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ELECTRICAL PHENOMENA AT THE ICE/WATER INTERFACE

by

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Electrical Phenomena at the Ice/Water Interface

I. Automatic apparatus for recording streaming potentials: application ice-water system.

II. Device for producing and measuring electric potentials at the ice/water interphase during freezing.

GENERAL INTRODUCTION

The aim of the present report is to describe the experimental equipment designed for the purpose of investigating electric phenomena which occur at the ice/water interphase. Two aspects of the same problem are to be studied: i) electric potentials generated whenever liquid water is forced through ice capillaries under pressure gradients; those are known as streaming potentials. ii) electric potentials which appear during the freezing of water of dilute aqueous solutions; these are called freezing potentials*. Although these two phenomena appear to occur in the case of the ice/water interface their mechanisms are entirely different. Electric phenomena occuring at the ice/water interphase is of importance

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* Freezing potentials are also present during the liquid/solid transition of polar liquids.

in the explanation of many natural phenomena where ice and water are involved.

I. Automatic apparatus for recording streaming potentials. Application to the ice-water system.

Introduction

Preliminary investigation on streaming potentials on ice/water system appears to support the view that ice must show an electrokinetic charge at the ice/water interface (1).

This charge could be obtained experimentally with the help of electrokinetic phenomena; streaming potential measurements seems to be the most appropriate for the ice/water interface. A comparative study of the several electrokinetic techniques, although interesting, are outside the scope of this report. However a few words must be said in support of the use of streaming potential technique to obtain electrokinetic data. It is true that this technique has been plagued by a number of difficulties which in turn lead to the controversial conclusion regarding the validity of the calculated zeta potentials. For example many authors seem to have observed a difference in behavior of streaming potential when altering the direction of flow; this observation does not find support in the theory of the phenomenon. Fortunately

it has been shown recently that many of these difficulties are originated in the electrodes themselves; the causes of the trouble seem to be the age of the electrode, flow potentials in absence of the surfaces, and the most serious of all, the polarization effects.[2,3,4] The use of fresh reversible electrodes appears to eliminate the majority of these troubles, the polarization effect in particular. Fortunately it is possible to obtain reproducible and reliable results for the zeta potentials despite these difficulties.[4] The apparatus to be described below records automatically the streaming potential versus pressure curves in approximately 10 to 20 seconds (or less if desired) as compared to 50 minutes obtained by the old recording methods. This fact alone constitutes an advantage of the present device; also another feature is that any anomalous behavior of the system can be detected immediately while streaming.

One of the major causes of errors in the calculation of zeta potentials lies in the fitting of the best line to the experimental points. This is made difficult because of the condition of a steady pressure required for streaming;

the reverse is true for the present "continuous" recording method. A percent error in the measurement of the slope of the Δ E versus Δ p curve contributes with the same percent error in the calculation of the zeta potential. (see later)

The Apparatus

The automatic recording apparatus consists of four main parts:

i) the streaming potential cell

ii) the solution reservoirs and pressure ballast

iii) the pressure gauge (pressure transducer)

iv) the electronic circuit.

i) The streaming potential cell.

Two streaming potential cells have been used in the present work; one for measurements of streaming potentials on quartz using the plug method. This experiment was carried out in order to check the measuring device; the cell used in the quartz work has been described previously.[5] Measurements of streaming potentials on ice were carried out using capillaries made of ice; for that purpose an elaborate lucite cell was constructed. The cell consists of the following parts:

a) the inner lucite tube; this part supports the ice capillary,

b) the ice jacket; this contains crushed ice and helps to maintain the equilibrium temperature of 0°C,

c) the electrode system; this part containing the electrodes is also with inlet and outlet for the liquid circulation through the ice capillary.

Because the cell is in the process of being modified a detail of construction of the cell is not given here.

ii) Solution reservoirs and pressure ballast.

The solution reservoirs and pressure ballast can be clearly seen in Figure (1). In the case of the ice work the solution reservoirs were placed inside two large Dewar flasks containing ice. The reservoirs have provisions for temperature measurements; the center mouth can be fitted with a simple device for pH determinations after which the small volume of solution withdrawn can be discarded. The output of the pH meter would be fed into one of the Y axis available, thereby recording the pH value on the same chart as the Δ E versus Δ P curve (see later). A large ballast reservoir is used to

store nitrogen under pressure (~12 cm Hg) for driving the liquid through the cell. Because the apparatus records simultaneously the changing applied pressure and the corresponding streaming potential it is necessary to make provisions for the continuous change in pressure with respect to time within the system. This is easily accomplished by fitting a three way stopcock to the ballast reservoir; one of the outlets would be fitted with a hypodermic needle of very small diameter thereby permitting the applied pressure to drop at a rate of 3-6 mmHg/sec. The three way stopcock allows the "bleeding" without emptying the ballast reservoir. Pressures up to 6 cm Hg were used is the present work which corresponding to 10 to 20 seconds for a complete tracing of a Δ E versus Δ P curve.

