

THE THERMODYNAMIC IONIZATION CONSTANTS OF d,l-MALIC ACID

by

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## INTRODUCTION

When a weak electrolyte is dissolved in water it does not dissociate completely. The extent of the dissociation depends upon a number of factors:- temperature, concentration of weak electrolyte, concentration of other components in the solution and on a parameter specific to the weak electrolyte under study. This parameter, the ionization constant (also referred to as the equilibrium or dissociation constant) of the weak electrolyte and its relation to free energy change, is a very valuable tool for describing the behavior of an electrolyte in solution.

A first approximation of the ionization constant may be calculated quite simply. For example, the ionization constant of a weak monobasic acid, HA, which dissociates according to the equation



may be approximated by the expression

$$K' = \frac{m_{\text{H}^+} \cdot m_{\text{A}^-}}{m_{\text{HA}}} \quad (2)$$

The quantities  $m_{\text{H}^+}$ ,  $m_{\text{A}^-}$ , and  $m_{\text{HA}}$  represent the equilibrium molal concentrations of the hydrogen ion, anion and undissociated acid respectively. The data required for an approximate calculation are the molality of one of the components and any property of the solution that depends upon the extent of dissociation:- conductance, pH, vapor pressure lowering, specific absorption at a given wave-length, etc.

Unfortunately, such first approximations may be greatly in error. Some of the assumptions introduced in order to simplify the computation are too drastic. Perhaps the most questionable assumption is the use of concentration in the place of activity. Molality and activity

are equivalent only in ideal solutions. Except at very great dilution, no real electrolyte in solution behaves ideally. The activity of the chloride ion for example is less than 0.08 in a 0.1 molal solution of hydrochloric acid. The activity of a polyvalent ion will be less than 50 per cent of the molality in a 0.1 molal solution.

The thermodynamic ionization constant of the acid HA is correctly defined by the expression

$$K = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \quad (3)$$

The quantities  $a_{H^+}$ ,  $a_{A^-}$ ,  $a_{HA}$  represent the activities of the several components. The relation between activity and molality is expressed by the equation

$$a_i = \gamma_i m_i \quad (4)$$

The new parameter,  $\gamma_i$ , is called the activity coefficient. Equation 3 may be rewritten in the form

$$K = \frac{m_{H^+} \cdot m_{A^-}}{m_{HA}} \cdot \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}} \quad (5)$$

It is evident that the first fraction on the right hand side of equation 5 is identical with the right side of equation 2. Therefore the relation between the thermodynamic ionization constant and the "apparent" ionization constant is simply

$$K = K' \cdot \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}} \quad (6)$$

In order to obtain some idea of the difference between  $K'$  and  $K$ , we may consider the case of the hypothetical monobasic acid HA. It is not unreasonable to assume that in dilute solution the activities of  $H^+$  and  $A^-$  will differ only slightly from the activity of other small monovalent



ions at the same molality. Further, the activity of an undissociated molecule is seldom very different from the molality in dilute solutions. If the ionic concentration of the acid solution is 0.1 molal, (This can be accomplished by the addition of an inert electrolyte or by the addition of the acid salt.) then a substitution of the value of 0.08 ( $a_{Cl^-}$  in a 0.1 molal solution) for  $a_{H^+}$  and  $a_{A^-}$  in equation 3, indicates that  $K$ , ( the ionization constant calculated on an activity basis) is only about two-thirds of  $K'$ , (the ionization constant calculated on a molality basis.) It is to be anticipated that at higher ionic concentrations the discrepancy will be much greater. A precise determination of the ionization constant therefore must take into account the fact that there is a difference between activities and molalities.

The case of an electrolyte with two dissociating groups introduces another source of uncertainty. In such cases there are two ionization constants to be determined. But the equilibrium constant for one dissociation cannot be evaluated without correcting for the effect of the other dissociation (5). That is, if the first ionization constant of the acid  $H_2A$  was being studied, interest would center around the reaction



But it is to be expected that some of the monovalent anion  $HA^-$  will dissociate further according to the reaction



There are a few dibasic acids that possess a very high ratio of first to second ionization constant (20). In such cases the interaction will be negligible. But most of the common dicarboxylic acids (20) and a number of the substituted benzoic acids that have been studied (35)

do not come under this category. When the ratio of first to second ionization constant is 500 or less, the interaction of the two equilibria is too great to be ignored.

In many instances, the following general procedure has been used to determine precisely the ionization constants of dibasic acids. A suitable reversible chemical cell is chosen. Preference has usually been given to cells that do not require a liquid junction between the half-cells. The electrolytic cell solution is prepared with a definite concentration of the weak electrolyte under study. By various means, correction terms for the overlapping of equilibria i.e. hydrolysis or dissociation, are evaluated. The activity coefficient terms are computed; usually by some form of the Debye-Hückel equation. Then the ionization constants may be found and used to make a recalculation of the correction terms. The ultimate values of the ionization constants are arrived at after a series of successive approximations.

A number of workers have determined the ionization constants of weak dibasic acids using variations of this procedure (4, 14, 15, 23, 24, 44). It is, at best, an involved and laborious computation.

Bates (5) has proposed a simpler method for the precise determination of one ionization constant of a dibasic acid, provided that the other ionization constant is known. The data of such a determination are obtained from cells without liquid junction. The electrolytic solution is prepared containing a definite quantity of the acid salt of the weak dibasic acid. The product of the ionization constants,  $K_1K_2$ , is determined graphically. The value of this method lies in the fact that the molality term in the calculation is insensitive to relatively large errors in the hydrolysis correction. Since it has been assumed

that one of the ionization constants is known, the other may be calculated readily from the product.

A simpler method for evaluating both the first and second ionization constants of a weak dibasic acid from a single set of observations had been suggested some years earlier by Speakman (46). In certain respects it is analogous to the method proposed by Bates. The method proposed by Speakman does reduce the errors that might otherwise be introduced when hydrolysis and activity coefficient corrections are neglected. In spite of this reduction in the effects of the usual approximations, a correction for the errors arising from the two sources discussed above must be introduced before Speakman's method can be used to determine the ionization constants of dibasic acids with some precision.

The method applied by Speakman to data obtained from pH titrations in cells containing a liquid junction, is amenable to use with any source of emf data. Furthermore, it is possible to modify the method of calculation so as to include the corrections.

The method proposed here and applied to the determination of the ionization constants of d,l- malic acid, is a modification of Speakman's method that will permit the simultaneous evaluation of the ionization constants of a dibasic acid using data that have been derived from cells without liquid junction.

The basis of the experimental method used here was first described by Harned and Ehlers (25, 26). The procedure was modified further by Hamer and Acree (30) and later by Bates and Acree (7). The apparatus and experimental procedure employed in this work was essentially that described by the latter.

## THEORETICAL DERIVATION

The first and second thermodynamic ionization constants of a dibasic acid are defined by the equations

$$K_1 = \frac{a_{H^+} \cdot a_{HA^-}}{a_{H_2A}} = \frac{a_{H^+} \cdot m_{HA^-}}{m_{H_2A}} \cdot \frac{\gamma_{HA^-}}{\gamma_{H_2A}} \quad (9)$$

and

$$K_2 = \frac{a_{H^+} \cdot a_{A^{2-}}}{a_{HA^-}} = \frac{a_{H^+} \cdot m_{A^{2-}}}{m_{HA^-}} \cdot \frac{\gamma_{A^{2-}}}{\gamma_{HA^-}} \quad (10)$$

The usual convention have been employed:-

- $a_i$  - the activity of the ion specified by the subscript.
- $m_i$  - the molality of the ion specified by the subscript.
- $\gamma_i$  - the activity coefficient on a molal basis of the ion specified by the subscript.

Three additional terms have been defined:-

- $\alpha$  - the quantity, in moles, of the acid salt added initially to the solution.
- $\beta$  - the quantity, in moles, of strong acid added initially to the solution. (If strong base is to be added instead of acid, the sign of  $\beta$  is negative.)

$$B = \beta - m_{H^+} + m_{OH^-} \quad (11)$$

Consider the solution of a monobasic salt of a weak acid, MHA, in a solution containing a completely dissociated (strong) acid, HC. At equilibrium, the acid salt will have dissociated completely into the cation  $M^+$  and into a certain amount of each of the three possible forms the anion may take. Some of the monovalent anion will have reacted with the hydrogen ion of the strong acid to produce the undissociated acid,  $H_2A$ , and a small portion of the monovalent anion will have dissociated

to produce the bivalent anion  $A^{2-}$  in accordance with equation 8.

Since the solution must be electrically neutral, the ionic equilibrium between positive and negative charges may be written

$$[M^+] + [H^+] = [C^-] + [OH^-] + [HA^-] + [2A^{2-}] \quad (12)$$

By definition,  $\alpha$  equals the number of moles of acid salt initially added. At equilibrium,  $\alpha$  will equal the sum of the three interconvertible forms of the anion of the acid salt.

$$\alpha = [H_2A] + [HA^-] + [A^{2-}] \quad (13)$$

At the same time

$$\alpha = [M^+] \quad (14)$$

Equation 12 may be rewritten in the form

$$\alpha + [H^+] = \beta + [OH^-] + [HA^-] + [2A^{2-}] \quad (15)$$

If equation 15 is rearranged and the definition of B (Equation 11) is introduced, then equation 15 may be written

$$B = \alpha - [HA^-] - [2A^{2-}] \quad (16)$$

$$\text{or} \quad \alpha - B = [HA^-] + [2A^{2-}] \quad (17)$$

If  $\alpha$  is added to both sides of equation 16 and the value of  $\alpha$  as defined by equation 13 is substituted into the right hand side of equation 16, then

$$\alpha + B = [HA^-] + [2H_2A] \quad (18)$$

Equation 18 may be used to eliminate  $m_{H_2A}$  from the equation for the first ionization constant (9).<sup>1</sup>

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<sup>1</sup>The use of number of moles and molality interchangeably is justified so long as the mass of the solvent does not figure in the derivation. The actual numerical computations must be made in terms of molality

$$K_1 = \frac{2(a_{H^+} \cdot m_{HA^-}) \cdot \gamma_{HA^-}}{(\alpha + B - m_{HA^-}) \cdot \gamma_{H_2A}} \quad (19)$$

In a like manner  $m_A^-$  may be eliminated from equation 10 by the introduction of equation 17.

$$K_2 = \frac{a_{H^+}(\alpha - B - m_{HA^-}) \cdot \gamma_{A^-}}{2m_{HA^-} \cdot \gamma_{HA^-}} \quad (20)$$

Both equations 19 and 20 may be rearranged to solve for  $m_{HA^-}$ .

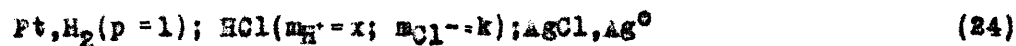
$$m_{HA^-} = \frac{K_1(\alpha + B) \cdot \gamma_{H_2A}}{\gamma_{HA^-} \cdot a_{H^+} + K_1 \gamma_{H_2A}} \quad (21)$$

$$m_{HA^-} = \frac{a_{H^+}(\alpha - B) \cdot \gamma_{A^-}}{a_{H^+} \gamma_{A^-} + 2K_2 \gamma_{HA^-}} \quad (22)$$

Equating 21 and 22 and rearranging terms:-

$$\frac{a_{H^+}(\alpha - B) \gamma_{A^-}}{(\alpha + B) \gamma_{H_2A}} = \frac{K_1 \cdot a_{H^+} \cdot B \gamma_{A^-}}{(\alpha + B) \gamma_{HA^-}} + K_1 K_2 \quad (23)$$

The experimental determination of  $a_{H^+}$  is made by measuring the potential of an electrical cell:-



The Nernst equation for this cell may be written

$$E = E^0 - \frac{RT}{F} \ln (a_{H^+} a_{Cl^-}) \quad (25)$$

or

$$(E - E^0)/k + \log m_{Cl^-} = -\log(a_{H^+} \gamma_{Cl^-}) \quad (26)$$

In order to make the notation less cumbersome several additional quantities have been defined:-

$$P = 10 \left( \frac{E - E^0}{k} + \log m_{Cl^-} \right) \quad (27)$$

$$X = \frac{PB}{\alpha + B} \quad (28)$$

$$Y = \frac{F^2(\alpha - \beta)}{(\alpha + \beta)} \quad (29)$$

$$\sigma = \frac{\gamma_{H_2A} \cdot \gamma_{Cl^-}}{\gamma_{HA^-}} \quad (30)$$

$$\rho = \frac{\gamma_{A^{2-}}}{\gamma_{H_2A} \gamma_{Cl^-}^2} \quad (31)$$

$$\rho \cdot \sigma = \frac{\gamma_{A^{2-}}}{\gamma_{HA^-} \gamma_{Cl^-}} \quad (32)$$

The new definitions permit equation 23 to be written in the form

$$\rho Y = K_1 \rho \sigma X + K_1 K_2 \quad (33)$$

or

$$Y = K_1 \sigma X + K_1 K_2 / \rho \quad (34)$$

To this point the derivation has been carried out without sacrificing thermodynamic exactness. Now we may consider how it can be used to calculate the two ionization constants in actual practice. The variables  $X$  and  $Y$  are quantities computed from the experimental cell voltage determinations and from the initial molalities. Since  $m_{H^+}$  is involved in the computation of the quantity  $B$  and consequently in the computation of  $X$  and  $Y$ , it must be determined in some way. The experimental conditions may be arranged so that  $\alpha$  and  $\beta$  are large when compared with  $m_{H^+}$  so that  $X$  and  $Y$  as they are calculated by equations 28 and 29 are quite insensitive to relatively large errors in  $m_{H^+}$ .

It can be seen that equation 34 will be a linear equation in  $X$  and  $Y$  if certain conditions can be met:- if the different values of the independent variables found in that equation do not appreciably affect the constancy of  $1/\rho$  and  $\sigma$ . Studies of salt effects indicate that the activity coefficients of ions in solution are largely independent of the concentration of any single ionic component but depend upon the ionic

strength of the solution. (9, 27) Therefore, it should be possible to maintain  $\rho$  and  $\sigma$  constant within the error of the determination, by comparing values of X and Y derived from experimental measurements of solutions containing different ratios of acid salt to strong acid ( or strong base) at constant ionic strength. If this is done, it is possible to obtain a family of straight lines corresponding to different values of the ionic strength.

The slopes of these lines ( $\sigma K_1$ ) are then plotted against ionic strength and the resultant curve is extrapolated to zero ionic strength. Since  $\sigma$  approaches unity at infinite dilution, the value at the intercept is considered to be  $K_1$ .

The operation may be reversed, and with the aid of the newly evaluated  $K_1$ , values of  $\sigma$  may be computed for different values of ionic strength. The quantity  $K_2/\rho$  can then be computed from equation 34.

The quantity  $K_2/\rho$  may now be plotted against ionic strength; a treatment analogous to the computation of  $K_1$ . In this case the intercept at zero ionic strength should be  $K_2$  since  $1/\rho$  approaches unity at infinite dilution.



## EXPERIMENTAL PROCEDURE

### A. Reagents

1. Potassium acid malate. Equimolar quantities of reagent grade d,l-malic acid and potassium hydrogen carbonate were dissolved in water. The solution was maintained at 60° C for several minutes, activated charcoal was added and the solution was filtered. The filtrate was cooled in an ice-water bath and ethyl alcohol (95 per cent) was poured into the solution until the volume had been doubled. The precipitate of crude potassium acid malate was separated by filtration. This precipitate was recrystallized five times by first dissolving the salt in hot water and reprecipitating it by the addition of ethyl alcohol. The salt collected after the fifth recrystallization was dried overnight at 130° C and was kept in a desiccator.

The potassium acid malate was assayed by acidimetric titration against a standard solution of potassium hydroxide. The standard base had previously been standardized against potassium acid phthalate (NBS Standard Sample 84b). After the first recrystallization, the dried salt was calculated to be 99.69 per cent potassium acid malate. After the third recrystallization the assay had risen to 99.92 per cent. After the fifth recrystallization it was 99.99 per cent.

Tests were made to determine whether the dried potassium acid malate was hygroscopic. Four samples, each weighing four grams, were placed in weighing bottles. The samples were dried for forty hours at 105° C and immediately placed in a desiccator. The samples were allowed to cool to room temperature and then weighed. After the weights had been taken, the bottles were left open for 48 hours in a room at 22° C, 45 per cent

relative humidity. The samples increased in weight by an average of 1.5 milligrams or about 0.04 per cent. After the samples had been left open for two weeks, the average increase in weight of sample was 2.4 milligrams or 0.07 per cent. Apparently potassium acid malate is not appreciably hygroscopic under normal laboratory conditions. However, as a precaution, the salt was dried for an hour at 105° C before the preparation of each set of solutions.

2. Potassium chloride. Potassium chloride, the source of chloride ion in the electrolytic cell, was prepared according to the procedure suggested by Pinching and Bates (37). Chlorine gas was bubbled into a saturated solution of potassium chloride for an hour. The solution was boiled to remove the gaseous chlorine and bromine and then cooled to 25° C. Hydrogen chloride gas, generated by the addition of sodium chloride to concentrated sulfuric acid, was bubbled into the potassium chloride solution until no more appeared to be absorbed. The solution was filtered; the precipitate was washed with cold absolute ethyl alcohol and dried in an oven at 130° C. The dried salt was fused under dry nitrogen in a platinum crucible and was allowed to solidify.

The fused potassium chloride was tested for the presence of free alkali. Several five-gram samples were titrated with 0.01 molar hydrochloric acid, using bromthymol blue as the indicator. The endpoint was estimated by comparing the test solution with a color standard prepared from the indicator and a phosphate buffer of pH 7(8).

The potassium chloride was also tested for bromide impurity using the procedure of R. G. Aickin (1) as modified by Pinching and Bates (37). In this test, bromine is detected by oxidizing bromide ion to free bromine and adsorbing the bromine on paper saturated with fluorescein.

The bromine displaces hydrogen from the fluorescein to form eosin (tetrabromfluorescein). A positive test for bromine is indicated by a pink spot of eosin. The test is extremely sensitive and will detect 0.001 per cent bromide.

After the purification procedure, the potassium chloride contained about 0.001 per cent potassium hydroxide and 0.002 per cent potassium bromide as indicated by the tests described above.

3. Potassium hydroxide. The standard solution of potassium hydroxide was prepared from J. T. Baker "ACS Standard " potassium hydroxide pellets. Two hundred grams of potassium hydroxide were dissolved in distilled water of "conductivity" grade to make a solution of about 400 ml. A solution of barium hydroxide was prepared by boiling an excess of barium hydroxide in Distilled water. The mixture was cooled to room temperature, centrifuged for ten minutes and the supernatant liquid was decanted. The amount of potassium carbonate contaminant was indicated on the label to be 1.8 per cent. An amount of barium hydroxide solution calculated to be sufficient to precipitate the carbonate impurity was added to the potassium hydroxide solution. Additional barium hydroxide solution was introduced dropwise until no further precipitation was observed. Approach to the end-point was estimated by the following procedure. One ml of the supernatant liquid was withdrawn and placed in a test-tube. It was then diluted with three ml of water and one ml of the barium hydroxide solution was added. The end-point was considered to have been reached when only very slight turbidity was observed.

A similar test using 0.5 ml of 1 normal sulfuric acid was made in order to determine whether barium ion had been added in excess. In this

case there also was a slight turbidity at the end-point.

The concentrated potassium hydroxide solution was centrifuged for fifteen minutes and the supernatant liquid pipetted into a paraffin lined carboy containing about seventeen liters of "conductivity" water. The water in the carboy had been scrubbed previously by bubbling purified nitrogen through it overnight. The concentrated potassium hydroxide was added to the water a little at a time without stopping the stream of nitrogen. A sample of the dilute solution was removed and titrated rapidly so that the molality could be more closely adjusted to 0.1 molal.

The dilute potassium hydroxide solution (0.1 molal) was standardized by a series of weight titrations against potassium acid phthalate ( NBS Standard Sample 84b) in a carbon dioxide-free atmosphere. Three drops of phenolphthalein solution were added as indicator. The titration was carried to a pale pink color comparable with a color standard prepared from a borate buffer ( pH 8.6 ) and the phenolphthalein indicator.

4. Perchloric Acid. Reagent grade perchloric acid (70 per cent) was diluted with "conductivity" water to make a solution about 0.1 molal. The acid solution was standardized by a series of gravimetric titrations against the potassium hydroxide solution described above. A test was made for chloride ion impurity in the perchloric acid using silver nitrate solution according to the procedure described by Hosin (41). The perchloric acid was found to contain less than 0.001 per cent of chloride ion.

## B. Preparation of Solutions

The solutions were prepared by weighing out samples of both the solid salts and the distilled water. Salts were weighed with a precision of  $\pm 0.1$  milligram. Solutions of less than 100 gram mass were weighed to  $\pm 5$  milligrams; between 100 and 500 grams they were weighed to  $\pm 10$  milligrams; solutions with greater mass than 500 grams were weighed to  $\pm 50$  milligrams.

Potassium chloride was added to make each solution 0.008000 molal with respect to the chloride ion.

Nine sets of solutions, five dilutions per set, were prepared. The experimental results of one of the sets were discarded because of exceptionally large drifts in the cell voltages. In several other cases, one of the five dilutions had to be discarded for similar reasons. The values of the buffer ratios and the dilution ratios employed in each run are presented in Table 1.

## C. Electromotive force Measurements

The glass vessel which served as the body of each cell and the method of making the dilutions and filling the cells in a hydrogen atmosphere were originally described by Bates and Acree (7). A photograph of the cell is reproduced in Figure 7.

A stream of purified hydrogen, prepared by passing the gas through copper turnings maintained at about  $400^{\circ}$  C, was saturated with water vapor by bubbling the gas through a reservoir of the solution "B", in the particular cell being filled. The hydrogen was then passed under the platinized electrodes, "C", and out through a side-arm and bubble trap, "E". The silver-silver chloride electrodes were inserted in the

second vertical member of the cell, "D". After the solution had been introduced, the solution flask line was removed and the hydrogen line affixed to the same standard taper "A". By suitable manipulation, the solution can be used to wash out, fill the cell and the side tubes.

The platinized "hydrogen" electrodes were prepared by a modification of the method of Popoff, Kuntz and Snow (38). Bright platinum foil electrodes were platinized in a solution of chloroplatinic acid containing 80 milligrams of lead acetate per 100 ml of solution. A current of 500 milliamperes applied for about a minute and a half seemed to produce the optimum coat of platinum black.

The silver-silver chloride electrodes were prepared by covering a tightly wound helix of platinum wire with a paste of silver oxide. The silver oxide was reduced to silver in a furnace maintained at  $540^{\circ}$  C. Each electrode was removed from the oven, cooled and then chloridized in 0.5 normal hydrochloric acid by applying a current of 5 to 7 milliamperes for forty five minutes (7). The chloridized electrodes were washed, set in a 0.1 normal solution of hydrochloric acid and intercompared in the hydrochloric acid solution after the electrodes had been standing for 24 hours. Electrodes that varied more than 0.05 millivolts from the mean were discarded.

A pair of silver-silver chloride electrodes and a pair of "hydrogen" electrodes were used in each cell. Each pair was mounted in a two-holed neoprene stopper and was jammed tightly into the proper arm of the glass cell.

Five cells, one for each dilution of a given buffer ratio, were run concurrently. Measurements of terminal voltage between the silver-silver chloride electrodes and the "hydrogen" electrodes were made in dup-

licate. The electrical apparatus employed in the measurement consisted of a Leeds and Northrup Type K-1 potentiometer and a Type HS galvanometer. Readings of potential were made to  $\pm 0.01$  millivolt.

The temperature of the bath containing the cells was maintained to better than  $\pm 0.02^\circ$  C. The temperature schedule used, with some minor exceptions, was  $25^\circ, 15^\circ, 0^\circ, 10^\circ, 20^\circ, 30^\circ, 40^\circ, 50^\circ, 45^\circ, 35^\circ, 25^\circ$ . Individual points were discarded if the cell potential measurement varied by more than 0.20 millivolts from the curve obtained by plotting emf against temperature. All points of a given dilution were discarded if the final value at  $25^\circ$  C differed from the initial value by more than 0.30 millivolts.

Normally the cells reached equilibrium in about thirty minutes. Equilibrium was judged to have been achieved when readings of the same set of electrodes taken ten minutes apart, differed by 0.03 millivolts or less.

## EXPERIMENTAL RESULTS

The potentiometric measurements for all eight successful runs are assembled in the second column of Table 2. The values of  $E$  and  $E^0$  were corrected in accordance with the changes in the fundamental electrical units decided upon at the 1947 conference of the International Union of Chemistry (10). The values of  $2.3026 RT/F$  used in the computations, modified in accordance with these changes, were obtained from NBS Circular C 459 (3) (Table 3).

### A. pH

Values of pH were computed by the use of the equation

$$\text{pH} = (E - E^0)/k + \log m_{\text{Cl}^-} \gamma_{\text{HCl}} \quad (35)$$

A plot of the mean activity coefficient of hydrochloric acid against ionic strength was prepared from data published by Harned and Owen (27). This plot has been reproduced as Figure 8. The values of the mean activity coefficient of hydrochloric acid were calculated by Harned and Ehlers (26) from the potentiometric data of cells without liquid junction.

Determinations of the activity of hydrochloric acid using similar cells have been made by N. J. Anderson (2) for the range of molality 0.00002 to 0.003 molal at 25° C. Their values of  $\gamma_{\text{HCl}}$  accord with those of Harned and Ehlers to  $\pm 0.0002$ . Shedlovsky and MacInnes (43) measured  $\gamma_{\text{HCl}}$  at 25° C from 0.001 to 0.1 molal using cells containing a liquid junction. The largest deviations in the values of  $\gamma_{\text{HCl}}$  between their results and the results of Harned and Ehlers is 0.002 at a single comparable point. All the other calculated points agree to 0.001.



There are no corroborative studies for temperatures above 25° C, but Randall and Young (40) computed  $\gamma_{\text{HCl}}^{\pm}$  from the freezing point measurements of Randall and Vanselow (39). Their data are in excellent agreement with the data of Harned and Ehlers and 0° C. The largest difference in the value of  $\gamma_{\text{HCl}}^{\pm}$  is 0.002 at 0.5 molal but in the range from dilute solution to 0.1 molal, the largest difference between the two sets of data is 0.0006.

### B. Ionic Strength

Ionic strength is defined by the equation

$$\mu = \frac{1}{2} \sum z_i^2 m_i \quad (36)$$

$z_i$  - the valence of the ion specified by the subscript.

The calculation of ionic strength of solutions prepared without the addition of strong acid or strong base, is somewhat different from the calculations that are required when either strong acid or strong base have been added to the solution of potassium acid malate.

A solution prepared solely with the acid salt will be a mixture of the ions  $M^+$ ,  $H^+$ ,  $HA^-$ ,  $A^{2-}$ .<sup>1</sup> The ionic strength of such a solution will be expressed by

$$\mu = \frac{1}{2}(m_{M^+} + m_{H^+} + m_{HA^-} + 4m_{A^{2-}}) \quad (37)$$

The quantity  $\alpha$  was defined earlier by the equations

$$\alpha = m_{A^{2-}} + m_{HA^-} + m_{H_2A} \quad (13)$$

---

<sup>1</sup>Here and in the subsequent treatment the contribution of the hydroxyl ion is neglected since the ratio of added base to acid salt is never so high that  $m_{OH^-}$  is greater than  $10^{-8}$  molal.

$$\alpha = m_{K^+} \quad (14)$$

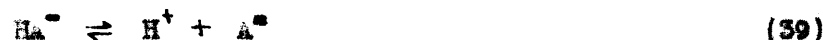
By the use of these definitions of  $\alpha$ , equation 37 may be rewritten:-

$$\mu = \frac{1}{2}(2\alpha - m_{H_2A} + 3m_{A^{2-}} + m_{H^+}) \quad (38)$$

The undissociated acid present at equilibrium must have been produced as a result of the reaction



while  $A^{2-}$  arises in part from the above reaction and in part from the reaction



The number of moles of  $A^{2-}$  produced by the reaction 8 is equal to the number of moles of  $H_2A$  produced by the same reaction. Consequently:-

$$[H^+] + [H_2A] = [A^{2-}] \quad (40)$$

This may be rearranged:-

$$[H_2A] = [A^{2-}] - [H^+] \quad (41)$$

A new formulation for ionic strength may be obtained by substituting equation 41 in equation 38.

$$\mu = \frac{1}{2}(2\alpha + 2m_{H^+} + 2m_{A^{2-}}) \quad (42)$$

$$\mu = \alpha + m_{H^+} + m_{A^{2-}} \quad (43)$$

A first approximation of ionic strength may be made by neglecting the second and third terms on the right of the equality.

