be observed, in passing, that the internal resistance of a set of electrodes can be expected to vary by a factor of 10 or more over the normal range of temperatures, so that it is important to have a very high input-impedance in the measuring instrument. No report can be made at the present time as to actual Resistance-Temperature Characteristics of the electrodes, except to quote a manufacturer's rating of 175 megohms for the glass electrode and 20,000 ohms for the calomel electrode. Actual measurements of the input resistance of the amplifier described above indicated resistances of from 2500 megohms to 10,000 megohms.

VII ACKNOWLEDGMENT

The work done by other investigators before the present author became associated with the project is acknowledged. Most of the circuits were developed by Mr. J.W. Bell, and assistance in the practical tests was given by engineers of the Biology Division of the National Research Council.

J.F. Davis
July 31st, 1946.



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FUNCTIONAL DIAGRAM AND CIRCUIT OF RELAY UNIT

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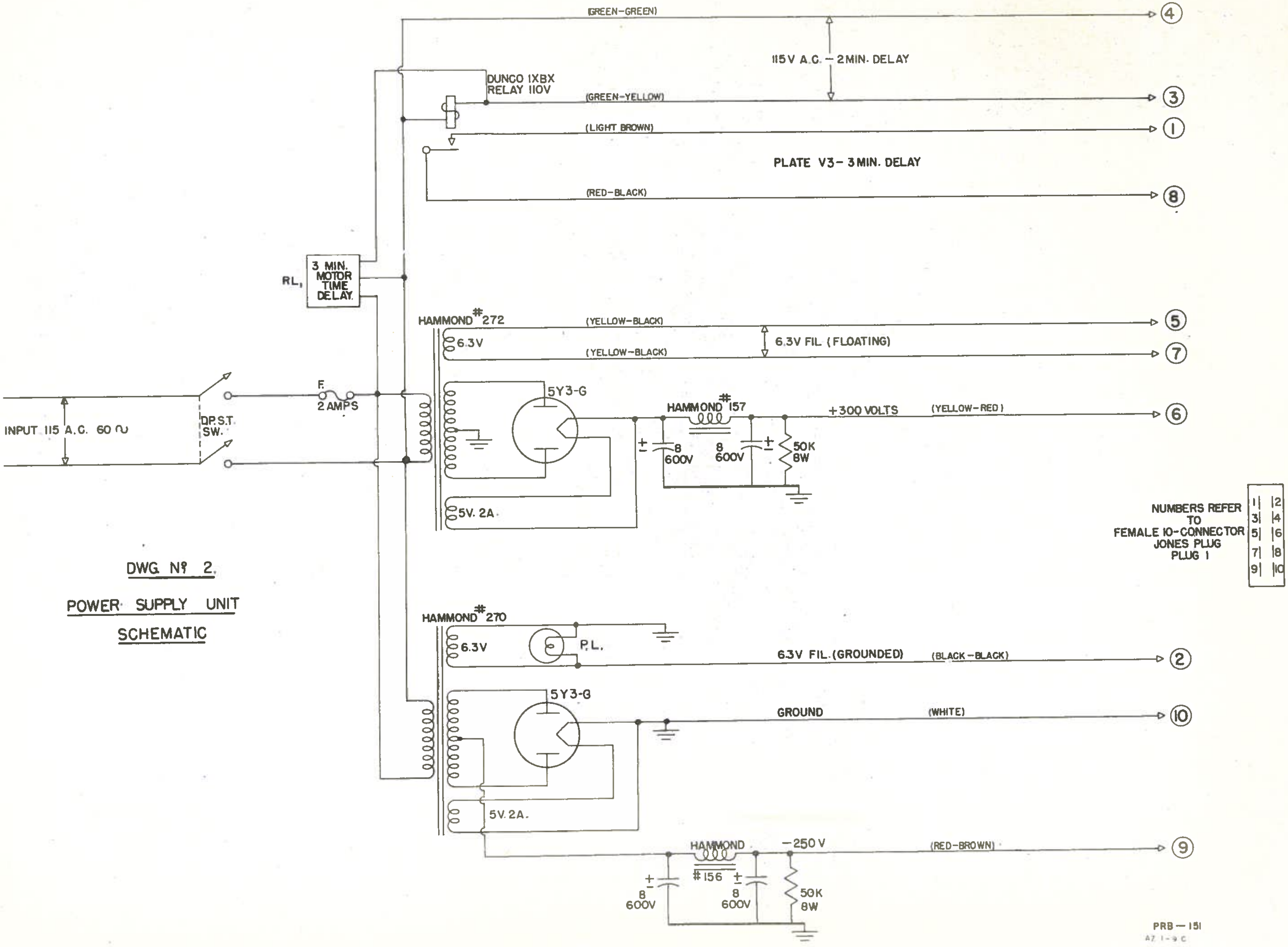

NUMBERS REFER
TO
FEMALE 10-CONNECTOR
JONES PLUG
PLUG 1

DWG. No. 2.