iii) <u>The pressure gauge</u>

The pressure gauge consists of a bellows and a differential transformer (Atcotran, model 6208A). This is essentially an electro-mechanical transducer that produces AC voltages proportional to the displacement of an armature from the electric center. The stationary element consists of a primary and a secondary wire winding; both circuits are composed of

two coils connected in series. The secondary coils are connected in such a manner as to produce output voltages of 180° out of phase. The primary is energized by an AC power supply thereby inducing a magnetic field in the secondary coils. The position of the armature (made of a magnetic material) determines the strength of the induced field and the voltage in the secondary coils. These are connected in series opposing; the output of the secondary is zero when the armature is positioned at the electrical center or null. If the armature is diplaced to either side of the null point, the coil nearest to the armature will show an electrical output much larger than that of the coil further away from the armature. The difference in output between the coils of the secondary is a linear function of the armature displacement. The characteristics of the 6208A transformer are: linear displacement $\pm$ 0.150" and 0.185 mV output per 0,001" per volt input.

The armature rests on top of the bellows; this expands under the pressure applied to the system for driving the liquid through the streaming cell. The excursion of the armature is a linear function of the bellows expansion, which

in turn is also a linear function of the applied pressure. The problem is simply that of transducing a linear motion of a bellows expansion into electric output. The transducer is calibrated by comparison with the appropriate manometer.

iv) The Electronic Circuit

The transducer output is amplified, demodulated and fed into the X axis of a double channel X-Y recorder (Moseley 4B). The streaming potentials are measured with the help of a Keithley electrometer (model 610A) whose output is fed into one of the Y axis of the recorder. The sensitivity of both the X and Y inputs can be adjusted in the Moseley recorder or in the measuring instruments. The sensitivities should not be too large otherwise pressure transients set up in the system at the beginning of flow may compromise the quality of the tracings. The recording device presented here could be further improved by using a ratio recorder; this would permit to obtain directly the tracing of the slope versus the pressure ($\Delta E / \Delta P$ versus P). A block diagram of the electronic circuit is shown in Figure (2).

Procedure for the work on quartz.

After loading the streaming cell with the material,

both solution reservoirs are open to the atmosphere. The recorder and the demodulator are set to zero, after selecting the appropriate sensitivities; the adequate electrometer range is selected next. The ballast reservoir is connected to one of the solution reservoirs making sure that the other is open to the atmosphere. At this moment the liquid flow is started (an electromagnetic valve could be used for this purpose); the ΔE versus ΔP curves will be obtained automatically. This procedure is also used for the streaming of water through the ice capillary.

Results on quartz.

The apparatus was checked with a quartz plug 28/35 mesh The material was cleaned with hot hydrochloric acid; traces of iron and chloride ion were eliminated by repeated washing with conductivity water. An actual recording is presented in Figure (3). These were obtained by streaming 5×10^{-4}M KCP pH = 5.8. The author believes that this is the first time that an actual recording of Δ E versus Δ P curves in different directions has ever been directly traced on the same chart. Careful examination of the curves shows that the slopes do slightly differ. Examination of the curves show that their slopes are equal within experimental error.

A slight curvature at low values of the applied pressure can also be observed. This slight curvature is due to an increasing hydrostatic head set up against the decreasing driving pressure. The transducer measures the applied pressure while the actual driving pressure is equal to the difference between the applied pressure and the corresponding hydrostatic head. This can be made small and of such a magnitude at the end of streaming as to have no appreciable effect on the Δ E versus Δ P curve at low values of Δ P. This can be achieved by building up a small hydrostatic head on the side of the applied pressure. At very low values of ΔP the effect of the hydrostatic head may be appreciable. The applied pressure is related to the streaming pressure by

$$\Delta P_{ST} = \Delta P \pm \frac{\Delta h}{13.6}$$

where Δ h is the values of the hydrostatic head in centimeters of water; if $\Delta P \gg \Delta h/13.6$, $\Delta P_{ST} \simeq \Delta P$. Assume that at the end of a run the value of Δ P = 1 cm Hg with an opposing head of h = 3cm H_2O. Assuming that the slope of the Δ E versus Δ P = 5 mv/cmHg there will be a decrease of 1 mV in the streaming potential at ΔE_{ST} = 5 mV due to the

opposing hydrostatic head to the streaming pressure. The zeta potentials were calculated at 20°C by the expression:

$$\zeta = -9.7 \times 10^{-4} \frac{\alpha k}{R_p}$$

where α = slope of the Δ E versus Δ P curve, R_p = resistance of the plug in the absence of flow and k = streaming cell constant. A reproducible value of - 39.2 mV was obtained for the zeta potential of a 1.0 cm plug. That value compares reasonably well with - 36 mV found previously for a plug of the same characteristics.(4)

Exploratory work on ice.

Ice capillaries were made by freezing water contained in the lucite tube (a). A tungsten rod of the appropriate diameter was placed in the center of the lucite tube prior to water freezing. After the ice is formed the wire is pulled out with a gentle rotatory movement; the ice was prepared by placing the lucite tube in a freezer. The lucite tube containing the ice annulus was then placed in the ice jacket (item b). The two solutions reservoirs were placed in two Dewar flasks containing ice. Thermic equilibrium was determined with the help of a few Chromel-Alumel thermocouples placed in the reservoirs and in the lucite tube near the ice phase. Ag/AgCl electrodes were employed.