When strong base, KOH, is added to the acid salt solution, the ions in solution will be  $M^+$ ,  $K^+$ ,  $H^+$ ,  $HA^-$  and  $A^{2-}$ . The ionic strength of such a solution may be computed by means of the equation

$$\mu = \frac{1}{2}(m_{M^+} + m_{K^+} + m_{H^+} + m_{HA^-} + 4m_{A^{2-}}) \quad (44)$$

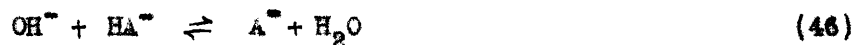
Using the two definitions of  $\alpha$ , (equations 13 and 14), as before

$$\mu = \frac{1}{2}(2\alpha + m_{K^+} + m_{H^+} - m_{H_2A} + 3m_{A^{2-}}) \quad (45)$$

As before, the only source of free acid is the reaction



But the added hydroxyl ion reacts with the monovalent anion according to the equation



Since the conditions have been so chosen that  $m_{\text{OH}^-}$  will be negligible at equilibrium, the  $\text{A}^{2-}$  produced by this last reaction will be equal to the quantity of strong base (KOH) added initially. A small amount of  $\text{A}^{2-}$  is also produced by the reaction



Therefore in this case, the number of moles of  $\text{A}^{2-}$  existing at equilibrium must be the same as the sum of the moles of strong base added, free acid produced and hydrogen ion produced.



Ionic strength of such a solution may now be formulated as

$$\mu = \frac{1}{2}(2\alpha + m_{\text{K}^+} + m_{\text{H}^+} - m_{\text{H}_2\text{A}} + 3m_{\text{K}^+} + 3m_{\text{H}^+} + 3m_{\text{H}_2\text{A}}) \quad (48)$$

$$\mu = \frac{1}{2}(2\alpha + 4m_{\text{K}^+} + 4m_{\text{H}^+} + 2m_{\text{H}_2\text{A}}) \quad (49)$$

$$\mu = \alpha - \beta + 2m_{\text{H}^+} + m_{\text{H}_2\text{A}} \quad (50)$$

As before, a first approximation of ionic strength may be made by neglecting the third and fourth terms on the right side of the equality.

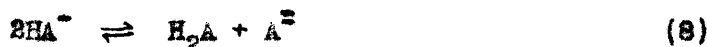
When a strong acid, HC, is added to the acid salt, ionic strength is defined by the equation

$$\mu = \frac{1}{2}(m_{\text{H}^+} + m_{\text{C}^-} + m_{\text{M}^+} + m_{\text{HA}^-} + 4m_{\text{A}^{2-}}) \quad (51)$$

If use is made of equation 13 and the definition of  $\beta$ , equation 51 may be rewritten

$$\mu = \frac{1}{2}(\alpha + \beta + m_{\text{H}^+} + m_{\text{HA}^-} + 4m_{\text{A}^{2-}}) \quad (52)$$

In this case, the free acid,  $H_2A$ , is produced by the two reactions



In this case,

$$H_2A = m_{Cl^-} - m_{H^+} + m_{A^{2-}} \quad (53)$$

$$= \beta - m_{H^+} + m_{A^{2-}} \quad (54)$$

$$\mu = \frac{1}{2}(2\alpha + \beta + m_{H^+} - m_{H_2A} + 3m_{A^{2-}}) \quad (55)$$

$$\mu = \frac{1}{2}(2\alpha + 2m_{H^+} + 2m_{A^{2-}}) \quad (56)$$

$$\mu = \alpha + m_{H^+} + m_{A^{2-}} \quad (57)$$

Here too, a first approximation of ionic strength may be made by neglecting the second and third terms to the right of the equality.

The correction terms in the various ionic strength equations may be evaluated by the following procedure. First, the values of  $\gamma_{HCl}^{\pm}$  corresponding to the approximate ionic strength at each experimental point may be interpolated from the data of Harned and Ehlers (26) plotted in Figure 8. Approximate values of  $K_1$  and approximate values of  $K_1'K_2'$  may be computed from the data of runs 1 and 8 by plotting  $X$  against  $Y$  in the manner described on pages 9 and 10. These approximate constants may then be used to compute the two additional terms in each of the ionic strength equations 43, 50 and 57.

A description of the method for calculating pH has already been presented on page 13. If the assumption is made that the activity coefficient of hydrogen ion is equal to the mean activity coefficient of hydrochloric acid, equation 35 may be used to calculate  $m_{H^+}$ .

$$pH = -\log m_{H^+} - \log \gamma_{H^+} = (E - E^0)/k + \log m_{Cl^-} - \gamma_{HCl}^{\pm} \quad (58)$$

$$-\log m_{H^+} = (E - E^0)/k + \log m_{Cl^-} - \gamma_{Cl^-}^2 \quad (59)$$

The molality of malate ion present in solutions prepared with added strong acid, may most readily be estimated by means of the approximate values of  $K_1K_2$ . The "apparent" ionization constants  $K'_1$  and  $K'_2$  are defined by the equations

$$K'_1 = \frac{m_{H^+} \cdot m_{HA^-}}{m_{H_2A}} \quad (60)$$

$$K'_2 = \frac{m_{H^+} \cdot m_{A^{2-}}}{m_{HA^-}} \quad (61)$$

The product of the two is :-

$$K_1K_2 = \frac{m_{H^+}^2 \cdot m_{A^{2-}}}{m_{H_2A}} \quad (62)$$

This can be rearranged to give :-

$$m_{A^{2-}} = \frac{K_1K_2 m_{H_2A}}{m_{H^+}^2} \quad (63)$$

On substituting the value of the molality of the undissociated acid given by equation 54 into equation 63 one obtains :-

$$m_{A^{2-}} = \frac{K_1K_2 (\beta - m_{H^+} + m_{A^{2-}})}{m_{H^+}^2} \quad (64)$$

Since  $\beta$  is much larger than  $m_{H^+}$  and  $m_{A^{2-}}$ , a sufficiently accurate estimate of  $m_{A^{2-}}$  may be made with the aid of the equation

$$m_{A^{2-}} = \frac{K_1K_2 \beta}{m_{H^+}^2} \quad (65)$$

A different equation was found to be more satisfactory for evaluating the correction term in the case of added strong base or in the case of the potassium acid malate taken by itself. An approximation of the thermodynamic ionization constant,  $K_1$ , rather than the "apparent"

dissociation constant  $K_1'$ , was obtained by extrapolating to infinite dilution, the approximate data obtained from run 8. Use was made of the equation describing the first dissociation of a dibasic acid:-

$$K_1 = \frac{a_{H^+} \cdot m_{HA^-} \cdot \gamma_{HA^-}}{m_{H_2A} \cdot \gamma_{H_2A}} \quad (9)$$

Since an approximate value of  $m_{H_2A}$  is all that is required, several assumptions may be made to simplify the calculations. It was assumed that the activity coefficient of the undissociated acid,  $\gamma_{H_2A}$ , is not significantly less than 1 and also that  $\gamma_{HA^-}$  is not significantly different from  $\gamma_{HCl}^{\pm}$ . It is impossible to evaluate the activity coefficient for a single ion but there are some data that may be cited as justification for this last assumption. For example, the mean activity coefficients of 38 1-1 electrolytes have been tabulated by Harned and Owen (27). In a few instances the value of the mean activity coefficient at 25° C, 0.1 molal, is different from the mean of these electrolytes by perhaps 5 per cent. In the majority of the salts the difference from the mean is less than 3 per cent. Bates, Diamond, Eden and Acree (9) have found that there are no specific effects in a study of the effects strong electrolytes on the activity coefficients of p-phenolsulfonate buffers.

Equation 9 may be rewritten on the basis of these assumptions:-

$$m_{H_2A} = \frac{m_{HA^-} \cdot m_{H^+} \cdot \gamma_{HCl}^2}{K_1} \quad (66)$$

If equation 18 is introduced in place of  $m_{HA^-}$  in equation 66, then

$$m_{H_2A} = \frac{(\alpha + \beta - 2m_{H_2A}) \cdot m_{H^+} \cdot \gamma_{HCl}^2}{K_1} \quad (67)$$

The quantity  $m_{H_2A}$ , appearing on the right side of equation 67, may

be neglected in this calculation of the molality of the free acid.

### C. The First Ionization Constant, $K_1$

The first approximation of ionic strength has been tabulated in the first column of Table 2. The final value of ionic strength has been tabulated in the last column of Table 2. Values of X and Y have been calculated by means of equations 28 and 29 and the results also tabulated in Table 2. These values of X and Y were plotted against ionic strength (Figures 1.1a to 1.7b). A family of curves was drawn, each curve being made up of values of X or of Y calculated for solutions of the same buffer ratio and temperature. The values of X and Y corresponding to values of ionic strength 0.06, 0.05, 0.04, 0.03, 0.025, 0.020 and 0.014 were interpolated from this family of curves. The values of X and Y obtained by this interpolation are presented in Table 4.

A second series of graphs (Figures 2.1 to 2.11) was prepared by employing the values assembled in Table 4. X was plotted against Y and a family of straight lines was drawn by joining the points corresponding to constant ionic strength and temperature but varying buffer ratio. The slopes of these lines ( $\sigma K_1$ ) were computed and assembled in Table 5.

The logarithms of these  $\sigma K_1$  values were plotted against ionic strength at each temperature (Figures 3.1, 3.2). It has been assumed that  $\log \gamma_{H_2Mal}$  is, to a first approximation, a linear function of ionic strength at these dilutions. Accordingly, the best straight line was drawn through the points and the line extrapolated to zero ionic strength. The values of  $p\sigma K_1$  ( $-\log \sigma K_1$ ) at different values of the

ionic strength, the extrapolated values of  $pK_1$  at zero ionic strength and the slopes of the straight lines are given in Table 6.

#### D. The second Ionization Constant, $K_2$

Use may once again be made of equation 34. The second ionization constant,  $K_2$ , may be computed from the values of the intercept of the plot of  $X$  against  $Y$  ( $K_1 K_2 / \rho$ ). If the experimental errors for all the measured points are about equal in magnitude, it is to be expected that the best values of the intercept may be obtained by the shortest extrapolations. For this reason, only the data derived from the five runs made with the more basic solutions ( and with the smallest values of  $X$  and  $Y$ ) were used in the computation of  $K_2$ .

Once  $K_1$  and  $\sigma K_1$  have been evaluated, the only remaining term in equation 34 is  $K_2 / \rho$ . Values of  $-\log K_2 / \rho$  were computed for each experimental value of  $X$  and  $Y$  obtained in these five runs. The results of the computation are assembled in Table 7. In this case however,  $\log \rho$  is not expressible as a linear function of ionic strength. The most successful description for the activity coefficients of ions in dilute solution is the familiar Debye-Hückel equation

$$\log \gamma_1 = \frac{-z_1^2 A \mu^{\frac{1}{2}}}{1 + B a_1 \mu^{\frac{1}{2}}} \quad (68)$$

This form of the Debye-Hückel equation has been used to compute the activity coefficient term,  $\rho$ , in equation 34. The quantity  $\rho$  (equation 34) is the product of several activity coefficients of ions in the solution. In such a case an empirical modification has been used so that  $\sum \log \gamma_1$  can be expressed simply. It has been assumed that  $a^*$ , an "average" value of the "ionic diameter", may be substituted for  $a_1$  in



equation 68. If this is done, the equation becomes

$$\log \rho = \frac{-2.3\mu^{\frac{1}{2}}}{1 + Ba^*\mu^{\frac{3}{2}}} \quad (69)$$

It is evident that if a proper value of  $a^*$  is found and  $\log \rho$  is computed, this quantity may be added to the experimentally derived quantity  $\log K_2/\rho$ . This sum should be a constant,  $\log K_2$ , at any specified temperature. The constancy of this sum constitutes a criterion for determining the correctness of the values of  $\log \rho$  computed by means of the Debye-Hückel equation. Accordingly, a plot of  $\log K_2/\rho$  (experimentally derived) and  $\log \rho$  (computed from the Debye-Hückel equation) against  $\mu$  was made at each temperature (Figures 4.1 and 4.2). If the proper value of  $\log \rho$  has been used, such a plot will be a straight line parallel to the abscissa.

The computed values of  $\log K_2/\rho$  at 25° C were plotted against ionic strength and a smooth curve was drawn through the points. The value of the ordinate for each of two arbitrarily chosen values of the abscissa ( $\mu = 0.025$  and  $\mu = 0.06$ ) were read from this curve. The difference between the ordinate values of these two points is

$$\log \frac{K_2}{\rho_1} - \log \frac{K_2}{\rho_2} = \log \frac{\rho_2}{\rho_1} \quad (70)$$

Equation 69 may be substituted into equation 70 and the resulting expression rearranged to solve for  $a^*$ .

$$a^{*2} + \frac{1}{B} \left( \mu_1^{-\frac{1}{2}} + \mu_2^{-\frac{1}{2}} \right) a^* - \frac{2A}{B^2} \left( \mu_1^{-\frac{1}{2}} - \mu_2^{-\frac{1}{2}} \right) \log \frac{\rho_1}{\rho_2} + \frac{\mu_1^{-\frac{1}{2}} \mu_2^{-\frac{1}{2}}}{B^2} = 0 \quad (71)$$

The value of  $a^*$  obtained by the solution of equation 71 is  $6.25 \times 10^{-8}$ . No significance is attached to the third figure. The term,  $\log \rho$ , is quite insensitive to changes in  $a^*$ . For example, if  $a^*$  is

assigned a value of  $6.0 \times 10^{-8}$ ,  $\log \rho$  will be  $-0.1706$  at  $\mu^{\frac{1}{2}} = 0.25$ . The value obtained for  $\log \rho$  ( $a^* = 6.25 \times 10^{-8}$ ) at the same ionic strength is  $-0.1680$ . The effect of different values of  $a^*$  on  $\log \rho$  will be even less at lower values of ionic strength.

The same value of  $a^*$  was used at all temperatures. The values of the parameters A and B in the Debye-Hückel equation (Table 3) were taken from the recomputation of these quantities by Manov, Bates, Hamer and Acree (34).

An average was taken of the values of  $-\log K_2$  (Figures 4.1 and 4.2) obtained by the procedure described above. An arbitrary weight of two was assigned to those values computed from runs 1 and 6, since these runs were prepared with no added strong acid or base and consequently furnished values of Y and X closest to the origin.

#### E. Thermodynamic Constants

Harned and Robinson (28) have suggested the use of the empirical equation

$$-\log K = pK = A/T + B + CT \quad (72)$$

to describe the behavior of the ionization constant as a function of temperature. The parameters of such an equation have been calculated for both ionization constants of malic acid.

For the first ionization constant of d,l-malic acid

$$pK_1 = \frac{1359.85}{T} - 5.1382 + 0.01355 T \quad (73)$$

The  $pK_1$  values derived from the experimental data and the  $pK_1$  values calculated from the equation above are assembled in Table 8 and represented graphically in Figure 5. The mean deviation between the computed points and the smoothed curve is  $\pm 0.0013$  pK units.

In the case of the second ionization constant,

$$pK_2 = \frac{1658.53}{T} - 6.2364 + 0.01935 T \quad (74)$$

was the equation obtained. The experimentally computed and the smoothed values of  $pK_2$  are compared in Table 9 and in Figure 6. In this case, the mean deviation between the computed and the smoothed points was calculated to be  $\pm 0.0011$  pK units.

The experimentally derived and the smoothed values of  $K_1$  and  $K_2$  have been assembled in Table 11.

The thermodynamic quantities associated with the equilibrium constants may be computed after performing simple operations on equation 72.

$$\Delta F^\circ = -RT \ln K = 2.3026 R (A + BT + CT^2) \quad (75)$$

$$\Delta H^\circ = RT^2 \frac{d \ln K}{dT} = 2.3026 R(A + 2CT) \quad (76)$$

$$\Delta S^\circ = \frac{-d\Delta F^\circ}{dT} = -2.3026 R(B + 2CT) \quad (77)$$

$$\Delta Cp^\circ = \frac{T d\Delta S^\circ}{dT} = -2.3026 R(2CT) \quad (78)$$

Values of these quantities for the two dissociation constants have been assembled in Table 11.

## DISCUSSION

A considerable number of determinations of the ionization constants of malic acid have been made in the last sixty years and a number of different methods have been used. The values of the ionization constants obtained by these earlier workers have been assembled in Table 12. The columns designated  $K_1$  and  $K_2$  list the values that have not been corrected for activity. In most of the determinations to be found in the literature, the author has made no mention of a calculation using activities rather than concentrations. Unless the author made a definite statement that activity coefficients had been used to correct the equilibrium equations, it was assumed that the ionization constants had been calculated on a concentration basis.

The values of the "apparent" ionization constants listed in Table 12 are uniformly higher than the thermodynamic ionization constants. This is to be anticipated since the activity coefficient correction would decrease the value of the ionization constant.

The first thermodynamic ionization constant of d,l-malic acid has been determined by Larsson (29) and by Hamer (21). The value for  $K_1$  computed in this paper is in quite good agreement with that of Larsson (at 15° C) but is about 4 per cent lower than the value of  $K_1$  computed by Hamer (at 25° C).

It is clear from Table 12 that agreement between the various workers is better for determinations of the first ionization constant than for the second ionization constant. Three previous workers have determined the thermodynamic ionization constant  $K_2$ . Larsson in particular, has determined  $K_2$  by three different experimental methods. (30,31,32) All

these previous determinations are somewhat lower than the values given here. The values of Duboux and Fremmel (19) and Larsson (32) obtained from solubility measurements agree fairly well with the value of  $K_2$  obtained by Hamer (21) on the basis of pH titrations. But these values are about  $0.5 \times 10^{-6}$  lower than the value obtained here. On the other hand the electrometric determination of Larsson (31) at  $18^\circ \text{C}$  is in fair agreement with the value of  $K_2$  obtained in this paper. No statement may be made about the relative accuracy of these determinations of  $K_2$ . The rather large differences do serve to emphasize the fact that the determination of the second ionization constant is not as satisfactory as the determination of the first ionization constant.

## DISCUSSION OF ERRORS

A rigorous determination of the errors involved in the computation of ionization constants is difficult because of the devious nature of the computation. However, a reasonable idea of the over-all error can be obtained by carrying through a sample calculation.

Even though the sensitivity of the potentiometric circuit is about  $\pm 0.01$  millivolt, the agreement between identical cells or even between sets of electrodes in the same cell are no better than  $\pm 0.10$  millivolt. It has been assumed for the purpose of this discussion that the error in the measurement of emf is about  $\pm 0.15$  millivolt.

The cell prepared with the lowest concentration of buffer solution of Run 4 developed a potential of 0.53133 v at 0° C. The values of the standard electrode potential,  $E^\circ$ , and the value of  $k = 2.3026 RT/F$  at 0° C are 0.23652 and 0.054201 respectively (Table 3). It may be safely assumed that the errors in  $E^\circ$  and  $k$  are negligible compared to the error in the experimentally determined value of  $E$ .

$$\frac{E - E^\circ}{k} = \frac{0.53133 \pm 0.00015 - 0.23652}{0.054201} \quad (79)$$

$$\frac{E - E^\circ}{k} = 5.4392 \pm 0.0027 \quad (80)$$

The quantity  $p_w H$  has been defined by Bates (6):-

$$p_w H = \frac{E - E^\circ}{k} + \log m_{Cl^-} \quad (81)$$

Since the molality of the chloride ion was maintained as close to 0.00800 molal as possible,

$$\log m_{Cl^-} = -2.0968 \pm 0.0001 \quad (82)$$

If this value is substituted into equation 81 :-

$$p_w H = 5.4392 \pm 0.0027 - 2.0968 \pm 0.0001 \quad (83)$$

$$p_w H = 3.3424 \pm 0.0028 \quad (84)$$

The quantity,  $P$ , has been defined earlier (Equation 27). It can be seen by inspection that  $P$  is the antilog of  $-p_w H$ . In this sample calculation:-

$$P = 10^{-3.3424 \pm 0.0028} \quad (85)$$

$$P = (4.546 \pm 0.030) \times 10^{-4} \quad (86)$$

The errors in the molal quantities  $\alpha$  and  $\beta$ , like the errors in  $m_{Cl^-}$ , are negligible in comparison with the error in  $E$ . But  $m_{H^+}$  is involved in the calculation of  $B$  (Equation 11). The values of  $m_{H^+}$  were computed by means of the following equation:-

$$- \log m_{H^+} = (E - E^0)/k + \log m_{Cl^-} + 2 \log \gamma_{HCl}^{\pm} \quad (87)$$

If equation 81 is substituted into the above equation, it becomes

$$- \log m_{H^+} = p_w H + 2 \log \gamma_{HCl}^{\pm} \quad (88)$$

The mean activity coefficient of hydrochloric acid has already been discussed on page 18. In the light of this discussion, an error of  $\pm 0.002$  has been assigned to each value of  $\gamma_{HCl}^{\pm}$ . The quantity  $p_w H$  for this example has already been computed (Equation 84). The mean activity coefficient of hydrochloric acid is 0.873 at ionic strength 0.02006 (Figure 8).

$$- \log m_{H^+} = 3.3424 \pm 0.0028 + 2 \log(0.873 \pm 0.002) \quad (89)$$

$$- \log m_{H^+} = 3.2244 \pm 0.0048 \quad (90)$$

$$m_{H^+} = (5.97 \pm 0.07) \times 10^{-4} \quad (91)$$

It can be seen that the error in  $m_{H^+}$  is over one per cent. This is larger than the errors in any of the quantities considered so far. But in most of the calculations, the quantity  $B$  is so large that it is quite insensitive to errors in  $m_{H^+}$ . In the example under discussion:-

$$\beta = 0.007352 \quad (92)$$

As was noted before

$$B = \beta \frac{-m}{H^+} \quad (11)$$

Substituting into equation 11 the proper numerical values:-

$$B = 0.006755 \pm 0.000007 \quad (93)$$

In this example

$$\alpha = 0.011394 \quad (94)$$

Therefore,

$$\alpha + B = 0.018149 \pm 0.000007 \quad (95)$$

$$\alpha - B = 0.004639 \pm 0.000007 \quad (96)$$

The quantities X and Y may now be computed by the use of equations 28 and 29 respectively.

$$X = \frac{PB}{(\alpha + B)} \quad (28)$$

$$X = \frac{(4.546 \pm 0.030) \times 10^{-4} \times (6.755 \pm 0.007) \times 10^{-3}}{(18.149 \pm 0.007) \times 10^{-3}} \quad (97)$$

$$X = (1.6919 \pm 0.0076) \times 10^{-4} \quad (98)$$

$$Y = \frac{P^2(\alpha - B)}{(\alpha + B)} \quad (29)$$

$$Y = \frac{(2.0662 \pm 0.026) \times 10^{-7} \times (4.639 \pm 0.007) \times 10^{-3}}{(18.149 \pm 0.007) \times 10^{-3}} \quad (99)$$

$$Y = (5.28 \pm 0.071) \times 10^{-8} \quad (100)$$

The evaluation of  $K_1'$  depends upon the slope of the plot of X against Y. The slope may be expressed by the equation

$$K_1' = \frac{Y_1 - Y_2}{X_1 - X_2} \quad (101)$$

Since this plot passes very close to the origin,  $X_2$  and  $Y_2$  can be chosen to be negligible when compared to  $X_1$  and  $Y_1$ . The slope,  $K_1'$ , may be approximated by the equation:-



$$K'_1 \approx Y_1/K_1 \quad (102)$$

If the equations 28 and 29 are substituted into this approximate expression:-

$$K'_1 \approx \frac{P^2(\alpha - B)(\alpha + B)}{(\alpha + B)PB} \quad (103)$$

$$K'_1 \approx \frac{P(\alpha - B)}{B} \quad (104)$$

The numerical values may be substituted into equation 104.

$$K'_1 \approx \frac{(4.546 \pm 0.030) \times 10^{-4} \times (4.639 \pm 0.007) \times 10^{-3}}{(6.755 \pm 0.007) \times 10^{-3}} \quad (105)$$

$$K'_1 \approx (3.122 \pm 0.021) \times 10^{-4} \quad (106)$$

This corresponds to a relative error in the determination of  $K'_1$  of 0.66 per cent. The precise value of  $K'_1$  determined graphically at this value of the ionic strength is  $(2.907 \pm 0.020) \times 10^{-4}$ . The value of  $pK'_1$  will be  $3.5365 \pm 0.0027$ .

The procedure employed in the computation of  $K_2$  depends upon the experimentally derived quantity  $K_1 K_2 / \rho$ , the intercept of the plot of  $X$  against  $Y$ . It is to be expected that this quantity will be in error to the same extent as any determination of  $Y$ . The error in  $Y$  has been evaluated in equation 100. The relative error in  $Y$  is about 1.3 per cent. The relative error in  $K_1$  as evaluated above is 0.66 per cent.

Finally, the error involved in the determination of  $\rho$  must be considered. Possible errors arising from the use of slightly different values of the parameter  $a^*$  of the Debye-Hückel equation, has already been touched upon on page 27. Errors arising from this source will be largest in the most concentrated solutions. For example,  $-\log \rho$  calculated for the most concentrated solution of Run 1 at  $0^\circ \text{C}$  will be 0.1682, if  $a^*$  is assumed to be  $6.25 \times 10^{-8}$ ; and 0.1708, if  $a^*$  is assigned

the value  $6.00 \times 10^{-8}$ . The values of  $\rho$ , for these values of  $a^*$ , will be 0.679 and 0.675 respectively.

If the same sort of calculation is made for the most dilute solution of Run 2 ( $\mu^{\frac{1}{2}} = 0.1149$ ), then  $\rho = 0.811$  when  $a^*$  is  $6.25 \times 10^{-8}$  and  $\rho = 0.810$  when  $a^*$  is  $6.00 \times 10^{-8}$ . Accordingly, the average relative error in the activity coefficient term,  $\rho$ , has been assumed to be 0.5 per cent.

The formula for the "propagation of error" has a simple expression for the product of a number of variables:-

$$\Delta R/R = \left[ (\Delta x/x)^2 + (\Delta y/y)^2 + (\Delta z/z)^2 \right]^{\frac{1}{2}} \quad (107)$$

If the values of the relative errors of  $Y$ ,  $K_1$  and  $\rho$  are substituted into equation 107:-

$$\Delta R/R = \left[ (0.0132)^2 + (0.0066)^2 + (0.0050)^2 \right]^{\frac{1}{2}} \quad (108)$$

$$\Delta R/R = 0.0156 \quad (109)$$

The average value of  $K_2$  at  $0^\circ \text{C}$  has been determined to be  $7.592 \times 10^{-6}$ . If the relative error is 1.56 per cent, the absolute error will be  $\pm 0.119 \times 10^{-6}$ . An independent check of the indeterminate errors may be had by using the data of Table 9. It has been found that the mean of 25 determinations of  $\text{p}K_2$  at  $0^\circ \text{C}$  is 5.1194. The mean deviation is  $\pm 0.0065$   $\text{p}K$  units. If the antilog of  $\text{p}K_2$  is determined for  $\text{p}K_2 = 5.1194$  and  $\text{p}K_2 = 5.1129$ ,  $K_2$  is computed to be 7.596 in the first case and 7.711 in the second case. The difference is  $0.115 \times 10^{-6}$ ; a value almost identical with the error term  $0.119 \times 10^{-6}$  calculated above.

In actuality, the precision of the average value of  $K_2$  should be somewhat better than the error calculated above, since the average values of  $K_2$  are based on 25 determinations at each temperature. The standard deviation of the mean will consequently be approximately  $0.0012$   $\text{p}K$  units or  $\pm 0.024 \times 10^{-6}$  "K" units. A further check can be found

in Tables 9 and 10 by comparing the experimental averages of  $pK_2$  and  $K_2$  with the values read from the smoothed curve. Here it can be seen that the average difference between the experimental and smoothed values for the temperature range  $0^\circ$  to  $50^\circ$  C is 0.0011 pK units or 0.021 "K" units. This remarkable agreement is fortuitous but it indicates the consistency of the estimation of error.

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Table 1. Buffer ratios and dilution ratios of runs  
1 to 8.

Dilution ratio		1	2	3	4	5
Run	Buffer ratio					
		$\frac{\text{HG10}_4}{\text{KHM}_{\text{al}}}$				
1	.0000	1	.6527	.3893	.2120	.09764
2	-.4002*	1	.6617	.3352	.2128	.09314
3a	-.6607	1	.7432	.4183	.3076	.19815
4	.6303	1	.6617	.3751	.2111	-
5	.3676	1	.6587	.3417	.2264	.09775
6	.0000	1	.6545	.4122	.2279	.08672
7	-.4161	1	.6448	.3643	.2247	.09827
8	.6695	1	.6654	.3372	.2152	.09442

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\*The minus sign was used to designate the ratio  
KOH/KHM<sub>al</sub>.

