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STILLSON

THE
KINETICS
OF THE
EXCHANGE

THE KINETICS OF THE EXCHANGE BETWEEN BENZYL IODIDE AND IODIDE ION

By

Paul Stillson

A Thesis
In partial fulfillment of the
Requirements for the Degree of
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DOCTOR OF PHILOSOPHY

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THE KINETICS OF THE EXCHANGE BETWEEN BENZYL IODIDE AND IODIDE ION

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CHAPTER I

INTRODUCTION

Theory of Replacement Reactions

A general form of an ion-molecule replacement reaction occurring at a saturated carbon atom may be represented by

$$Y^- + R\text{-}X \rightleftharpoons Y\text{-}R + X^-$$

where Y^- is a negatively charged atom or group which can replace an atom or group X in the molecule R-X and R is any organic radical which is saturated at the point of attachment of X. The mechanisms which have been postulated[1,2,3] for the above reaction may be divided into the following two groups: (1) those which assume primary dissociation of the neutral organic reactant into ions as the rate-determining step; (2) those which postulate the formation of an activated complex from the two reactants as the rate-determining step.

The first mechanism implies a two-stage process, in which a rate-determining dissociation is followed by a fast reaction between the carbon cation formed and the substituting reagent. For example, the reaction, $Y^- + R\text{-}X \rightleftharpoons R\text{-}Y + X^-$, may take place in two steps:

(1) $R\text{-}X \xrightarrow{\text{slow}} R^{+} + X^{-}$ rate-determining step (ionization)

(2) $Y^{-} + R^{+} \xrightarrow{\text{fast}} Y\text{-}R.$

In this mechanism only one reactant, R-X, is concerned in the rate-determining stage and the mechanism is termed "unimolecular."

The second mechanism implies that the process is initiated by the attack of the reagent Y^{-} on the molecule R-X. An activated complex is then formed wherein the reagent Y^{-} adds to the R-X molecule. The final step is the expulsion of the group X^{-} from the activated complex to yield the substituted product Y-R. For example, the reaction, $Y^{-} + R\text{-}X \rightleftharpoons R\text{-}Y + X^{-}$, may take place in one step,

$$Y^{-} + R\text{-}X \xrightarrow[\text{rate-determining}]{\text{slow}} \overset{\delta-}{Y}\cdots R\cdots\overset{\delta-}{X} \xrightarrow{\text{fast}} Y\text{-}R + X^{-},$$

where the δ's represent partial charges. The mechanism shown above represents a one-stage process, simultaneously involving both reactants, and is termed "bimolecular."

Duality of Mechanism

The first indications of the duality of mechanism in substitution reactions were obtained in a study of the alkaline hydrolysis of several alkyl bromides[4], namely,

methyl bromide, ethyl bromide, isopropyl bromide, and tertiary butyl bromide. The purpose of these experiments was to determine the rate of hydrolysis as a function of the ability of an alkyl group to release electrons to the seat of substitution. It was found that the rate of hydrolysis decreased in the order methyl > ethyl > isopropyl and the kinetics observed were of second order. In the region of the isopropyl group the rate passed through a minimum and a mixture of first and second order kinetics were observed, either of which could be brought into prominence by altering the conditions of the hydrolysis. Finally, the rate of hydrolysis increased in the region of the tertiary butyl group and the kinetics observed were first order with respect to the tertiary butyl bromide and independent of the hydroxide concentration. Since the experimental conditions were not varied throughout the investigation, it may be assumed that a change in the order of the hydrolysis reaction was indicative of a change in reaction mechanism. Thus, it is seen that the critical region of mechanistic change was located at the isopropyl group under the conditions employed in this investigation.

The dual mechanism theory was then applied to the aralphyl chlorides namely, methyl chloride, benzyl chloride, methyl bromide, ethyl bromide, isopropyl bromide, and tertiary butyl bromide. The purpose of these experiments was to determine the mode of hydrolysis as a function of the ability of an alkyl group to release electrons to the seat of substitution. It was found that the rate of hydrolysis decreased in the order given (methyl to isopropyl) and the kinetics observed were of second order. In the region of the isopropyl group the rate passed through a minimum and a mixture of first and second order kinetics was observed, either of which could be brought into prominence by altering the conditions of the experiment. Finally, the rate of hydrolysis increased in the region of the tertiary butyl group and the kinetics observed were first order with respect to the tertiary butyl bromide and independent of the hydroxide concentration. Since the experimental conditions were not varied throughout the investigation, it was assumed that a change in the order of the hydrolysis reaction was indicative of a change in reaction mechanism. Thus, it is seen that the critical region of mechanistic change was located at the isopropyl group under the conditions employed in this investigation.

