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A kinetic study of the base catalyzed esterification of acetic anhydride with ethyl alcohol using a high frequency oscillometer

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A KINETIC STUDY OF THE BASE CATALYZED ESTERIFICATION OF ACETIC ANHYDRIDE WITH ETHYL ALCOHOL USING A HIGH FREQUENCY OSCILLOMETER

A THESIS
PRESENTED TO
THE FACULTY OF THE DEPARTMENT OF CHEMISTRY
COLLEGE OF PACIFIC

IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE

by
WILLIAM E. LOWERY
JUNE 1958

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ACKNOWLEDGEMENT

The writer wishes to express appreciation to the members of the faculty of the Department of Chemistry of the College of the Pacific, and especially to Dr. Herschel Frye for his guidance and help during this investigation.

CHAPTER I

THE NATURE OF THE PROBLEM

In recent years considerable interest has been aroused in the chemical oscillometer as an analytical tool. To the chemist eager for methods which will improve and expidite his knowledge of the various substance concentration in homogenous solutions, this type instrument has become of increasing importance.

Since the article by Jensen and Parrack (1946) describing an inductively coupled instrument operating at high frequency, many developments and uses have been made of this type instrument. The E.H. Sargent Co. (1957) has an excellent review of the work which has been done to date with references. The fields of endeavour have included titrations, examination of binary solutions, applications to chromotography, and the study of complexes. However, one of the most valuable uses for this type instrument, yet one which has received relatively little attention, is the study of reaction rates in homogenous solutions.

Crystallization velocity and precipitation velocity were studied by Asada (1954), and Duke, Beaver, and Diehl (1949)studied the rate of precipitation of Barium Sulphate from Barium Acetate.

Jensen, Watson, and Beckham (1951) used a high frequency apparatus to follow the saponification reaction of ethyl acetate. Flom and Elving (1953) were successful in applying this method to the rate of hydrolysis of lower aliphatic esters.

All of the published kinetic studies using this type instrument have been done in aqueous solution in which the principle instrumental effect is conductimetric. To the best of the writer's knowledge no kinetic studies have been made to date utilizing the binary solution method of analysis wherein the instrumental effect is essentially capacitative.

It is the purpose of this investigation to determine the feasibility of using a 120 megacycle oscillometer for kinetic studies in non-aqueous solutions by studying the reaction rate of the base catalyzed esterification of acetic anhydride.

CHAPTER II

A DESCRIPTION OF THE INSTRUMENT AND PRINCIPLES OF OPERATION

The high frequency oscillometer used in this investigation is a capacitatively coupled, heterodyne type of instrument, operating in the 120 megacycle range. A complete electronic description of the instrument may be found in the Master's Thesis (1957), by John Clinkscales who built the instrument.

Essentially, the instrument is composed of two separate oscillators, mechanically shielded from each other, and isolated by two identical electrical buffer systems. As a part of the circuit in one oscillator, called the working circuit, is included the cell which contains the sample to be studied. The frequency of the working circuit is determined by the conducting and (or) dielectric properties of the sample. The frequency of the second oscillating circuit, called the reference circuit, is adjusted by means of two parallel condensers in the circuit. As the two oscillators approach the same frequency, a heterodyne or resonant beat frequency will be heard. This is a null or zero beat when the two frequencies are exactly the same. The beat is fed through an amplifier, into an audio stage, and picked up by means of earphones.

In practice, the cell containing the sample is placed in the cell holder, which is part of the working circuit. The condensers in the reference circuit are then adjusted to match the frequencies of the two circuits, and a zero beat is heard. This reading on the condenser system dial constitutes the initial reading and is recorded. As the dielectric or conducting properties of the sample change, the frequency of the working circuit is changed, and the reference circuit adjusted to again produce a zero beat, thus giving a new scale reading. By this method it is possible to follow the course of many reactions, the type of reaction determining the number and frequency of readings which must be obtained.

The instrument exhibits good stability after an initial warm-up period of two hours. "Drift", after this period, is very slight, and can be eliminated completely from interfering with experimental results by maintaining a second cell with a standard sample for retuning the instrument periodically during the course of a given experiment.

The influence of external capacitance upon the working circuit is significant, particularly body capacitance. This problem may produce erratic results unless the operator determines where he may safely touch the instrument, and what is the best position with reference to the instrument for operation. With experience, this factor is easily controlled.

A minimum of one hundred ml must be used in the sample cell. It is so constructed that a ground ring is included at this level in the cell holder. With the ground ring in place, a shift in frequency is observed as the cell is filled with sample, only up to the ninety ml mark. Above this ring there is no change in frequency with increased volume. If a minimum of one hundred ml is used at the start of every experiment, the shift in frequency is due to a change in the composition of the sample, and not to a change in physical capacitance.

The National dial used as a scale on the variable condenser system in the reference circuit can be read to three places directly, and estimated, in the opinion of this investigator, to plus or minus 0.05 divisions. This is also the amount the dial can be moved without affecting the signal. The precision obtainable is plus or minus 0.166% over a dial range of thirty units.

In general, the instrument exhibits good stability, but careful operation is essential to good results. The instrument should not be jarred or moved during the course of an experiment, as this will change the frequency of the working circuit.

CHAPTER III

THEORETICAL CONSIDERATIONS FOR HIGH FREQUENCY OSCILLOMETERS

Since the high frequency oscillometer is a relatively new instrument in chemical analysis, the pertinent theory relative to the operation of such an instrument is of interest. The following presentation is a compilation of the many theoretical interpretations which have been made concerning the operation of such an instrument.

Two types of oscillometric instruments are known, the type dependent upon the mode of coupling the sample to the oscillating circuit. If the sample is placed in the field of the plate coil, it is inductively coupled, and if exposed to the electrostatic field of the condenser, it is capacitatively coupled. Since the instrument used in the present investigation is the latter type, it is this type which will here be discussed.

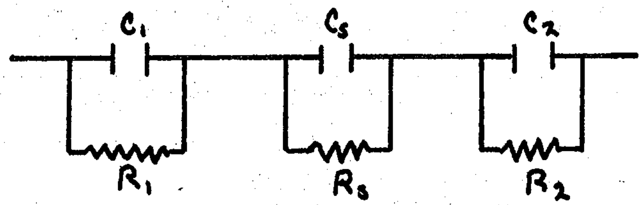
As described in a previous chapter, the frequency of the oscillating circuit containing the sample cell is dependent upon the nature of the sample in the cell. It is not the purpose of this thesis to present a detailed discussion of this frequency dependence. Falkenberg (1943) has an excellent treatment of the frequency dependence of conductivity and dielectric constant, while Debye (1929) presents a detailed analysis of both the electrophoretic and the time of relaxation effects.

Essentially, it may be said that the addition of a sample produces an increase in capacitance which results in a decrease in the frequency of the circuit in accordance with the relationship,

$$f = 1/ 2\pi(LC)^{\frac{1}{2}} \tag{1}$$

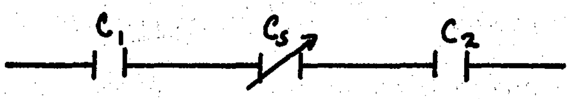
where f is the frequency, L, the inductance of the circuit, and C, the total series capacitance. In order to match the frequencies of the sample oscillator with the reference oscillator, the frequency of the reference circuit is adjusted by means of a variable condenser system. Since the circuits are identical, L is assumed to be the same in both circuits, and hence the scale reading produced by turning the reference oscillator may be considered in terms of capacitance units. However, since the change in frequency of the sample oscillator cannot in all cases be attributed to the capacitative effect of the sample, but must, in some cases, include a resistive effect, the measured change in the reference circuit is more properly referred to as apparent capacitance.

The sample cell may be represented electrically as a combination of capacitances and resistances,

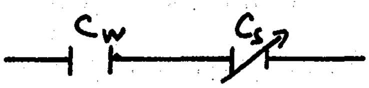


where C_1,C_2 and R_1,R_2 are the capacitances and resistances of the cell walls and C_s and R_s,the capacitance and resistance of the sample liquid. R_1 and R_2 are of such magnitude as to be infinite, while R_s will depend upon the conductivity of the sample. In dealing with electrolytic samples, R_s is considered to be important. However, with most organic liquids the conductivity is low enough that the effect of this shunting resistance can be neglected. At precisely which point, and in what organic liquids, R_s can safely be ignored is a problem worthy of further investigation.

If the effect of the three shunting resistances, R_1 ,R_2 ,and R_s,are neglected, the circuit may be considered as,



or, since C_1 and C_2 are fixed capacitances of the cell wall, a single series equivalent may be used.



The expression for the capacitance(apparent) is then

$$C = C_W C_s /(C_W+C_s) . \tag{2}$$

If the quantity, C_s ,is defined as

$$C_s = C_o K , \tag{3}$$

where C_o is the capacitance of the area between the walls in vacuum, and K is the dielectric constant of the sample, then

$$C = C_W C_o K /(C_W + C_o K) . \tag{4}$$

If the cell is filled with air (K= 1),

$$C = C_W C_o / (C_W + C_o) \; . \qquad (5)$$

Any reading produced in the scale of the variable condenser in the reference oscillator will be the difference between the initial capacitance, C_a, (if tuned on air $C_a = C_W C_o/(C_W + C_o)$ and the final capacitance, C_b, or

$$C_A = C_W C_o K/(C_W + C_o K) - C_W C_o/(C_W + C_o) \qquad (6)$$

where C_A is apparent capacitance or scale reading.

The quantities, C_W and C_o , are constants of a particular cell and may be calculated in terms of scale units, or, if the scale is calibrated in capacitance units, in terms of capacitance units as follows.

Consider

$$S_1 = (C_W C_o K_1 / C_W + C_o K_1) - (C_W C_o / C_W + C_o) \qquad (7)$$

and

$$S_2 = (C_W C_o K_2 / C_W + C_o K_2) - (C_W C_o / C_W + C_o) \qquad (8)$$

where S_1 and S_2 are scale readings, and K_1 and K_2 are known dielectrics. Dividing equation (7) by equation (8) and rearranging the form below is obtained.

$$C_o/C_W = \frac{S_2(K_1 - 1) - S_1(K_2 - 1)}{K_1 S_1(K_2 - 1) - K_2 S_2(K_2 - 1)} \; . \qquad (9)$$

hence

$$C_W = \frac{S\ (C_W/C_o + 1) + KS\ (C_o/C_W + 1)}{K - 1} \qquad (10)$$

By a similar method C_o may be evaluated.

From the expression in equation (6), which may be rearranged to give,

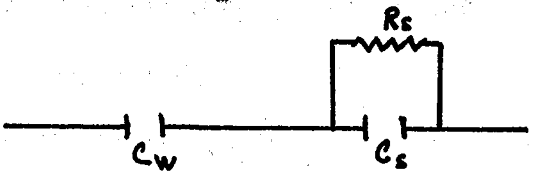
$$C_A = \frac{C_o\ (K-1)}{C_o/C_W(K(C_o/C_W+1)+1)+1} \quad . \tag{11}$$

It is readily seen that the apparent capacitance reading of the instrument is not a linear function of the dielectric constant of the sample. Figure 1 is a graph of dielectric constant for various liquids plotted against the scale readings. The limiting value is the value of C_W, which is dependent upon the thickness of the cell walls, the dielectric of wall material, the distance between the plates, etc. This is readily shown by the following equations.

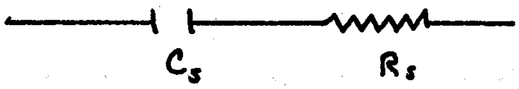
$$C_A = \lim_{C_o K \to 0} C_W\ C_o\ K/(C_W + C_o\ K) = 0 \tag{12}$$

$$C_A = \lim_{C_o K \to \infty} C_W\ C_o\ K/(C_W + C_o\ K) = C_W \tag{13}$$

For samples having appreciable conducting properties, the sample resistance, R_s, must be included. The circuit then becomes,



or as an equivalent series circuit,



By calculating the total impedance and separating this into real and imaginary components the following equation is obtained.

$$R = R_s / (R_s^2 w^2 C_s^2 + 1) \qquad (14)$$

where R_s is the effective resistance of the sample, C_s is the capacitance which would be produced in the absence of the conductive effect, and is proportional to the dielectric of the sample, and w is equal to 2 pi f. The expression for the capacitance then has the form,

$$C = \frac{C_w\ (R_s^2\ w^2\ C_s^2 + 1)}{R_s^2\ w^2\ C_w\ C_s + R_s^2\ w^2\ C_s^2\ 1} \qquad (15)$$

In terms of the dielectric constant, K, for any sample, equation (15) becomes,

$$C = \frac{C_w\ (R_s^2\ w^2\ C_o^2\ K2 + 1)}{(R_s^2\ w^2\ C_w\ C_o\ K) + (R_s^2\ w^2\ C_o^2\ K^2) + 1} \quad . \qquad (16)$$

The final scale reading, C_A, is then the difference between equation (16) and the quantity $C_w C_o / (C_w + C_o)$.

Various methods have been outlined for determining R_s independently. These have included using the specific resistance of the liquid sample and the cell geometry to calculate R_s or its measurement by high frequency impedance bridges. Sargent's, MANUAL OF CHEMICAL OSCILLOMETRY, (1957) has an outline of several methods with mathematical calculations presented.

CHAPTER IV

EXPERIMENTAL PROCEDURE

1. PREPARATION OF SOLUTIONS AND REAGENTS

The materials used in the work presented in this thesis included acetic anhydride, ethyl alcohol, pyridine, acetic acid, and ethyl acetate prepared and purified as indicated below.

The acetic anhydride was Matheson Co.'s 90% reagent, which was triply distilled in a 120 x 2 cm helix packed column. The cut having a boiling point range of 139.5-140 degrees centigrade was retained for use in the work. This reagent had a density of 1.087 $^{20/4}$ gms/ml.

Glacial acetic acid of 99.7% composition was distilled in the helix column. The fraction used had a boiling point range of 117.9-118.5 degrees centigrade. The density of this reagent was 1.050 $^{20/4}$ gms/ml.

The ethyl acetate used was reagent grade further purified by distillation in the helix column. The fraction retained for experimental work had a boiling point range of 76.9-77.2 degrees centigrade and a density of 0.900 $^{20/4}$ gms/ml.

Absolute ethyl alcohol (100%) from commercial source was used without further purification. Density of this reagent was 0.788 $^{20/4}$ gms/ml.

Reagent grade pyridine, triply distilled in the helix column, was used. The fraction having a boiling point range of 115.1-115.4 degrees centigrade was retained. The density of this reagent was 0.983 $^{20/4}$ gms/ml.

All reagents were maintained in glass stoppered flasks, and normal precautions taken to avoid contamination.

The volume of each reagent used, both for the calibration curves and the actual runs, was calculated from the density measurement of the particular reagent and delivered by means of calibrated burrettes. Table I is a comparison of the volume of each reagent to the number of moles it contains.

II. OPERATIONS AND PROCEDURE

The instrument was allowed to warm up at least twenty four hours prior to each use to avoid any possibility of drift due to lack of thermal equilibrium in the electronic components. During all of the present work a constant source of 250 volts was maintained from a Heathkit model PS-3 power supply unit.

For the calibration of scale units to concentrations of reactants and products, the procedure consisted, firstly, of filling the sample holder with the calculated volume of the reactants and products at twenty five degrees centigrade. The sample holder was then immediately inserted into the instrument, the timer started, and the desired amount of pyridine catalyst added. The mixture was stirred and the instrumental reading taken. A series of timed readings were continued in order to extrapolate back to zero time for the actual reading desired. A retuning "zero", consisting of a mixture of ethyl alcohol and ethyl acetate, was contained in an identical sample holder, and used prior to and after each instrumental reading.

The instrument was tuned so that the "zero" gave a reading of 70 scale units .

For the runs to determine the instrumental response to concentration change during the actual reaction, the procedure consisted of filling the sample holder with the desired volume of acetic anhydride and ethyl alcohol. These reagents were maintained at twenty five degrees centigrade by means of a thermostat. The sample cell was then inserted into the cell holder, and the desired amount of catalyst added. The stirrer was started and the timer turned on when one half of the catalyst had been delivered.

A stopper, through which a hole was drilled for the stirrer, was kept in place on the sample cell to minimize the loss by vaporization of the ethyl acetate formed.

The temperature was maintained at twenty five degrees centigrade (as measured by a calibrated 17-32 deg thermometer) by means of an ice-water thermostat. Prior to, and after each reading, the EtOH-EtAc "zero" was inserted in the cell holder, and the instrument retuned to 70 to avoid any error due to instrumental drift.

No attempt was made to insure that readings were taken at definite time intervals, as the maintenance of constant temperature conditions prevented this. As often as possible, two or three readings were taken very close together in order to determine the precision of the instrumental response.

In each case the initial scale reading of the reactants was obtained by extrapolation.

CHAPTER V

BASIS FOR KINETIC CALCULATIONS

The derivation of the fundamental expression for second order reactions is well known. However, it will be briefly presented here in order that methods of treating the oscillometric data may be shown.

Since the rate of a second order reaction is dependent upon two concentrations, if a and b are the initial concentrations of the reactants, and x is the amount reacted after time, t, then

$$dx/dt = k(a-x)(b-x) \ . \qquad (1)$$

The integrated form of this expression becomes,

$$k = 2.303/t(a-b) \log b(a-x)/a(b-x) \qquad (2)$$

where k is the rate constant.

The general methods for determining the rate constant include substitution of the values for a, b, and x into the equation at varying values of t to see if k is a constant value. Graphical treatment consists of plotting t against log $a-x/b-x$, which should yield a straight line, the slope of which is $k(a-b)/2.303$.

In order to utilize data obtained from the oscillometer, it must be interpreted in terms of the reaction variable, x. If the variable is a linear function of the scale readings obtained, then the scale readings may be used directly to evaluate x. Flom and Elving (1953) reported this method to be successful in evaluating the reaction variable in the alkaline hydrolysis of lower aliphatic esters. Their work was done on dilute aqueous solutions of electrolytes and, hence, the data obtained was primarily due to a conductive phenomenom.

A determination of scale readings with varying composition of reactants and products in the present investigation showed the reaction variable, x, to be a non-linear function of the scale readings. In order to compensate for this, it is necessary to first construct a calibration curve by plotting scale readings against varying concentrations of reactants and products. The calibration is done by relating a definite sdale value to a series of known concentrations of reactants and products. In this manner, the scale reading may be interpreted in terms of molar concentrations.

If it is desired, the scale values may be utilized to interpret the reaction variable directly by drawing a straight line from the initial to the final scale reading. The experimental scale reading falling on the curved line, may then be read as an actual scale reading on the straight line at the same time value. Since the total scale change is proportional to the total concentration change, and the initial concentration of the reactant present in the lesser amount, b, is also proportional to the total concentration change providing the reaction goes to completion, then the initial concentration, b, is proportional to $S_o - S_\infty$ and the decrease after time, t, is proportional to $(S_o - S_t)/(S_o - S_\infty)$. This may be expressed as,

$$x = ((S_o - S_t) / (S_o - S_\infty))\, b = yb \tag{3}$$

where S_t is the scale reading at time, t, corrected to the straight line to compensate for non linearity of x as a function of scale units.

The method of utilizing scale units directly to evaluate x is very valuable where it can be shown that x is a linear function of the scale, since it eliminates the necessity of calibration. However, in the present investigation, the calibration method is considered more useful.

Since there is a possibility that a consecutive, competing reaction in the substances studied may be important, the method presented by Frost and Pearson was utilized to check this possibility. The complex reaction considered is shown below.

$$Ac_2O + EtOH \longrightarrow HAc + EtAc$$

and

$$EtOH + HAc \longrightarrow H_2O + EtAc$$

In terms of symbols these substances are defined as ETOH = A, Ac_2O = B, HAc = C, EtAc = E, and H_2O = D. The following relationship is then apparent.

$$A + B \xrightarrow{k1} C + E$$

$$A + C \xrightarrow{k2} D + E$$

The differential expression for the rates of reaction becomes,

$$dA/dt = -k_1AB - k_2AC \qquad (4)$$

By imposing the condition that $A_o = 2B_o$, it follows that $C = A - 2B$, and equation (4) becomes,

$$dA/dt = (2k_2 - k_1)AB - k_2A^2 \ . \qquad (5)$$

Frost and Schweneer have studied and obtained solutions for various limiting cases where the reactions are second order. The first of these is where k_1 is very much greater than k_2 so that the first step is very rapid compared to the second. The reaction studied was thought to be this case, and the calculations following indicate this to be true.

