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KINETICS OF THE REACTION OF CARBON DIOXIDE WITH HYDROXYL ION

Chiu-chuan Shirley Hsu
(M. S. Thesis)

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I. INTRODUCTION

The kinetics of the combination of carbon dioxide and hydroxyl ion is of considerable industrial interest. The reaction is second-order in the forward direction

$$CO_2 + OH^- \xrightarrow{K} HCO_3^-$$

and the rate is given by:

$$\text{Rate (g mole/l s.)} = -\frac{d(CO_2)}{dt} = K\,(CO_2)(OH^-)$$

where K is the second-order rate constant for OH^-, (ℓ/g mole-s),(CO_2 and (OH^-) are the concentrations of CO_2 and OH^- at any stage of the reaction respectively, g mole/ℓ .

The data of the kinetic constant K in various temperatures and salt solutions are very useful in the calculations for designing the process of using hydroxide solutions to remove carbon dioxide from gas mixtures. The calculation of the actual rate of the reaction between carbon dioxide and hydroxyl ion in salt solutions is very complicated because of the effect of ionic strength and the nature of salts. A discussion on the theoretical approach to the calculation will be given in the next section.

The value of K has been measured by some workers. Except the data reported by Pinsent (26) and Nijsing (24), few data are useful for industrial applications. The kinetic constant K is strongly affected by the ionic strength and the nature of the ions present and, therefore, its value cannot be

accurately predicted for the salt solutions in which it has not been measured. A review of the methods which have been used for measuring the kinetic constant will be given in a later section. The results obtained by various methods will be compared and the best method for measuring K in the salt solutions will be discussed.

II. THEORETICAL BACKGROUND

1. Kinetics in unbuffered solutions

When carbon dioxide reacted with hydroxyl ion in excess concentration of hydroxide, the reaction can be expressed as:

$$CO_2 + OH^- \xrightarrow{K} HCO_3^- \qquad (1)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^= + H_2O \qquad (2)$$

and the over-all reaction is

$$CO_2 + 2OH^- \longrightarrow CO_3^= + H_2O \qquad (3)$$

Reaction (2) can be considered as instantaneous and the rate for the over-all reaction is determined by reaction (1).

Solution of the differential rate equation gives the following expression from which K may be obtained:

$$\log \frac{b-2y}{a-y} = \frac{b-2a}{2.303} Kt + \log \frac{b}{a} \qquad (4)$$

where: a = the initial concentration of CO_2, g mole/ℓ

b = the initial concentration of OH^-, g mole/ℓ

y = the concentration of carbonate formed at time t, g mole/ℓ

K = the kinetic constant of the reaction (1), ℓ/ g mole, sec.

The concentration of hydroxide at any stage can be determined from thermal (26), pH (39) and CO_2(24) measurements. The concentration of carbonate y can be calculated from the measured hydroxide concentration.

2. Kinetics in buffered solutions

In the carbonate-bicarbonate buffer solutions, hydroxide concentration at any stage in the reaction depends on the buffer ratio, the buffer Ka and various activity coefficients. It is usually calculated by the equation:

$$(OH^-) = \frac{K_w}{K_a} \frac{(CO_3^=)}{(HCO_3^-)} \qquad (5)$$

where

$$K_a = \frac{a_{H^+} a_{CO_3^=}}{a_{HCO_3^-}} = \frac{(H^+)\ (CO_3^=)}{(HCO_3^-)} \times \frac{f_{H^+}\ f_{CO_3^=}}{f_{HCO_3^-}} \qquad (6)$$

$$K_w = a_{H^+}\ a_{OH^-} \qquad (7)$$

K_a = dissociation constant of HCO_3^-

a_{H^+}, $a_{CO_3^=}$, $a_{HCO_3^-}$ are the activity of H^+, $CO_3^=$ and HCO_3^- respectively, expressed as the product of the molar concentration, i.e. (H^+), $(CO_3^=)$, (HCO_3^-) and the activity coefficient, f_{H^+}, $f_{CO_3^=}$, $f_{HCO_3^-}$

K_w = dissociation constant of water

K_a and K_w at any temperature depend on ionic strength of the solution and the nature of the ions present. Thus the concentration of hydroxide will also depend on the ionic strength and the species of the ions.

Näsänen (23) measured K_w/K_a at 25°C in solutions of NaCl

KCl ($I<2$ g ion/ℓ) and expressed the relation of log K_w/K_a and I as:

$$\log \frac{K_w}{K_a} = -3.677 - \frac{1.01\sqrt{I}}{1+\alpha\sqrt{I}} - \beta I \qquad (8)$$

where I = ionic strength, g ion/liter, as defined in eq. (19)

for KCl: $\alpha = 1.49$, $\beta = 0.061$

NaCl: $\alpha = 1.27$, $\beta = 0.125$

From this equation, it can be seen that in potassium solutions K_w/K_a is higher than that in sodium solutions.

So far, there is practically no information about the concentration of hydroxyl ion in concentrated carbonate-bicarbonate solutions ($I > 1$ g ion/ℓ). Because of the uncertainty of hydroxide concentration in buffers, the integrated form of the second order rate law will be a complex expression which requires an elaborate ionic strength correction.

3. The effect of temperature on the kinetic constant

The variation of rate constant with temperature can be represented by the equation:

$$\log K = \left(\frac{-E_a}{2.303\,R}\right) \frac{1}{T} + C \qquad (9)$$

where K = the reaction rate constant

T = the absolute temperature

R = the gas constant in calories

E_a = Activation energy, calories

C = the constant of integration

According to Eq. (9), a plot of log K against 1/T should be a straight line with a slope expressed by Equation 10:

$$\text{slope} = \frac{-E_a}{2.303\ R} \qquad (10)$$

4. The effect of ionic strength on the kinetic constant

A general theory of the influence of ionic strength on the rate of reactions between ions was given by Brønsted (4), Bjerrum (2), Christiansen (6) and Scatchard (34) for the influence of the ionic strength on the rate. Consider a reaction of the general type

$$A + B \longrightarrow AB^{\neq} \longrightarrow \text{Products} \qquad (11)$$

From transition-state theory, the rate of the reaction is given by:

$$K_I = \frac{k\ T}{h} \quad \frac{(AB^{\neq})}{(A)\ (B)} \qquad (12)$$

where k: Boltzmann's constant

h: Planck's constant

T: Temperature

$(AB^{\neq})$, (A) and (B): Concentrations of $AB^{\neq}$, A and B respectively, in moles/liter

If A and B are ions, the equilibrium constant is given by

$$K^{\neq} = \frac{a_{AB^{\neq}}}{a_A\ a_B} = \frac{(AB^{\neq})}{(A)(B)} \quad \frac{f_{AB^{\neq}}}{f_A f_B} \qquad (13)$$

$$\frac{(AB^{\neq})}{(A)(B)} = K^{\neq} \frac{f_A\ f_B}{f_{AB^{\neq}}} \qquad (14)$$

Substituting eqn. (14) to eqn. (12) yields

$$K_I = \frac{k\,T}{h}\ K^{\neq}\ \frac{f_A\ f_B}{f_{AB}} = K_o\ \frac{f_A\ f_B}{f_{AB}} \tag{15}$$

where K_o is the reaction constant at infinite dilution. Taking logarithms,

$$\log K_I = \log K_o + \log \frac{f_A\ f_B}{f_{AB^{\neq}}} \tag{16}$$

According to the Debye-Hückel theory, the activity coefficient of an ion is related to its valency Z and the ionic strength according to the equation:

$$\log f = -\ Q\ Z^2\sqrt{I} \tag{17}$$

The coefficient Q in this expression is given by

$$Q = \frac{N^{1/2}\ e^3\ (2\pi)^{1/2}}{2.303\ (\epsilon kT)^{3/2}(1000)^{1/2}} \tag{18}$$

where N: Avogadro constant

e: electric charge of the ion

ϵ: Dielctric constant

k: Botzmann's constant.

T: Temperature

and the ionic strength is defined, following G. N. Lewis, by the equation:

$$I = \frac{1}{2} \sum C_i\ Z_i^2 \tag{19}$$

hydroxide, the influence of the cation on the activity coefficient is in the order of K > Na > Li. This phenomenon was explained by Robinson and Harned (30). They introduced the idea of "localized hydrolysis" to account for the effect: In the hydration shell around a cation the water molecules must be highly polarized with the positive charges directed away from the cation:

$$Na^{+} \ldots\ldots\ldots\ldots \quad OH^{-} \quad \ldots\ldots\ldots\ldots \quad H^{+}$$

It is possible that the bound hydrogen ion can exert sufficient force on a comparatively small ion like the hydroxyl to lead to a short-life binding:

$$Na^{+} \ldots\ldots\ldots\ldots \quad OH^{-} \quad \ldots\ldots\ldots \quad H^{+} \quad \ldots\ldots\ldots \quad OH^{-}$$

with the formation of a kind of ion-pair but differing in that the water molecule acts as intermediary. The smaller the cation the more polarized will be the solvent molecules so that the effect would decrease from lithium to potassium. As such interaction would lead to reduced activity coefficients, it would explain why lithium hydroxide has a low, and potassium hydroxide a high, activity coefficient.

The effects of chlorides and sulfates on the activity coefficients of sodium and potassium hydroxide were measured by some workers. The data are shown in Table 15. From the table , we can see that the activity coefficients of hydroxides in chloride solutions are higher than those in sulfate solutions.

(ii) The influence of ionic strength on the activity coefficient of carbon dioxide: (i.e. eqn. 22)

The salt effect on the activity coefficient of CO_2 has been discussed by many authors, but it is still not possible to make reliable estimates of its magnitude. Table (16) shows the b_B value used in eqn. (22) to express the salt effect on the activity coefficient of CO_2 for various salts as calculated from the data obtained by Marham and Kobe (22). From the table, it shows that the order of the effect of cations is in the reverse order of ion size. Increasing the concentration of lithium salt increases the CO_2 activity coefficient more than sodium salt. This was discussed by Long and McDevit (21). The basic assumption is that the interactions which occur between acidic and basic nonelectrolytes and water molecule are greatly affected by the orientation of the water molecules in the hydration sphere of an ion. With cations the surrounding water molecules will be oriented with their protons outward and there will be a repulsion with an acidic nonelectrolytes. From this picture, one would expect for CO_2, which is an acidic nonelectrolyte, its activity will be increased in the reverse order of the molecular weights of the salts in solution, i.e. Li > Na > K.

From the discussion shown above, the effect of some salts on the activity coefficients of carbon dioxide and hydroxide, are shown in Tables (14), (15) and (16). However, it is still not possible to calculate the value of b in the equation:

the chemical reaction is the elimination or separation of diffusion effects from kinetic effects. The experimental methods used for measuring the kinetic constant of the reaction between carbon dioxide and hydroxide have followed two approaches. One approach is to determine the over-all reaction rate in a flow or batch process, and then correct this value for the effect of diffusion, such as manometric method. The other approach is to design the experiment so that the influence of diffusion is negligible, such as continuous flow method and isotope exchange method. Among these methods, the results obtained by Pinsent (26) using continuous flow method are the best and will be discussed first. The other methods will also be described and the results are compared with Pinsent's data.

1. Continuous flow method

The continuous flow method was devised by Hartridge and Roughton (15) for measuring the velocity of rapid chemical reactions. It can be applied to the studies of those reactions whose half periods range from 10 sec. or more, down to 0.001 sec. The principle of their method was that the two reacting solutions were mixed and then passed down an observation tube. At various cross sections of the tube the composition of the streaming fluid was determined by optical, thermal, electrical, chemical or other methods of analysis applicable to rapidly moving fluids. From the composition at each cross section and the corresponding reaction time, the velocity of the reaction could be followed. The main disadvantage of this method is

the need for large quantity of reagents.

(i) Thermometric, Pinsent (26)

In this work, thermocouples were used for measuring the extent of the reaction by measuring temperature rise of the mixed flowing fluid due to the evolution of the heat of reaction. Various salts were added to study the effect of ionic strength.

The results are shown in Table 2. They covered a temperature range from $0^{o}C$ to $40^{o}C$, Fig. (1), and studied the effects of NaCl, KCl, Na_2CO_3, $NaNO_3$ and Na_2SO_4 on the kinetic constant, Fig. 10. This work is so well established that the results have been used as a reference in many other kinetic studies using the thermal flow method (31).

(ii) Conductivity, Saal (36)

In this work, the replacement rate of hydroxide by carbonate was determined by measuring the conductivity changes. Pairs of platinum wires were sealed at intervals into the observation tube. The data obtained were used to calculate the velocities of the reaction. The results are shown in Table 3. The corrected value of kinetic constant at infinite dilution is plotted in Figure 1. It is in agreement with Pinsent's data.

(iii) Photo-electric, Brinkman (3)

The carbon dioxide was mixed in a rapid flow apparatus with NaOH solution. The pH changes were followed photo-electrically by use of 0.01 per cent tropaeolin as indicator.

This indicator, giving a suitable color change from yellow to red, was added in equal amounts to both reacting solutions. One solution would thus be yellow in color and the other red. The two solutions were allowed to mix in the mixing chamber and flowed down to the observation tube. The mixing chamber and observation tube were mounted in a vertical carriage, which could be moved up and down, so that various parts of the observation tube could be brought into the path of the beam of light illuminating the photoelectric cell. A calibration curve was obtained by running through the observation tube a series of buffer solutions of known pH, containing the same concentration of indicator. Then the pH of the moving mixed fluid at various points in the observation tube could be obtained. From the pH of the solution the values of (CO_2), (H_2CO_3) and (HCO_3^-) could be calculated. The results are shown in Table 4 and are plotted in Figure 1. The data obtained in this work are somehow much lower than the others.

2. Carbamino quenching method

The carbamino quenching method was used by Faurholt in 1924 (11). He established the rate laws for the reactions of carbon dioxide with hydroxide ion and carbon dioxide with water. The apparatus he used was very simple, containing only a flask and a separation funnel, yet he was able to obtain a result which compared favorably with other works. The principle of his method was that alkyl amines react extremely rapidly with unhydrated CO_2 to form carbamates:

$$CO_2 + 2\ R_2NH \longrightarrow (R_2NCO_2^-)(NH_2R_2^+) \quad (25)$$

Experimentally, carbon dioxide solution was mixed with a carbonate-bicarbonate buffer of known pH in a flask. The carbon dioxide reacted with hydroxyl ion to form bicarbonate ion. After the desired reaction time had elapsed, a large excess of 4-M amine was added. Unreacted CO_2 combined with the amine to form carbamates. $BaCl_2$ was then added to precipitate carbonate, from which the CO_2 which had not reacted with hydroxyl ion could be determined. When the solution was heated, carbamate gradually changed to carbonates and precipitated as the barium salts. The concentration of reacted CO_2 could thus be determined. The chief sources of error in the carbamino quenching method lay in the mixing which he accomplished merely by pouring the contents of one flask into another with shaking. The data are shown in Table 5 and are plotted in Fig. 2 to compare with Pinsent's data. Faurholt did not pay attention to the ionic strength effect. The data reported are not at zero ionic strength but rather at the experimental conditions shown in Table 5. Since there is no sufficient data to predict the relation between ionic strength and kinetic constant the points on Fig. 2 are not at infinite dilution.

3. Boat method or manometric method.

The boat method was first introduced by Brinkman, Margaria and Roughton (3) for studying the reaction of CO_2 and hydroxide. It is of a manometric type; the absorption of CO_2 from a gas

The results are shown in Table 8. They estimated that at $0^{o}C$, the reaction constant should be corrected by 5-7%, but at $10^{o}C$, the corrected constant is not accurate to better than $\pm$ 15% and they concluded that the manometric method is not suitable for studying rapid reactions at higher temperatures.

Meda (26) followed Pinsent's method but used veronal buffer at pH 8.6 to 8.7 instead of pH 10. The reaction velocity was reduced by a factor of ten. Thus he was able to measure the reaction constant at higher temperature. The results agree satisfactorily with those obtained by the thermal flow method. They are shown in Table 9 and Fig. 3.

4. Stopped flow method

The major disadvantage of the continuous flow method is the large expenditure of reagents. The stopped flow method was introduced by Roughton (32). This method has recently been very widely used in biochemical studies owing to the strict economy with reagents. The basic idea of this method is that the two reacting solutions are mixed together just before they enter a cell which has observation ports or other sensors. Flow is then mechanically stopped and measurements may be made with a minimum of turbulence. The transient of the current or voltage of the detector system as a function of time is recorded for analysis. The apparatus is now available commercially. Measurement techniques include absorption spectroscopy in visible or near ultraviolet regions, calorimetry, pH, polarography, electron paramagnetic resonance. The details can be found in Schechter's paper (38).

Sirs (39) applied the stopped flow method to study the reaction $CO_2 + OH^- \longrightarrow HCO_3^-$. The two reacting solutions were fed from two stainless steel vessels, via three-way taps, to two glass syringes. The taps were then orientated so that when the two syringes were driven up together by a sliding platform, the reactants were driven into the mixing chamber and observation tube. The mixing chamber was based on a system of symmetrical tangential jets, which fed into an observation tube. The measurement was done by two screwed, stainless steel electrodes located in the observation tube on either side of the tube at a certain distance from the mixing chamber. The measured conductivity change was used to calculate the extent of the reaction. In another setup, he used Tropaeolin O to follow the hydrogen ion change optically as Saal (36) did.