POWER SUPPLY UNIT

SCHEMATIC

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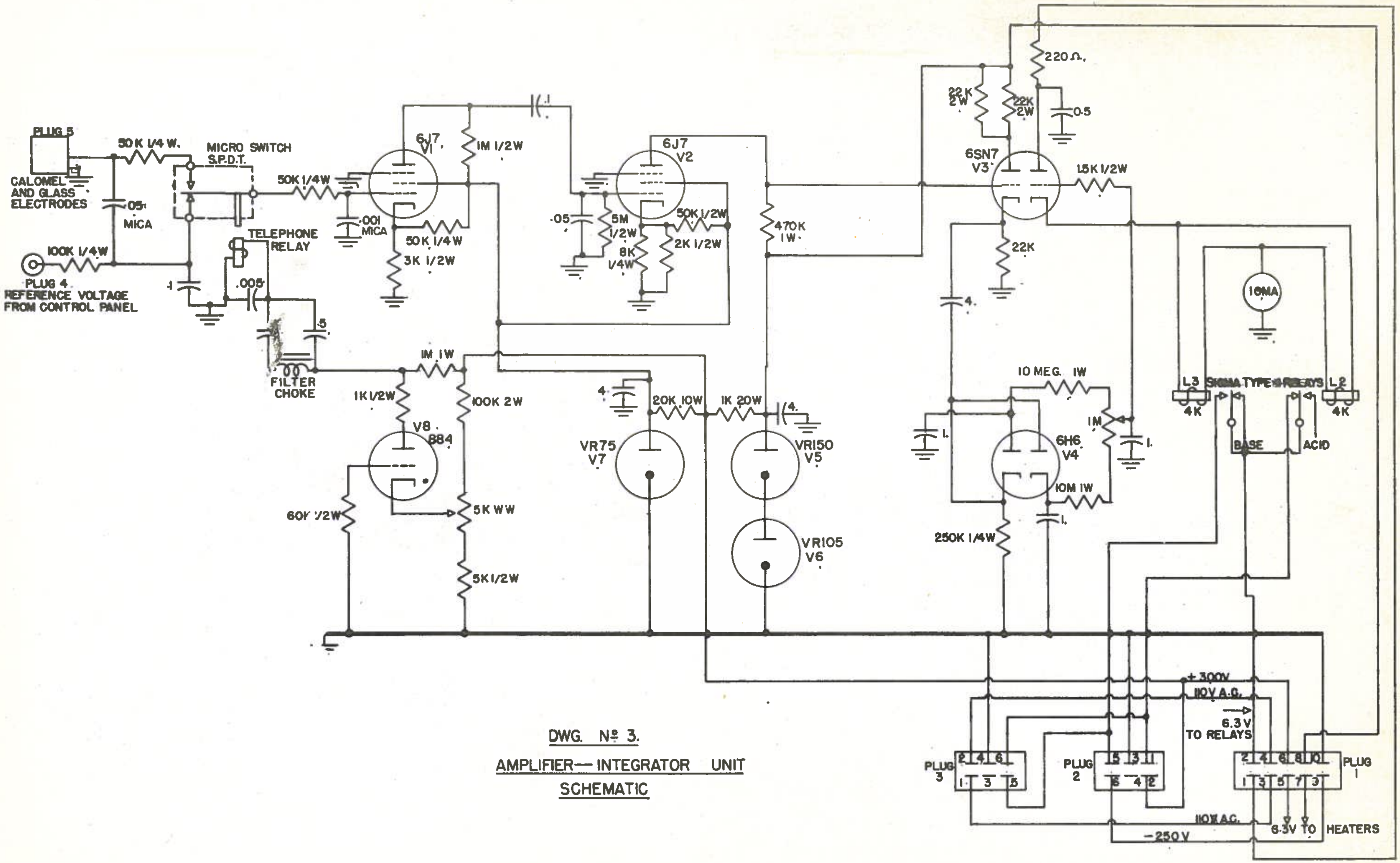
AZ 1-9 C