The dual mechanism theory was then applied to the aralkyl chlorides namely, benzyl chloride, [illegible] and benzhydryl chloride, by Hughes, Ingold, and Patel.[5] The rates of hydrolysis of each chloride in the above series were investigated and the minimum rate was observed in the benzyl group. The rate of hydrolysis increased rapidly upon moving further to the right in the series. It has been seen previously that the alkaline hydrolysis of methyl bromide proceeded through a "bimolecular" mechanism. Therefore, it might be expected that a critical region of mechanistic change would occur within the benzyl group and the "unimolecular" mechanism would predominate in all the groups to the right of the benzyl group in the aralphyl series. This was confirmed by Bateman, Hughes, and Ingold[6] who investigated the exchange reaction of benzhydryl chloride with fluoride ion in liquid SO_2, and Ward[7] who investigated the alkaline hydrolysis of benzhydryl chloride in aqueous alcohol. Both found the mechanism of the substitution to be "unimolecular."

Other types of reactions of benzyl halides have been investigated with similar results. In reactions of benzyl bromide with sodium sulfite[8], it was reported that the kinetics observed correspond to no simple type, but could only be approximated as the sum of two reactions. Baker and Nathan[9,10], utilizing the reaction of substituted benzyl

bromides with pyridine, also confirmed these results.

It was suggested by Hughes[1] in the formulation of the dual mechanism theory that, although each of the mechanisms must exist throughout a series, only one mechanism could be observed on each side of the critical point. Since then, only one attempt has been made to quantitatively separate mechanistic mixtures, but without appreciable success.[11]

Effect of Solvent

Since the replacement reaction discussed above is characterized by charge transfers which occur in the rate-determining step, one would predict that both the rate of reaction and the type of mechanism would vary with the solvent. One of the effects to consider in connection with the influence of solvent on reaction rate is the possibility of solvation of the substances concerned in the reaction.[12] In this instance, the main concern is with the effect of solvation on the energy required for the formation of the activated complex. In order to illustrate this effect, consider a reaction in a particular solvent in which neither the reactants, nor the activated complex, is solvated. If in a second solvent the activated complex is solvated but the reactants are unaffected, then the energy of activation provides with particl[illegible] [illegible] [illegible] [illegible] [illegible].

It was suggested by [illegible] [illegible] [illegible] [illegible] [illegible] the dual mechanism theory [illegible], although many of the mechanisms [illegible] which [illegible] [illegible] [illegible] could be observed in [illegible] of the [illegible] [illegible]. [illegible] then, only [illegible] [illegible] has been made to [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible].

SOLVENT EFFECTS.

Since the [illegible] [illegible] [illegible] [illegible] characterised by [illegible] [illegible] [illegible] [illegible] [illegible] determining [illegible] [illegible] [illegible] the [illegible] reaction and the [illegible] mechanism [illegible] [illegible] solvent. One of the [illegible] [illegible] [illegible] [illegible] the influence of solvent [illegible] [illegible] the possibility of solvation of the substance, [illegible] [illegible] [illegible]. In this instance, the [illegible] [illegible] [illegible] [illegible] solvation on the energy required [illegible] [illegible] of the activated complex. In order to [illegible] of [illegible], consider a reaction in a [illegible] [illegible] neither the reactants, nor the activated complex, is solvated. [illegible] in a second solvent, the activated complex [illegible] [illegible] the reactants [illegible] [illegible] [illegible] [illegible] [illegible] for the reaction in the latter solvent will be lower than that for the reaction in which there is no solvation. Therefore, solvation of the activated complex would tend to bring about an increase in reaction rate.

If the reactants are solvated by the second solvent and the activated complex is unaffected, the activation energy would be greater and the rate of the reaction in the second solvent would be retarded. There is the third possibility that both the reactants and the activated complex would be solvated by the second solvent. In this case, there may be little change in the energy of activation, and the effect on the rate of the reaction would be small.