The results obtained for both the conductivity and photoelectric technique were significantly lower than the values obtained thermally. He then traced the discrepancy to the dissolved gas in the solution. He found formation of CO_2 gas bubbles during turbulent flow. The pressure changes and turbulence of the mixing and flow of solutions gave rise to small gas bubbles via minute gas nuclei. These bubbles caused a decrease in conductivity and light absorption. He then made a new set of observations using only one quarter or less saturated CO_2 as the reagent solution. The data are shown in Table 10 and the corrected value at infinite dilution are plotted in Fig. 4. They are in excellent agreement with those

obtained by the thermal flow method.

5. Laminar jets absorption

In his study of the kinetics of the absorption of CO_2 by caustic solutions, Nijsing (24) measured the kinetic constant for high OH^- concentrations. His theoretical approach involved the assumption that at sufficiently high $(OH^-)/(CO_2)$ ratios and sufficiently small contact times between gas and liquid, the reaction taking place in the liquid between CO_2 and OH^- may be regarded as a pseudo first-order reaction. The kinetic constant of $CO_2 + OH^- \longrightarrow HCO_3^-$ can be obtained from measurements of the total absorption rate of CO_2 as a function of jet length.

Experimentally, the rate of absorption was obtained from the rate of decrease of the gas volume in the absorber at constant temperature and pressure. This was obtained by measuring the velocity of displacement of a soap film in a calibrated tube. A linear relation between the rate of absorption and the jet length was observed:

$$\phi m = \pi d c^* \sqrt{D K (OH^-)} \ \ell \qquad (26)$$

where

ϕm: the rate of absorption, in mass per unit time

d: the diameter of the jet,

c*: the equilibrium concentration of CO_2 at the gas-liquid interface, in mass per unit volume.

D: the diffusivity of CO_2 in the liquid phase.

K: the kinetic constant

ℓ: the jet length

When ϕm is plotted against ℓ, a straight line is obtained,

$$\text{slope} = \pi\, d\, c^* \sqrt{D\, K\, (OH^-)} \qquad (27)$$

c* was calculated using the formula:

$$\log \frac{c^*}{c^*_w} = - k_s\, I \qquad (28)$$

where: c^*_w: the solubility of the CO_2 in water

I: ionic strength

k_s: constant depending on the type of the solution

D was estimated by correcting for the viscosity of the solution according to the equation:

$$D\mu^{0.85} = \text{constant, at constant temperature} \qquad (29)$$

K can be calculated by using Eqn. (27). The results obtained together with the estimated c* and D are shown in Table 11. The kinetic constant data in KOH, NaOH and LiOH solutions are plotted against ionic strength in Fig. (9). It shows that KOH has more effect on the kinetic constant than NaOH and NaOH than LiOH. The value at zero ionic strength obtained is lower than Pinsent's datum. (see Fig.5).

The results of this method are believed to be less accurate than the results of the other methods because it is impossible to measure c* and D. Those two values were obtained merely by estimation. This work is valuable in that he determined the influences of ionic strength and types of ions on K.

6. Isotope Exchange Method:

The isotope exchange method provides an advantage in avoiding the correction for mass transfer effects experienced in the manometric methods.

(i) Radioactive CO_2:

1. Radioactive CO_2 was used to determine the kinetic reaction rate constants by Himmelblau and Babb (16). The essence of the procedure is to operate the CO_2-$NaHCO_3$-Na_2CO_3-H_2O system at chemical equilibrium but at isotopic disequilibrium. With samples taken from a closed vessel at periodic intervals after initially injecting tracer in the form of $NaHC^*O_3$, it is possible to follow the rates of reaction by analysis of the percentage of tracer in the solution in the form of $C^{14}O_2$. They measured the rates of these two reactions

$$H^+ + HC^*O_3^- \rightleftharpoons H_2O + \overset{*}{C}O_2 \qquad (30)$$

$$\overset{*}{HCO_3^-} \rightleftharpoons OH^- + \overset{*}{C}O_2 \qquad (31)$$

Then, by varying the $(CO_2)/(HCO_3^-)$ ratio in the solutions, they were able to separate the effect of reaction (30) from the supposed effect of reaction (31).

The results shown in Table 1 obtained by this method are about 50-130 times as fast (depending on the temperature) as other reported values. The discrepancy is too large to be explained by ionic strength or specific ion effects. Danckwerts and Melkersson (8) treated the thermodynamic coefficients differently and obtained a set of corrected values shown in

Table 1. The results still show a large discrepancy when compared with other values. Another reaction path was suggested to explain the results (8).

$$\overbrace{CO_2 \cdot OH^- \rightleftharpoons \overset{*}{H}CO_3^-}^{A}$$

$$B \left\{ \begin{array}{l} CO_2 \cdot OH^- \\ + CO_2 \\ \overset{*}{CO}_2 + \\ \\ CO_2 \cdot OH^- \rightleftharpoons HCO_3^- \end{array} \right. \qquad (32)$$

A species written as $\overset{*}{CO}_2 \cdot OH^-$ was assumed to exist and it was assumed that this species can react with CO_2 with the exchange of the OH^- group (reaction B) and that this process is much faster than reaction A. This reaction path would only be observable by the isotopic labelling technique.

2. Goodridge and Taylor (13) also used the radioactive tracer method for investigating the mechanism of gas absorption. It was done by introducing a small amount of radioactive solute gas into the system. The use of small amounts of solute gas has an advantage over the use of large amounts of solute gas used by other methods. The concentration of absorbent molecules even at high dilutions remains sensibly constant this way. Experimentally, the rate of absorption was measured continuously by circulating the gas phase containing the radioactive solute $C^{14}O_2$ through a scintillation head where $C^{14}O_2$ could be counted. Under the experimental conditions, the concentration of hydroxyl

ions remained constant and the reaction of CO_2 and OH^- became pseudo first-order. The kinetic constant was obtained by neglecting the ionic strength effect. It is impossible to apply this method for the study of the effect of ionic strength. The value obtained at infinite diluted are plotted in Fig. 6, it agrees with Pinsent's line.

(ii) Oxygen - 18:

Poulton and Baldwin (27) used the O^{18} exchange method. The reaction kinetics were studied by dissolving sodium carbonate and bicarbonate in a weighed amount of oxygen-18 enriched water. At various intervals aliquots of the solution were taken for isotopic analysis of the carbonate-bicarbonate. The results are shown in Table 12. It was found that the kinetic constant decreased with increasing ionic strength. This phenomenon can not be explained. Their datum at the lowest ionic strength measured, however, was in agreement with other reports (Fig.6).

7. Steady State Method:

Koefoed and Engel (19) studied the reaction between CO_2 and OH^- under conditions of enforced stationarity. To perform the measurement, a solution of sodium carbonate is kept saturated with carbon dioxide. When the pH of the solution has attained its equilibrium value, strong acid or base is supplied at a constant rate. After a few minutes the pH is again stationary. The dependence of the change of pH on the rate of strong acid or base addition is

analysed according to the over-all reaction mechanism. It is quite complicated and will not be shown here. The results are shown in Table 13. The value shown in Fig. 7 was obtained at ionic strength = 0.75. There is insufficient data to obtain the reaction constant at zero buffer concentration. However, the estimated value, using the value of log K/I = 0.26, is higher than the other values shown. The discrepancy might be caused by the high CO_2 pressure used. Also, the changes in bicarbonate ion concentration, due to the addition of the strong acid or base used, may have been higher than they had assumed.

IV. INTERPRETATION OF THE EXPERIMENTAL DATA

1. The effect of temperature on the kinetic constant of the reaction $CO_2 + OH^- \longrightarrow HCO_3^-$

The data reported for the kinetic constant at zero ionic strength are plotted against the inverse of the temperature in Fig. 8. The straight line shown was suggested by Pinsent (26). It can be written as:

$$\log K_o = 13.635 - \frac{2895}{T} \qquad (33)$$

The energy of activation was calculated:

$$E_a = 13{,}250 \text{ cal}$$

The results obtained by using other methods are in excellent agreement with this line except for those data obtained by Brinkman, et al (3) and Himmelblau (16).

2. The effect of ionic strength on the kinetic constant of the reaction $CO_2 + OH^- \longrightarrow HCO_3^-$

(1) Unbuffered solutions

The effect of ionic strength on the kinetic constant is expressed as:

$$\log K_I = \log K_o + bI \qquad (24)$$

where K_I and K_o are the kinetic constant in salt solutions and infinite dilution respectively. If $\log K_I$ is plotted against I, a straight should be obtained with a slope equal to b.

The data obtained by Nijsing (24) in KOH, NaOH and LiOH solutions as shown in Table 11 and Fig. 9 coincide with this approach. However, the data obtained by Pinsent (26) as shown in Fig. 10 do not coincide with eq. (24).

In order to investigate alternate methods of correlation, the data of Pinsent and of Nijsing were corrected to a common temperature, 25°C assuming the temperature effect to be the same as that shown in Fig. 8 for dilute solutions. It was found that the data could be brought closer together by plotting K_I v. s. the product of the ionic strength and the mean activity coefficient of the salt as shown in Figures 11 and 12. The activity coefficients of these salts are given in Table 17. From Fig. 11 and Fig. 12, we can conclude that for the reaction between carbon dioxide and hydroxyl ion in salt solutions, a plot of log K_I against I x f for the salts with a common cation will lie on a single curve and the corresponding plot for the salts with a common anion will result in a family of curves. The latter curves fall in the same order as the order of the sizes of the respective cations, i.e. K > Na > Li. According to the "localized hydrolysis" described previously, this is the same order as the influence of the cations on the activity coefficients of the hydroxyl ion.

Fig. 13 and Fig. 14 are the plots of log K_I against I x f x a. Where a is the radius of the respective cation as tabulated below*.

* From V. M. Goldshmidt, Chem. Ber, 60, 1263 (1927).

ion	K^+	Na^+	Li^+
Radius, Ångstrom	1.33	0.98	0.78

This method appears to bring the date into a single curve which should be useful for prediction of ionic strength effects. Further study of this method on additional system may be desirable.

(2) Buffer solutions:

In bicarbonate-carbonate mixtures, the salt effects on the rate of the reaction between CO_2 and OH^- are more complicated. The concentration of hydroxide depends on the ratio of carbonate and bicarbonate:

$$(OH^-) = \frac{K_w}{K_a} \frac{(CO_3^=)}{(HCO_3^-)} \qquad (9)$$

where

$$K_w = a_{H^+} \; a_{OH^-} \qquad (11)$$

$$K_a = \frac{a_{H^+} \; a_{CO_3^=}}{a_{HCO_3^-}} \qquad (10)$$

Ka and K_w vary markedly with the ionic strength and composition of the solution. Fig. 15 shows the value of K_w/K_a as a function of ionic strength in KCl and NaCl solutions. Roberts (29) combined the values of Kw/Ka with the value of K_I at 20°C given by Pinsent (26) in KCl and NaCl solutions as shown in Figure 16. The two straight lines on Figure 16 are the values

reported by Nijsing (24) in CO_3/HCO_3 buffers of ionic strengths 1.2-2.1 g ion/l. It shows that the rate in potassium solution is higher.

There do not appear to be sufficient data available to permit a general correlation for the prediction of K_I in buffered solutions. The curves of Figures 15 and 16 suggest that the introduction of activity coefficients as in the case of the non-buffered solution may be worthy of future study.

V. EXPERIMENTAL STUDIES ON THE THERMAL FLOW METHOD

1. Theory

The continuous flow method devised by Hartridge and Roughton in 1924 (14) was used for many studies of rapid reactions in the liquid phase. A review of this method was written in detail by Roughton (35). The principle of the method was that two reagent solutions were placed in separate containers and driven thence continuously into a special mixing chamber where they were rapidly mixed. The emerging mixed fluid passed down an observation tube of uniform bore, at various cross sections of which the composition of the streaming fluid was determined by optical, thermal, electrical, chemical or other methods of analysis applicable to the rapidly moving fluids. Those properties indicated the progress of the reaction. Since only the optical and thermal measurements are useful for a general purpose apparatus where the reagent solutions contain a buffer or other foreign electrolyte, thermal flow method was chosen for the purpose of our studies.

If d is the distance in cm between the mixing chamber and the cross section under examination, and $\bar{u}$ is the average linear velocity in cm per second of the streaming fluid, then the average time for which the reaction has proceeded before reaching the place of observation is simply $d/\bar{u}$ seconds. The value of $\bar{u}$ is given by $\bar{V}/A$, where $\bar{V}$ is the average volume velocity of the streaming fluid as

measured in cm^3/sec and A is the cross-sectional area of the observation tube. From observations at several cross sections the usual type of concentration-time curve could readily be plotted.

The reaction under study was:

$$CO_2 + OH^- \longrightarrow HCO_3^- \qquad (1)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^= + H_2O \qquad (2)$$

At excess concentrations of OH^-, if we assume that all the bicarbonate is transformed to carbonate.

In reactions (1) and (2), there is an evolution of an appreciable amount of heat. If the total heat evoluted is known, the corresponding temperature changes can accordingly be used to follow quantitatively the progress of the reaction. Thermistors were inserted into the observation tube in order to determine the temperature of the streaming fluid at various distances from the mixing chamber.

2. Apparatus

The main elements of the apparatus are shown in Fig. (17). It consisted of two feed tanks, rotameters, pumps, mixing chamber, observation tube and temperature measuring device.

(a) Reagent containers:

The reagent containers are made of two stainless steel tanks of capacity 35 liters. They are capable of standing up to 4 atmospheres pressure. The temperature of the reagent is maintained by the constant temperature water coil which goes

into each tank. The solutions are continually stirred with motor-driven stirrer. The constant temperature water bath is controlled to $\pm$ 0.05°C. The temperature of the reagent in the tank is then controlled to $\pm$ 0.002°C.

(b) Mixing chamber and observation tube

Two types of mixing chambers have been constructed and tested. One is simply a 1/4 inch stainless steel tee. The two reacting fluids come in from two stems and the other stem connected to a 1/4 in O. D., 0.196 in I.D., stainless steel tubing used as the observation tube. At 0.7 GPM from each tank, mixing was only 75% complete at the last measuring point which was corresponding to 7.5 msec after mixing. The half time of the reaction under study is from 1 msec to 2 msec, this mixing chamber is not suitable for the purpose.

The other mixer is constructed of plexiglas. The general construction is shown in Fig.(18), in which a mixing chamber with 14 jets is illustrated. The jets and the observation tube are drilled out from 1 in. diameter solid plexiglas cylinder. The jets are 1 mm in diameter and are constructed in a way that they deliver the fluids tangentially rather than radially and thus impart a rotary motion to the fluid in the mixer. The fluid from one of the feed tanks flowed into a ring which had seven inlets going into every other one of the fourteen jets, the other fluid flowed into the remaining seven jets. Thus the two reagents were mixed in the mixing chamber of 0.05 cm^3 in volume and then flowed

down to an observation tube of uniform bore 5 mm in diameter and 8 cm in length. The end of the tube was connected to a control valve which maintained a back pressure to prevent the bubble formation from the flowing fluid. The valve was connected to $\frac{1}{2}$ O. D. nylon tube which went down to the drain. The mixing chamber and the observation tube were immersed in an oil bath. The temperature of the bath was controlled to $\pm$ 0.005°C by a YSI Model 72 proportional controller.

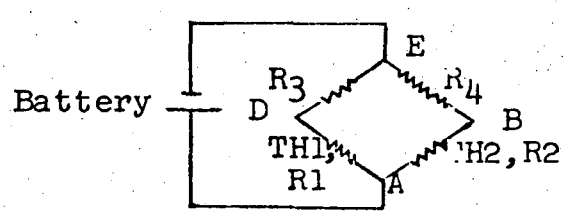
(c) Temperature measuring device

The differential measurements of the temperature of the reacting solution were made by employing thermistors. A thermistor is in essence a piece of semiconductor material attached to two electrical leads. The chief characteristic of semiconductors is their large negative coefficient of resistance change with temperature. A review of theory and applications of thermistors was written by Boucher (5). So far as we know, the thermistors have not been used for the purpose of studying the reaction of carbon dioxide and hydroxide. Giladi et al, (17) applied the thermistors to the measurement of temperature for some reactions having half period of 0.05 second. The measuring devices necessary for satisfactory performance are much simpler in using thermistors than using thermocouples in some cases.

The thermistors used in our study were YSI Precision Thermistor Probe Part 44105 which had a resistance of 3 KΩ at 25°C, sensitivity of 100Ω/°C at 30°C. The

reference thermistor were located at the inlet of KOH solution and the other eight thermistors were located at the other inlet of the mixing chamber, the center of the mixing chamber and at some different places along the observation tube. Each lead from the thermistor was inserted in a 1/8 inch stainless steel tube which was then sealed with epoxy resin cement. Swagelok fittings were used to insert the thermistors to the wall of the observation tube. The output from the thermistors was recorded using a recorder designed by meter shop, LRL. It can measure the temperature differences to thousandths of one degree Centigrade. The circuit diagram is shown in Fig. (18).