The second case is where k_2 is very much greater than k_1, and the third case where $k_1 = 2k_2$. By introducing dimensionless variables p, q, r, and a parameter, s, where $p = A/A_o$, $q = B/B_o$, $r = B_ok_1t$, and $s = k_2/k_1$, and substituting these values into equation (5), the subsequent integral may be evaluated to give for these special calculations of cases the following solutions:

For $s = 0$ (k_1 much greater than k_2)

$$r = \ln((q+1)/2q) \quad \text{and} \quad p = (q+1)/2 \qquad (6)$$

For $s = \frac{1}{2}$ ($k_1 = 2k_2$)

$$r = 1/p - 1 \quad \text{and} \quad p^2 = q \qquad (7)$$

For $s = \infty$ (k_2 much greater than k_1)

$$r = \tfrac{1}{2}(1/q - 1) \quad \text{and} \quad p = q$$

Table X shows the strict adherence the reactions studied in this investigation maintain with the first case, and the writer assumes this is the condition imposed upon the reaction.

CHAPTER VI

CALCULATIONS AND RESULTS

The rate constant in the following tables are calculated according to the second order expressions presented in the preceding chapter. In all cases the initial concentration of Ac_2O was 0.5 moles and EtOH was 1.0 moles. The concentration variable, x, is found for any time, t, from the plot of b-x (moles) against t.

As an example, consider the run using two ml of pyridine catalyst. At twenty minutes reaction time (t=20), b-x = 0.325 moles and a-x = 0.825 moles. Then the calculations are as shown below.

$$k = (2.303/t\ (a-b))\log(b(a-x)/a(b-x))$$

$$k = (2.303/20\ \text{min} \times .5\ \text{moles})\log(.5 \times .825/.325) \times .106\ \text{liters}$$

$$k = 0.002539\ \text{liters min}^{-1}\text{moles}^{-1}$$

All calculations of k are done in this manner except that the volume used is the actual volume of the solution at a given concentration of reactants and products. This volume varies from 104 to 108 ml dependent upon the concentration of pyridine.

Figures 7, 10, 15, 18, 22, 25, 29, and 32 are plots of log b(a-x)/ a(b-x) vs. time (min). The slope of the straight line is equal to k (a-b)/2,303

Table XI shows the comparison of k calculated from substitution in the second order equation, with k calculated from the slope of the line in the log plot.

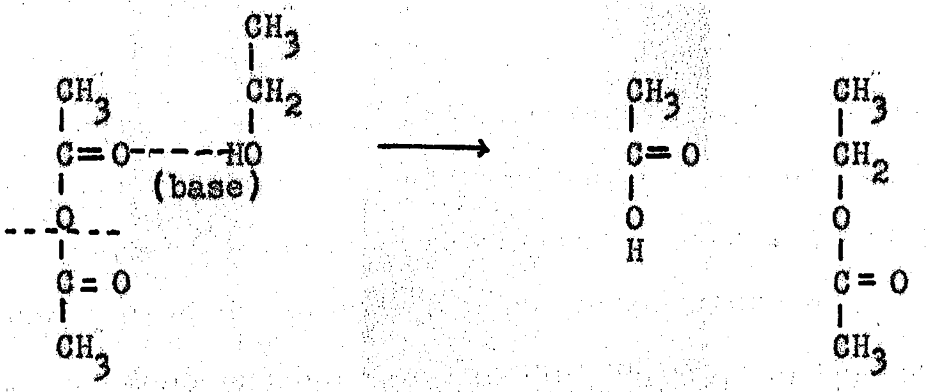
Table X is a comparison of the rate constant as calculated from experimental data with a constant calculated according to the methods previously presented for handling competitive reactions. It is readily seen that only the case where k_1 is very much greater than k_2 agrees with the experimental data.

In the present work only the values for k between ten and eighty percent reaction are used. These are considered to be the most reliable. The small deviation in the values of the rate constants within the 10-80% range is taken as evidence of their reliability; the values prior to 10% reaction being obtained, in most cases, by extrapolation, and those over 80% reaction considered inaccurate due to loss of EtAc by evaporation.

The experimental data obtain ed in this investigation indicate the rate constant of the reaction between Ac_2O and EtOH to produce HAc and EtAc to be a linear function of the amount of pyridine used as a catalyst (Fig. 33).

Jarama and Kubota (1953,1954) studied this reaction by means of the vapor pressure method and also reported their observation of this linear relationship. However, since no data is available from their work under conditions similar to those in which the present investigation was carried out, the exact values for the rate constants are not comparable. It is nonetheless interesting to note the similarity of results obtained by the two different methods as to the linearity of the pyridine concentration as a function of the rate constant.

The mechanism for this reaction has been proposed as shown below.



The pyridine (or other organic base) facilitates the transfer of the proton from the ethanol,and the cleavage of the anhydride molecule is analagous to the same procedure in the hydrolysis of acetic anhydride.

The decrease in the rate of reaction as the reaction progresses is partially attributed to the neutralization of pyridine by the HAc formed, and hence, a lessening in its ability to facilitate the removal of a proton from the EtOH molecule. However, the remaining AcO^- will compensate for this somewhat. Jarama and Kubota (1954) investigated the effect upon the rate constant of adding Hac to the reaction mixture. They found some evidence of catalyst poisoning. The reader is referred to the original paper for a more complete treatment of this effect.

CHAPTER VII

SUMMARY

A one hundred twenty megacycle oscillometer was used to study the kinetics of the reaction of Ac_2O and EtOH to produce HAc and EtAc. Pyridine was used to catalyze this esterification, and a linear relationship noted between the pyridine concentration and the rate constant.

It was shown that the effect of a competing reaction (HAc plus EtOH to give H_2O plus EtAc) is negligible by comparing the experimental values of the two rate constants with values for these constants as calculated by methods for special limiting relationships.

The instrument is considered to be entirely satisfactory for kinetic studies in polynary solutions providing there is sufficient difference in the capacitative effects of the reactants and products, as indicated by their dielectric constants.

Two graphs are presented showing the instrumental response to dielectric change and to electrolytic concentration change. The instrument, using the present sample cell construction, is not sufficiently sensitive for use with electrolytic solutions.

TABLE I

COMPARISON OF VOLUME TO MOLES OF REAGENT

EtOH		Ac_2O		HAc		EtAc	
VOLUME (ml)	MOLES	VOLUME (ml)	MOLES	VOLUME (ml)	MOLES	VOLUME (ml)	MOLES
58.30	1.0	46.80	0.5	0	0	0	0
56.85	0.95	42.10	0.45	2.86	0.05	4.89	0.05
52.45	0.9	37.50	0.4	5.71	0.1	9.78	0.1
46.64	0.8	28.10	0.3	11.42	0.2	19.55	0.2
40.78	0.7	18.70	0.2	17.15	0.3	29.35	0.3
34.98	0.6	9.35	0.1	22.86	0.4	38.93	0.4
29.15	0.5	0	0	28.56	0.5	48.89	0.5

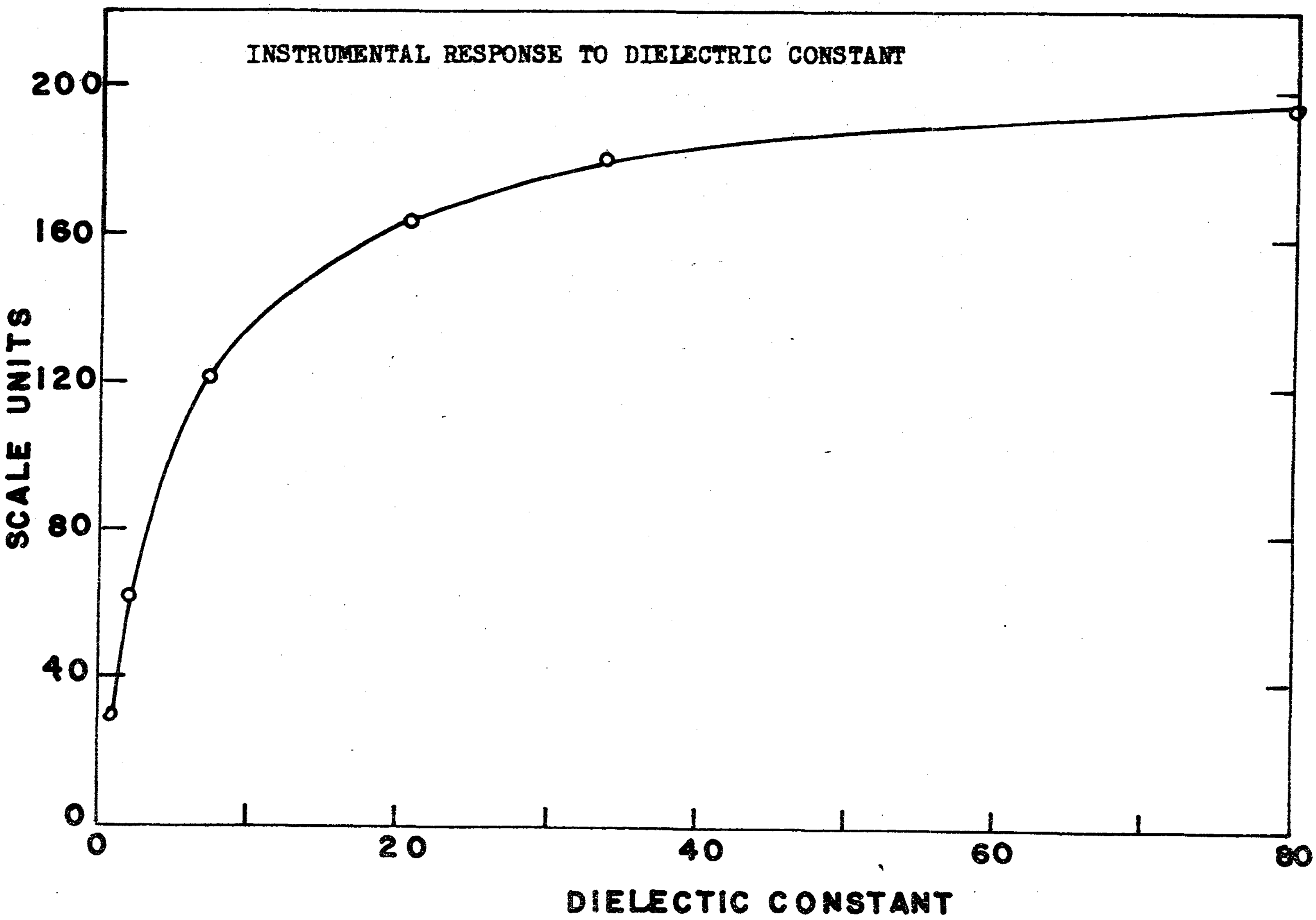

INSTRUMENTAL RESPONSE TO DIELECTRIC CONSTANT
SCALE UNITS
200
160
120
80
40
0
0
20
40
60
80
DIELECTIC CONSTANT

FIGURE I

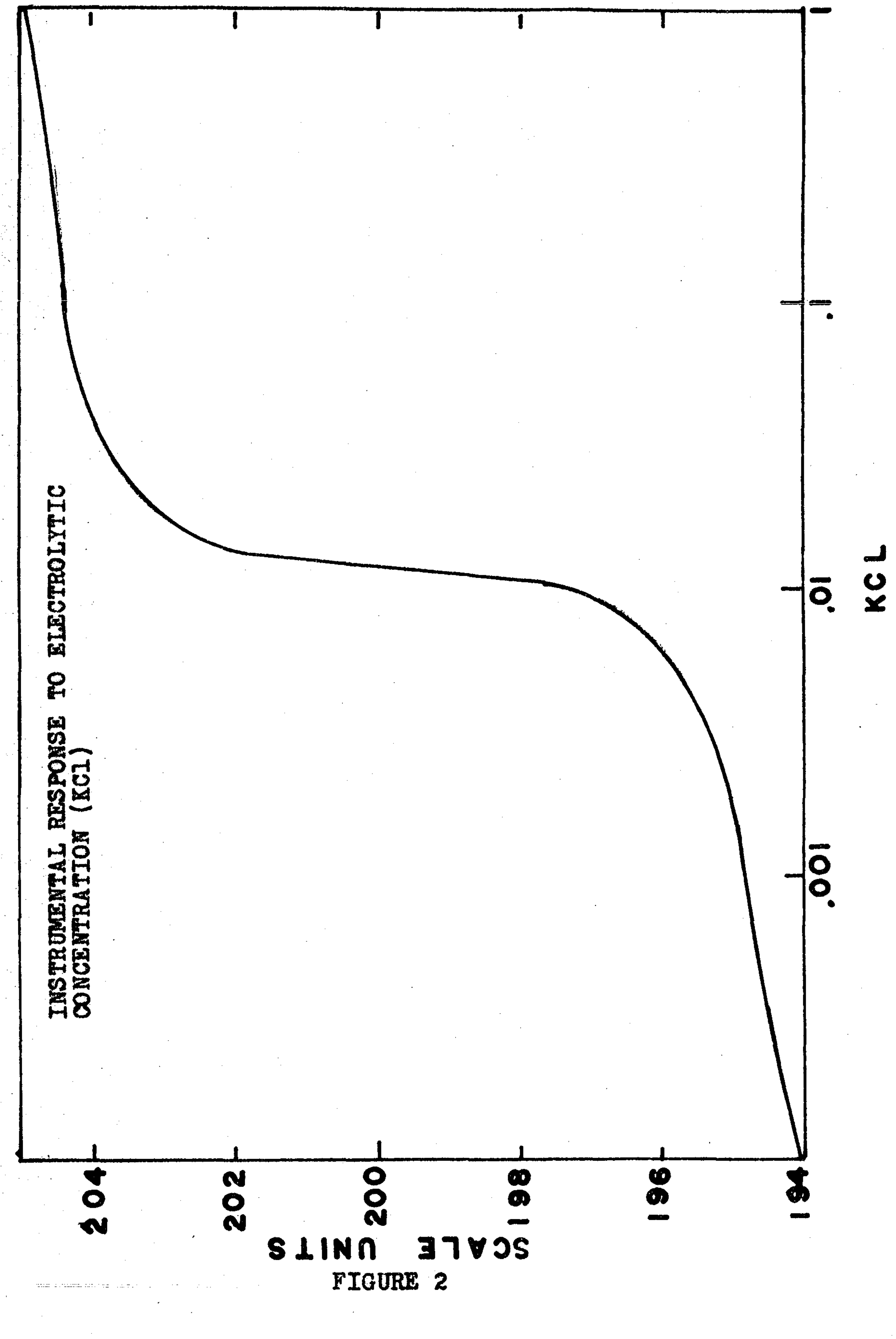

INSTRUMENTAL RESPONSE TO ELECTROLYTIC CONCENTRATION (KCl)
204
202
200
198
196
194
SCALE UNITS
.001
.01
.1
KCL

FIGURE 2

TABLE II

EXPERIMENTAL DATA - RUN # 1

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $(\frac{\text{moles}}{\text{min l}})$
5	0.43	0.93	0.034	0.922	0.003319
10	0.387	0.887	0.060	0.461	0.002905
15	0.354	0.854	0.082	0.308	0.002660
20	0.325	0.825	0.104	0.2303	0.002539
25	0.299	0.799	0.126	0.1842	0.002461
30	0.277	0.777	0.147	0.1537	0.002395
35	0.253	0.753	0.173	0.1318	0.002415
40	0.235	0.735	0.195	0.1151	0.002375
45	0.215	0.715	0.221	0.1024	0.002395
50	0.198	0.698	0.236	0.0922	0.002398
55	0.182	0.682	0.273	0.0838	0.002420
60	0.169	0.669	0.297	0.0768	0.002415
65	0.156	0.656	0.323	0.0709	0.002425
70	0.145	0.645	0.347	0.0658	0.002420
75	0.134	0.634	0.374	0.0615	0.002435
80	0.127	0.627	0.393	0.0576	0.002400

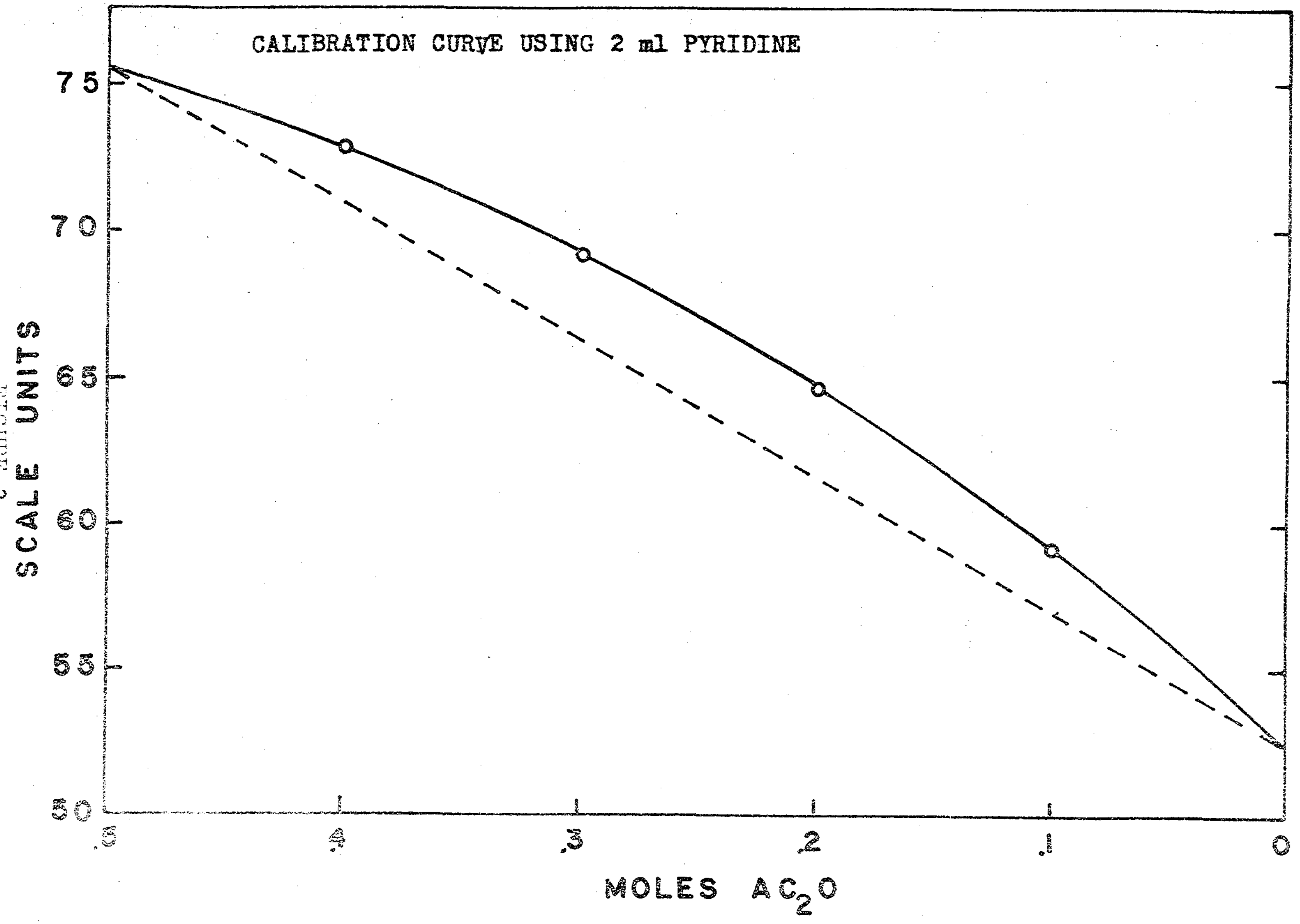
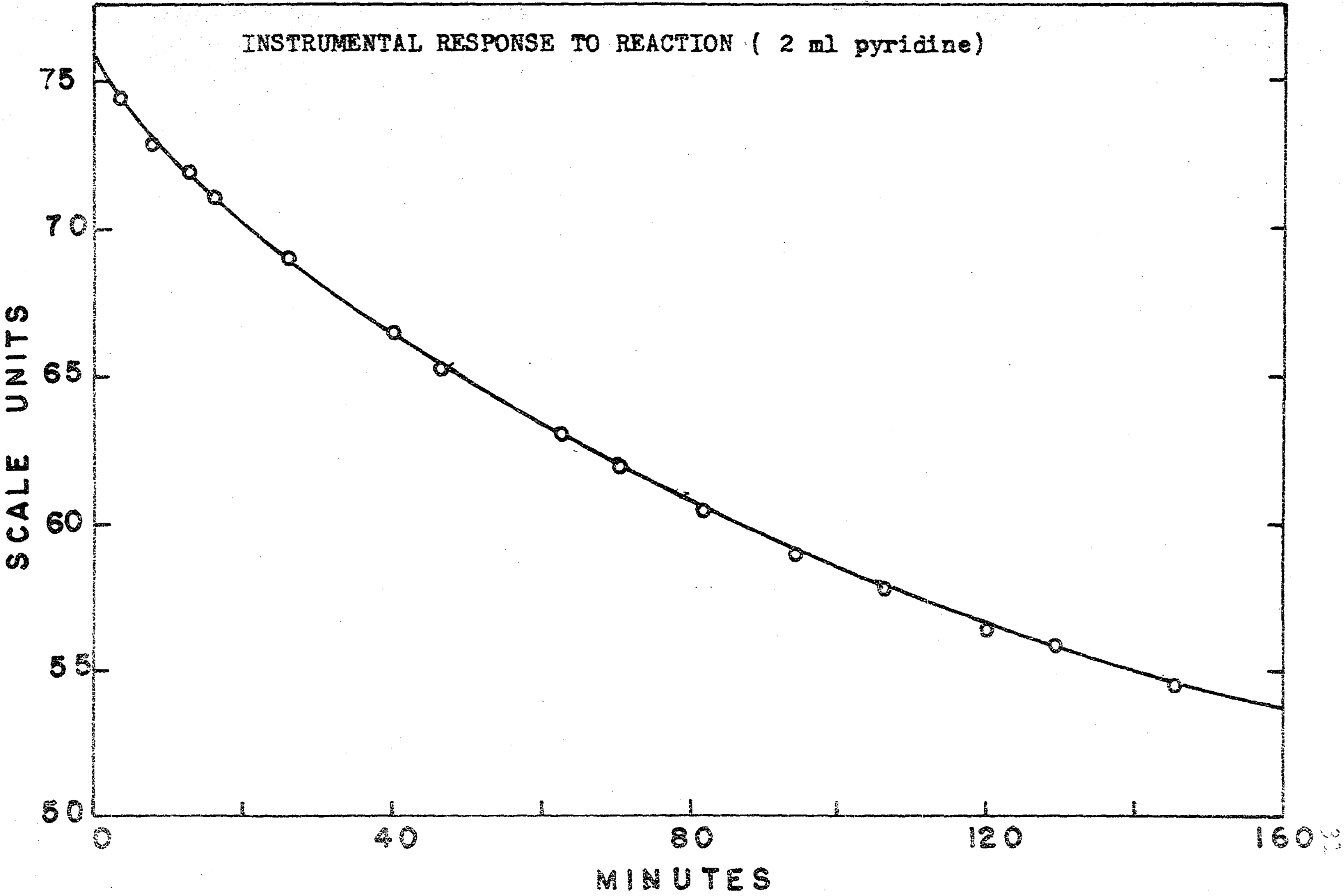