It may be noticed that only the solvation of the reactants and activated complex have been considered. The solvation of the products formed in the reaction would have no direct influence on the reaction rate as they are not concerned in the rate-determining stage of the reaction.

Another effect to consider is the influence of the dielectric constant of the solvent medium on the reaction rate. One relationship, which has been derived by Laidler and Eyring[13] for ion-molecule reaction, may be expressed mathematically as

$$\frac{d \ln k_o}{d(1/D)} = \frac{\varepsilon^2 Z_A{}^2}{2KT} \left(\frac{1}{r_A} - \frac{1}{r_{\ddagger}} \right) \qquad (1)$$

where k_o = specific rate constant at zero ionic strength.

D = dielectric constant of the solvent.

ε = unit charge.

Z_A = number of unit charges of reacting ion A.

K = Boltzmann constant.

T = absolute temperature.

r_A = radius of ion A.

$r_{\ddagger}$ = radius of activated complex.

It is seen from equation (1) that a plot of $\ln k_o$ vs $1/D$ should be linear.* Since $r_{\ddagger}$, the radius of the activated complex, is usually greater than r_A, the slope will generally be positive. This indicates that the rate of reaction should decrease with increasing dielectric constant of the solvent medium. Examples of this type of behavior are to be found in the reaction between isopropyl bromide and hydroxyl ions[14] and between water and a sulfonium cation.[15] Both of these reactions proceed through a "bimolecular" mechanism.

---

* Fair results may be obtained by plotting ln k at any ionic strength against 1/D.

The "unimolecular" mechanism, on the other hand, is characterized by the ionization of the organic molecule in the rate-determining step. An increase in the ionizing power of the solvent, thereby increasing the dielectric constant of the medium, will, in this case, tend to enhance the ionic character of the R-X bond and accelerate the reaction rate. An example of this type of behavior is found in the reaction between tertiary-butyl bromide and hydroxyl ions.[16]

Thus, it is seen that the effect of varying the dielectric constant of the medium will depend upon the mechanism of the replacement reaction. These effects are summarized in the following table.

TABLE I

Solvent Effect in the Replacement of Halogen in Alkyl Halides[17]

Mechanism	Reactants	Transition State	Effect of Ionizing Media on Rate
"unimolecular"	R-X	$R^{+}.......X^{-}$	strong acceleration
"bimolecular"	Y^{-} + R-X	$Y^{-}...R...X^{-}$	weak retardation

In the discussion of the aliphatic and aralphyl series, it was pointed out that the critical region of mechanistic change was located in the isopropyl and benzyl

groups respectively for the particular solvents used in the investigation. According to the theory of solvent action discussed above, the critical point should shift to the left of the series for more strongly ionizing solvents and to the right of the series for less strongly ionizing solvents. This prediction has been confirmed by a series of experiments involving the hydrolysis of alkyl bromides in various solvents.[18] It was found that the minimum rate occurred at the isopropyl group in a weakly aqueous acetone medium, at the ethyl group when the hydrolysis was carried out in strongly aqueous ethanol, and at the methyl group in aqueous formic acid. Similar results were obtained in a study of solvent effect on the hydrolysis of the appropriate chlorides in the aralphyl series. Here, the critical point was shifted to the benzhydryl group when anhydrous acetone was used as the solvent medium[19] and to the methyl group when the solvent used was water.[20]

Scope of Investigation

Since the C-I bond in benzyl iodide requires less energy for bond rupture than the C-Br and C-Cl bonds in benzyl bromide and benzyl chloride,[21] respectively, it was thought that a study of the kinetics of the exchange reaction groups respectively for the particular solvent used in the investigation. According to the theory of solvent action discussed above, the critical point should shift [illegible] of the series for [illegible] ionizing solvents and to the right of the center for [illegible] ionizing solvents. This prediction has been confirmed by a study of [illegible] involving the hydrolysis of [illegible] in [illegible] solvent.[18] It was found that the critical point was at the isopropyl group in a [illegible] aqueous acetone medium, at the ethyl group when the hydrolysis was carried out in [illegible] aqueous ethanol, and at the methyl group in [illegible] formic acid. Similar results were obtained in a study of [illegible] effect on the hydrolysis of the [illegible] in the [illegible] series. Here, the critical point was shifted to the [illegible] group when [illegible] was used as the solvent [illegible] when the solvent was [illegible].