Distilled water was used in these exploratory experiments. The manipulation of the ice and instrumentation at 0°C has shown that it is extremely difficult to make measurements of any significance with such a simplified device. Although some measurements seem to indicate the presence of charges at the ice/water interface we feel it is too premature to attach any significance to the results obtained. The streaming cell for ice studies is being modified; it will permit ice formation in s'tu. The ice capillary and both solution reservoirs will be cooled by thermoelectric pumping thereby permitting a better control of the equilibrium temperature in the different parts of the apparatus (see part II of this report).

II. Freezing Potential Apparatus

Introduction

It is a well established fact that solidification of water is accompanied by charge separation between the ice and water phases [6,7]. This effect was explained by Workman and Reynolds [6] in terms of ion entrapment in the ice lattice. For example amonium ions impart a positive charge to ice while Cl^- ions confer to the ice a negative charge. The validity of the ion entrapment mechanism has been challenged by Mason[8]

who supports the theory of temperature gradients across the interface as the cause of the freezing potentials. It is opportune to recall here that the potentials which result from thermal gradients are small compared to the enormous potentials developed during freezing of aqueous solutions; these may reach 200 volts for NH_4^+ as compared to a few millivolts for a typical thermal effect on ice.(8)

Before trying to give a quantitative basis for a physical phenomena efforts must be made to reproduce the phenomena and measure with precision the fundamental parameters. Unfortunately the measurements on freezing potentials of aqueous solutions are not easily reproducible. This fact makes comparison difficult if not impossible with the values reported in previous papers.(6) Most of the devices employed until the present moment use a metal block cooled by liquid air; water in contact with this block solidifies and produces the freezing potential. Two factors at least appear to contribute to the lack of reproducibility of the phenomena. They are: a) lack precise temperature control in the system, b) gases dissolved in the water phase and entraped in the ice. The lack of a convenient method to afford temperature control in the block and in the ice

itself seems to be the major cause of the trouble. Because it is difficult to reproduce a certain value of freezing potential for the same solution it is customary to make a series of experiments and report the largest value for the freezing potential.[6] An improved apparatus and freezing cell was designed; this is the subject of the present paper.

The freezing potential apparatus.

The freezing potential apparatus has three main parts. They are:

i) the freezing potential cell,

ii) the freezing well,

iii) the measuring and recording devices.

A brief description of each part follows.

i) The freezing potential cell consists of a small Teflon cup (~1 ml) fitted with a gold bottom. This is thick enough to accommodate a Chromel-Alumel thermocouple. The cell sits on a brass block placed in the freezing well. Previous calibration allows both the temperature of the block and the bottom to be known at any moment, thereby permitting adequate temperature control to be obtained. The cell is

depicted in Figure (4); it will allow studies to be performed in the absence of CO_2 which may be an interfering factor.

ii) The freezing well

The freezing well is cooled by thermoelectric pumping; temperatures as low as - 40°C can be obtained in a few minutes. The heart of the device is a thermoelectric module; the whole freezing unit shown in Figure (5) and measuring 4" x 5" x 2" was made to order by Frigitronic (Bridgeport, Conn.)

The freezing unit was supplied on request with a Copper-Constantan thermocouple which permits, after calibration, the determination of the well temperature as a function of the power pack output. Calibration curves were run to establish the dependence of the temperatures of both the block and well as a function of the input current. These are given in Figure (7). A third thermocouple introduced in the ice permits to obtain its temperature; this is well above that of the block. Preliminary studies with ammonium hydroxide solutions gave potentials of + 90 volts (for 1×10^{-5}N). The experiments performed show that the temperature of the ice is of importance and to the best of our knowledge has never been reported.

iii) Electronic Circuit

The electronic circuit whose block diagram is given in Figure (6) consists of the Moseley Autograph 4B and Keithley 610A; this measures the potentials. A Keithley microvoltmeter 150A measures the output of the several thermocouples used in the experiment. The output of both Keithley electrometers are fed into the two Y axis of the recorder; the X axis records time. The apparatus after calibration of the thermocouple was checked using the cell depicted in Figure (4). Dilute solutions of ammonium hydroxide were employed. Potentials up to + 90 V were measured for 1×10^{-5}N $HONH_4$ at - 30°C, block temperature. These values are lower than 200 volts reported early in the literature.(6) It was observed that those values could be reproduced wtihin $\pm$ 4 volts; carbon dioxide was not eliminated from the system. A concentration dependence curve was obtained and shows a very sharp discontinuity at certain critical concentration. Below and above this critical point the values of the freezing potential were either trivial or non existent. Full details will be given in the next report.