The basic idea for the design of this meter is that the resistance of a thermistor is a function of the ambient temperature and the variation of resistance can be measured very accurately by Wheatstone's bridge with an amplifier. An idealized Wheatstone's bridge is shown as follows:



In the figure, R3 = R4, TH1 and TH2 are two identical thermistors with resistances R1 and R2 respectively. If the ambient temperature of TH1 and TH2 are the same, then R1 = R2 and the potential difference between point D and point B is zero. On the other hand, if there is a slight

temperature difference between TH1 and TH2, then R1 $\neq$ R2 and there will be a small potential difference V_{DB} between the points D and B. Although V_{DB} is small when the temperature difference is small, V_{DB} can be amplified by an electrical amplifier and then fed into an indicator for clear reading. There are nine thermistors totally, the temperature of the eight thermistors will be compared to the same reference temperature TH1.

All the connecting lines in the system were $\frac{1}{2}$ O. D. Nylon tubing and the flow rate was measured by Brooks Model 1112A size A, full view rotameter with 1.4 GPM max.

3. Experimental procedure

(a) Thermistor response time measurement

Time constant of each thermistor was measured as follows: One beaker was maintained at 30°C and the other at 30.1°C. At first, both reference and the thermistor under investigation were put in the 30°C beaker. When the differential reading was stable, the thermistor was taken out and immersed immediately into the other beaker at 30.1°C. The temperature reading was recorded continuously and a curve of differential temperature versus time was obtained. The time constant was calculated using the following equation from Ref. (36):

$$\frac{Tt}{T_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-Kn^2\pi^2 t/r^2} \qquad (7)$$

where Tt is the temperature reading at time t, T_∞ is the final temperature reading and $K = \frac{k}{\rho c_p}$. k is the time constant

of the thermistor, ρ the density of the teflon covering the thermistor tip, and c_p the heat capacity of the teflon.r is the thickness of the teflon.

From the data, K can be calculated and by the relation $K = k/\rho c_p$, k is obtained for each thermistor. The time constant reported by the manufacturer for this type of thermistor is 2.5 sec. The measured time constants were from 2.4 to 6 sec. Thermistors were then inserted along the observation tube in the order of increasing time constants.

(b) Mixing test

The mixing efficiency of the mixing chamber was tested by mixing potassium hydroxide with hydrochloric acid. The reaction is an instantanuous reaction and should complete at the same time when they are mixed. The heat of neutralization at 30°C is -13,360 cal/mole (26). When 0.01282M HCl was mixed with 0.01755M KOH total temperature rise should be 0.166°C, the temperature rise measured was 0.165°C along the observation tube and 0.148°C in the mixing chamber. The mixing efficiency was thus concluded about 90% in mixing chamber and 100% complete before reaching the first measuring point along the tube at the velocity tested.

(c) Thermistor response test

When 0.04226M KOH was mixed with 0.01454M HCl, concentrated HCl was injected into the observation tube at the point before the measuring thermistor and after the mixing chamber at the rate of 0.08 ml/sec. The calculated temperature rise due to

the injection of conc. HCl was 0.0577°C and the value measured was 0.049°C. The response of the thermistor was fairly satisfactory.

(d) Experimental procedure

(i) Before each run, thermistors were calibrated with blank experiment. Distilled water was charged into both tanks, allowed to attain temperature equilibrium with constant temperature water bath, pumped through the observation tube at the desired flow rate, recorded each reading.

(ii) The carbon dioxide solution was prepared by bubbling carbon dioxide at different pressures according to the desired concentrations into distilled water contained in one of the feed tank.

(iii) The potassium hydroxide solution of the desired concentration, determined by titration to the neutral point with hydrochloric acid, was charged to another tank.

(iv) After temperature equilibrium was attained, the tanks were pressurized by nitrogen. Then both solutions were pumped to the mixing chamber. Steady differential temperature readings from the reference thermistor and all the other thermistors were attained on the recorder.

(v) The extent of the reaction was calculated from the heat of reaction and the measured temperature rise at each point.

(vi) Total concentration of $CO_3^{=}$ and OH^- in runnings were determined by titration with HCl.

(e) Example of calculation of data

Partial pressure in CO_2 feed tank: $P_{CO_2} = 3.94$ psi

Concentration of CO_2 dissolved in water calculated from Henry's law:

$$X_{CO_2} = \frac{P_{CO_2}}{H}$$

Where X_{CO_2} is the mole fraction of CO_2 in the liquid phase

PCO_2 is the partial pressure in atm in gas phase

H is Henry's constant, at 30°C is 1.86×10^3 for CO_2. (Perry's Handbook 14-4)

$$(CO_2) = 0.008M$$

therefore the concentration of CO_2 at reactin nozzle:

$$(CO_2)_{t=0} = 0.004M$$

The initial concentration of potassium hydroxide:

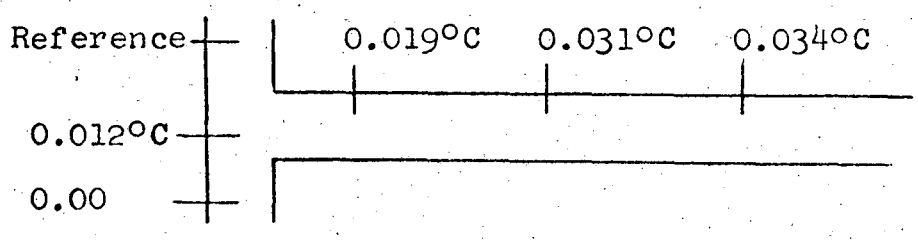
$$(OH^-)_{t=0} = 0.01045 \text{ M}$$

The concentrations of both reagent were checked by titrating the running:

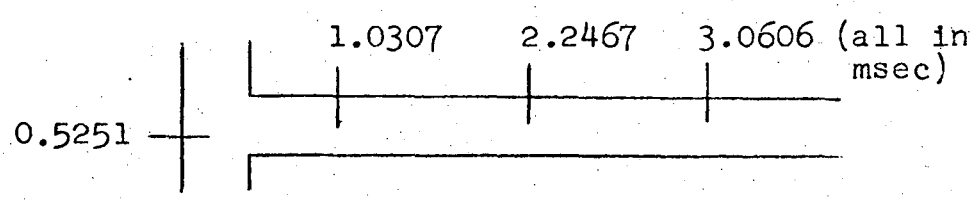
$$a = (CO_2)_{t=0} = 0.004465 \text{ M}$$

$$b = (OH^-)_{t=0} = 0.01099 \text{ M}$$

The data obtained after calibrated with blank are shown in the following according to their position along the observation tube:



The time elapsed when the reacting solution reached each thermistor was calculated from the flow rate measured by flowmeter:



The concentration of $CO_3^{=}$ at each cross section was calculated from the corresponding temperature change by

$$\Delta T = \frac{\Delta H\, y}{\rho C_p \times 10^3}$$

where ρ is the density and C_p the specific heat of the solution

$$\Delta H = 21{,}200 \text{ cal} \qquad (26)$$

t, msec	y	$\log \frac{b-2y}{a-y}$
0	0.	0.39100
0.5251	0.0005714	0.40300
1.0307	0.0009048	0.41100
2.2476	0.0014762	0.42900
3.0606	0.0016190	0.43500

After applying the least squares method, a straight line of $\log \frac{b-2y}{a-y}$ versus t was drawn and the slope was determined. It is shown in Fig. (20). The slope was 0.0141 $msec^{-1}$ in this case, from eqn. (8):

$$\text{slope} = \frac{b-2a}{2.303} K$$

$$K = \text{slope} \times \frac{2.303}{b-2a}$$

$$= 0.0141 \times \frac{2.303}{0.01099 - 0.004465 \times 2} \times 10^3$$

$$= 15{,}800 \quad (\ell/\text{g mole, sec.})$$

4. Results

A series of experiments have been done by varying hydroxide concentrations. The results are shown in the following:

T=30°C	Run	(OH^-)mole/ℓ	(CO_2),mole/ℓ	I,mole/e	K_I ℓ/g mole, sec.
	1	0.01099	0.004465	0.011	15,800
	2	0.01269	0.003960	0.013	18,600
	3	0.01556	0.003300	0.016	21,000
	4	0.01782	0.005110	0.0178	17,800
	5	0.01802	0.004437	0.018	24,700
	6	0.01807	0.004953	0.018	18,800
	7	0.01957	0.005197	0.0196	14,000
	8	0.04182	0.004760	0.042	9,930
				(KCl)	I K_I
	9	0.01325	0.002960	0.008	0.0214 20,100
	10	0.01046	0.003490	0.0336	0.0441 16,600

The data obtained had a large discrepancy, for the concentration of potassium hydroxide ranging from 0.01M to 0.02M, the kinetic constants obtained were ranging from 14,000 to 24,700. For the four runs, Run 4, 5, 6, 7, the concentration of OH^- was about the same but the values of K varied from run to run. The effect of ionic strength was tested by adding potassium chloride at the same concentration to both carbon dioxide and hydroxide solutions. The results shown in Run 9 and Run 10 indicated that the discrepancy was too large to be accounted for the effect of ionic strength. The heat of dilution of KOH solution has been measured and the effect was found to be small. Taking the data of first seven runs, the kinetic constant at zero ionic strength was obtained by extrapolating the straight line of log K_I versus I to I = 0. The K_o obtained was 16,920 compared to 12,400 at 30°C reported by Pinsent (26).

5. Dissusion

The use of the present apparatus for the purpose of measuring the kinetic constant of the reaction of carbon dioxide and potassium hydroxide has been found to be unsatisfactory. The data obtained varied from run to run. The major sources of the error are discussed in the following:

(a) The measurement error of the device

The accuracy of the amplifier and the recorder used are 0.25% of full scale, which from -0.05°C to +0.05°C is 100 μV. Taking a conservative estimate of the repeatability as ± 1.0%, then the maximum error was ± 1 μV corresponding to ± 0.001°C.

The thermistors used had different temperature sensitivities ($\Delta\Omega/\Delta T$) when nulled at 30°C, the differential varied from 0.0 to 0.01°C between 29°C and 31°C. The maximum actural temperature change measured in the flow apparatus was 0.1°C. Therefore, the calculated maximum error from differing sensitivities was 0.0005°C.

Total maximum error from electronic and thermistor sensitivity difference was 0.0015°C corresponding to 4-10% of anticipated readings (0.02°C to 0.08°C).

(b) Error due to power dissipation in the thermistor

The electric power dissipated in the thermistor caused it to assume a steady state temperature Δt above that of the adjacent fluid. The following calculations are based on the discussion in Baker's book (1). In the present device, the current flowing through the thermistor was 25.1 mA, the resistance of the thermistor was 2.417 KΩ at 30°C and 2.407 KΩ at 30.1°C. The electric-power dissipation in the thermistor was

$$W_e = I^2R = 1.55\times10^{-6} \text{ watts} \qquad (1)$$

The error Δt due to power dissipation was expressed by:

$$\Delta t = q_e / UA \quad \text{in } ^\circ F \qquad (2)$$

where q_e/A was the electric-power dissipation in the sensitive element per unit of outer-surface area, BTU/hr, ft^2. $q_e = W_e/J$ and J = 0.293 W hr/BTU. U was the thermal boundary conductance referred to the outer-surface area, BTU/hr ft^2 °F and was calculated from:

$$U = 1/\ (1/U_i + 1/U_w + 1/U_o\ ) \qquad (3)$$

where U_i was the boundary conductance, referred to the outer-surface area, from the sensitive element to the inner surface of the casing, in this case, the air film between the thermistor tip and the teflon covering, BTU/hr ft^2 ^oF.

U_w was the boundary conductance, referred to the out-surface area, of the casing wall which was teflon in this case, BTU/hr ft^2 ^oF.

U_o was the boundary conductance over the outer-surface area to those portions of the parent-body material sufficient distant to be undisturbed in temperature by the presence of the sensitive element, BTU/hr ft^2 ^oF.

After proper values were substitute into eqns. (2) and (3), the maximum error Δt was calculated and the value was 0.003^oC.

(c) Error due to friction

The thermistors were first calibrated by immersing them in a beaker which was filled with oil, the beaker was immersed in an oil bath. The temperature of the oil bath was controlled to 30$\pm$0.005^oC and the temperature of the oil in the beaker was controlled to 30 $\pm$ 0.001^oC. The differential readings of the thermistors were calibrated to zero referring to the reference thermistor. When the thermistors were inserted into the observation tube in the way described before and the distilled water at 30^oC was pumped through, the differential readings of the thermistors changed from zero

to positive readings ranging from 0.02 to 0.04°C. The change was believed to be caused by the pressure drop in the observation tube. The pressure drop between the inlet of the mixing chamber and the downstream of the tube was 15 psi at the flow rate used. If the pressure drop occurred between the reference thermistor and the measuring thermistor, the calculated temperature rise due to friction was 0.025°C.

The thermistors were therefore calibrated again with constant temperature water flowing through. Since the calibration and actual experiment were carried out in two separate runs, the experimental conditions might have changed. Experimentally, the stability of two blank experiments was ± 0.001°C.

(d) Error due to the bubble formation

The carbon dioxide solution was prepared by bubbling CO_2 and N_2 gas mixture into distilled water at about 27 psi. The back pressure maintained at the downstream of the observation tube was 24.7 psi. The temperature drop due to the bubble formation was calculated and the value was 0.002°C. Experimentally, no bubble formation was observed.

One other source of error might come from lead conductance, however because of lack of some information on the surface conditions of the leads, a significant value can not be obtained.

Among the errors discussed above, some would cause a positive error on the differential reading and some would cause a negative reading, they might cancel out one another.

The measure errors discussed above are summarized in the following table:

Sources of error	Δ Te (measure error)
(a) Amplifier and recorder	$\pm$ 0.0015°C
(b) Thermistors	
1. Self heating due to power dissipation	$\pm$ 0.0030°C
2. Differing sensitivities for total differential reading 0.1°C	$\pm$ 0.0005°C
3. Zero tolerance	$\pm$ 0.0020°C
$\Sigma \Delta$ Te =	$\pm$ 0.0060°C

In the experiment given as an example for the calculation of data, for the measuring range of 0.012°C to 0.04°C, the measure error of 0.006°C corresponds to 50 to 15% error. For the anticipated reading in most experiments (0.02°C to 0.08°C), a maximum measure error of 0.006°C corresponds to an error of 30 to 8%. For our purpose of studying the salt effect on the kinetic constant of the reaction of carbon dioxide and potassium hydroxide, the error that can be tolerated can not be more than $\pm$ 0.002°C, the measuring device is concluded to be unsatisfactory.

Before further research is done, the data obtained by Pinsent (26) as shown in Fig. 8 can be used for estimating the value of kinetic constant at infinite dilution between 0°C and 40°C. Figs. 13 and 14 can be used for estimating the effect of the salts not measured.

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VII. REFERENCES

1. Baker, H. D., Ryder, E. A. and Baker, N. H., "Temperature measurement in engineering", Copyright 1961 by John Wiley & Sons, Inc., Vol. 2.
2. Bjerrum, N., Z. Physik. Chem., 108, 82 (1924).
3. Brinkman, R., Margaria, R. and Roughton, F. J. W., Phil. Trans. Roy., A232, 65 (1933).
4. Brønsted, J. N., Z. Physik. Chem., 102, 169 (1922)
5. Boucher, E. A., J. of Chem. Edu., 44, No. 11, A935 (1967).
6. Christiansen, J. A., Z. Physik. Chem., 113, 35 (1924)
7. Crank, J., in "Mathematics of Diffusion", p. 86 (1956), Oxford University Press.
8. Danckwerts, P. V. and Helkersson, K. A., Tran. Far. Soc., 58, 1832 (1962).
9. Davies, C. W. J. Chem. Soc., 448, 2093 (1938)
10. Debye, P. and McAuley, J., Physik. Z., 26, 22 (1925).
11. Faurholt, C., J. Chim. Phy., 21, 400 (1925).
12. Giladi, E., Lifshitz, A. and Perlmutter-Hayman, B., Bull. Res Counc. of Israel, Vol. A8, 75 (1959).
13. Goodridge, F. and Taylor, M. D., Trans. Far. Soc., 59, 2868 (1963).
14. Harned, H. S., J. Am. Chem. Soc., 47, 684 (1925); Harned and Swindells, ibid, 48, 126 (1926).
15. Hartridge, H. and Roughton, F. J. W., Proc. Roy. Soc., A104, 376 (1923).

16. Himmelblau, D. M. and Babb, A. L., A. I. Ch. E. J., 4, 143 (1958).

17. Hückel, Physik. Z., 26, 93 (1925).

18. Kern, D. M., J. Chem. Edu., 37, No. 1, 14 (1960).

19. Kiese, M. and Hastings, A. B., J. Biol. Chem., 132, 267 (1940).

20. Koefoed, J. and Engel, K., Acta. Chem. Scand., 15, No. 6, 1319 (1961).

21. Long, F. A. and McDevit, W. F., Chem. Rev., 51, 119 (1952).

22. Markham, A. E. and Kobe, K. A., J. Am. Chem. Soc., 63, 449 (1941).

23. Näsänen, R., Acta. Chim. Fenn., B19, 90 (1946).

24. Nijsing, R. A. T. O., Hendriksz, R. H. and Kramers, H., Chem. Eng. Sci., 10, 88 (1959).

25. Pinsent, B. R. W. and Roughton, F. J. W., Trans. Far. Soc., 47, 263 (1951).

26. Pinsent, B. R. W., Pearson, L. and Roughton, F. J. W., Trans. Faraday Society, 52, 1512 (1956).

27. Poulton, D. J. and Baldwin, H. W., Canadian J. Chem., 45, 1045 (1967).

28. Righellato, E. C. and Davies; C. W. Trans. Faraday. Soc., 26, 592 (1930).

29. Roberts, D. and Danckwerts, P. V., Chem. Eng. Sci., 17, 961 (1962).

30. Robinson, R. A. and Harned, H. S., Chem. Rev., 28, 419 (1928).

31. Robinson, R. A. and Stokes, R. H., "Electrolyte Solutions", Academic Press Ins., New York, 1955, Appendix 8. 10.

32. Roughton, F. J. W., Proc. Roy. Soc., B115, 473 (1934).

33. Roughton, F. J. W. and Booth, V. H., Biochem. J., 32, 2094 (1938).

34. Roughton, F. J. W., J. Biol. Chem., 141, 129 (1941).

35. Roughton, F. J. W., in Weissberger, A., "Technique of organic chemistry", Vol. 8, Chapter 14, Interscience Publishers Inc., N. Y., (1953).

