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A kinetic study of the reaction between acetic anhydride and isobutyl alcohol using a chemical oscillometer

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A KINETIC STUDY OF THE REACTION BETWEEN ACETIC ANHYDRIDE AND ISOBUTYL ALCOHOL USING A CHEMICAL OSCILLOMETER

A Thesis
Presented to
the Faculty of the Department of Chemistry
The College of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
Charles Huffman Lewis, Jr.
June, 1959

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CHAPTER I

A DESCRIPTION OF THE PROBLEM

To the organic chemist, there is no phase of physical chemistry of more interest or importance than the study of reaction rates. By applying the information obtained from a kinetic or rate investigation, it is often possible to propose or speculate the mechanism of the reaction, the problem which more than any other has excited the imagination of organic chemists.

The object of this research project is to investigate the base catalyzed reaction of acetic anhydride and isobutyl alcohol reacting to form acetic acid and isobutyl acetate. In this investigation, a high frequency oscillometer is used to observe the progress of the reaction as it proceeds to the formation of products.

The chemical oscillometer, in one form or another, has been in existence for over twenty years. During this time it has developed from a laboratory curiosity to a practical instrument with a great number of applications. However, its use in connection with kinetic studies has not been too active because of the fact that it has been used primarily as a purely analytical device. A more detailed description of the instrument as well as a brief background of its use will be presented in the following chapter.

Another purpose of this investigation is to determine how the velocity of the reaction in question is dependent upon the temperature of the vessel or environment in which the reaction is taking place. In other words, several rate determinations will be made at various temperatures in order to establish the relationship between these two variables. From the data obtained from this series of rate determinations, it becomes possible to calculate a theoretical term known as the energy of activation, the significance of which will be explained in Chapter IV.

CHAPTER II

THE HIGH-FREQUENCY OSCILLOMETER AND ITS APPLICATION TO CHEMICAL KINETICS

The basic method for using the chemical oscillometer as an analytical or kinetics tool consists of placing the sample to be examined in a component of an oscillating circuit where it will affect the capacitance, resistance or the inductance of the circuit. The sample may be connected into the circuit either by being placed in the field of the plate coil or by being exposed to the electrostatic field of a condenser. One of the advantages found in the use of this type of instrument is that at no time is there any physical contact made with the sample with the exception of the containing vessel.

The original work in this area was performed by Jensen and Parrack (1946). They constructed a very simple apparatus that would indicate changes in the electrical properties of solutions under chemical analysis. When the results were interpreted, they indicated a definite endpoint in the analysis. Since this time, a fairly large number of related instruments have been constructed and have been applied to different phases of chemistry. Some of the functions include the analysis of binary mixtures, titrations, and as a means of locating bands in column chromatography. In all these cases, successful operation is dependent on a frequency change of an oscillator resulting from a change in capacitance or conductance or both in the sample. Blaedel (1950) gives an excellent survey of high-frequency oscillometers and discusses their advantages as well as their limitations.

The device used in this study is an original one and for an exact description of the circuitry and operating characteristics the reader should refer to the Master's thesis (1957) of John Clinkscales who built the instrument. The instrument is a heterodyne type, operating in the 120 megacycle range. In general, it consists of two identical oscillators, each shielded and isolated from the other and connected to mixer, detector, and audio stages. One of these oscillators is known as the working oscillator and its frequency is dependent on the electrical characteristics of the solution under investigation. The other oscillator, known as the reference oscillator, is adjusted so that its frequency matches that of the working oscillator. When the two approach the same frequency, a heterodyne or beat frequency is heard over ear phones. As the two oscillators reach the exact same frequency, a zero or null is heard. By this method of balancing, it becomes possible to detect any change of frequency in the working oscillator due to a change in electrical characteristics of the sample which is determined by a change in chemical composition. The change if any can be read directly from the National dial on the front of the apparatus. It should be mentioned that these dial readings have no significance themselves unless some means of calibration is used to relate them to units of concentration.

The nature and magnitude of the property or properties being measured is determined by such things as the composition of the sample, the geometry of the sample cell and the frequency of the oscillator. Debye (1929) presents material that somewhat explains the effects involving the relationship between conductivity and dielectric constant but this phase is considered beyond the scope and not the purpose of this study. Although an exact relationship between change in frequency of an oscillator and the capacitative-conductive effect is not known, the fact that instruments of this type have found practical applications and operate successfully justifies their existence.

This study is carried out in basically the same manner as that performed by Lowery (1958), who investigated the reaction of acetic anhydride and ethyl alcohol. He attempted to derive a method that would relate the dial units directly to concentration. However, in both investigations it was necessary to employ a more indirect method of calibration due to the non-linear response of the instrument to changes in concentration. The method that is used is adequate for the purpose and is discussed along with the operating procedure in Chapter V.

CHAPTER III

THE FOUNDATION FOR A KINETIC INVESTIGATION

The field of chemical kinetics is generally considered as being composed of two sub-divisions. The sub-divisions are the studies of (1) homogeneous reactions, those reactions that take place entirely in one phase, and (2) heterogeneous reactions, those reactions that occur at the interface or junction between various phases. The former case represents the type involved in this investigation.

Because many organic reactions proceed relatively slowly with respect to the majority of those of an ionic-inorganic nature, they are often suitable for investigation leading to the determination of the specific reaction constant. In a great number of instances where numerous products and competing reactions are involved, evaluation of the rate-constant or the specific reaction rate is difficult or impossible. However, it is sometimes possible to overcome these obstacles by altering the concentrations of the reactants so as to force one of the possible reactions to predominate or proceed much faster than the others.

The data obtained from an investigation of this type will ordinarily consist of listings of concentrations of the reactants or products at various intervals of time. Usually these listings are obtained under the conditions of constant temperature--preferably at as many different temperatures as possible. The data are then evaluated by insertion in the general differential equation for the rate expression, $dc/dt = f(c_1, c_2 \ldots\ldots c_n)$. It is the basic assumption of all reaction-rate investigations that the number of moles reacting in unit time is proportional to the product of the concentrations of the reacting substances and is independent of the concentrations of other substances that do not take part in the reaction. This assumption is made with the understanding that the environment in which the reaction takes place remains reasonably constant.

The rate of a chemical reaction--which is also known as the velocity or speed--can be expressed in several different ways. Obviously, a convenient method would be to use the concentration of one of the changing components at any time t. There are some investigations of gaseous reactions where k--the rate-constant--is reported in terms of pressure. For example, in the kinetic study of the thermal decomposition of acetaldehyde, there is an increase in pressure at constant volume on dissociation, and this change in pressure as observed on a manometer attached to the system may be employed to follow the course of the reaction. If concentrations are expressed in moles per liter and time is expressed in seconds, then k will have the units of liters/mole-seconds. This is the method used in this study and is commonly found in the literature.

After the concentration of a reactant or product has been determined at various intervals of time, the reaction-rate and the order of the reaction may be calculated. The order of a chemical reaction is defined as the sum of the exponents of the concentration terms in the general rate expression. Thus for the typical reaction

$$A + B \longrightarrow Z$$

the rate is proportional to $C_A C_B$ where C refers to the molar concentrations of the substances in question. This rate can be expressed as

$$dC_Z/dt = kC_A^m C_B^n$$

The reaction is therefore mth order with respect to A and nth order with respect to B. The over-all order for the reaction is $(m + n)$th order.

In the particular case under investigation, a bimolecular situation exists. This means that the reaction involves two reacting molecules coming together with sufficient energy for reaction. All bimolecular chemical reactions are of second order. This is equivalent to saying that the reaction-rate is proportional to the concentration of each of the two reacting substances.

The derivation of the second order rate expression will now be considered. In the reaction

$$A + B \longrightarrow AB$$

if
$$-dC_A/dt = -dC_B/dt = kC_A C_B$$

then the reaction is said to be of second order. If A and B represent the initial concentrations of reactants and X represents the reaction variable or the amount of either A or B that has reacted at time t, then the rate can be expressed by the relationship

$$dX/dt = k(A - X)(B - X) \tag{1}$$

In an example where the reactants are of equal initial concentration, the expression simplifies to:

$$dX/dt = k(A - X)^2 \tag{2}$$

However, in the majority of kinetic studies, it is beneficial to have the reactants at non-equal concentrations for reasons already mentioned. Consequently, equation (1) proves to be the most useful of the two. When this equation is integrated, the following relationship is obtained:

$$kt = \frac{1}{(A - B)} \ln \frac{B(A - X)}{A(B - X)}$$

or on rearrangement

$$k = \frac{2.303}{t(A - B)} \log \frac{B(A - X)}{A(B - X)} \tag{3}$$

Thus k can be evaluated directly from equation (3) and when these values do not vary appreciably with time, the reaction can be taken as second order.

The value for the rate-constant can also be calculated very easily graphically. When log $\frac{B(A - X)}{A(B - X)}$ is plotted as ordinate against time, a straight line is obtained if the reaction is second order. The slope of this line is equal to $\frac{k(A - B)}{2.303}$ and therefore the rate-constant can be determined.

It becomes obvious that the over-all reaction as written on paper will usually have little bearing on the actual path followed during the course of reaction. Only a few chemical reactions are straightforward first, second, or third, order reactions; usually, several reactions are taking place at the same time. There are three important types of complications that may arise and each will be described separately.

A consecutive reaction may be represented as:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

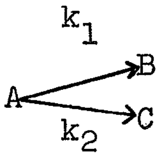
where k_1 is the rate-constant for the first step and k_2 is the rate-constant for the second step. An example of this type is found in the oxidation of hydrocarbons where the final products are carbon dioxide and water. However, there are intermediate steps where alcohols, ketones, and acids are formed.

Reverse reactions may be represented as:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D$$

where k_1 is the rate-constant of the forward reaction and k_2 is the rate-constant for the reaction proceeding to the left.

Competing reactions are of the following general form:



Examples of this type are many as in the case of the nitration of phenol to give both ortho-nitrophenol and para-nitrophenol. The amounts of each isomer will of course depend on the relative magnitudes of k_1 and k_2. If the situations that have been described exist and the rate-constants are known, then it is more than likely that conditions can be established so as to favor one of the possible reactions at the expense of the others.

This investigation is concerned with the reaction of acetic anhydride and isobutyl alcohol to form isobutyl acetate and acetic acid. For purposes of abbreviation, the following notations are made:

Isobutyl Alcohol	A
Acetic Anhydride	B
Acetic Acid	C
Isobutyl Acetate	D
Water	E

The following reactions are probable for this system.

$A + B \longrightarrow C + D$ (Desired Reaction)

$C + D \longrightarrow A + B$ (Reverse Reaction)

$A + C \longrightarrow D + E$ (Consecutive-Competing Reaction)

The possibility of a reverse reaction is considered to be negligible because preliminary test on solutions containing acetic acid and isobutyl acetate showed that there was no appreciable disappearance of acid over a period of time.

A consecutive-competing reaction is ruled out on the basis of data taken from Royals (1954), who reported that this particular reaction proceeds to only 44.36% completion over a period of one hour. Royals also reported that the maximum value for this reaction at infinite time was 67.38%. These figures are based upon experiments carried out at 155 degrees Centigrade. Since the temperatures involved in this investigation are considerably lower, the formation of sufficient ester to seriously affect the calculations is considered non-important.

CHAPTER IV

THE ENERGY OF ACTIVATION AND THE INFLUENCE OF TEMPERATURE UPON THE RATE-CONSTANT

It has been known for many years that a relationship did exist between the rate-constant and the temperature of reaction. The effect is quite pronounced and in a large number of organic reactions, the velocity of reaction is doubled or even trebled for every ten degree rise in temperature.

