

CATION ERRORS OF THE
GLASS ELECTRODE AT HIGH TEMPERATURES

Max F. Smith

A THESIS SUBMITTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE MASTER OF SCIENCE

May 30, 1939

CONTENTS

Introduction	Page 1
Apparatus	5
Experimental Procedure	8
Experimental Results	10
Theory of Glass Electrode	15
Summary	18

CATION ERRORS OF THE
GLASS ELECTRODE AT HIGH TEMPERATURES

INTRODUCTION

Cremer (1) discovered that a definite potential existed between an acid and an alkaline solution when the two solutions were separated by a thin glass membrane. He surmised that the glass membrane was permeable only to hydrogen ions, from earlier work on ion migration through glass, but did not realize that the potential was a function of the hydrogen ion concentration in the two solutions. Haber and Klemensiewicz (2) were the first investigators to show that the glass membrane functioned as a hydrogen electrode and that the potential followed the Nernst equation

$$E = \frac{RT}{F} \ln \frac{H_2}{H_1} \quad (1)$$

where H_1 and H_2 are the hydrogen ion concentrations in the solutions on either side of the membrane. The glass membrane used by these investigators was a simple thin-walled bulb blown on the end of a test tube. The tube was filled with a solution of fixed hydrogen-ion concentration and was immersed in other solutions of various hydrogen

ion concentrations. Calomel reference electrodes dipped into the internal and external solutions. The potential developed by the cell was measured by means of a potentiometer and quadrant electrometer. The bulb-type glass membrane was subsequently used by many investigators for the measurement of hydrogen ion concentration and became known as the Haber Glass Electrode.

The glass electrode is unique among hydrogen ion electrodes in that it is unaffected by the presence of oxidizing or reducing substances and is not poisoned by substances which often interfere with the use of other electrodes, such as the hydrogen, quinhydrone, antimony, etc. The glass electrode may be used in the presence of colloids and suspended solids and in various viscous materials. Despite these advantages, the glass electrode was not widely used for many years because the high electrical resistance of the glass membrane necessitated the use of a quadrant electrometer for the potential measurement. The development of modern electronic circuits which could be used in place of the delicate quadrant electrometer has brought about a wide-spread use of the glass electrode and today, the glass electrode is one of the most

commonly used means for the measurement of hydrogen-ion concentration.

The glass electrode deviates in several respects from the behavior theoretically expected from a hydrogen-ion electrode. If identical solutions are placed on the two sides of the glass membrane and identical reference electrodes dipped into the two solutions, the theoretical potential between the two electrodes is zero. Actually there is usually a slight potential, known as the "Asymmetry Potential". The potential is presumably due to slight differences in the compositions of the two surfaces of the glass membrane. The potential usually does not exceed a few milli-volts and remains substantially constant over long periods of time, at room temperatures, so that no error from this source is ordinarily encountered in practical measurements. The glass electrode is usually standardized by means of buffer solutions of known hydrogen ion concentration (pH) so that the correction for asymmetry potential is automatically included in the standardization.

A more serious error of the glass electrode, from the standpoint of industrial pH measurements,

is the error caused by high alkali-ion concentrations in the high pH region. Particularly in the presence of sodium ions, the glass electrode yields pH values which are smaller than the true pH values. The magnitude of the error increases with increasing pH, increasing alkali-ion concentration and increasing temperature. Metallic cations other than sodium produce similar errors but their effects are very much smaller than that of sodium ions.

Dole (3) made an extensive study of alkali-ion errors at 25° C. Dole and Wiener (4) measured sodium and lithium-ion errors at 10°, 25° and 50° C. Gardner and Sanders (5) measured the sodium-ion errors of two commercial electrodes at 30°, 50° and 60° C. Unfortunately these investigators used electrical measuring equipment which was not provided with temperature compensation so that the published values combine sodium errors with an indefinite temperature error.

There is evidence that the magnitude of the alkali-ion error depends upon the composition of the glass from which the membrane is made. Ssokalov and Passynsky (6) stated that a lithium glass containing 80% SiO₂, 10% CaO and 10% Li₂O showed much smaller errors than the soda-lime

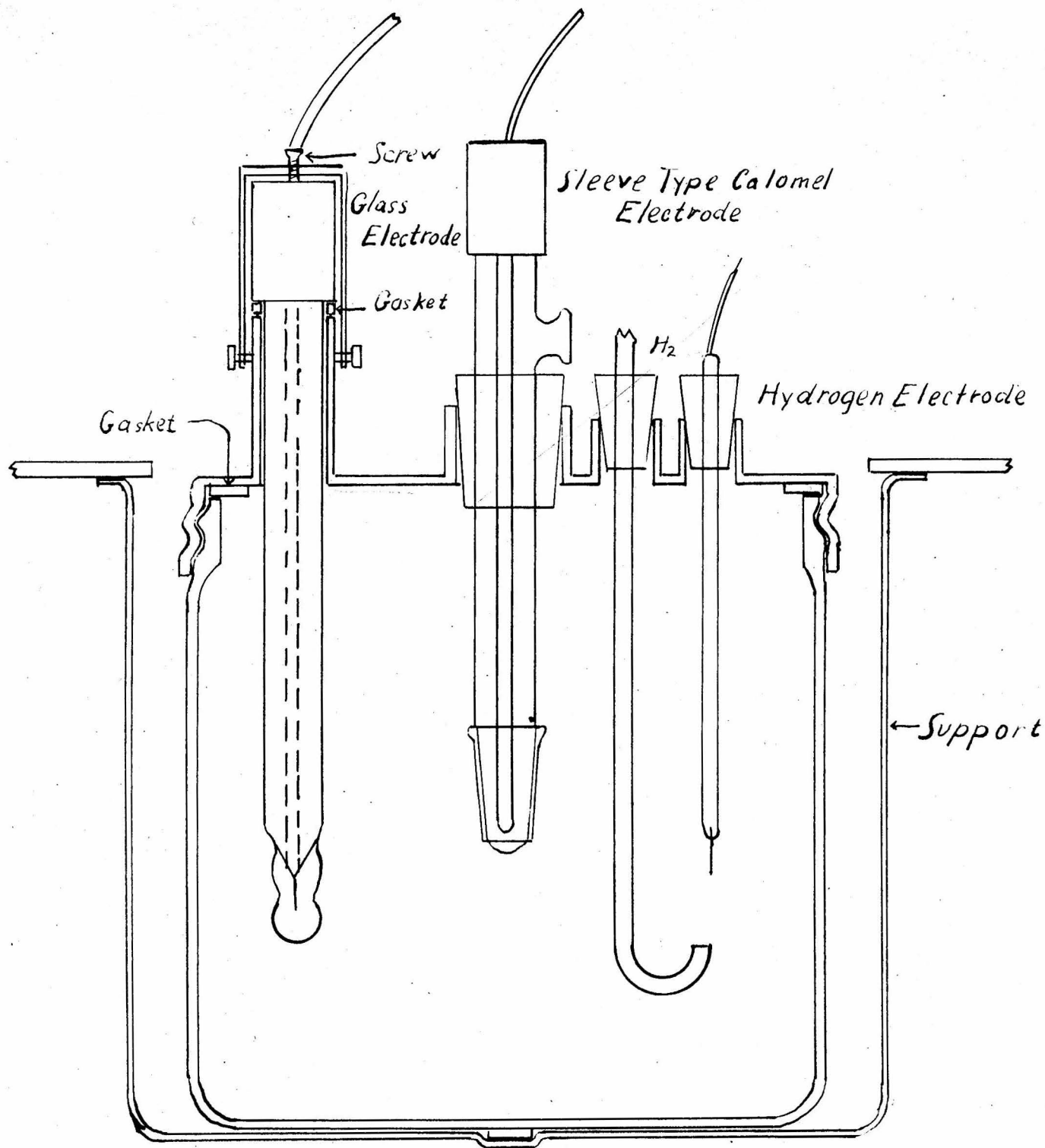


fig I Arrangement of Cell

glass usually used. Gabbard and Dole (7) attempted to make glass electrodes of this composition but found them unsatisfactory. At present, commercial glass electrodes are made of a soda-lime-silica glass known as Corning 015, consisting of approximately 22% Na_2O , 6% CaO and 72% SiO_2 .

Despite future improvements in glass which may provide better glass electrodes, there is an immediate need for reliable and extensive measurements of alkali-ion errors of electrodes made from the 015 glass. The recent extension of glass electrode applications into high temperature regions makes high temperature values particularly desirable. The present work was undertaken for the purpose of supplying the needed data.

APPARATUS

The glass electrodes were supplied by the National Technical Laboratories and were made as follows: Corning 015 glass was blown into a bulb on the end of a ten millimeter diameter lead glass tube; the lead glass being of very high resistivity, reduced the electrical leakage to a minimum. The glass membranes themselves were about 0.0075 of an inch thick and had resistances at