Table 2.1. The experimental values of terminal voltage, ionic quantities and the second approximation of ionic

Run	$\mu$ $\times 10^3$	E volts	$\frac{E - E^0}{k}$	p <sub>WH</sub>	$\gamma_{\text{HCl}}$	$-\log m_{\text{H}^+}$	$m_{\text{H}^+}$ $\times 10^4$	B $\times 10^3$	$\alpha + B$ $\times 10^3$	$\alpha - B$ $\times 10^3$	P $\times 10^5$	p <sup>2</sup> $\times 10^{10}$	X $\times 10^6$	Y $\times 10^9$	$\mu_2$ $\times 10^3$
8	70.41	.52226	5.2719	3.1749	.808	2.9897	10.24	42.636	105.046	19.774	66.85	4469	271.3	84.13	71.57
	49.53	.52298	5.2851	3.1881	.828	3.0241	9.46	28.105	69.635	13.425	64.85	4206	261.7	81.09	50.58
	29.04	.52486	5.3198	3.2229	.853	3.0849	8.22	13.900	34.945	7.145	59.86	3583	238.1	73.32	29.93
	21.43	.52591	5.3577	3.2608	.869	3.3188	7.26	8.670	22.101	4.761	54.85	3009	215.2	64.82	22.21
	13.89	.53095	5.4324	3.3355	.890	3.2343	5.83	3.539	9.432	2.354	46.19	2133	173.3	53.24	14.50
4	62.44	.52749	5.3684	3.2720	.815	3.0944	8.05	88.010	88.010	19.956	53.45	2857	206.6	64.79	62.98
	44.06	.52793	5.3755	3.2800	.833	3.1213	7.56	58.015	58.015	13.429	52.49	2755	201.7	63.77	44.62
	28.50	.52949	5.4053	3.3086	.854	3.1715	6.74	32.542	32.542	7.858	49.13	2414	187.1	58.30	29.02
	19.57	.53133	5.4392	3.3424	.873	3.2244	5.97	18.149	18.149	4.639	45.46	2066	169.2	52.31	20.06
1	61.15	.58026	6.3420	4.2454	.815	4.0678	.855		53.060	53.230	56683	32.30	-.0916	3.241	68.44
	42.72	.58074	6.3508	4.2543	.824	4.0966	.801		34.609	34.769	5.569	31.00	-.1288	3.115	47.41
	28.69	.58134	6.3619	4.2653	.853	4.1272	.746		20.614	20.764	5.428	29.47	-.1965	2.968	31.62
	19.29	.58216	6.3770	4.2805	.873	4.1625	.688		11.197	11.337	5.243	27.49	-.3221	2.783	20.98
	13.20	.58319	6.3960	4.2995	.892	4.2002	.631		5.126	5.252	5.018	25.13	-.6174	2.580	14.06
6	62.45	.58026	6.3420	4.2450	.815	4.0674	.856		54.361	54.533	5.682	32.35	-.0896	3.246	69.94
	43.64	.58094	6.3508	4.2543	.834	4.1000	.794		35.558	35.720	5.526	30.54	-.1235	3.067	48.47
	30.44	.58135	6.3619	4.2651	.850	4.1239	.752		22.366	22.526	5.431	29.49	-.1825	2.969	33.43
	20.41	.58211	6.3770	4.2792	.871	4.1592	.692		12.339	12.480	5.258	27.64	-.2954	2.796	22.13
	12.72	.58315	6.3960	4.2984	.895	4.2020	.628		4.659	4.785	5.031	25.31	-.6782	2.599	13.42
2	62.51	.61330	6.9515	4.8546	.814	4.6759	.211	-12.137	18.136	42.410	1.398	1.954	-9.354	.4569	63.36
	34.38	.61435	6.9709	4.8740	.832	4.7142	.193	- 8.036	11.995	28.068	1.337	1.787	-8.956	.4181	44.92
	26.27	.61543	6.9908	4.8939	.857	4.7599	.174	- 4.078	6.051	14.225	1.277	1.639	-8.605	.3834	26.54
	19.60	.61611	7.0034	4.9064	.873	4.7884	.163	- 2.594	3.847	9.035	1.240	1.539	-8.365	.3614	19.78
	13.08	.61785	7.0355	4.9385	.892	4.8392	.145	- 1.143	1.677	3.963	1.152	1.327	-7.854	.3137	13.15
7	63.60	.61511	6.9849	4.8880	.814	4.7093	.195	-12.647	17.699	42.993	1.294	1.675	-9.248	.4068	64.38
	43.85	.61533	6.9890	4.8921	.833	4.7334	.185	- 8.161	11.407	27.729	1.282	1.644	-9.172	.3995	44.34
	28.25	.61705	7.0207	4.9238	.854	4.7867	.163	- 4.616	6.438	15.670	1.192	1.420	-8.545	.3457	28.54
	20.50	.61730	7.0253	4.9284	.871	4.8085	.155	- 2.853	3.966	9.672	1.179	1.391	-8.482	.3391	20.67
	13.46	.61908	7.0582	4.9613	.891	4.8610	.138	- 1.255	1.727	4.237	1.093	1.195	-7.941	.2932	13.54
3a	61.83	.63651	7.3798	5.2845	.814	5.1058	.0784	-15.319	7.856	38.494	.5193	.2697	-10.127	.1321	61.98
	48.01	.63767	7.4012	5.3055	.828	5.1416	.0722	-11.386	5.837	28.609	.4948	.2449	-9.653	.1200	48.12
	30.62	.63848	7.4161	5.3200	.850	5.1788	.0663	- 6.412	3.283	16.107	.4787	.2291	-9.348	.1124	30.68
	24.56	.63916	7.4287	5.3322	.861	5.2022	.0628	- 4.720	2.413	11.844	.4653	.2165	-9.103	.1063	24.81
	18.67	.63978	7.4401	5.3435	.875	5.2275	.0592	- 3.040	1.552	7.632	.4534	.2056	-8.873	.1011	18.70

strength, molality; terms of equation 23 derived from these strength. ° Centigrade.



Table 2.2. The experimental values of terminal voltage, ionic strength, molality; terms in equation 23 derived from these quantities and a second approximation of ionic strength. 5° Centigrade.

Run	$\mu_1$ x10 <sup>3</sup>	E volts	$\frac{E - E^0}{k}$	p <sub>w</sub> H	$\gamma_{\pm HCl}$	-log m <sub>H+</sub>	m <sub>H+</sub> x10 <sup>4</sup>	B x10 <sup>3</sup>	$\alpha + B$ x10 <sup>3</sup>	$\alpha - B$ x10 <sup>3</sup>	P x10 <sup>5</sup>	P <sup>2</sup> x10 <sup>10</sup>	X x10 <sup>6</sup>	Y x10 <sup>9</sup>	M <sub>2</sub> x10 <sup>3</sup>
8	70.41	.52395	5.2526	3.1556	.808	2.9704	10.95	42.565	104.975	19.845	69.89	4884	283.4	92.33	71.65
	49.53	.52477	5.2674	3.1704	.828	3.0064	9.85	28.066	69.596	13.464	67.55	4563	272.4	88.27	50.62
	29.04	.52671	5.3026	3.2057	.855	3.0697	8.52	13.870	34.915	7.175	62.27	3878	247.4	79.69	29.96
	21.43	.52873	5.3392	3.2423	.870	3.1213	7.56	8.640	22.071	4.791	57.24	3276	224.1	71.12	22.24
	13.89	.53316	5.4194	3.3325	.890	3.2213	6.01	3.521	9.414	2.372	47.59	2265	278.0	57.06	14.52
4	62.44	.52921	5.3479	3.2515	.816	3.0749	8.42	33.990	87.793	19.993	56.04	3140	216.5	71.36	63.00
	44.06	.52967	5.3562	3.2597	.834	3.1020	7.91	22.258	57.980	13.464	55.00	3025	211.1	70.23	44.64
	28.50	.53123	5.3845	3.2878	.856	3.1527	7.04	12.362	32.612	7.888	51.54	2657	195.4	64.26	29.05
	19.57	.53326	5.4212	3.3245	.873	3.2065	6.22	6.730	18.074	4.664	47.38	2244	176.4	57.92	20.08
5	62.03	.55238	5.7677	3.6709	.816	3.4943	3.20	19.544	73.575	34.487	21.33	455.1	56.67	21.33	63.03
	43.59	.55293	5.7776	3.6808	.833	3.5221	3.01	12.783	48.373	22.807	20.85	434.9	55.11	20.50	44.38
	26.46	.55361	5.7899	3.6931	.860	3.5621	2.74	6.514	24.977	11.949	20.27	411.0	52.87	19.60	27.04
	20.23	.55437	5.8037	3.7069	.872	3.5879	2.58	4.239	16.470	7.992	19.64	385.7	50.55	18.72	20.70
	13.28	.55645	5.8414	3.7445	.891	3.6443	2.27	1.714	6.997	3.567	18.01	324.3	44.14	16.53	13.63
1	61.15	.58316	6.3253	4.2288	.816	4.0522	.887		53.055	53.233	5.905	34.87	-.0987	3.499	68.49
	42.72	.58369	6.3349	4.2384	.835	4.0818	.828		34.606	34.772	5.776	33.36	-.1383	3.352	47.45
	28.69	.58423	6.3447	4.2482	.855	4.1122	.772		20.612	20.766	5.647	31.89	-.2116	3.213	31.55
	19.29	.58511	6.3607	4.2641	.873	4.1462	.714		11.196	11.338	5.444	29.63	-.3473	3.001	20.91
	13.20	.58621	6.3806	4.2830	.891	4.1828	.656		5.123	5.255	5.212	27.16	-.6678	2.786	14.04
6	62.45	.58316	6.3253	4.2284	.815	4.0508	.889		54.358	54.536	5.910	34.93	-.0967	3.504	69.96
	43.64	.58386	6.3380	4.2411	.835	4.0845	.823		35.791	35.555	5.740	32.95	-.1329	3.310	48.52
	30.44	.58430	6.3460	4.2491	.853	4.1109	.775		22.364	22.518	5.636	31.76	-.1952	3.198	33.44
	20.41	.58507	6.3599	4.2630	.872	4.1440	.718		12.336	12.480	5.457	29.73	-.3175	3.013	22.11
	12.72	.58615	6.3795	4.2826	.894	4.1852	.653		4.657	4.787	5.217	27.22	-.7313	2.793	13.44
2	62.51	.61715	6.9412	4.8442	.815	4.6665	.216	-12.138	18.135	42.411	1.432	2.049	-9.581	.4792	63.33
	44.33	.61811	6.9586	4.8616	.833	4.7029	.198	-8.037	11.994	28.069	1.375	1.892	-9.216	.4426	44.90
	26.27	.61920	6.9783	4.8813	.860	4.7503	.178	-4.079	6.051	14.226	1.314	1.727	-8.859	.4061	26.53
	19.60	.61991	6.9911	4.8942	.873	4.7762	.167	-2.595	3.846	9.036	1.276	1.628	-8.606	.3824	19.77
	13.03	.62084	7.0080	4.9111	.891	4.8109	.155	-1.144	1.676	3.964	1.227	1.506	-7.378	.3563	13.15
7	63.60	.61820	6.9710	4.8741	.814	4.694	.202	-12.647	17.699	42.993	1.336	1.735	-9.548	.4337	64.36
	43.85	.61902	6.9750	4.8781	.835	4.720	.191	-8.162	11.406	27.730	1.324	1.753	-9.473	.4261	44.33
	28.25	.62082	7.0077	4.9107	.857	4.775	.168	-4.616	6.438	15.670	1.229	1.510	-8.811	.3675	28.53
	20.50	.62106	7.0120	4.9151	.872	4.795	.160	-2.854	3.965	9.674	1.216	1.473	-8.749	.3606	20.66
	13.46	.62292	7.0457	4.9388	.891	4.838	.145	-1.255	1.727	4.237	1.125	1.266	-8.181	.3107	13.54
3a	61.83	.64053	7.3648	5.2695	.815	5.0919	.0794	-15.319	7.856	38.494	.5376	.2890	-10.483	.1416	61.79
	42.01	.64169	7.3858	5.2902	.829	5.1275	.0746	-11.388	5.837	28.609	.5127	.2628	-10.002	.1288	48.11
	30.62	.64249	7.4003	5.3041	.851	5.1640	.0685	-6.412	3.283	16.107	.4965	.2465	-9.695	.1209	30.67
	24.56	.64329	7.4148	5.3183	.863	5.1903	.0645	-4.716	2.413	11.844	.4805	.2308	-9.392	.1133	24.81
	18.67	.64401	7.4278	5.3312	.875	5.2152	.0609	-3.040	1.552	7.632	.4664	.2176	-9.135	.1070	18.70







Table 2.6. The experimental values of terminal voltage, ionic strength, molality, terms of equation 23 derived from these quantities and a second approximation of ionic strength 25° Centigrade.

Run	$\mu_1$ x10 <sup>3</sup>	E volts	$\frac{E - E^0}{k}$	p <sub>w</sub> H	V <sub>t</sub> HCl	-log m <sub>H+</sub>	m <sub>H+</sub> x10 <sup>4</sup>	B x10 <sup>3</sup>	$\alpha + B$ x10 <sup>3</sup>	$\alpha - B$ x10 <sup>3</sup>	P x10 <sup>5</sup>	P <sup>2</sup> x10 <sup>10</sup>	X x10 <sup>6</sup>	Y x10 <sup>9</sup>	$\mu_2$ x10 <sup>3</sup>
8	70.41	.53028	5.2031	3.1061	.806	2.9193	12.04	42.456	104.866	19.954	78.33	6135	317.1	116.73	71.73
	49.53	.53125	5.2196	3.1226	.825	2.9556	11.08	27.943	69.473	13.587	75.41	5686	303.3	111.20	50.73
	29.04	.53346	5.2569	3.1600	.852	3.0208	9.53	13.769	34.814	7.276	69.18	4786	273.6	100.03	30.05
	21.43	.53603	5.3004	3.2035	.868	3.0805	8.31	8.565	21.996	4.866	62.59	3917	243.7	86.66	22.31
	13.89	.54102	5.3847	3.2878	.889	3.1856	6.52	3.470	9.363	2.423	51.55	2657	191.0	68.77	14.57
4	62.44	.53605	5.3007	3.2044	.813	3.0246	9.45	33.887	87.870	20.096	62.46	3902	240.9	89.23	63.10
	44.06	.53655	5.3022	3.2126	.831	3.0518	8.88	22.161	57.883	13.561	61.29	3756	234.6	87.99	44.72
	28.50	.53839	5.3403	3.2436	.852	4.1045	7.86	12.280	32.530	7.970	57.07	3257	215.4	79.79	29.13
	19.57	.54068	5.3790	3.2822	.873	3.1642	6.85	6.667	18.061	4.727	52.22	2727	192.8	71.37	20.15
5	62.03	.56085	5.7199	3.6231	.813	3.4433	3.60	19.504	73.535	34.527	23.32	567.2	63.17	26.63	63.03
	43.59	.56142	5.7295	3.6327	.830	3.4709	3.38	12.746	48.336	22.844	23.30	542.8	61.43	25.65	44.38
	26.46	.56225	5.7436	3.6467	.856	3.5116	3.08	6.480	24.943	11.983	22.56	508.8	58.60	24.45	27.05
	20.23	.56310	5.7579	3.6611	.872	3.5421	2.87	4.212	16.441	8.021	21.82	476.3	55.91	23.24	20.72
	13.28	.56564	5.8009	3.7070	.891	3.6038	2.49	1.693	6.974	3.589	19.77	390.0	47.99	20.12	13.64
1	61.15	.59446	6.2887	4.1921	.813	4.0123	.972		53.045	53.243	6.425	41.28	-.1177	4.143	68.28
	42.72	.59509	6.2936	4.2021	.831	4.0413	.909		34.598	34.730	6.279	39.43	-.1650	3.964	47.32
	22.60	.59583	6.3112	4.2146	.851	4.0744	.843		20.605	20.773	6.101	37.22	-.2495	3.753	31.46
	19.29	.59662	6.3245	4.2280	.874	4.1110	.774		11.189	11.345	5.916	35.00	-.4095	3.549	20.91
	13.20	.59810	6.3500	4.2535	.892	4.1543	.701		5.119	5.259	5.579	31.12	-.7640	3.197	14.02
6	62.45	.59463	6.2909	4.1939	.812	4.0131	.970		54.350	54.544	6.399	40.95	-.1143	4.110	69.77
	43.64	.59523	6.3010	4.2040	.831	4.0432	.905		35.546	35.728	6.252	39.08	-.1592	3.928	48.39
	30.44	.59600	6.3140	4.2170	.849	4.0748	.842		22.357	22.525	6.067	36.81	-.2284	3.709	33.35
	20.41	.59688	6.3289	4.2319	.871	4.1119	.773		12.331	12.485	5.863	34.37	-.3675	3.480	22.11
	12.72	.59813	6.3500	4.2530	.894	4.1556	.699		4.652	4.792	5.524	31.18	-.8389	3.212	13.42
2	62.51	.63179	6.9190	4.8220	.811	4.6400	.229	-12.139	18.134	42.412	1.507	2.270	-10.085	.5308	63.26
	44.38	.63292	6.9381	4.8411	.830	4.6793	.209	- 8.038	11.993	28.070	1.442	2.079	- 9.563	.4865	44.85
	26.27	.63390	6.9546	4.8577	.856	4.7226	.189	- 4.080	6.049	14.227	1.388	1.926	- 9.360	.4530	26.51
	19.60	.63497	6.9727	4.8758	.873	4.7578	.175	- 2.595	3.845	9.036	1.331	1.772	- 8.984	.4164	19.76
	13.08	.63608	6.9915	4.8945	.891	4.7943	.161	- 1.145	1.675	3.964	1.275	1.625	- 8.711	.3847	13.15
7	63.60	.63357	6.9491	4.8522	.812	4.6712	.213	-12.648	17.698	42.994	1.406	1.976	-10.046	.4800	64.32
	43.85	.63408	6.9577	4.8608	.829	4.6980	.200	- 8.162	11.406	27.730	1.378	1.899	- 9.861	.4617	44.29
	28.25	.63588	6.9821	4.8912	.853	4.7530	.177	- 4.617	6.437	15.671	1.285	1.651	- 9.216	.4013	28.50
	20.50	.63620	6.9935	4.8966	.870	4.7756	.168	- 2.854	3.966	9.673	1.269	1.610	- 9.134	.3928	20.64
	13.46	.63814	7.0263	4.9294	.891	4.8292	.148	- 1.257	1.726	4.239	1.177	1.384	- 8.569	.3401	13.54
3a	61.83	.65694	7.3441	5.2489	.811	5.0669	.0857	-15.319	7.856	38.494	.5638	.3179	-10.996	.1558	61.96
	43.01	.65831	7.3672	5.2716	.825	5.1045	.0786	-11.387	5.836	28.610	.5350	.2863	-10.439	.1403	48.10
	30.62	.65924	7.3830	5.2868	.848	5.1436	.0718	- 6.412	3.283	16.107	.5167	.2669	-10.091	.1310	30.67
	24.56	.65994	7.3948	5.2983	.860	5.1674	.0680	- 4.716	2.412	11.844	.5031	.2531	- 9.836	.1243	24.61
	18.67	.66088	7.4107	5.3141	.875	5.1981	.0634	- 3.040	1.552	7.632	.4852	.2354	- 9.504	.1158	18.70

Table 2.7. The experimental values of terminal voltage, ionic strength, molality, terms of equation 23 derived from these quantities and a second approximation of ionic strength. 30° Centigrade

Run	$\mu_1$ x10 <sup>3</sup>	E volts	$\frac{E - E^0}{k}$	$p_{\text{wH}}$	$\gamma_{\text{HCl}}^+$	$-\log m_{\text{H}^+}$	$m_{\text{H}^+}$ x10 <sup>4</sup>	B x10 <sup>3</sup>	$\alpha + B$ x10 <sup>3</sup>	$\alpha - B$ x10 <sup>3</sup>	P x10 <sup>5</sup>	P <sup>2</sup> x10 <sup>10</sup>	X x10 <sup>6</sup>	Y x10 <sup>9</sup>	$\mu_2$ x10 <sup>3</sup>
8	70.41	.53172	5.1957	3.0987	.805	2.9103	12.29	42.431	104.841	19.979	79.67	6348	322.5	120.96	71.75
	49.53	.53272	5.2123	3.1153	.825	2.9483	11.26	29.925	69.455	13.605	76.68	5880	308.3	115.19	50.75
	29.04	.53502	5.2505	3.1536	.852	3.0144	9.67	13.755	34.800	7.290	70.21	4929	277.5	103.26	30.07
	21.43	.53763	5.2939	3.1970	.869	3.0750	8.41	8.555	21.986	4.876	63.53	4036	247.2	89.52	22.32
	13.89	.54269	5.3780	3.2811	.888	3.1779	6.64	3.458	9.351	2.435	52.35	2740	193.6	71.35	14.58
4	62.44	.53758	5.2931	3.1968	.812	3.0159	9.66	33.866	87.849	20.117	64.57	4041	245.1	92.54	63.12
	44.06	.53814	5.3024	3.2059	.831	3.0451	9.01	22.148	57.870	13.574	62.25	3875	238.2	90.89	44.73
	28.50	.54002	5.3363	3.2370	.853	3.0989	7.96	12.270	32.520	7.980	57.94	3357	218.6	82.38	29.14
	19.57	.54244	5.3739	3.2771	.873	3.1591	6.93	6.659	18.053	4.735	52.84	2792	194.9	73.22	20.15
5	62.03	.56291	5.7142	3.6174	.812	3.4333	3.69	19.495	73.526	34.536	24.13	582.4	63.99	27.35	63.02
	43.59	.56344	5.7230	3.6262	.830	3.4644	3.43	12.741	48.331	22.849	23.65	559.3	62.35	26.44	44.37
	26.46	.56429	5.7371	3.6403	.857	3.5063	3.12	6.476	24.939	11.978	22.89	524.1	59.45	25.19	27.04
	20.23	.56519	5.7521	3.6552	.872	3.5362	2.91	4.208	16.437	8.025	22.12	489.3	56.63	23.89	20.72
	13.28	.56783	5.7960	3.6991	.890	3.5979	2.52	1.689	6.971	3.592	20.00	399.8	48.46	20.60	13.64
1	61.15	.59731	6.2860	4.1995	.812	4.0086	.980		53.046	53.242	6.464	41.79	-.1195	4.194	68.27
	42.72	.59791	6.2960	4.1995	.831	4.0378	.915		34.597	34.781	6.317	39.91	-.1670	4.012	47.30
	28.69	.59873	6.3096	4.2131	.852	4.0740	.843		20.605	20.773	6.122	37.43	-.2506	3.779	31.50
	19.29	.59942	6.3211	4.2246	.873	4.1066	.782		11.189	11.345	5.963	35.55	-.4169	3.605	20.90
	13.20	.60098	6.3470	4.2505	.889	4.1483	.711		5.118	5.260	5.617	31.55	-.7800	3.243	14.02
6	62.45	.59726	6.2852	4.1882	.812	4.0074	.983		54.339	54.535	6.483	42.03	-.1173	4.218	69.76
	43.64	.59805	6.2983	4.2013	.831	4.0405	.911		35.540	35.722	6.290	39.57	-.1612	3.977	48.37
	30.44	.59882	6.3111	4.2141	.850	4.0729	.845		22.352	22.522	6.107	37.30	-.2310	3.758	33.39
	20.41	.59973	6.3263	4.2293	.871	4.1093	.778		12.328	12.484	5.898	34.79	-.3720	3.523	22.10
	12.72	.60101	6.3475	4.2505	.893	4.1523	.704		4.650	4.791	5.617	31.55	-.8505	3.250	13.42
2	62.51	.63539	6.9191	4.8221	.811	4.6401	.229	-12.139	18.134	42.412	1.506	2.269	-10.083	.5306	63.25
	44.38	.63664	6.9399	4.8429	.830	4.6811	.208	-8.038	11.993	28.070	1.436	2.062	-9.623	.4825	44.85
	26.27	.63781	6.9593	4.8624	.857	4.7284	.187	-4.080	6.051	14.226	1.373	1.885	-9.257	.4432	26.51
	19.60	.63874	6.9748	4.8778	.873	4.7598	.174	-2.595	3.846	9.036	1.325	1.755	-8.941	.4125	19.76
	13.08	.63993	6.9946	4.8975	.890	4.7964	.160	-1.145	1.675	3.964	1.266	1.603	-8.651	.3794	13.15
7	63.60	.63724	6.9498	4.8529	.811	4.6709	.213	-12.648	17.698	42.994	1.403	1.969	-10.028	.4783	64.31
	43.85	.63768	6.9572	4.8602	.828	4.6962	.201	-8.162	11.406	27.731	1.380	1.903	-9.871	.4626	44.28
	28.25	.63964	6.9897	4.8928	.854	4.7558	.176	-4.617	6.437	15.671	1.280	1.638	-9.181	.3988	28.50
	20.50	.64000	6.9957	4.8988	.871	4.7788	.166	-2.854	3.965	9.674	1.262	1.594	-9.087	.3888	20.64
	13.46	.64196	7.0283	4.9314	.890	4.8302	.148	-1.257	1.725	4.239	1.171	1.372	-8.531	.3370	13.54
3a.	61.83	.66108	7.3461	5.2509	.811	5.0689	.0853	-15.319	7.856	38.494	.5612	.3149	-10.943	.1543	61.96
	48.01	.66250	7.3698	5.2741	.826	5.1081	.0780	-11.387	5.836	28.610	.5320	.2830	-10.379	.1387	48.10
	30.62	.66345	7.3855	5.2894	.849	5.1472	.0713	-6.412	3.283	16.107	.5136	.2638	-10.031	.1294	30.67
	24.56	.66411	7.3965	5.3001	.861	5.1701	.0676	-4.716	2.412	11.844	.5011	.2511	-9.797	.1233	24.61
	18.67	.66516	7.4140	5.3174	.875	5.2014	.0629	-3.040	1.552	7.632	.4815	.2319	-9.432	.1140	18.70

Table 2.8. The experimental values of terminal voltage, ionic strength, molality, terms of equation 23 derived from these quantities and a second approximation of ionic strength. 35° Centigrade.

Run	$\mu_1$ x10 <sup>3</sup>	E volts	$\frac{E - E^0}{k}$	p <sub>w</sub> H	$\gamma_{HCl}$	-log m <sub>H+</sub>	m <sub>H+</sub> x10 <sup>4</sup>	B x10 <sup>3</sup>	$\alpha + B$ x10 <sup>3</sup>	$\alpha - B$ x10 <sup>3</sup>	P x10 <sup>5</sup>	P <sup>2</sup> x10 <sup>10</sup>	X x10 <sup>6</sup>	Y x10 <sup>9</sup>	$\mu_2$ x10 <sup>3</sup>
8	70.41	.53313	5.1912	3.0942	.802	2.9026	12.51	42.409	104.319	20.001	80.50	6480	325.7	123.65	71.77
	49.53	.53420	5.2087	3.1117	.822	2.9415	11.44	27.907	69.437	13.623	77.32	5979	310.8	117.30	50.76
	29.04	.53651	5.2465	3.1496	.851	3.0094	9.79	13.744	34.789	7.301	70.36	5021	279.9	105.38	30.08
	21.43	.53902	5.2875	3.1916	.866	3.0666	8.58	8.539	21.970	4.892	64.33	4138	250.0	92.14	22.34
	13.89	.54433	5.3743	3.2774	.887	3.1732	6.71	3.451	9.344	2.442	52.80	2787	195.0	72.85	14.57
4	62.44	.53915	5.2896	3.1933	.809	3.0092	9.79	33.853	87.836	20.130	64.08	4106	246.9	94.09	63.13
	44.06	.53972	5.2990	3.2024	.828	3.0385	9.15	22.134	57.856	13.588	62.74	3937	240.0	92.46	44.74
	28.50	.54164	5.3304	3.2337	.852	3.0946	8.05	12.261	32.511	7.989	58.38	3403	220.2	83.75	29.15
	19.57	.54418	5.3719	3.2743	.870	3.1533	7.03	6.653	18.047	4.741	53.17	2827	196.0	74.28	20.16
5	62.03	.56492	5.7111	3.6143	.809	3.4302	3.71	19.493	73.524	34.528	24.30	590.7	64.44	27.75	63.01
	43.59	.56549	5.7204	3.6236	.837	3.4586	3.48	12.736	48.326	22.854	23.79	566.0	62.70	26.77	44.37
	26.24	.56639	5.7351	3.6383	.855	3.5022	3.14	6.474	24.937	11.989	23.00	529.0	59.71	25.43	27.04
	20.23	.56729	5.7498	3.6530	.869	3.5310	2.94	4.205	16.434	8.028	22.23	494.4	56.89	24.14	20.71
	13.28	.57000	5.7942	3.6973	.888	3.5941	2.54	1.687	6.969	3.594	20.08	403.1	48.61	20.79	13.63
1	61.15	.60018	6.2877	4.1912	.809	4.0071	.984		53.046	53.242	6.439	41.46	-.1194	4.161	69.19
	42.72	.60075	6.2971	4.2005	.829	4.0376	.917		34.597	34.781	6.302	39.72	-.1671	3.993	47.23
	19.29	.60224	6.3214	4.2249	.870	4.1039	.787		11.188	11.346	5.958	35.50	-.4192	3.600	20.89
	13.20	.60389	6.3484	4.2519	.888	4.1487	.710		5.118	5.260	5.599	31.35	-.7769	3.222	14.01
6	62.45	.60000	6.2848	4.1878	.809	4.0036	.992		54.338	54.536	6.489	42.11	-.1184	4.226	69.68
	43.64	.60080	6.2979	4.2009	.828	4.0368	.919		35.539	35.722	6.297	39.65	-.1628	3.985	48.30
	30.44	.60165	6.3118	4.2158	.848	4.0716	.848		22.352	22.522	6.099	37.19	-.2314	3.748	33.35
	20.41	.60259	6.3272	4.2302	.869	4.1082	.780		12.328	12.484	5.886	34.65	-.3722	3.509	22.09
	12.72	.60387	6.3481	4.2511	.891	4.1509	.707		4.650	4.791	5.609	31.46	-.8523	3.242	13.41
2	62.51	.64096	6.9547	4.8578	.808	4.6726	.213	-12.139	18.134	42.412	1.488	2.214	-9.960	.5177	63.24
	44.38	.64038	6.9452	4.8482	.827	4.6832	.207	- 8.038	11.993	28.070	1.418	2.011	-9.506	.4708	44.84
	26.27	.64160	6.9651	4.8682	.855	4.7321	.185	- 4.080	6.051	14.226	1.386	1.922	-9.348	.4519	26.50
	19.60	.64254	6.9805	4.8836	.870	4.7626	.173	- 2.595	3.846	9.036	1.308	1.710	-9.923	.4017	19.76
	13.08	.64374	7.0001	4.9032	.888	4.8000	.159	- 1.145	1.675	3.964	1.250	1.562	-8.536	.3695	13.15
7	63.60	.64096	6.9547	4.8578	.808	4.6726	.213	-12.648	17.698	42.994	1.388	1.925	-9.916	.4677	64.30
	43.85	.64124	6.9609	4.8640	.826	4.6980	.200	- 8.162	11.406	27.731	1.368	1.871	-9.789	.4549	44.28
	28.25	.64349	6.9960	4.8991	.852	4.7599	.174	- 4.617	6.437	15.671	1.261	1.591	-9.048	.3874	28.50
	20.50	.64388	7.0024	4.9055	.869	4.7835	.165	- 2.854	3.965	9.674	1.243	1.545	-8.947	.3770	20.64
	13.46	.64588	7.0351	4.9381	.889	4.8360	.146	- 1.257	1.725	4.239	1.153	1.329	-8.395	.3265	13.54
3a	61.83	.66527	7.3522	5.2570	.808	5.0713	.0848	-15.319	7.856	38.494	.5533	.3062	-10.790	.1500	61.96
	42.01	.66675	7.3764	5.2808	.823	5.1116	.0766	-11.387	5.836	28.610	.5238	.2744	-10.219	.1345	42.10
	30.62	.66770	7.3920	5.2958	.847	5.1516	.0722	- 6.412	3.283	16.107	.5060	.2561	- 9.884	.1256	30.67
	24.56	.66827	7.4013	5.3049	.859	5.1729	.0672	- 4.716	2.412	11.844	.4956	.2456	- 9.689	.1206	24.61
	18.67	.66952	7.4217	5.3252	.873	5.2072	.0611	- 3.040	1.552	7.632	.4730	.2237	- 9.264	.1100	18.70









Table 3. The standard electrode potential of the silver-silver chloride half-cell, the value of the parameters A and B of the Debye-Hückel equation and the parameter  $2.3026 RT/F$  for the temperature range  $0^{\circ}$  to  $50^{\circ}$  Centigrade.

t	$E^{\circ}$	$k = RT/F$	A	B
$^{\circ}C$	abs v	$\times 2.3026$		$\times 10^{-8}$
0	0.23652	0.054201	0.4883	0.3241
5	.23404	.055194	.4921	.3249
10	.23140	.056186	.4960	.3258
15	.22854	.057178	.5000	.3266
20	.22557	.058170	.5042	.3273
25	.22245	.059162	.5085	.3281
30	.21918	.060154	.5130	.3290
35	.21571	.061146	.5170	.3297
40	.21214	.062138	.5221	.3305
45	.20829	.063131	.5270	.3314
50	.20439	.064123	.5319	.3321

Table 4.1. Values of X and Y for each experimental run interpolated at equal values of ionic strength.