In 1889, Arrhenius attempted to derive a more quantitative expression relating the two variables. Since the van't Hoff equation for the temperature coefficient of the equilibrium constant is

$$\frac{d\ \ln K_c}{dT} = \frac{\Delta H}{RT^2} \tag{1}$$

Arrhenius proposed that a reasonable relationship involving the rate-constant and temperature change might be

$$\frac{d\ \ln k}{dT} = \frac{\Delta Ha}{RT^2} \tag{2}$$

where the term Ha is known as the energy or heat of activation. When this quantity is assumed to be constant, that is, temperature independent, expression (2) on integration gives

$$\ln k = -\frac{\Delta Ha}{RT} + S \tag{3}$$

in which S is the constant of integration. Expression (3) is then simplified to

$$k = Se - \frac{\Delta Ha}{RT}$$

If equation (2) is integrated, between limits, the following relationship is obtained:

$$\log \frac{k_2}{k_1} = \frac{\Delta Ha}{2.303R} \frac{(T_2 - T_1)}{(T_2 T_1)} \qquad (4)$$

From (4), it is possible to solve for the term ΔHa when the value for the rate-constant is known at two or more temperatures.

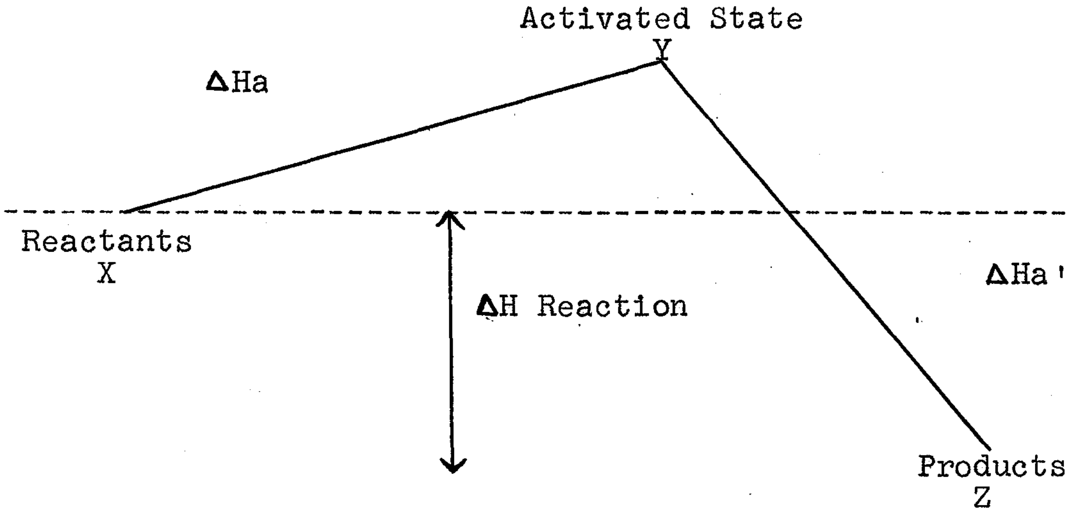
The modern concept of reaction-mechanism is that reactant molecules must be brought or raised to an activated state before conversion into products is possible. The existence of an activated state, specific for every system, is indicated by the fact that all chemical reactions are not equally reactive. If this were the case, it would be impossible to explain the variations in the velocities of different systems.

Thermodynamics is concerned with only initial and final steps in rate-processes. However, in the study of chemical kinetics, it is necessary to consider intermediate steps which lead to the final products. In accordance with this, a typical reaction might be represented as

$$\begin{array}{ccccc} \text{Reactants} & \xrightarrow{\text{slow}} & \text{Activated State} & \xrightarrow{\text{fast}} & \text{Products} \\ X & & Y & & Z \end{array}$$

where interest is centered on the slow or the rate-determining step. To reach this activated state it is necessary to have an activation energy equal to ΔHa.

The relation between the heat of reaction and the heats or energies of activation is represented in the following diagram:



The heat of reaction as determined in a calorimeter at constant pressure is equal to the difference between the heats of activation of the forward and reverse reactions.

$$\Delta H = \Delta Ha - \Delta Ha'$$

Generally, the heat evolved in proceeding from Z to Y is greater than going from X to Y. If the converse situation exists, then the reaction is endothermic.

It can be said that the amount of energy required to attain the activated state is the main factor in determining the speed of a chemical reaction. The greater the energy requirements for reaction, the smaller the number of molecules having this energy at any given temperature and consequently the lower the velocity of reaction.

One point should be emphasized. The heat evolved in a chemical reaction has no bearing on the reaction rate. This is easily seen because it is not possible to break down the heat of reaction into the individual components of activation.

Actually, unless the measurements are made under conditions of limited temperature range, the values obtained for the activation energies will not remain constant. One explanation for this is that the heat of reaction (ΔH) varies with temperature. Since there is a relationship between the energies of activation for the forward and reverse reactions with the over-all heat of reaction, it can be seen that activation energies will not be a constant value under wide temperature ranges.

In this investigation, the reaction between acetic-anhydride and isobutyl alcohol is catalyzed by a small amount of pyridine. The function of the catalyst is to bring about the reaction by lowering the energy requirements. The net result is that a more rapid reaction will occur at a given temperature because a larger number of reactant molecules have sufficient energy for reaction.

In many instances, the use of a catalyst results in the formation of a new compound with less energy consumption, and when this intermediate decomposes into one or more of the final products, the catalyst is reformed.

A study of a similar system, the reaction between acetic anhydride and ethyl alcohol catalyzed by pyridine, was performed and is described in the Master's thesis (1958) by William Lowery. Lowery found a nearly linear relationship to exist between the rate constant and the amount of catalyst used. One would expect a somewhat identical situation to exist in this investigation because of the similarity of the two systems.

Since this study is concerned with the determination of the rate-constant at several different temperatures, it was decided to keep the amount of catalyst constant in each case. The addition of pyridine to this type of system results in the generation of heat, and it is necessary to use only a small amount (one milliliter in every case) so that conditions of constant temperature could be maintained.

CHAPTER V

EXPERIMENTAL PROCEDURE

I. SELECTION AND PREPARATION OF SOLUTIONS AND REAGENTS

The substances used in this study included acetic anhydride, isobutyl alcohol, acetic acid, isobutyl acetate and pyridine. These particular compounds were chosen on the basis of dielectric constants and with respect to the magnitude of the instrumental response for the system. As has already been said, a system that is well suited for a kinetic investigation using the chemical oscillometer must be one in which a relatively large difference in dielectric or other electrical properties exist between reactants and products. The following list gives the dielectric constants for the substances in question.

Acetic Anhydride	20.5
Isobutyl Alcohol	31.7
Isobutyl Acetate	5.6
Acetic Acid	7.1
Pyridine	12.5

Because the presence of other substances, especially water, will not only promote certain complications such as mentioned in Chapter III but will often induce misleading measurements in the instrument, it was necessary to further purify the materials even though they were obtained from commercial sources. This was accomplished by successive distillation using a 120 x 2 cm. helix packed column. The boiling point range and the specific gravity of the fraction of each compound retained for use in the investigation are presented in the following list.

Compound	Boiling Point	Specific Gravity
Acetic Anhydride	137.9-140.2	1.079 gms/ml
Isobutyl Alcohol	108.0-108.3	0.801 gms/ml
Isobutyl Acetate	117.9-118.4	0.872 gms/ml
Acetic Acid	117.6-118.4	1.047 gms/ml
Pyridine	115.0-115.3	0.983 gms/ml

After each fraction was obtained, it was stored in glass stoppered bottles and care was taken to prevent contamination.

Table I gives the comparison of the volume of each reagent to the number of moles. This was calculated from the specific gravity and the molecular weight of each compound. These values were used throughout this investigation.

II. EXPERIMENTAL TECHNIQUE

The oscillometer was permitted to warm up at least twelve hours before any measurements were to be made. By doing this, any shift in frequency or instability in the electrical components due to lack of thermal equilibrium was avoided. The electrical source for the instrument consisted of a Heathkit model PS-3 power supply. During the course of an experimental run, the power supply was adjusted so that approximately 275 volts were delivered to the oscillometer. Because of the identical nature of the oscillators within the instrument, the amount of electricity supplied is not critical. Any change or fluctuation of the input voltage has the same effect on both oscillators so that the instrumental response does not vary.

It was decided to establish a calibration curve for each of the experimental runs in order to eliminate the possibility of errors due to changes in dielectric or conductive properties of the solutions because of changes in temperature. The calibration curves that were constructed do show differences in the degree of curvature. The curves, going from thirty five to sixty degrees Centigrade respectively, progress from a near linear condition to one that is convex. The cause or causes of these differences were not investigated. However, this might be an interesting project for future work.

In order to establish a relationship between the dial units and concentration, the procedure consisted of filling the polyethylene sample holder with the calculated volume of reactants and products after the solutions had been brought to the desired temperature in a constant temperature bath. The exact volumes of reactants and products were delivered using calibrated burets. The catalyst, which was at the same temperature as the solutions, was added and an electric stirrer was inserted to insure homogeneity. A rubber stopper through which a hole was drilled for the stirrer was used to cover the sample holder. A series of timed readings were taken and recorded graphically and the value at zero time was obtained in every case by extrapolation. In this manner, a graph could be constructed that would relate the dial reading directly to the concentration of acetic anhydride in the reacting solution.

It should be mentioned that a zero or standard solution was employed to prevent any drift in the instrument. This solution consisted of a mixture of acetic acid and benzene and was used throughout the investigation to retune the instrument to a value of eighty five as read on the National dial. The dial can be read to an accuracy of approximately plus or minus 0.05 dial units.

In order to determine the instrumental response to the actual reaction, the procedure consisted of bringing the reactants to the desired temperature in the constant temperature bath and then adding the pyridine catalyst. The stirrer was inserted and an electric timer activated. The reacting solution remained in the constant temperature bath until the desired time and was then transferred to the sample holder and the dial reading was recorded. Readings were made at intervals of 300 seconds and no difficulty was encountered in maintaining conditions of constant temperature. A calibrated thermometer was used to insure that the temperature of the reacting solution was at the appropriate value. Before and after each measurement, the zero solution was inserted in the instrument and the necessary adjustment, if any, was made.

A third graph was constructed directly from the two graphs already mentioned and it related the concentration of acetic anhydride in the reacting solution to time. In this manner, it was possible to measure the disappearance of one of the reactants over a known period of time and to ultimately calculate the rate constant.

CHAPTER VI

CALCULATIONS AND RESULTS

The rate constants that are listed in the following tables are calculated on the basis of the relationships presented in Chapter III. The initial concentration of the reactants was 0.5 moles acetic anhydride and 1.0 moles isobutyl alcohol. This initial concentration was used in all experimental runs. The reaction variable, x, is determined directly from the plots of (B - X) versus time.

For a typical calculation, consider the experimental run at 35 degrees Centigrade. At t = 3,300 seconds, (B - X) is equal to 0.207 moles acetic anhydride and (A - X) is equal to 0.707 moles isobutyl alcohol. These values are inserted into the following expression.

$$k = \frac{2.303}{t(A - B)} \times \log \frac{B(A - X)}{A(B - X)}$$

On substitution,

$$k = \frac{(2.303)}{(3{,}300)(0.5)} \times \log \frac{(0.5)(0.707)}{(0.207)}$$

$$\times\ 0.1408 \text{ liters}$$

$$k = 0.0000455 \text{ liters seconds}^{-1}\text{moles}^{-1}$$

The volume of reactants was 0.1408 liters in all instances and this figure must be used in all of the calculations in order express the rate constant in proper units. The rate constant was also determined from the slope of the line formed by the plot of log B(A - X)/A(B - X) versus time. To obtain the value for the rate constant, the slope of the line is multiplied by 2.303/(A - B). The product of these numbers is then multiplied by the volume, 0.1408 liters. In the case of the experimental run at 35 degrees Centigrade, the slope of the line is equal to 0.698×10^{-4}. The calculation would then be as follows.

$$k = \frac{(2.303)(0.698 \times 10^{-4})}{(A - B)} \times 0.1408 \text{ liters}$$

$$= 0.0000455 \text{ liters seconds}^{-1}\text{moles}^{-1}$$ 45267

The activation energy is calculated from the following expression.

$$\log \frac{k_2}{k_1} = \frac{\Delta H_a}{2.303R} \times \frac{(T_2 - T_1)}{(T_2 T_1)}$$

The constant R is equal to 1.987 calories $\text{degree}^{-1}\text{mole}^{-1}$. As an example of a typical calculation, consider the determination of the activation energy from the rate constants at 35 and 60 degrees Centigrade.