[illegible] of Investigation

Since the C-H bond [illegible] less energy for bond rupture than the C-C and C-H bonds in benzyl bromides has been [illegible],[19] [illegible], it was thought that a study of the kinetics of the [illegible] reaction between benzyl iodide and iodide ion would yield interesting results on the dependence of both the rate and the mechanism of the reaction on the solvent. The exchange reaction may be written as

$$C_6H_5CH_2I + I^{-*} = C_6H_5CH_2I^* + I^-$$

where the asterisked atoms are radioactive.

Tuck[22] studied this reaction in liquid sulfur dioxide using radioactive I^{128} as tracer. He found the rate of exchange of this reaction to be measureable at 0°C and -38°C. The rate of the reaction was postulated as being first order with respect to the benzyl iodide and independent of the iodide ion concentration. This rate law suggests the ionization of benzyl iodide as the rate-determining step.

In the investigation to be described here, the exchange reaction was carried out in methyl alcohol, ethyl alcohol, and acetone-alcohol mixtures. Radioactive I^{131} was used as tracer throughout the investigation. A mechanism was postulated for this reaction in each solvent and activation energies were determined.

CHAPTER II

Radiochemical Exchange

In investigations of the mechanism of replacement reactions useful simplifications are introduced by examining symmetrical exchanges of the type

$$X^- + R\text{-}X = X\text{-}R + X^-$$

It is in this connection that experiments with radioactive halogens have proved to be of great value.

The radiochemical exchange reaction may in general be written

$$AX + BX^* = AX^* + BX$$

where X^* represents a radioactive atom of X. The reasonable assumption is made that AX and AX^* are chemically identical as are the species BX and BX^*. Calculations have been made which demonstrate that this assumption introduces an error of less than 0.5% when working with iodine isotopes.[23]

The simplifying features of the isotopic exchange reaction as compared to ordinary chemical reactions are the following:

1. The internal energy of the reactants equals that of the products, and since there is no pressure or volume change, the heat of reaction is zero. The negative free energy of the exchange reaction arises solely from the

entropy increase due to the redistribution of the radioactive atoms.

2. The composition of the reaction mixture remains constant throughout the experiment because the system is always at chemical equilibrium.

3. Since the reactants and products are chemically identical the bonds ruptured are the same as those formed.

4. The solvation energy of the reactants are equal to that of the products.

The application of isotopic exchange data to chemical kinetic problems was first postulated by McKay[24] and developed in 1946 on a more quantitative basis by Duffield and Calvin.[25] They derived the quantitative exchange law which states that the increase in concentration of the radioactive atoms in the previously inactive species is first order with respect to the concentration of the originally radioactive species regardless of the actual kinetics of the exchange reaction under consideration. Mathematically, the exchange law is expressed:

$$- \ln (1-F) = \frac{R\,(a+b)}{ab}\, t \qquad (2)$$

where F, the fraction exchanged at time t, is the ratio of the radioactivity present in the originally inactive reactant at the time t to the radioactivity that would be

present in the reactant when the exchange reaction has gone to completion. The rate of the reaction, R, is a function of total concentrations, temperature, and solvent, and will be a constant for any given experiment. The terms a and b are the total concentrations of the reacting species and are expressed in units of moles per liter.

The general procedure used in carrying out exchange reactions is to establish the fraction exchanged, F, as a function of time. This is accomplished by removing aliquots of the reaction mixture at various time intervals, separating the reactants, and determining the amount of radioactivity present in each reactant. The fraction exchanged is calculated for each time interval, and ln(1-F) is plotted against t. It is seen from equation (2) that this plot should be linear for any given total concentrations of reactants and for a specified temperature and solvent.

A term frequently used to compare rates of exchange is the half-time of exchange, $t_{\frac{1}{2}}$, which is the time that it takes for the exchange reaction to proceed half-way towards completion. Since the value of F at this particular time of exchange is equal to one-half, the half-time of exchange may be evaluated from the slope of the line obtained by plotting ln (1-F) against t. An equation relating the half-present in the reactant [illegible] exchange [illegible] to completion. The rate of the exchange reaction, R, is a function of total concentrations, temperature, pH etc., and will be a constant for any given experiment. [illegible] are the total concentrations of the reacting species, [illegible] expressed in units of moles per litre.