Ionic Strength	X $\times 10^6$							Y $\times 10^9$							
	0.06	0.05	0.04	0.03	0.025	0.020	0.014	0.06	0.05	0.04	0.03	0.025	0.020	0.014	
Run t															
0g															
8	0	266.8	261.5	253.1	238.4	225.2	205.2	170.0	82.65	81.00	78.65	73.35	68.45	61.55	51.35
	5	278.1	271.9	262.8	247.5	234.0	213.8	173.2	90.45	88.15	85.20	79.80	74.75	67.60	55.95
	10	288.0	281.3	271.3	255.0	240.9	219.5	176.0	97.40	94.75	91.40	85.40	79.80	71.70	59.00
	15	296.5	289.2	279.1	262.2	246.3	223.0	181.0	103.20	100.70	97.40	90.70	83.75	74.80	62.65
	20	303.8	296.7	286.2	268.4	251.1	225.0	184.4	109.15	106.30	102.65	95.80	88.90	79.00	65.20
	25	310.5	302.7	291.9	273.4	256.6	230.4	186.0	113.85	110.95	107.00	99.95	92.55	81.60	67.30
	30	316.0	308.8	296.3	277.2	260.1	233.6	189.6	118.05	115.00	111.00	103.15	95.10	84.35	69.70
	35	318.4	310.1	298.6	279.6	262.7	237.0	190.0	120.30	117.00	112.60	105.20	97.50	86.85	71.50
	40	320.1	311.7	300.0	280.8	264.8	240.3	190.6	121.60	118.20	113.65	106.30	99.75	89.50	71.80
	45	319.0	310.4	299.8	279.2	264.1	240.5	190.0	120.65	117.40	112.85	105.60	99.20	89.00	70.80
	50	317.5	309.3	299.6	279.2	263.6	239.0	189.0	119.70	116.65	112.40	105.30	98.75	88.20	70.00
4	0	206.3	204.0	198.8	188.4	180.0	169.1		64.82	64.32	62.85	58.80	55.95	52.75	
	5	216.0	213.4	208.2	197.0	187.6	176.4		71.33	70.90	69.28	64.82	61.53	57.84	
	10	224.0	220.4	214.1	202.8	194.2	181.6		77.00	76.50	74.60	69.42	65.85	62.12	
	15	231.0	227.8	221.6	208.8	199.1	185.8		81.78	81.33	79.06	73.63	69.80	65.60	
	20	236.2	233.0	227.1	213.3	203.0	189.4		86.17	85.48	83.11	77.50	73.35	68.78	
	25	240.1	237.0	231.5	217.8	205.5	192.2		89.12	88.57	86.52	80.50	76.12	71.20	
	30	244.4	241.2	234.6	220.6	208.9	194.7		92.40	91.68	89.48	83.15	78.48	73.06	
	35	246.4	243.0	236.3	222.0	210.0	195.4		94.00	93.40	90.96	84.52	79.65	74.10	
	40	247.5	244.2	237.5	223.2	211.0	195.9		94.98	94.38	91.85	85.30	80.18	74.30	
	45	246.6	243.2	236.2	222.2	210.6	195.4		94.30	93.80	91.20	84.80	79.80	74.10	
	50	245.5	242.2	235.1	221.2	210.0	194.8		93.42	92.80	90.40	84.00	79.25	73.75	
5	0														
	5	56.41	55.60	54.70	53.23	52.25	50.15	44.50	21.20	20.77	20.33	19.80	19.37	18.58	16.70
	10	58.58	57.72	56.78	55.37	54.10	51.92	45.95	22.88	22.43	21.96	21.40	20.91	19.96	17.82
	15	60.30	59.41	58.35	56.90	55.57	53.20	47.13	24.27	23.76	23.25	22.64	22.12	20.98	18.72
	20	61.75	60.85	59.79	58.28	56.88	54.40	48.20	25.50	24.98	24.46	23.80	23.24	22.08	20.63
	25	62.93	62.02	60.95	59.38	57.93	55.45	48.90	26.48	25.97	25.41	24.73	24.15	23.03	20.38
	30	64.75	62.91	61.85	60.23	58.72	56.08	49.35	27.21	26.85	26.22	25.52	24.91	23.68	20.94
	35	64.33	63.38	62.18	60.50	59.02	56.37	49.55	27.60	27.10	26.51	25.75	25.13	23.90	21.07
	40	64.58	63.70	62.55	60.85	59.32	56.65	49.75	27.94	27.44	26.86	26.05	25.42	24.15	21.24
	45	64.16	63.35	62.30	60.37	58.82	56.25	49.05	27.56	27.17	26.64	25.73	25.01	23.86	21.00
	50	63.88	63.21	62.03	59.97	58.33	56.00	48.70	27.30	26.96	26.42	25.36	24.61	23.57	20.83

Table 4.2. Values of X and Y for each experimental run interpolated at equal values of ionic strength.

Ionic Strength	X $\times 10^6$							Y $\times 10^9$							
	0.06	0.05	0.04	0.03	0.025	0.020	0.014	0.06	0.05	0.04	0.03	0.025	0.020	0.014	
Run t															
$\rho_0$															
1	0	.101	.121	.152	.208	.258	.344	.625	3.184	3.115	3.037	2.928	2.852	2.753	2.600
	5	.111	.131	.164	.221	.272	.368	.673	3.435	3.355	3.270	3.162	3.081	2.973	2.790
2	10	.119	.141	.176	.238	.292	.394	.710	3.665	3.577	3.485	3.363	3.276	3.157	2.960
	15	.123	.146	.181	.242	.298	.400	.737	3.992	3.830	3.640	3.502	3.396	3.260	3.070
6	20	.130	.150	.189	.255	.311	.427	.767	4.114	3.965	3.748	3.612	3.518	3.390	3.170
	25	.134	.155	.193	.257	.314	.439	.774	4.210	4.052	3.845	3.693	3.590	3.454	3.215
	30	.136	.159	.196	.260	.316	.444	.780	4.270	4.125	3.895	3.738	3.636	3.500	3.255
	35	.134	.159	.194	.265	.320	.441	.777	4.263	4.110	3.895	3.736	3.632	3.490	3.250
	40	.130	.158	.191	.258	.322	.438	.762	4.060	3.966	3.853	3.688	3.572	3.422	3.190
	45	.128	.152	.184	.251	.313	.428	.737	3.928	3.834	3.718	3.570	3.468	3.333	3.090
	50	.126	.147	.181	.241	.297	.412	.700	3.784	3.702	3.592	3.435	3.342	3.203	2.935
2	0	-9.218	-9.080	-8.920	-8.710	-8.568	-8.370	-7.950	.04455	.04320	.04163	.03955	.03815	.03625	.03390
	5	9.468	9.336	9.172	8.952	8.820	8.647	8.413	.04675	.04535	.04370	.04170	.04035	.03875	.03645
	10	9.676	9.533	9.316	9.142	9.000	8.830	8.594	.04920	.04740	.04550	.04325	.04180	.04010	.03765
	15	9.786	9.644	9.466	9.240	9.098	8.930	8.687	.05040	.04860	.04660	.04430	.04270	.04105	.03860
	20	9.937	9.760	9.552	9.304	9.158	8.990	8.759	.05133	.04940	.04750	.04515	.04360	.04180	.03925
	25	9.970	9.776	9.560	9.312	9.168	9.005	8.765	.05175	.05000	.04830	.04580	.04425	.04230	.03950
	30	9.948	9.755	9.543	9.310	9.158	8.970	8.700	.05190	.04980	.04760	.04500	.04335	.04145	.03885
	35	9.798	9.630	9.447	9.190	9.030	8.845	8.580	.05025	.04843	.04645	.04385	.04225	.04045	.03800
	40	9.652	9.485	9.300	9.078	8.922	8.720	8.430	.04860	.04692	.04505	.04270	.04110	.03920	.03650
	45	9.412	9.217	9.082	8.832	8.662	8.464	8.185	.04575	.04434	.04265	.04056	.03895	.03712	.03460
	50	9.038	8.930	8.790	8.590	8.436	8.240	7.955	.04320	.04200	.04045	.03820	.03675	.03500	.03235
7	0	-9.245	-9.21	-9.10	-8.85	-8.66	-8.40	-7.96	.0408	.0406	.0392	.0363	.0344	.0324	.0295
	5	9.540	9.49	9.38	9.13	8.92	8.64	8.21	.0435	.0431	.0416	.0386	.0366	.0343	.0313
	10	9.785	9.71	9.52	9.21	9.05	8.77	8.40	.0452	.0449	.0433	.0402	.0382	.0359	.0328
	15	9.925	9.85	9.66	9.35	9.15	8.90	8.53	.0470	.0464	.0447	.0414	.0393	.0370	.0337
	20	10.010	9.91	9.73	9.44	9.23	8.98	8.60	.0478	.0470	.0452	.0420	.0399	.0376	.0342
	25	10.010	9.91	9.73	9.44	9.23	8.98	8.60	.0479	.0472	.0453	.0421	.0400	.0377	.0344
	30	10.000	9.92	9.77	9.49	9.29	9.02	8.58	.0478	.0471	.0452	.0416	.0395	.0371	.0339
	35	9.910	9.84	9.68	9.38	9.16	8.87	8.40	.0467	.0462	.0443	.0406	.0384	.0361	.0329
	40	9.760	9.68	9.51	9.21	8.99	8.72	8.29	.0452	.0447	.0437	.0391	.0370	.0347	.0317
	45	9.490	9.42	9.24	8.93	8.71	8.45	8.04	.0429	.0424	.0405	.0372	.0351	.0329	.0298
	50	9.240	9.15	8.96	8.66	8.45	8.19	7.77	.0407	.0400	.0382	.0351	.0332	.0310	.0282

Table 4.3. Values of X and Y for each experimental run interpolated at equal values of ionic strength

		X $\times 10^6$					
Ionic Strength		0.06	0.05	0.04	0.03	0.025	0.020
Run	t						
		°C					
3a	0	- 9.99	- 9.82	- 9.60	- 9.30	-9.11	-8.90
	5	10.34	10.17	9.96	9.64	9.43	9.19
	10	10.60	10.40	10.15	9.82	9.61	9.37
	15	10.75	10.54	10.30	9.96	9.75	9.51
	20	10.83	10.65	10.40	10.07	9.85	9.59
	25	10.79	10.65	10.40	10.07	9.85	9.59
	30	10.65	10.57	10.32	9.99	9.76	9.49
	35	10.43	10.43	10.18	9.85	9.63	9.34
	40	10.33	10.23	10.00	9.67	9.45	9.16
	45	10.16	9.97	9.72	9.38	9.21	8.89
	50	9.840	9.65	9.43	9.10	8.89	8.60
		Y $\times 10^9$					
	0	.0176	.0174	.0169	.0162	.0158	.0152
	5	.0186	.0182	.0178	.0171	.0165	.0159
	10	.0195	.0189	.0183	.0175	.0170	.0163
	15	.0199	.0193	.0187	.0178	.0173	.0166
	20	.0201	.0196	.0189	.0180	.0175	.0168
	25	.0200	.0196	.0190	.0181	.0175	.0168
	30	.0198	.0194	.0188	.0180	.0174	.0166
	35	.0193	.0188	.0183	.0176	.0170	.0162
	40	.0187	.0183	.0178	.0171	.0165	.0158
	45	.0180	.0176	.0171	.0165	.0159	.0152
	50	.0172	.0169	.0164	.0158	.0153	.0146

Table 5. Slopes of the plots of X against Y obtained from Figures 2.1 to 2.11.

Ionic Strength	0.06	0.05	0.04	0.03	0.025	0.020	0.014
Temperature							
°C							
0	2.990	2.995	3.014	2.970	2.957	2.907	2.923
5	3.139	3.124	3.123	3.100	3.059	3.032	3.058
10	3.273	3.261	3.270	3.231	3.215	3.233	3.226
15	3.357	3.386	3.382	3.349	3.328	3.325	3.297
20	3.480	3.476	3.475	3.445	3.450	3.425	3.370
25	3.540	3.535	3.530	3.520	3.519	3.513	3.480
30	3.612	3.620	3.620	3.594	3.586	3.561	3.535
35	3.643	3.640	3.643	3.633	3.610	3.601	3.576
40	3.670	3.663	3.672	3.656	3.635	3.619	3.604
45	3.665	3.665	3.660	3.653	3.620	3.598	3.580
50	3.635	3.635	3.655	3.632	3.615	3.605	3.590

Table 6. Values of  $p^{\circ}K_1$  ( $-\log \sigma K_1$ ) as a function of temperature and ionic strength and  $d(p^{\circ}K_1)/d\mu$  at each 5 degree interval in the range 0 to 50° C.

t °C	Ionic strength						
	0.06	0.05	0.04	0.03	0.025	0.020	0.014
0	3.5243	3.5236	3.5209	3.5272	3.5291	3.5365	3.5342
5	3.5032	3.5053	3.5054	3.5072	3.5144	3.5183	3.5146
10	3.4851	3.4866	3.4855	3.4907	3.4928	3.4904	3.4913
15	3.4740	3.4703	3.4708	3.4751	3.4778	3.4782	3.4819
20	3.4584	3.4589	3.4590	3.4628	3.4622	3.4653	3.4724
25	3.4510	3.4516	3.4522	3.4535	3.4536	3.4543	3.4584
30	3.4423	3.4413	3.4413	3.4444	3.4454	3.4484	3.4516
35	3.4385	3.4389	3.4385	3.4397	3.4425	3.4436	3.4466
40	3.4353	3.4362	3.4351	3.4370	3.4395	3.4414	3.4432
45	3.4359	3.4359	3.4365	3.4373	3.4413	3.4439	3.4461
50	3.4395	3.4395	3.4371	3.4399	3.4419	3.4431	3.4449

t °C	Extrapolated Value	$\frac{d(p^{\circ}K_1)}{d\mu}$
	0.00	
0	3.5377	-.285
5	3.5202	-.185
10	3.4945	-.251
15	3.4825	-.249
20	3.4725	-.193
25	3.4586	-.164
30	3.4520	-.204
35	3.4469	-.170
40	3.4440	-.179
45	3.4463	-.138
50	3.4452	-.136



Table 7. Values of  $-\log K_2/\rho$  computed from the experimental data of runs 1, 6, 2, 7 and 3a.

Run	Ionic Strength	Temperature °C										
		0	5	10	15	20	25	30	35	40	45	50
1	.2615	4.9479	4.9361	4.9241	4.9198	4.9176	4.9190	4.9209	4.9292	4.9385	4.9522	4.9663
	.2177	4.9634	4.9531	4.9426	4.9379	4.9353	4.9362	4.9383	4.9451	4.9551	4.9708	4.9851
	.1777	4.9814	4.9683	4.9549	4.9529	4.9562	4.9606	-	-	-	-	-
	.1449	5.0032	5.0014	4.9807	4.9763	4.9739	4.9733	4.9736	4.9789	4.9899	5.0032	5.0178
	.1187	5.0212	5.0082	5.0016	4.9986	4.9973	5.0010	5.0014	5.0087	5.0205	5.0377	5.0585
6	.2645	4.9474	4.9356	4.9256	4.9232	4.9207	4.9223	4.9186	4.9226	4.9313	4.9448	4.9596
	.2202	4.9704	4.9587	4.9504	4.9367	4.9440	4.9403	4.9423	4.9462	4.9531	4.9649	4.9790
	.1826	4.9819	4.9709	4.9635	4.9616	4.9602	4.9621	4.9637	4.9696	4.9784	4.9930	5.0055
	.1487	5.0025	5.0011	4.9828	4.9806	4.9805	4.9832	4.9811	4.9915	5.0006	5.0153	5.0297
	.1158	5.0155	5.0036	5.0063	4.9942	4.9949	4.9962	4.9976	5.0030	5.0108	5.0228	5.0426
2	.2517	4.9359	4.9426	4.9283	4.9249	4.9243	4.9259	4.9248	4.9934	4.9411	4.9561	4.9699
	.2119	4.9721	4.9647	4.9540	4.9510	4.9493	4.9495	4.9511	4.9589	4.9671	4.9815	4.9959
	.1628	5.0064	4.9875	4.9775	4.9746	4.9726	4.9683	4.9736	4.9702	4.9903	5.0043	5.0176
	.1407	5.0122	5.0029	4.9944	4.9961	4.9877	4.9893	4.9917	4.9992	5.0085	5.0222	5.0348
	.1149	5.0455	5.0181	5.0103	5.0068	5.0036	5.0069	5.0098	5.0171	5.0258	5.0305	5.0548
7	.2538	4.9567	4.9494	4.9357	4.9303	4.9360	4.9323	4.9312	4.9402	4.9363	4.9633	4.9758
	.2105	4.9917	4.9540	4.9445	4.9409	4.9542	4.9447	4.9435	4.9495	4.9586	4.9731	4.9871
	.1688	5.0044	4.9946	4.9837	4.9789	4.9791	4.9798	4.9815	4.9901	4.9992	5.0136	5.0270
	.1422	5.0105	4.9996	4.9893	4.9854	4.9846	4.9855	4.9882	4.9967	5.0063	5.0211	5.0341
	.1162	5.0447	5.0340	5.0244	5.0189	5.0173	5.0181	5.0205	5.0291	5.0381	5.0530	5.0666
3a	.2491	4.9584	4.9496	4.9357	4.9395	4.9300	4.9316	4.9318	4.9403	4.9481	4.9635	4.9775
	.2193	4.9839	4.9734	4.9586	4.9556	4.9552	4.9573	4.9583	4.9671	4.9759	4.9902	5.0040
	.1752	5.0034	4.9904	4.9782	4.9738	4.9734	4.9753	4.9770	4.9848	4.9934	5.0080	5.0211
	.1575	5.0168	5.0061	4.9949	4.9896	4.9868	4.9878	4.9889	4.9948	5.0039	5.0179	5.0323
	.1366	5.0299	5.0196	5.0100	5.0051	5.0033	5.0040	5.0071	5.0159	5.0255	5.0293	5.0536

Table 8. A comparison of the experimentally determined values of  $pK_1$  and the values computed on the basis of equation 73.

Temperature	$pK_1$ experimental	$pK_1$ calculated by equation 73	$\Delta pK_1$
00			
0	3.5377	3.5377	.0000
5	3.5202	3.5161	-.0041
10	3.4945	3.4975	.0030
15	3.4825	3.4821	-.0004
20	3.4725	3.4693	-.0032
25	3.4586	3.4595	.0009
30	3.4520	3.4519	-.0001
35	3.4469	3.4470	.0001
40	3.4440	3.4443	.0003
45	3.4463	3.4439	-.0024
50	3.4452	3.4455	.0003
		Average $\Delta pK_1$	$\pm .0013$

Table 9. A comparison of the experimentally determined values of  $pK_2$  and the values computed on the basis of equation 74.

t °C	Number of Det'ns	$pK_2$ experimental average	Mean deviation	$pK_2$ calculated by equation 74	$\Delta pK_2$
0	25	5.1194	.0065	5.1210	.0016
5	25	5.1085	.0064	5.1088	.0003
10	25	5.0988	.0053	5.1002	.0014
15	25	5.0960	.0059	5.0954	-.0006
20	25	5.0962	.0053	5.0939	-.0023
25	25	5.0974	.0052	5.0960	-.0014
30	25	5.0995	.0055	5.1008	.0013
35	24	5.1046	.0064	5.1027	-.0019
40	24	5.1179	.0058	5.1196	.0017
45	24	5.1330	.0070	5.1332	.0002
50	24	5.1494	.0059	5.1494	.0000
Average mean deviation			.0059	Average $\Delta pK_2$ $\pm$ .0011	

Table 10. A comparison of the experimentally determined values of  $K_1$  and  $K_2$  with the values computed from equations 73 and 74 respectively.

Ionization Constant	t °C	$K_1$ experimental $\times 10^4$	$K_1$ Calculated by equation 73 $\times 10^4$	$\Delta K_1$ $\times 10^4$
$K_1$	0	2.900	2.900	.000
	5	3.019	3.047	.028
	10	3.203	3.181	-.022
	15	3.292	3.295	.003
	20	3.369	3.394	.025
	25	3.479	3.471	-.008
	30	3.532	3.533	.001
	35	3.574	3.573	-.001
	40	3.597	3.595	-.002
	45	3.579	3.598	.019
	50	3.588	3.585	-.003
Average difference				.010
$K_2$		$\times 10^6$	$\times 10^6$	$\times 10^6$
	0	7.596	7.568	-.028
	5	7.789	7.784	-.005
	10	7.965	7.940	-.025
	15	8.017	8.028	.011
	20	8.013	8.056	.043
	25	7.991	8.017	.026
	30	7.952	7.929	-.023
	35	7.860	7.894	.034
	40	7.622	7.593	-.029
	45	7.362	7.359	-.003
50	7.089	7.089	.000	
Average difference				.021

Table 11. The thermodynamic quantities  $\Delta F^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta C_p^\circ$  derived from the smoothed values of the first and second ionization constants.

Ionization t	$\Delta F^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta C_p^\circ$	
Constant °C	kcal.	cal.	cal.	cal.	
$K_1$	0	4.421	1591.7	-10.36	-33.87
	5	4.475	1420.6	-10.98	-34.49
	10	4.531	1246.8	-11.60	-35.11
	15	4.591	1069.7	-12.22	-35.73
	20	4.654	889.4	-12.84	-36.35
	25	4.719	706.0	-13.46	-36.97
	30	4.788	519.8	-14.08	-37.59
	35	4.860	329.9	-14.70	-38.21
	40	4.935	137.7	-15.32	-38.83
	45	5.013	-58.1	-15.94	-39.45
50	5.095	-257.1	-16.56	-40.07	
$K_2$	0	6.399	982.3	-19.80	-48.37
	5	6.501	738.0	-20.69	-49.26
	10	6.607	489.6	-21.57	-50.14
	15	6.717	236.5	-22.46	-51.03
	20	6.831	-65.9	-23.35	-51.91
	25	6.951	-282.2	-24.23	-52.80
	30	7.074	-548.6	-25.12	-53.68
	35	7.197	-819.0	-26.00	-54.57
	40	7.330	-1094	-26.89	-55.45
	45	7.467	-1374	-27.77	-56.34
50	7.608	-1658	-28.66	-57.22	

Table 12. Values of the first and second ionization constants of malic acid obtained from the literature.

Author	Year	Method	t °C	$K_1'$ $\times 10^4$	$K_1$ $\times 10^4$	$K_2'$ $\times 10^6$	$K_2$ $\times 10^6$	Reference
Ostwald	1889	Conductivity	25	3.95				36
"	"	"	"	3.99				
Bertaelot	1891	"	17	3.83				12
Walden	1896	"	25	4.0				47
Smith	1898	Inversion of sucrose	100	3.99 <sup>a</sup>		8.3		45
Wegscheider	1902	Conductivity	17	4.0 <sup>a</sup>		7.5		48
Dhar-Datta	1913	Solubility	-			9.		17
Larsson	1922	Electrometric	18	4.0 <sup>a</sup>			7.8	31
Auerbach-Smolozyk	1924	"	20	3.86		13.9		4
Bjerrum	1924	"	15	4.0				13
Coops	1924	Conductivity	25	3.76				16
Larsson	1924	"	15		3.32			29
"	"	"	18	4.0 <sup>a</sup>			6.9	30
Roth-Wilms	1926	"	25	3.93				42
Mizutani	1925	Electrometric	18	4.7		13.5		33
Larsson	1926	Solubility	25	4.0 <sup>a</sup>			7.3	32
Duboux-Frommelt	1927	"	25	3.95 <sup>a</sup>			7.4	19
Hamer	1943	Electrometric	25		3.63		7.59	21
Eden	1951	"	25		3.48		7.99	
			20		3.37		8.01	
			15		3.29		8.02	

<sup>a</sup>The values of  $K_1'$  have been obtained from the original determination by Ostwald (36) and used by these authors in order to calculate  $K_2$ .