k_2(60 degrees Centigrade) = 0.000202

k_1(35 degrees Centigrade) = 0.0000455

T_2 = 333.16 degrees Absolute

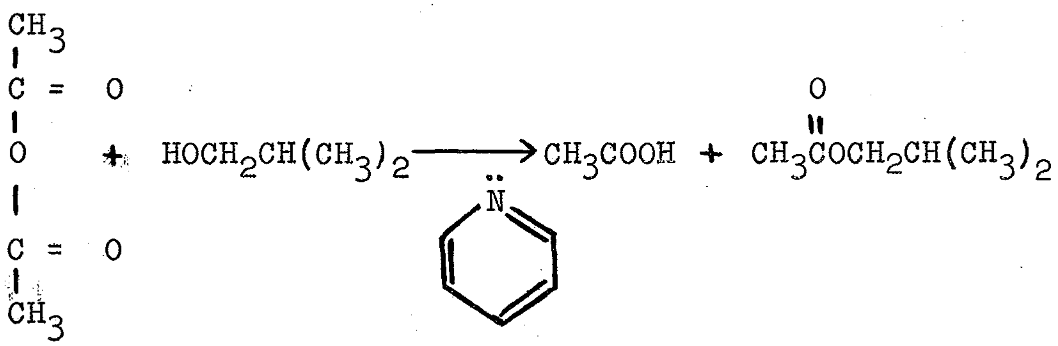
T_1 = 308.16 degrees Absolute

$$\log \frac{0.0002020}{0.0000455} = \frac{\Delta Ha}{(2.303)(1.987)} \times \frac{(333.16-308.16)}{(333.16)(308.16)}$$

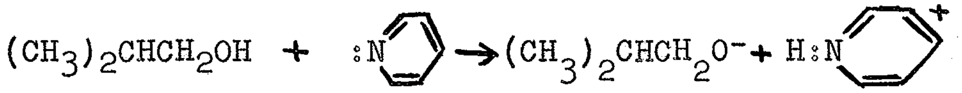
ΔH_a = 12,150 calories mole^{-1}

A more accurate value for the energy of activation is obtained from the slope of the line formed from the plot of log k versus the reciprocal of the Absolute temperature. To calculate ΔH_a, the slope is multiplied by -2.303R. The slope of the graph was determined to be -2,610. The energy of activation is therefore -(-2,610)(2.303)(1.987) or 11,900 calories $mole^{-1}$.

The over-all reaction for the system can be represented as follows.



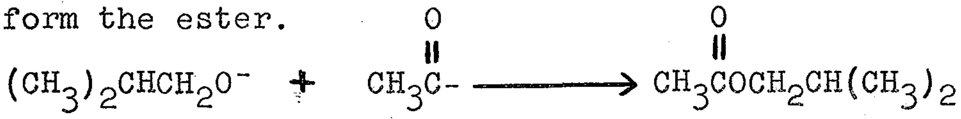
The probable mechanism for the individual steps involves the pyridine catalyst accepting a proton from the alcohol and then donating it to the acetate ion, one of the products of the cleavage of the anhydride molecule. The catalyst is reformed.



(1)

(2)

The isobutoxide radical then combines with the acetyl radical, another cleavage product of acetic anhydride, to form the ester.



$$(CH_3)_2CHCH_2O^- + CH_3\overset{O}{\overset{\|}{C}}- \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_2CH(CH_3)_2 \qquad (3)$$

Conant and Bramann (1928) investigated a similar reaction, the acetylation of napthol by acetic anhydride using pyridine as a catalyst. Their article discussed the use of both acid and base catalyst for this type of system.

An interesting point of the reaction is that the alcohol acts as a proton donor. Reactions between carboxylic acids and alcohols are of a similar nature. In considering the ionization data, this may seem strange but the reaction is not ionic and is not to be compared with the neutralization of an acid with a base.

One of the proofs for this mechanism is the reaction between a sulfur acid and oxygen alcohol.

$$RCOSH + R'OH \longrightarrow RCOOR' + H_2S$$

The formation of hydrogen sulfide indicates which substance contributes the proton.

The values obtained for the rate constant at the initial measurements are not considered to be very reliable. This can be attributed to errors involved in extrapolation and to the possibility that the system had not achieved temperature equilibrium at that time.

There is a possibility of the pyridine being neutralized by the formation of acetic acid. This would not seriously affect the calculations because the ionization of acetic acid in non aqueous solutions is very low. Also, if a competitive situation did exist between the acid product and the alcohol reactant as to which would contribute a proton to the pyridine, the amount of pyridium ion formed by the action of the acid would be negligible until the reaction had approached equilibrium. All of the measurements taken throughout this investigation were made before equilibrium was established.

The value for the activation energy, around 12,000 calories per mole, seems rather small for this system. A search through the literature did not reveal any values for this or a similar reaction. However, in considering the use of a catalyst as a method for lowering the energy requirements, this value becomes reasonable.

It should be mentioned that all values obtained from this study, both for the rate constant and also for the activation energy, are significant and specific for this particular system and the amount of catalyst used.

Aside from lowering the energy requirements for a chemical reaction, a catalyst can also be considered as having some effect on the frequency factor term in the Arrhenius equation.

$$k = Se^{-\Delta H_a/RT}$$

It is easily seen that the value of S, the frequency factor will affect the magnitude of the rate constant. This point was not investigated in this study.

CHAPTER VII

SUMMARY

The base catalyzed esterification of acetic anhydride and isobutyl alcohol was investigated with the purpose of determining the velocity of reaction. The mechanism of the reaction as well as that of the pyridine catalyst was proposed. The experiment was carried out at temperatures of 35, 45, 55, and 60 degrees Centigrade in order to ascertain the effect of temperature change on the speed of the reaction. From the data obtained, a theoretical term, the energy of activation was calculated.

Some of the possible complications involved in the reaction itself as well as the catalyst were discussed and certain conclusions were made on the significance that these would have on the final results.

A rather novel method was used to perform this investigation. It was not an original one, but an adaptation of the method used by Lowery (1958) who studied a similar reaction at constant temperature with varying amounts of catalyst. The method used involved a high frequency chemical oscillometer operating in the 120 megacycle range to measure the changing electrical properties of the reacting solution and consequently relate these changes to the progress of the reaction. This procedure, using this particular instrument, is considered to be a useful method for studying chemical reactions of this particular nature.

TABLE I

COMPARISON OF VOLUME(ML) TO MOLES OF REAGENT

ANHYDRIDE		ALCOHOL		ESTER		ACID	
VOLUME-	MOLES	VOLUME-	MOLES	VOLUME-	MOLES	VOLUME-	MOLES
47.27	0.50	92.51	1.00	0	0.00	0	0.00
42.50	0.45	87.91	0.95	6.66	0.05	2.87	0.05
37.80	0.40	83.25	0.90	13.35	0.10	5.74	0.10
28.35	0.30	74.00	0.80	26.70	0.20	11.48	0.20
18.92	0.20	64.65	0.70	40.10	0.30	17.22	0.30
9.45	0.10	55.50	0.60	53.45	0.40	22.92	0.40
0	0.00	46.29	0.50	66.60	0.50	28.69	0.50