CALIBRATION CURVE USING 2 ml PYRIDINE
SCALE UNITS
75
70
65
60
55
50
.5
.4
.3
.2
.1
0
MOLES AC_2O

FIGURE 3

FIGURE 4


INSTRUMENTAL RESPONSE TO REACTION (2 ml pyridine)
SCALE UNITS
75
70
65
60
55
50
0
40
80
120
160
MINUTES

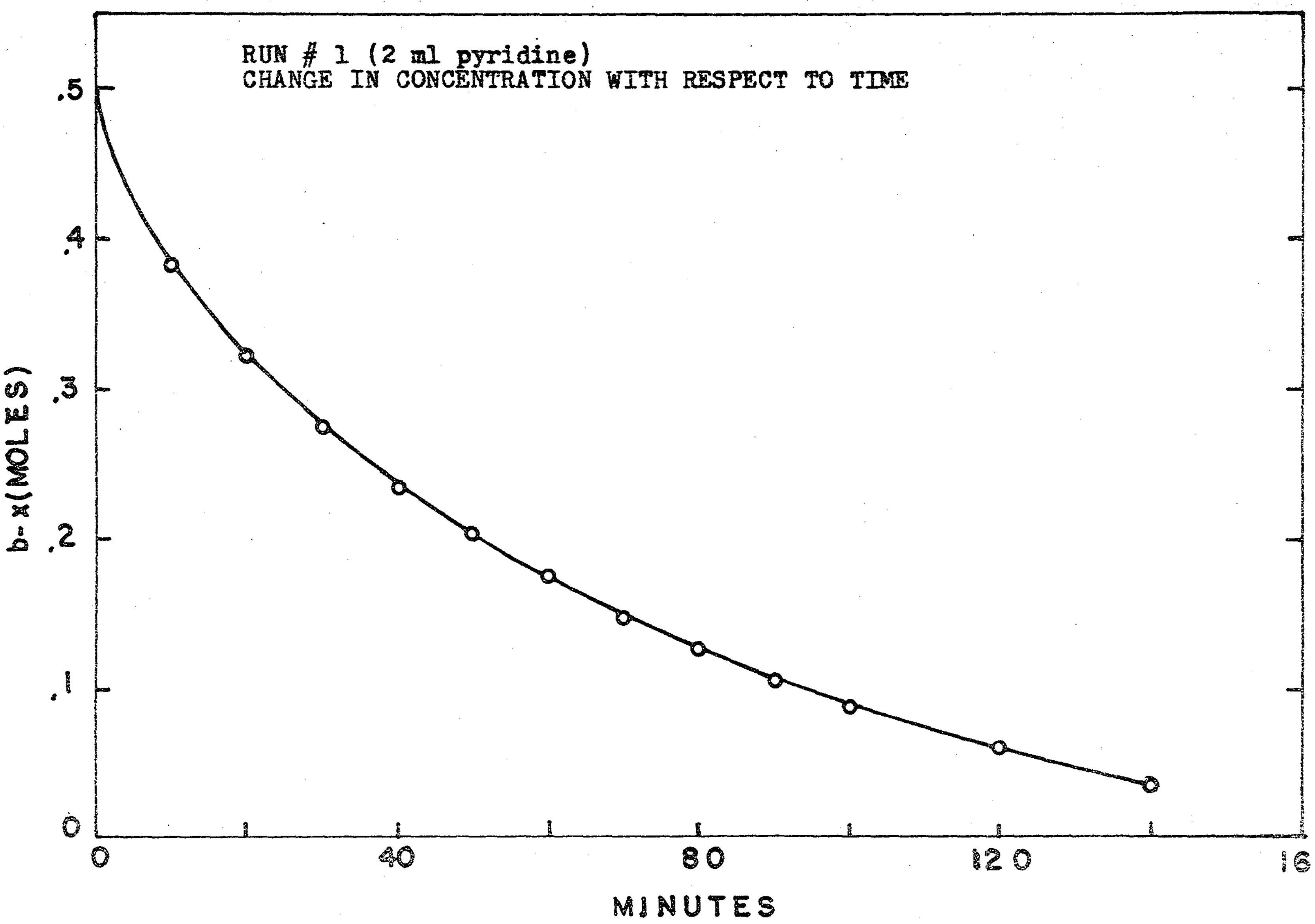

RUN # 1 (2 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
b-x(MOLES)
.5
.4
.3
.2
.1
0
0
40
80
120
160
MINUTES

FIGURE 5

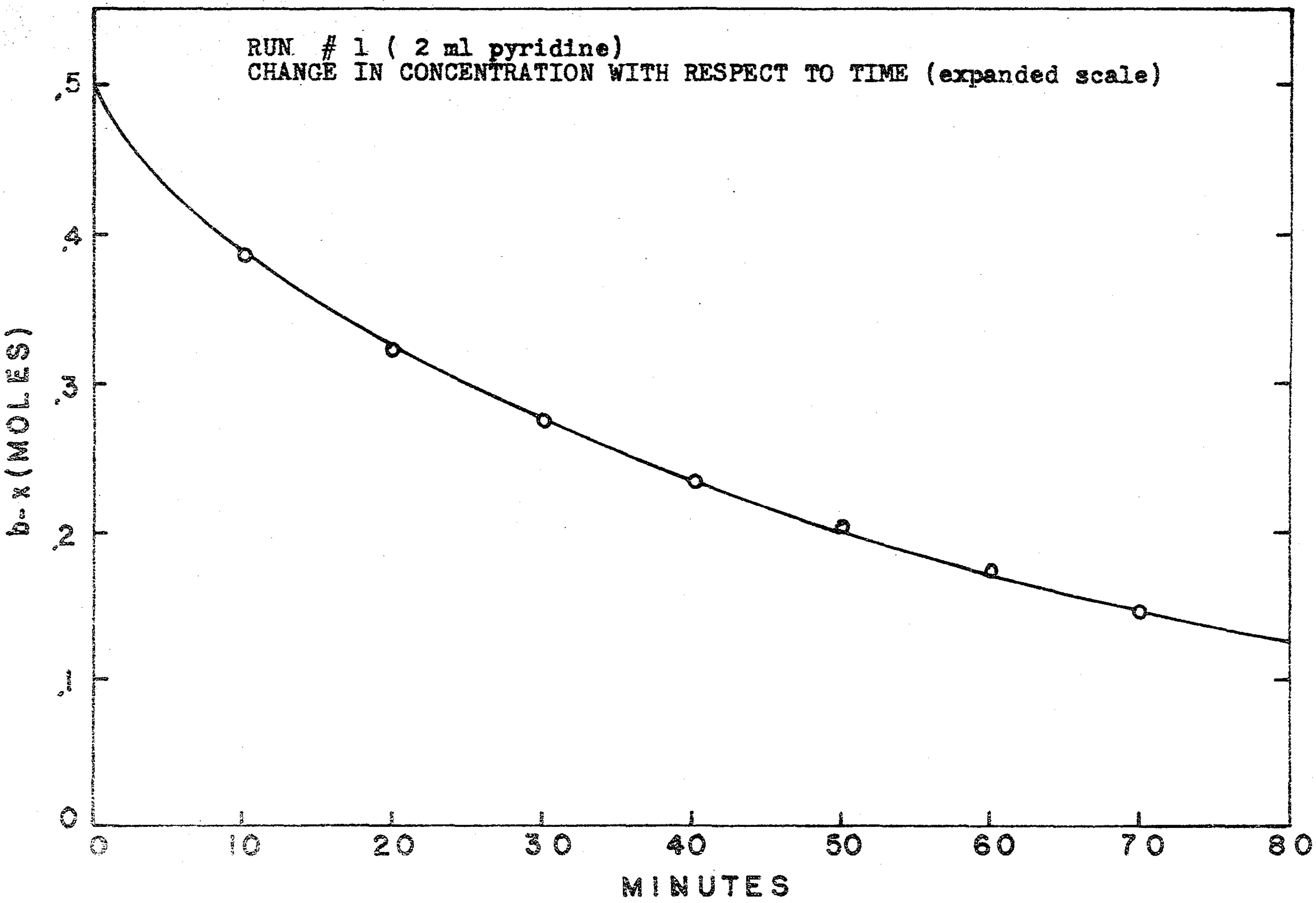

RUN # 1 (2 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME (expanded scale)
b-x (MOLES)
.5
.4
.3
.2
.1
0
0
10
20
30
40
50
60
70
80
MINUTES

FIGURE 6

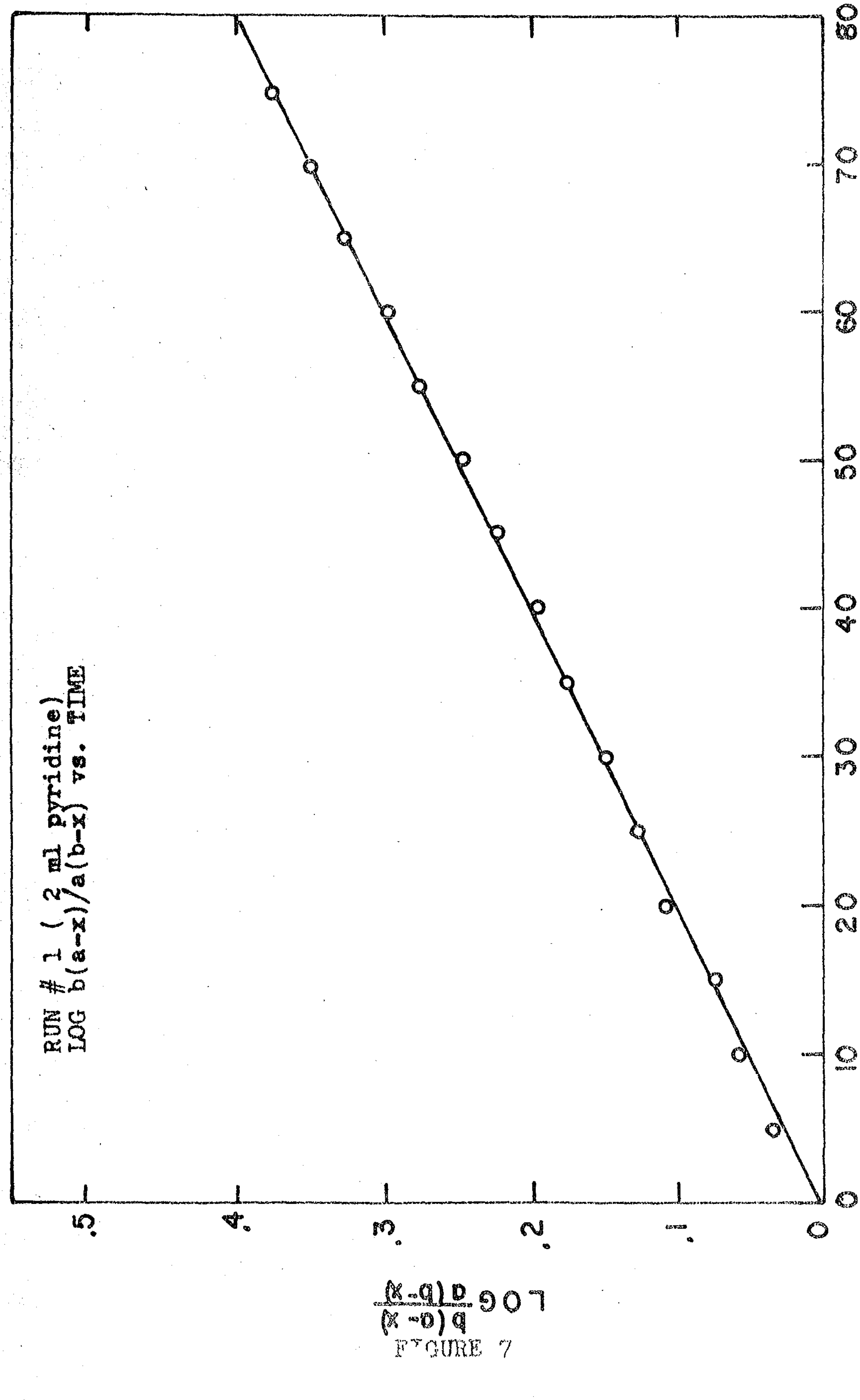

RUN # 1 (2 ml pyridine)
LOG b(a-x)/a(b-x) vs. TIME
0
10
20
30
40
50
60
70
80
MINUTES
0
.1
.2
.3
.4
.5
LOG $\frac{b(a-x)}{a(b-x)}$

FIGURE 7

TABLE III

EXPERIMENTAL DATA - RUN # 2

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $\left(\frac{\text{moles}}{\text{min l}}\right)$
10	0.388	0.888	0.0589	0.461	0.002881
20	0.329	0.829	0.1005	0.2303	0.002450
30	0.282	0.782	0.1427	0.1537	0.002321
40	0.244	0.744	0.1830	0.1151	0.002235
50	0.210	0.710	0.2281	0.0922	0.002225
60	0.185	0.685	0.2683	0.0768	0.002182
70	0.258	0.658	0.3190	0.0658	0.002231
80	0.133	0.633	0.3762	0.0576	0.002294
90	0.114	0.614	0.4303	0.0512	0.002335

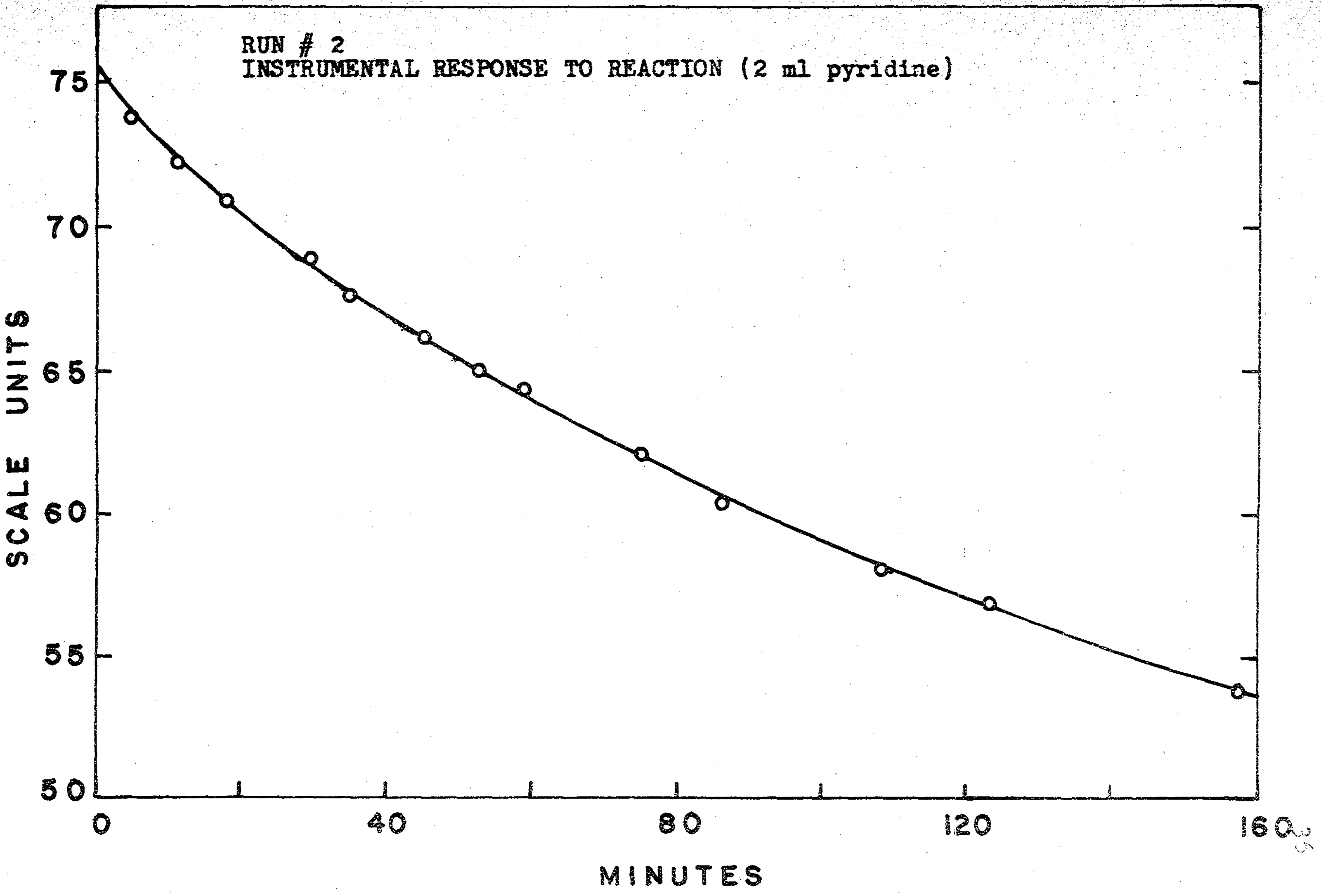

RUN # 2
INSTRUMENTAL RESPONSE TO REACTION (2 ml pyridine)
SCALE UNITS
75
70
65
60
55
50
0
40
80
120
160
MINUTES

FIGURE 8

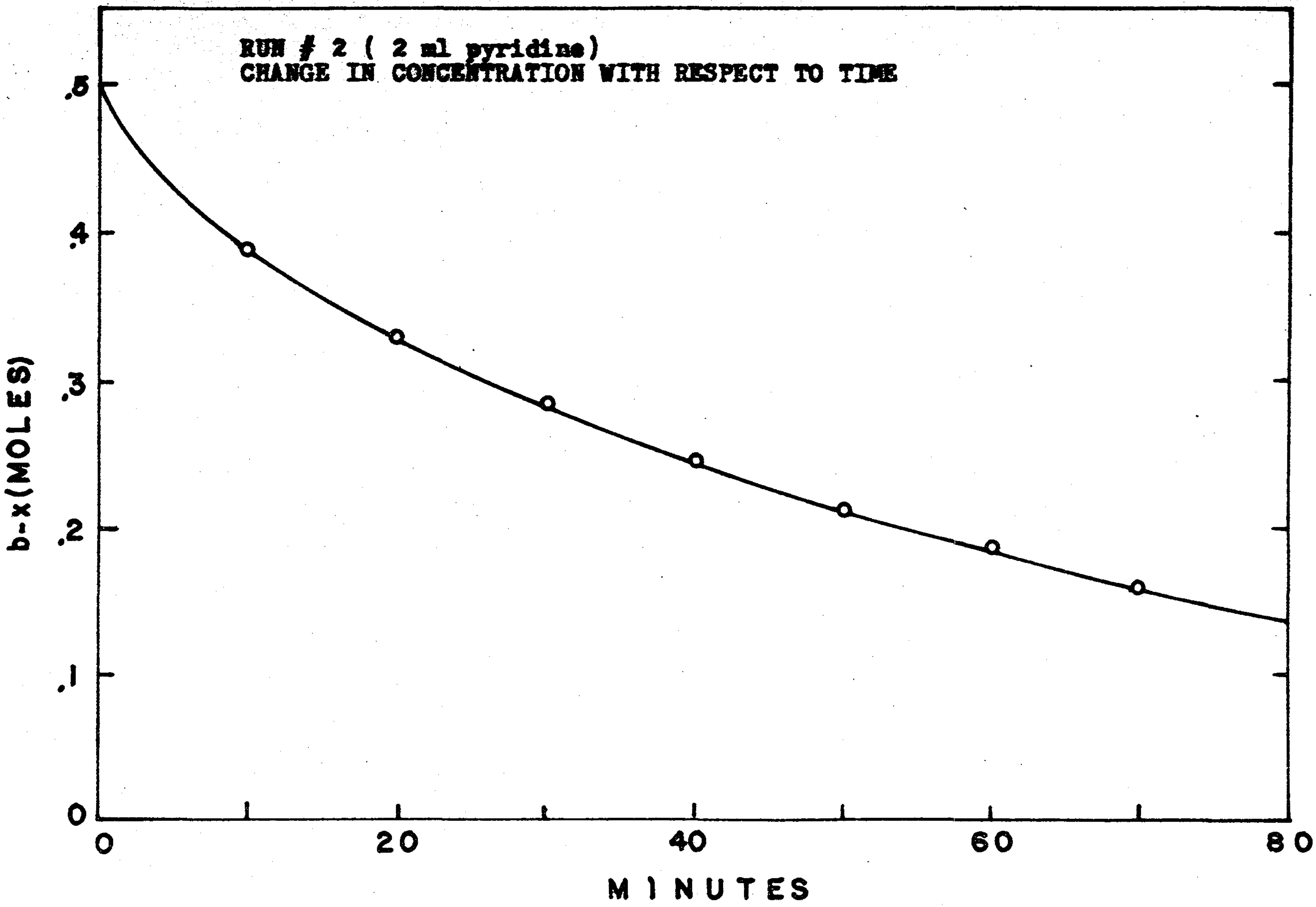

RUN # 2 (2 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
b-x(MOLES)
.5
.4
.3
.2
.1
0
0
20
40
60
80
MINUTES