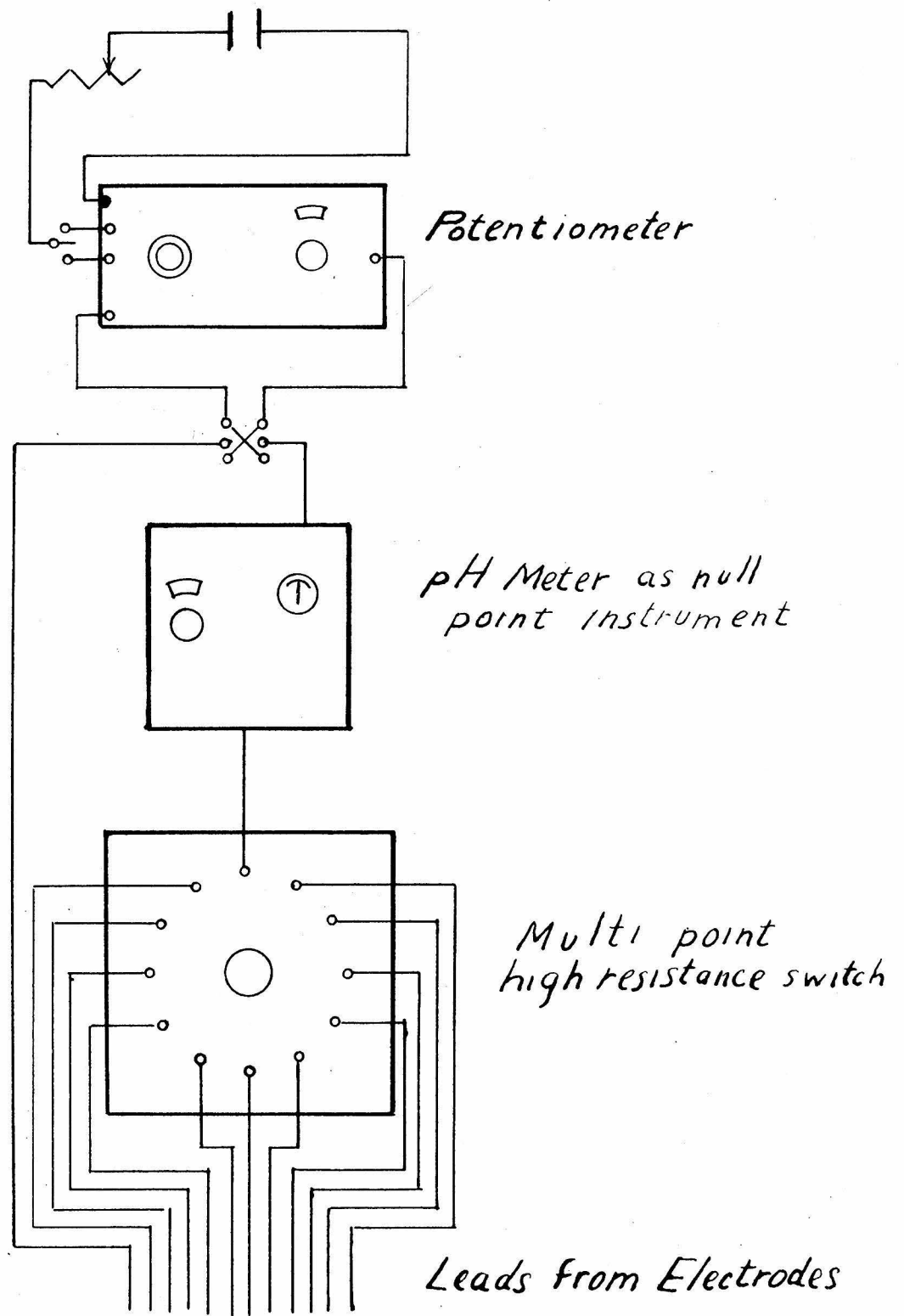


fig II Potentiometer Circuit

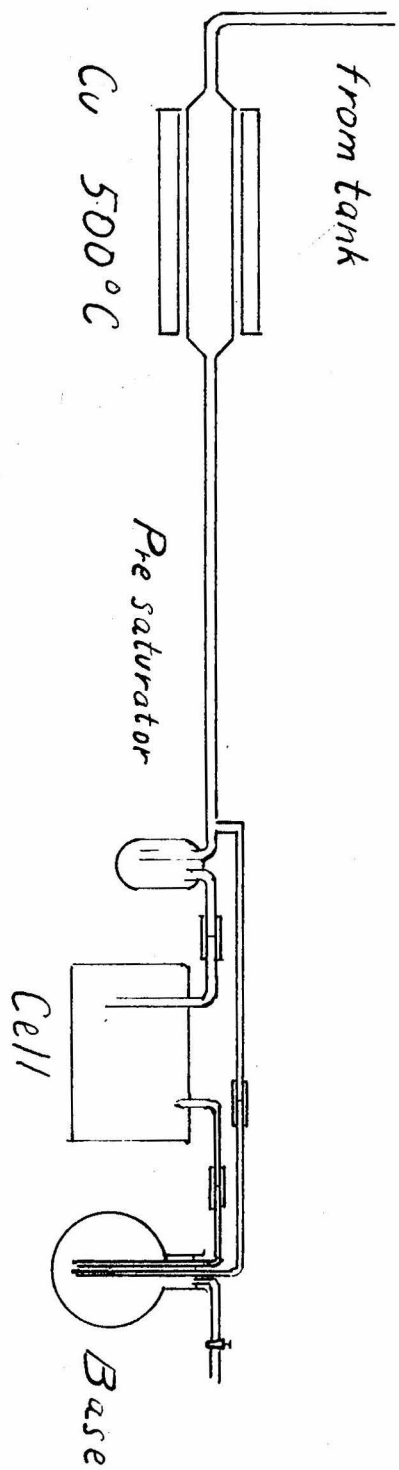


Fig III Hydrogen Gas Train

25° C. of 100 to 150 megohms. Permanent internal solutions and electrodes were sealed in. Shielded leads extended into the electrode to within an inch of the bottom so that electrostatic disturbances were completely avoided.

The glass electrodes were compared directly with hydrogen electrodes in the cell illustrated in figure 1. There were fifteen openings for; six glass electrodes, three hydrogen electrodes, one calomel electrode, a hydrogen inlet and outlet, a thermometer, a glass tube for adding and a siphon for removing solution. The cell was supported in an oil-filled thermostat.

The circuit used for measurement of the potentials is shown in figure 11. The glass and hydrogen electrode leads were connected to a Beckman pH meter amplifier through a multi-point high resistance switch which made the comparison of many glass electrodes a simple matter. The potentiometer was a Leeds and Northrup student type, which could be read within ± 0.1 mv.

Hydrogen electrodes made of platinum wire were entirely satisfactory. The platinizing solution was prepared by dissolving cleaned waste platinum wire in aqua regia, evaporating the

solution to dryness, adding water and evaporating to dryness again. The residue was dissolved in distilled water and was used without further treatment such as the addition of lead acetate. It was found that the pH of the platinizing solution made very little difference in the action of the hydrogen electrodes as long as a steady stream of hydrogen was used. The electrodes were cleaned in aqua regia and then purged of chlorine by electrolyzing in 1.0 N. H_2SO_4 for fifteen minutes or by dipping alternately in boiling concentrated HNO_3 and boiling 10% sodium acid sulphite. The same effect was produced by allowing them to stand in distilled water for two or three days.

A Beckman sleeve-type saturated KCl-calomel electrode was used for the reference electrode. This electrode was checked against two other saturated KCl-calomel electrodes and three 0.1 N. KCl-calomel electrodes. An experiment to determine the leakage of KCl solution out of this type of electrode showed a maximum value of 0.003 moles of KCl in twenty-four hours; this was not enough to effect the results of the experiments in any way.

The cell used for the comparison of the glass and hydrogen electrodes was kept in a thermostat filled with low conductivity transformer oil. The constant temperatures that were required

were maintained by a 100 c.c. mercury regulator connected through a vacuum tube relay to two knife heaters. An electric motor was used for agitating the oil bath, but it was disconnected while the readings were being taken. A separate thermostat was kept at 25° C.; this thermostat contained two standard cells and the 0.1 N. KCl-calomel half-cells.

The hydrogen gas train is shown in figure 111. Thick-walled rubber tubing connections were used where necessary; this tubing was first boiled in concentrated NaOH and then impregnated with paraffin. The hydrogen was saturated with water vapor before entering the cell in order to keep the concentration of the cell solution constant during a run.

EXPERIMENTAL PROCEDURE

The procedure was a modification of that used by Dole(8) in which the concentration of the cation is kept constant during the experiment. The glass and hydrogen electrodes were compared in the same solution as was first done by Hughes(9).

A buffered solution of the acetate and phosphate of the cation under investigation was placed in the cell; the electrodes were then placed in position and the entire assembly lowered into the thermostat. The hydrogen was started through

the cell and through the flask containing the base solution to be used for changing the pH of the cell solution. When the hydrogen electrodes gave constant values, usually in two to two and one-half hours, the potentials of the glass and hydrogen electrodes were recorded. The pH of the solution in the cell was then changed by closing the stopcock on the hydrogen outlet from the flask and letting the pressure of the hydrogen force the base solution from the flask into the cell. When the stopcock was opened the base solution in the line to the cell ran back into the flask. Since the base added had been saturated with hydrogen and it was introduced without allowing oxygen to enter the cell, the hydrogen electrodes came to equilibrium at once. The potentials of the glass electrodes became constant in about ten minutes; they took somewhat longer in potassium solutions below 40° C. Thirty to forty minutes were usually allowed to make certain that equilibrium was reached.

The potentiometer circuit was standardized against the two standard cells that were kept in the 25° C. thermostat. The standardization was done through the amplifier. The low input current of the electronic circuit (2×10^{-13} amps.) allowed the standard cells to be connected without polarization even though the circuit might be far out of balance.

EXPERIMENTAL RESULTS

The cells which were considered in this investigation were:

1. Pt H₂ | solution X || saturated KCl | Hg₂Cl₂ | Hg
2. Ag | AgCl | $\begin{array}{c} \text{Const. Cl}^- \\ \text{Const. H}^+ \end{array}$ | Glass | solution X || saturated KCl | Hg₂Cl₂ | Hg

If we subtract the potentials of these two cells we obtain the potential for the cell

3. Pt H₂ | solution X | glass | $\begin{array}{c} \text{const. Cl}^- \\ \text{const. H}^+ \end{array}$ | AgCl | Ag

Using the same terminology as Dole and Wiener (4) and calling this potential ΔG , then by definition

$$\Delta G = E_1 - E_2$$

It has been pointed out that at high pH ΔG varies with the metallic cation present, its concentration and the pH of the solution. If the potential which would be observed, if the glass electrode functioned as a perfect hydrogen-ion electrode, is called ΔG_0 , then the error of the glass electrode ΔE can be found.

$$\Delta E = \Delta G - \Delta G_0$$

ΔG_0 is found by making measurements in the low pH range where the glass electrode does act as a perfect hydrogen-ion electrode. The preceding discussion will be illustrated later by the consideration of a specific case.

The pH of the buffer solutions at the various temperatures was determined^e by the hydrogen electrode; i.e. the potential of cell 1. Since the E.M.F.-temperature

relations of the saturated KCl-calomel electrode are not well established at the higher temperatures used in this investigation, the pH values were referred to 0.05 N. potassium hydrogen phthalate with the assumption that the pH of this solution does not change with temperature. Clark (10) gives the pH of this solution as 3.98. Recently MacInnes, Belcher and Shedlovsky (11) have recommended^d the values 4.00 at 12°C, 4.00 at 25°C and 4.015 at 38°C. Despite the probable greater accuracy of this work, the value 3.98 was used in the following computations because the other values have not been widely accepted. The uncertainty in the pH values of the potassium hydrogen phthalate buffer at the various temperatures is only of secondary importance in this investigation for it does not enter directly into the alkali-ion errors. It appears only in the indicated pH values of the solutions. A large change in the pH values of these solutions would cause only a slight shift in the error curves shown in the following figures.

At each temperature the hydrogen and calomel electrodes were immersed in 0.05 N potassium hydrogen phthalate solution and the cell potential (E) determined. From the equation

$$E - E' = \frac{2.303 RT}{F} \text{pH} \quad (2)$$

the quantity E' was found for each temperature. This quantity includes the E.M.F. of the calomel reference cell, the liquid junction potential and the correction

for the reduced partial pressure of the hydrogen gas at the hydrogen electrode. The experimental values are shown in the following table

TABLE 1

<u>Temperature</u>	<u>E' (volts)</u>
30° C	-0.2420
40°	-0.2338
50°	-0.2255
60°	-0.2174
70°	-0.2093

The experiments included in this investigation are the measurements of cation errors of the glass electrode at the following temperatures and concentrations.