TABLE II

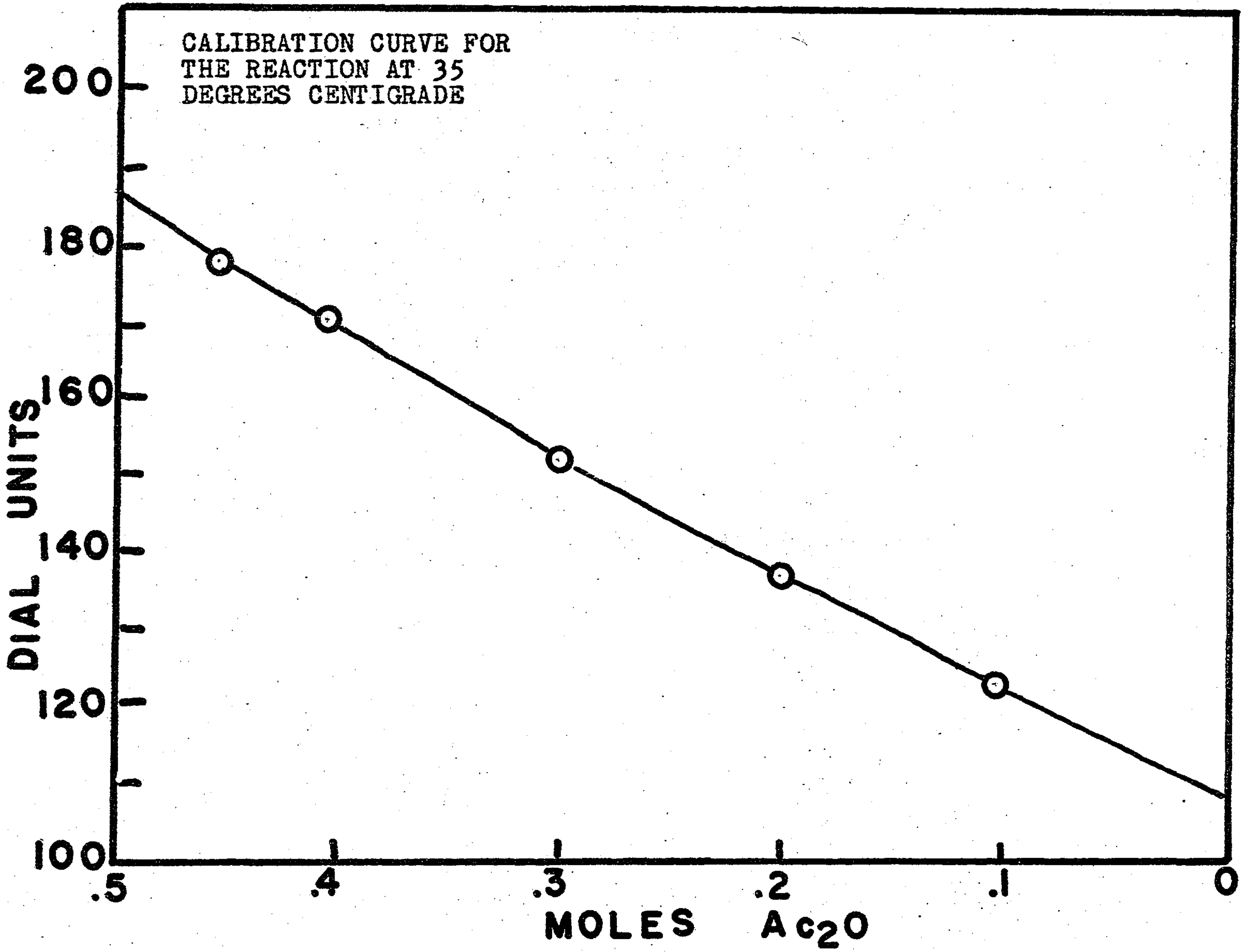
EXPERIMENTAL DATA FOR THE REACTION AT 35 DEGREES CENTIGRADE

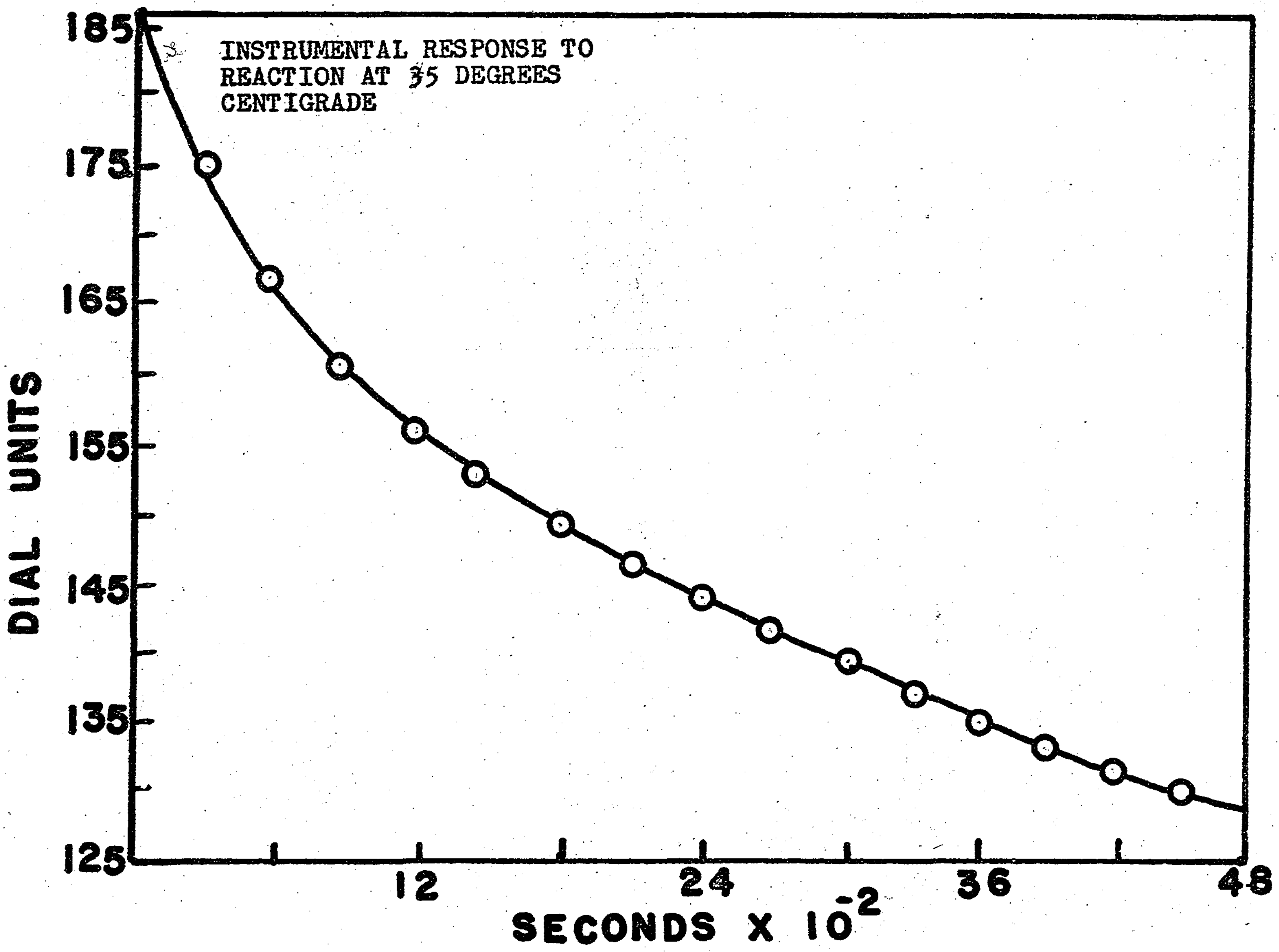
TIME (SEC)	(B - X)	(A - X)	LOG $\frac{B(A - X)}{A(B - X)}$	$\frac{2.303}{(A - B)t}$	k(LITERS-MOLE^{-1}SEC^{-1})
300	0.435	0.935	0.0314	0.01535	0.0000678
600	0.393	0.893	0.0549	0.00768	0.0000594
900	0.358	0.858	0.0791	0.00512	0.0000570
1200	0.330	0.830	0.0965	0.00384	0.0000522
1500	0.310	0.810	0.1156	0.00307	0.0000500
1800	0.290	0.790	0.1335	0.00256	0.0000481
2100	0.270	0.770	0.1538	0.00219	0.0000474
2400	0.253	0.753	0.1728	0.00192	0.0000467
2700	0.235	0.735	0.1945	0.00171	0.0000468
3000	0.220	0.720	0.2135	0.00154	0.0000463
3300	0.207	0.707	0.2317	0.00140	0.0000455
3600	0.190	0.690	0.2588	0.00128	0.0000467
3900	0.180	0.680	0.2765	0.00118	0.0000460
4200	0.172	0.672	0.2903	0.00110	0.0000463
4500	0.160	0.660	0.3143	0.00103	0.0000457
4800	0.152	0.652	0.3308	0.00096	0.0000447

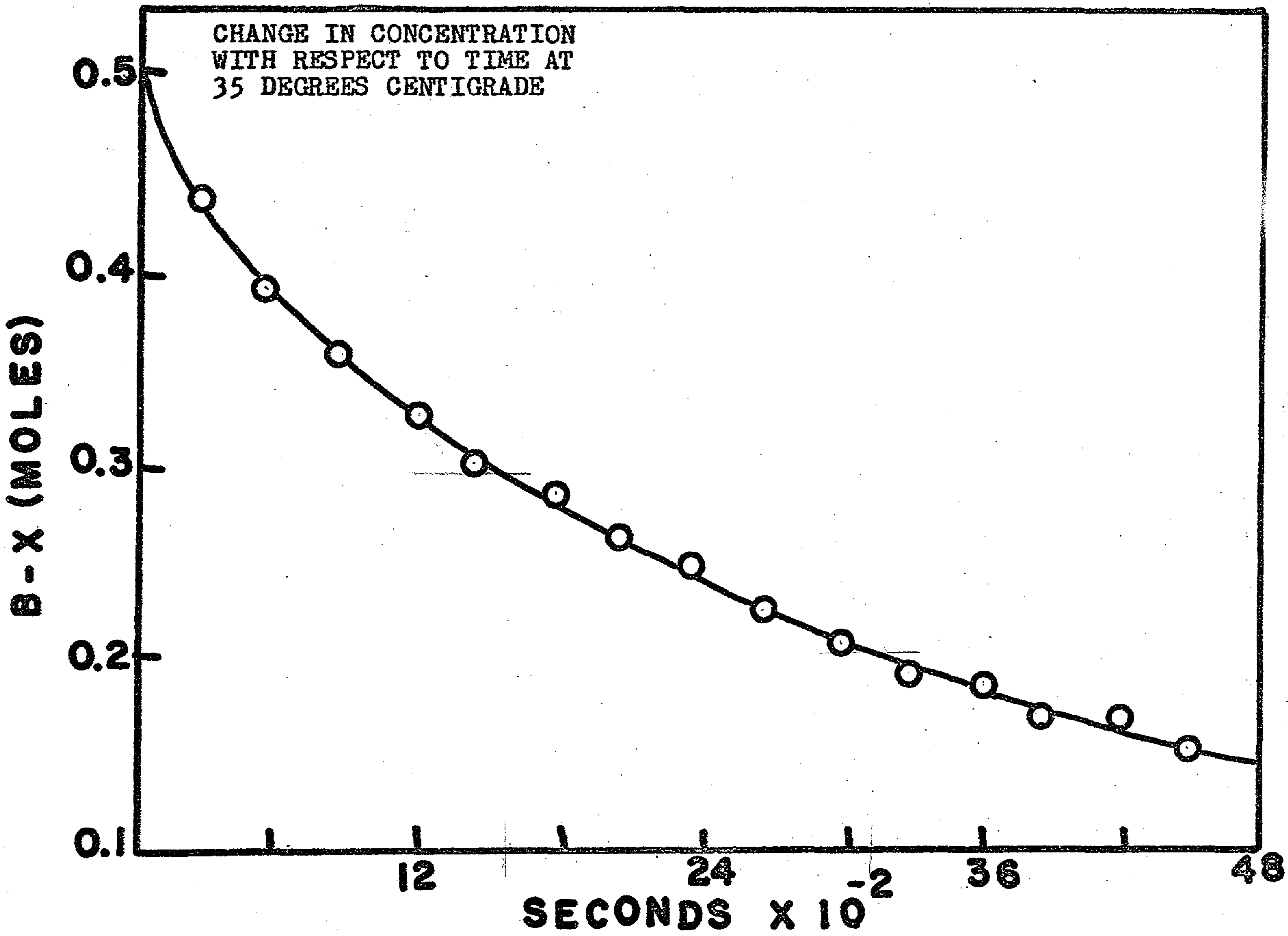
$$\text{SLOPE OF LINE} = \frac{k(A - B)}{2.303} = 0.698 \times 10^{-4}$$

$$k = (2.303)(0.698 \times 10^{-4})/(A - B) \quad \times \quad 0.1408 \text{ LITERS}$$

$$= 0.0000455 \text{ LITERS-MOLE}^{-1}\text{SEC}^{-1}$$


CALIBRATION CURVE FOR
THE REACTION AT 35
DEGREES CENTIGRADE
DIAL UNITS
200
180
160
140
120
100
MOLES Ac_2O
.5
.4
.3
.2
.1
0


INSTRUMENTAL RESPONSE TO
REACTION AT 35 DEGREES
CENTIGRADE
DIAL UNITS
185
175
165
155
145
135
125
12
24
36
48
SECONDS X 10⁻²

CHANGE IN CONCENTRATION
WITH RESPECT TO TIME AT
35 DEGREES CENTIGRADE
B-X (MOLES)
0.5
0.4
0.3
0.2
0.1
12
24
36
48
SECONDS X 10^{-2}

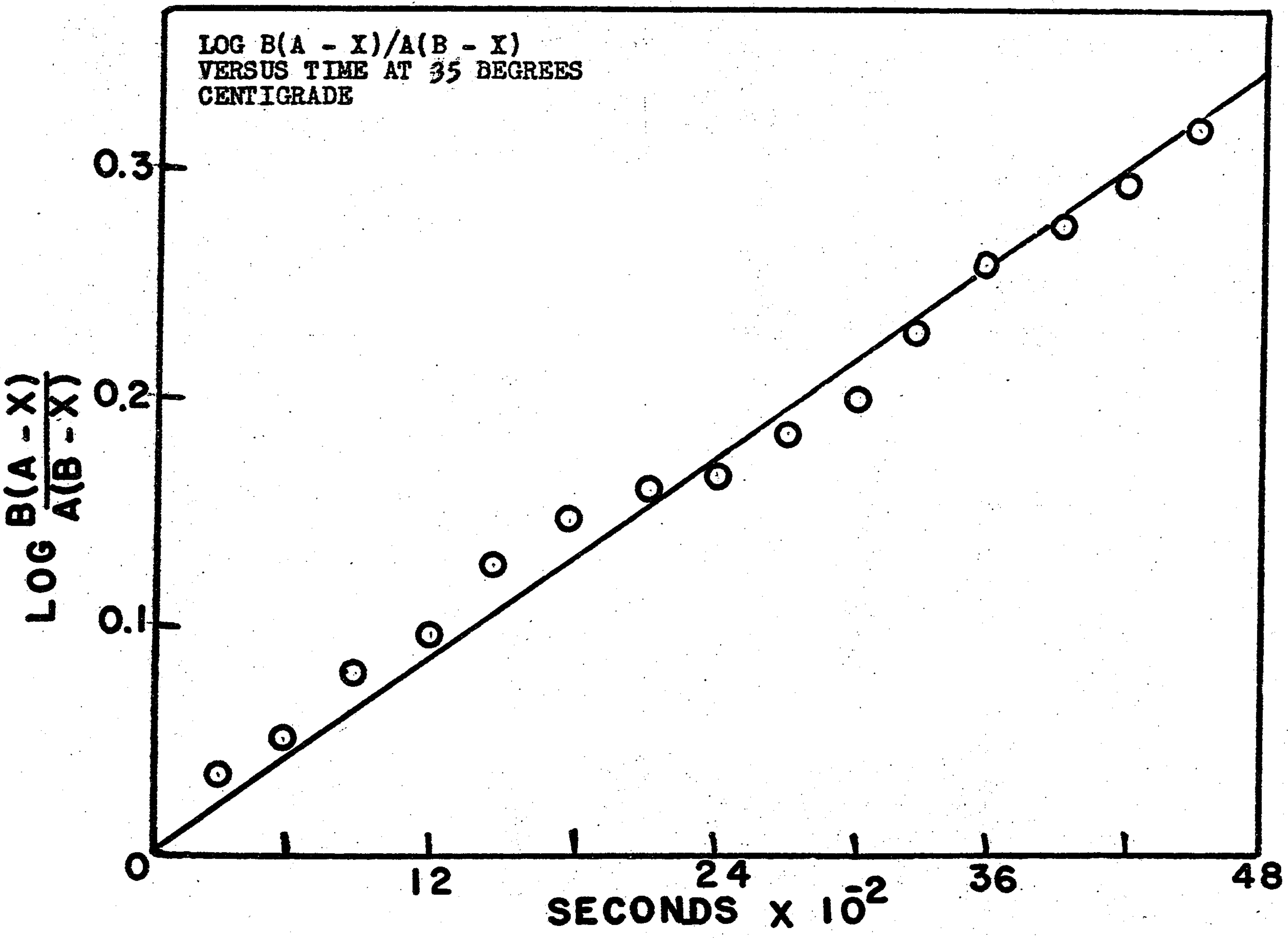

LOG B(A - X)/A(B - X)
VERSUS TIME AT 35 DEGREES
CENTIGRADE
0.3
0.2
0.1
0
LOG $\frac{B(A-X)}{A(B-X)}$
12
24
36
48
SECONDS X 10^{-2}