FIGURE 9

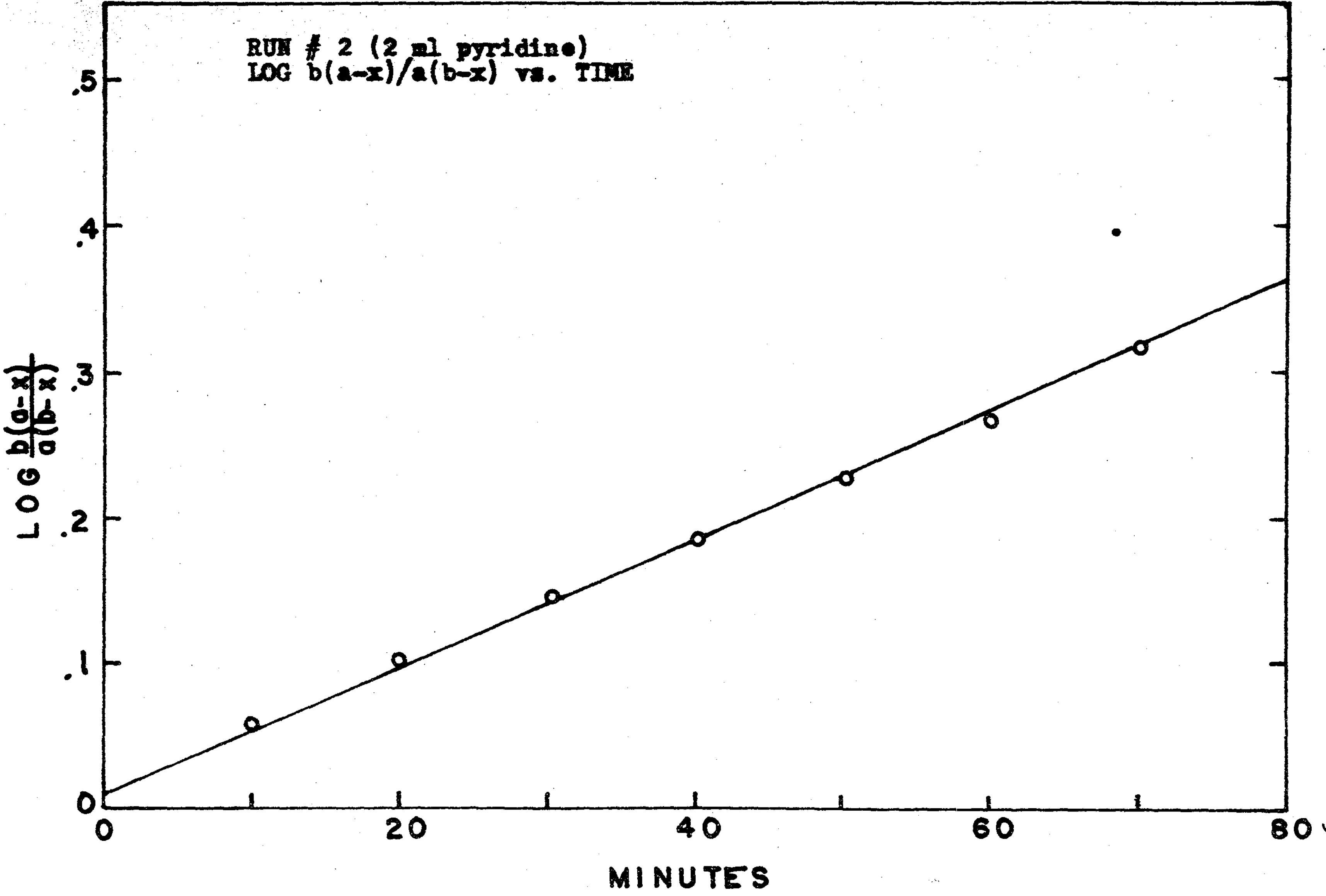

RUN # 2 (2 ml pyridine)
LOG b(a-x)/a(b-x) vs. TIME
LOG $\frac{b(a-x)}{a(b-x)}$
.5
.4
.3
.2
.1
0
0
20
40
60
80
MINUTES

FIGURE 10

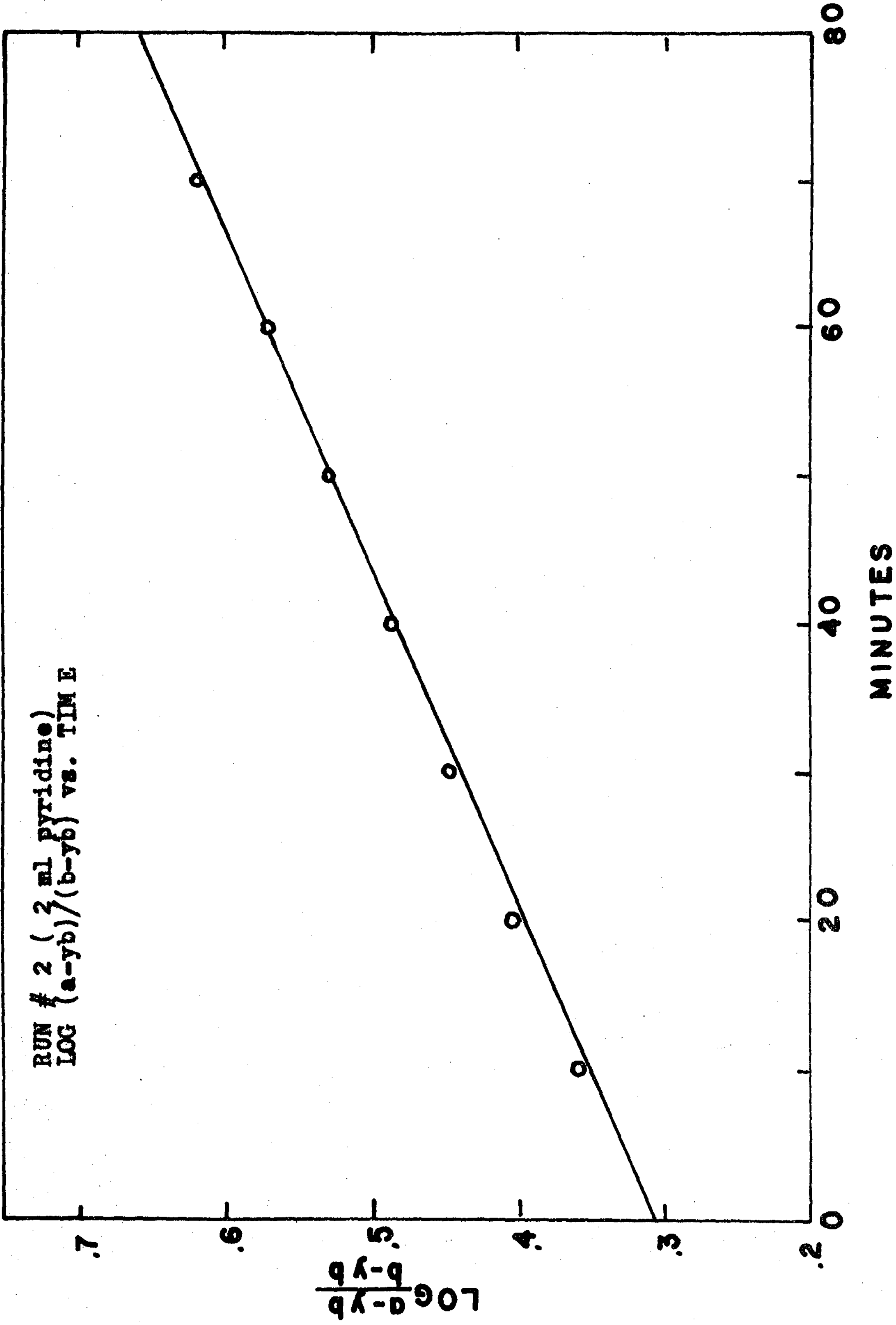

RUN # 2 (2 ml pyridine)
LOG (a-yb)/(b-yb) vs. TIM E
.7
.6
.5
.4
.3
.2
$\text{LOG}\frac{a-yb}{b-yb}$
0
20
40
60
80
MINUTES

FIGURE 11

TABLE IV

EXPERIMENTAL DATA - RUN # 3

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $\left(\frac{moles}{min\ l}\right)$
5	0.371	0.871	0.070	0.922	0.00684
10	0.304	0.804	0.1215	0.461	0.00594
15	0.259	0.759	0.166	0.307	0.00541
20	0.221	0.721	0.212	0.2303	0.00517
25	0.189	0.689	0.2608	0.184	0.00510
30	0.162	0.662	0.311	0.1535	0.00506
35	0.138	0.638	0.364	0.1318	0.00509
40	0.118	0.618	0.4185	0.1151	0.00511
45	0.099	0.599	0.480	0.1023	0.00521

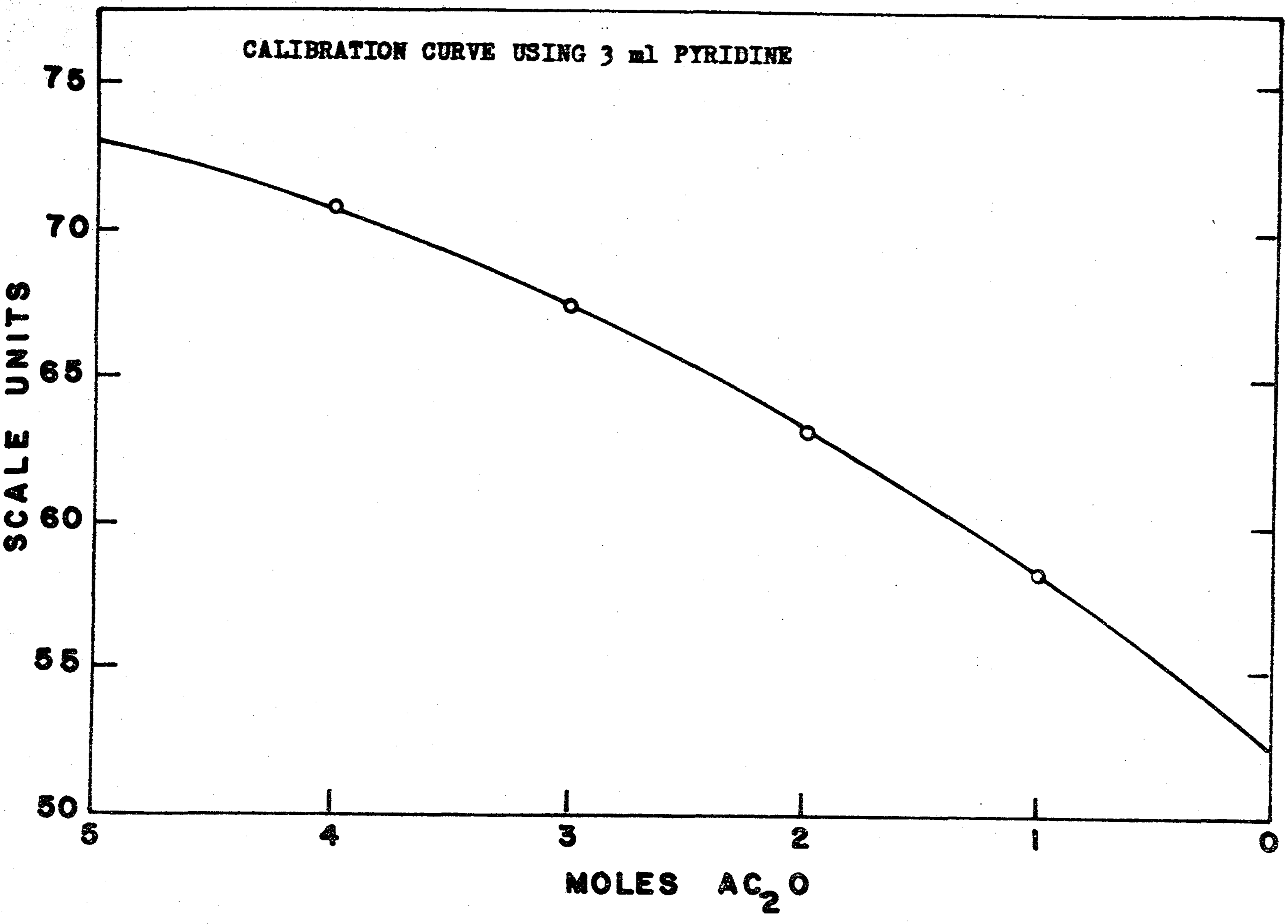

CALIBRATION CURVE USING 3 ml PYRIDINE
SCALE UNITS
75
70
65
60
55
50
5
4
3
2
1
0
MOLES AC_2O

FIGURE 12

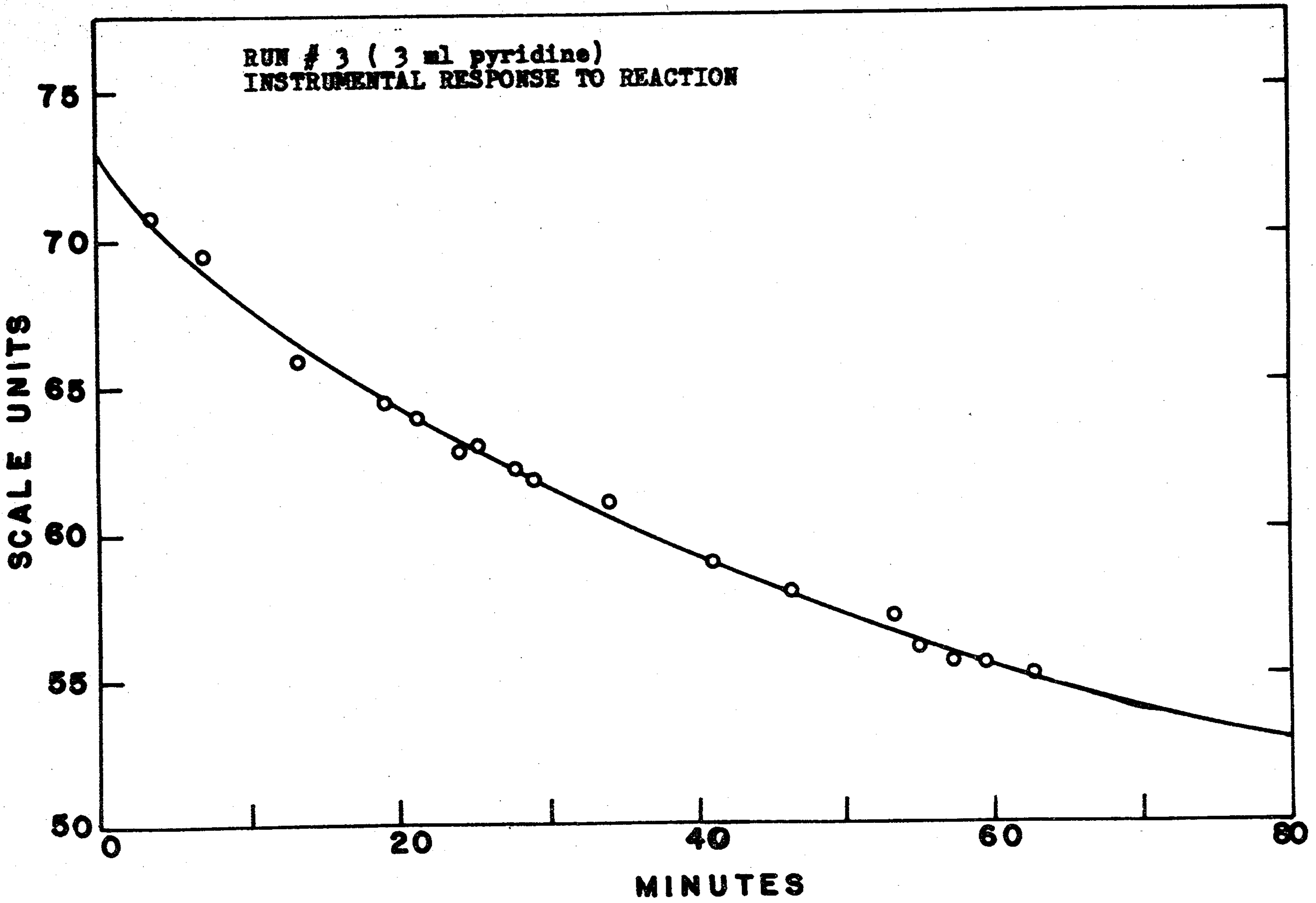

RUN # 3 (3 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION
SCALE UNITS
75
70
65
60
55
50
MINUTES
0
20
40
60
80