<u>Temperature</u>	<u>Cation Concentration</u>
30°, 40°, 50°, 60°, 70° C	0.1, 1.0, 2.5 N sodium-ion
30°, 40°, 50°, 60°, 70°	0.1, 1.0 N potassium-ion
30°, 50°, 60°	2.5 N potassium-ion
30°, 40°, 50°, 60°	1.0 N lithium-ion
30°, 40°	2.0 N lithium-ion
40°, 50°, 60°, 70°	0.1 N lithium-ion
30° 60°	0.01 N calcium-ion

Typical experimental data and computed results are given in table II. The values are for 2.5 N sodium-ion at 50°C. H_1 , H_2 and H_3 are the measured potentials (in volts) of the cells composed of a calomel reference electrode and three individual hydrogen electrodes. This is the potential of cell

1 given above. $G_1, G_2 \dots G_7$ are the corresponding potentials of the same calomel electrode and seven individual glass electrodes. This comprises cell 2 given above. The measurements were made on nine different solutions. The pH values shown were obtained by the use of equation 2, the value of E' for the temperature in question and the average value of H_1, H_2 and H_3 . $\Delta G_1 \dots \Delta G_7$ are the algebraic differences between $G_1 \dots G_7$ and the average value of H_1, H_2 and H_3 . This of course is the potential of cell 3. $\Delta E_1 \dots \Delta E_7$ are the sodium-ion errors of the respective glass electrodes; i.e., the differences between the measured glass electrode-calomel electrode potentials and the corresponding potentials which would have been obtained if the glass electrode functioned as an ideal hydrogen-ion electrode. The latter potentials were obtained from the values of ΔG in the low pH region, where the alkali-ion errors are negligible. This procedure will also eliminate the asymmetry potential. If there were no alkali-ion error, the values of ΔG , for a given electrode, would remain constant with increasing pH. If the average value of ΔG in the region of negligible cation error is called ΔG_0 , then the cation errors are obtained by subtracting ΔG_0 from the measured values of ΔG .

The age of the glass electrode appears to have very little effect upon the cation errors except in the

case of sodium-ions. There is some evidence that freshly blown glass electrodes show somewhat smaller sodium-ion errors than are shown by old electrodes. In Table II, electrodes G₄ and G₇ were freshly blown electrodes. The effect of age, however, appears to be less than the variations normally found among individual electrodes.

All experimental results are summarized in Figures 4 to 17. The points shown on the graphs represent the average values obtained for at least five glass electrodes in each case.

In Table III alkali-ion errors published by other workers are compared with the corresponding values obtained in this investigation. In general the agreement is satisfactory for most practical measurements. For refined pH determinations where large sodium-ion errors are involved and where the age of the glass electrode may be an important factor, direct determination of the sodium-ion error should be made under the actual operating conditions.

TABLE IIIa

Rounded off values of glass electrode errors at 30° C.

<u>pH</u>	<u>0.1 Na</u>	<u>1.0 Na</u>
9	0 (2) mv.	2 mv.
9.5	1 (4)	5 (5.5)
10	2 (6.4)	12 (11.5)
10.5	7 (9.4)	21 (18.5)
11	13 (14.4)	34 (30.3)
11.5	23 (21.3)	52 (45.2)
12	34 (38.5)	75 (63.1)

Values in parenthesis are those of J. L. Gabbard and Dole (7).

TABLE IIIb

Rounded off values of glass electrode errors at 50° C.

<u>pH</u>	<u>0.1 Li</u>	<u>1.0 Li</u>	<u>0.1 Na</u>	<u>1.0 Na</u>
9	3 mv.	0 (3) mv.	2 (21) mv.	14 (7.1) mv.
9.5	5 (1)	10 (8)	7 (4.3)	25 (12.9)
10	7 (3)	20 (17)	15 (10)	40 (25.4)
10.5	13 (7.5)	34 (30)	27 (18)	59 (39.0)
11	19 (14.2)	51 (46)	41 (27)	83 (58.5)
11.5	27 (25.5)	71 (68)		108 (75.5)
12		94 (98)		

Values in parenthesis are those of Dole and Wiener (4).

TABLE II

2.5N Na 50° C

	H ₁	H ₂	H ₃	G ₁	G ₂	G ₃	G ₄	G ₅	G ₆	G ₇
1.	.5630	.5630	.5630	-.1137	-.0814	-.0820	-.0321	-.0621	-.1518	-.0178
2.	.6312	.6312	.6312	-.0475	-.0157	-.0148	.0345	-.0037	-.0959	.0482
3.	.7168	.7166	.7167	.0343	.0687	.0694	.1184	.0872	-.0013	.1324
4.	.7914	.7915	.7915	.0864	.1255	.1277	.1793	.1415	.0582	.1922
5.	.9562	.9561	.9561	.1355	.1803	.1832	.2457		.1153	.2578
6.	.8410	.8410	.8410	.1104	.1538	.1556	.2080	.1782	.0862	.2208
7.	.8998	.8998	.8998	.1268	.1708	.1744	.2308	.1861	.1048	.2420
8.	.9562	.9560	.9561	.1342	.1787	.1821	.2420	.1954	.1130	.2518
9.	.9995	1.0115	1.0115	.1355	.1842	.1877	.2483	.1991	.1191	.2582

	H (average)	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7
1.	.5630	.6767	.6444	.6450	.5951	.6251	.7148	.5808
2.	.6312	.6784	.6469	.6460	.5967	.6275	.7363	.5830
3.	.7166	.6823	.6479	.6472	.5982	.6294	.7189	.5842
4.	.7915	.7051	.6660	.6638	.6122	.6500	.7333	.5993
5.	.9561	.8206	.7759	.7729	.7104		.8408	.6983
6.	.8410	.7306	.6972	.6854	.6330	.6728	.7548	.6202
7.	.8998	.7730	.7290	.7254	.6600	.7137	.7950	.6578
8.	.9561	.8219	.7774	.7740	.7141	.7607	.8386	.6998
9.	1.0115	.8720	.8233	.8298	.7592	.8085	.8884	.7493

	pH	Ave. ΔE mv.	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7
2.	6.407	2.1	.0027	.0025	.0010	.0016	.0024	.0215	.0022
3.	7.665	3.8	.0056	.0035	.0022	.0031	.0043	.0041	.0034
4.	8.832	21.2	.0284	.0216	.0198	.0171	.0249	.0185	.0185
5.	11.402	127.6	.1439	.1315	.1279	.1153		.1260	.1175
6.	9.602	44.6	.0539	.0528	.0404	.0379	.0477	.0400	.0394
7.	10.527	83.3	.0963	.0846	.0804	.0649	.0896	.0802	.0670
8.	11.402	129.2	.1452	.1330	.1290	.1190	.1356	.1238	.1190
9.	12.202	182.4	.1993	.1829	.1888	.1681	.1874	.1776	.1725

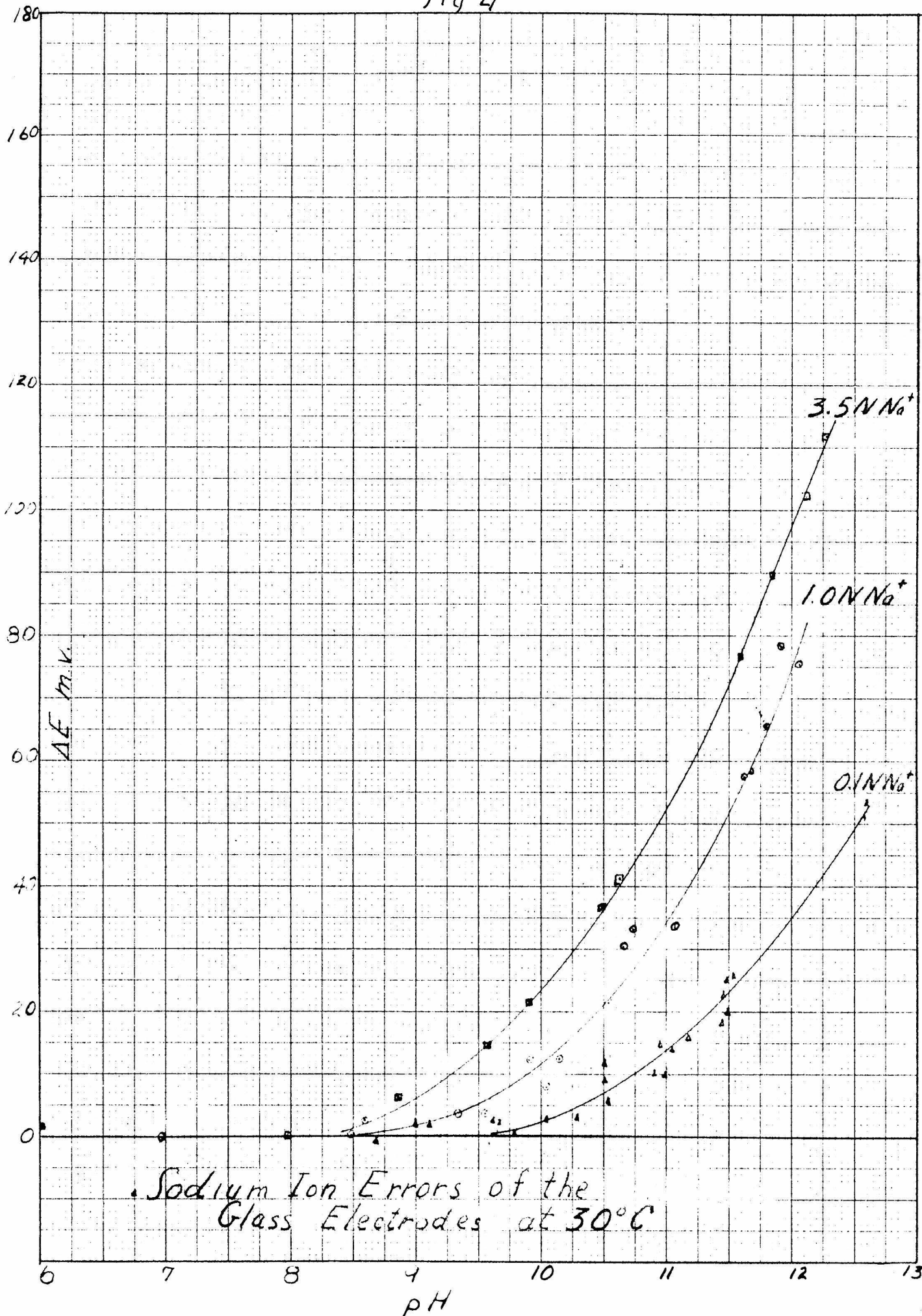
H₁ - 3 The potential in volts of three hydrogen electrodes.

G₁ - 6 The potential in volts of six glass electrodes.

ΔG_1 - 6 The difference in volts of the potential of the average hydrogen electrode and the potential of the individual glass electrodes.

E₁ - 6 $\Delta G - G_0$ or the increase of G caused by the presence of sodium ions.