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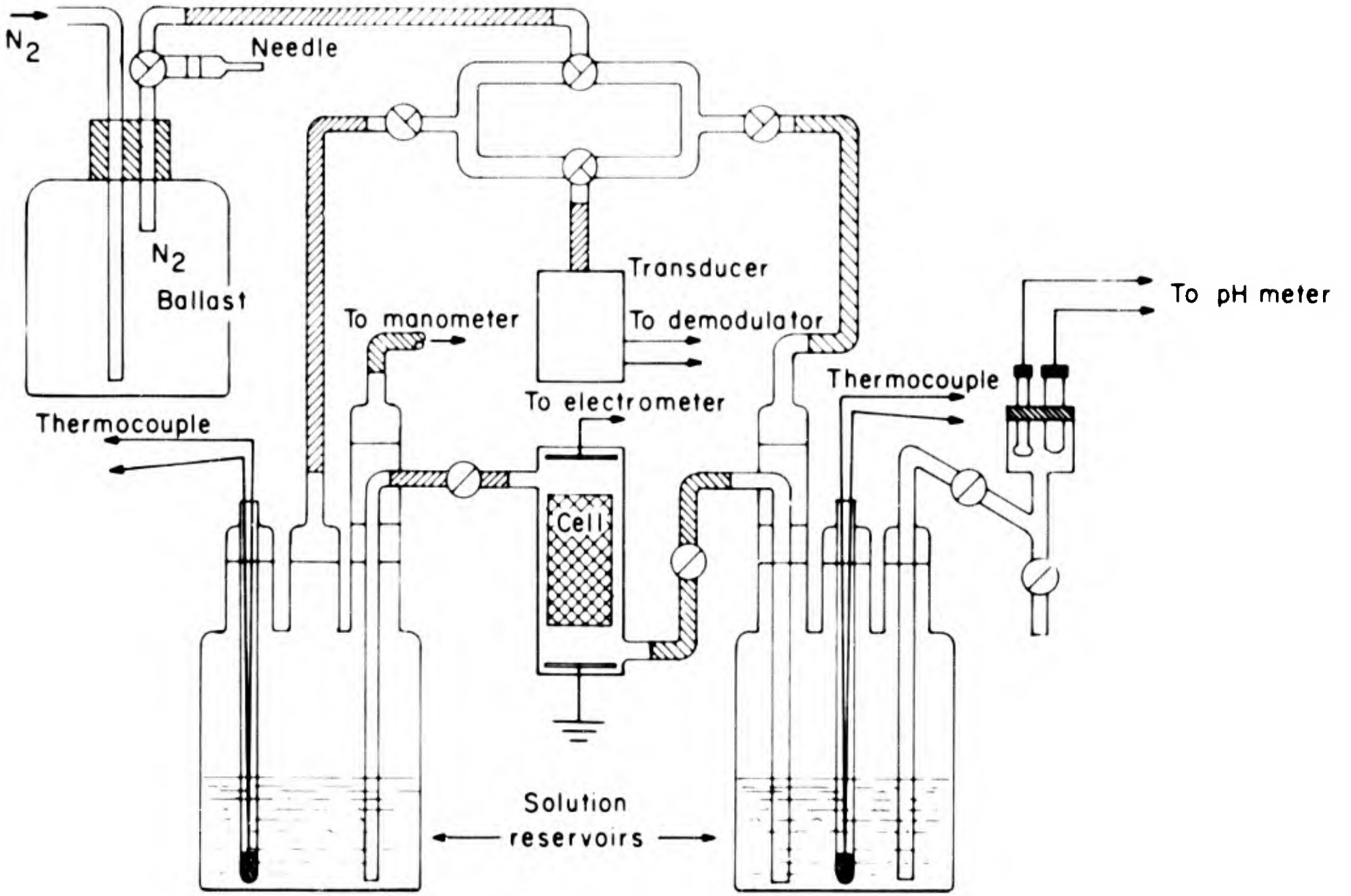
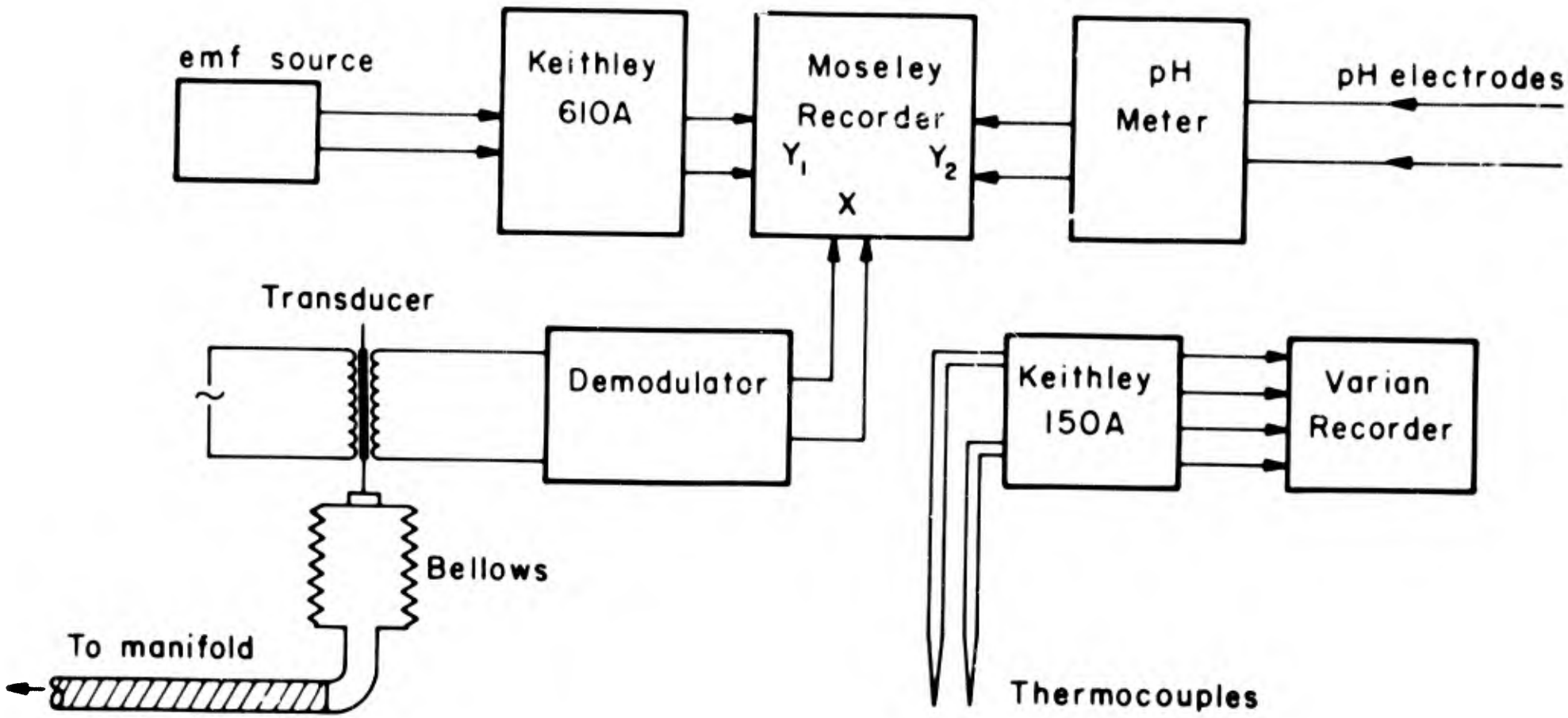