FIGURE 13

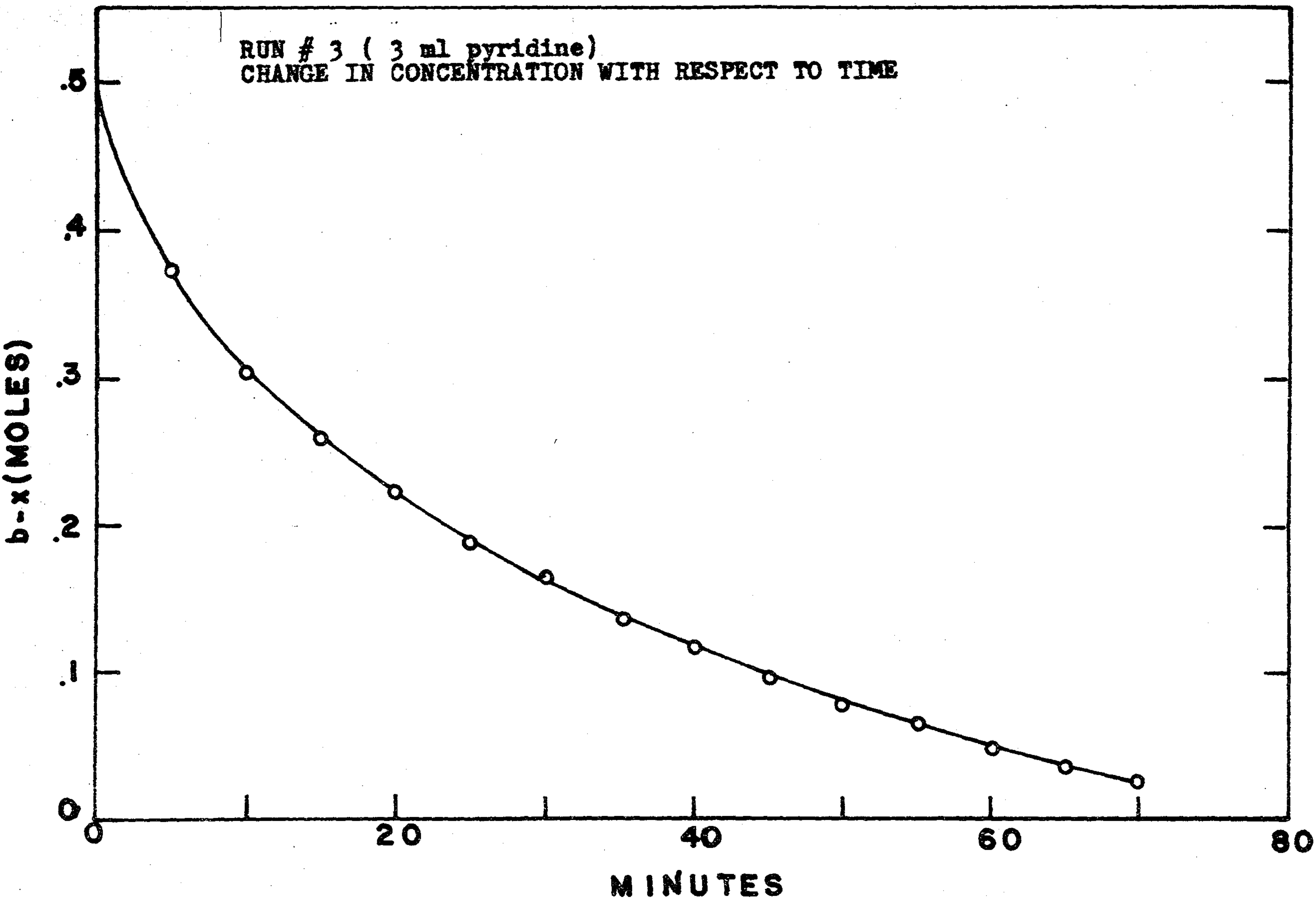

RUN # 3 (3 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
b-x(MOLES)
.5
.4
.3
.2
.1
0
0
20
40
60
80
MINUTES

FIGURE 14

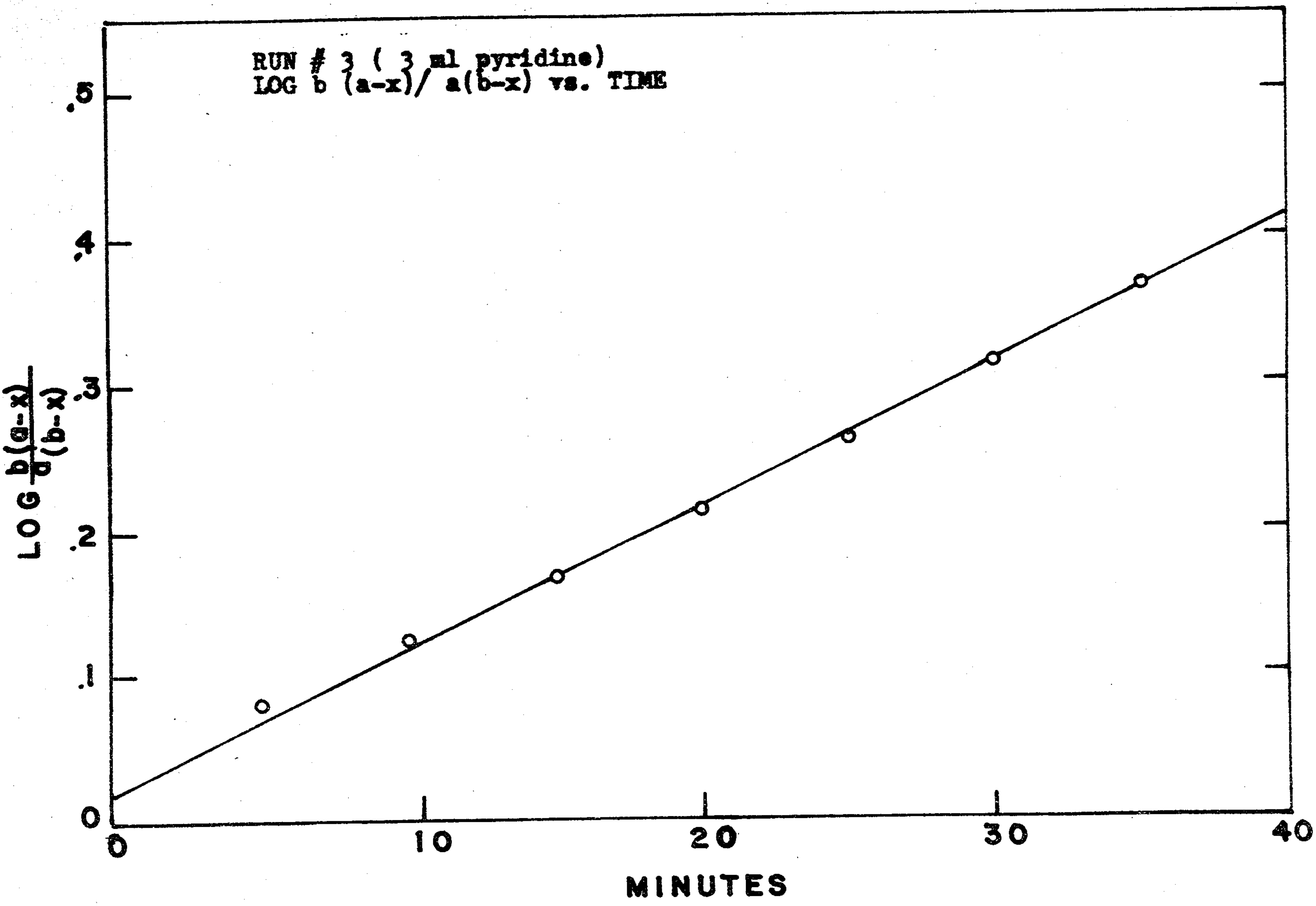
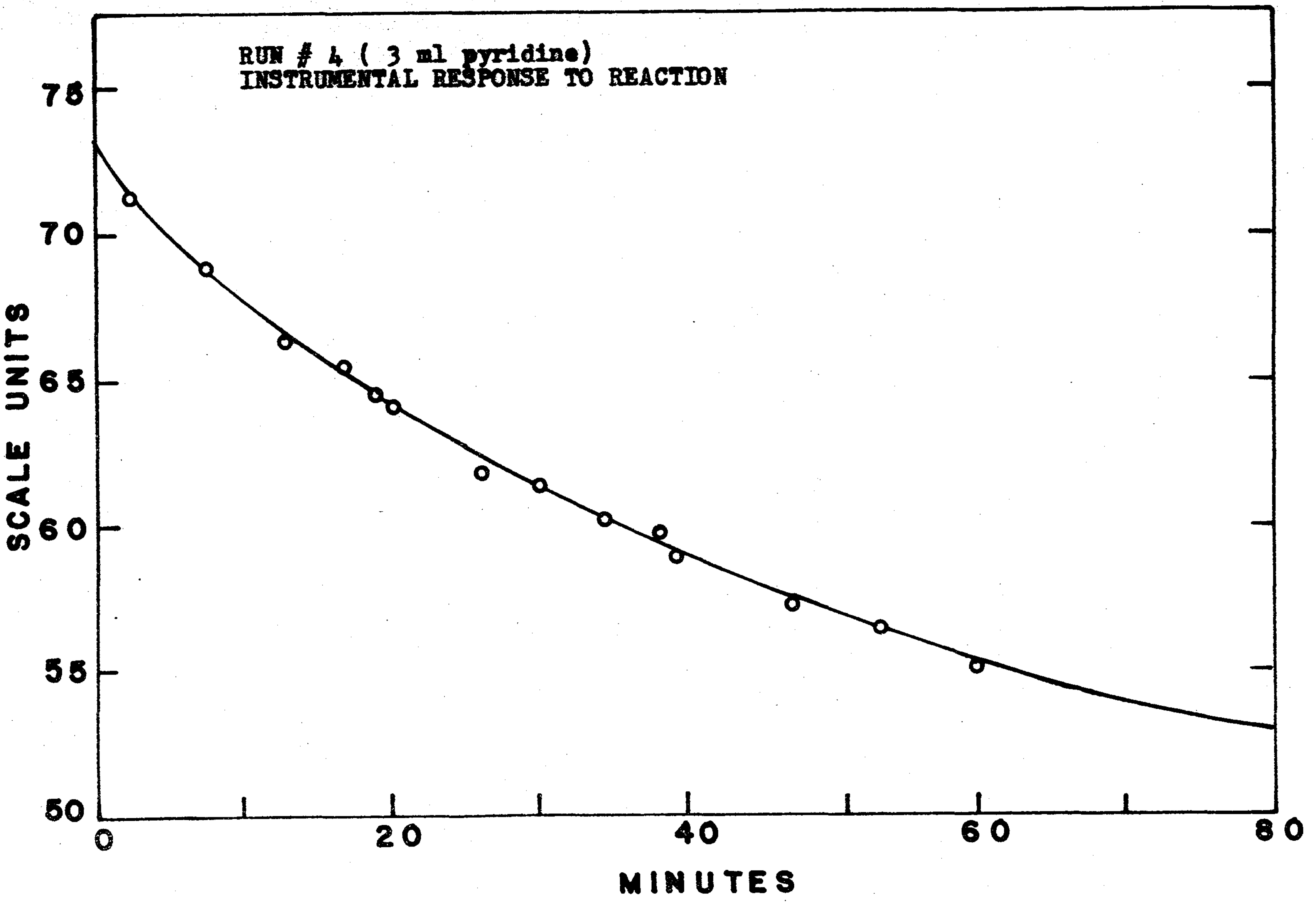

RUN # 3 (3 ml pyridine)
LOG b (a-x)/ a(b-x) vs. TIME
.5
.4
.3
.2
.1
0
LOG $\frac{b(a-x)}{a(b-x)}$
0
10
20
30
40
MINUTES

FIGURE 15

TABLE V

EXPERIMENTAL DATA - RUN # 4

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $(\frac{\text{moles}}{\text{min l}})$
5	0.374	0.874	0.068	0.922	0.00665
10	0.302	0.802	0.123	0.461	0.00600
15	0 .251	0.751	0.176	0.307	0.005725
20	0.211	0.711	0.228	0.2303	0.00556
25	0.180	0.680	0.277	0.184	0.00540
30	0.152	0.651	0.332	0.1535	0.00540
35	0.129	0.629	0.387	0.1318	0.00540
40	0.108	0.608	0.449	0.1151	0.00547
45	0.090	0.590	0.516	0.1023	0.00559



RUN # 4 (3 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION

FIGURE 16

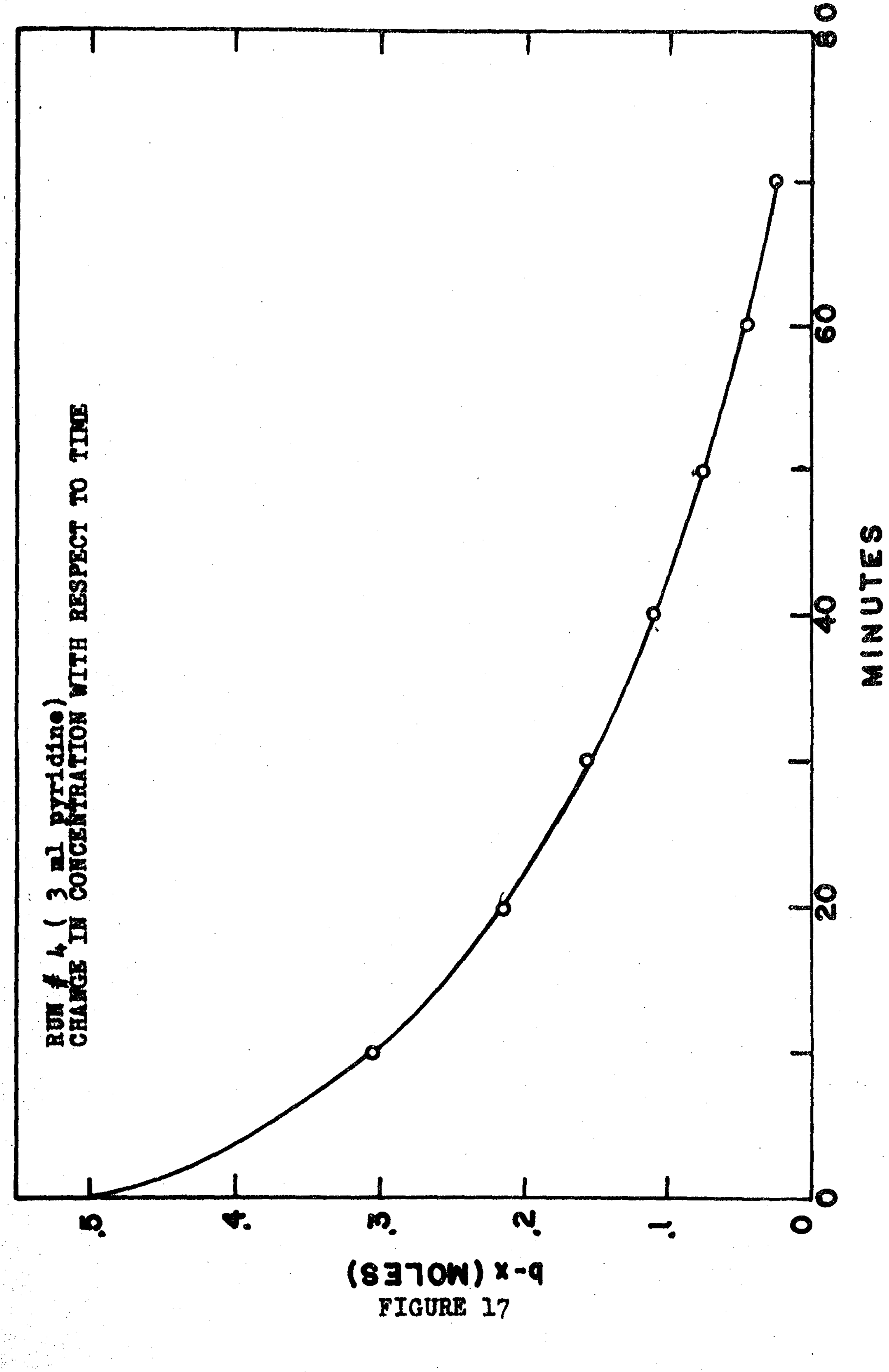

RUN # 4 (3 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
MINUTES
0
20
40
60
80
.5
.4
.3
.2
.1
0
b-x (MOLES)

FIGURE 17

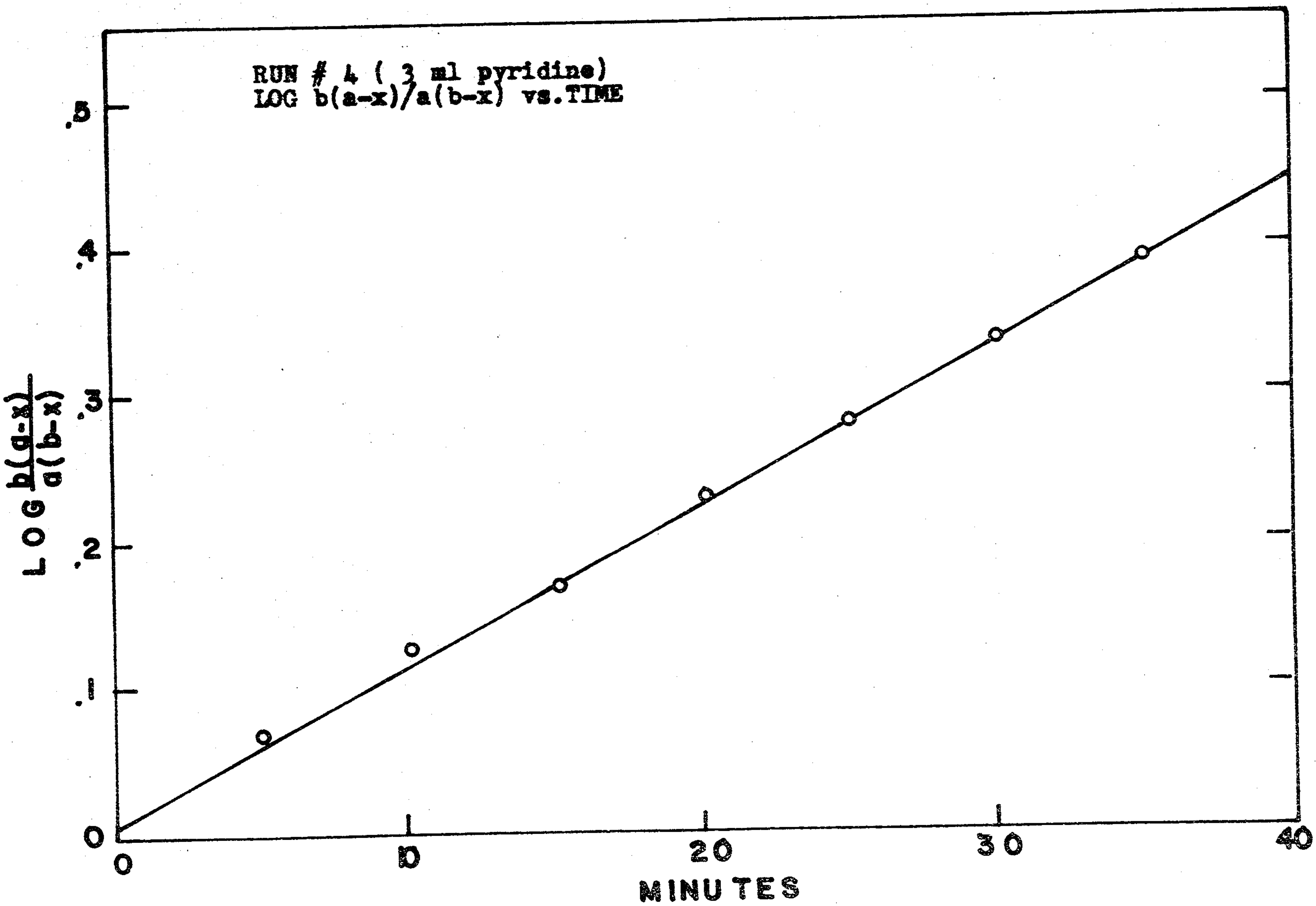

RUN # 4 (3 ml pyridine)
LOG b(a-x)/a(b-x) vs.TIME
LOG $\frac{b(a-x)}{a(b-x)}$
0
.1
.2
.3
.4
.5
0
10
20
30
40
MINUTES

FIGURE 18

TABLE VI

EXPERIMENTAL DATA - RUN # 5

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $(\frac{\text{moles}}{\text{min l}})$
2	0.436	0.936	0.031	2.303	0.00764
4	0.389	0.889	0.058	1.151	0.00715
6	0.348	0.848	0.086	0.769	0.00706
8	0.313	0.813	0.114	0.576	0.007025
10	0.284	0.784	0.140	0.461	0.00690
12	0.252	0.752	0.174	0.384	0.00713
14	0.229	0.729	0.202	0.329	0.00710
16	0.206	0.706	0.234	0.288	0.00721
18	0.186	0.686	0.266	0.256	0.00727
20	0.167	0.667	0.301	0.2303	0.00741
22	0.151	0.651	0.333	0.209	0.00745
24	0.135	0.635	0.372	0.192	0.00764
26	0.120	0.620	0.412	0.177	0.00780
28	0.107	0.607	0.454	0.1645	0.00790