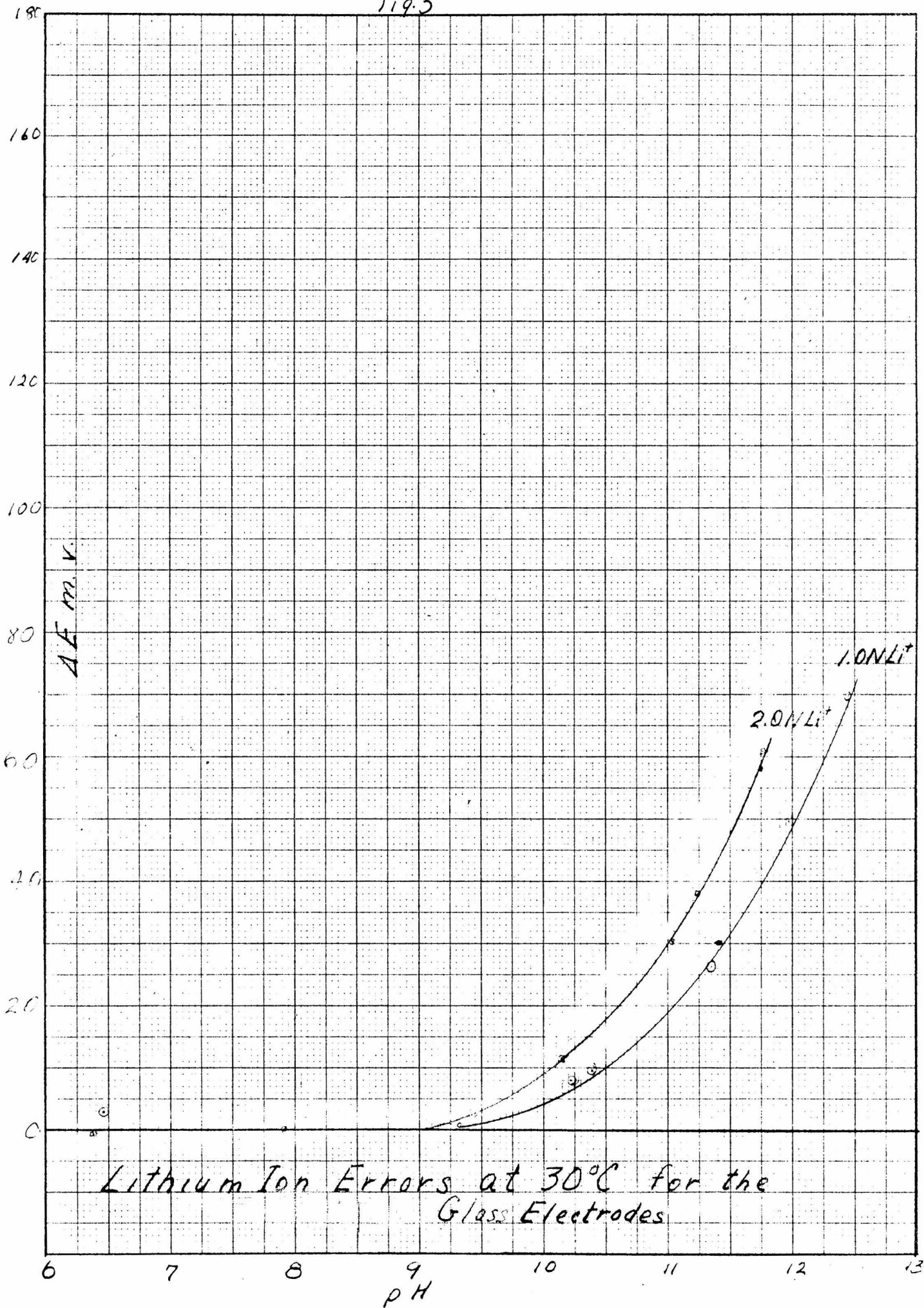
fig 4



Sodium Ion Errors of the Glass Electrodes at 30°C

KEUFFEL & ESSER CO., N. Y. NO. 35-411
25 N. 2ND ST. PHILADELPHIA, PA.
MADE IN U.S.A.

fig. 5



KEUFFEL & ESSER CO. N. Y. NO. 351-11
200 E. 42nd St. New York 17, N. Y.

Lithium Ion Errors at 30°C for the Glass Electrodes

fig. 6

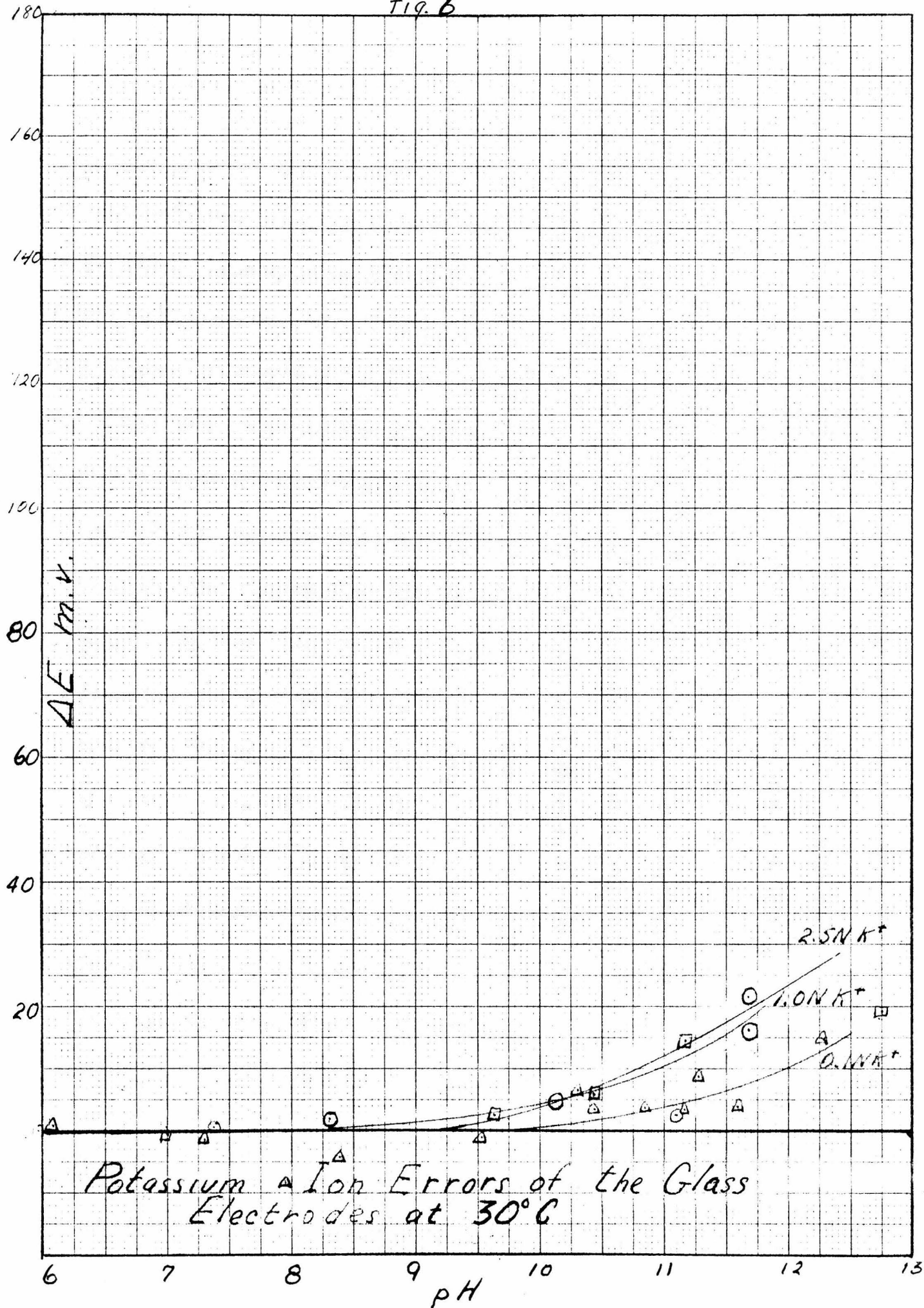
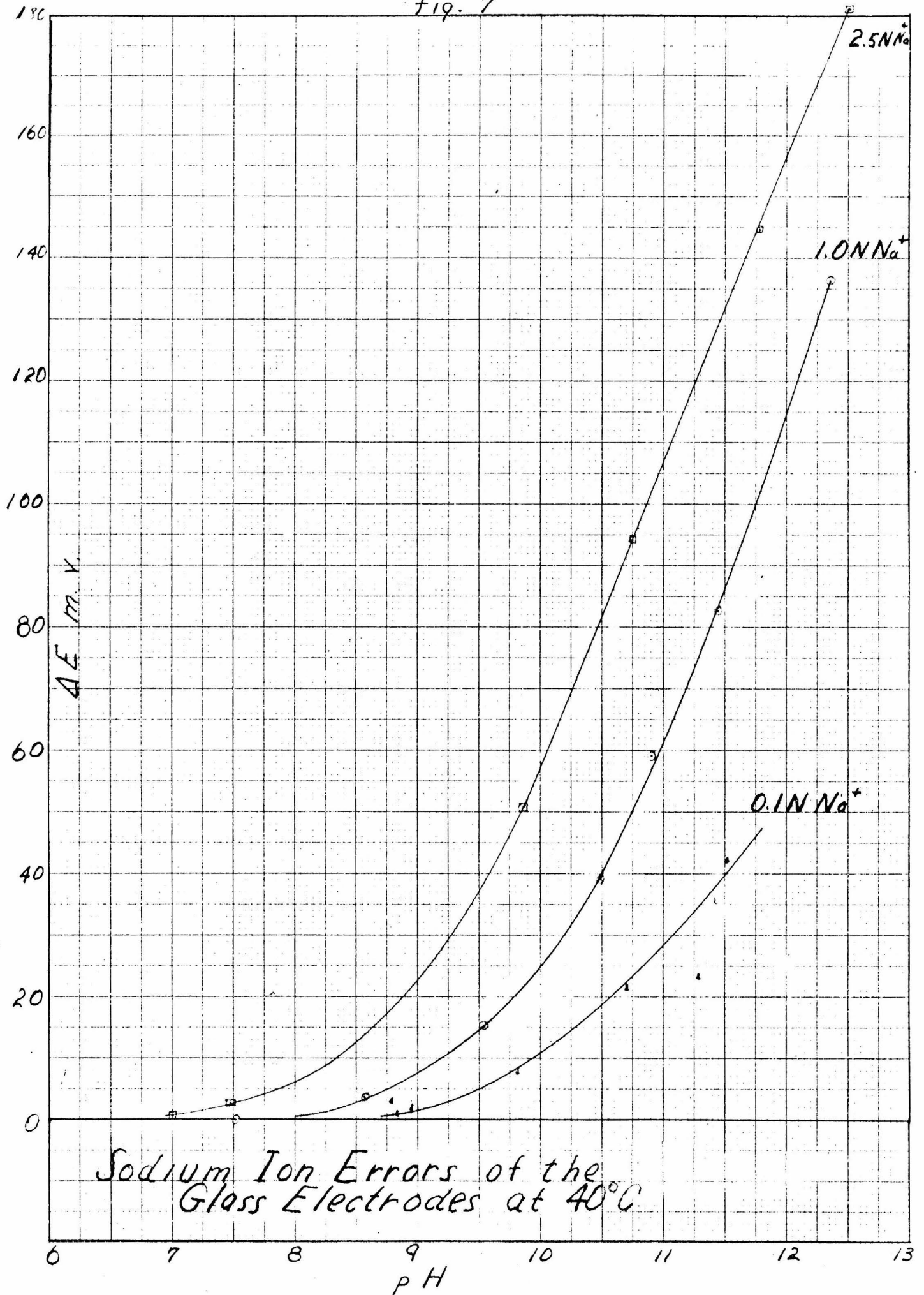
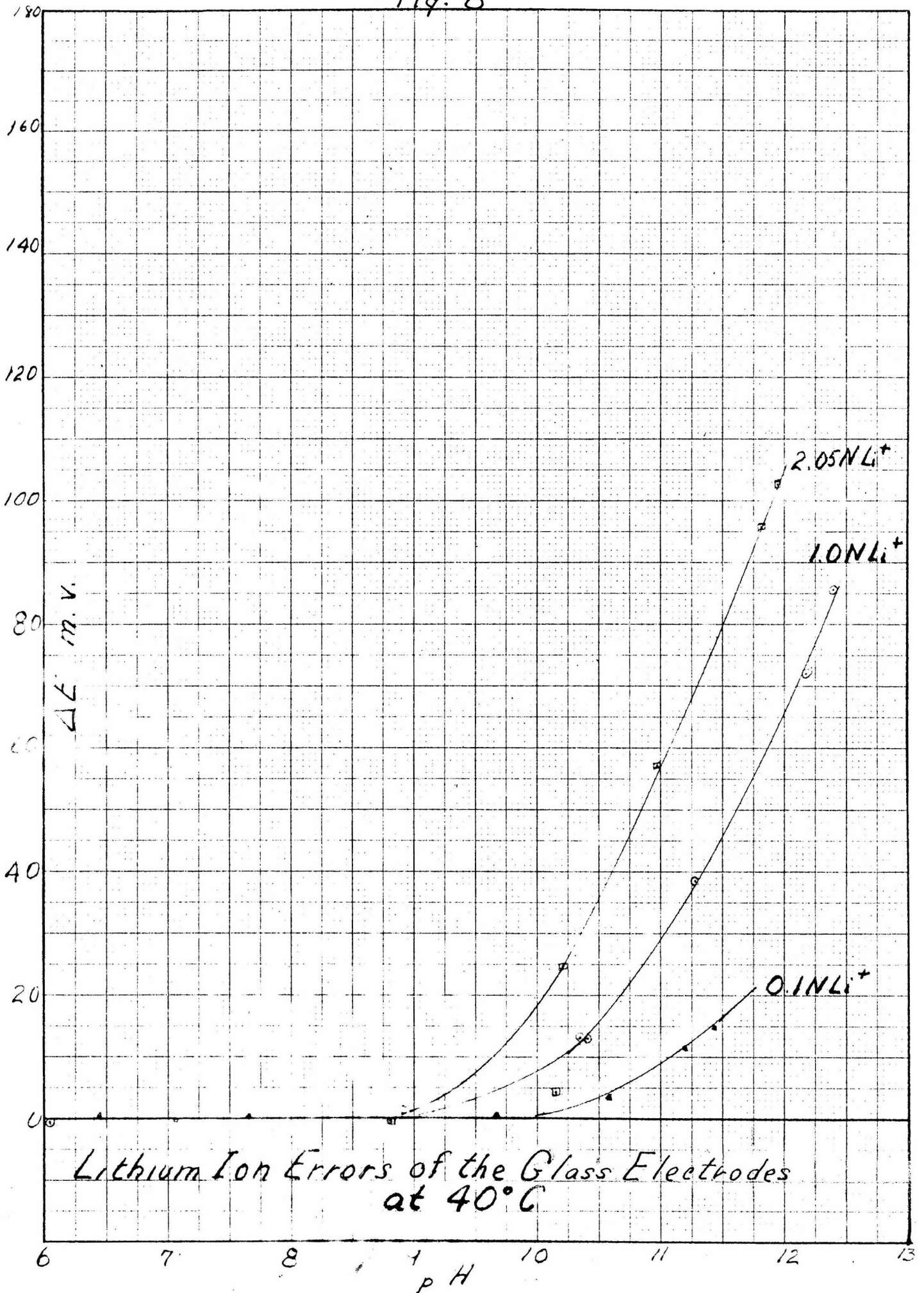