STREAMING POTENTIAL APPARATUS

Fig. 1

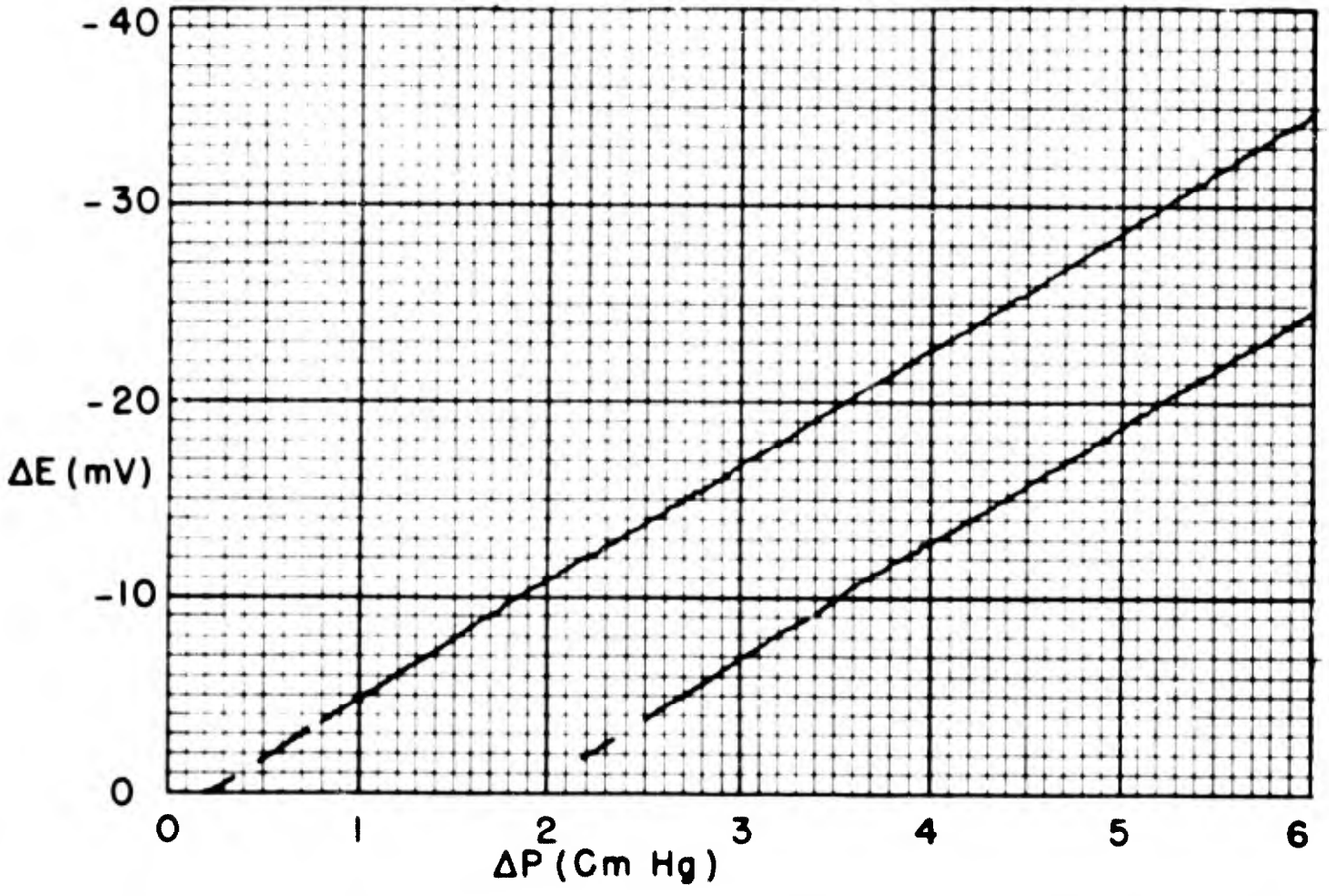


STREAMING POTENTIAL APPARATUS
BLOCK DIAGRAM OF ELECTRONIC CIRCUIT.