The general procedure used in a study of exchange reactions is to establish the fraction exchange, F, as a function of time. This is achieved by removing aliquots of the reaction mixture at [illegible] intervals, separating the reactants, and determining the amount of radioactivity present in each reactant. The fraction [illegible] is calculated for each time interval, and log (1-F) is plotted against t. It is seen from equation (7) that this plot should be linear for any given total concentrations of reactants and for a specified temperature and pH, etc.

A term frequently used in connection with exchange is the half-time of exchange, $t_{\frac{1}{2}}$, which is the time that is taken for the exchange reaction to proceed half-way towards completion. Since [illegible] of exchange is equal to one-half, [illegible] of exchange may be evaluated from the [illegible] by plotting ln (1-F) against t, [illegible]-

time, $t_{\frac{1}{2}}$, to the rate of exchange, R, can be obtained from equation (2) by setting the fraction of exchange, F, equal to one-half;

$$t_{\frac{1}{2}} = \frac{a\ b\ \ln 2}{R(a+b)} \qquad (3)$$

The rate of exchange, R, may then be evaluated from equation (3) for any given concentration of a and b. By varying the concentrations of the reacting species, the rate of exchange, R, may be established as a function of the concentrations of a and b, namely,

$$R = k\ [a]^m\ [b]^n \qquad (4)$$

where k, m, and n are constants. Constant temperature is, of course, implied.

Another method which may be utilized in setting up a rate expression similar to equation (4) is through a consideration of the probable mechanism involved in the exchange reaction. Since the isotopic exchange discussed above is an example of a simple symmetrical substitution reaction, in which an active atom replaces an inactive atom, we may adopt the mechanisms of substitution reactions discussed in Chapter I. If the exchange reaction follows the "bimolecular" mechanism, the rate of the reaction would be first order with respect to each of the reacting species. The rate equation time, $t_{1/2}$, to the [illegible]

equation (12), by setting [illegible]

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The rate of change, [illegible]

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for such a path would be shown as $R = k_1 [a][b]$. In the event that the rate-determining step consists of an ionization of one of the reacting species, the rate equation would be $R = k_2 [a]$. If the reaction proceeds through both the bimolecular and unimolecular paths, the over-all rate equation may be written as

$$R = k_1 [a][b] + k_2 [a] \qquad (5)$$

Upon rearrangement, equation (5) may be expressed as

$$\frac{R}{[a]} = k_1 [b] + k_2 \qquad (6)$$

It is seen from equation (6) that a plot of $\frac{R}{[a]}$ vs. $[b]$ would be linear for any specified temperature and solvent. If the reaction mechanism is completely "bimolecular," the straight line produced would pass through the origin and have a slope equal to the specific reaction rate constant for the "bimolecular" path. If the exchange reaction mechanism is completely "unimolecular," the straight line produced would be parallel to the $[b]$ axis and would intercept the $\frac{R}{[a]}$ axis at a point equal to the value for the specific reaction rate constant of the "unimolecular" mechanism. In the event that both mechanisms are operating simultaneously during the course of the reaction, a straight line would still be obtained with a slope and intercept equal to the

For such a mechanism the rate is proportional to [a][b]. In the event that any rate-determining step involves the formation of one of the reacting species, the rate equation would be R = k_2[a]. If the reaction proceeds through both the bimolecular and unimolecular routes, the over-all rate equation may be written

$$R = k_1[a][b] + k_2[a] \qquad (4)$$

Upon rearrangement, equation (4) can be expressed as

$$\frac{R}{[a]} = k_1[b] + k_2 \qquad (5)$$

It is seen from equation (4) that a plot of $\frac{R}{[a]}$ vs. [b] would be linear for any specified temperature and solvent. If the reaction mechanism is completely "bimolecular," the straight line produced would pass through the origin and have a slope equal to the specific reaction rate constant for the "bimolecular" path. If the reaction mechanism is completely "unimolecular," the plot of $\frac{R}{[a]}$ vs [b] would be parallel to the [b] axis and would intersect the $\frac{R}{[a]}$ axis at a point equal to the value of the specific reaction rate constant of the "unimolecular" reaction. In the event that both mechanisms are operating simultaneously during the course of the reaction, a straight line would still be obtained with a slope and intercept equal to the respective specific rate constants for the two paths. The failure of any data to conform to the linear plot described above would be an indication of other operating paths.