TABLE III

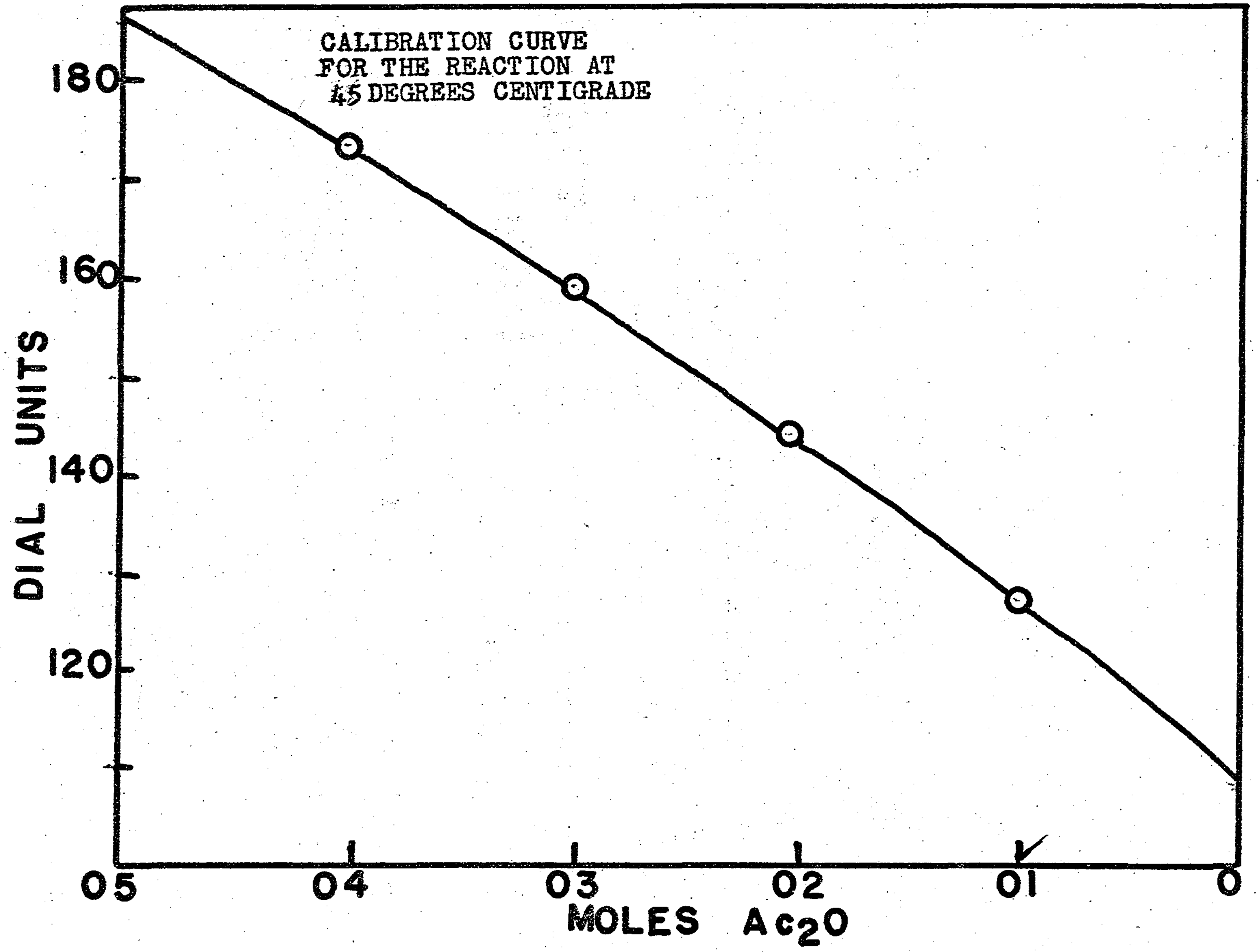
EXPERIMENTAL DATA FOR THE REACTION AT 45 DEGREES CENTIGRADE

TIME (SEC)	(B - X)	(A - X)	$\log\frac{B(A - X)}{A(B - X)}$	$\frac{2.303}{(A - B)t}$	k(LITERS-MOLE^{-1}SEC^{-1})
300	0.410	0.910	0.0453	0.01535	0.0000977
600	0.347	0.847	0.0864	0.00768	0.0000943
900	0.322	0.822	0.1055	0.00512	0.0000761
1200	0.261	0.761	0.1644	0.00384	0.0000887
1500	0.230	0.730	0.1974	0.00307	0.0000853
1800	0.203	0.703	0.2380	0.00256	0.0000830
2100	0.180	0.680	0.2753	0.00219	0.0000846
2400	0.157	0.657	0.3202	0.00192	0.0000865
2700	0.135	0.635	0.3720	0.00171	0.0000893
3000	0.119	0.619	0.4150	0.00154	0.0000897

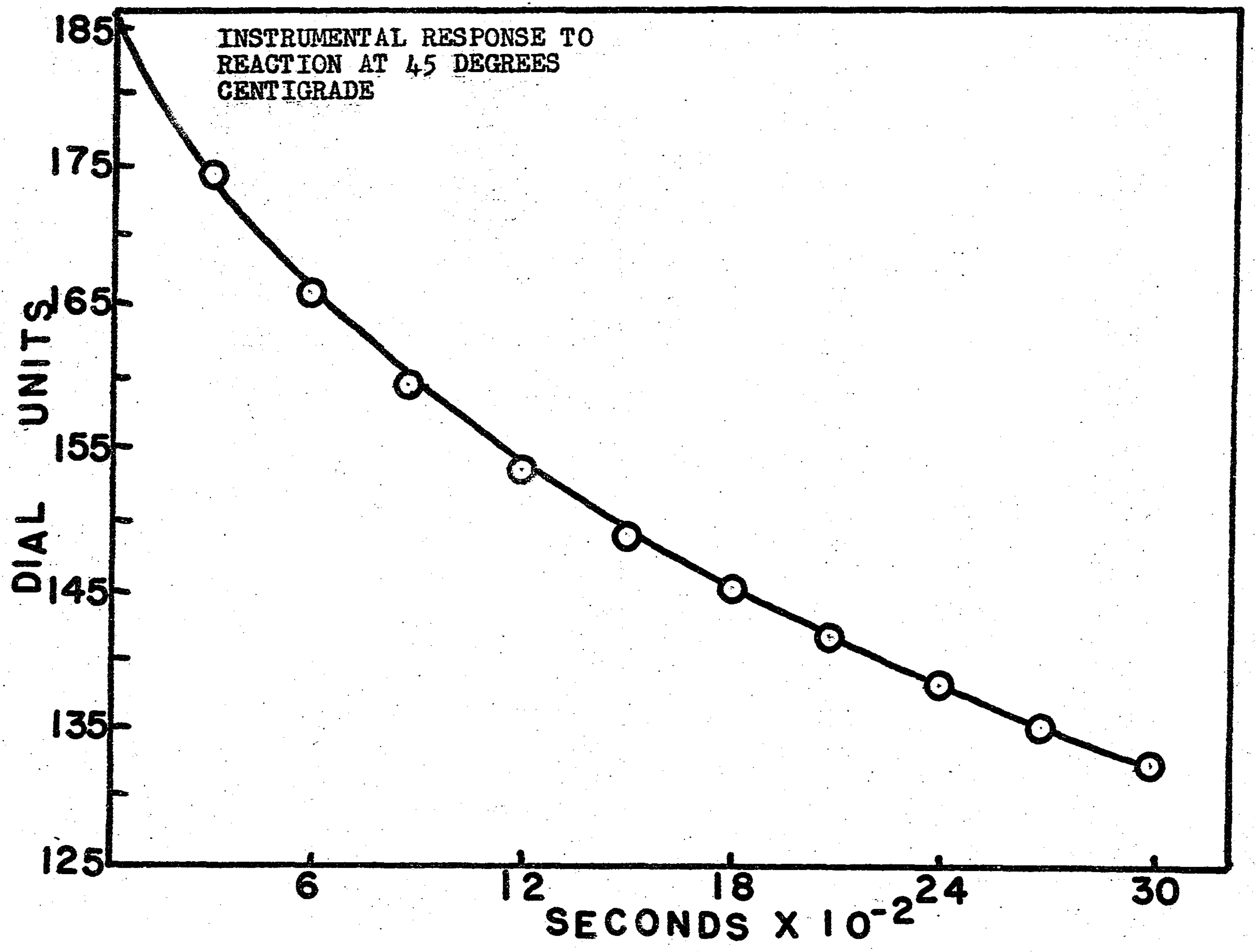
$$\text{SLOPE OF LINE} = \frac{k(A - B)}{2.303} = 1.38 \times 10^{-4}$$

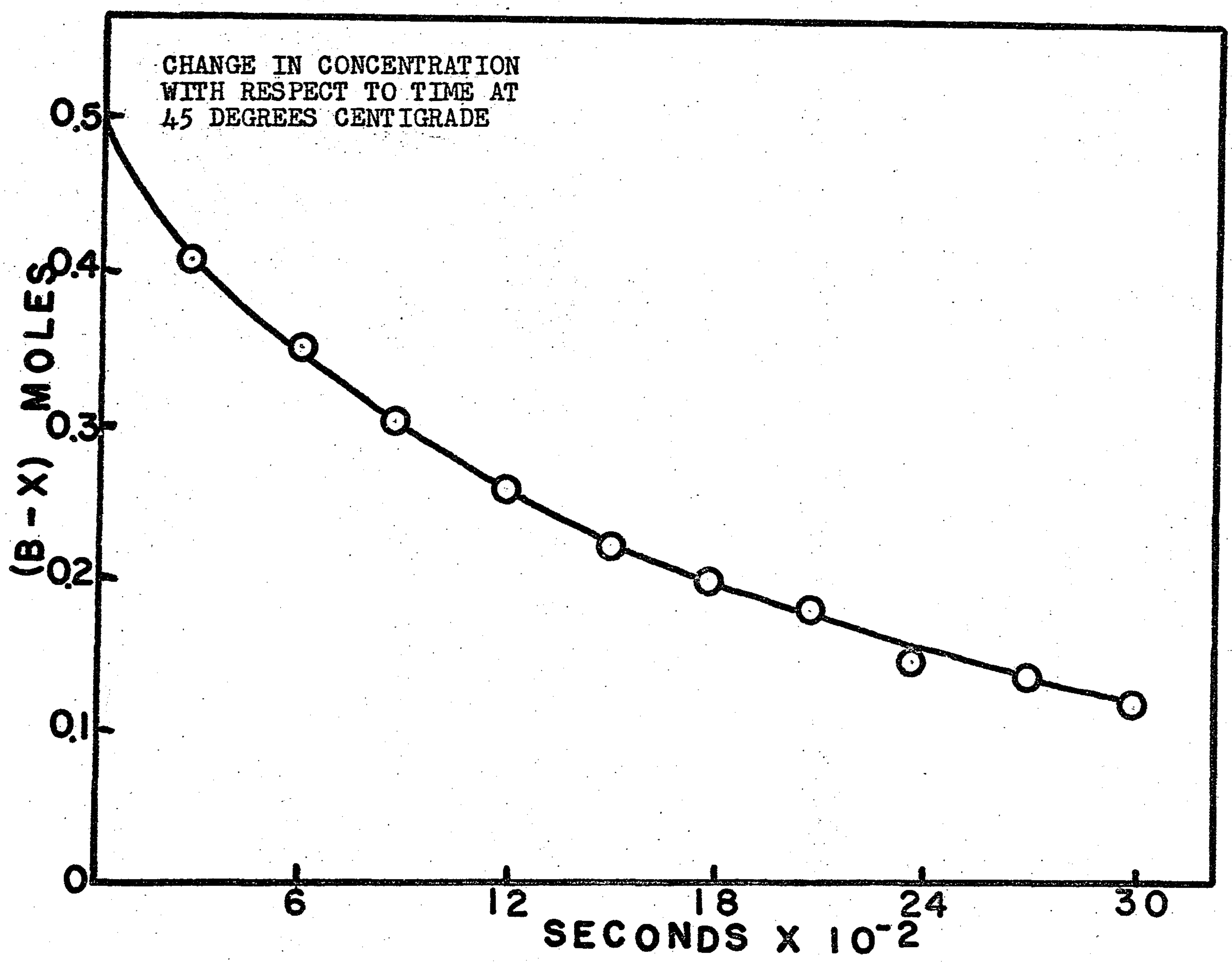
$$k = (2.303)(1.38 \times 10^{-4})/(A - B) \times 0.1408 \text{ LITERS}$$