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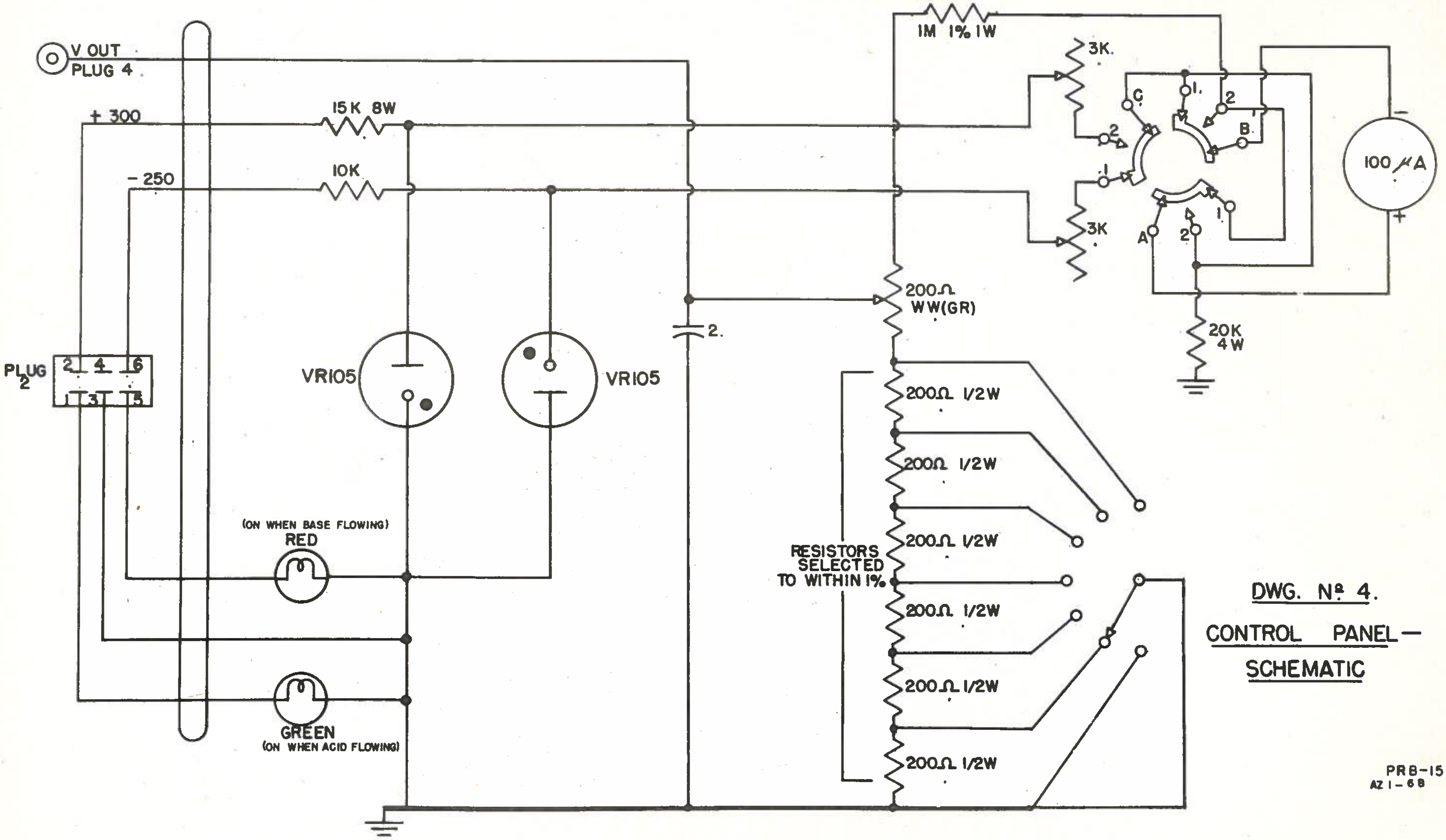
AMPLIFIER— INTEGRATOR UNIT SCHEMATIC



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CONTROL PANEL —
SCHEMATIC

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CHART I.