Fig 1.1.a

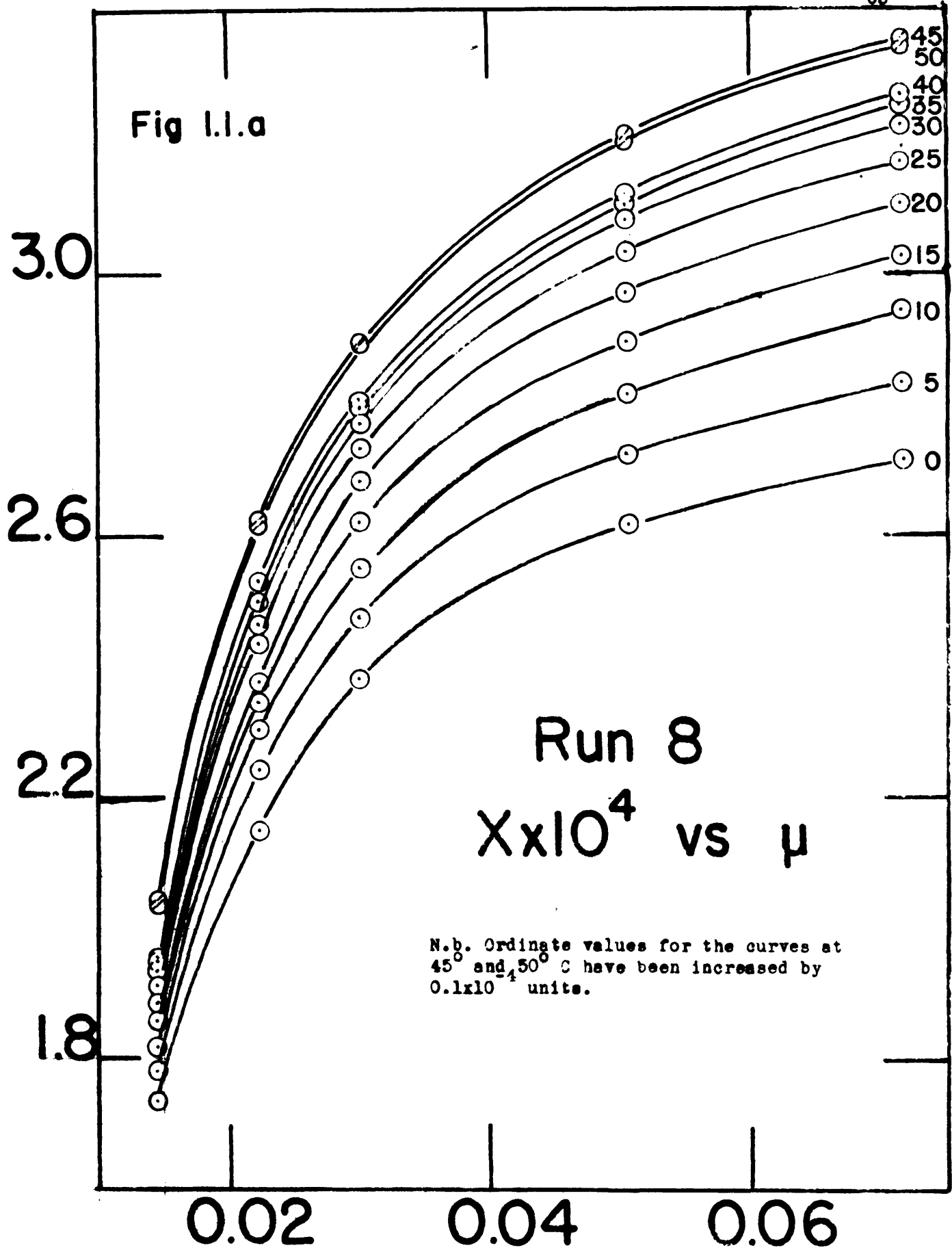
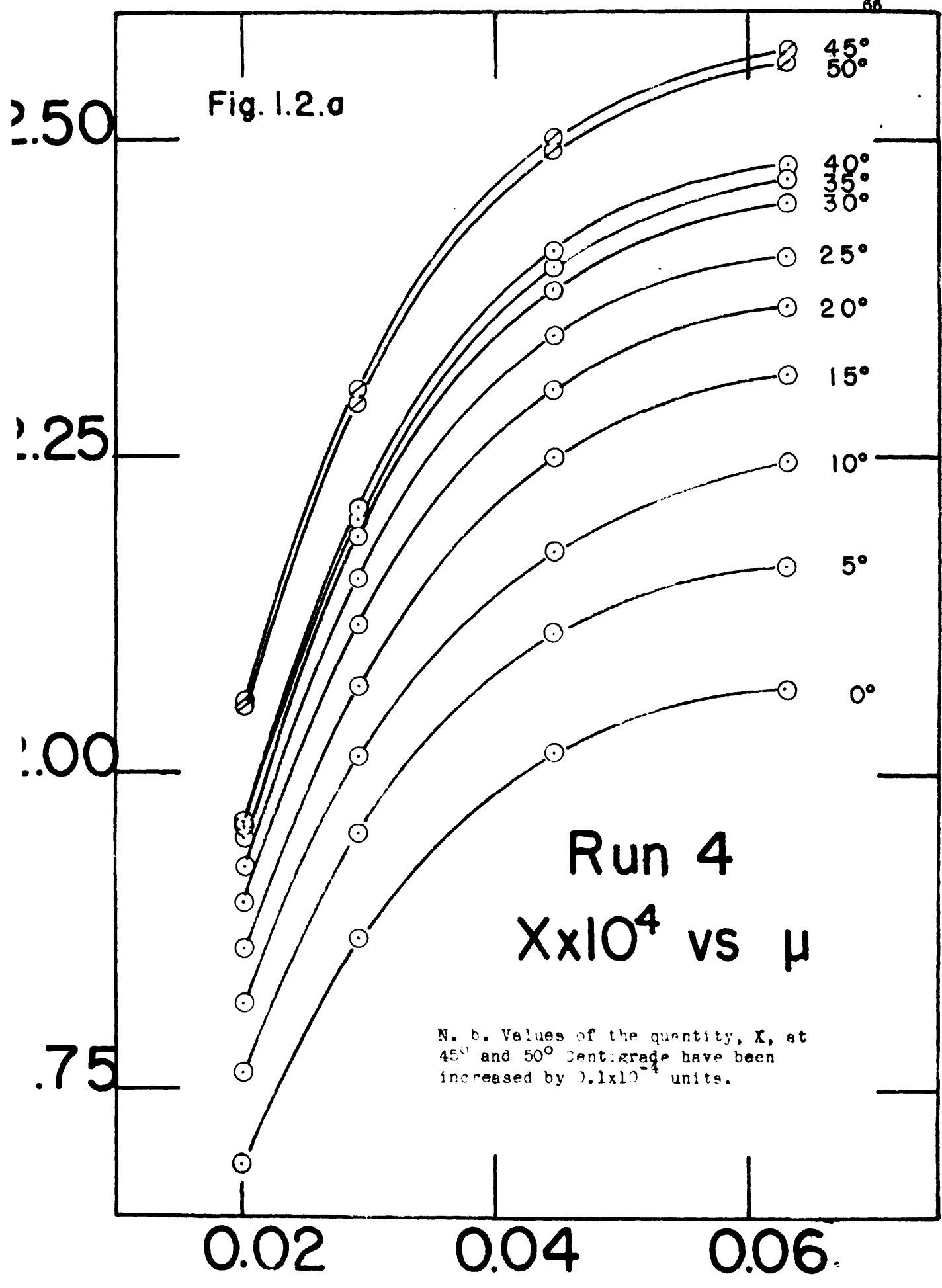
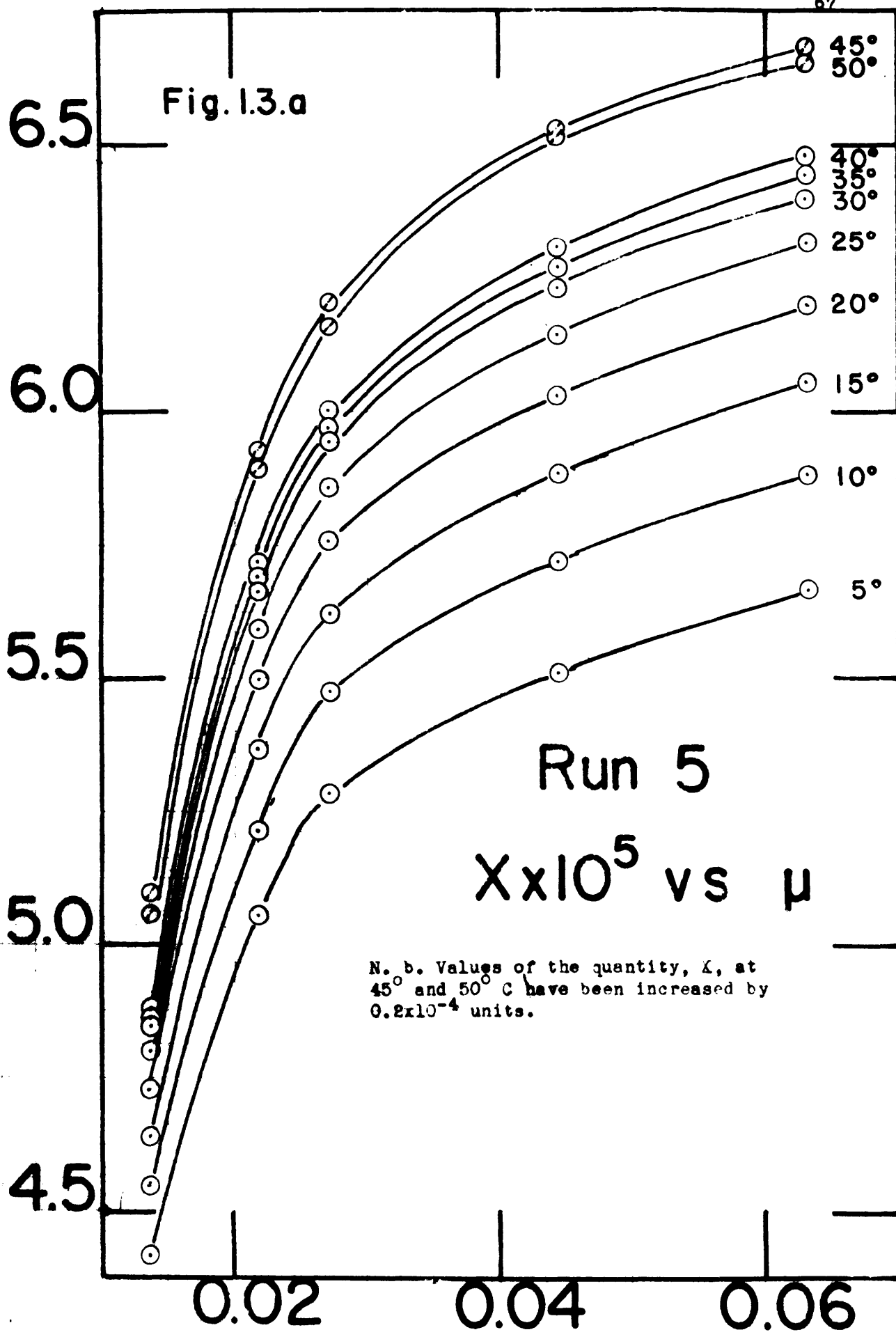
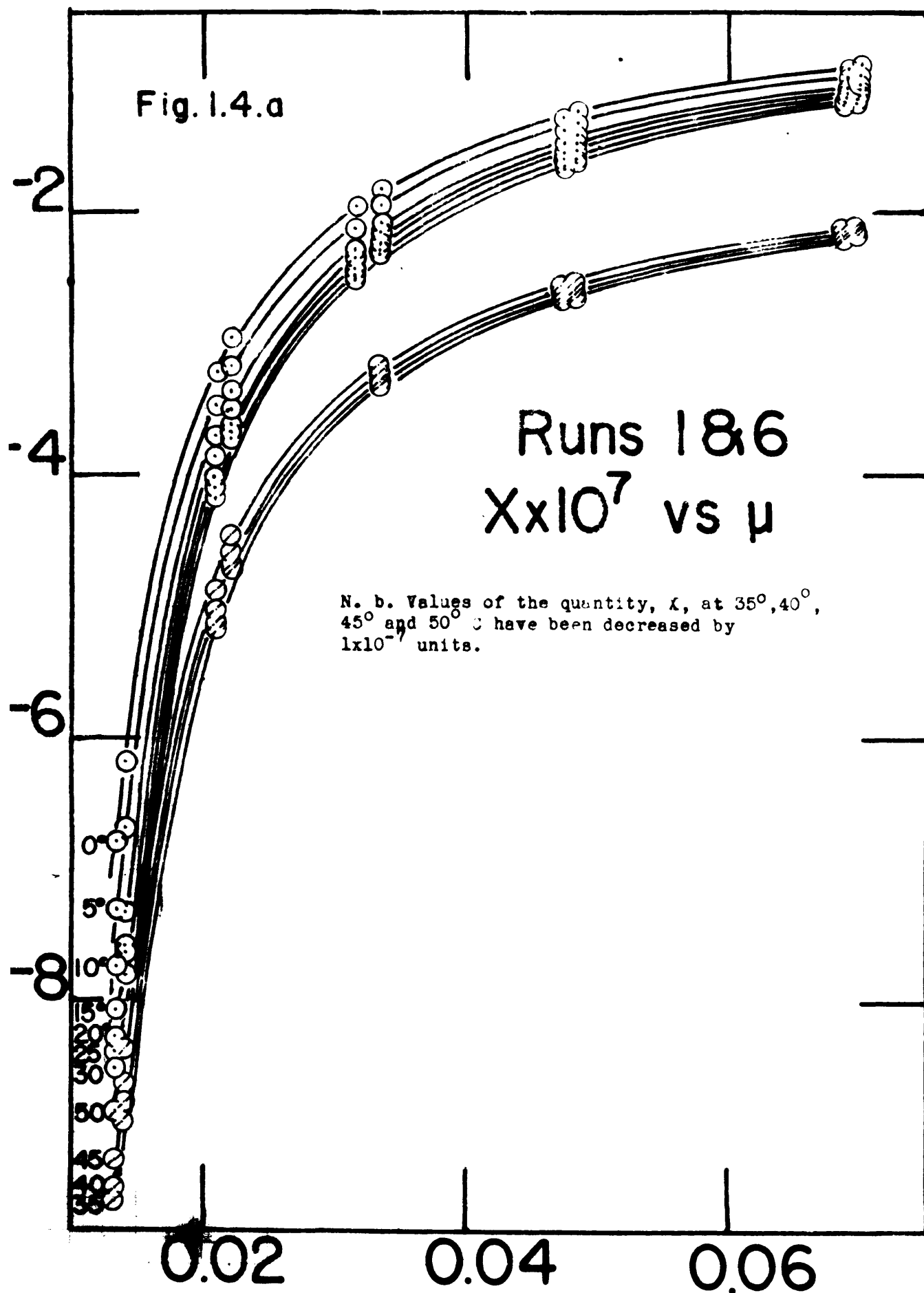


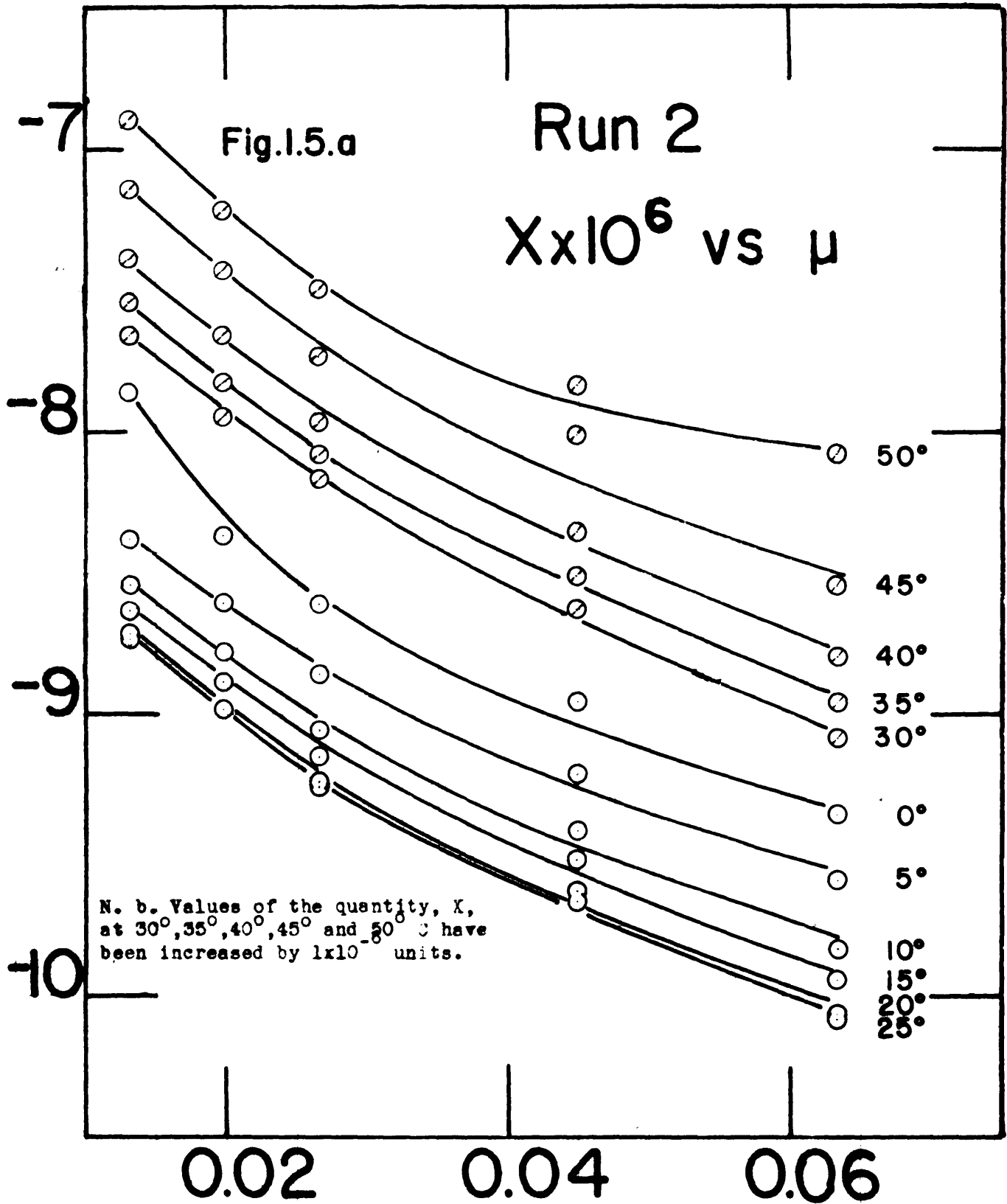
Figure 1. The computed quantity, X, as a function of ionic strength for the temperature range 0° to 50° Centigrade.











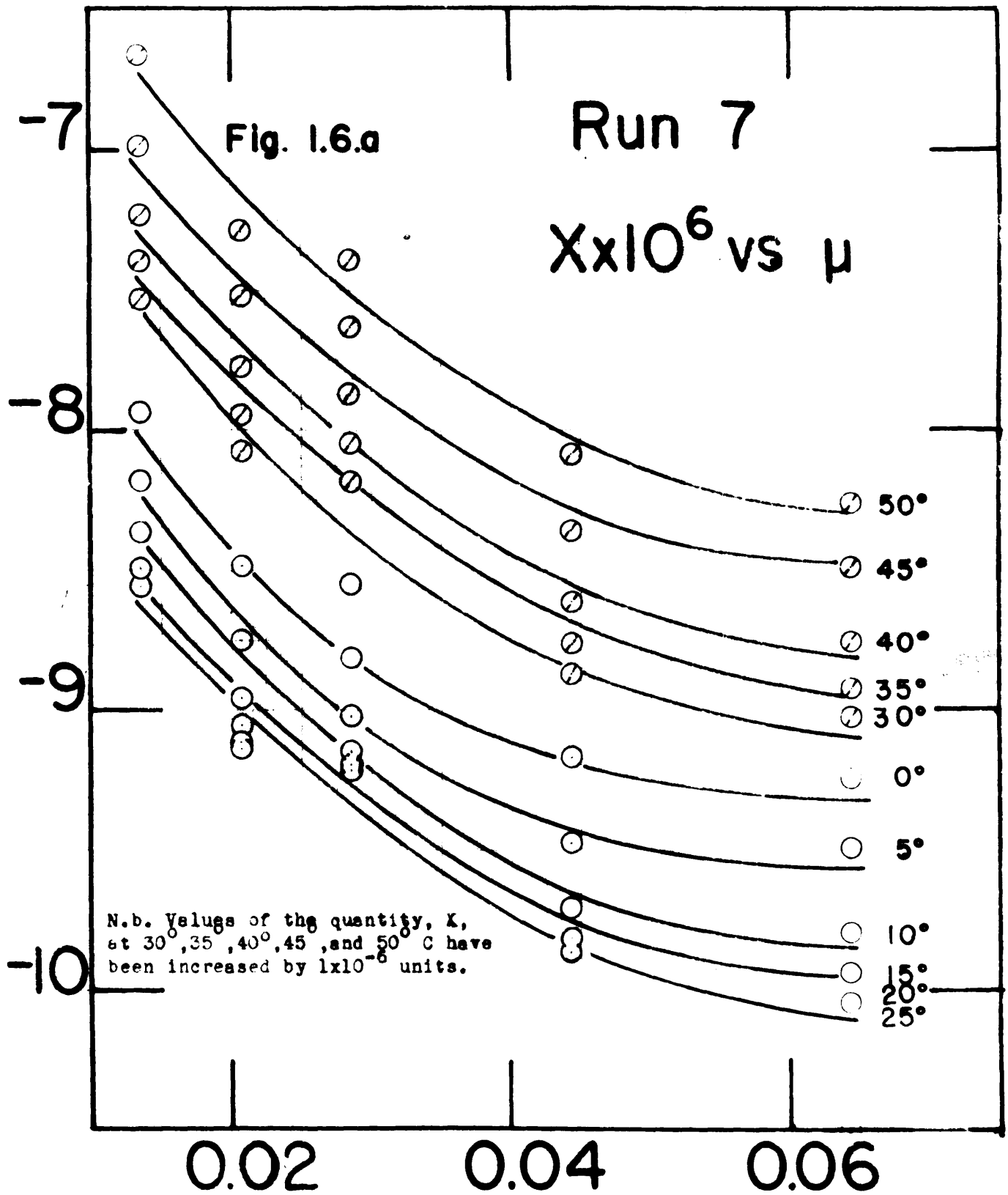
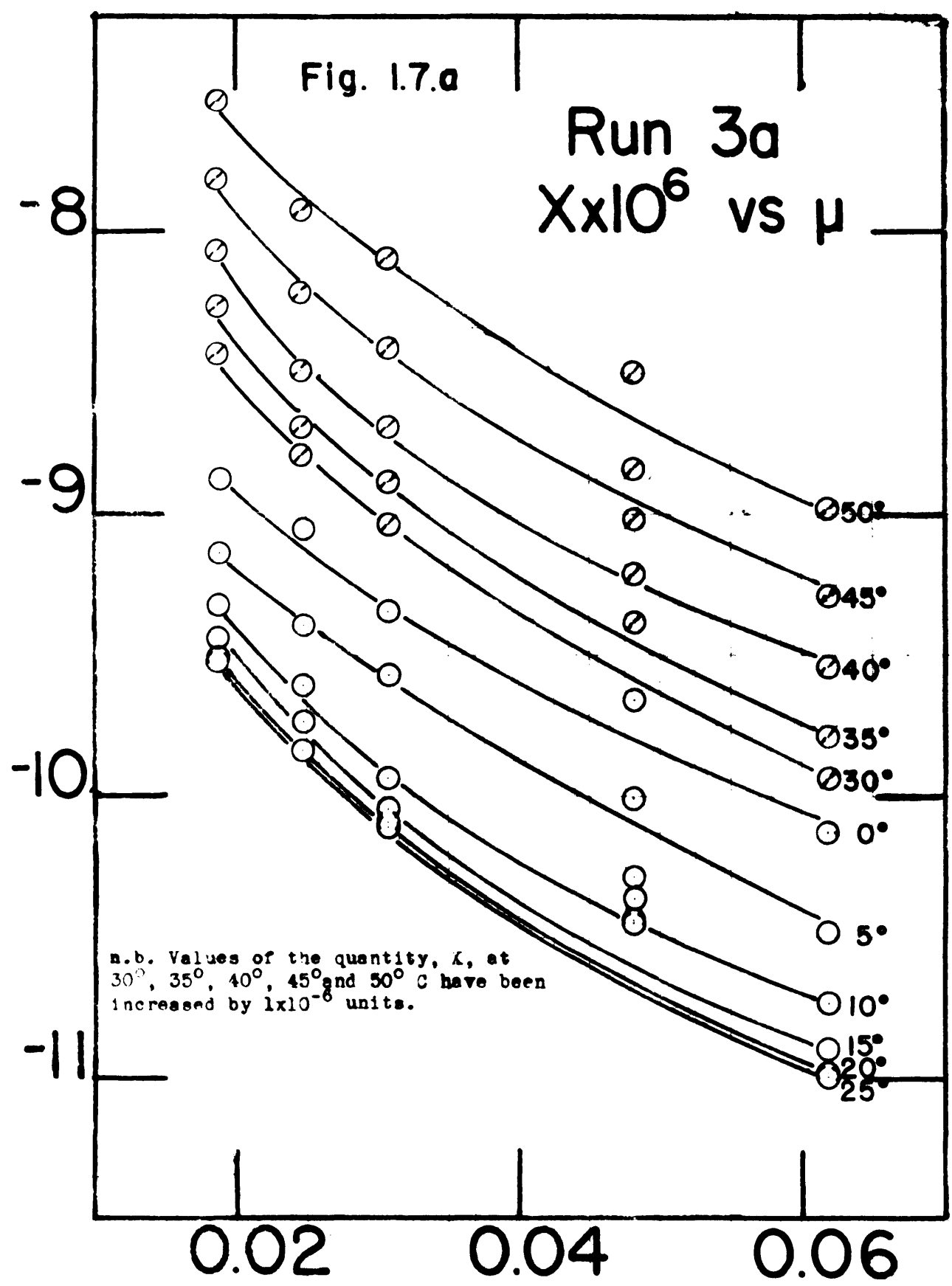


Fig. 1.7.a

Run 3a  
 $X \times 10^6$  vs  $\mu$



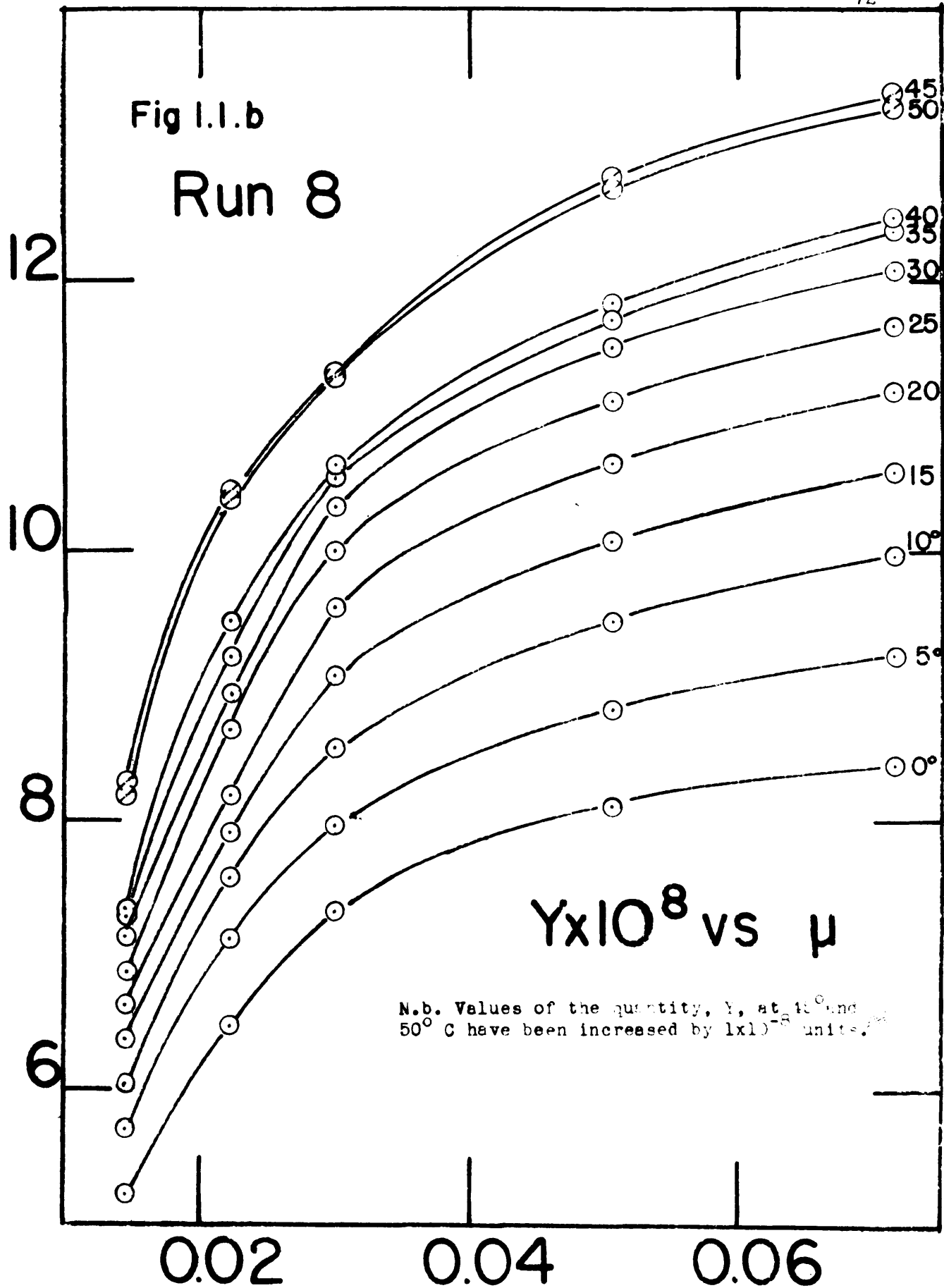
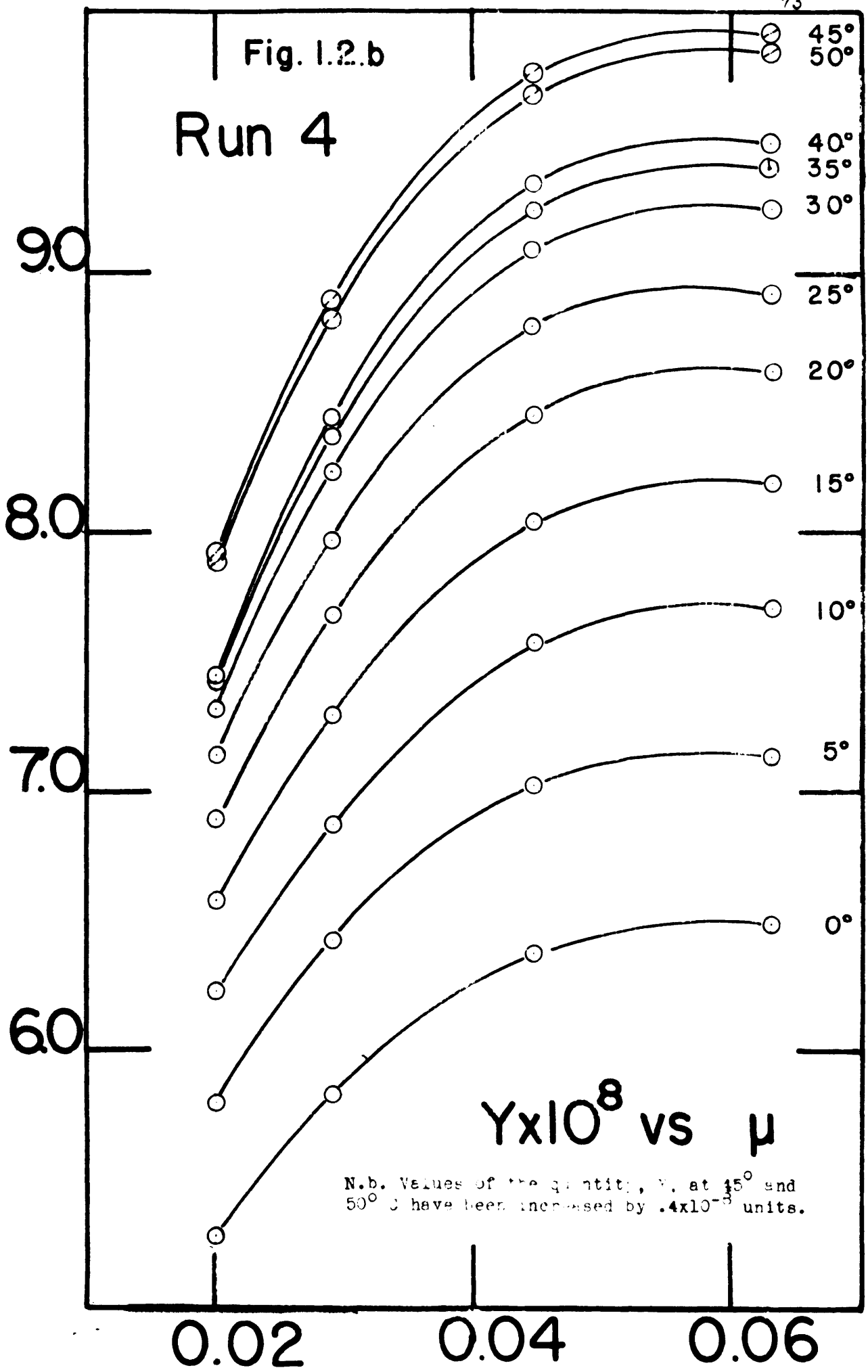