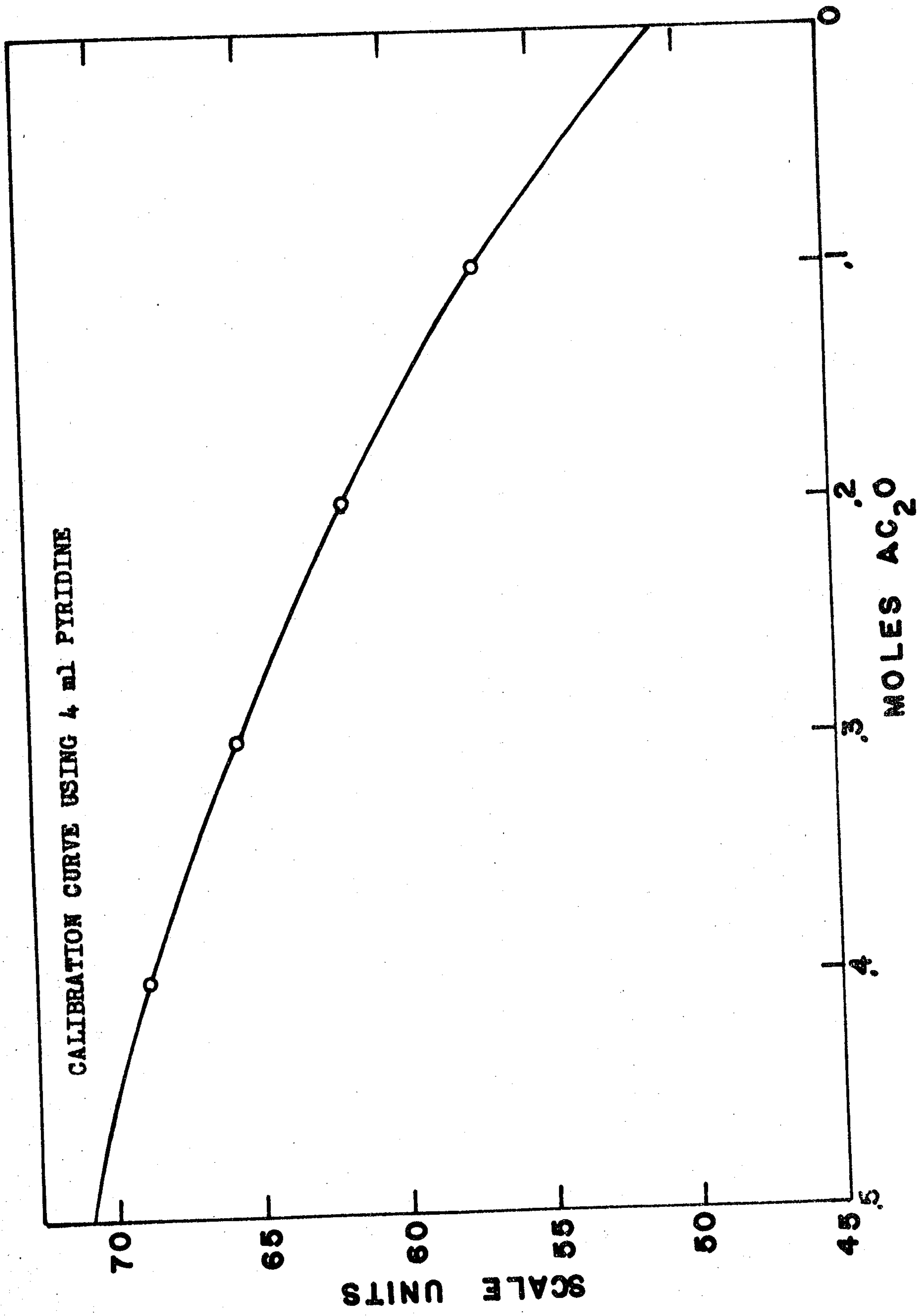

CALIBRATION CURVE USING 4 ml PYRIDINE
MOLES AC_2O
0
.1
.2
.3
.4
.5
SCALE UNITS
45
50
55
60
65
70

FIGURE 19

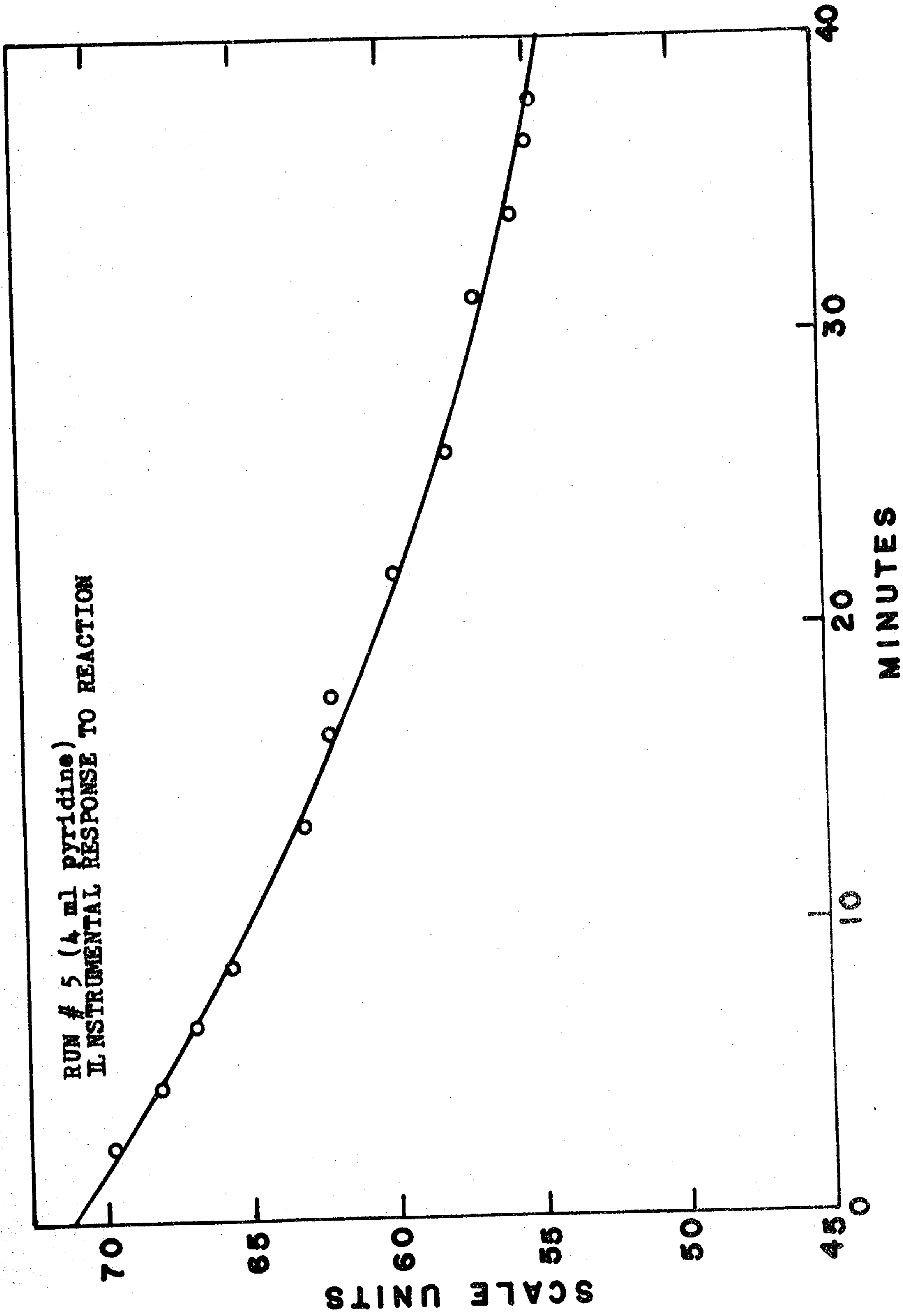

RUN # 5 (4 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION
MINUTES
0
10
20
30
40
SCALE UNITS
45
50
55
60
65
70

FIGURE 20

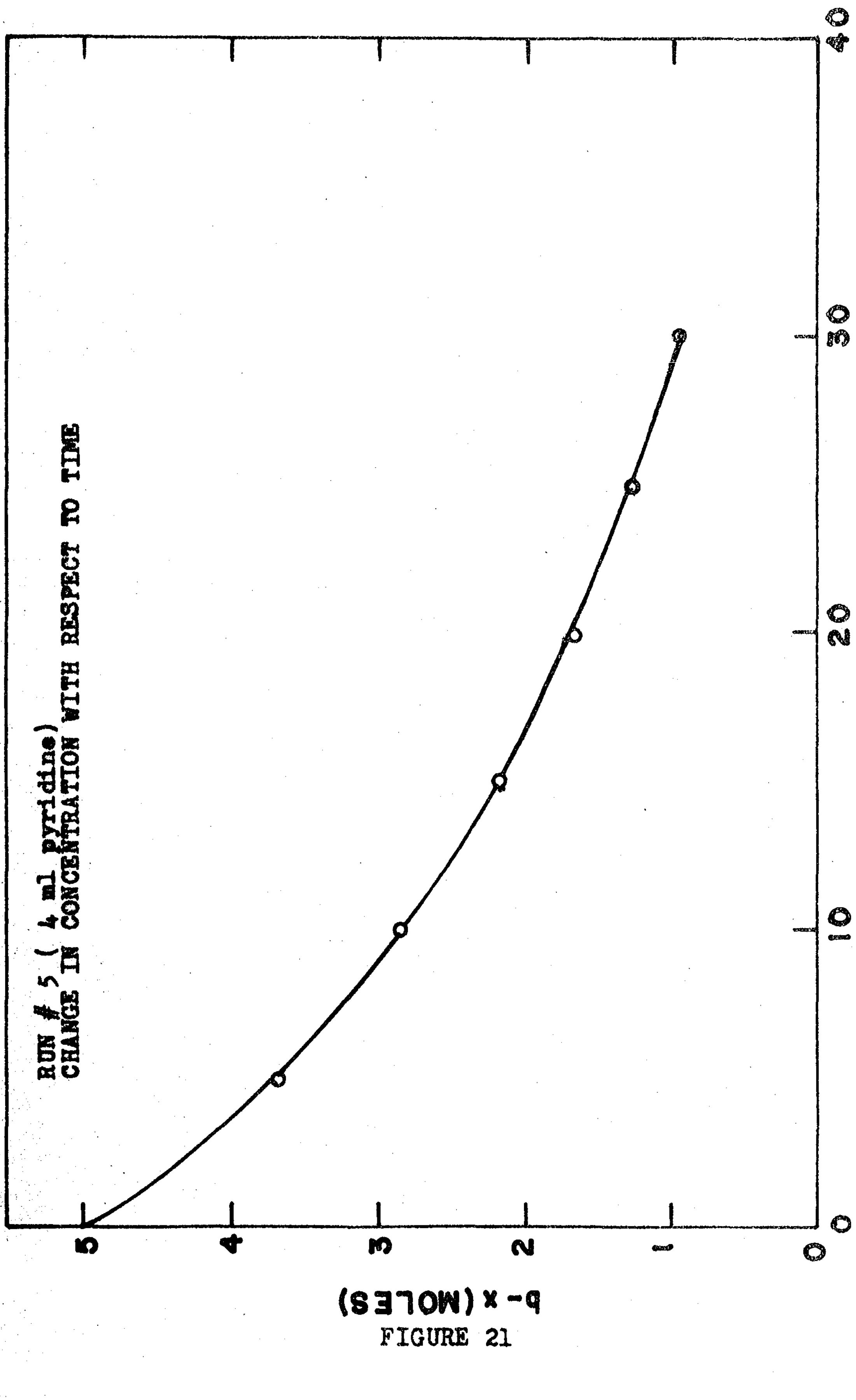

RUN # 5 (4 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
b- x (MOLES)
5
4
3
2
1
0
MINUTES
0
10
20
30
40

FIGURE 21

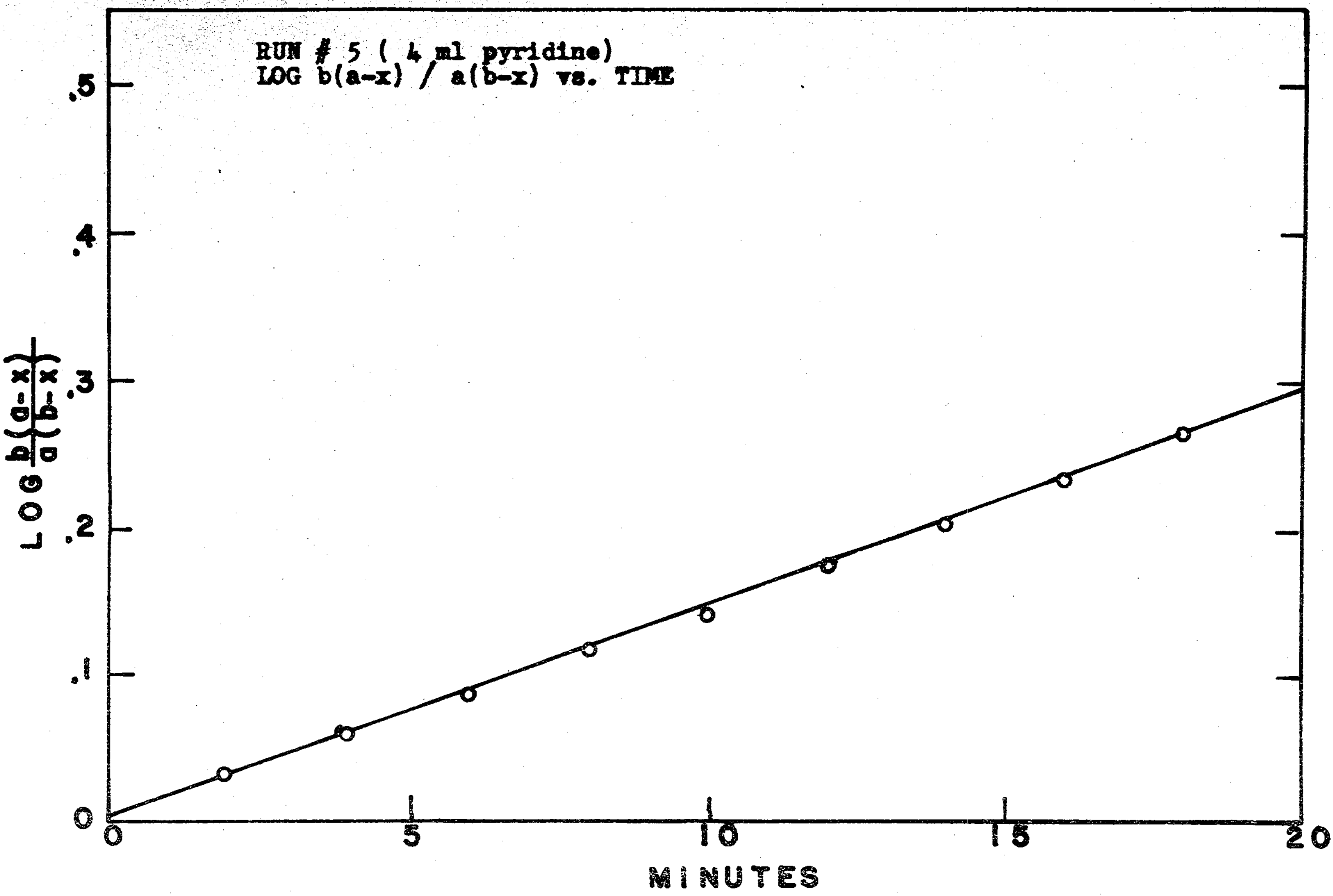

RUN # 5 (4 ml pyridine)
LOG b(a-x) / a(b-x) vs. TIME
.5
.4
.3
.2
.1
0
LOG $\frac{b(a-x)}{a(b-x)}$
0
5
10
15
20
MINUTES

FIGURE 22

TABLE VII

EXPERIMENTAL DATA - RUN # 6

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $(\frac{\text{moles}}{\text{min l}})$
2	0.430	0.930	0.0335	2.303	0.00773
4	0.383	0.883	0.0615	1.151	0.00752
6	0.344	0.844	0.089	0.764	0.00731
8	0.310	0.810	0.116	0.576	0.00714
10	0.282	0.782	0.142	0.461	0.00699
12	0.256	0.756	0.170	0.384	0.00699
14	0.232	0.732	0.198	0.329	0.00696
16	0.211	0.711	0;226	0.288	0.006975
18	0.191	0.691	0.257	0.256	0.00702
20	0.173	0.673	0.289	0.2303	0.00713
22	0.157	0.657	0.321	0.209	0.00720
24	0.140	0.640	0.360	0.192	0.00739
26	0.125	0.625	0.398	0.177	0.00754
28	0.111	0.611	0.439	0.1645	0.00772

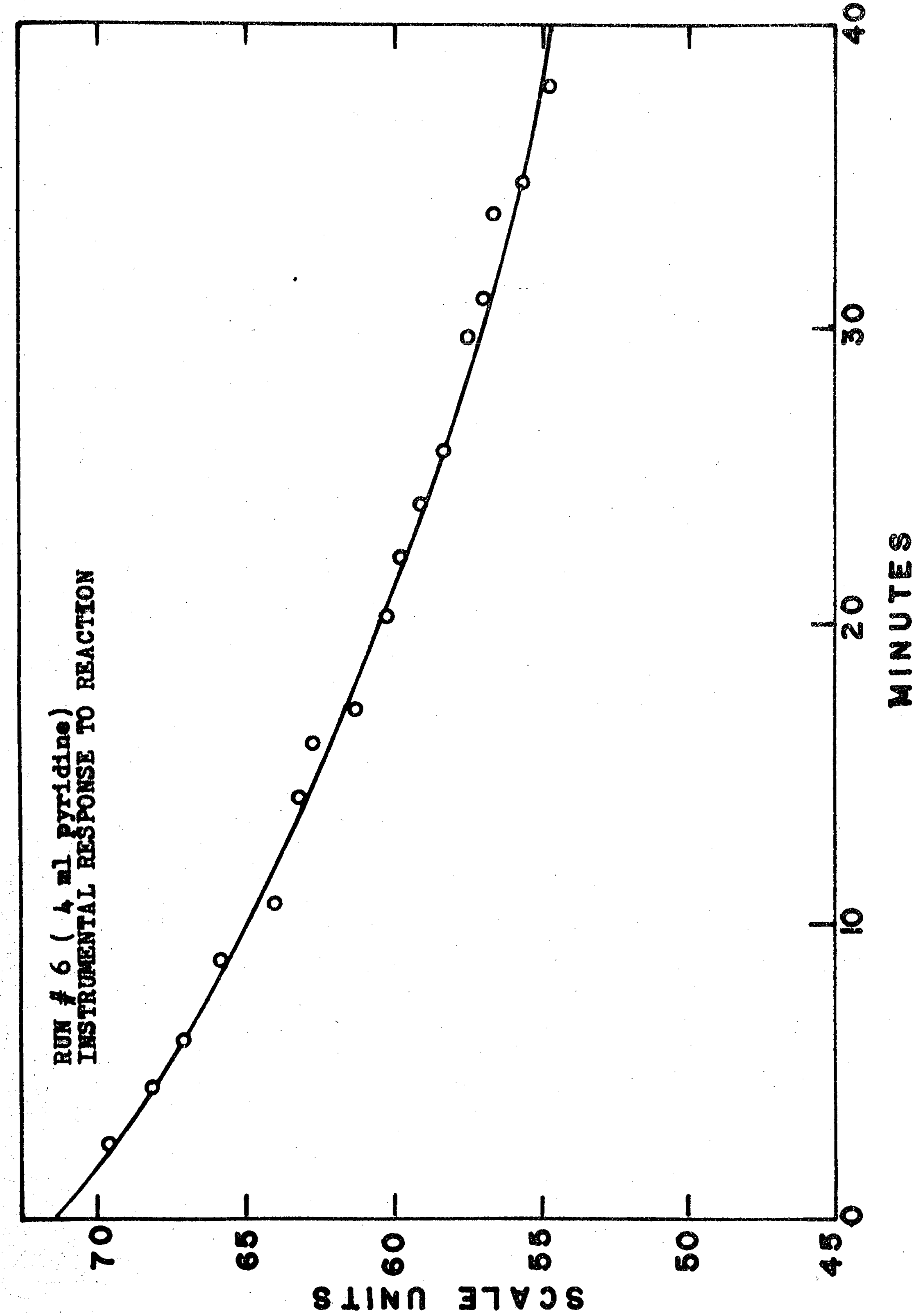

RUN # 6 (4 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION
SCALE UNITS
70
65
60
55
50
45
MINUTES
0
10
20
30
40