PRINCIPLE OF OPERATION

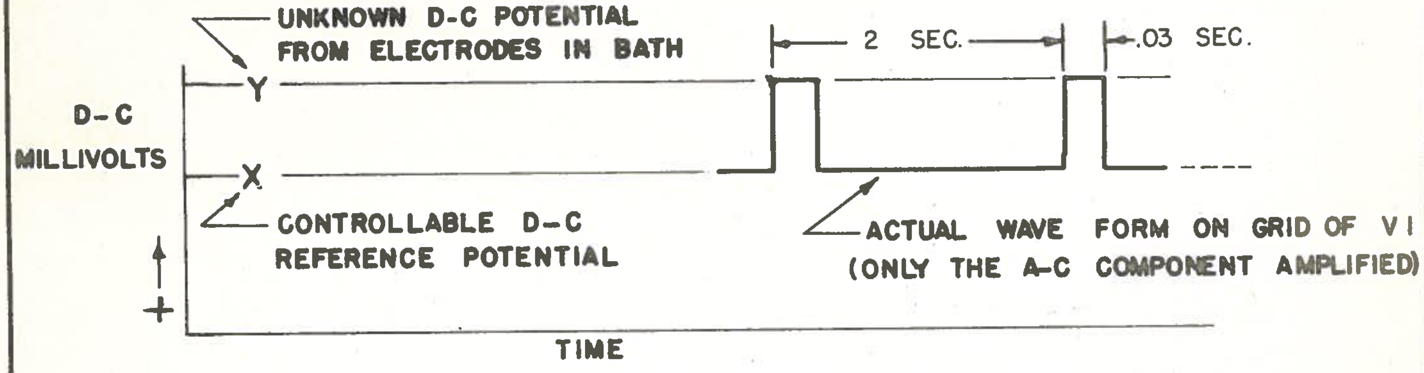

FIG. 1.—PULSE POSITIVE WHEN Y IS MORE POSITIVE THAN X.

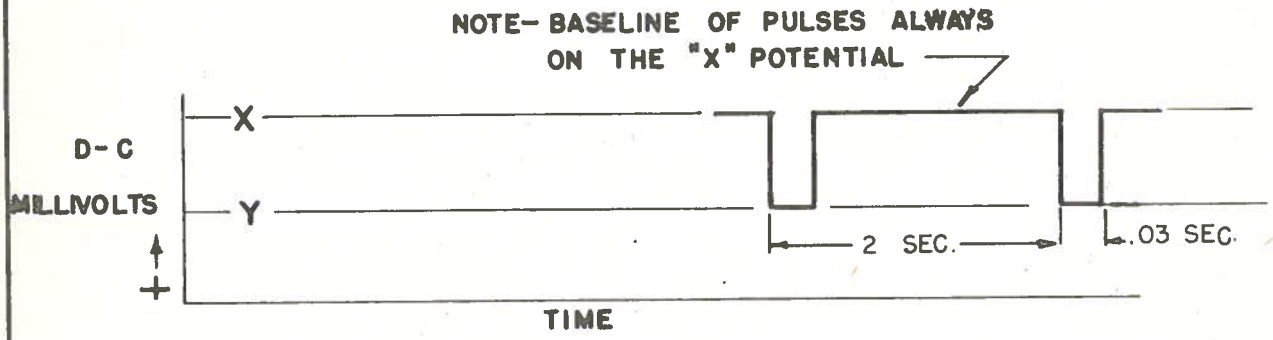

FIG. 2.- PULSE NEGATIVE WHEN Y IS MORE NEGATIVE THAN X.

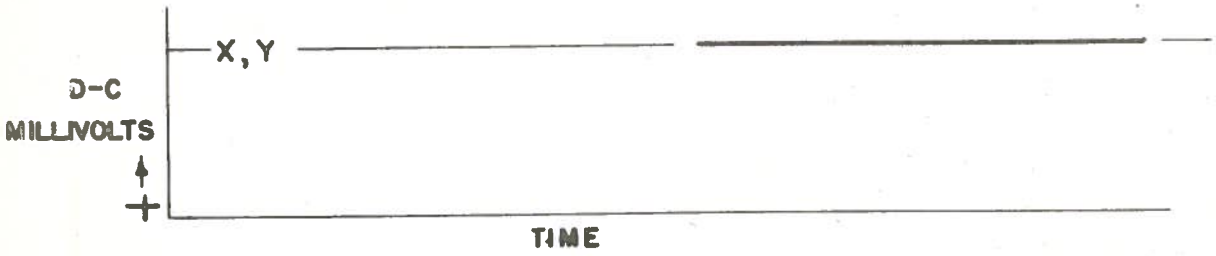

FIG. 3.— NO PULSE WHEN Y AND X ARE EQUAL

CHART 2.