Fig. 2

Streaming from right to left (+ΔE); upper curve

Streaming from left to right (−ΔE); lower curve



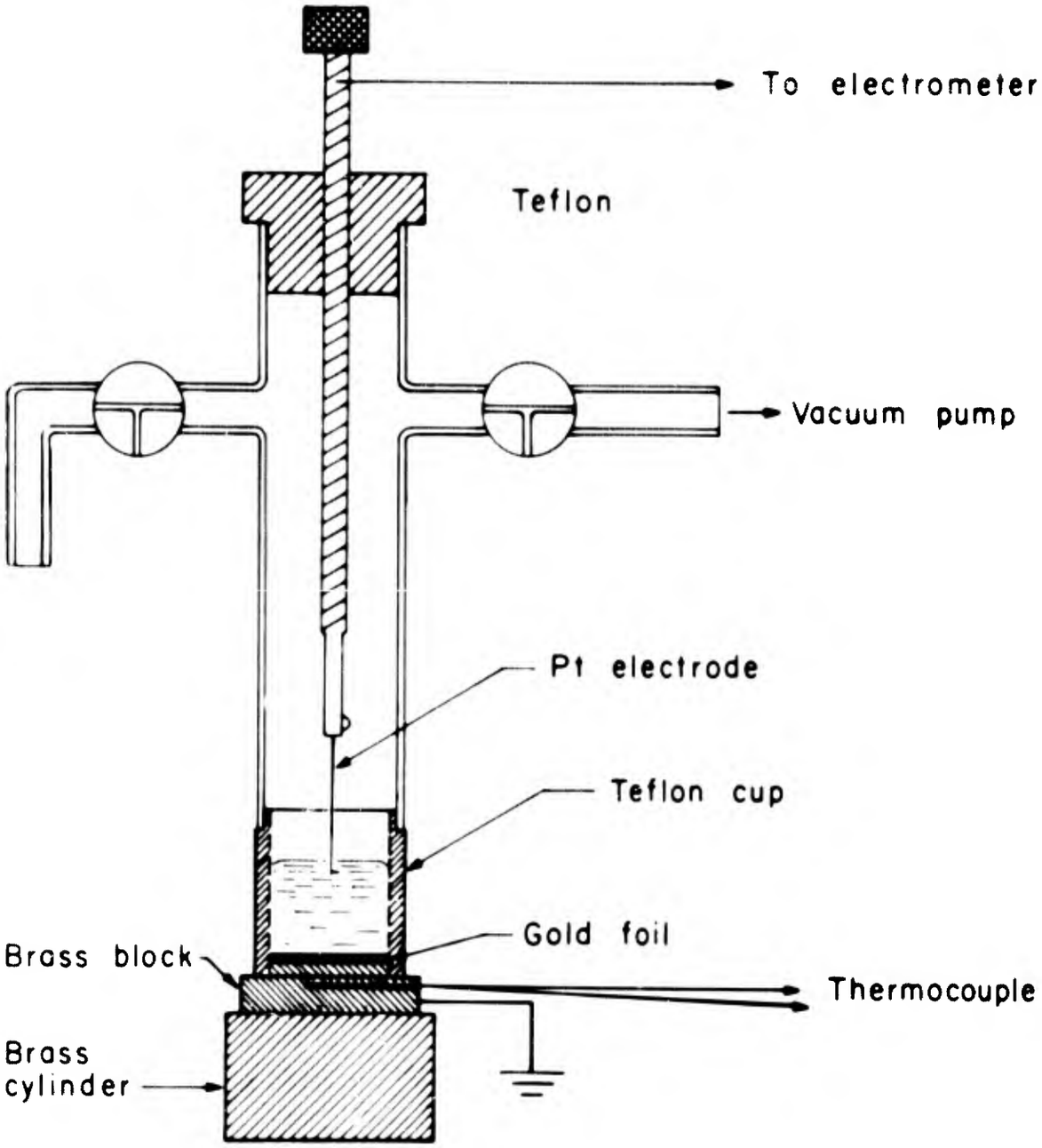
Material : quartz 28/35 mesh