36. Saal. R. N. J., Rec. Trav., 47, 73, 264 (1928).

37. Scatchard, G., Chem. Revs., 10, 229 (1932).

38. Schechter, A. N., Science, 170, 273 (1970).

39. Sirs, J. A., Trans. Far. Soc., 54, 201 (1958).

40. Srivastava, R. D., Mcmillan, A. F. and Harris, I. J., Candian J. Chem. Eng., 46, 181 (1968).

Table 1. Values reported for rate constant of the reaction $CO_2 + OH^- \xrightarrow{K} HCO_3^-$

	$K_o \times 10^{-3}$ (ℓ/g mole, sec.)				
	0°C	10°C	20°C	25°C	30°C
1. Continuous Flow Method					
Thermometric, Pinsent (26)	1.095	2.55	5.9		12.4
Conductivity, Saal (36)		2.733			
Photoelectric, Brinkman (3)		1.28	2.75		
2. Carbamino Quenching Method					
Manometric, Faurholt (11)	0.93*		4.675*		
3. Boat Method					
Manometric, Brinkman (3)	0.84*		2.1*		
Manometric, Kiese (19)	1.19				
Manometric, Pinsent (25)	1.05*	2.3*			
Manometric, Meda (26)			5.5	8.5	11.6
4. Stopped Flow Method					
Photoelectric, Sirs (39)	0.536*	3.05*	5.27*	8.5*	13.0*
Conductometric, Sirs (39)	0.993*	2.60*	5.00*		
5. Laminar Jets Absorption					
Volumetric, Nijsing (24)			4.7	6.7	
6. Isotope Exchange Method					
Radioactive CO_2, Himmelblau (3)	144	241	277		
Corrected, Danckwerts (8)	79	154	171		
Radioactive CO_2, Goodrige (13)				8.1	
Oxygen-18, Poulton (29)				8.4*	
7. Steady State Method					
pH measurement, Koeffoed (20)	5.5				

*: The data shown are not at zero buffer solution but at low ionic strength.

Table 2 Pinsent, Pearson and Roughton (26)

Temp. °C	K_o (ℓ/g mole, sec.)
0	1,095
10	2,550
20	5,900
30	12,400
40	24,000

Temp. = 20°C

(KCl)	(KOH)	I (g mole/ℓ)	K_I (ℓ/g mole, sec.)
1.0	0.0208	1.02	9,800
2.0	0.0134	2.01	13,700
3.0	0.0196	3.02	18,200
	(NaOH)		
2.0	0.0244	2.02	13,700
(Na_2CO_3)	(NaOH)		
0.0247	0.0246	0.099	6,280
0.122	0.0244	0.360	6,800
0.241	0.0233	0.746	7,800
0.457	0.0288	1.394	10,500
($NaNO_3$)	(NaOH)		
2.35	0.0203	2.37	11,100
3.60	0.207	3.62	12,400
(Na_2SO_4)	(NaOH)		
0.5	0.269	1.53	8,700
1.0	0.0203	3.02	10,800

Table 3 Saal (36)

temp. = 13.7°C	I (g mole/ℓ)	K_I (ℓ/g mole, sec)
	0.0115	3,700
	0.013	3,800
	0.0215	3,600
Avg.	0.0153	3,700

Table 4 Brinkman, Margaria and Roughton (3)

Temp.	(NaOH)	(CO_2)	I (g mole/ℓ)	K_I (ℓ/g mole,sec.)
15.5°C	0.0423	0.0173	0.0423	2,000
18.0°C	0.062	0.045	0.062	2,300

Table 5 (Faurholt (11)

Temp.	(HCO_3^-)/($CO_3^=$)	I (g mole/l)	K_I (l/g mole,sec.
0°C	0.04/0.06	0.22	906
	0.02/0.03	0.11	959
			Avg.932
18°C	0.04/0.06	0.22	4,000

Table 6 Brinkman, Margaria and Roughton (3)

Temp.	($NaHCO_3$)	(Na_2CO_3)	I (g mole/l)	K_I (l/g mole,sec.
0.5°C	0.036	0.067	0.237	780
0.5°C	0.073	0.034	0.175	890
				Avg.840
16°C	0.036	0.067	0.237	1,660
18°C				1,800

Table 7 Kiese and Hastings (19)

Temp.	Buffer	pH	K_o (l/g mole,sec.)
5°C	Pyrophosphate	8.1	2,950
	"	8.55	2,900
	"	9.0	2,850
	Borate	9.0	2,850
	Carbonate	10.1	1,840

Table 8 Pinsent and Roughton (25)

Temp.	(HCO_3^-)/($CO_3^=$)	pH	K_o (l/g mole, sec.)
0°C	3	10.18	1,040
	4	10.06	1,060
	5	9.97	1,050
			Avg.1,050
10°C	3 to 5	10.04 to 9.94	2,300 ± 15%

Table 9 Meda (4)

Temp.	(NaOH)	I (g mole/l)	K_I (l/g mole,sec.)
20°C	3.9×10^{-6}	3.9×10^{-6}	5,500
25°C	4.81×10^{-6}	4.81×10^{-6}	8,500
30°C	5.96×10^{-6}	5.96×10^{-6}	11,600

Table 10 Sirs (39)

Photoelectric

Temp., °C,	(NaOH)	I (g mole/l)	K_I (l/g mole, sec.)
3.3	0.0166	0.02	975
11	0.0218	0.02	3,310
11.0	0.0163	0.02	2,410
16.3	0.0166	0.02	4,570
16.6	0.0201	0.02	4,380
20.7	0.0109	0.01	5,590
22.0	0.0163	0.02	5,580
27.0	0.0201	0.02	10,150
30.0	0.0109	0.01	13,000

Conductively

2.7	0.0127	0.0127	1,260
10.4	0.0130	0.0130	2,690
11.6	0.0127	0.0127	3,350
16.9	0.0127	0.0127	3,870
20.0	0.0129	0.0129	5,000

Table 11 Nijsing, Hendriksz and Kramers (24)

Temp. = 20°C	(NaOH)	I (g mole/l)	K_I(l/g mole, sec.)	D	c*
		0	4,700		
	0.46	0.46	5,450	1.55	2.91
	1.05	1.05	6,200	1.41	2.38
	2.07	2.07	9,000	1.14	1.68
	(KOH)	I	K_I		
	0.44	0.44	5,800	1.61	3.04
	0.89	0.89	7,000	1.55	2.70
	3.14	3.14	17,300	1.23	1.55
	(LiOH)	I	K_I		
	0.51	0.51	5,350	1.56	2.94
	1.02	1.02	5,400	1.41	2.54

Table 12 Poulton and Baldwin (27)

Temp. = 25°C	In the solution of NaCl ↓ carbonate buffer	I	K_I (1/g mole, sec.)
		0.5	8,400
		1.5	8,000
		2.5	4,800

Table 13 Koefoed and Engel (20)

Temp. = 0°C	($NaHCO_3$)	(NaCl)	I (g mole/l)	K_I (1/g mole,sec.)
	0.25	0.50	0.75	5,450
	0.50	0.25	0.75	5,460
	0.75	0	0.75	5,470

Table 14 Activity coefficient of hydroxides (31)

Temp. = 25°C	m (mole/l)	f_{KOH}	f_{NaOH}	f_{LiOH}
	0.1	0.798	0.766	0.760
	0.2	0.760	0.727	0.702
	0.3	0.742	0.708	0.665
	0.4	0.734	0.697	0.638
	0.5	0.732	0.690	0.617
	0.6	0.733	0.685	0.599
	0.7	0.736	0.681	0.585
	0.8	0.742	0.679	0.573
	0.9	0.749	0.678	0.563
	1.0	0.756	0.678	0.554
	1.2	0.776	0.681	0.542
	1.4	0.800	0.686	0.532
	1.6	0.827	0.692	0.525
	1.8	0.856	0.700	0.518
	2.0	0.888	0.709	0.513
	2.5	0.974	0.743	0.503
	3.0	1.081	0.784	0.494
	3.5	1.215	0.835	0.487
	4.0	1.352	0.903	0.481
	4.5	1.530	0.985	
	5.0	1.720	1.077	
	5.5	1.950	1.181	
	6.0	2.200	1.299	

Table 15 Salt effects on the activity coefficients of hydroxides(13

1. The effect of chloride

Temp.= 25°C, (NaOH) = 0.1 mole/liter; (KOH) = 0.1 mole/liter

(NaCl), moles/liter	f_{NaOH}:	(KOH), moles/liter	f_{KOH}
0.000	0.775	0.0000	0.789
0.204	0.700	0.2022	0.706
0.5019	0.660	0.506	0.666
1.024	0.636	1.009	0.643
2.041	0.620	2.005	0.645
3.099	0.6305	3.025	0.669

2. The effect of sulfates

Temp. = 25°C, (NaOH) = 0.1 mole/liter; (KOH) = 0.1 mole/liter

(Na_2SO_4), mole/liter	f_{NaOH}	; (K_2SO_4), moles/liter	f_{KOH}
0.0	0.767	0.0	0.783
0.0312	0.713	0.0039	0.778
0.0625	0.680	0.0078	0.764
0.125	0.650	0.0156	0.753
0.250	0.602	0.0312	0.735
0.500	0.547	0.0625	0.701
1.000	0.505	0.125	0.673
1.50	0.491	0.25	0.627
2.0	0.495	0.5	0.578
2.5	0.501	0.625	0.565

Table 16 Effect of some salts on the activity coefficient of CO_2, (22)

$$\log f_B = b_B I$$

Salt	b_B, 0.2°C	b_B, 25°C	b_B, 40°C
$MgSO_4$	0.341	0.285	0.269
Na_2SO_4		0.322	0.280
$Mg(NO_3)_2$	0.175	0.123	0.109
NaCl	0.132	0.105	0.099
$NaNO_3$	0.107	0.067	
KCl	0.085	0.064	0.066
KNO_3	0.059	0.027	0.022

Table 17 Activity coefficients of some salts at 25°C (31)

M (moles/liter)	f_{NaCl}	f_{KCl}	f_{NaNO_3}	$f_{Na_2SO_4}$
0.1	0.778	0.770	0.762	0.445
0.2	0.735	0.718	0.703	0.365
0.3	0.710	0.688	0.666	0.320
0.4	0.693	0.666	0.638	0.289
0.5	0.681	0.649	0.617	0.266
0.6	0.673	0.637	0.599	0.248
0.7	0.667	0.626	0.583	0.233
0.8	0.662	0.618	0.570	0.221
0.9	0.659	0.610	0.558	0.210
1.0	0.657	0.604	0.548	0.201
1.2	0.654	0.593	0.530	0.186
1.4	0.655	0.586	0.514	0.1746
1.6	0.657	0.580	0.501	0.1654
1.8	0.662	0.576	0.489	0.1580
2.0	0.668	0.573	0.478	0.152
2.5	0.688	0.569	0.455	0.1418
3.0	0.714	0.569	0.437	0.1365
3.5	0.746	0.572	0.422	0.1345
4.0	0.783	0.577	0.408	0.1354
4.5	0.826	0.583	0.396	
5.0	0.874		0.386	
5.5	0.928		0.378	
6.0	0.986		0.371	

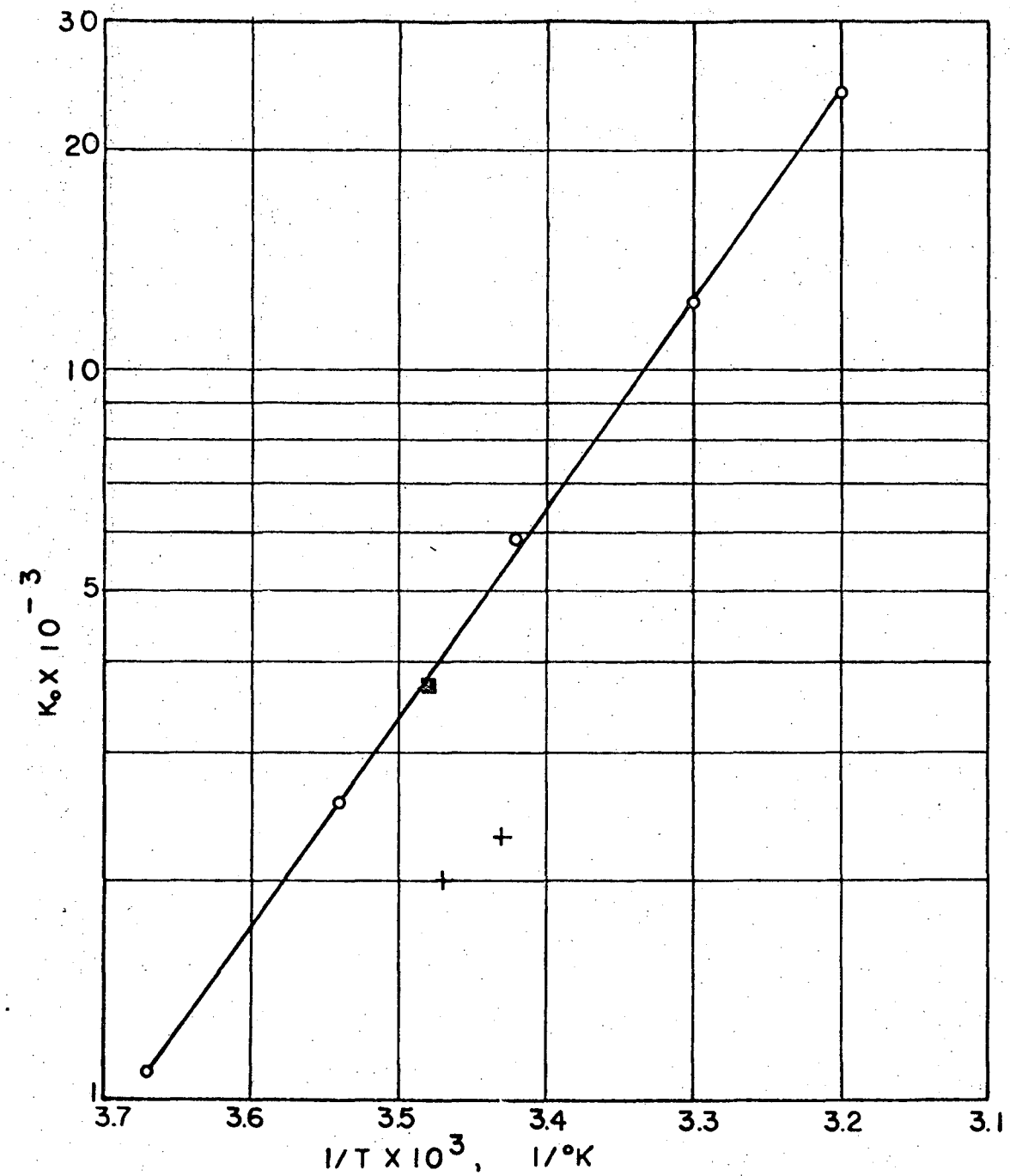

FIG.1. CONTINUOUS FLOW METHOD

O PINSENT, (26); ■ SAAL (36); + BRINKMAN (3)