After the mechanism has been established and the velocity constants, k, of each path determined, a series of exchange reactions are carried out in which the reaction temperature is varied. Values of specific rate constants are then obtained at several different temperatures. From these data the Arrhenius energy of activation for each path may be calculated using the equation

$$\ln k = -\frac{E}{RT} + C \qquad (7)$$

where k is the velocity constant

E is the activation energy in calories mole^{-1}

R is the gas constant in calories mole^{-1} degree^{-1}

T is the temperature in degrees absolute

C is an experimentally determined constant.

respective should be [illegible]
failure of any [illegible] by the [illegible]
above would be [illegible]

After the [illegible]
velocity constants, [illegible]
exchange reactions were carried out [illegible]
temperature is [illegible]
are then [illegible] as [illegible]
these data the [illegible]
may be calculated using [illegible]

$$\ln k = -\frac{E}{RT} + C$$

where k is the velocity constant

E is the activation energy [illegible]

R is the gas constant [illegible]

T is the temperature in degrees Absolute

C is an experimentally determined constant.

CHAPTER III

Radioactivity

Preparation of Radioactive Materials

The radioactive isotope of iodine used as a tracer in this investigation was 8.0-day I^{131} which decays by beta and gamma emission to stable Xe^{131}. This iodine isotope is formed through the beta decay of Te^{131} which is produced, in turn, from Te^{130} by thermal neutron capture.

Naturally occurring tellurium has several stable isotopes which may capture thermal neutrons. These are listed in Table II, together with their abundances, cross sections for thermal neutron capture, and the mode of decay of the irradiated product.

TABLE II

Stable Isotopes of Tellurium[26]

Stable Isotope Mass Number	Abundance, per cent	Thermal neutron cross section, $cm^2 \times 10^{24}$	Mode of Decay
120	0.091	Not Known	K capture to stable Sb^{121}
122	2.49	"	stable
123	0.89	"	stable
124	4.63	"	stable

TABLE II (CONTINUED)

Stable Isotopes of Tellurium[26]

Stable Isotope Mass Number	Abundance, per cent	Thermal neutron cross section, $cm^2 \times 10^{24}$	Mode of Decay
125	7.01	Not Known	stable
126	18.72	0.80	beta decay to stable I^{127}
128	31.72	0.137	beta decay to I^{129} (Ref. a)
130	34.46	0.21	beta decay to I^{131} (Ref. b)

Ref. a. I^{129} decays by beta emission with a very long half-life.

b. I^{131} decays by beta and gamma emission with a half-life of 8.0 days.

It is seen from the table that radioactive isotopes of iodine having mass numbers 129 and 131 would be produced by the (n, γ) reaction. Practically all of the iodine activity will be due to the I^{131} since I^{129} is a very long-lived beta emitter.

The method used for the extraction of the active iodine isotope from the tellurium sample was similar to the one used for the preparation of carrier-free iodine from tellurium samples.[27,28] Powdered tellurium metal was sealed in lucite containers and irradiated with thermal neutrons

for 4-14 days. A 20 gram sample of the irradiated tellurium metal was placed in a two-liter flask fitted with a standard tapered joint. The sample was then treated with 52 milliliters of a 50% chromic trioxide solution and 60 milliliters of 9M sulfuric acid. Two milliliters of 0.1M potassium iodide carrier were added and the mixture refluxed for one hour. In this step the tellurium is oxidized to the tellurate ion and the iodine, in whatever form it exists, is oxidized to iodate ion according to the equations

$$Te + 2CrO_3 + 4\,H^+ = TeO_4^{=} + 2Cr^{+++} + 2H_2O$$

$$[I^*] = [I^*O_3]$$

After cooling the solution, 20 grams of solid oxalic acid dihydrate and 40 milliliters of 9M sulfuric acid were added in small portions through the condenser. The reaction mixture changes from a dark brown color to a dark green as the chromate ion is reduced to chromic ion and the iodate reduced to free iodine. The tellurate ion is not reduced by the oxalic acid. The reduction proceeds according to the equations