AMPLIFIER-INTEGRATOR CHARACTERISTIC

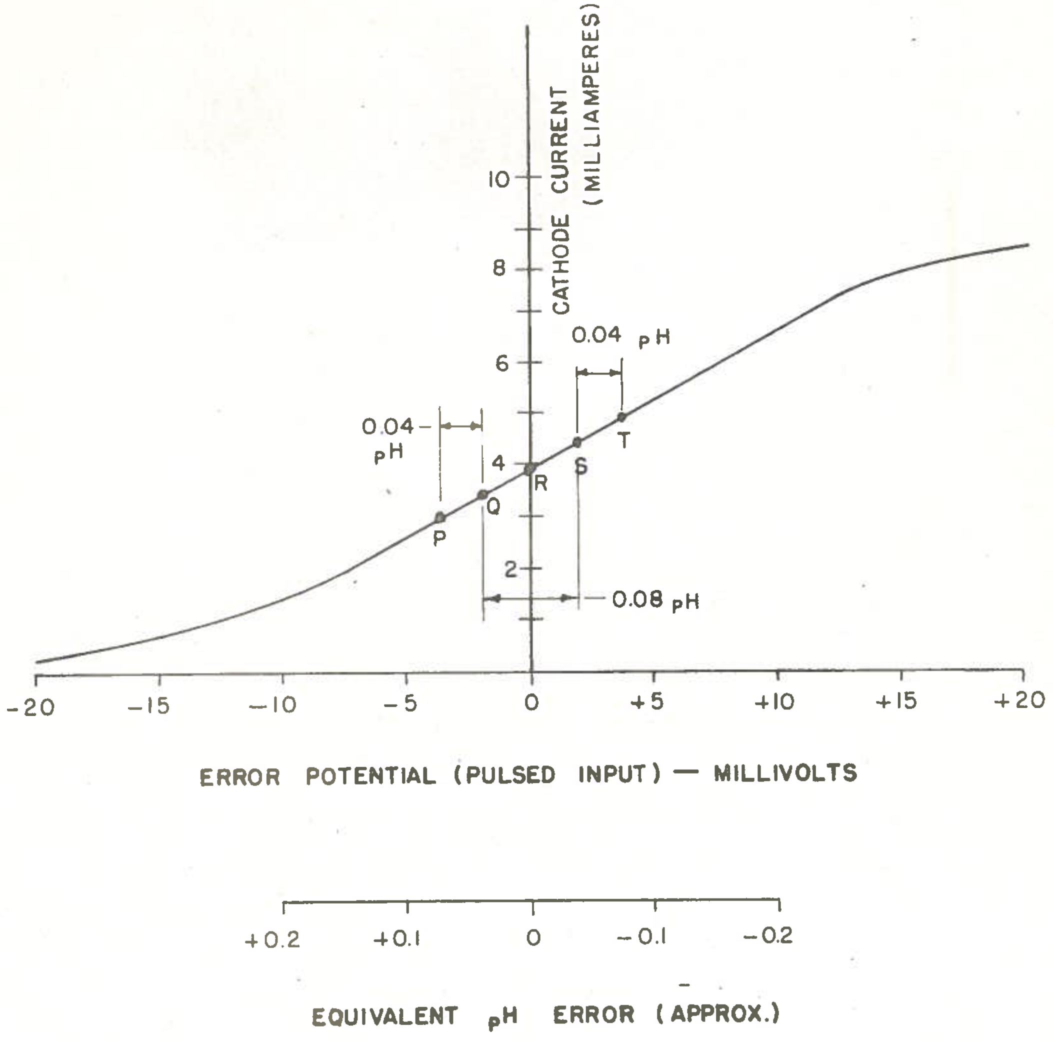

CHART 3

CALIBRATION AS A MILLIVOLTMETER

(MEAN CALIBRATION OVER A 3 1/2 DAY PERIOD)