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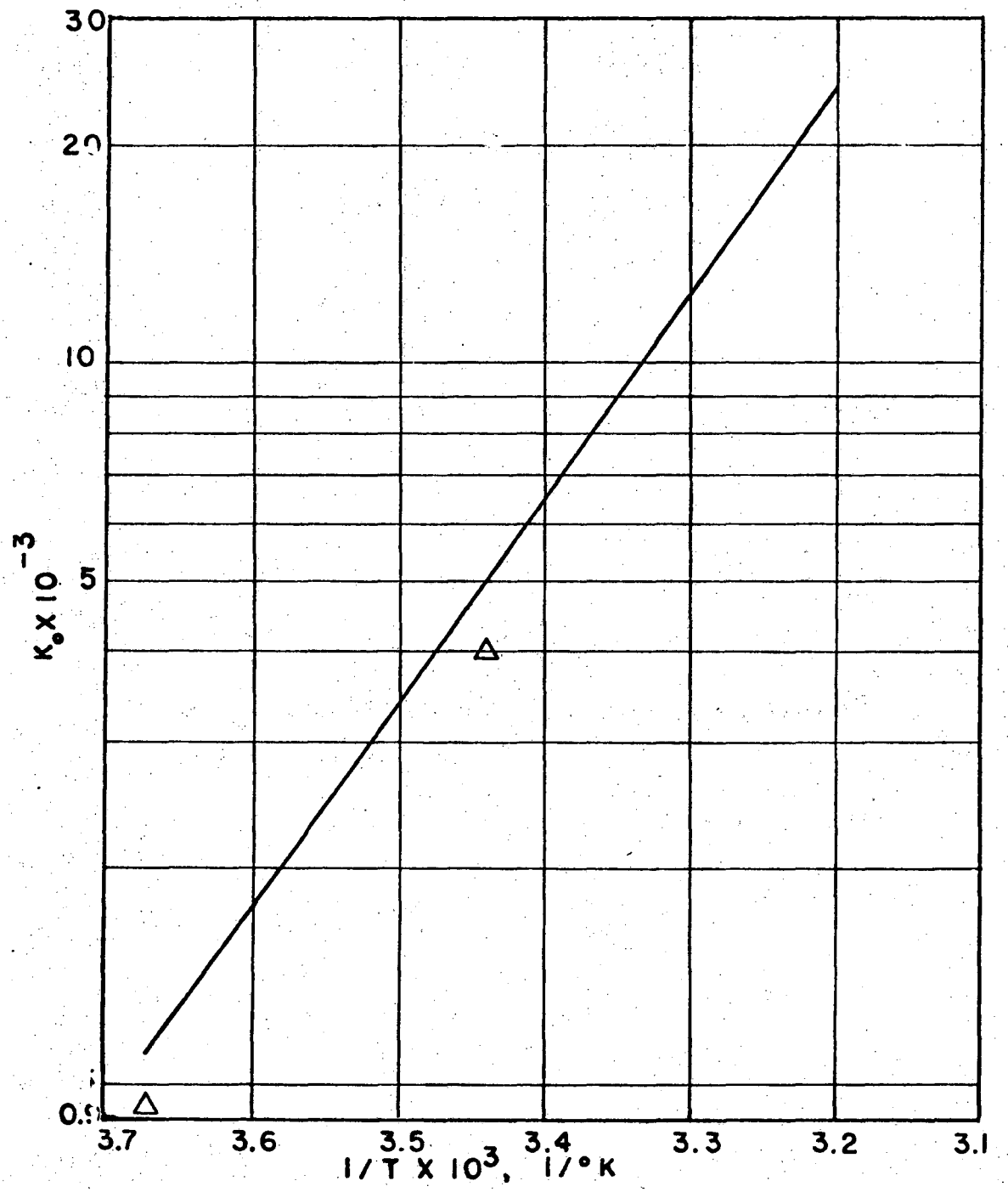

FIG.2. CARBAMINO QUENCHING METHOD

△ FAURHOLT (11)

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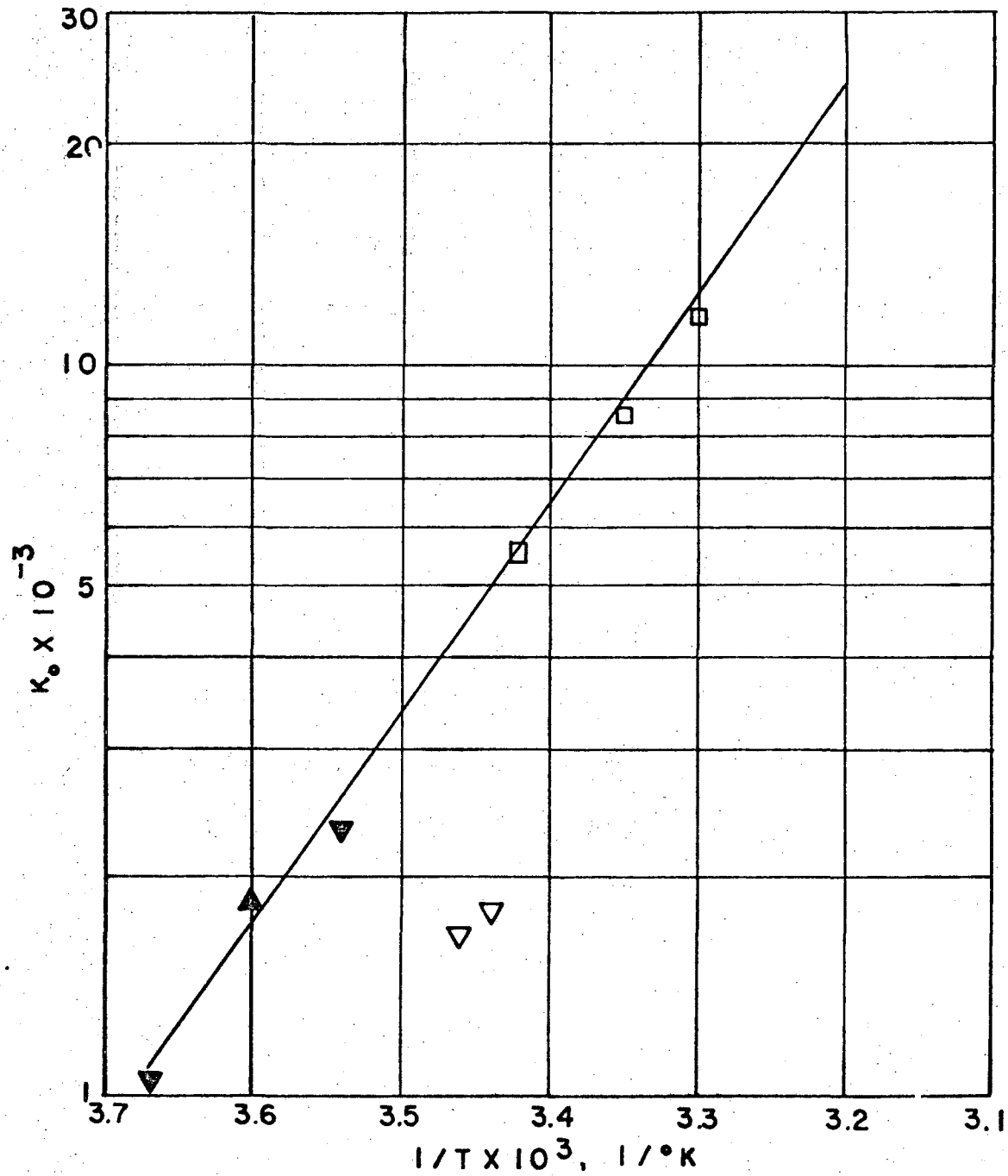

FIG.3. BOAT METHOD

▽ BRINKMAN (3); △ KIESE (19);

▼ PINSENT (25); □ MEDA (26)

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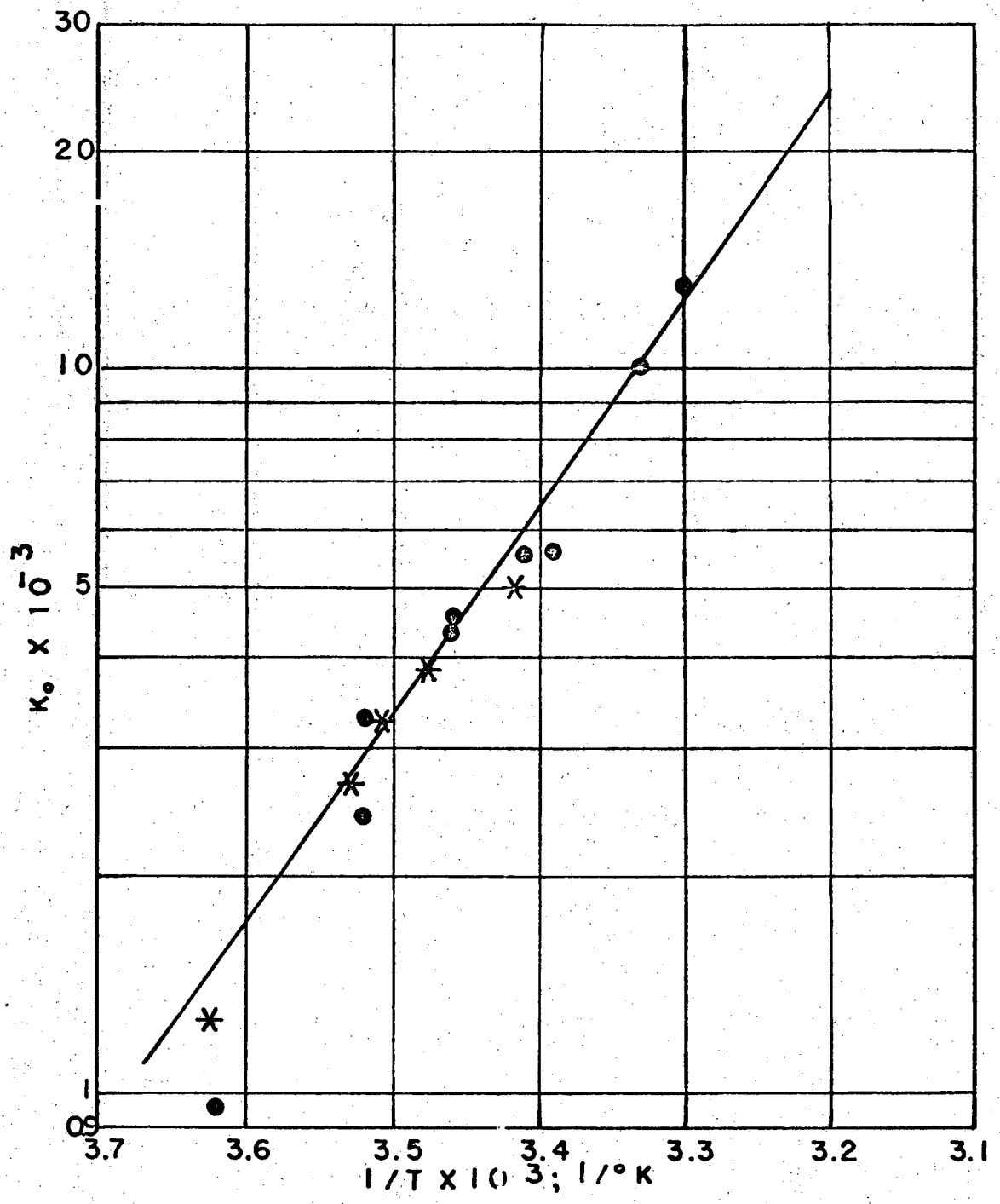

FIG.4. STOPPED FLOW METHOD

● PHOTOELECTRIC; SIRS (39)

✱ CONDUCTIVITY, SIRS (39)

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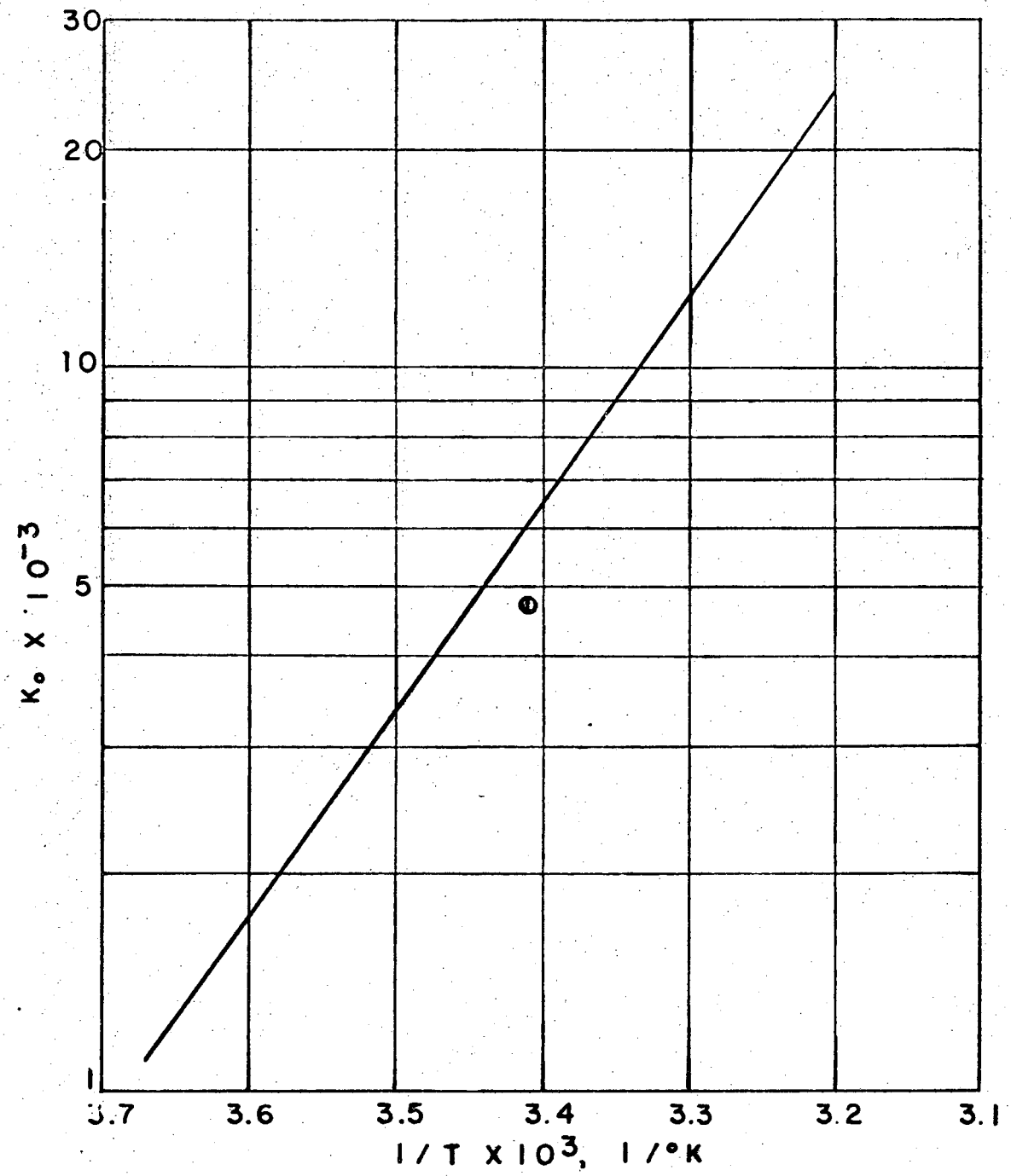

FIG.5. LAMINAR JET ABSORPTION

● NIJSING (24)

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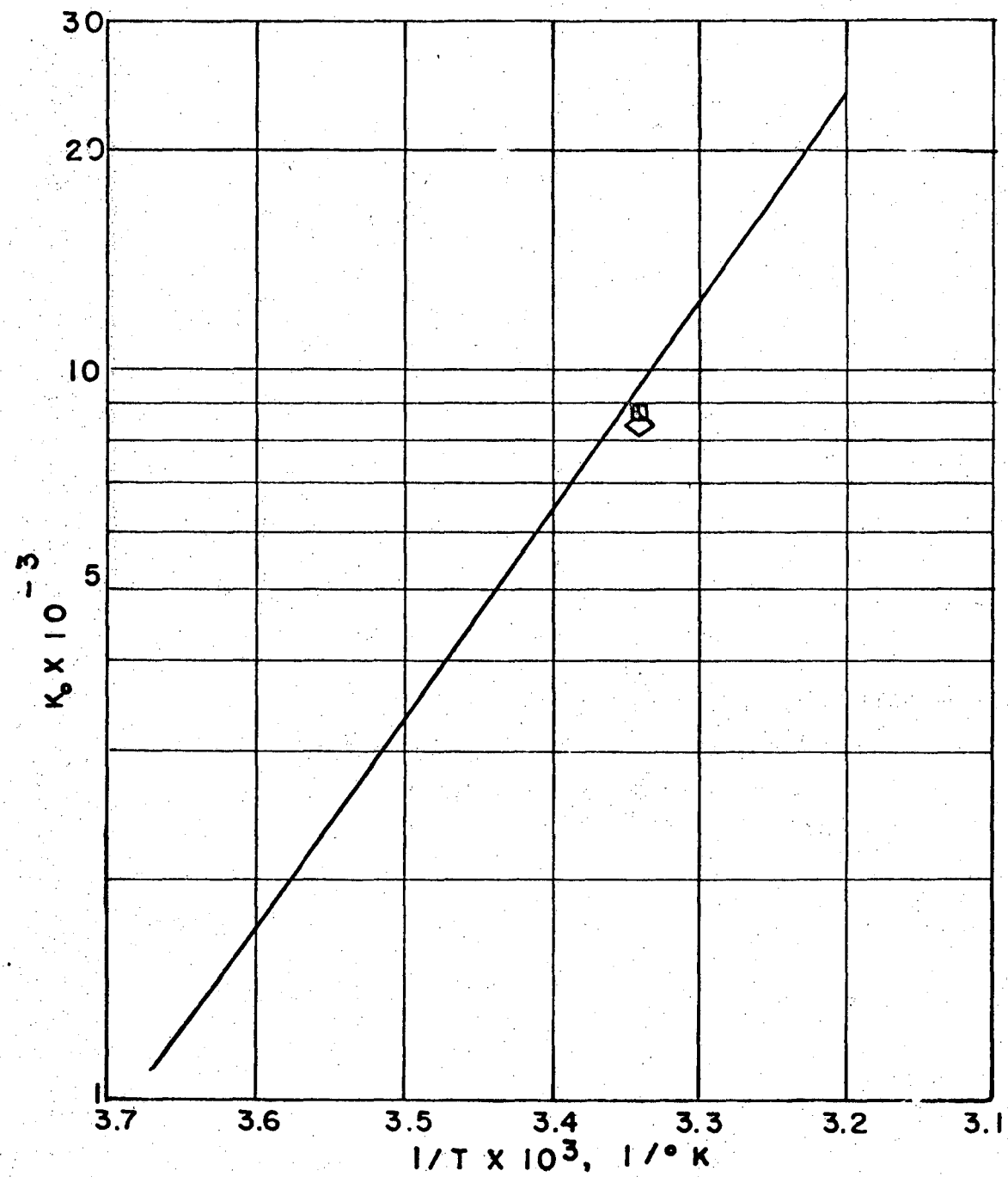