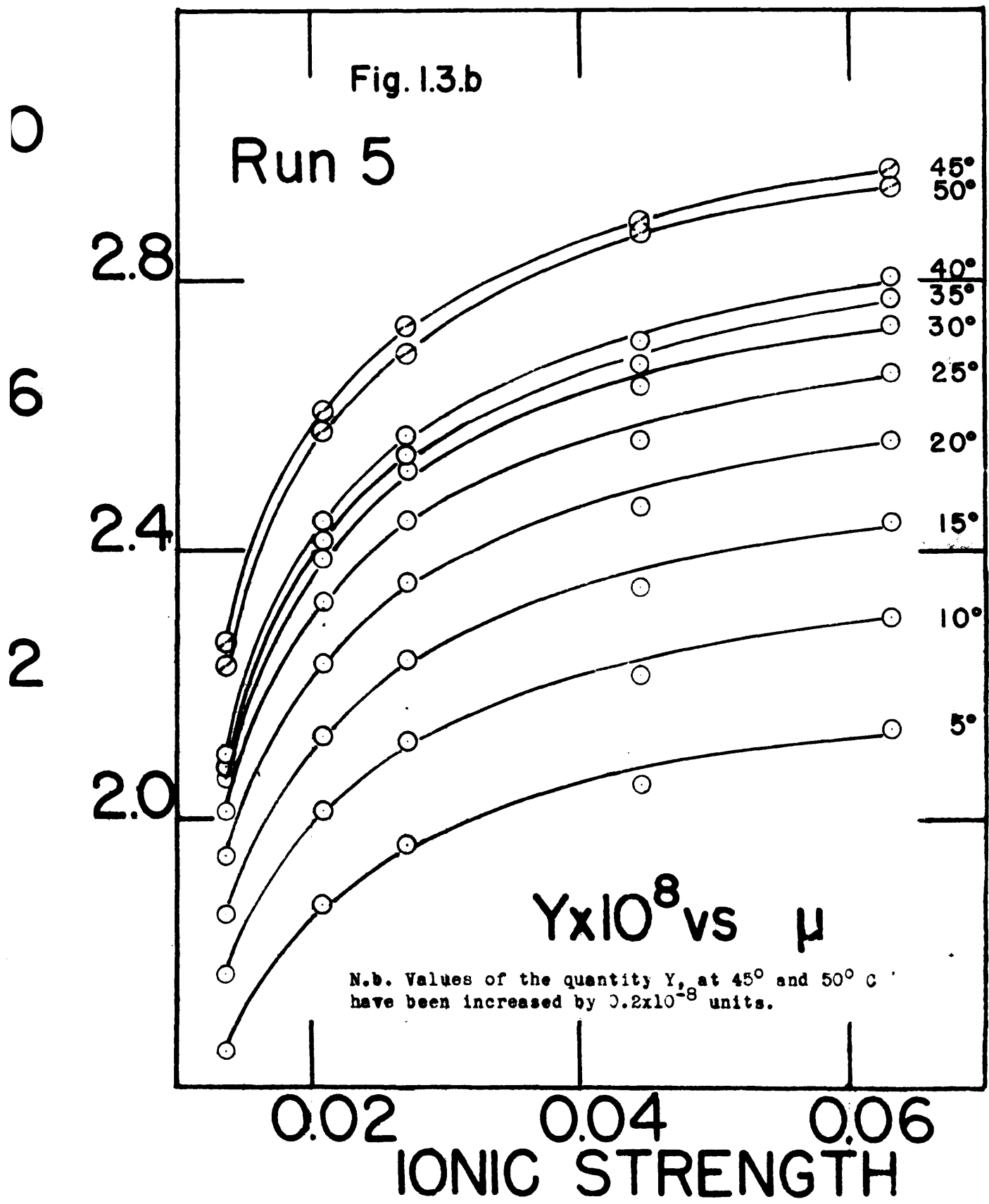
Figure 1b. The computed quantity, Y, as a function of ionic strength for the temperature range 0° to 50° Centigrade.

Fig. 1.2.b

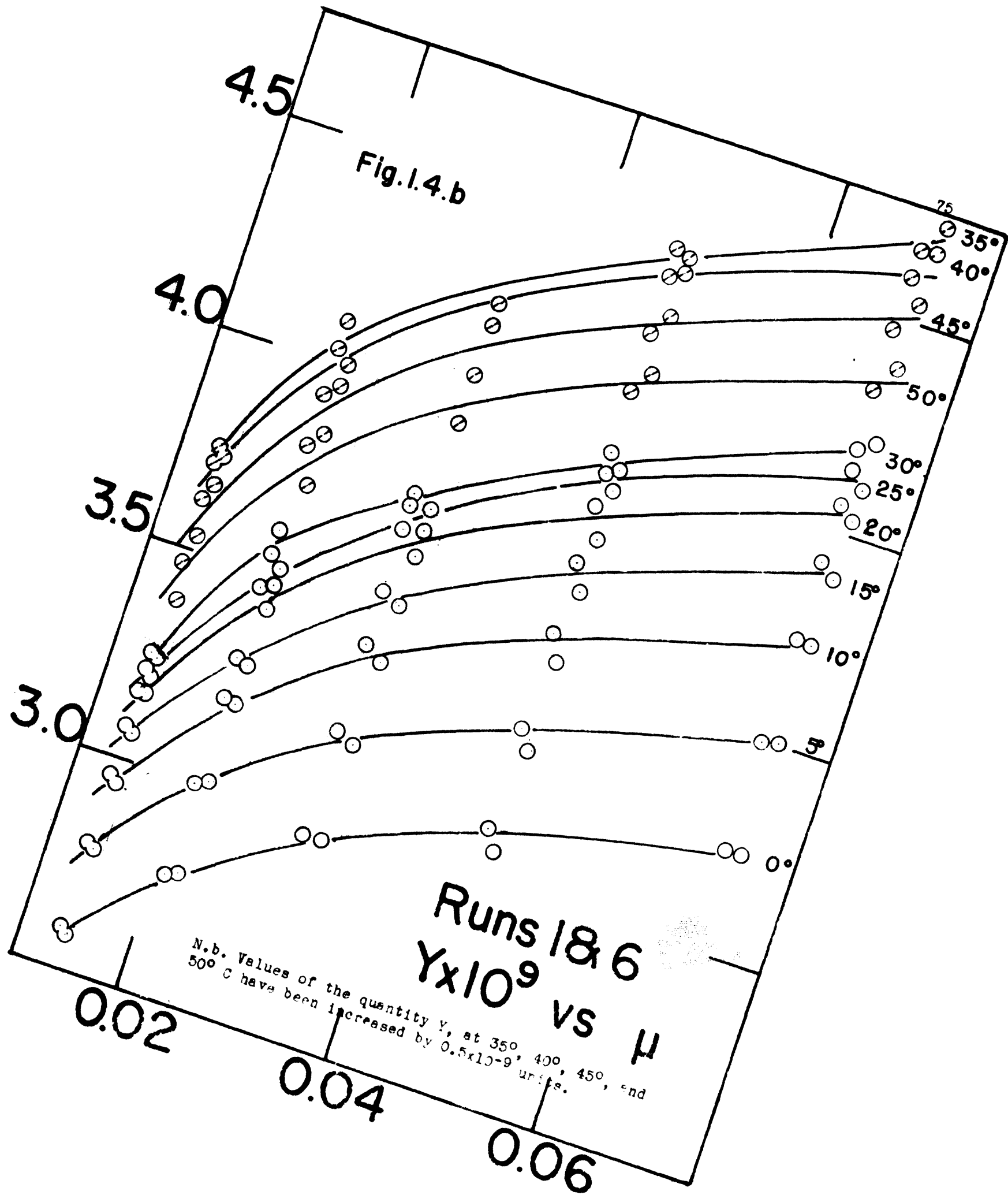
Run 4



N.b. Values of the quantity,  $Y$ , at 45° and 50° C have been increased by  $.4 \times 10^{-3}$  units.







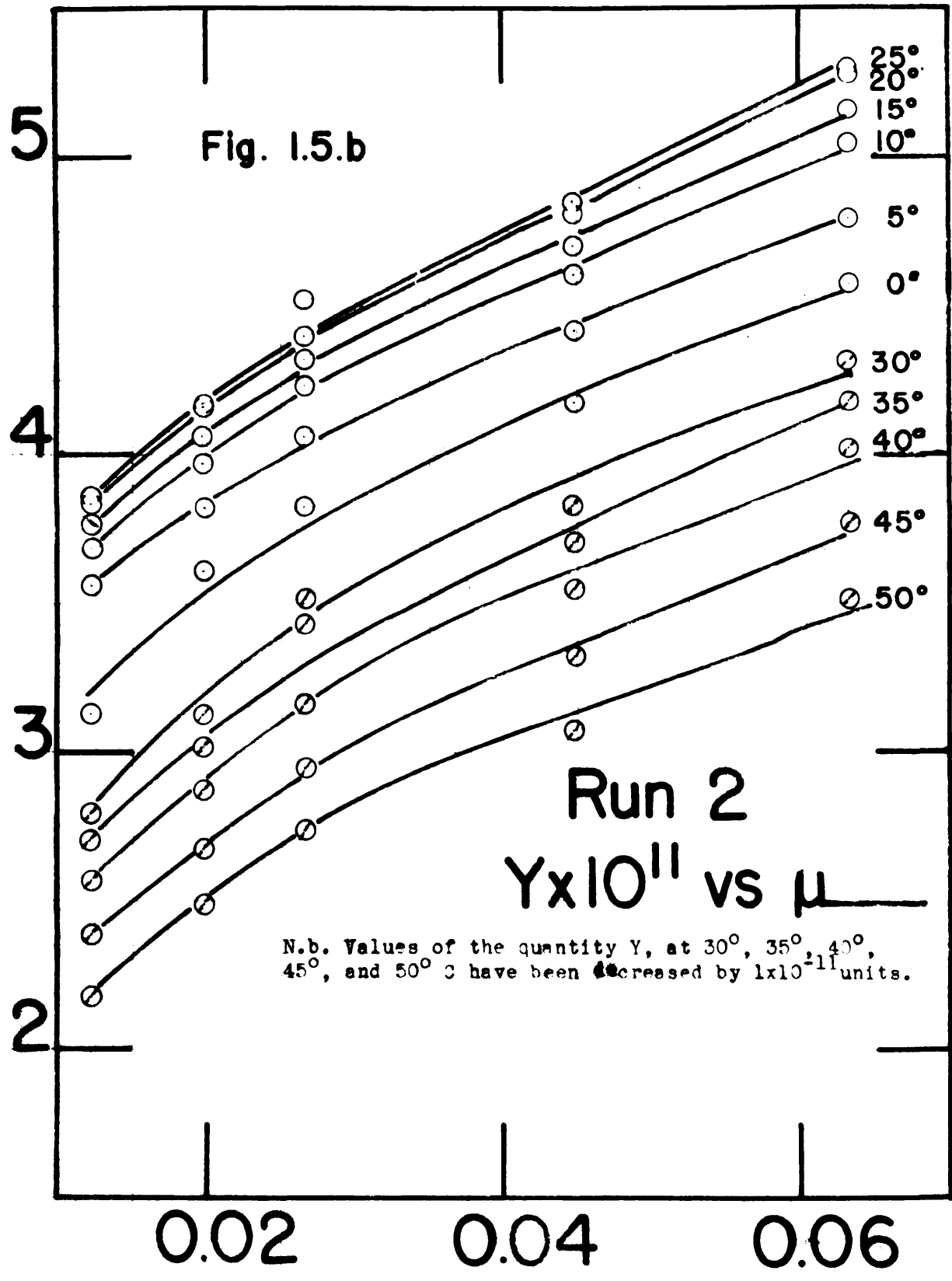
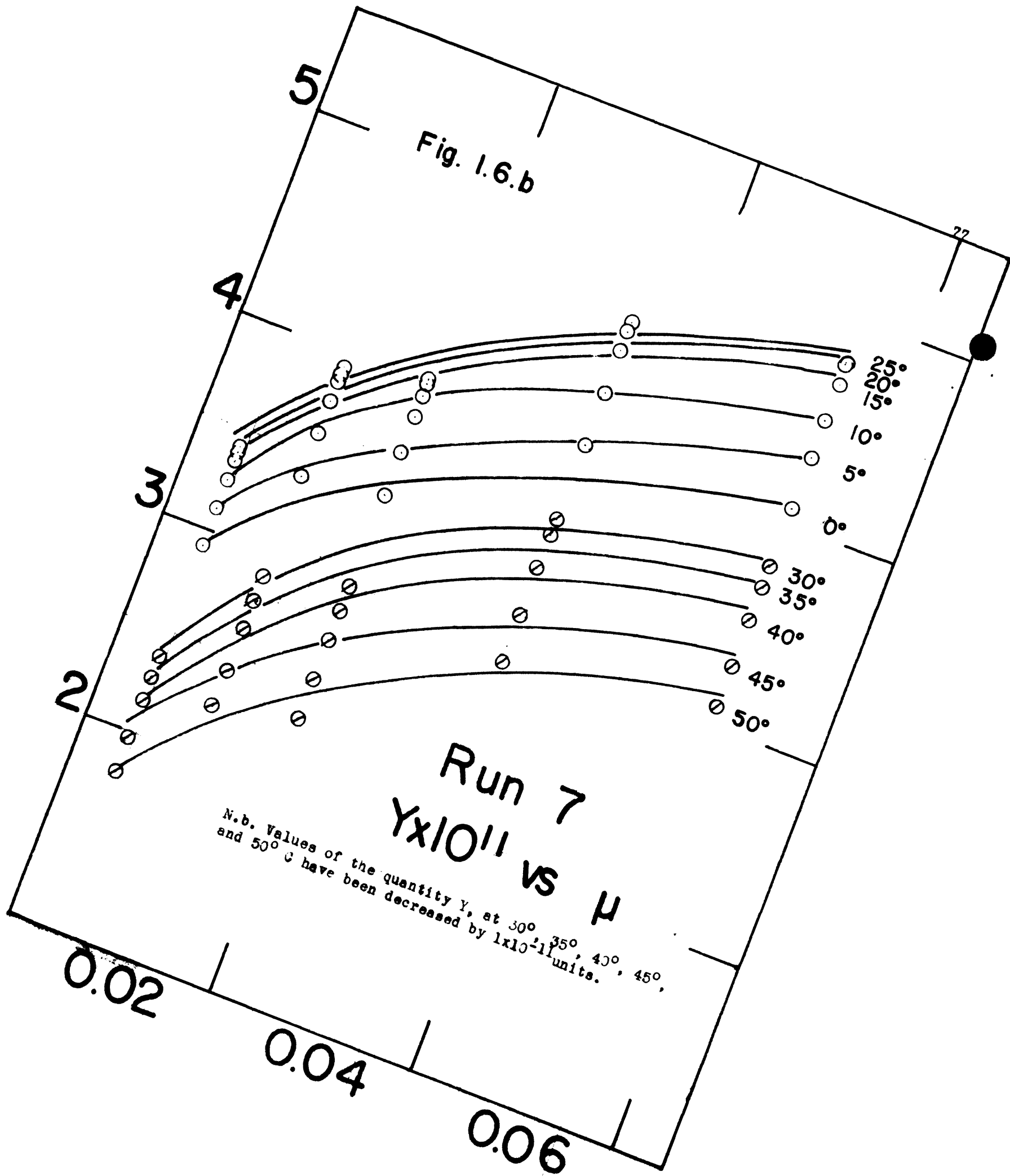
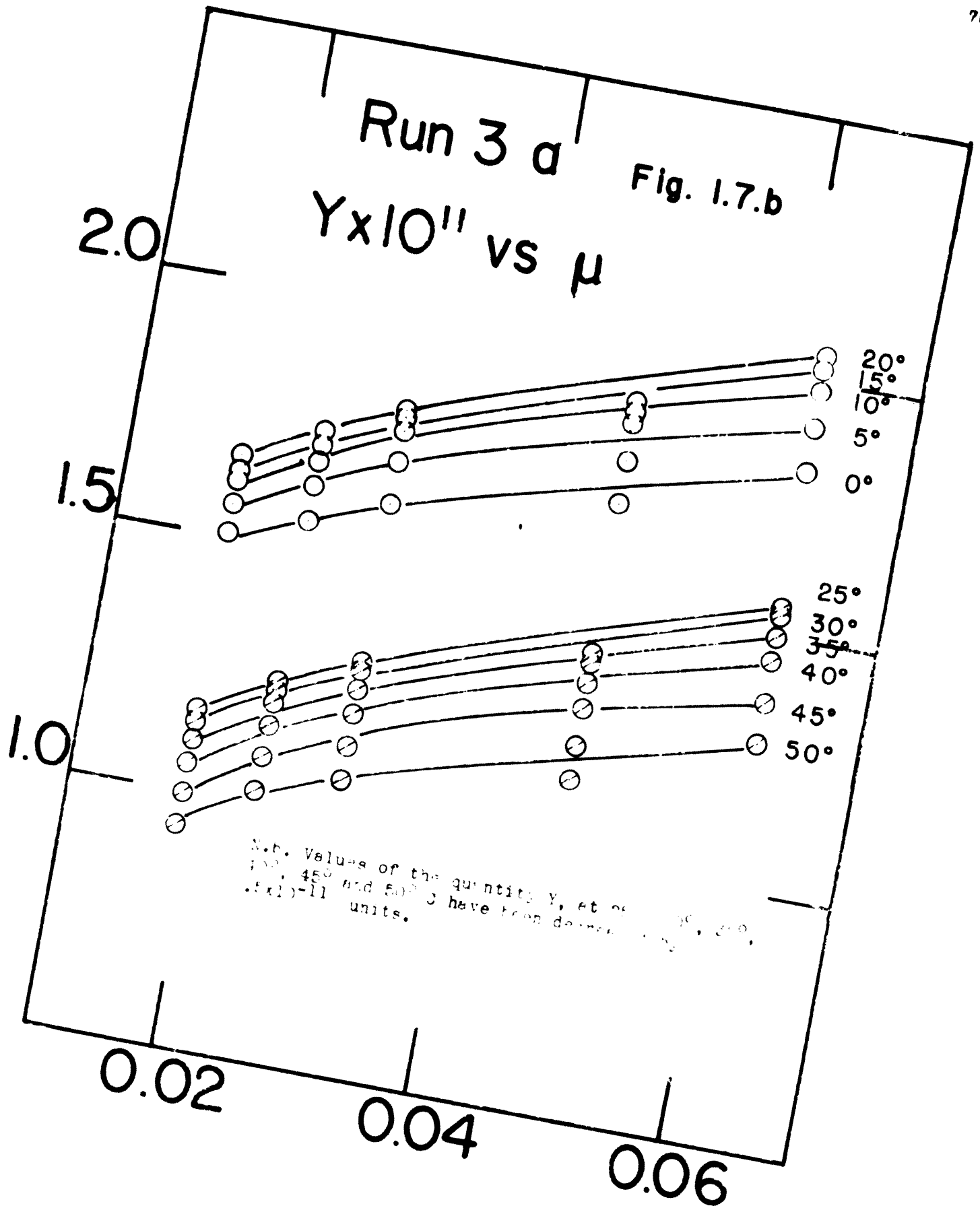


Fig. 1.6.b



Run 7  
 $Y \times 10^{11}$  vs  $\mu$

N.b. Values of the quantity Y, at 30°, 35°, 40°, 45°, and 50° C have been decreased by  $1 \times 10^{-11}$  units.



0°

Fig. 2.1

$Y \times 10^8$  vs  $X \times 10^4$

7.5

Figures 2.1 to 2.11. A series of plots of  $K$  against  $Y$  at constant ionic strength at each temperature in the range 0° to 50° Centigrade.

5.0

$\mu = .06$

.05

.04

.03

.025

.02

.014

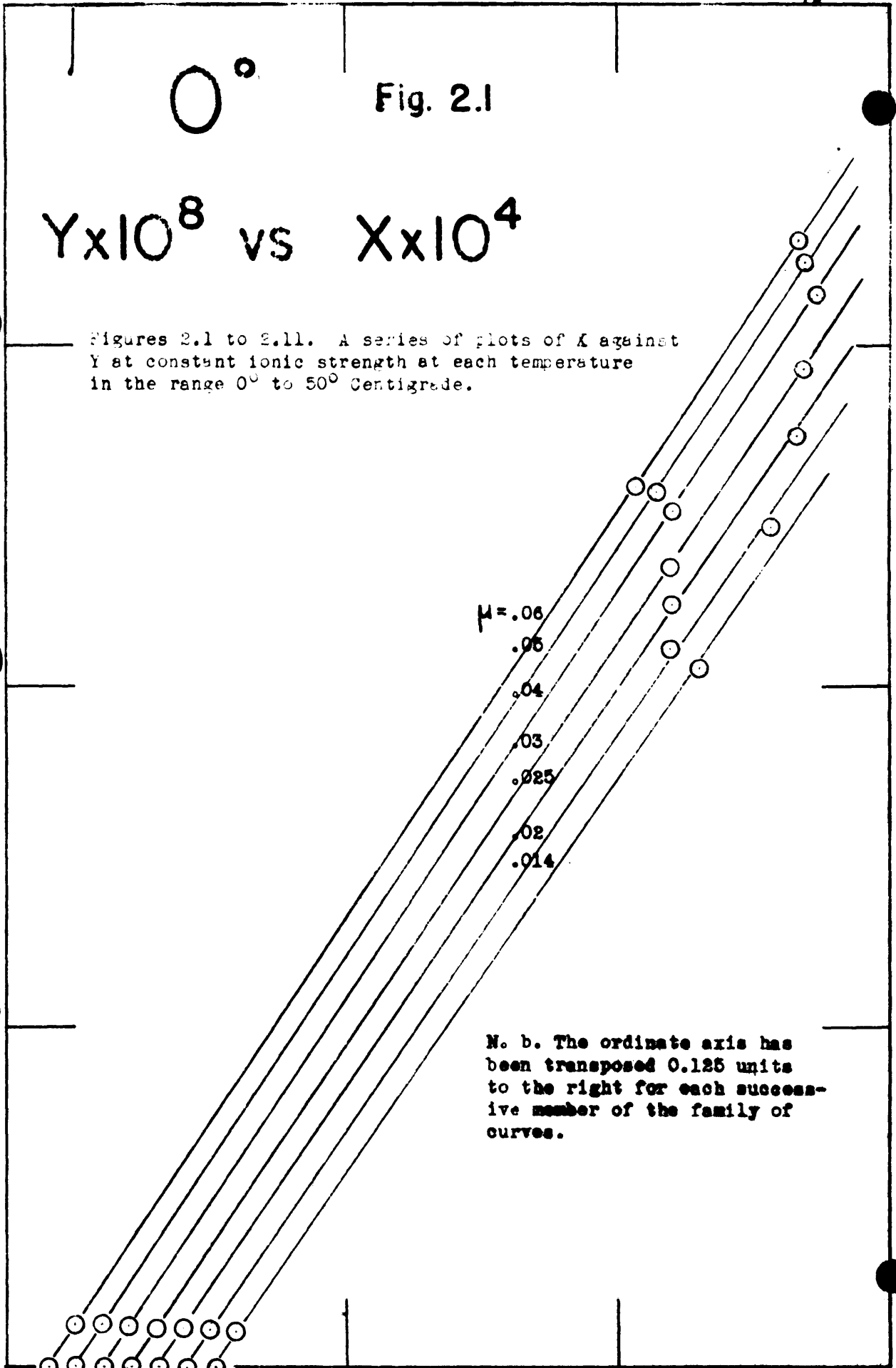
2.5

N. b. The ordinate axis has been transposed 0.125 units to the right for each successive member of the family of curves.

0.0

1.0

2.0



5°

Fig. 2.2

$Y \times 10^8$  vs  $X \times 10^4$

7.5

5.0

2.5

0.0

1.0

2.0

$\mu = .06$

.05

.04

.03

.025

.02

.014

N.b. The ordinate axis has been transposed 0.125 units to the right for each successive member of the family of curves.