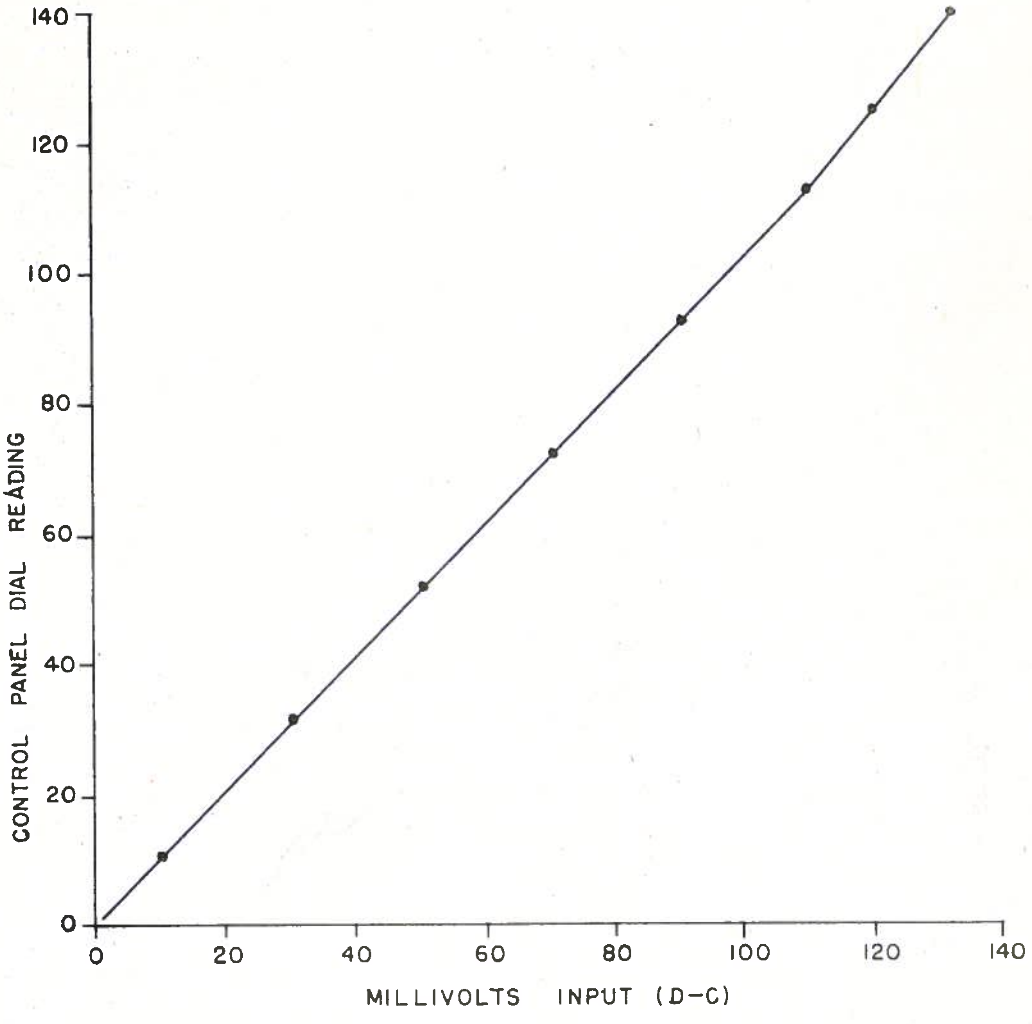

CHART 4.

STABILITY

(SEVEN DEPARTURE CURVES ARE SHOWN,
TAKEN OVER A 3 1/2— DAY PERIOD.)