FIG.6. ISOTOPE EXCHANGE METHOD

■ RADIOACTIVE CO_2, GOODRIGE (13)
◇ OXYGEN-18, POULTON (27)

XBL 712-2837

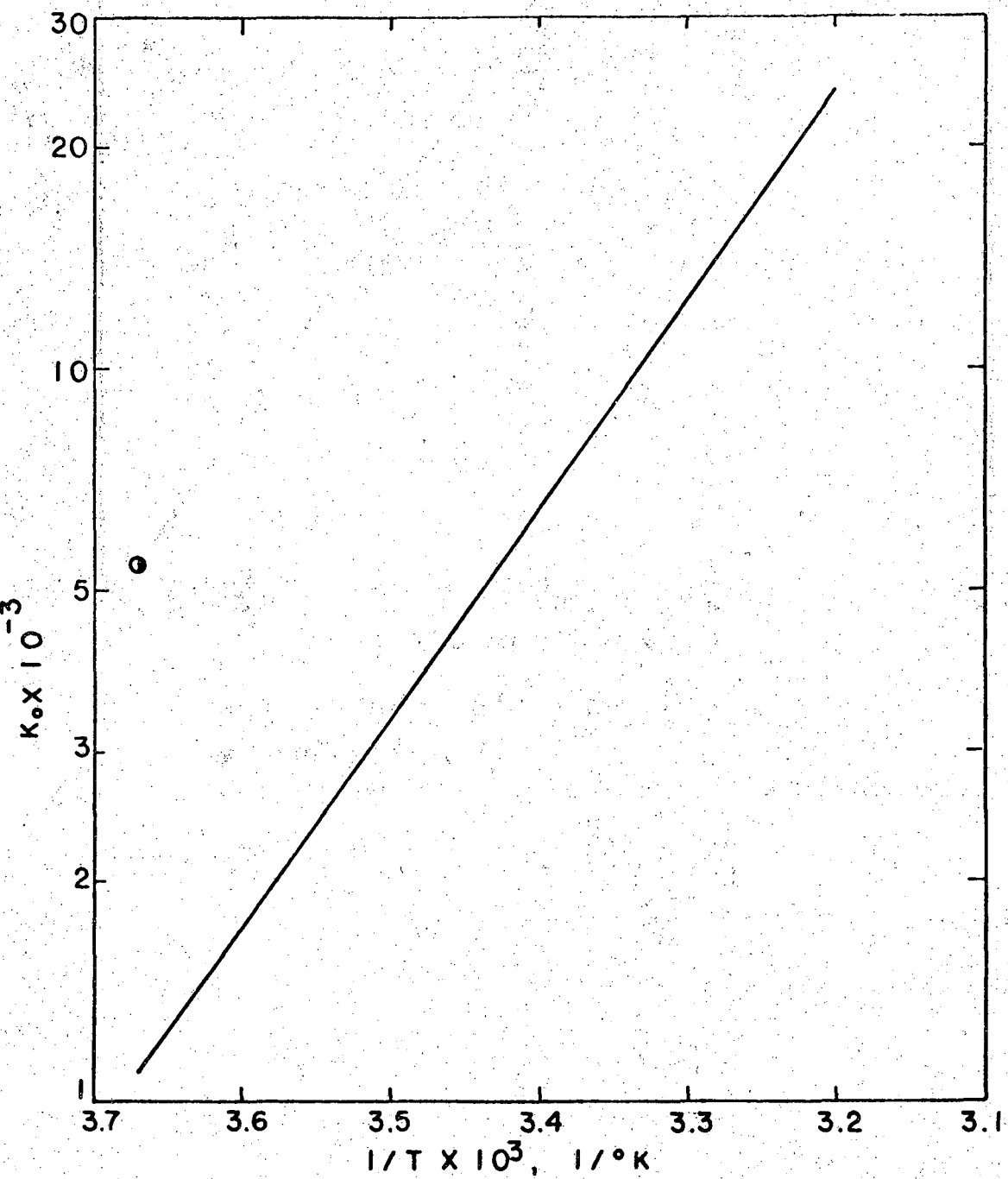

FIG.7. STEADY STATE METHOD

● KOEFOED (20)

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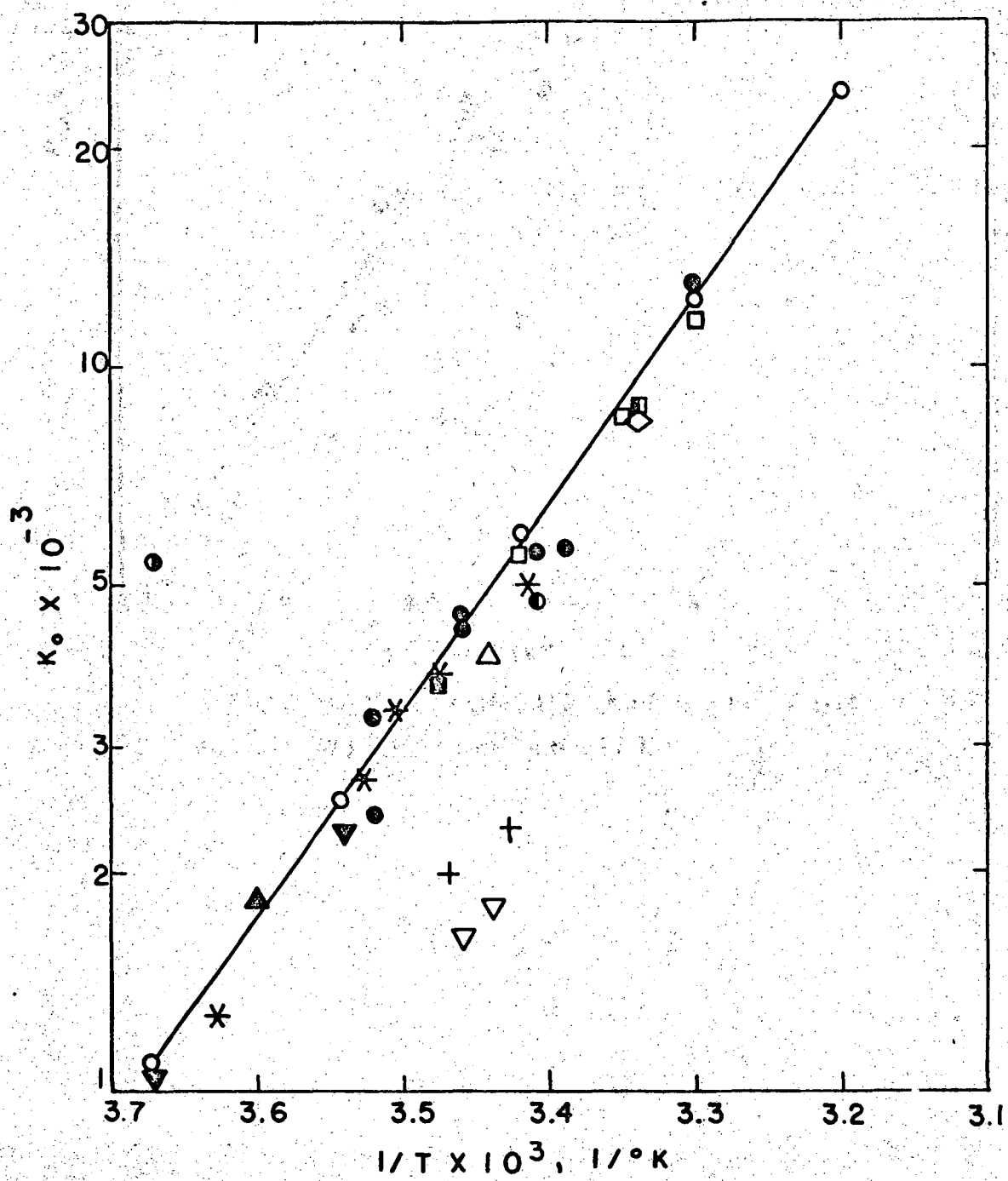

FIG.8 VARIATION OF KINETIC CONSTANT WITH TEMPERATURE

XBL 712-2839

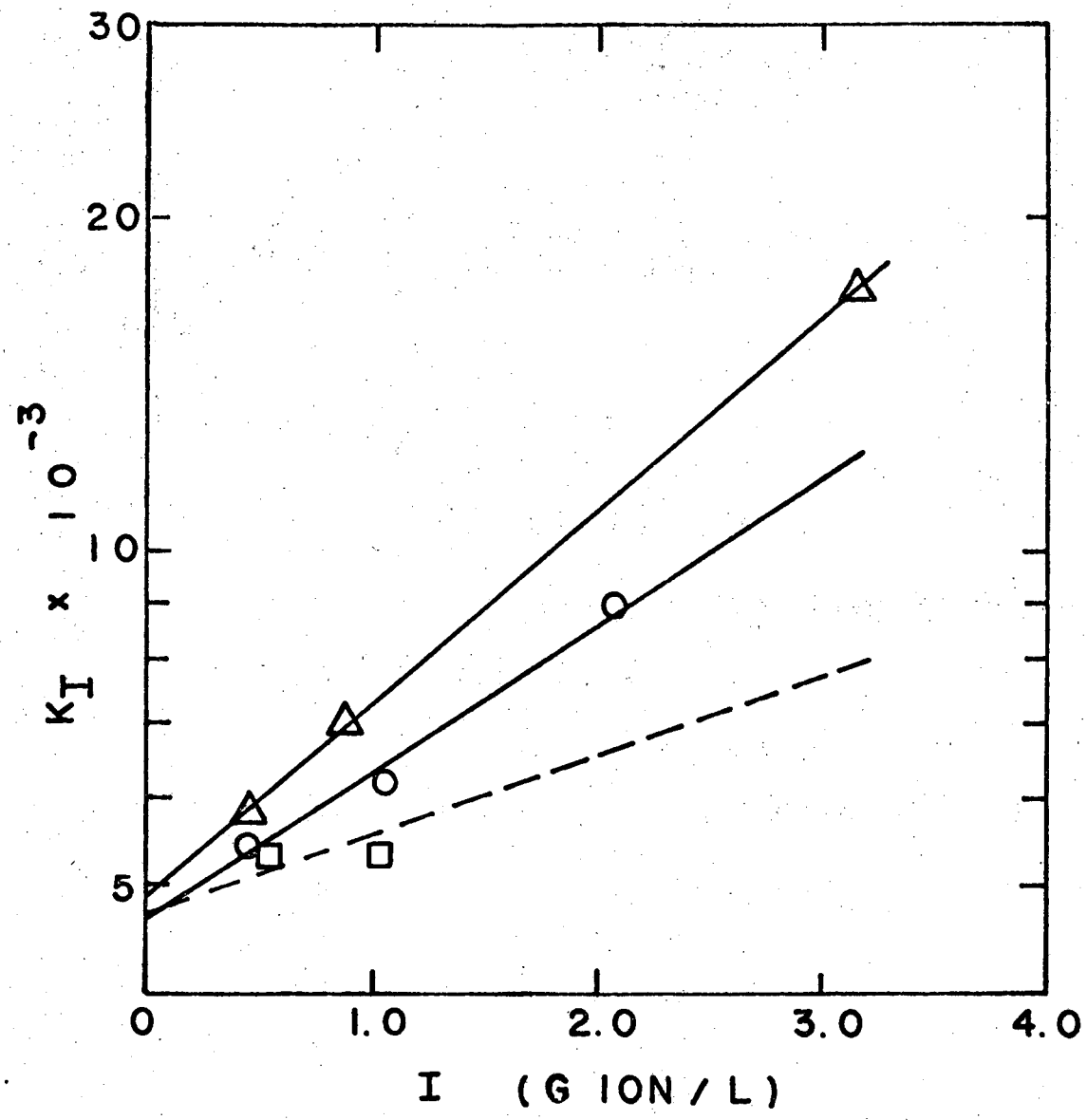

FIG.9. SALT EFFECT ON THE KINETIC CONSTANT (24)

△ KOH, ○ NaOH, □ LiOH

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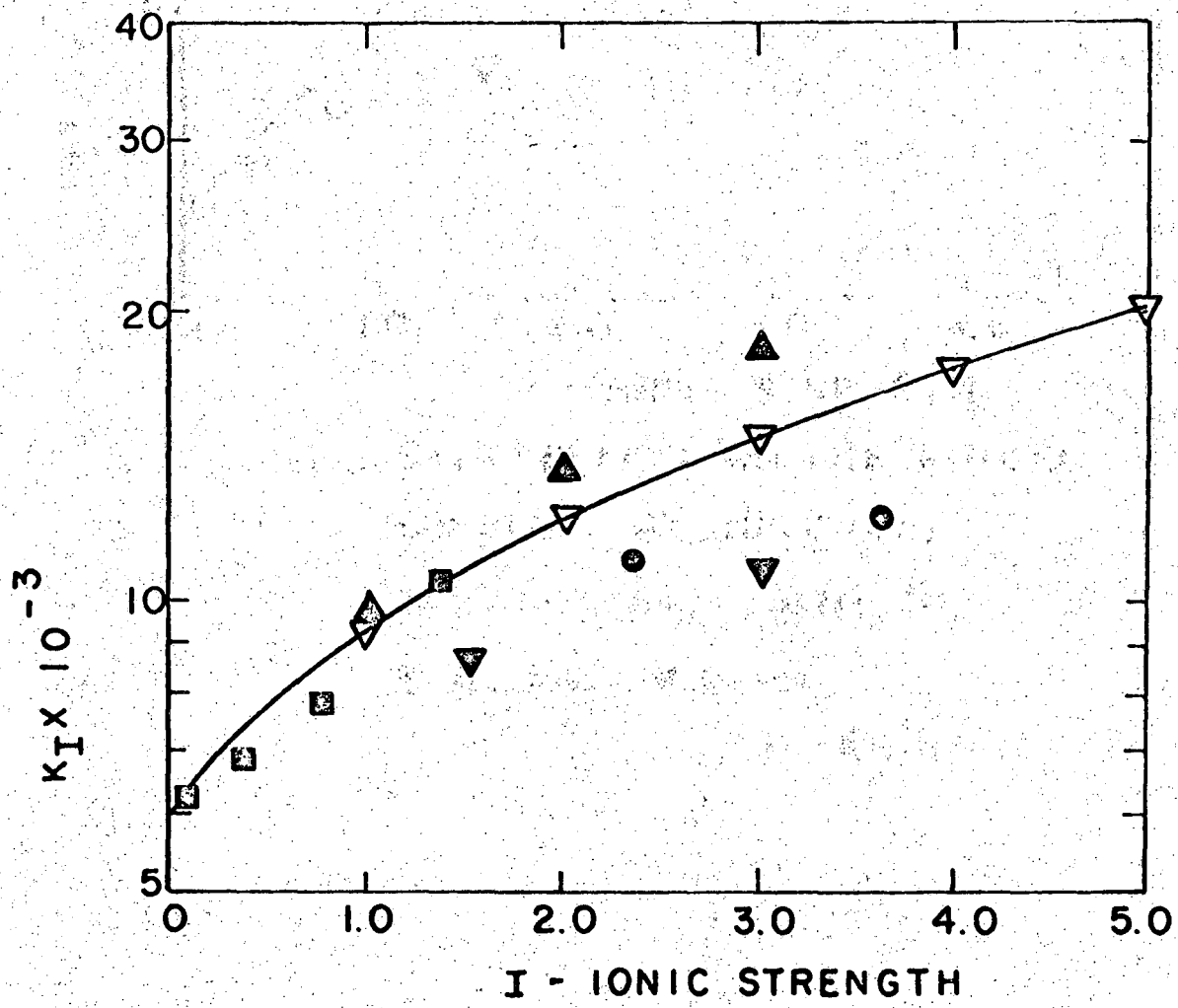

FIG.10 SALT EFFECT ON THE KINETIC CONSTANT AT 20° C (26)