fig. 7



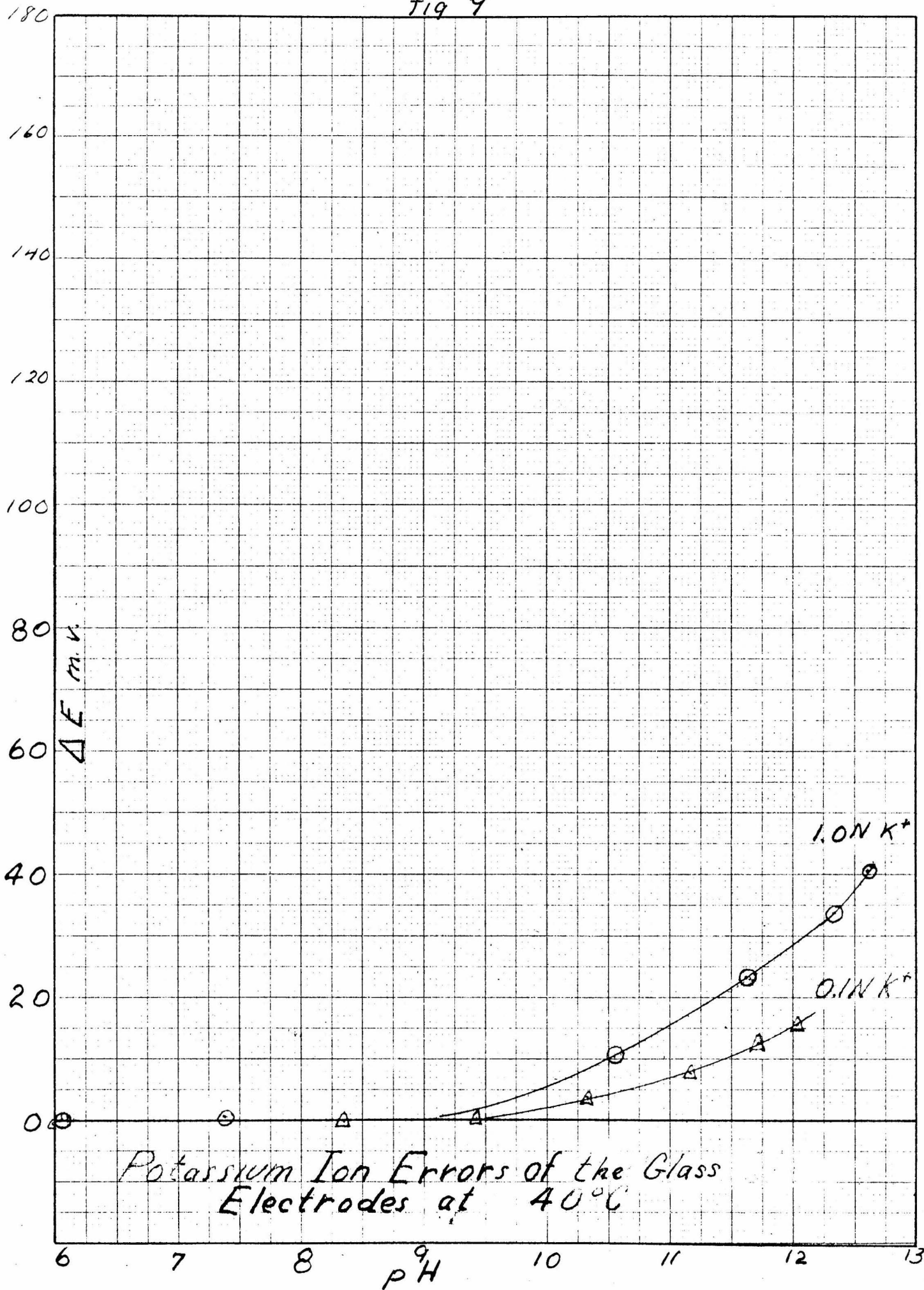
Sodium Ion Errors of the Glass Electrodes at 40°C

fig. 8



Lithium Ion Errors of the Glass Electrodes at 40°C

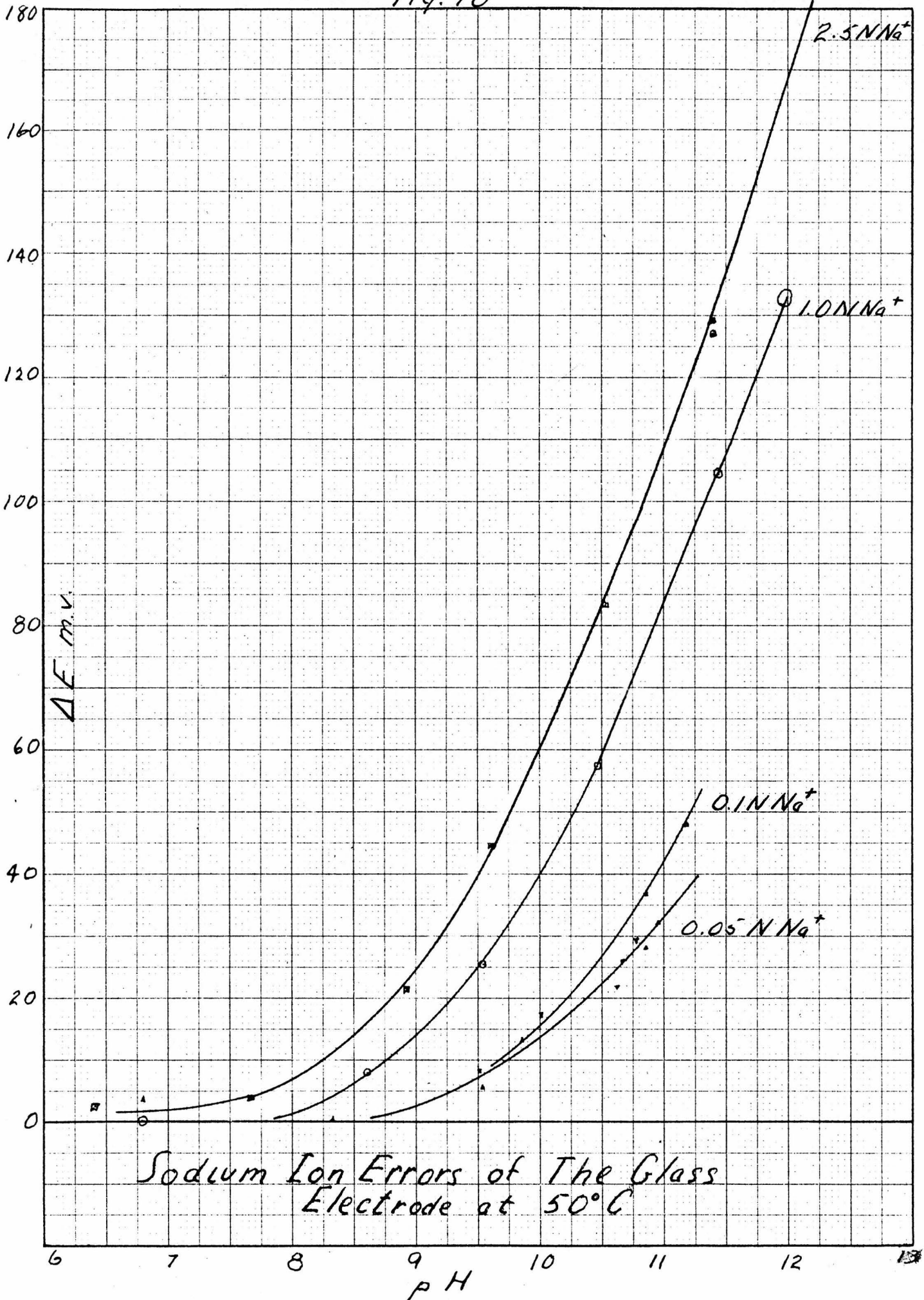
fig 9



Potassium Ion Errors of the Glass Electrodes at 40°C

KEUFFEL & ESSNER Co., N.Y. (CO. 23-111)
200 East 42nd Street, New York 17, N.Y.