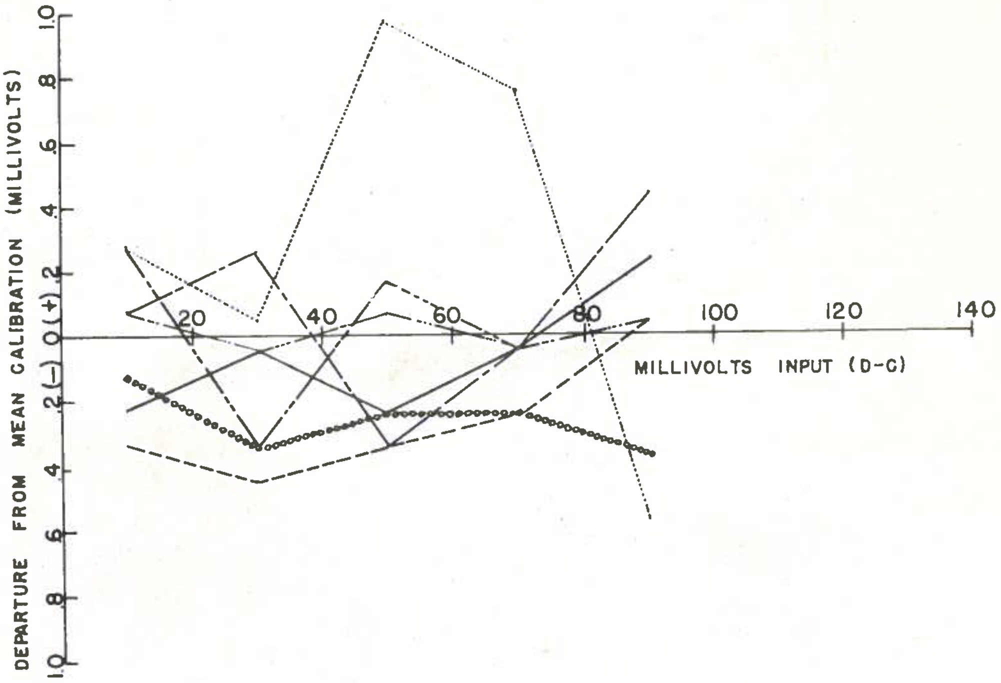

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CHART 5.