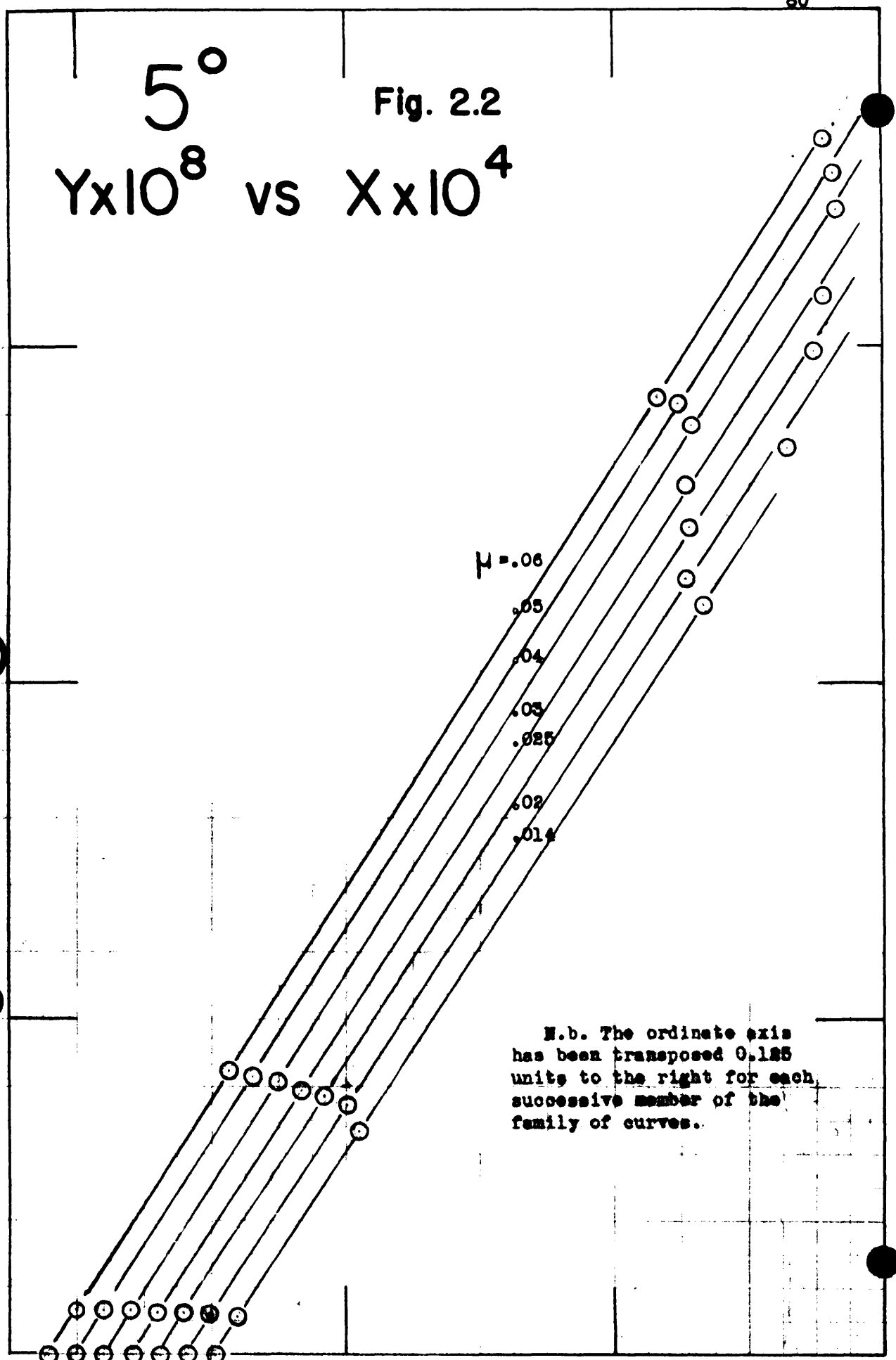


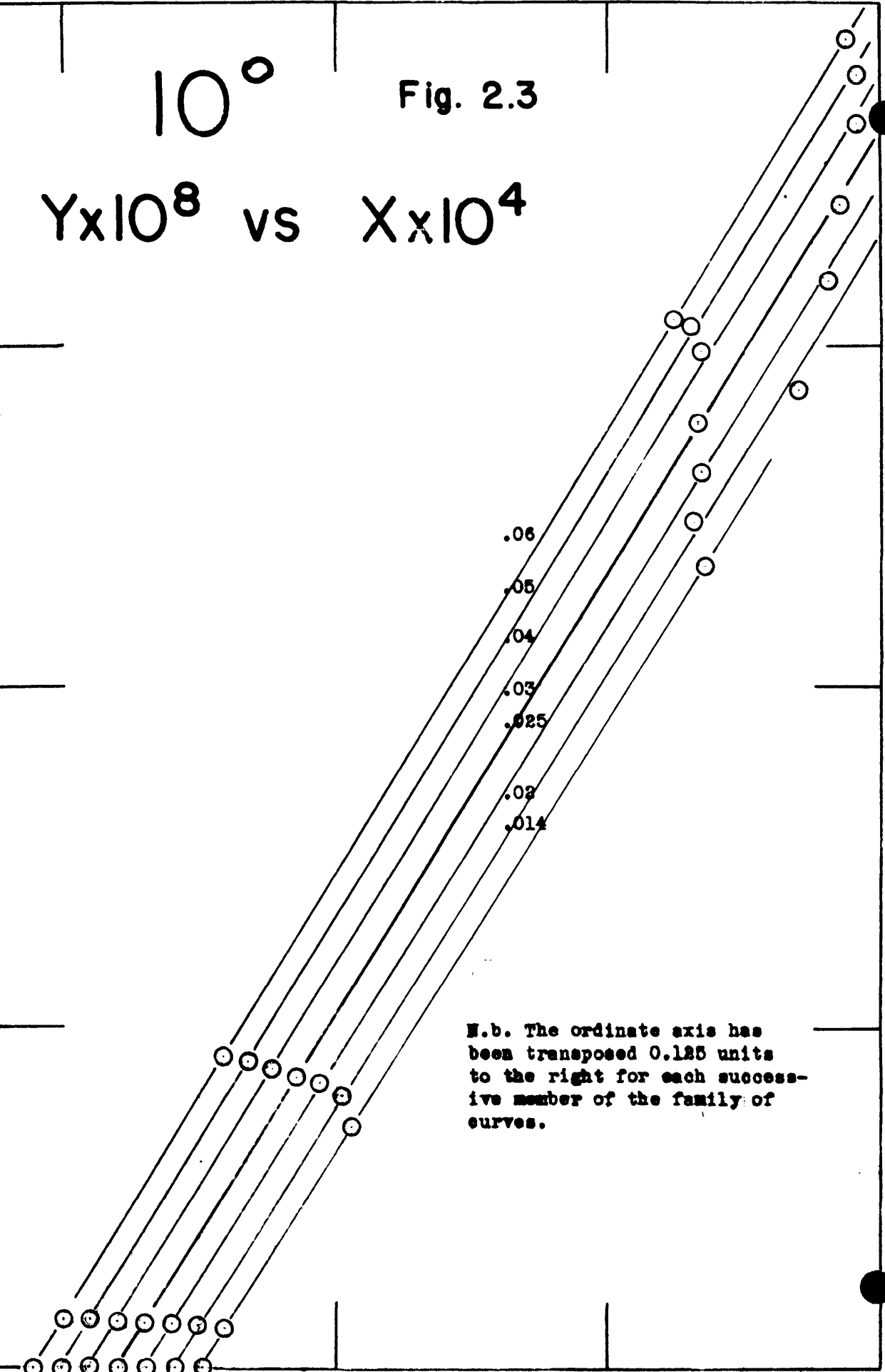
Fig. 2.3

$10^{\circ}$   
 $Y \times 10^8$  vs  $X \times 10^4$

7.5

5.0

2.5



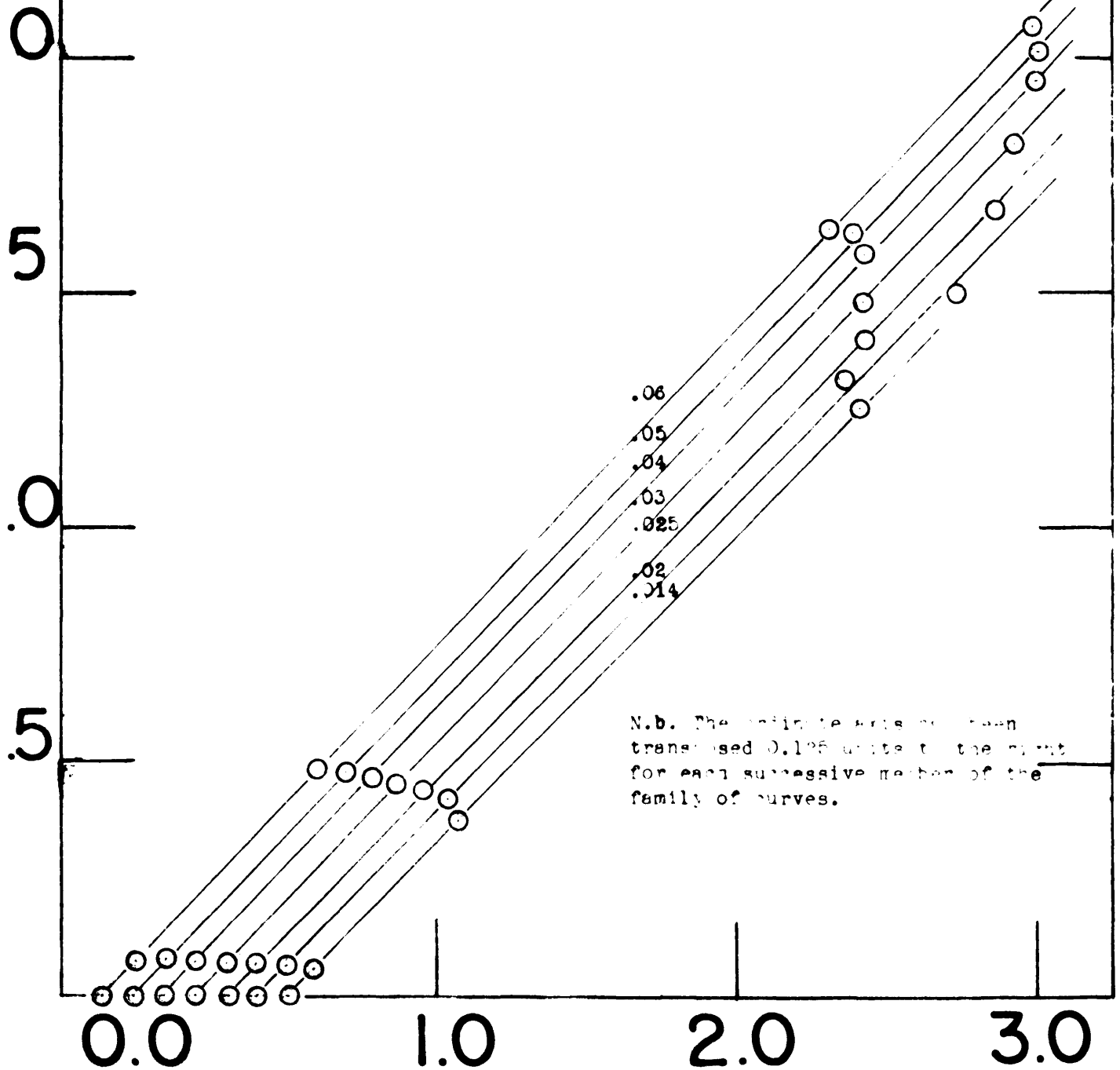
N.b. The ordinate axis has been transposed 0.125 units to the right for each successive member of the family of curves.

0.0

1.0

2.0

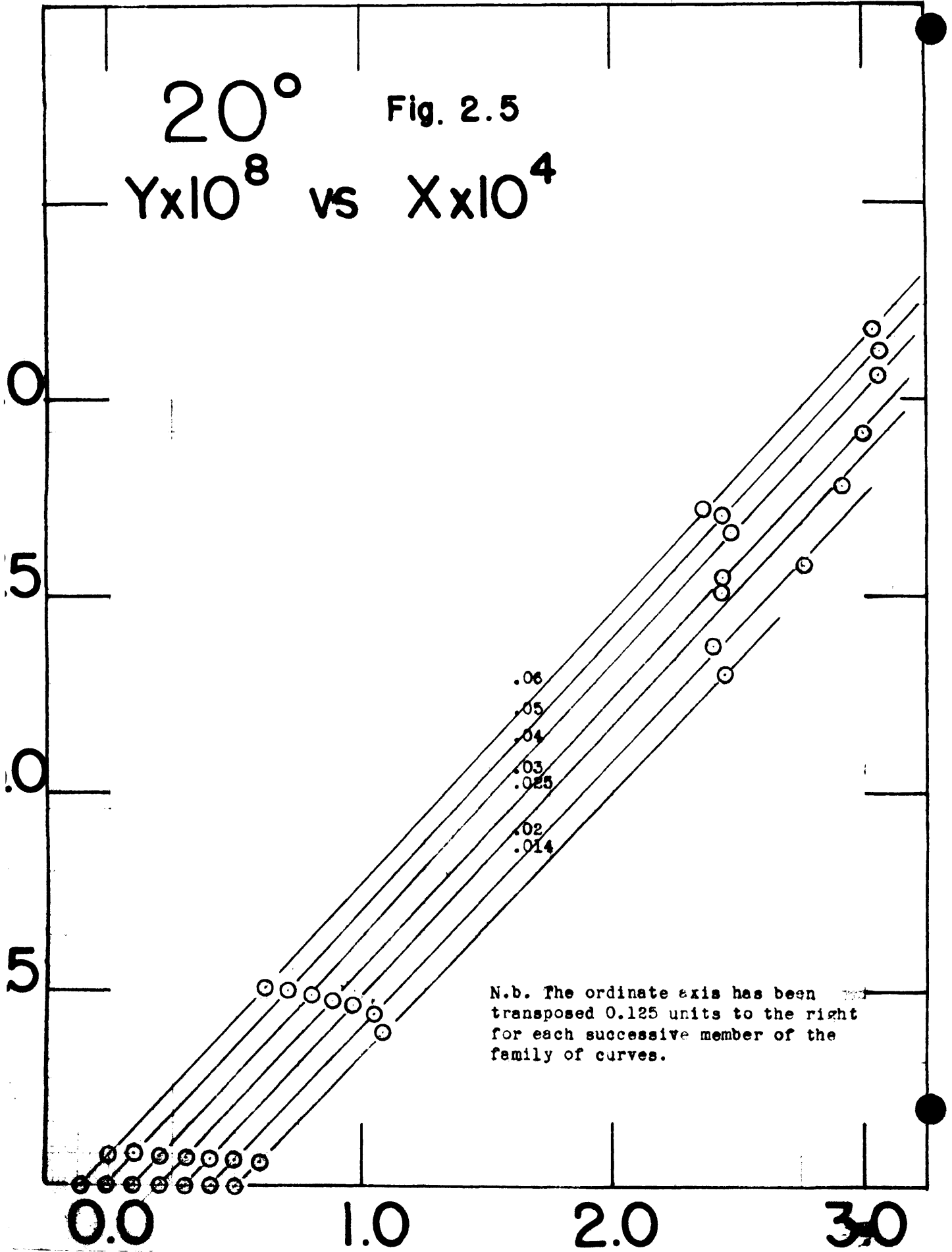
Fig. 2.4

 $15^\circ$   
 $Y \times 10^8$  vs  $X \times 10^4$ 




$20^\circ$   
 $Y \times 10^8$  vs  $X \times 10^4$

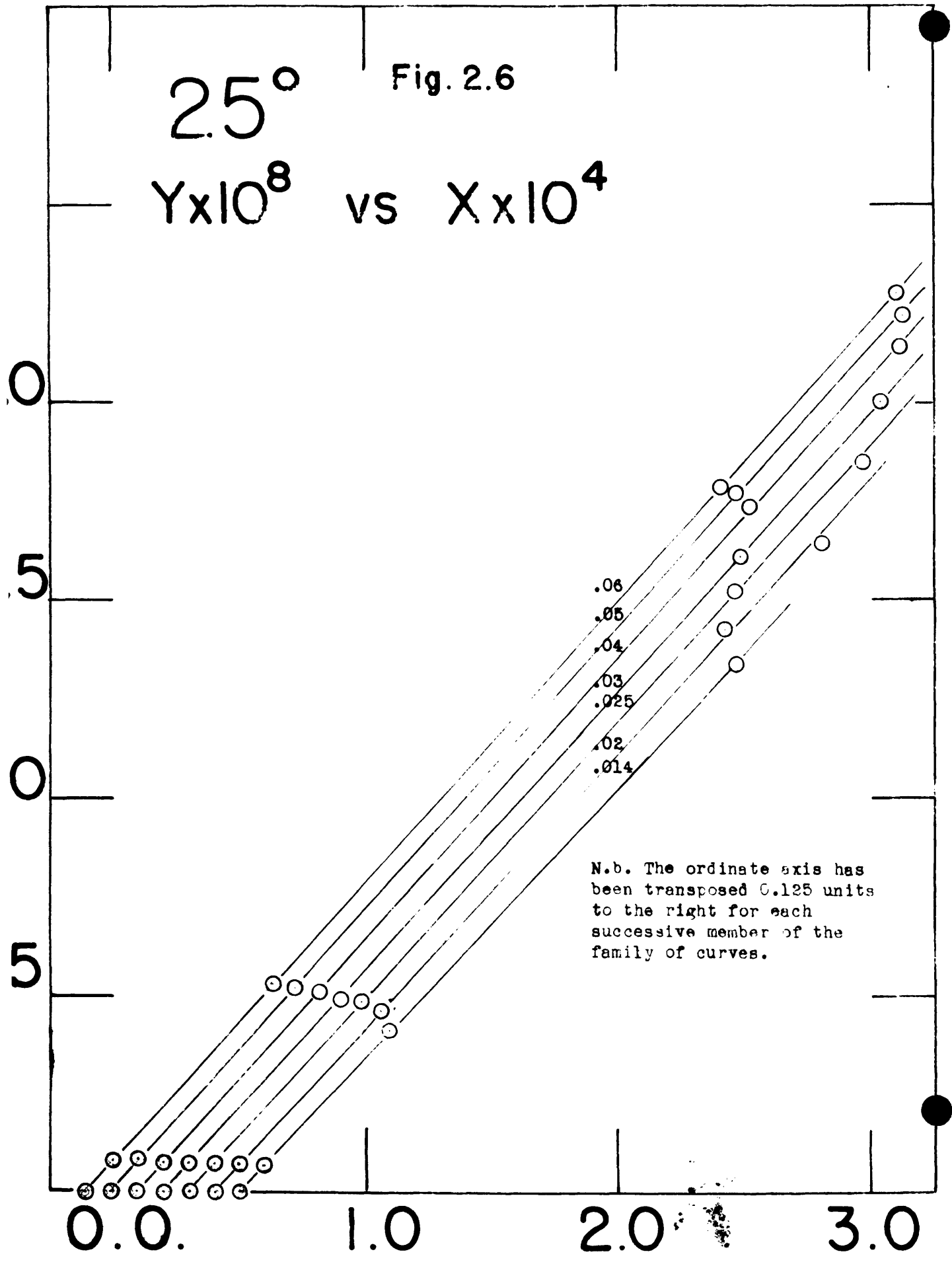
Fig. 2.5

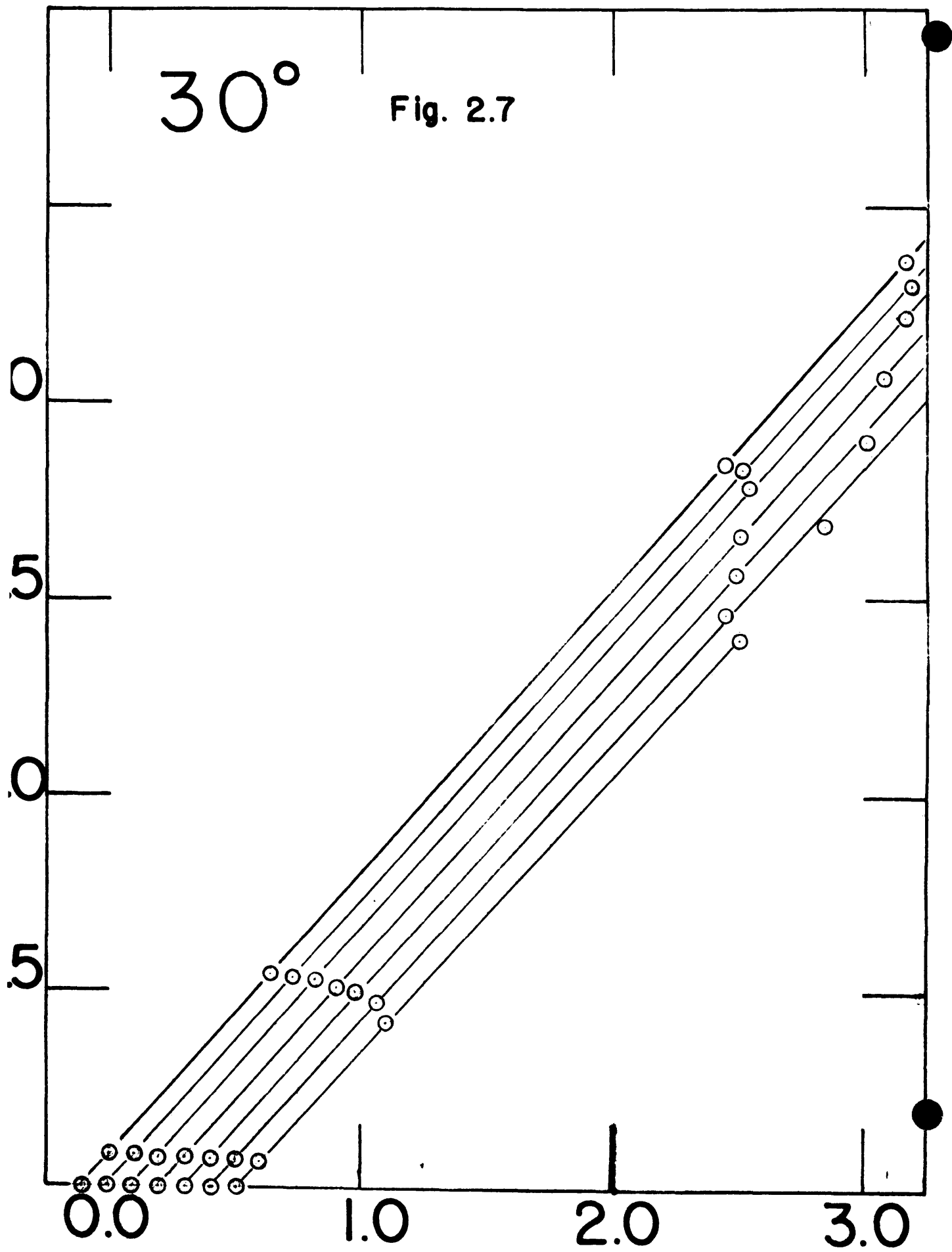


N.b. The ordinate axis has been transposed 0.125 units to the right for each successive member of the family of curves.

Fig. 2.6

$25^\circ$   
 $Y \times 10^8$  vs  $X \times 10^4$





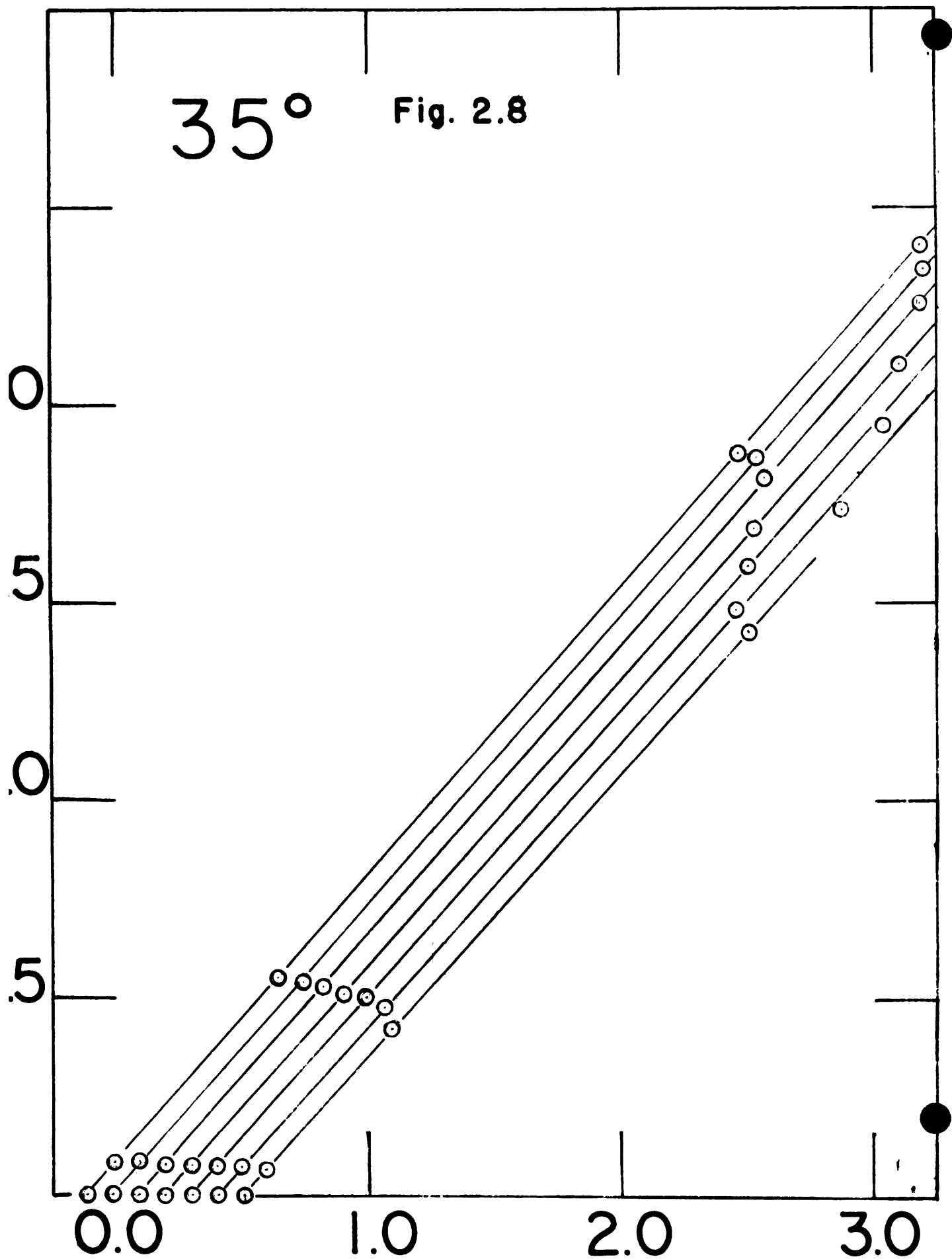
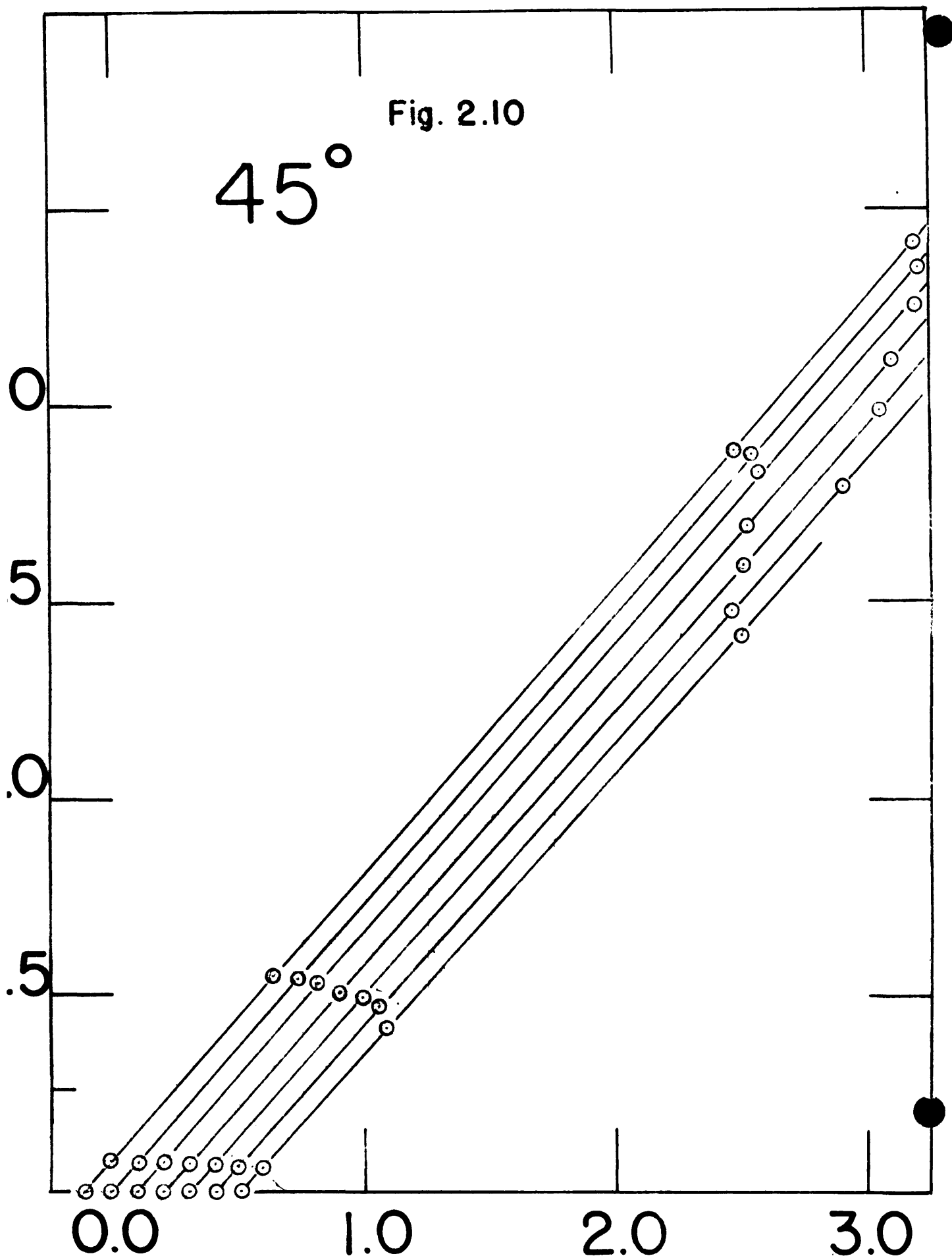