▲ KCl, ▽ NaCl, ■ Na_2CO_3,

▼ Na_2SO_4, ● $NaNO_3$

XBL712-2846

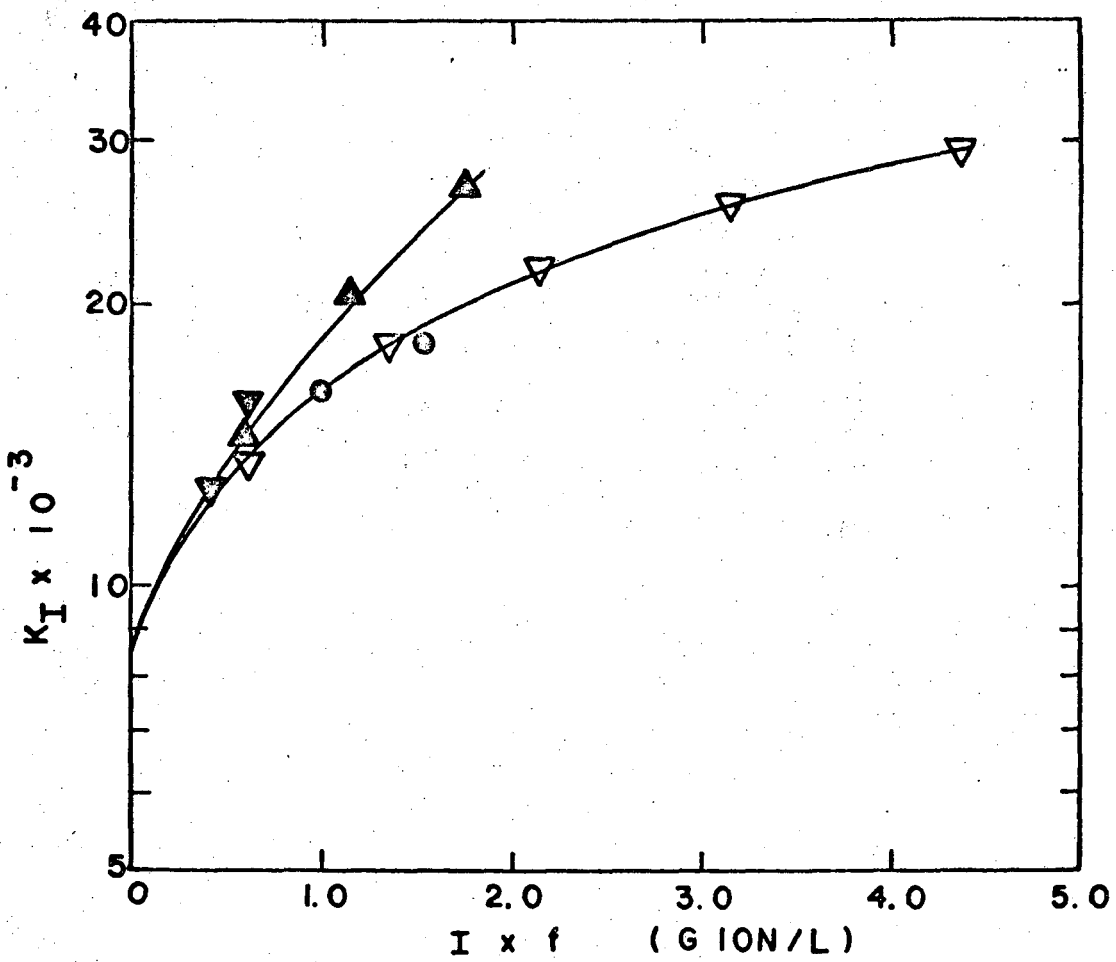

FIG.11 DATA OF LOG K_I PLOTTED AGAINST I x f

△ KCl , ○ $NaNO_3$, ▽ Na_2SO_4 , ▽ NaCl

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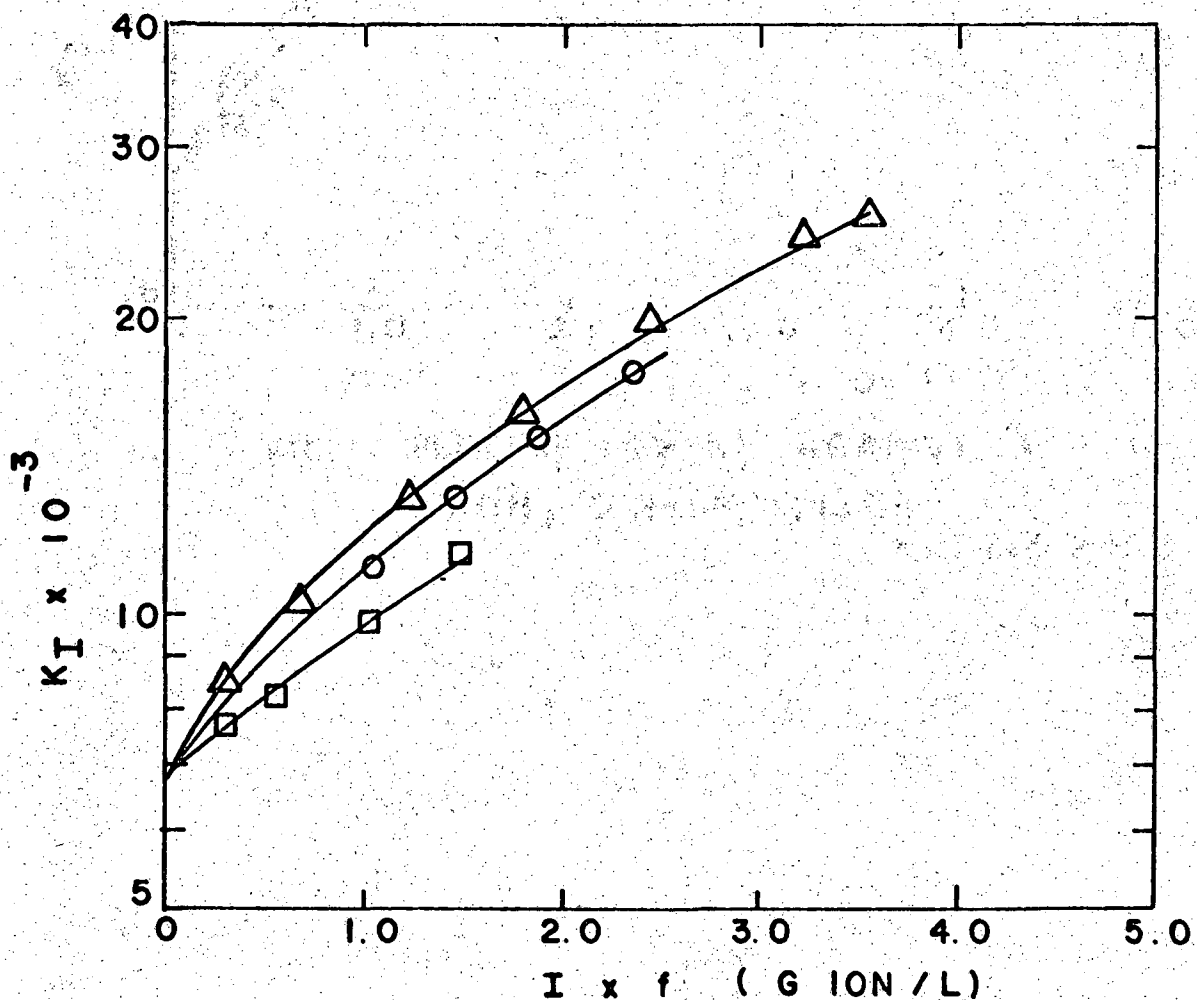

FIG.12. PLOT OF LOG K_I AGAINST I x f

△ KOH, ○ NaOH, □ LiOH

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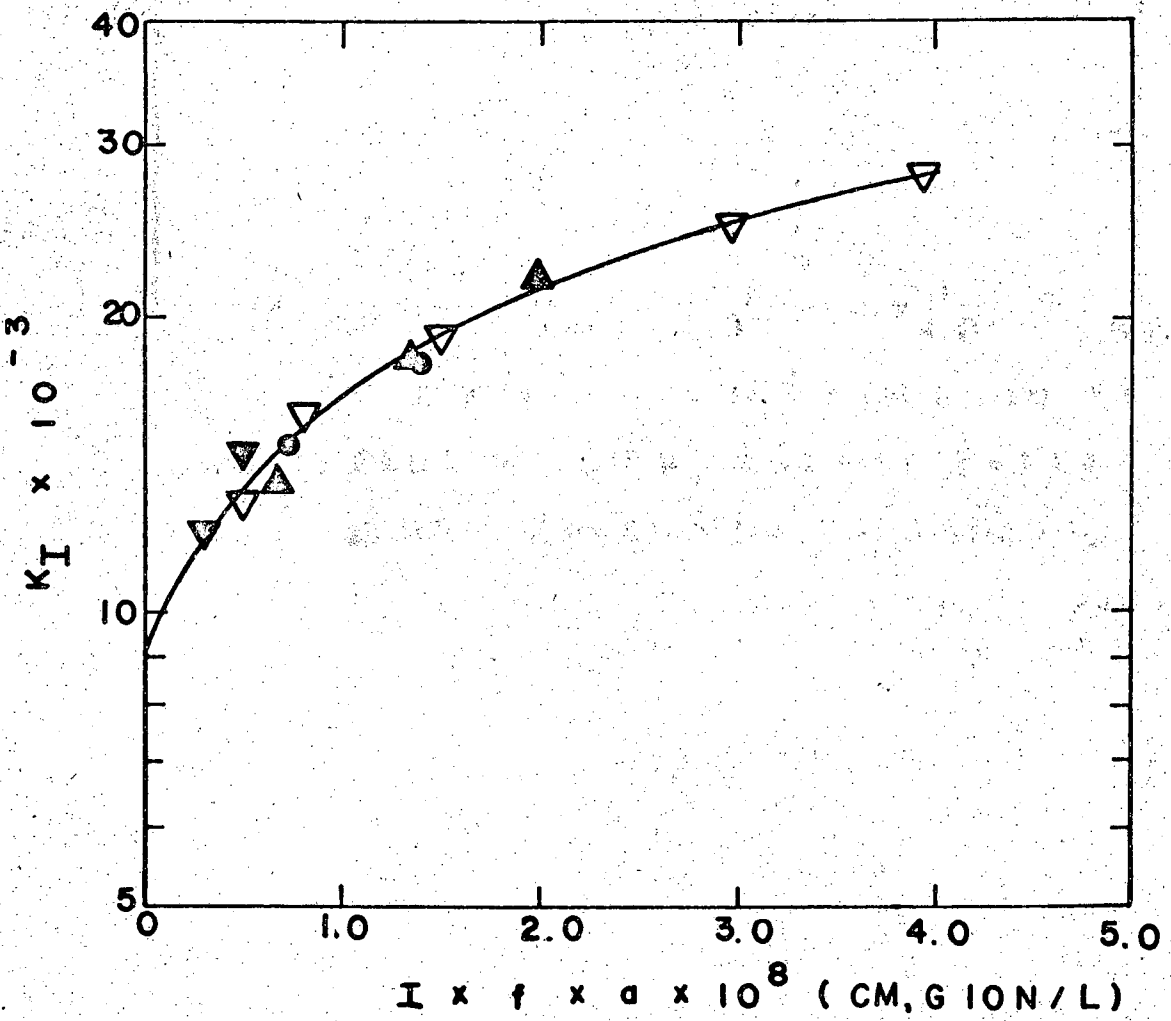

FIG.13. PLOT OF LOG K_I AGAINST $I \times f \times a$

▲ KCl, ▽ NaCl, ▽ Na_2SO_4, ⊙ $NaNO_3$

XBL712-2849

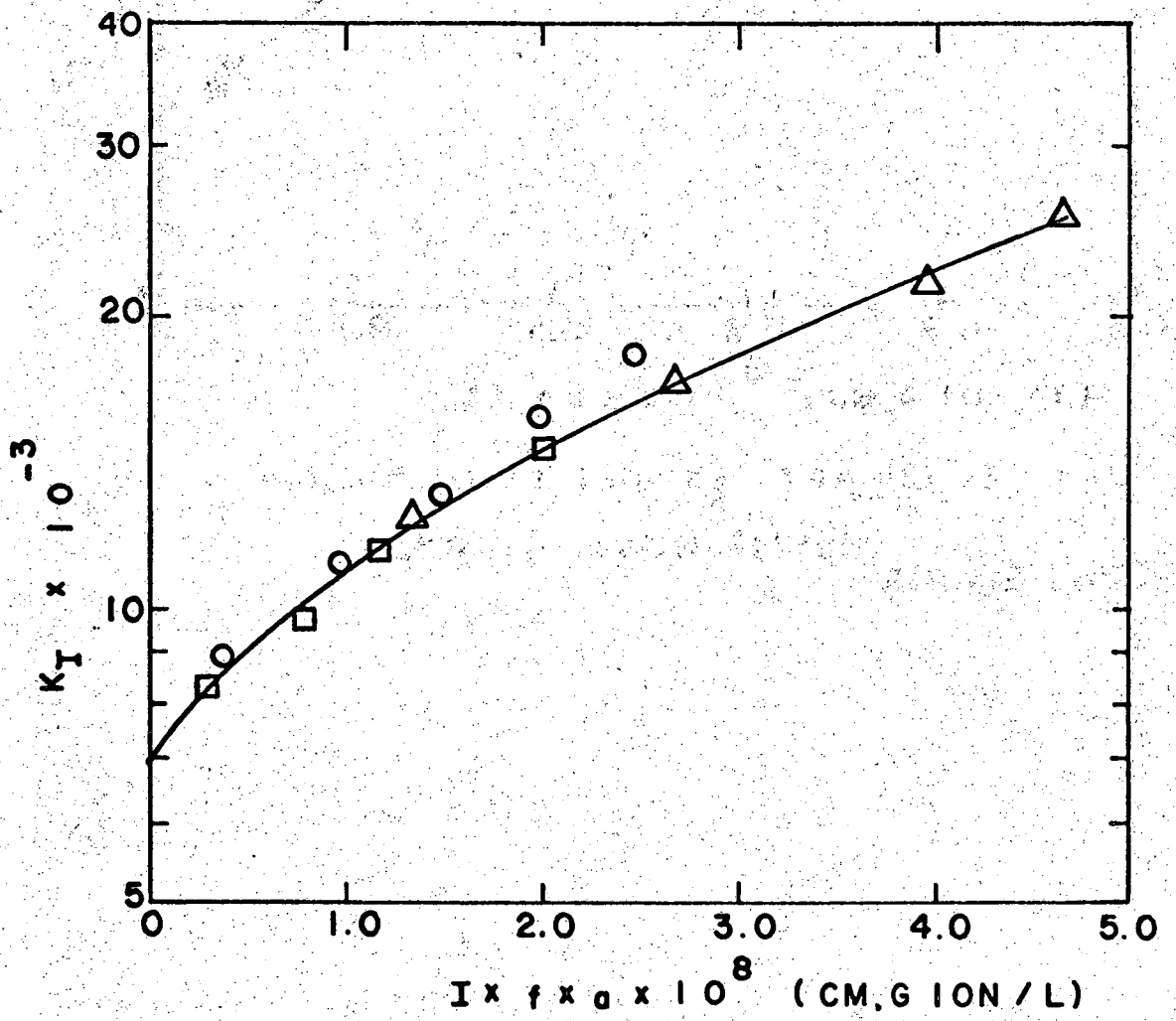

FIG.14.PLOT OF LOG K_I AGAINST $I \times f \times a$

△KOH, ○ NaOH, □ LIOH

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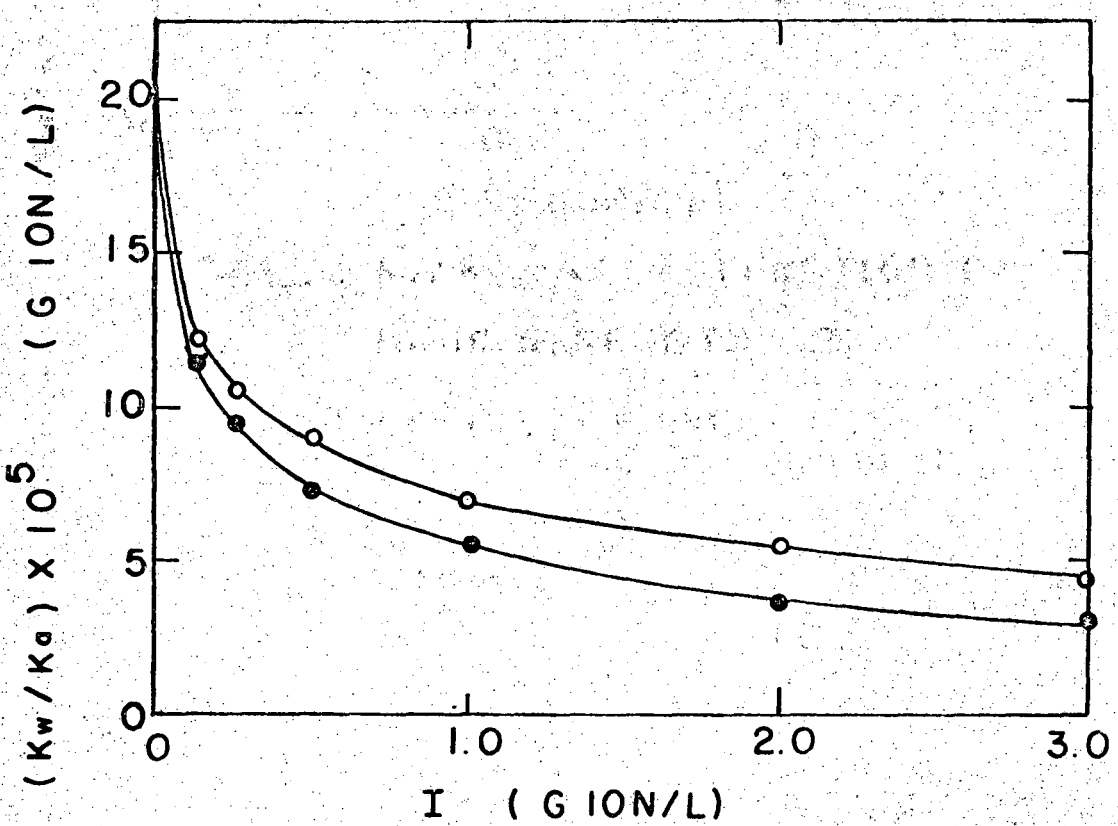