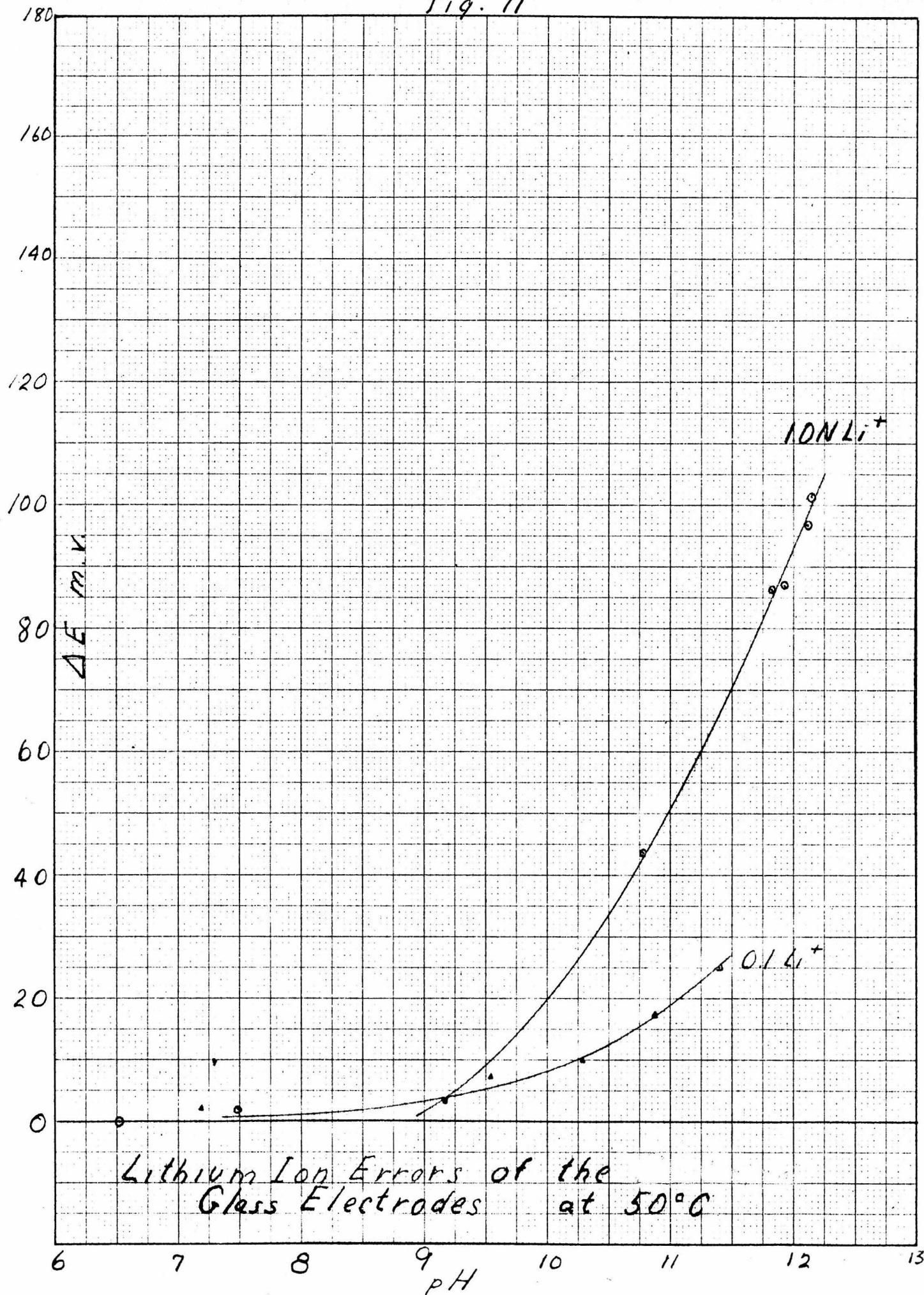
fig. 10



Sodium Ion Errors of The Glass Electrode at 50°C

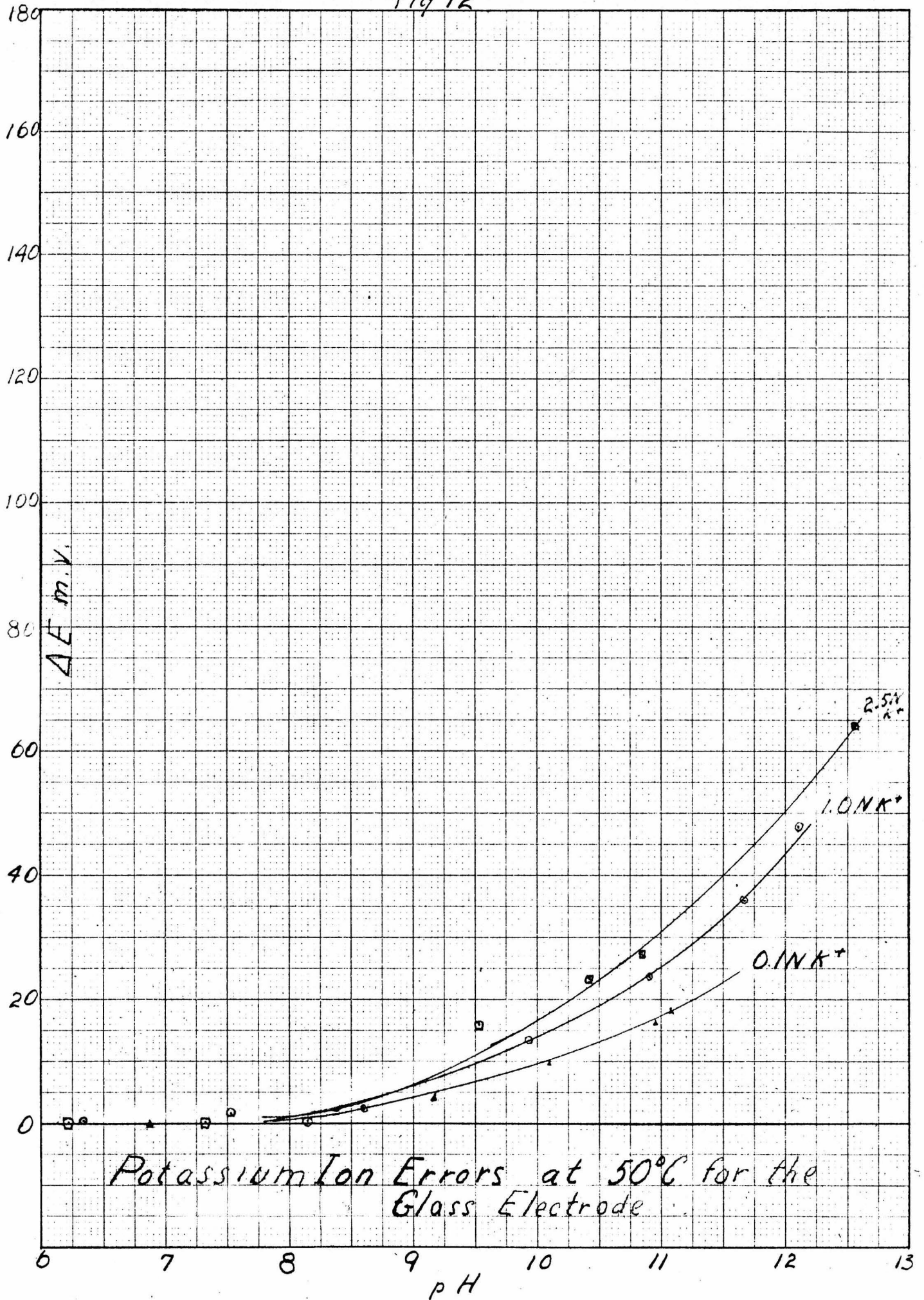
KTUFFEL & ESSER CO., N. Y. NO. 35-11
30 E. 23rd Street, New York, N. Y.
MADE IN U.S.A.

fig. 11



Lithium Ion Errors of the Glass Electrodes at 50°C

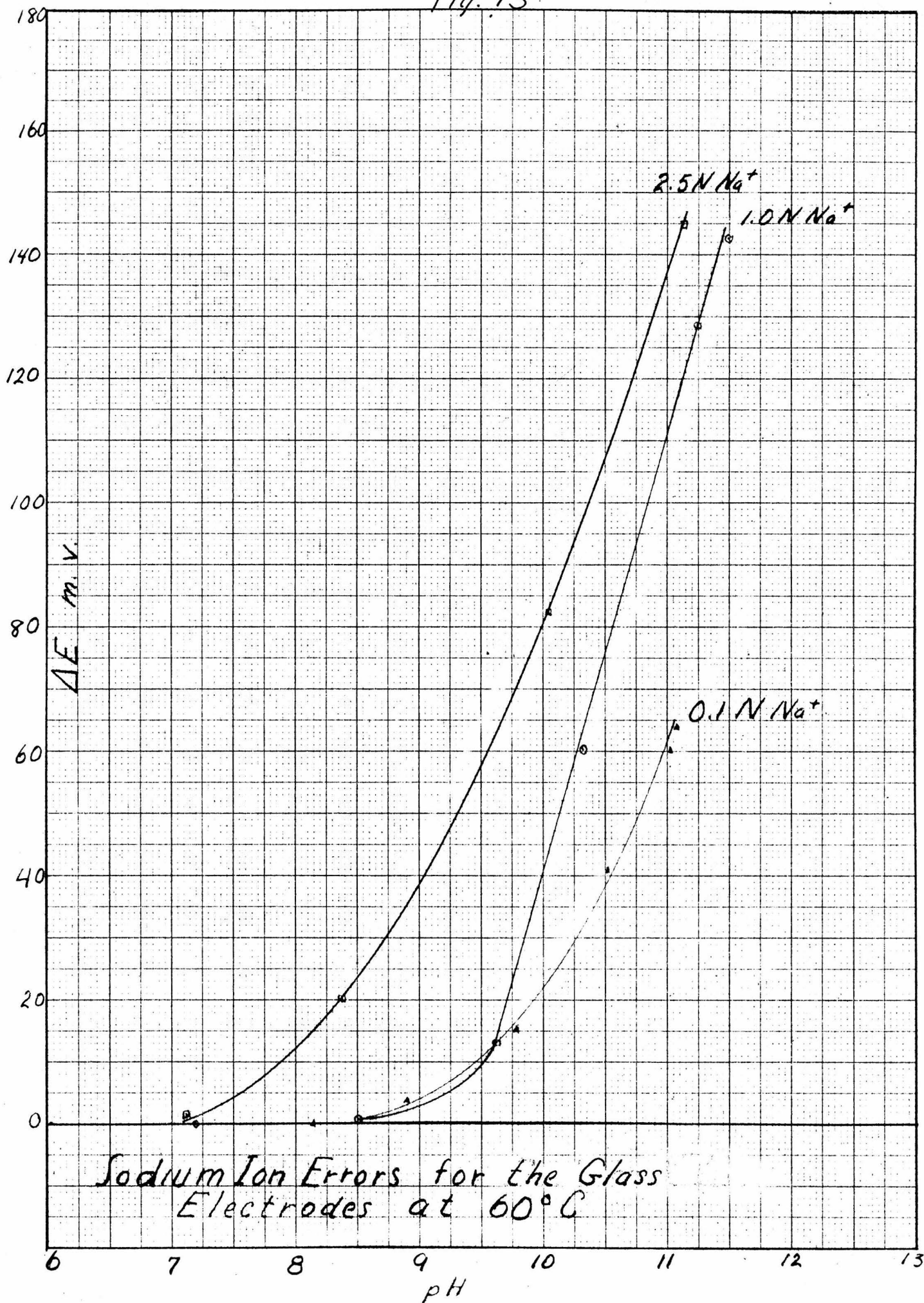
fig 12



KEUFFEL & ESSER CO., N. Y. NO. 359-11
2 1/2" x 3 1/2" to the top with 100 divisions
MADE IN U.S.A.