CONVERSION FROM pH TO VOLTAGE

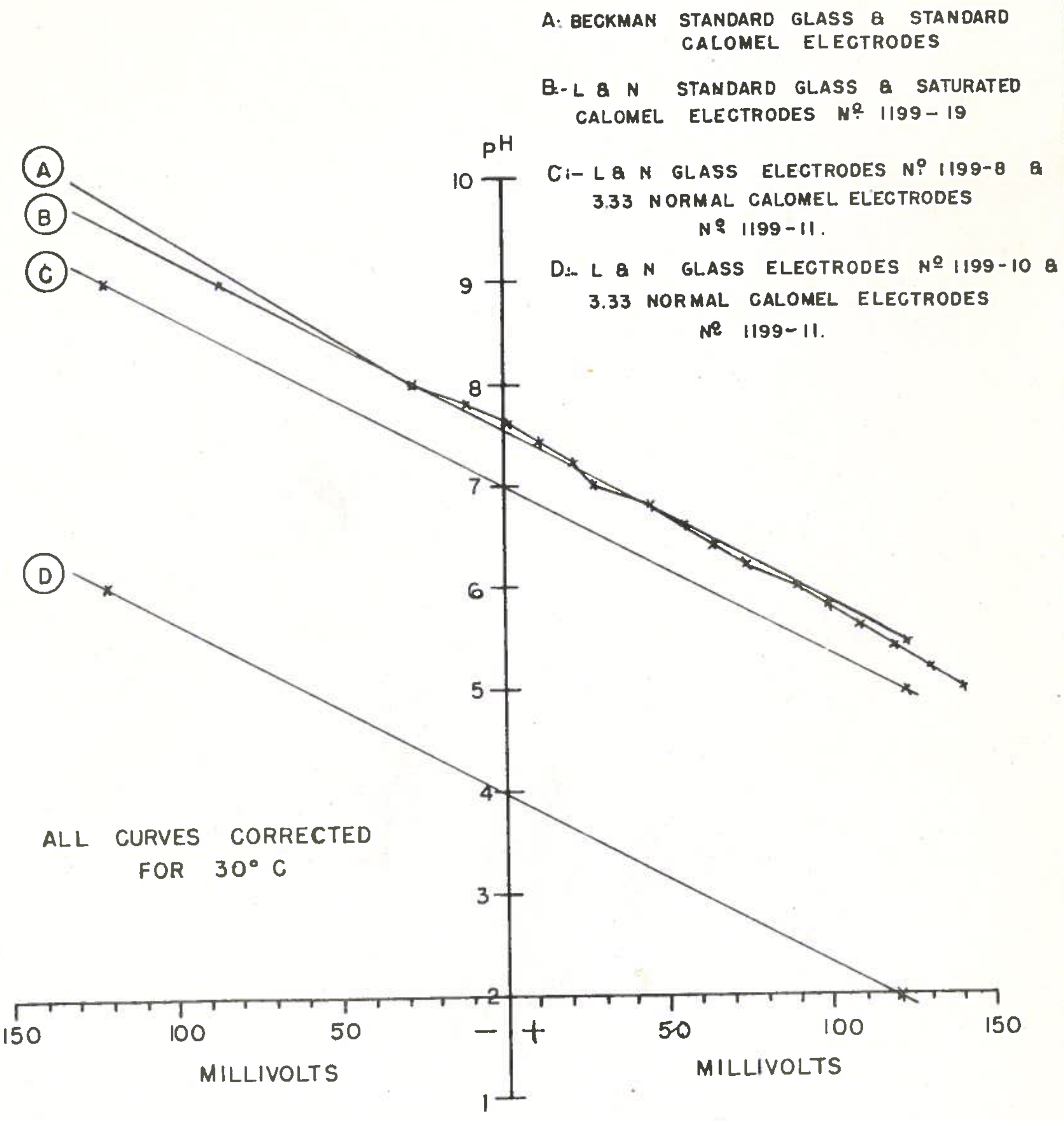
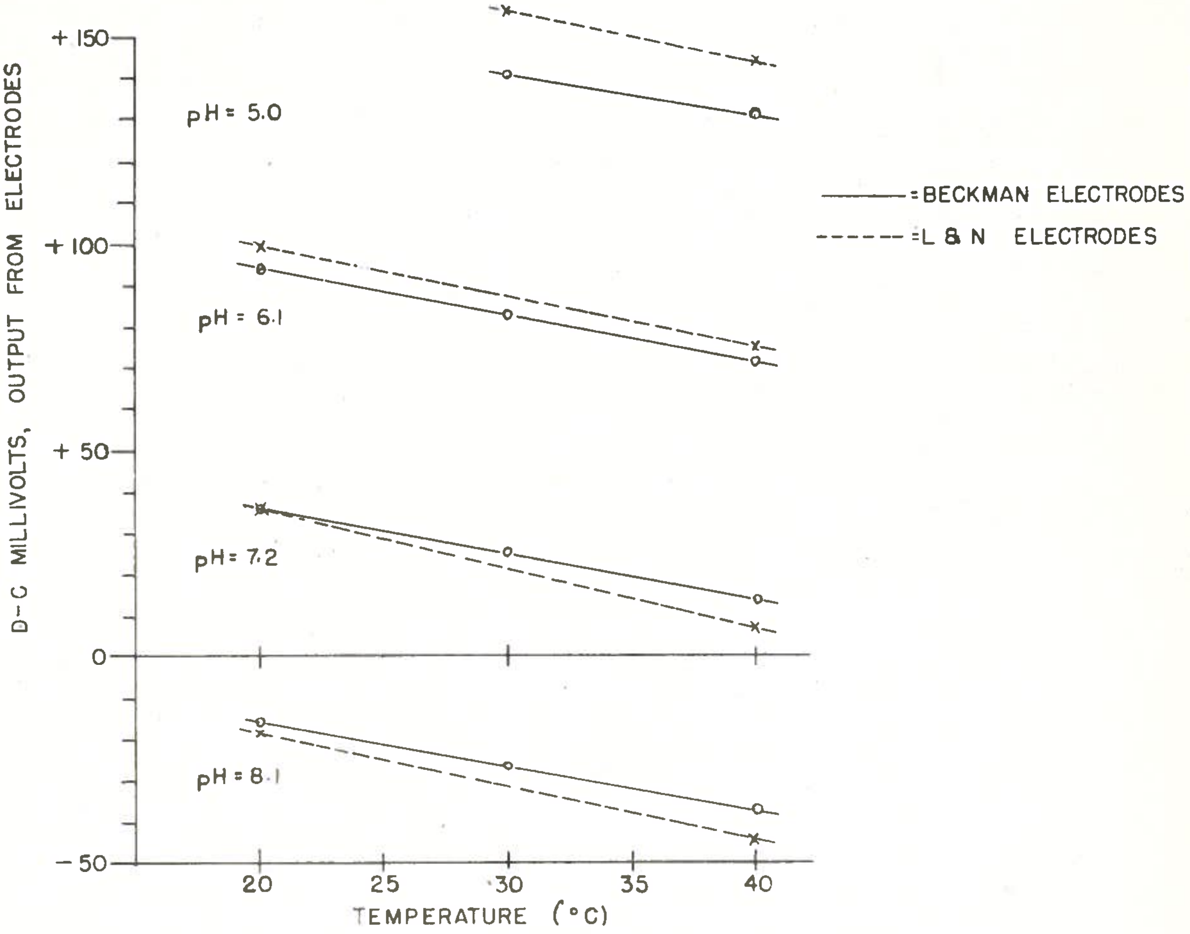


CHART 6.

TEMPERATURE CHARACTERISTIC OF TYPICAL ELECTRODES



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