Fig. 2.10

 $45^\circ$ 

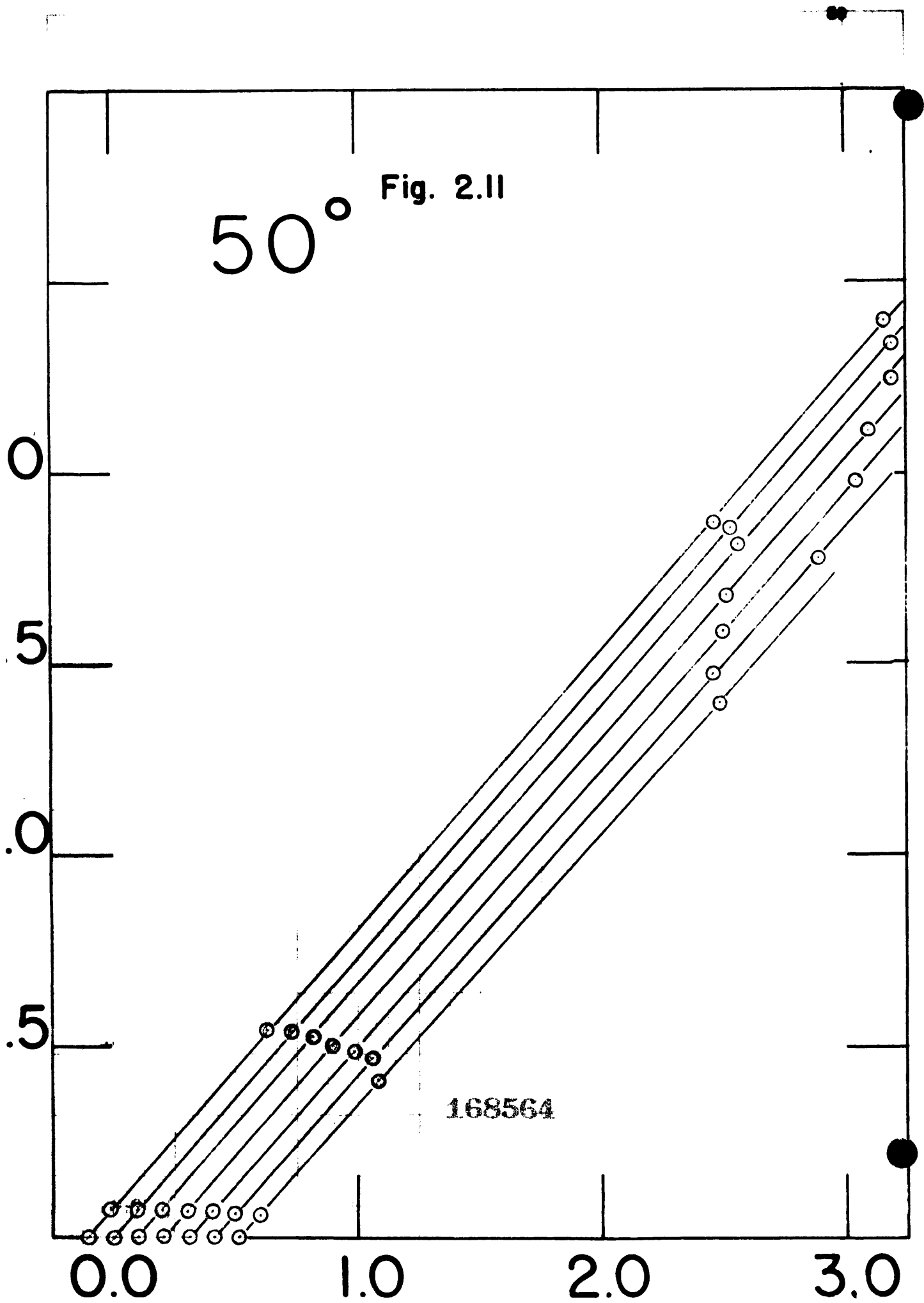
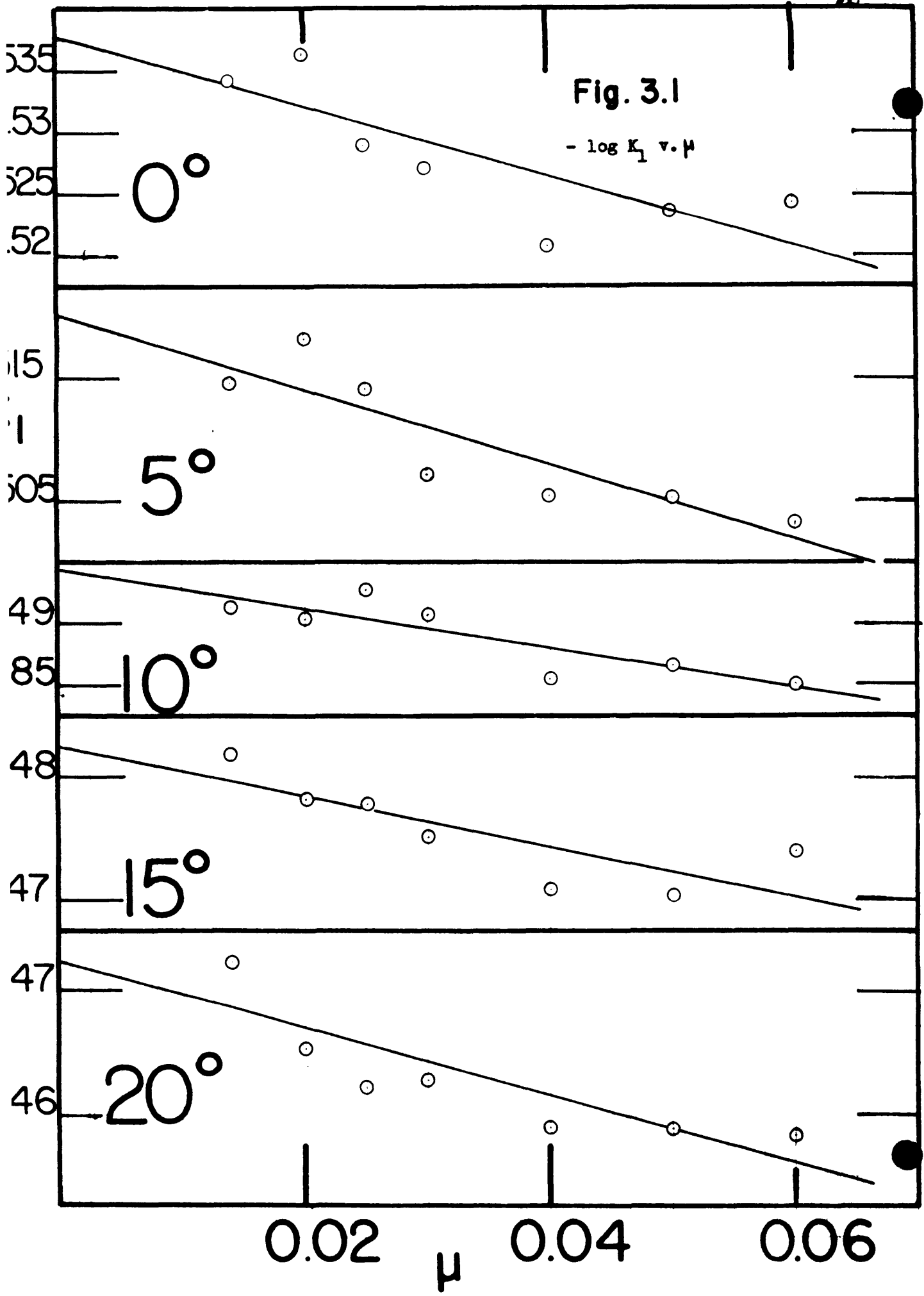
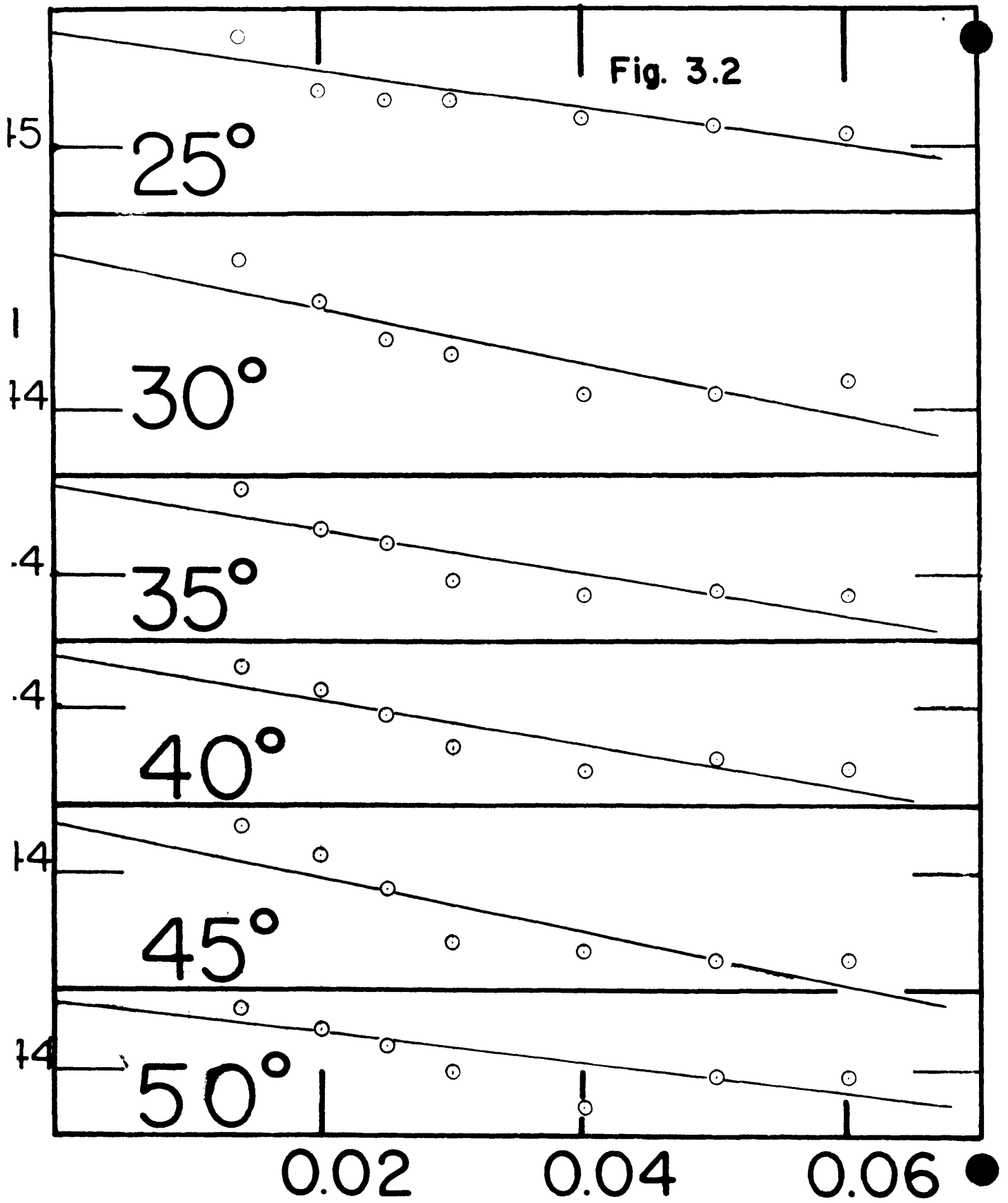


Fig. 3.1  
- log K<sub>1</sub> v. μ







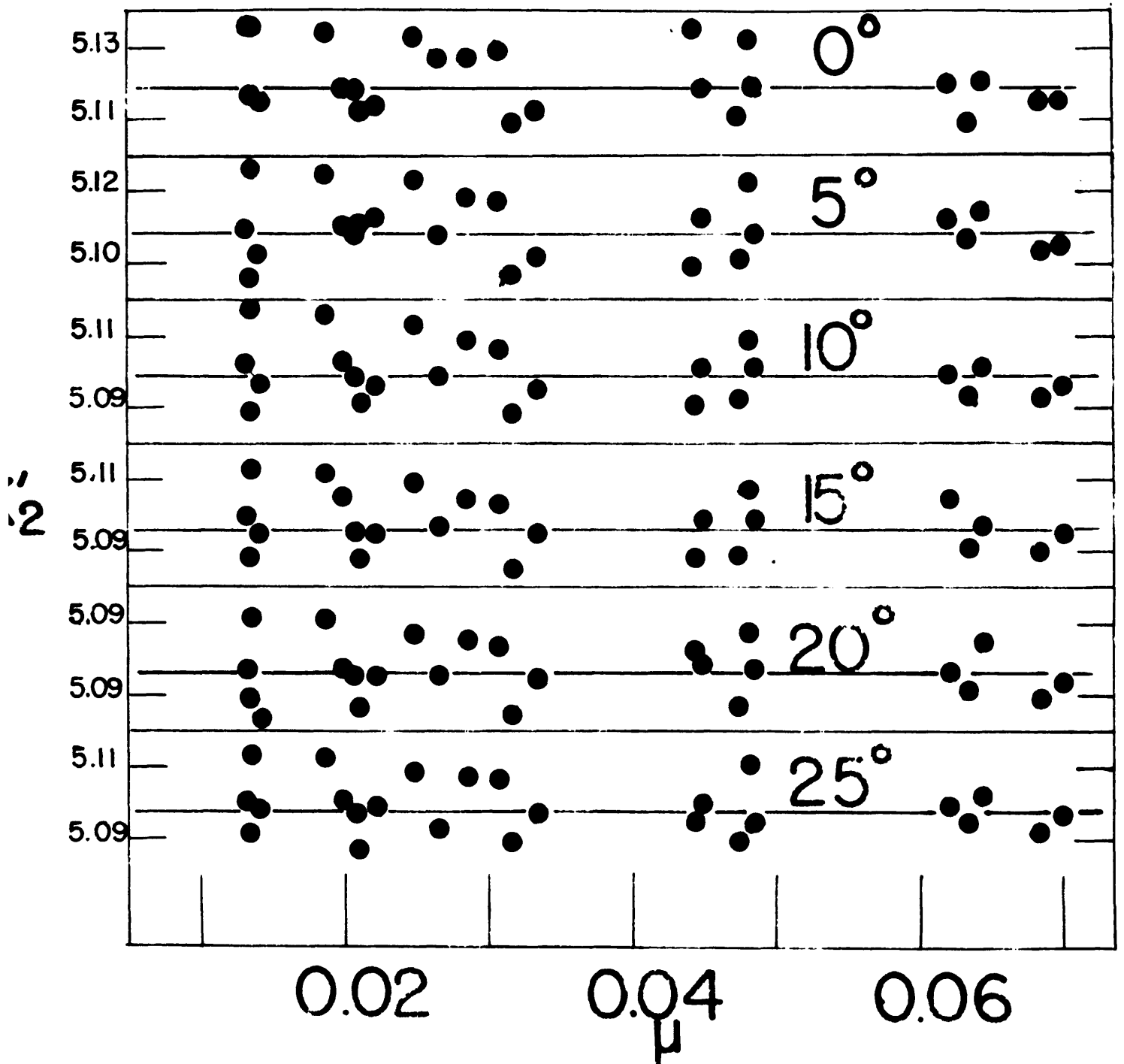
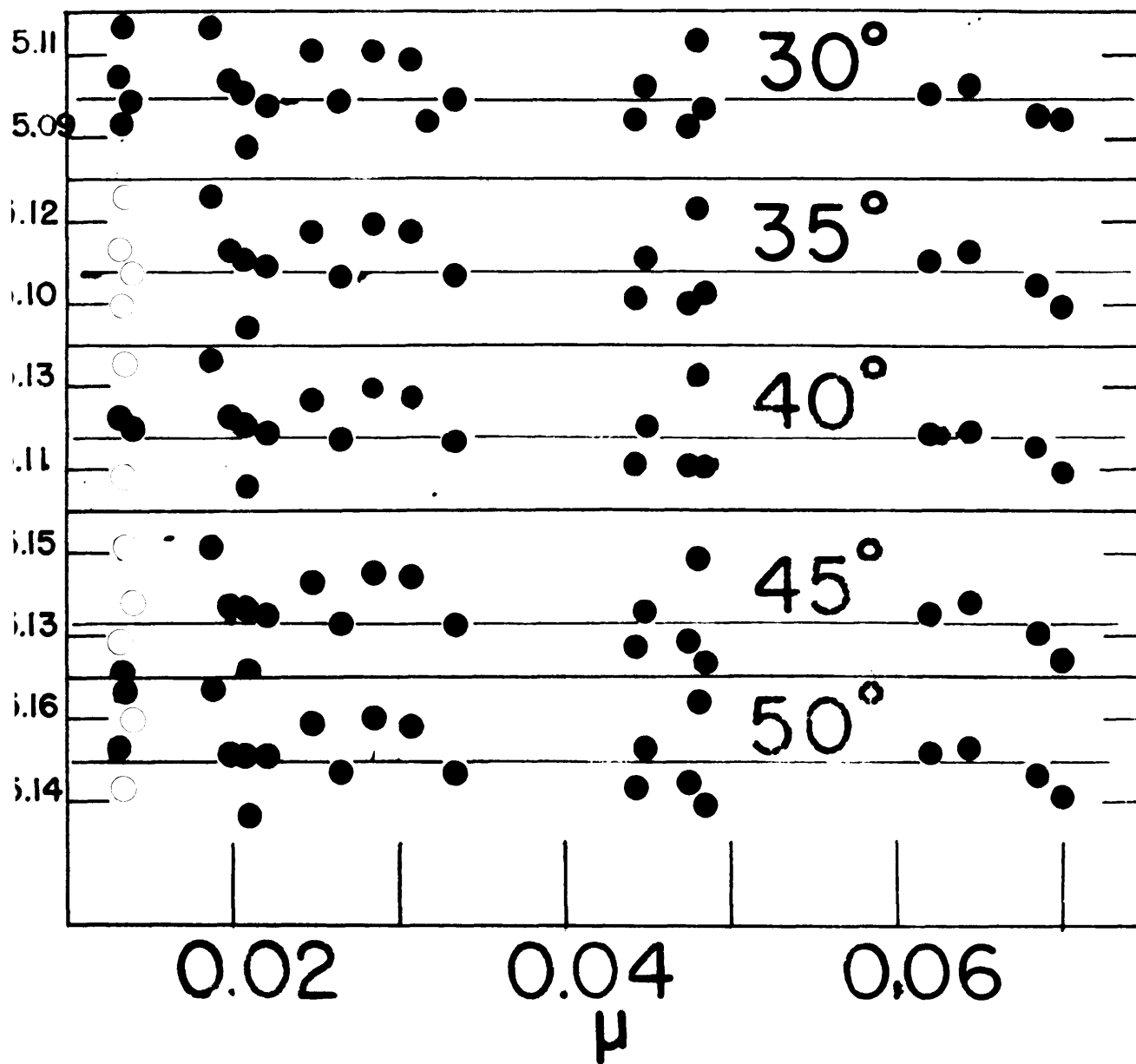


Fig. 4.1

Figure 4. Plot of  $-\log K_p/p^+ \log p^-$  vs. ionic strength for the temperature range 0° to 50° Centigrade.

Fig. 4.2



525

Fig. 5

Figure 5. A comparison of the experimentally derived values of  $pK_1$  and the values of  $pK_1$  calculated by means of equation 73.

500

$pK_1$

475

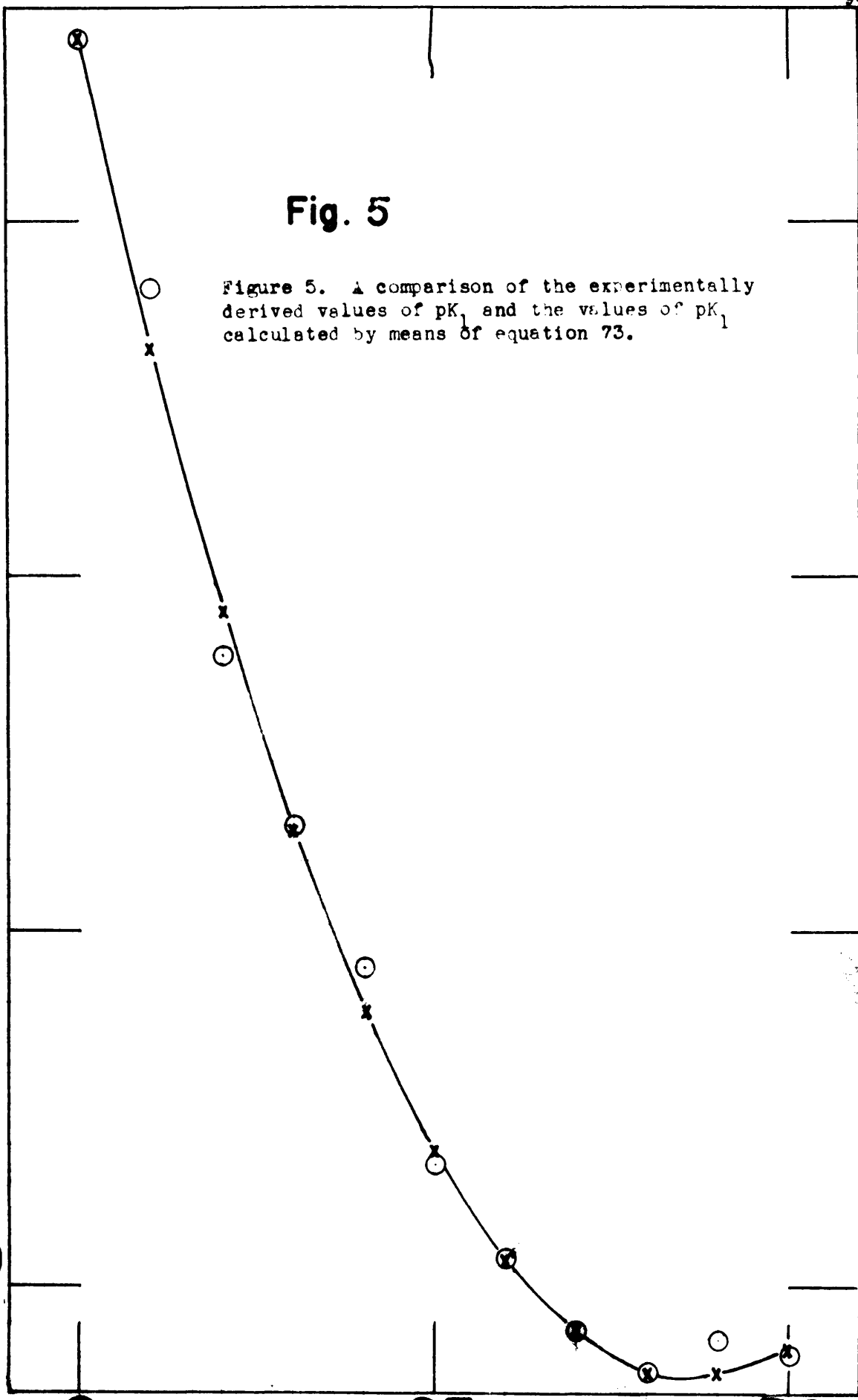
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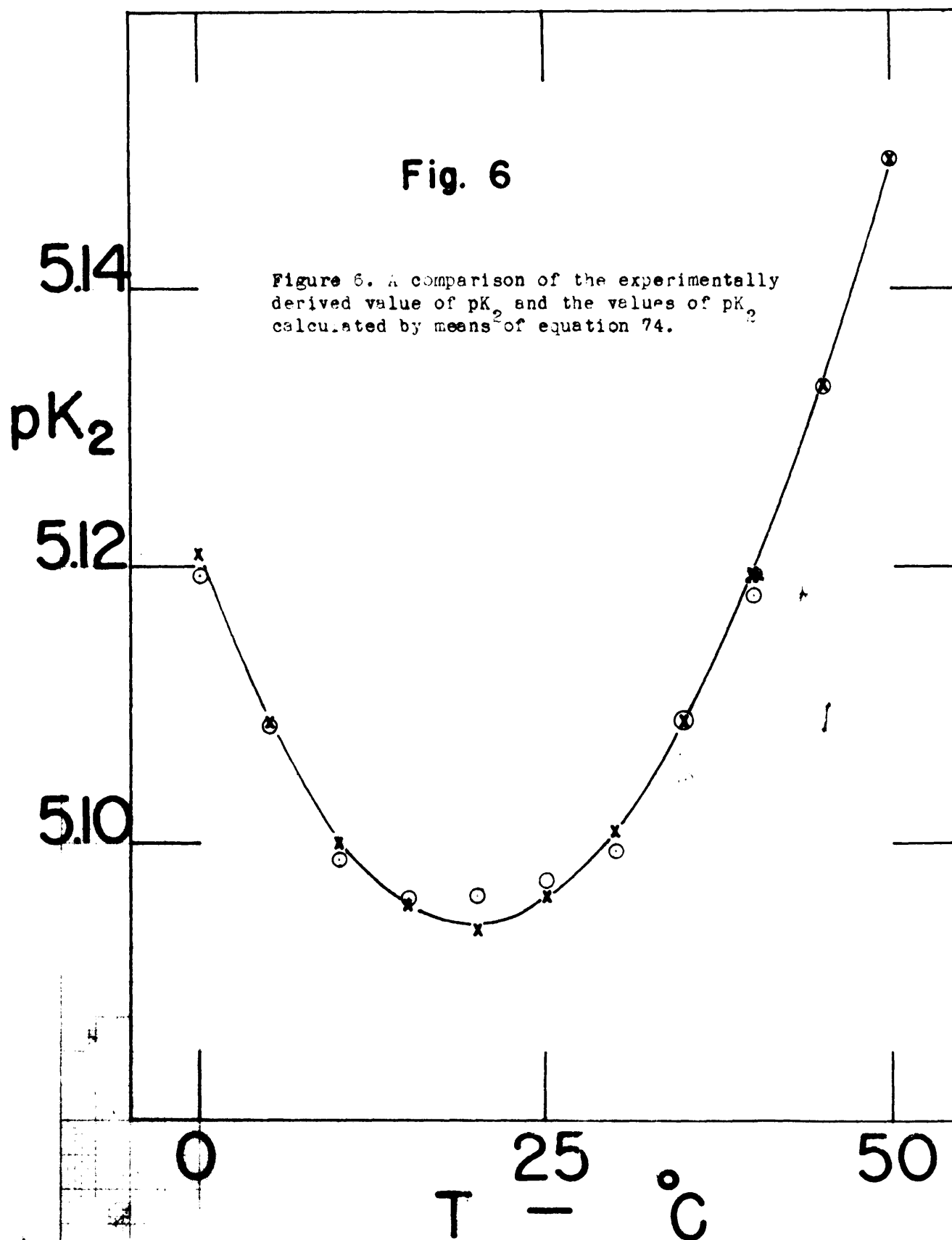
0

T = °C

25

50





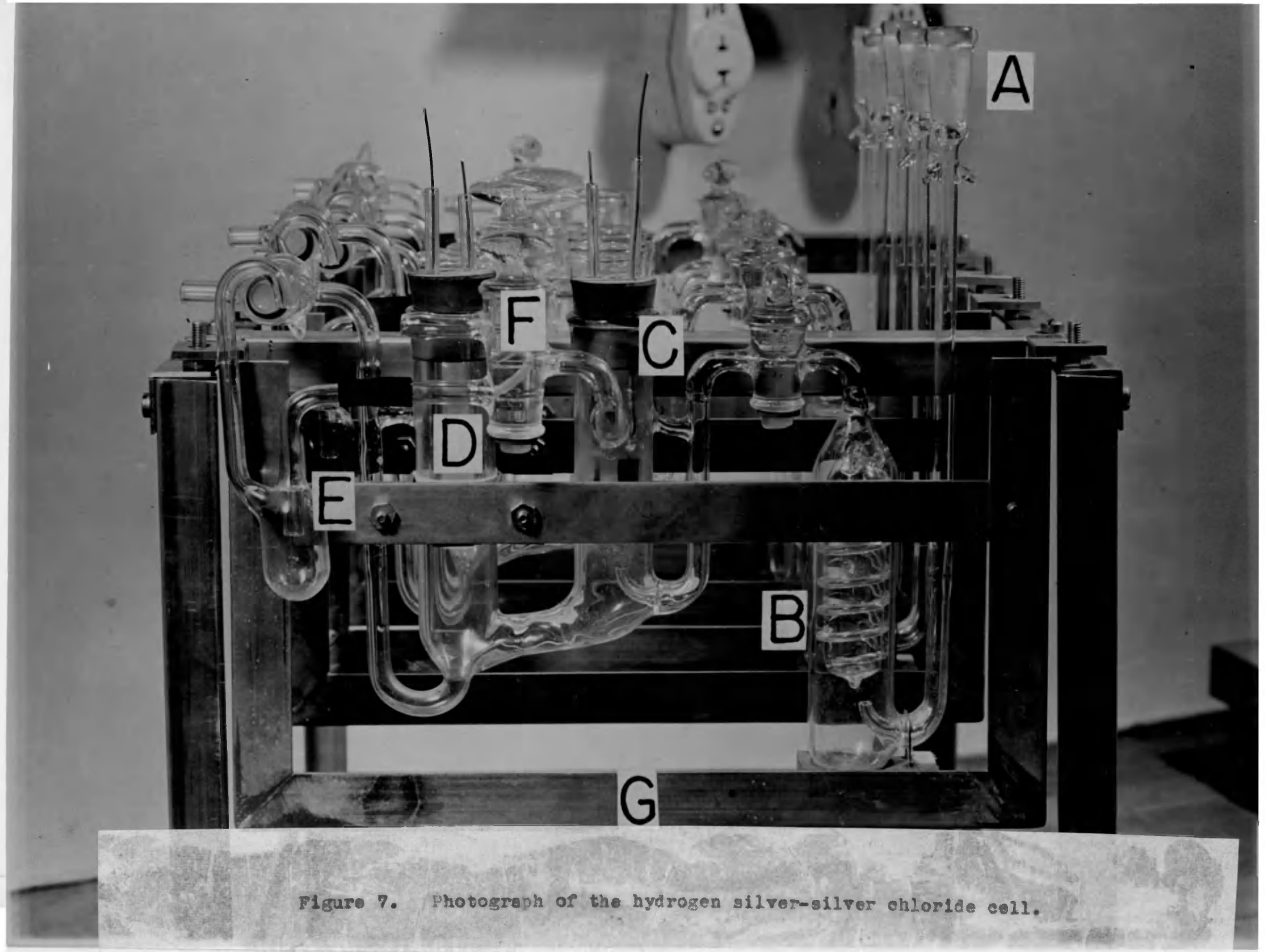


Figure 7. Photograph of the hydrogen silver-silver chloride cell.

Fig. 8

Figure 8. A plot of the mean activity coefficient of hydrochloric acid against ionic strength, for the temperature range 0° to 50° Centigrade; obtained from the data of Harned and Owen (27).