Potassium Ion Errors at 50°C for the Glass Electrode

fig. 13



KEUFFEL & ESSER CO., N. Y. NO. 359-11
2nd fl. to the left of 1st fl. in heavy
MAY 1958, U.S.A.

Sodium Ion Errors for the Glass Electrodes at 60°C

fig. 14

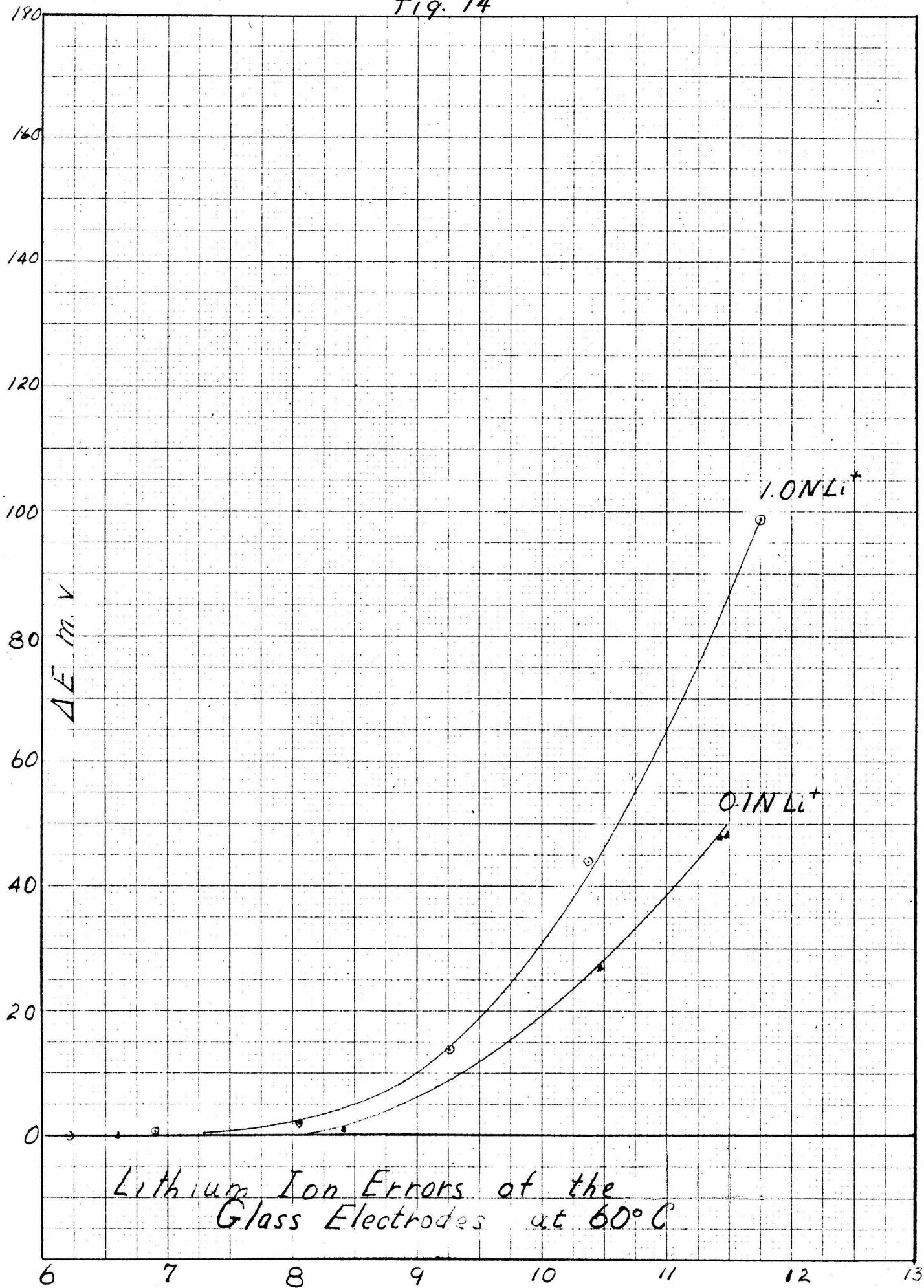
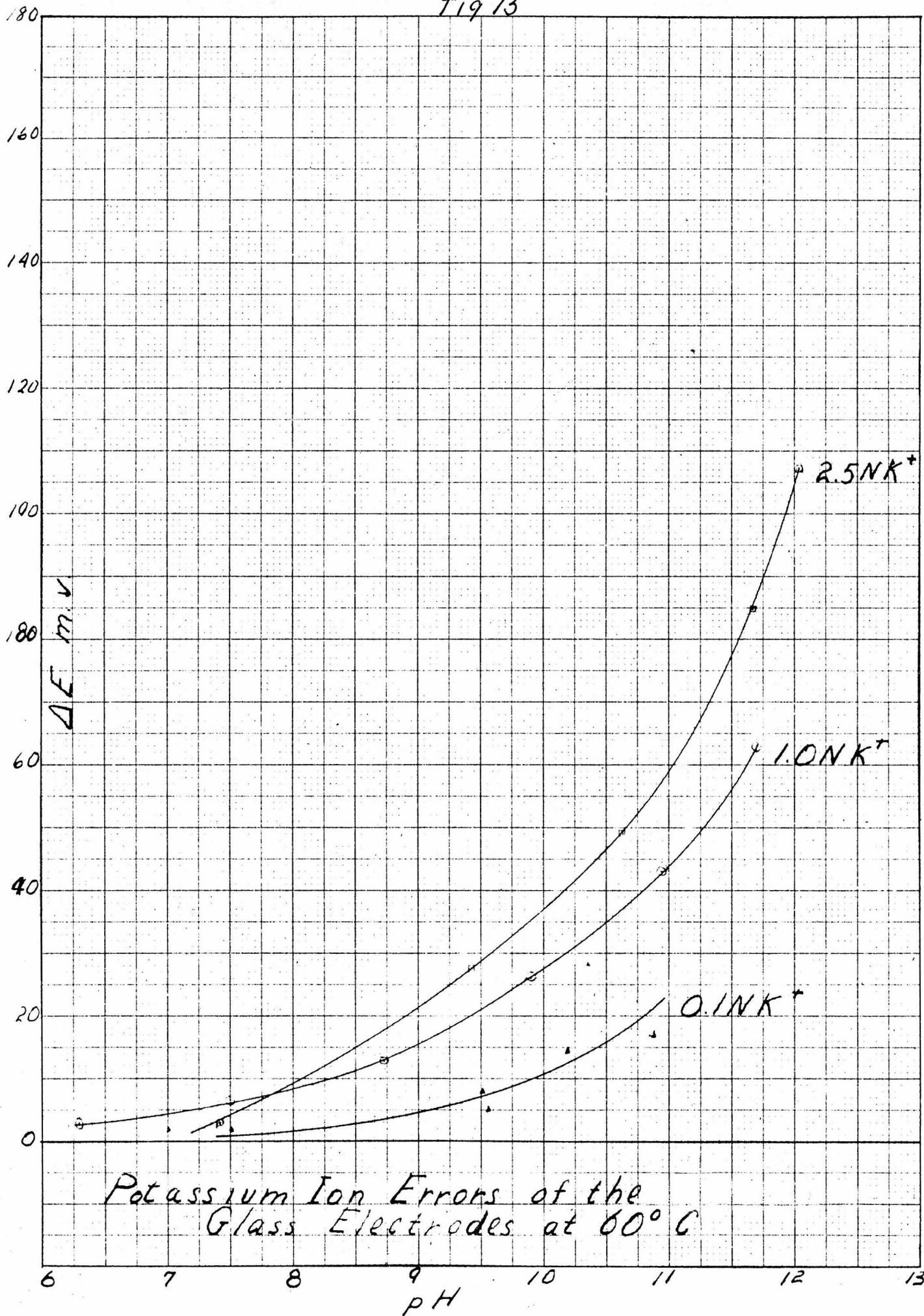