FIGURE 23

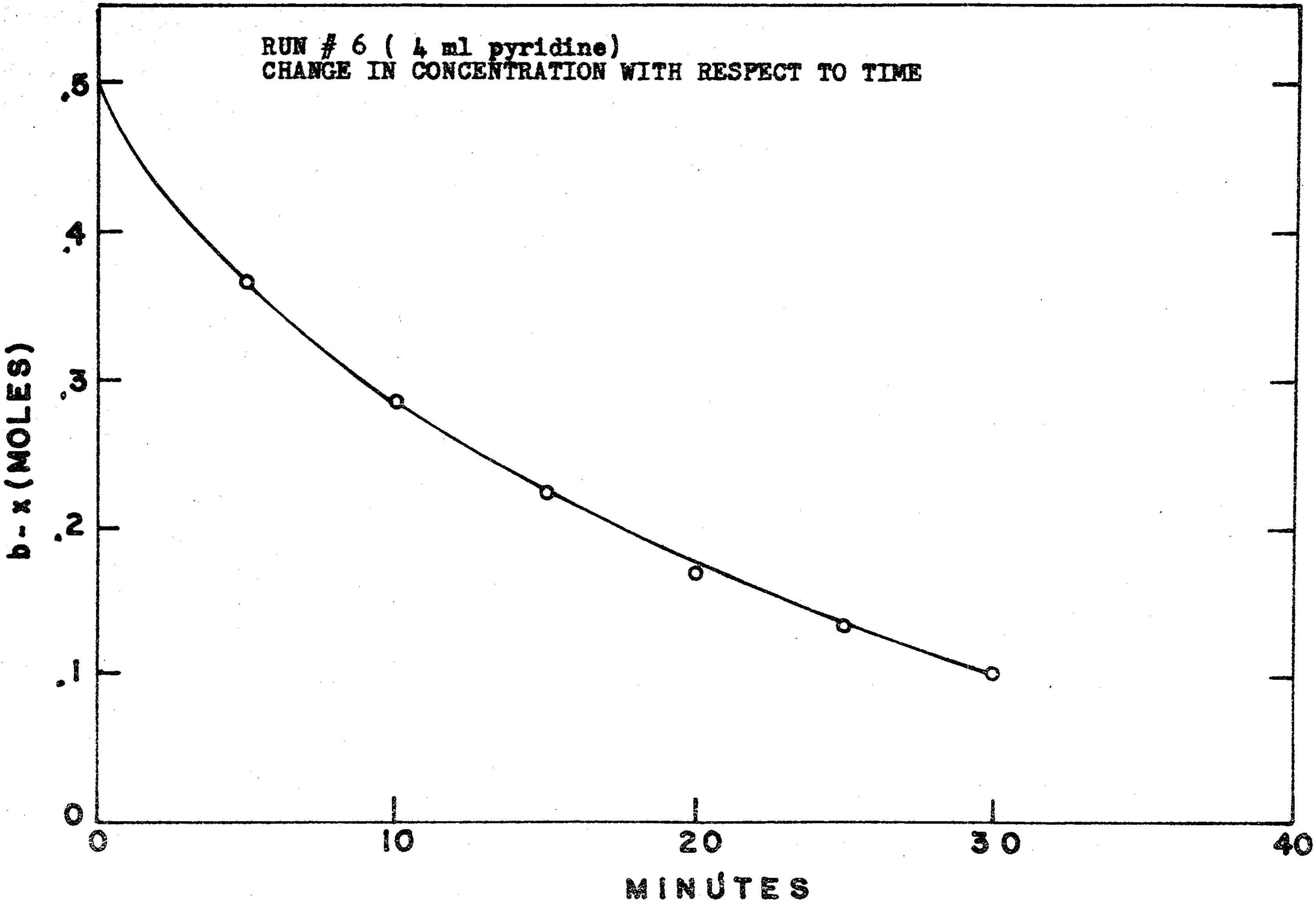

RUN # 6 (4 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
b - x (MOLES)
.5
.4
.3
.2
.1
0
0
10
20
30
40
MINUTES

FIGURE 24

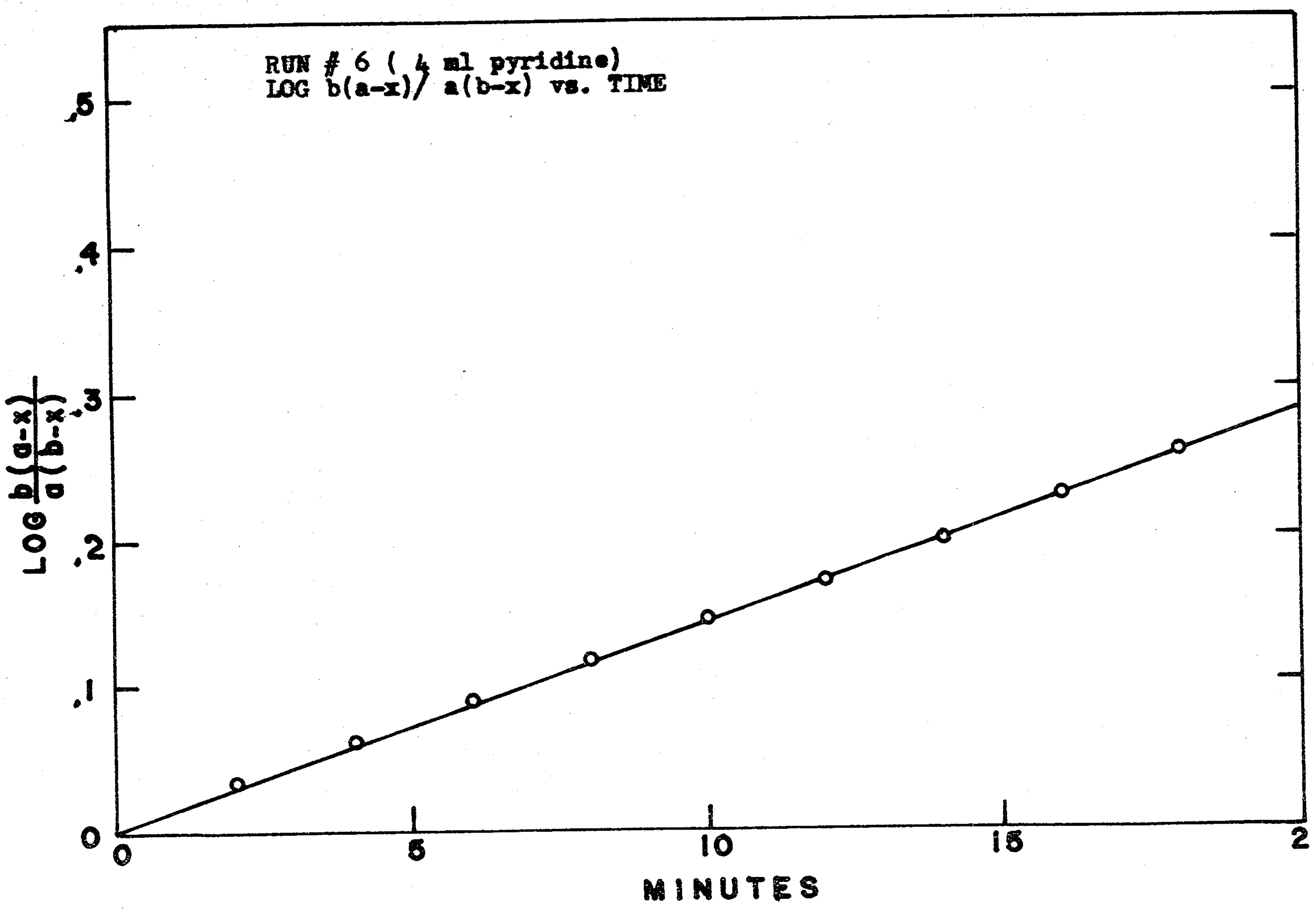

RUN # 6 (4 ml pyridine)
LOG b(a-x)/ a(b-x) vs. TIME
LOG $\frac{b(a-x)}{a(b-x)}$
.5
.4
.3
.2
.1
0
0
5
10
15
20
MINUTES

FIGURE 25

TABLE VIII

EXPERIMENTAL DATA - RUN # 7

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $\left(\frac{\text{moles}}{\text{min l}}\right)$
2	0.382	0.882	0.063	2.303	0.01533
4	0.325	0.825	0.104	1.151	0.01261
6	0.282	0.782	0.143	0.769	0.01151
8	0.249	0.749	0.177	0.576	0.01080
10	0.218	0.718	0.218	0.461	0.01065
12	0.190	0.690	0.259	0.384	0.01052
14	0.169	0.669	0.296	0.329	0.01030
16	0.149	0.649	0.338	0.288	0.01030
18	0.130	0.630	0.385	0.256	0.01042
20	0.113	0.603	0.434	0.2303	0.01060
22	0.098	0.598	0.485	0.209	0.01078

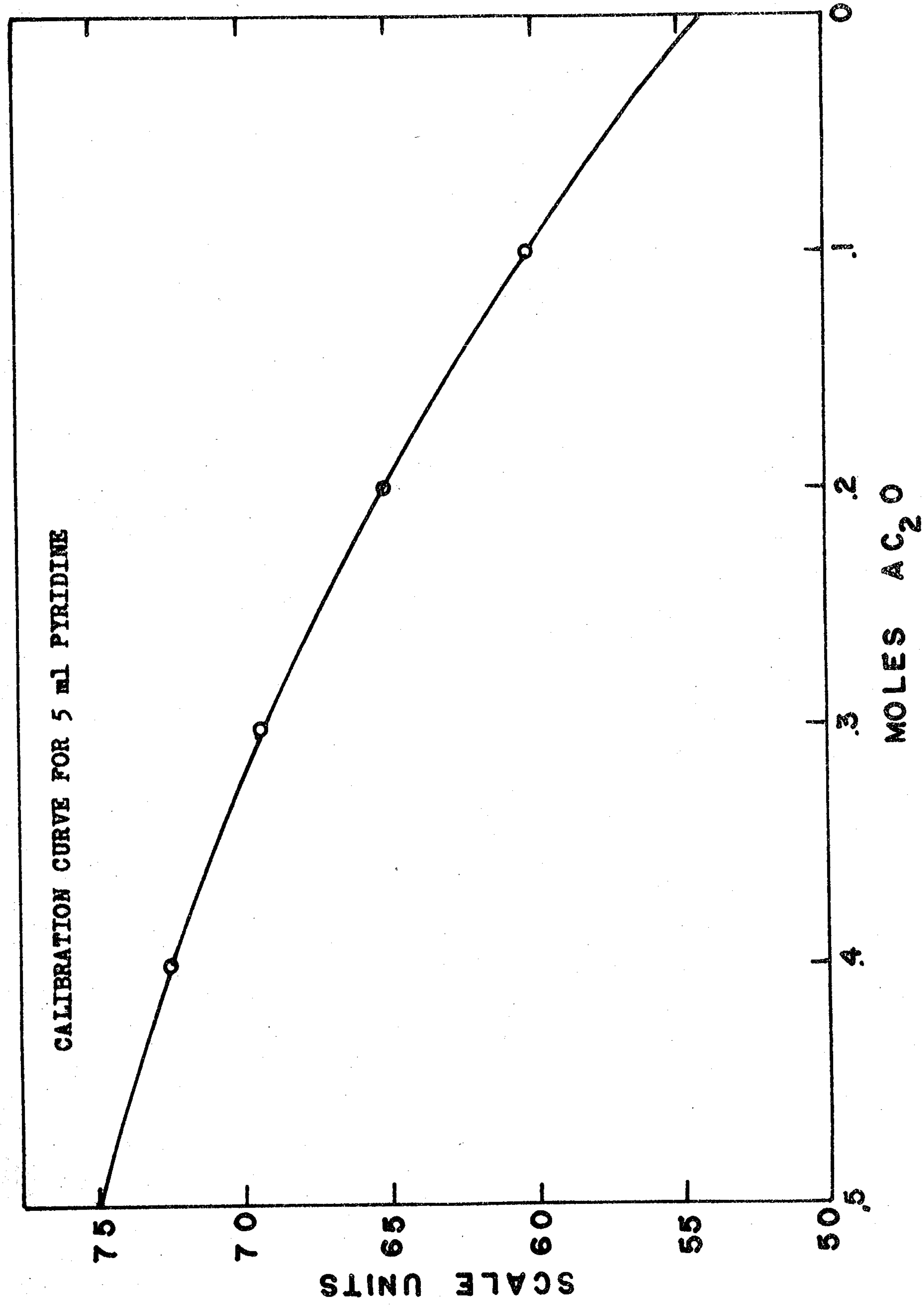

CALIBRATION CURVE FOR 5 ml PYRIDINE
MOLES AC_2O
0
.1
.2
.3
.4
.5
SCALE UNITS
75
70
65
60
55
50

FIGURE 26

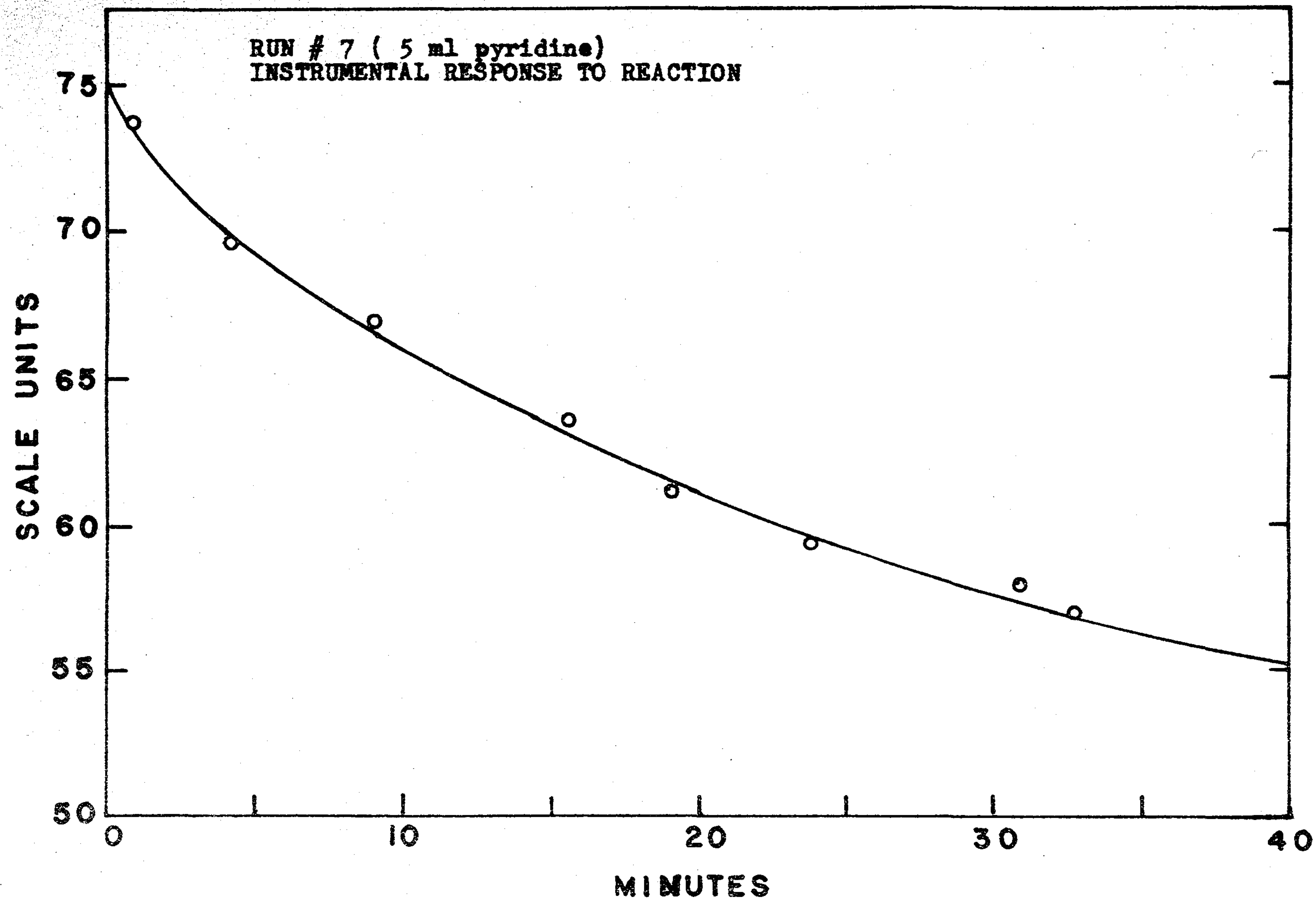

RUN # 7 (5 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION
SCALE UNITS
75
70
65
60
55
50
0
10
20
30
40
MINUTES

FIGURE 27

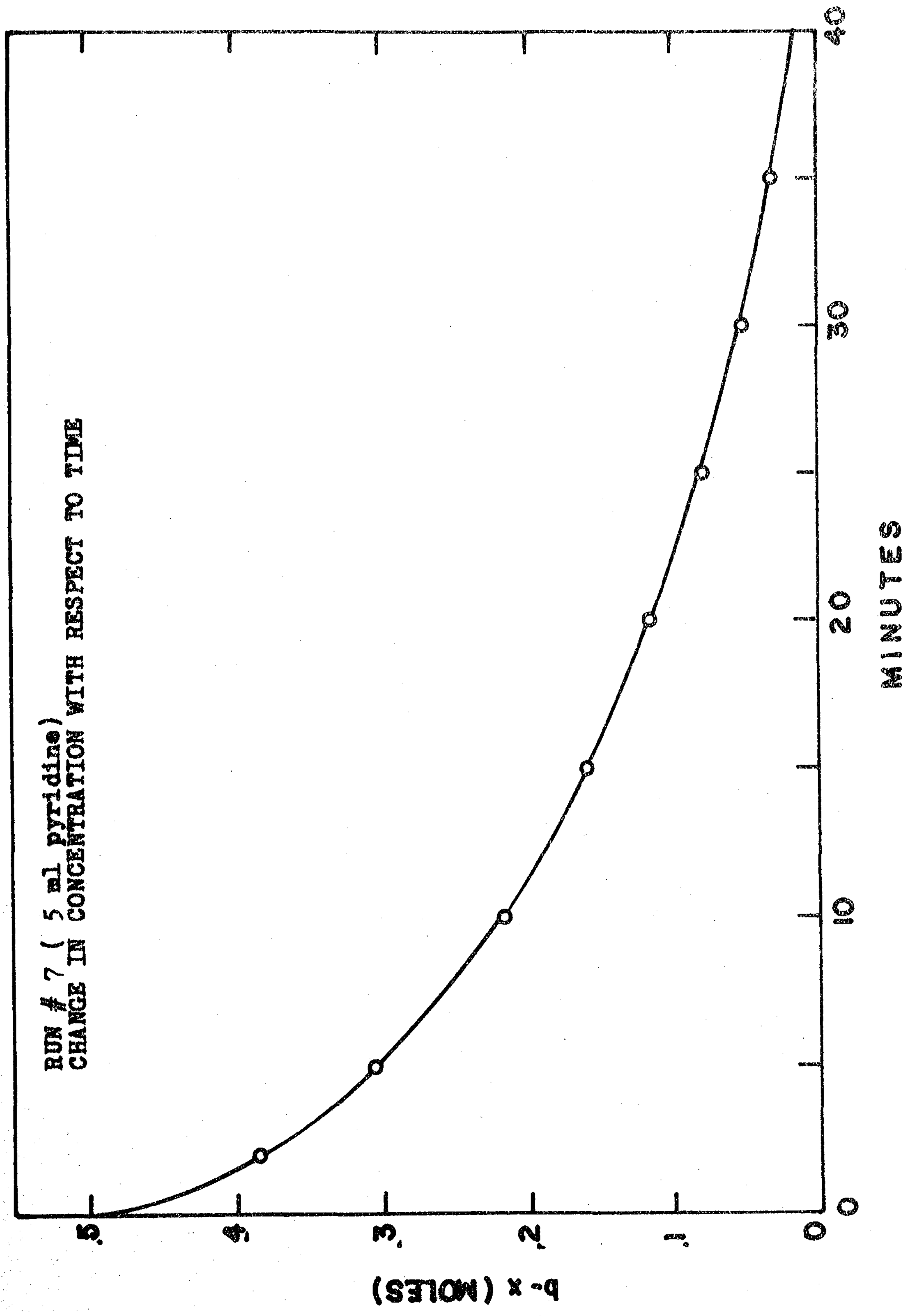

RUN # 7 (5 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME
.5
.4
.3
.2
.1
0
b- x (MOLES)
0
10
20
30
40
MINUTES