FIG.15. K_w / K_a AS A FUNCTION OF IONIC STRENGTH (23)

○ KCl ; ● NaCl

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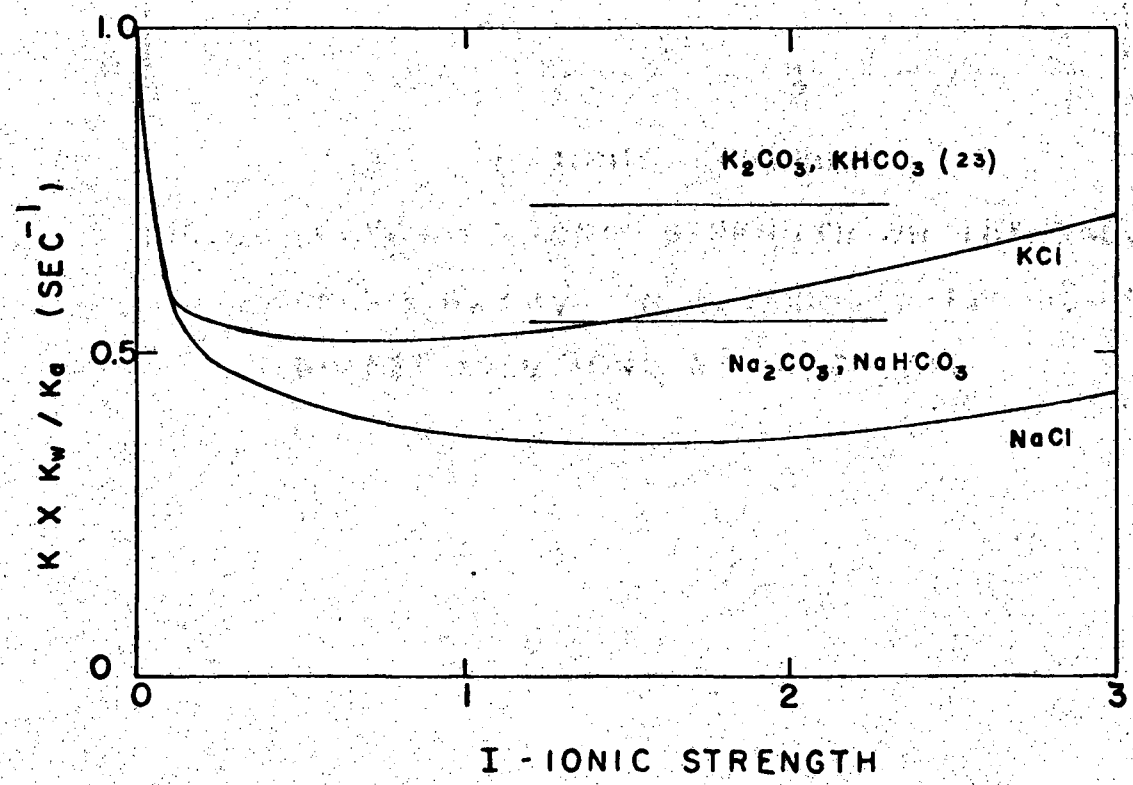

FIG.16. EFFECT OF IONIC STRENGTH ON THE VALUE OF K X K_w / K_a IN CARBONATE-BICARBONATE BUFFER SOLUTIONS AT 20°C (29)

XBL 712-2845

Fig.17. Flow diagram of experimental apparatus

1. KOH feed tank; 2. CO_2 feed tank; 3. Rotameter; 4. Mixing chamber; 5. Observation tube; 6. Thermistors; 7. Nitrogen supply tank; 8. Carbon dioxide supply tank; 9. Constant temperature water bath; 10. Constant temperature oil bath.

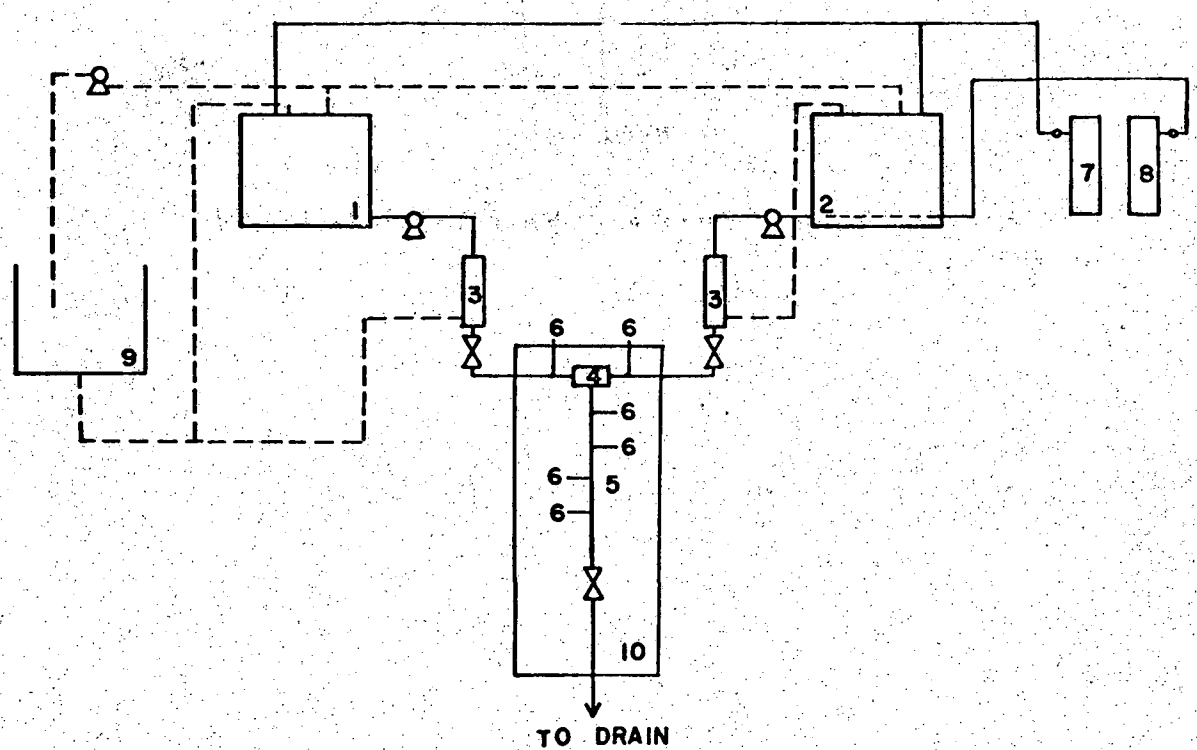

FIG. 17. FLOW DIAGRAM OF EXPERIMENTAL APPARATUS

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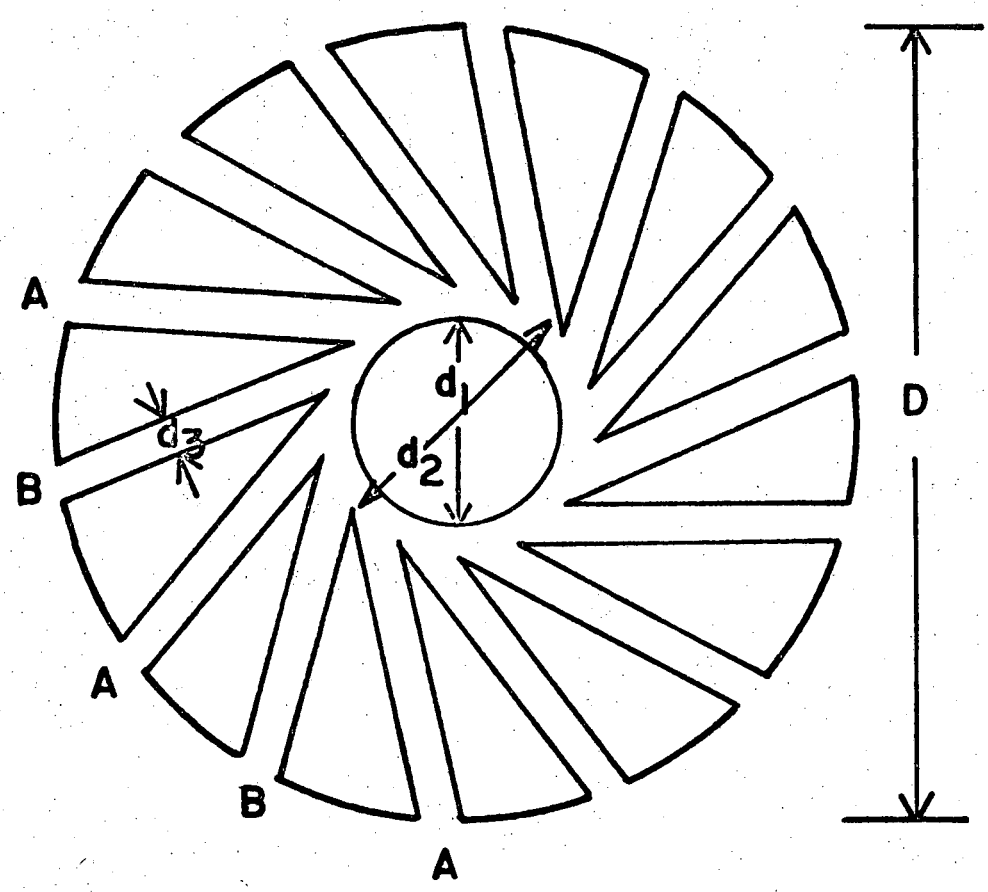

FIG.18. STRUCTURE OF THE MIXING CHAMBER

d_1 = 5 mm, d_2 = 7.13 mm, d_3 = 1.38 mm

D = 1.5 cm, d_4 = 3 mm

XBL712-2855

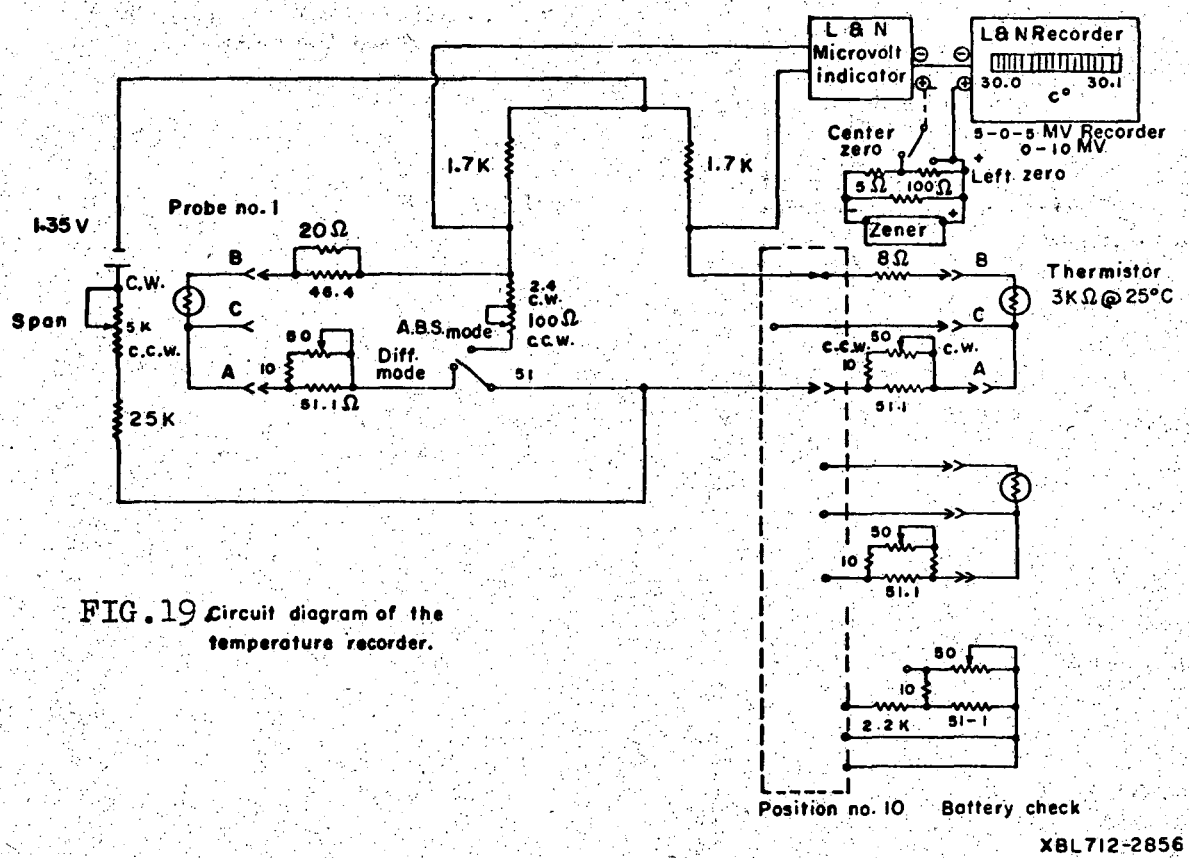

FIG. 19 Circuit diagram of the temperature recorder.

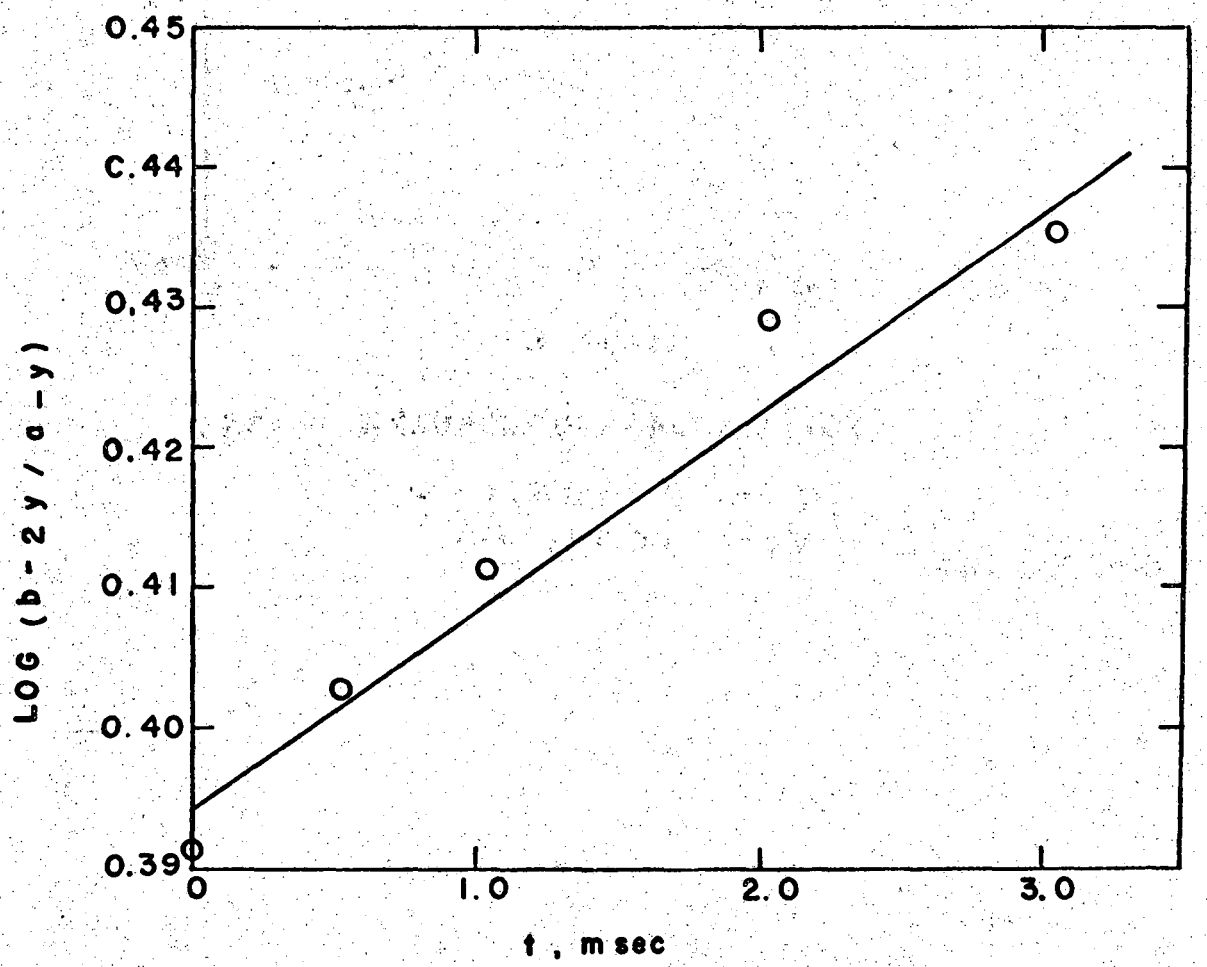

FIG.20. EXAMPLE OF CALCULATION

$b = (OH)_o = 0.01099$ M

$a = (CO_2)_o = 0.004465$ M

XBL712-2857

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TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720