Fig 15



Potassium Ion Errors of the Glass Electrodes at 60°C

KEUFEL & FISHER CO., N. Y. NO. 1000-11
110th St., Astoria, Ore.
1955

fig 16

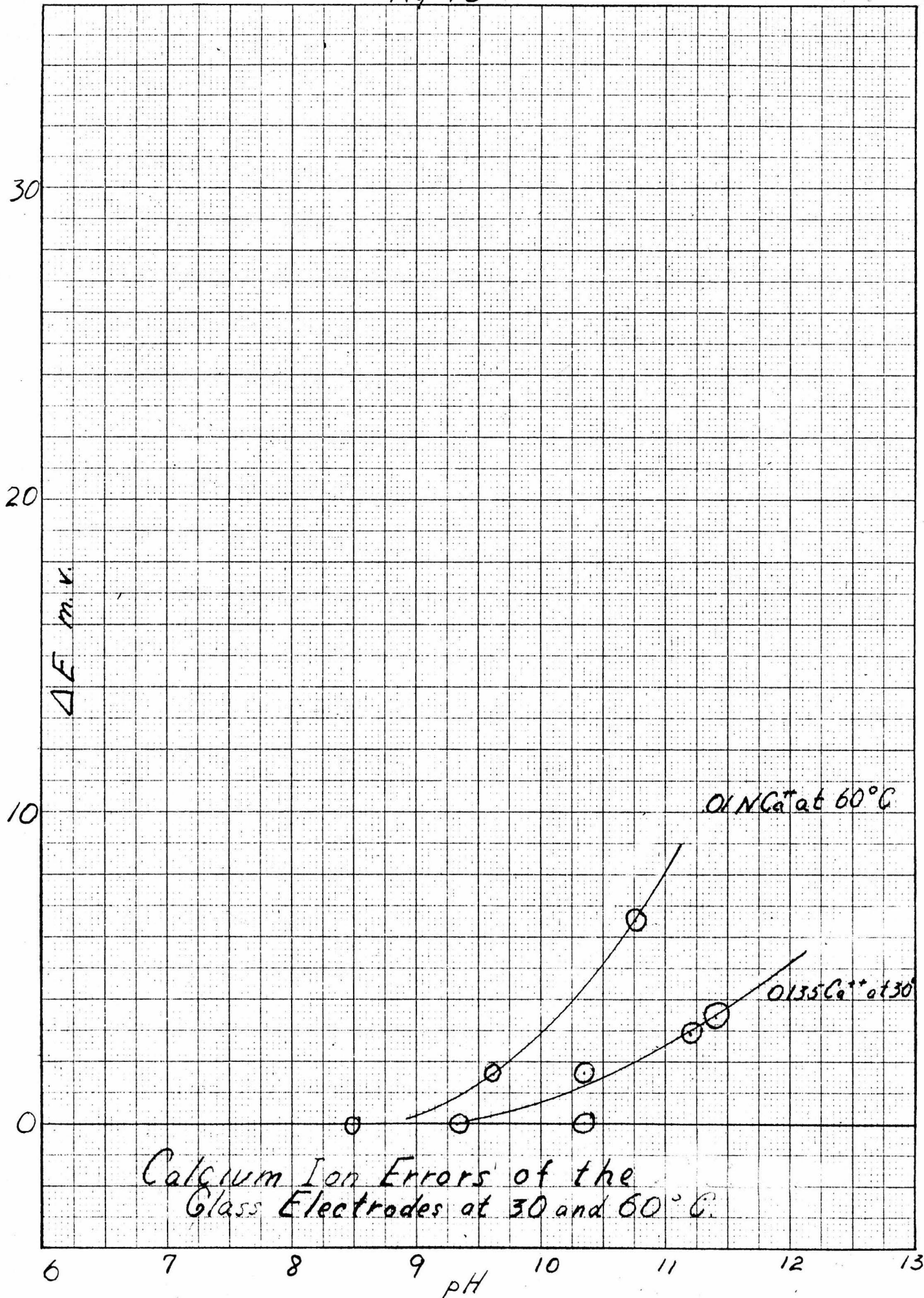
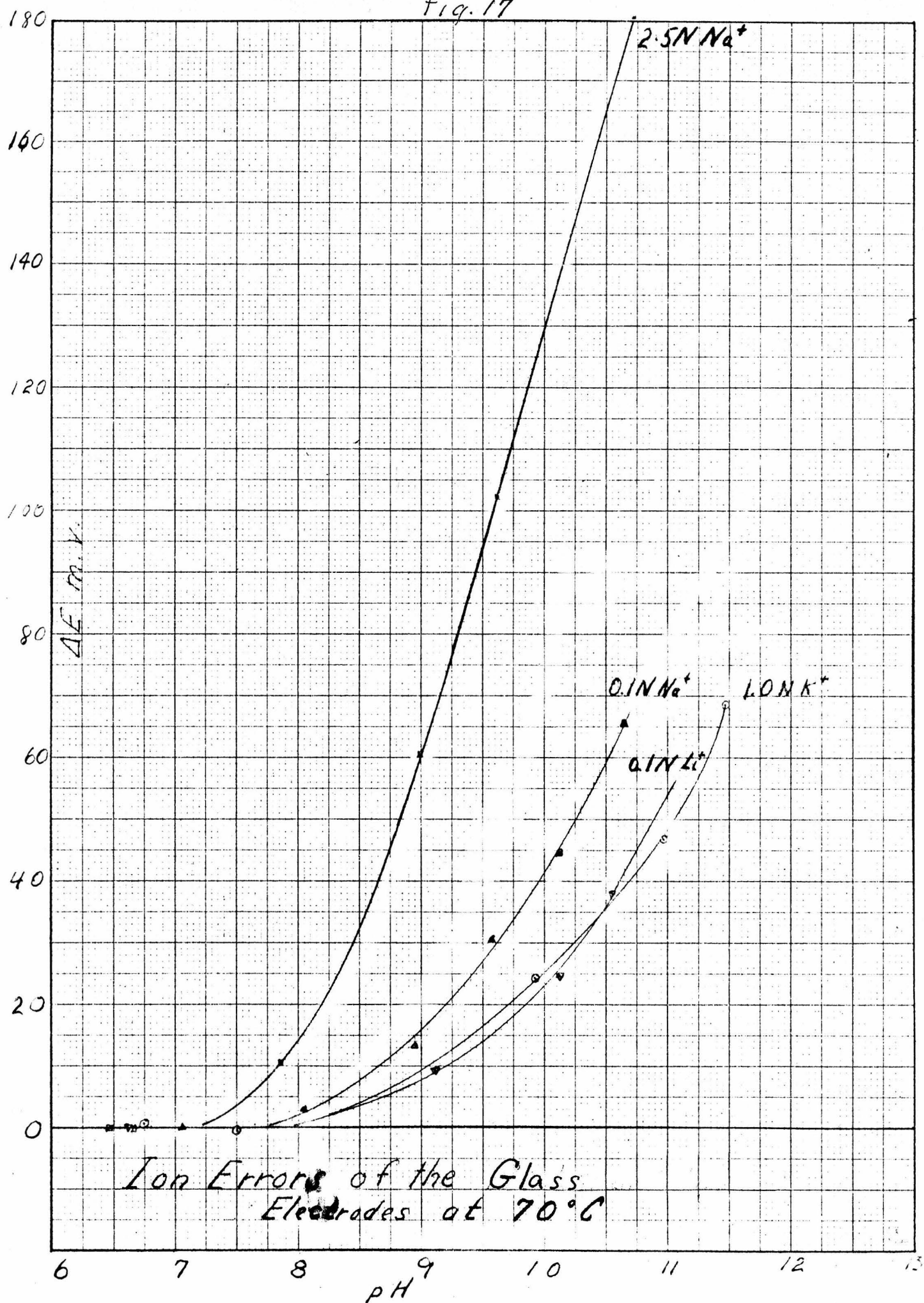


Fig. 17



ROUPEL & ESSER CO., N. Y. NO. 30-111
201 E. 42nd St. New York 17, N. Y.

Ion Errors of the Glass Electrodes at 70°C

THEORY OF THE GLASS ELECTRODE

There are three general theories for glass electrode behavior: the phase boundary potential theory, the membrane-diffusion potential theory, and the ion adsorption theory. M. Cremer (1), as stated before, assumed the glass was permeable only to hydrogen ions. He arrived at this conclusion because the work of E. Warburg showed that the electrical conductivity of glass was of electrolytic-type. Michaelis (19) extended this theory by considering the diffusion of other cations at high pH. Dole (3) showed this idea to be erroneous by doing two parallel experiments in which he measured the potentials between 0.1N NaOH solution and (a) pure 0.1N HCl solution and (b) 0.1N HCl solution which was 0.1N with respect to sodium-ion; the two potentials were found to be the same. If the sodium error was due to the diffusion of sodium-ion, the potential would be a function of the sodium-ion concentration on both sides of the glass membrane.

Horovitz (12) assumed an ion adsorption on the glass surface. He later modified this theory to include an ion interchange between the glass surface and solution; he again changed his theory to take into account the ionic mobility of the ions (13) and the heat of the mixture on the surface of the glass.

Schiller (14) and Lengyel (15) also advanced ion adsorption theories. Lengyel used quartz for his work; it is doubtful if the action of quartz and glass membranes are similar since the quartz acts essentially as a condenser while the low-resistance glass does not.

Haber (2), as already mentioned, advanced the first phase boundary theory. He neglected the action of metallic cations at high pH values. Hughes (16) stated that the buffer action of sodium silicate kept constant the hydrogen-ion concentration within the glass. While he mentions alkali-ion errors, he makes no attempt to explain them.

Gross and Halpern (17) attempted to account for the alkali-ion errors by assuming a dissolving of the glass in the water and the water in the glass. They postulate that in low pH regions the ionic concentration in the glass is due to hydrogen and hydroxol ions but at higher pH the metal ion also has an effect on the ionic concentration. In order to make these assumptions, it was necessary to assume a region of mutual solubility; it is difficult to visualize this film as existing in view of the slowness with which glass dissolves and the rapidity with which glass electrodes come to equilibrium.

Dole (3) used the Henderson and Planck formulas for liquid junction potentials to derive an

equation which fitted the measured alkali-ion errors up to a pH value of 12. The equation contained several constants that were neither constant nor theoretically determinable. Dole (18) later applied statistical mechanics to the problem and obtained an equation that predicts increased cation error at higher temperatures.

The equation is:

$$\Delta E = \frac{RT}{F} \frac{\left[\frac{B_{Me}}{B_H} \cdot c_{Me} \cdot f_{Me} e^{\left(\frac{Q_{Me} - Q_H}{RT} + C_H f_H \right)} \right]}{C_H f_H}$$

ΔE is the error of the glass electrode.

R, T, and F have their usual significance.

B is the ratio of the probability of a transition to the glass surface to the reverse transition at equilibrium. (Dole takes these as unity)

c is the concentration in moles per liter.

f is the activity coefficient.

Q is the difference between the energy of an ion in the interior of the solution and the energy of an ion on the glass surface.

The subscript Me refers to any cation other than H

Dole calculated values of $Q_H - Q_{Na}$ from measured errors and found them to be around 13 to 15 k. cal. per mole. The values increased with increasing pH, but at 50° C they became more constant.

The many constants in this equation can only be evaluated by experimental measurement and the experiment removes the need for the equation. It is, therefore, of no value from the standpoint of providing a means by

which glass electrode errors may be computed. Even though the constants could be evaluated, the equation fails to explain either the individual action of glass electrodes or the increasing reproducibility of the potassium-ion errors as the temperature is increased. The modified ionic exchange theory of Horovitz might offer a better explanation, but it would be of no greater value in predicting the glass electrode errors.

SUMMARY

1. The cation errors of Corning 615 glass electrodes were determined for various concentrations of lithium, potassium and sodium ions at 30°, 40°, 50°, 60° and 70° C and for calcium ion at 30° and 60° C. The errors were found to increase with increasing temperature.

2. Fresh glass electrodes showed slightly smaller errors than those which had been used for some time.

3. Potassium-ion errors, which were variable at low temperatures, became definite at temperatures above 40° C.

ACKNOWLEDGMENT

The writer wishes to take this opportunity to acknowledge his indebtedness to Dr. A. O. Beckman for his helpful suggestions and to the National Technical Laboratories for supplying the glass electrodes and much of the equipment used in this investigation.

BIBLIOGRAPHY

- 1- M. Cremer, Zytache F. Biol. 47, 1 (1906)
- 2- Haber and Klemensiewicz, Ann. D. Physik. (4) 26,
927 (1908)
- 3- M. Dole, J. Am. Chem. Soc. 53, 4260 (1931)
- 4- M. Dole and B. Z. Wiener, Trans. Electrochem.
Soc. 72, 107 (1937)
- 5- Gardner and H. W. Sanders, Anal. Ed. Ind. Eng.
Chem. 9, 274 (1937)
- 6- Ssokalov and Passynsky, Z. Physik. Chem.
A 160, 366 (1932)
- 7- J. L. Gabbard and M. Dole, Trans. Electrochem.
Soc. 72, 129 (1937)
- 8- M. Dole, J. Am Chem. Soc. 53, 4260 (1931)
- 9- W. S. Hughes, J. Am. Chem. Soc. 44, 2860 (1922)
- 10- "The Determination of Hydrogen Ions", W. M. Clark
- 11- D. A. MacInnes, D. Belcher and Shedlovsky,
J. Am. Chem. Soc. 60, 1094-9 (1938)
- 12- K. Horovitz, Z. Physik. 15, 369 (1923)
- 13- K. Horovitz, Z. Physik. 115, 424 (1925)
- 14- H. Schiller, Ann. Physik. 74, 105 (1924)
- 15- Lengyel, Z. Physik. Chem. 154, 371 (1931)
- 16- W. S. Hughes, J. Chem. Soc. 491 (1928)
- 17- F. Gross and O. Halpern, Z. Physik. Chem. 115, 54 (1925)
118, 255 (1925)
- 18- M. Dole, J. Chem. Phys. 2, 862 (1934)
- 19- L. Michaelis, Die Naturwiss., 14, 33 (1926)