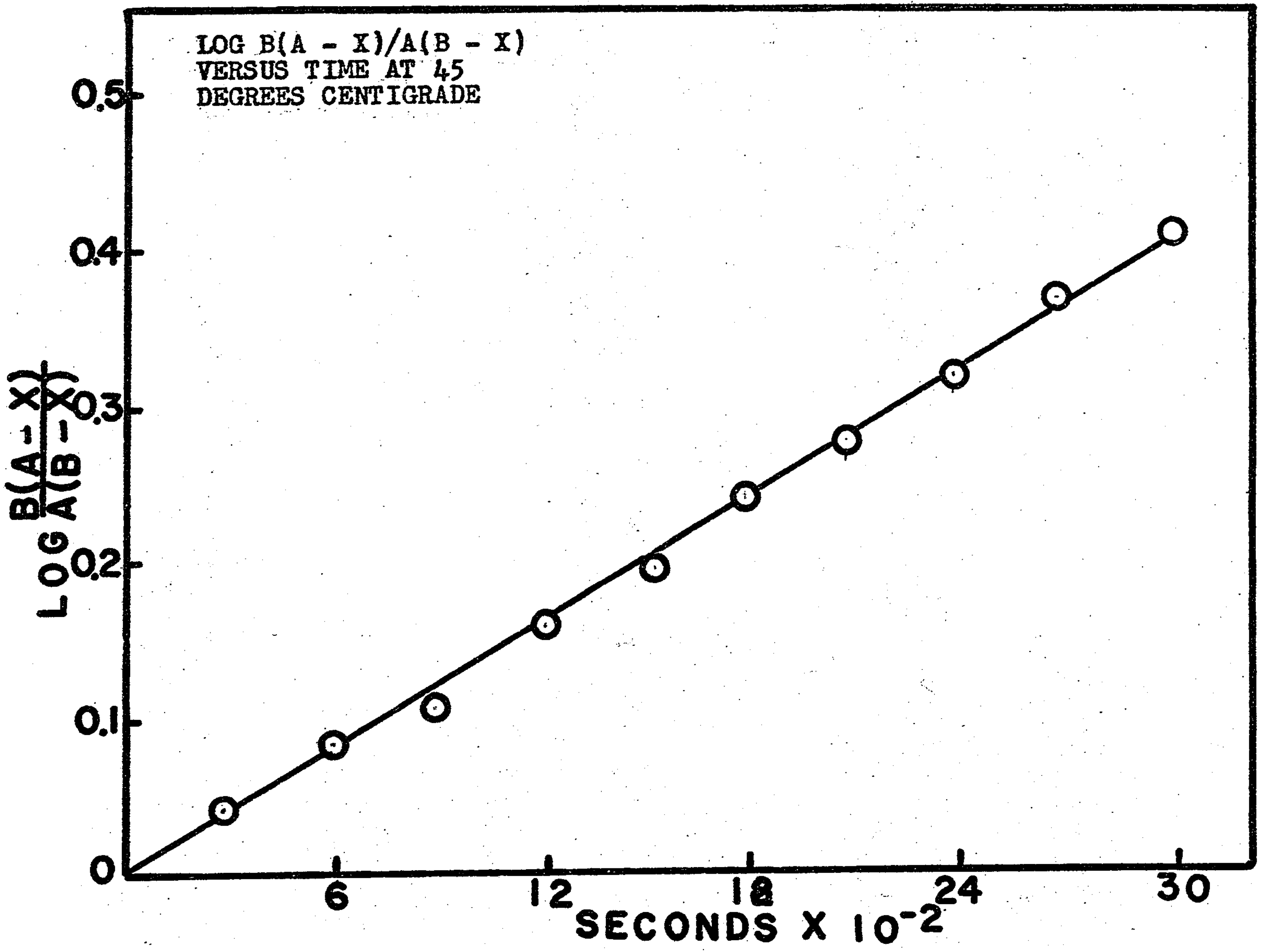
$$= 0.0000896 \text{ LITERS-MOLE}^{-1}\text{SEC}^{-1}$$



CALIBRATION CURVE
FOR THE REACTION AT
45 DEGREES CENTIGRADE
DIAL UNITS
180
160
140
120
MOLES Ac_2O
05
04
03
02
01
0


INSTRUMENTAL RESPONSE TO
REACTION AT 45 DEGREES
CENTIGRADE
185
175
165
155
145
135
125
DIAL UNITS
6
12
18
24
30
SECONDS X 10^{-2}


CHANGE IN CONCENTRATION
WITH RESPECT TO TIME AT
45 DEGREES CENTIGRADE
(B - X) MOLES
0.5
0.4
0.3
0.2
0.1
0
6
12
18
24
30
SECONDS X 10^{-2}



LOG B(A - X)/A(B - X)
VERSUS TIME AT 45
DEGREES CENTIGRADE

TABLE IV

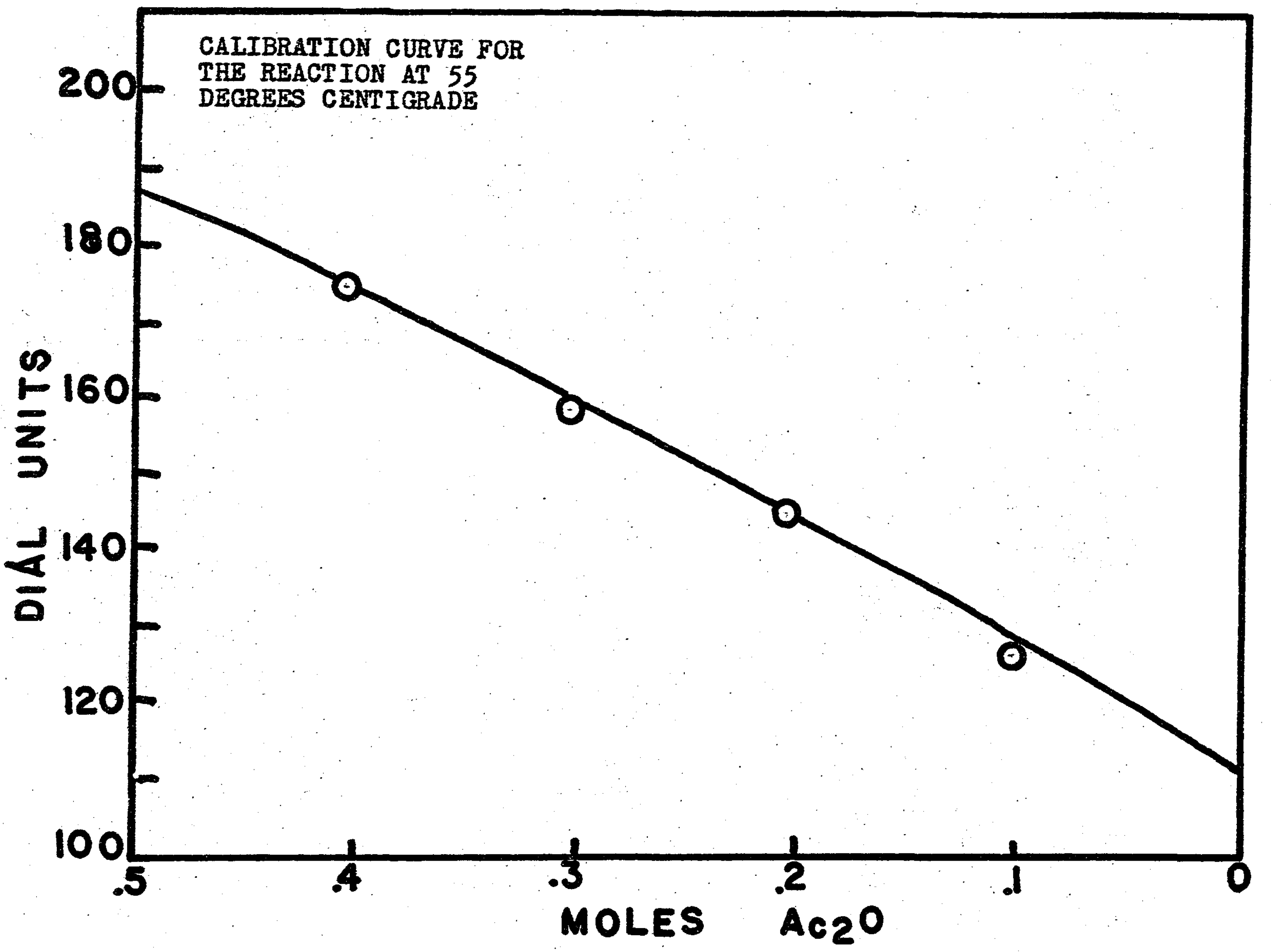
EXPERIMENTAL DATA FOR THE REACTION AT 55 DEGREES CENTIGRADE

TIME (SEC)	(B - X)	(A - X)	$\mathrm{LOG}\frac{B(A - X)}{A(B - X)}$	$\frac{2.303}{(A - B)t}$	k(LITERS-MOLE^{-1}SEC^{-1})
300	0.400	0.900	0.0647	0.01535	0.000139
600	0.300	0.800	0.1255	0.00768	0.000136
900	0.225	0.725	0.2068	0.00512	0.000149
1200	0.181	0.681	0.2744	0.00384	0.000148
1500	0.143	0.643	0.3541	0.00307	0.000153
1800	0.122	0.622	0.4065	0.00256	0.000147
2100	0.100	0.600	0.4771	0.00219	0.000147
2400	0.083	0.583	0.5478	0.00192	0.000155
2700	0.063	0.563	0.6484	0.00171	0.000156
3000	0.051	0.561	0.7324	0.00154	0.000158