Electrolyte : 2.5 M Kcl, pH = 5.8

Plug size : 1.0 x 1.0 cm

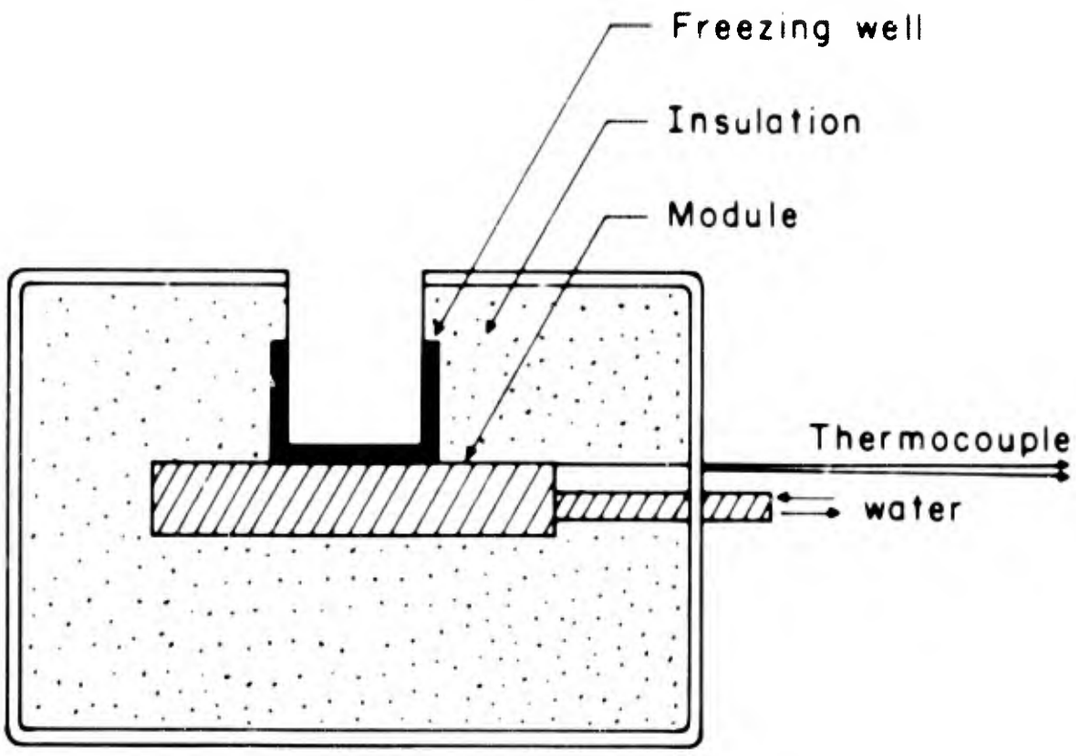
Electrodes : Ag / Ag Cl

Fig. 3



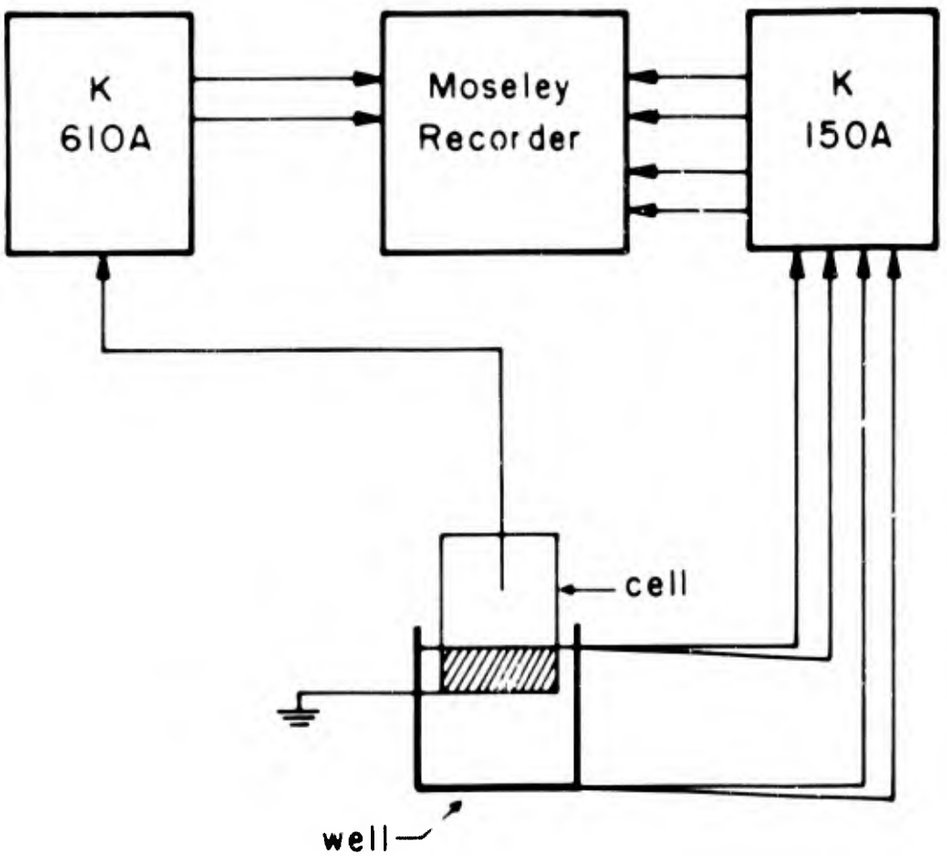