FIGURE 28

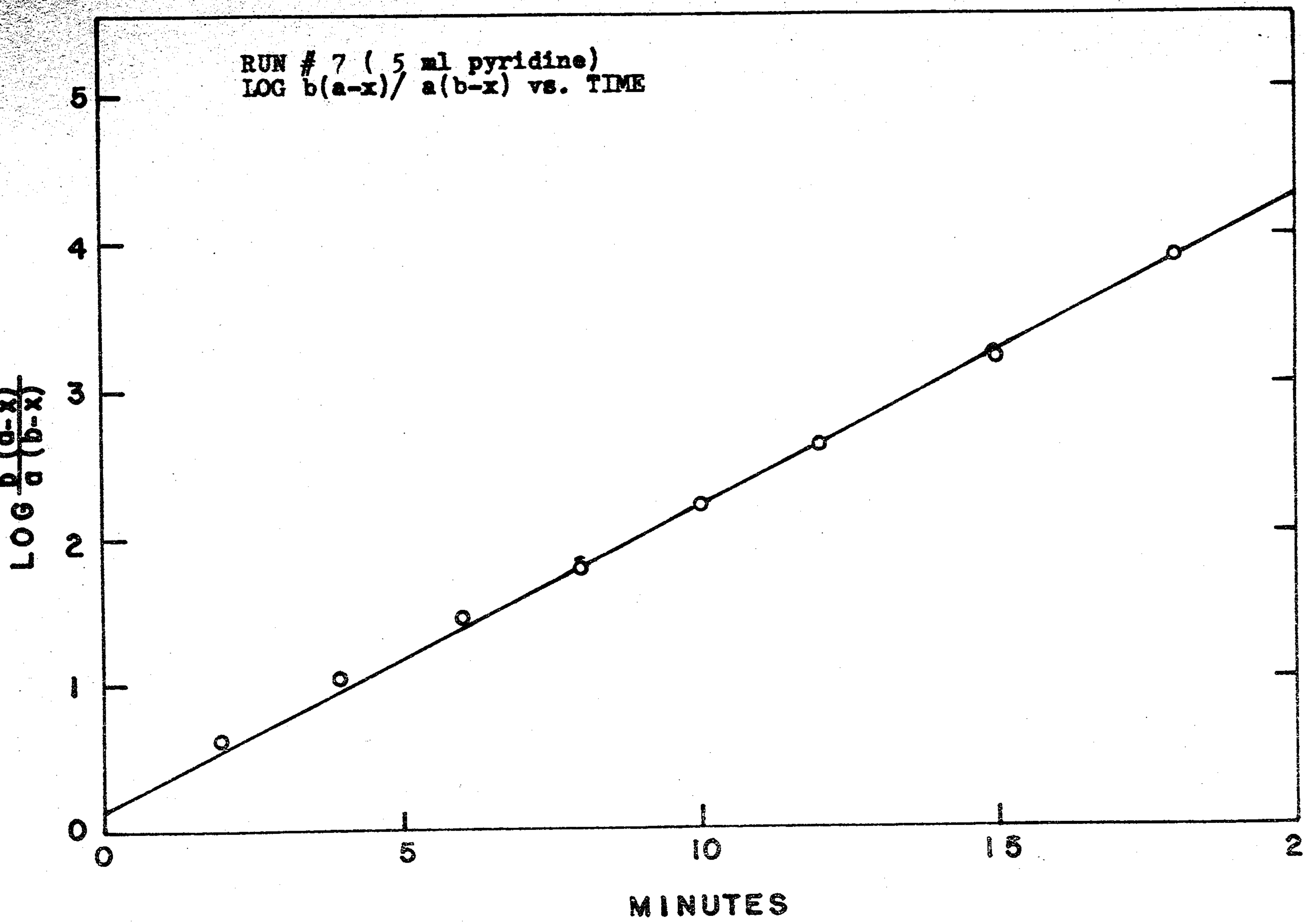

RUN # 7 (5 ml pyridine)
LOG b(a-x)/ a(b-x) vs. TIME
LOG $\frac{b(a-x)}{a(b-x)}$
0
1
2
3
4
5
0
5
10
15
20
MINUTES

FIGURE 29

TABLE IX

EXPERIMENTAL DATA - RUN # 8

time (min)	b-x (moles)	a-x (moles)	$\log\frac{(a-x)b}{(b-x)a}$	$\frac{2.303}{t(a-b)}$	k $(\frac{\text{moles}}{\text{min l}})$
2	0.392	0.892	0.057	2.303	0.01391
4	0.334	0.834	0.097	1.151	0.01185
6	0.287	0.787	0.238	0.769	0.01123
8	0.249	0.749	0.177	0.576	0.01080
10	0.219	0.719	0.215	0.461	0.01049
12	0.191	0.691	0.258	0.384	0.01051
14	0.168	0.668	0.298	0.329	0.01040
16	0.145	0.645	0.347	0.288	0.01059
18	0.127	0.627	0.292	0.256	0.01060
20	0.110	0.610	0.444	0.2303	0.01084
22	0.098	0.598	0.485	0.209	0.01082

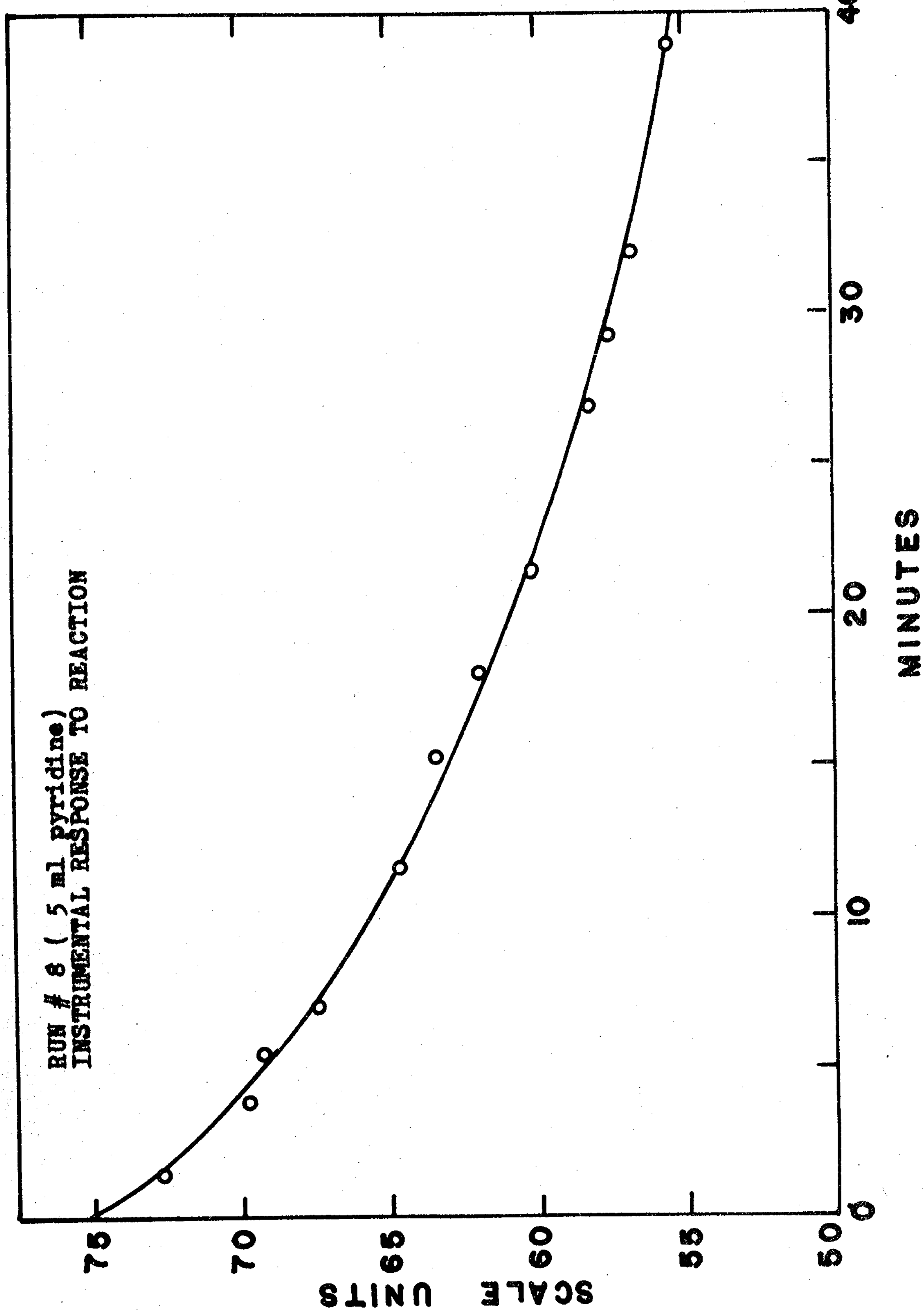
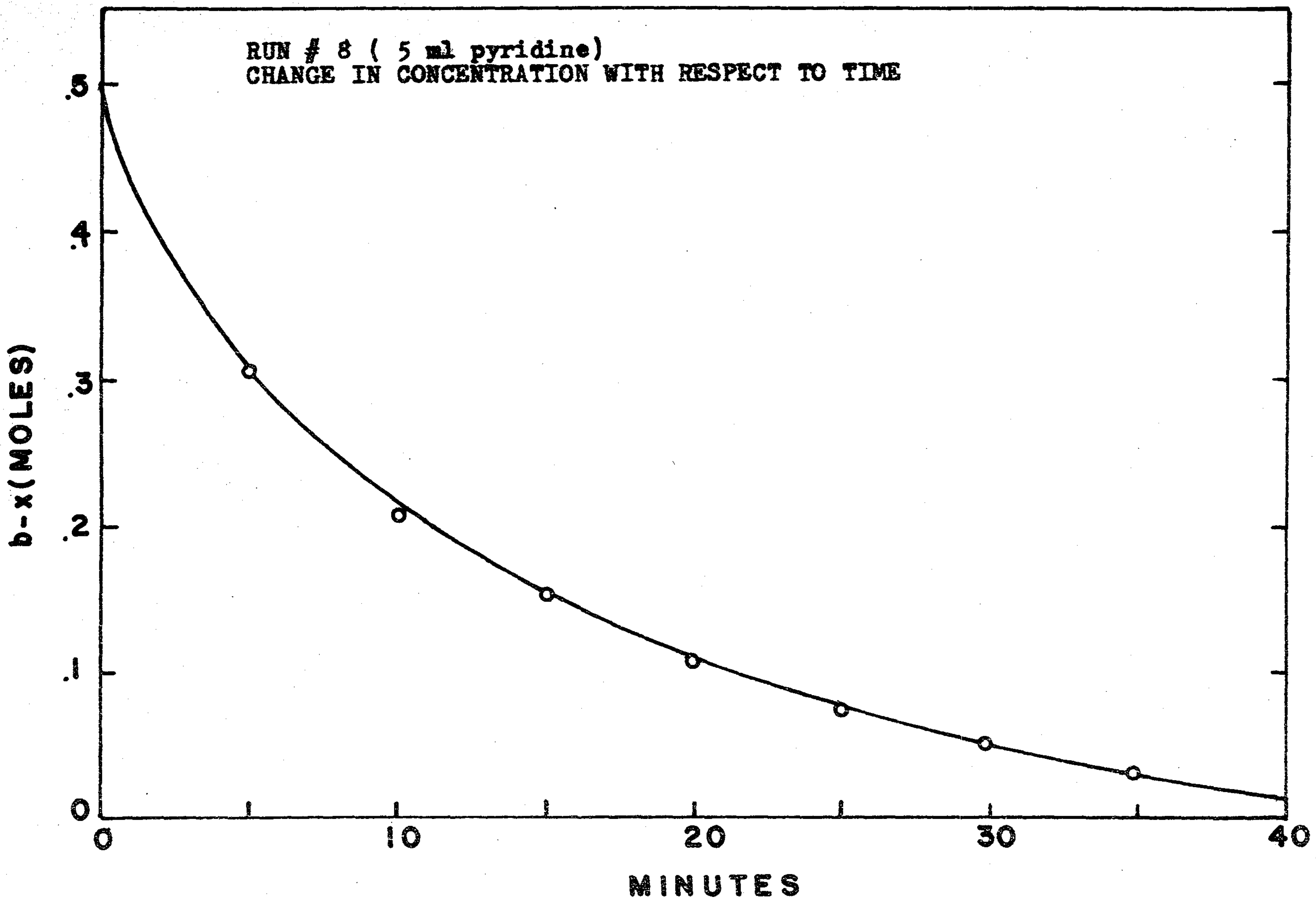

RUN # 8 (5 ml pyridine)
INSTRUMENTAL RESPONSE TO REACTION
SCALE UNITS
75
70
65
60
55
50
MINUTES
0
10
20
30
40

FIGURE 30



RUN # 8 (5 ml pyridine)
CHANGE IN CONCENTRATION WITH RESPECT TO TIME

FIGURE 31

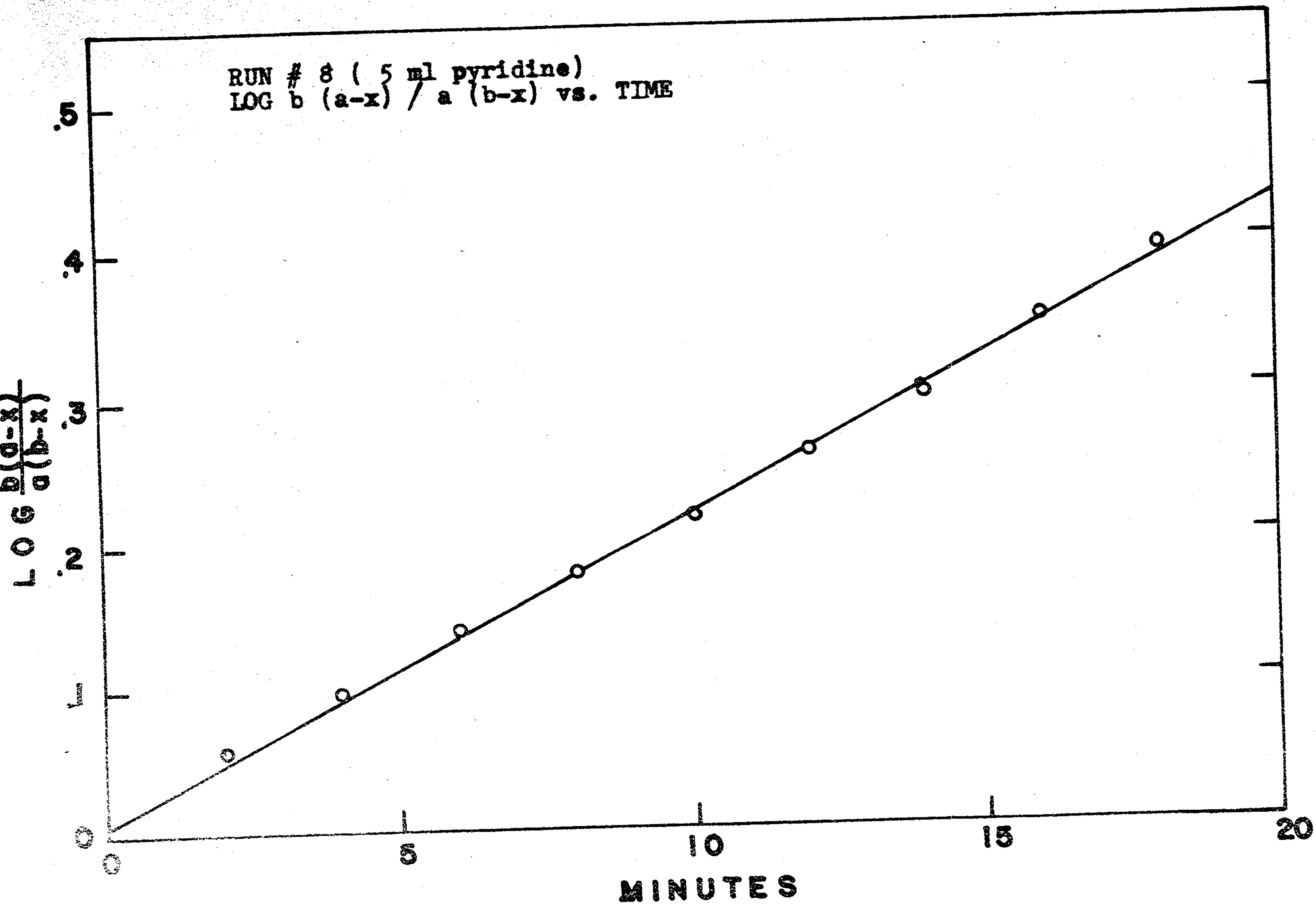

RUN # 8 (5 ml pyridine)
LOG b (a-x) / a (b-x) vs. TIME
.5
.4
.3
.2
.1
0
LOG $\frac{b(a-x)}{a(b-x)}$
0
5
10
15
20
MINUTES

FIGURE 32

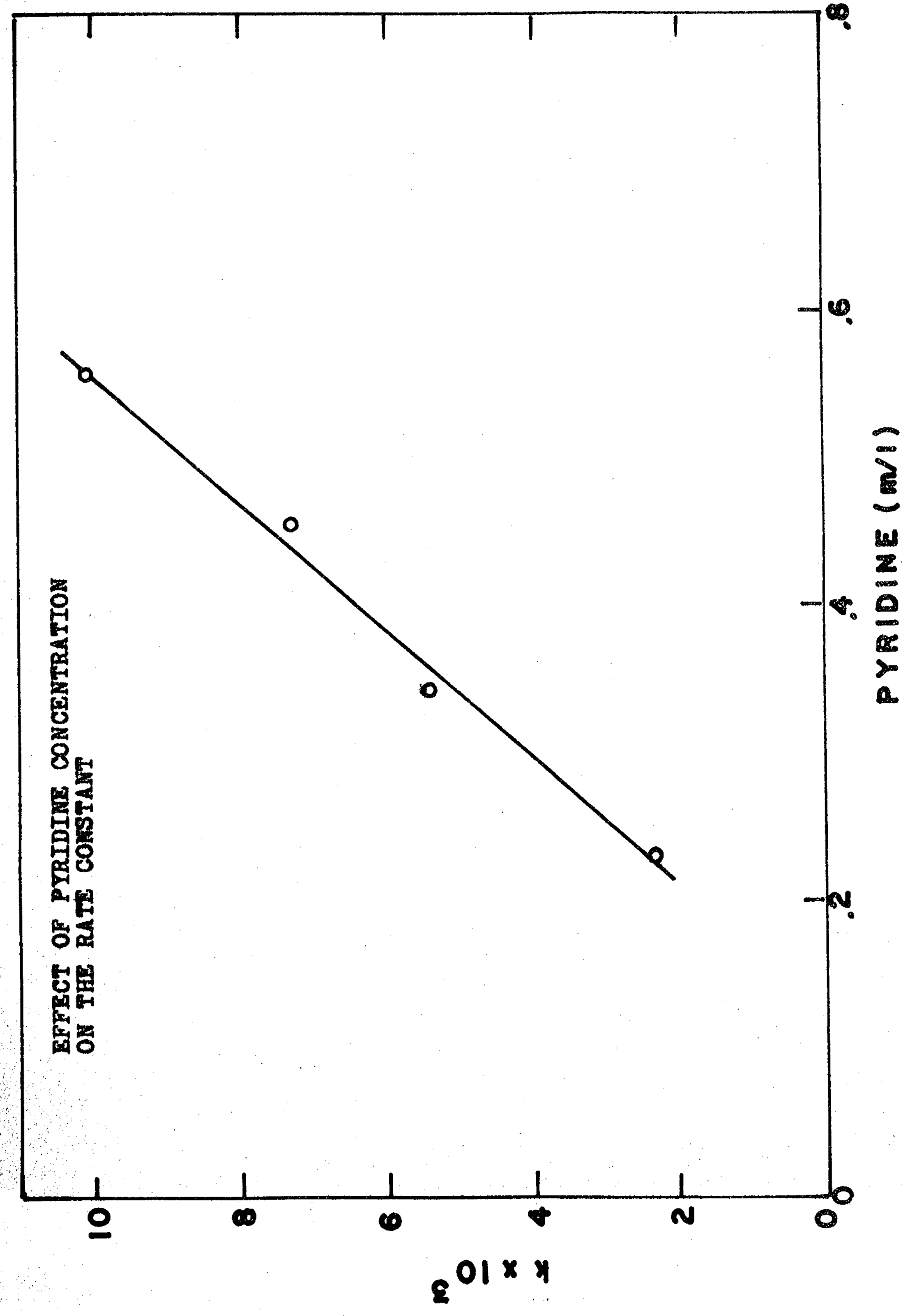

EFFECT OF PYRIDINE CONCENTRATION
ON THE RATE CONSTANT
PYRIDINE (m/l)
0
.2
.4
.6
.8
k x 10^3
0
2
4
6
8
10

FIGURE 33

TABLE X

COMPARISON OF RATE CONSTANTS BY METHOD OF FROST

TIME (min)	EXP k_1	CASE 1 k_1 k_2	CASE 2 k_1 k_2	CASE 3 k_1 k_2
30	0.002395	0.002375	0.002015	0.001909
40	0.002375	0.002373	0.001915	0.002120
50	0.002398	0.002395	0.001843	0.002395
60	0.002415	0.002410	0.001758	0.003465
70	0.002420	0.002415	0.001670	0.003705
80	0.002400	0.002395	0.001581	0.003900

TABLE XI

COMPARISON OF RATE CONSTANTS USING GRAPHICAL AND MATHEMATICAL TREATMENT

run	k (from eq.)	k (from slope)
1	0.002470	0.002465
2	0.002283	0.002180
3	0.005261	0.004925
4	0.005568	0.005370
5	0.007302	0.007260
6	0.007222	0.007020
7	0.01084	0.01042
8	0.01084	0.01055

TABLE XII

TABULATION OF DATA

RUN #	PYRIDINE (M conc)	k	avg k
1	0.2295	0.002470	0.002376
2	0.2295	0.002283	
3	0.3420	0.005261	0.005415
4	0.3420	0.005568	
5	0.4512	0.007302	0.007262
6	0.4512	0.007222	
7	0.5575	0.01084	0.010825
8	0.5575	0.01081	

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