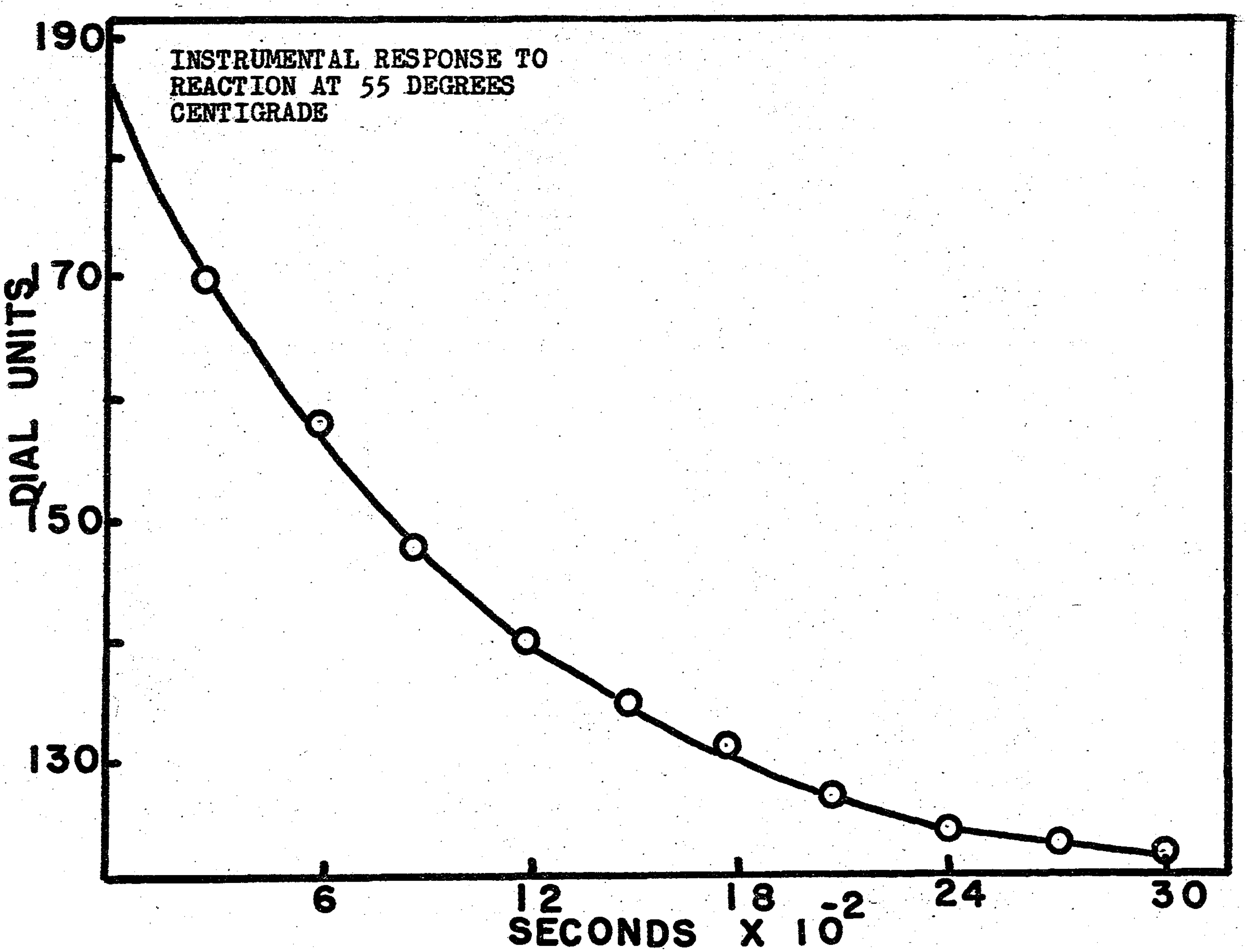
$$\text{SLOPE OF LINE} = \frac{k(A - B)}{2.303} = 0.227 \times 10^{-3}$$

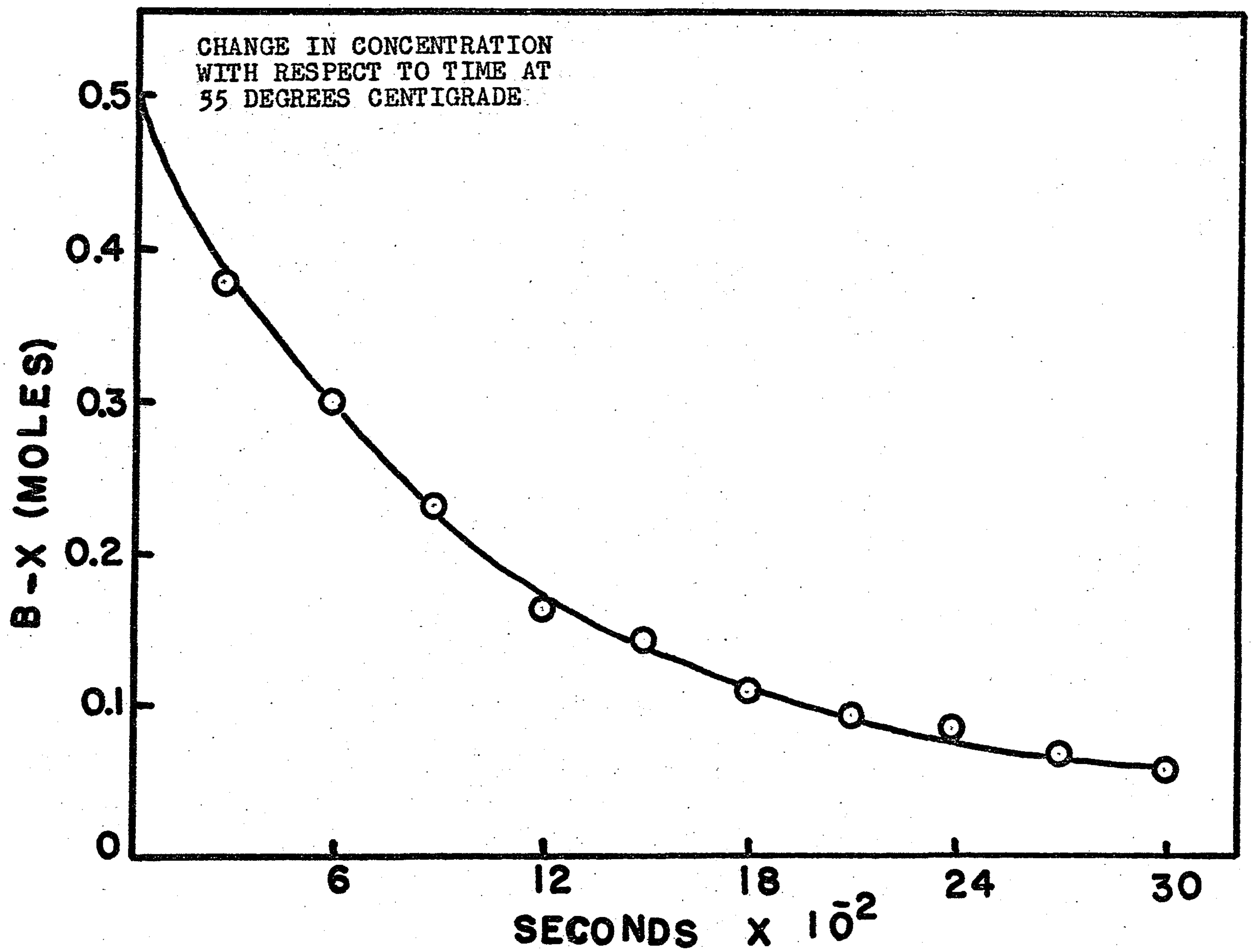
$$k = (2.303)(0.227 \times 10^{-3})/(A - B) \times 0.1408 \text{ LITERS}$$

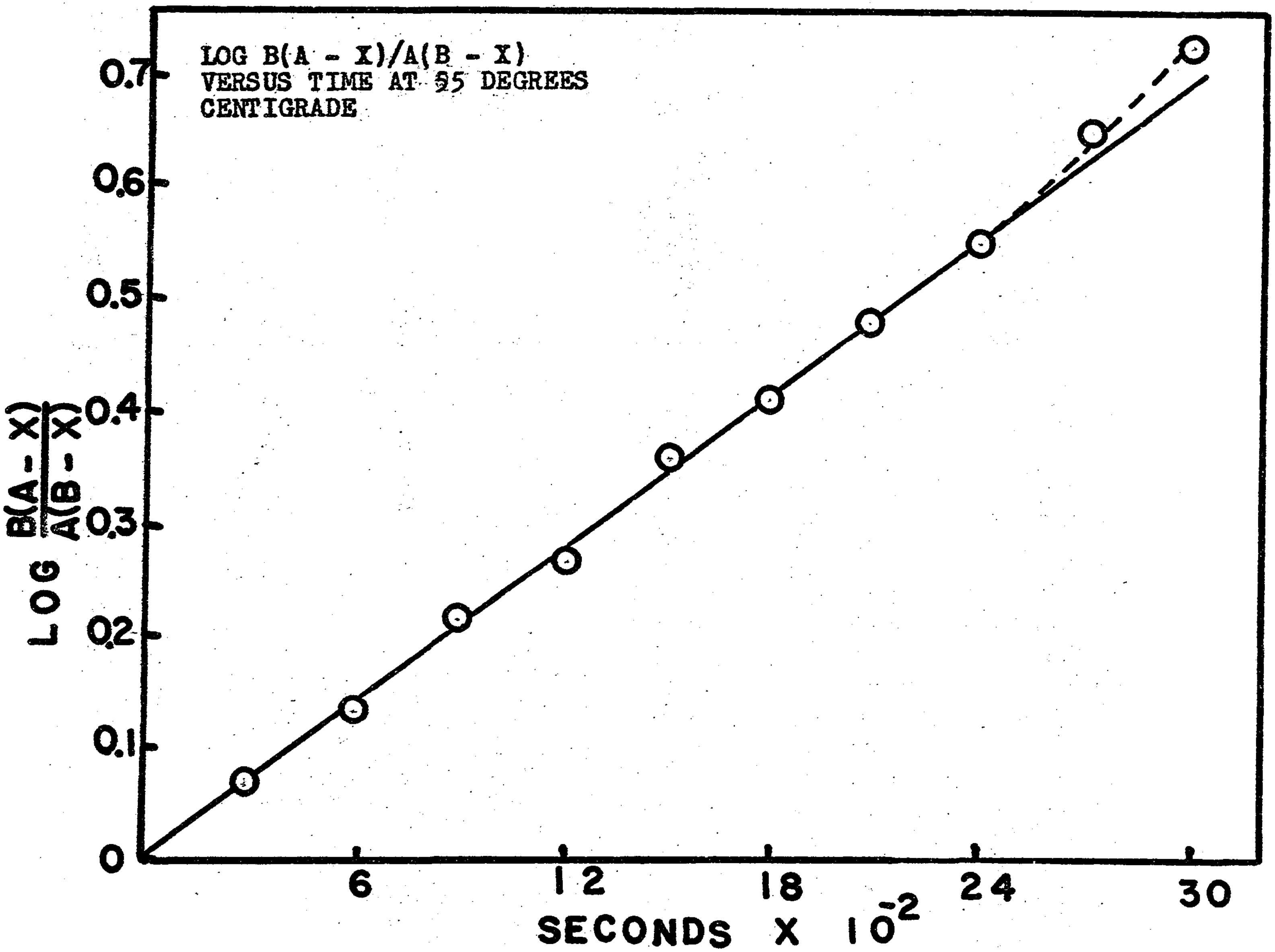
$$= 0.000147 \text{ LITERS-MOLE}^{-1}\text{SEC}^{-1}$$



CALIBRATION CURVE FOR
THE REACTION AT 55
DEGREES CENTIGRADE


INSTRUMENTAL RESPONSE TO
REACTION AT 55 DEGREES
CENTIGRADE
190
170
150
130
DIAL UNITS
6
12
18
24
30
SECONDS X 10⁻²


CHANGE IN CONCENTRATION
WITH RESPECT TO TIME AT
55 DEGREES CENTIGRADE
B-X (MOLES)
0.5
0.4
0.3
0.2
0.1
0
6
12
18
24
30
SECONDS X 10^{-2}