FREEZING POTENTIAL CELL

Fig. 4



FREEZING WELL

Fig. 5



FREEZING POTENTIAL APPARATUS
BLOCK DIAGRAM

Fig. 6

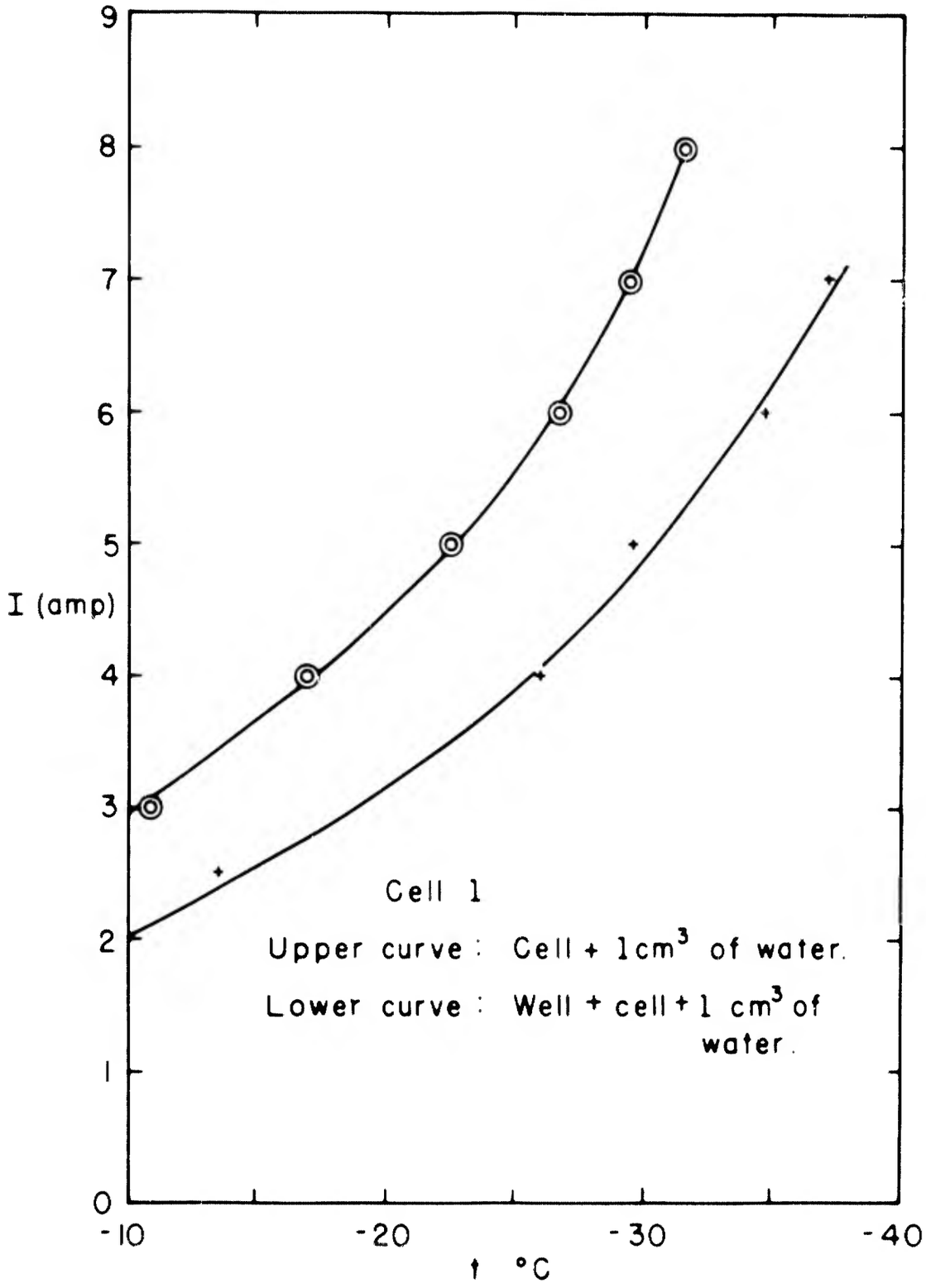


FIG. 7 MODULE CURRENT vs. TEMPERATURE