LOG B(A - X)/A(B - X)
VERSUS TIME AT 25 DEGREES
CENTIGRADE

TABLE V

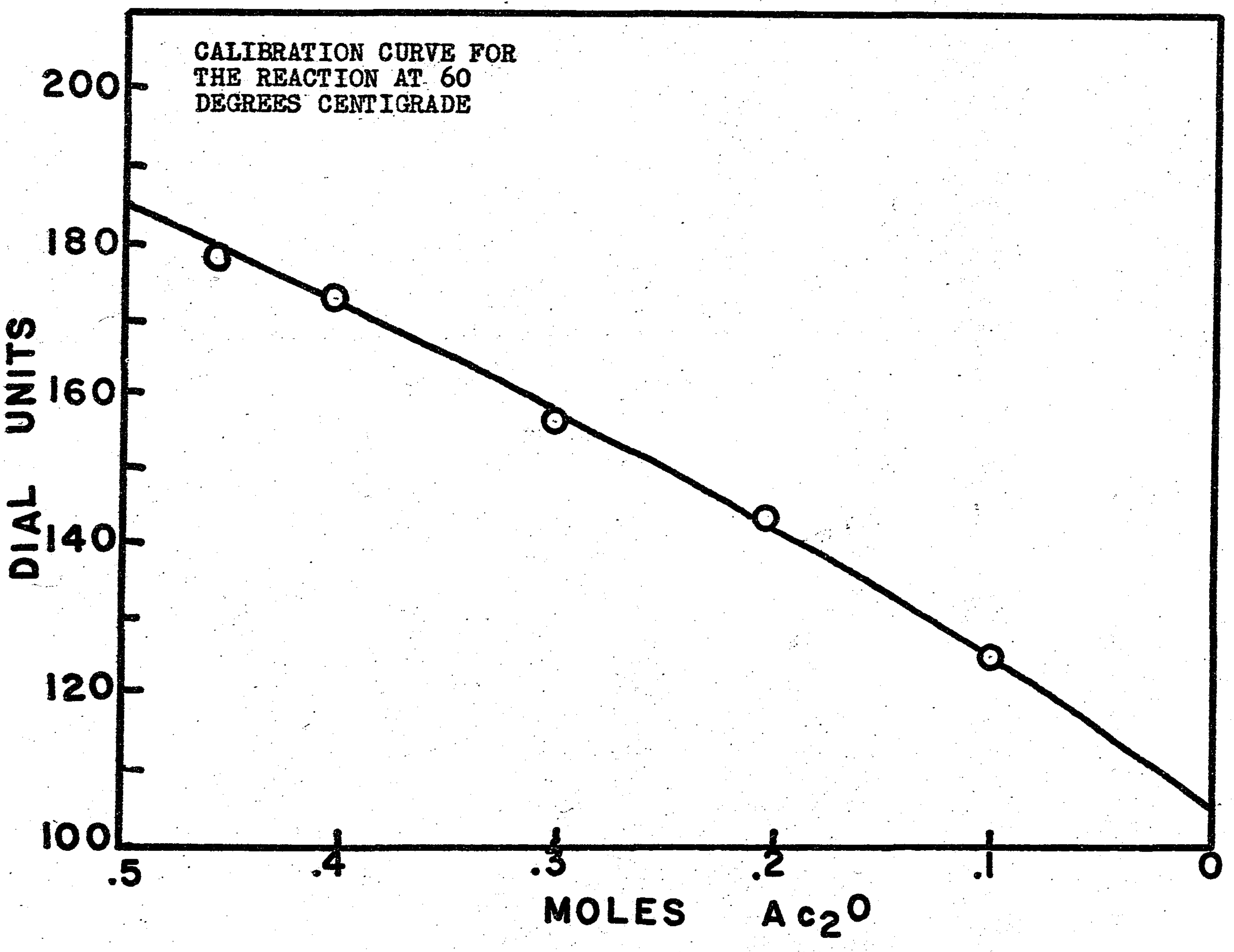
EXPERIMENTAL DATA FOR THE REACTION AT 60 DEGREES CENTIGRADE

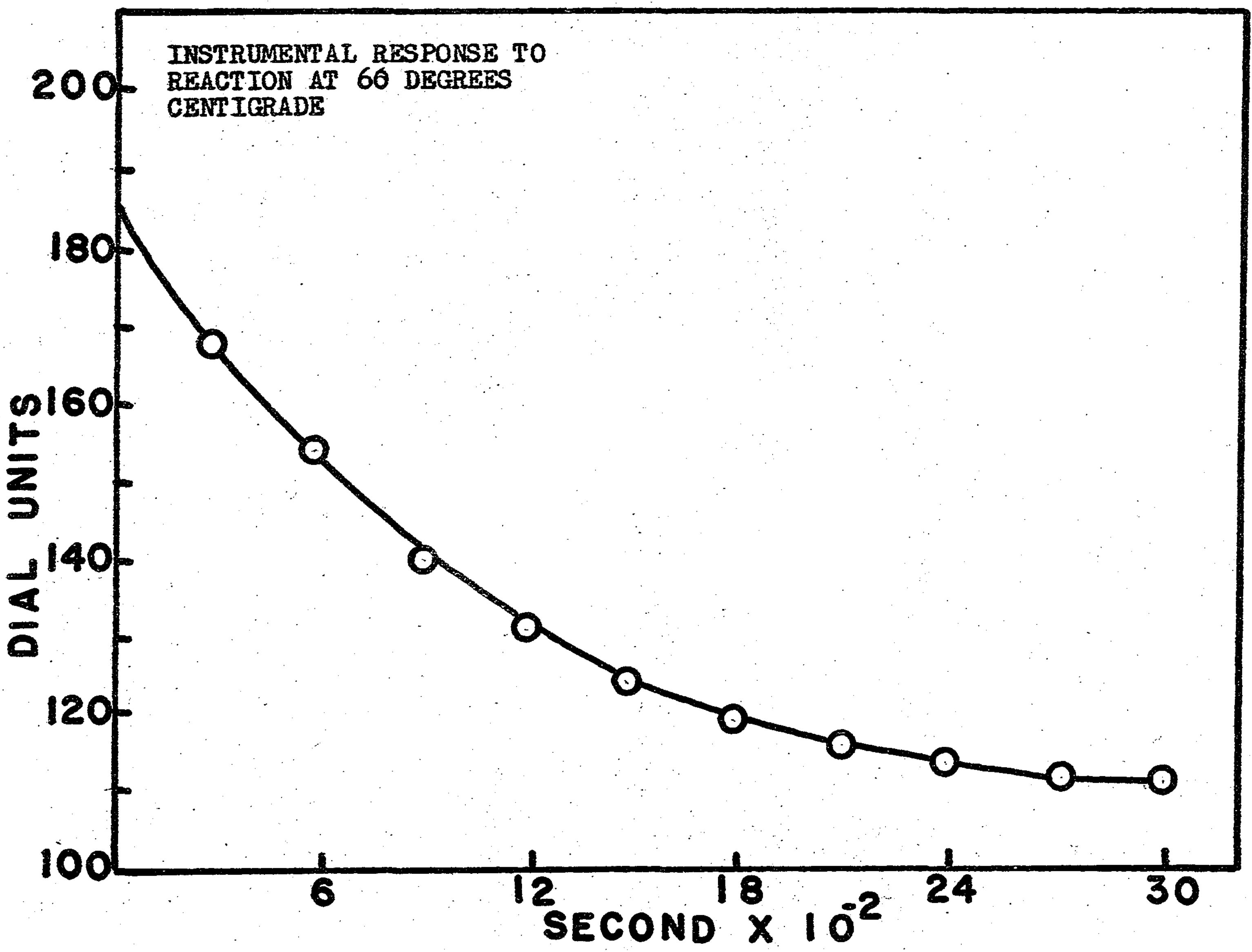
TIME (SEC)	(B - X)	(A - X)	$\log\frac{B(A - X)}{A(B - X)}$	$\frac{2.303}{(A - B)t}$	k(LITERS-MOLE^{-1}SEC^{-1})
300	0.332	0.832	0.0976	0.01535	0.000210
600	0.234	0.734	0.1956	0.00768	0.000211
900	0.174	0.674	0.2867	0.00512	0.000206
1200	0.131	0.631	0.3821	0.00384	0.000206
1500	0.109	0.609	0.4456	0.00307	0.000192
1800	0.075	0.575	0.5832	0.00256	0.000209
2100	0.060	0.560	0.6693	0.00219	0.000205
2400	0.047	0.547	0.7642	0.00192	0.000206
2700	0.034	0.534	0.8949	0.00171	0.000215
3000	0.028	0.528	0.9741	0.00154	0.000211

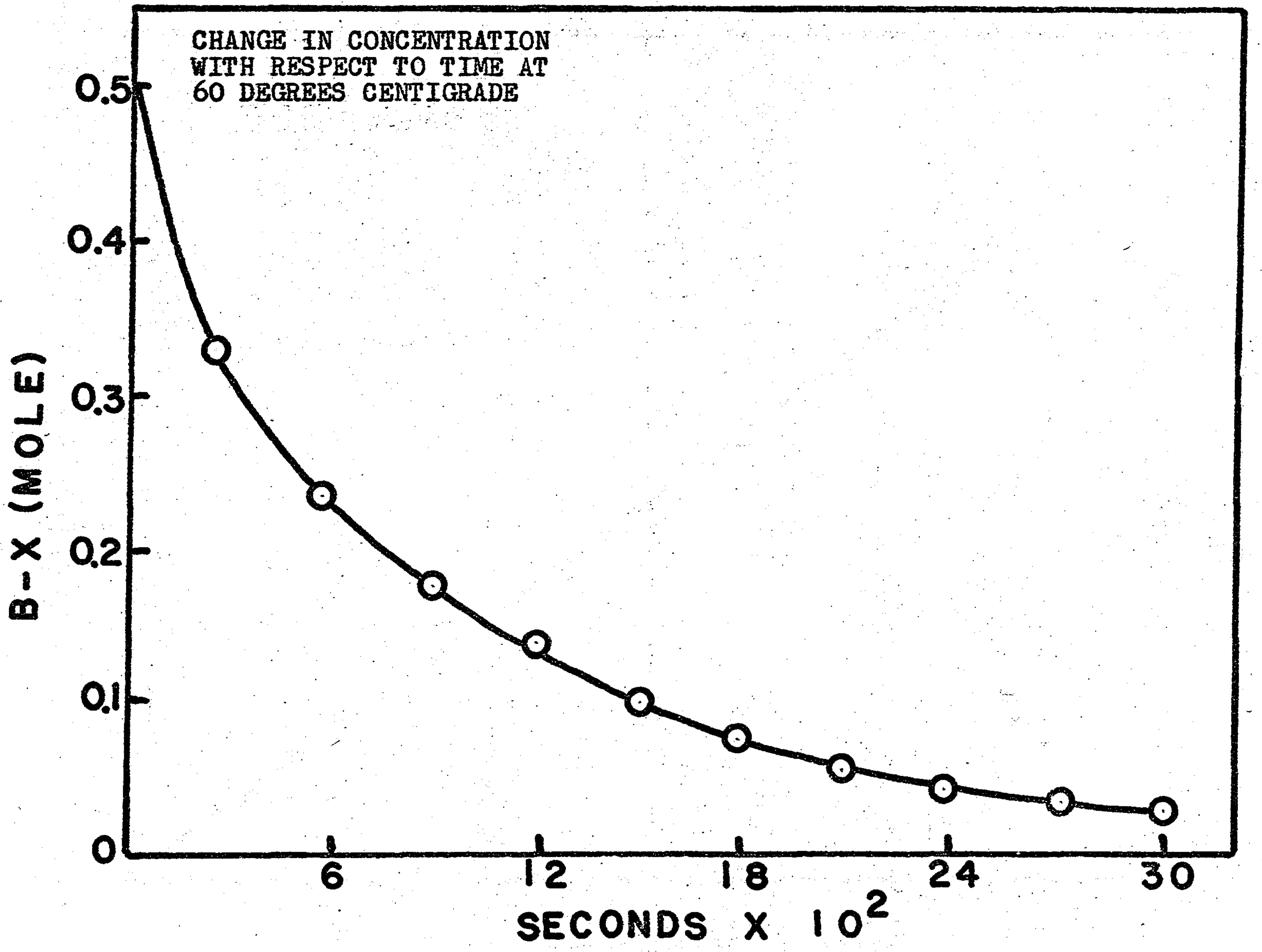
$$\text{SLOPE OF LINE} = \frac{k(A - B)}{2.303} = 0.315 \times 10^{-3}$$

$$k = (2.303)(0.315 \times 10^{-3})/(A - B) \times 0.1408 \text{ LITERS}$$

$$= 0.000202 \text{ LITERS-MOLE}^{-1}\text{SEC}^{-1}$$


CALIBRATION CURVE FOR
THE REACTION AT 60
DEGREES CENTIGRADE
DIAL UNITS
200
180
160
140
120
100
.5
.4
.3
.2
.1
0
MOLES Ac_2O


INSTRUMENTAL RESPONSE TO REACTION AT 66 DEGREES CENTIGRADE
DIAL UNITS
200
180
160
140
120
100
6
12
18
24
30
SECOND X 10^{-2}


CHANGE IN CONCENTRATION
WITH RESPECT TO TIME AT
60 DEGREES CENTIGRADE
B-X (MOLE)
0.5
0.4
0.3
0.2
0.1
0
6
12
18
24
30
SECONDS X 10^2

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