$$2\,CrO_3 + 3H_2C_2O_4 + 6H^+ = 2Cr^{+++} + 6CO_2 + 6H_2O$$

$$2I^*O_3^- + 5H_2C_2O_4 + 2H^+ = I_2^* + 10CO_2 + 6H_2O$$

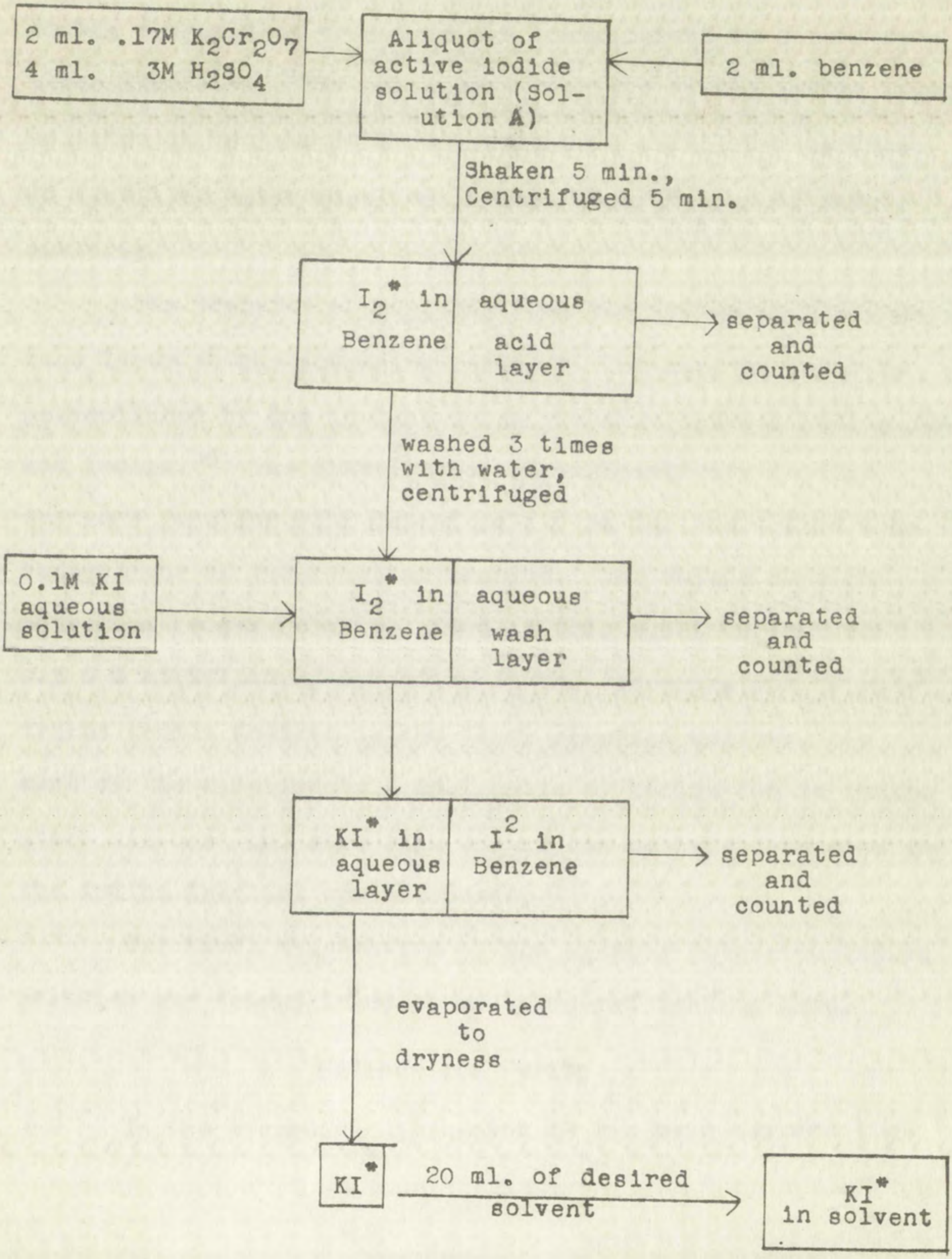
From 15 to 30 minutes were required for the addition of the oxalic acid reagent. When the evolution of carbon dioxide was no longer noticeable, the reaction mixture was refluxed for 15 minutes to insure complete reduction. The iodine was distilled into a 250 ml. glass-stoppered flask containing 10 milliliters of a solution of 0.1M sodium bisulfite and 0.1M sodium carbonate. Approximately 200 milliliters of water were distilled into the receiving vessel during the course of the distillation to yield a final iodide concentration of approximately 10^{-3} molar. This solution will hereafter be referred to as solution (A). The progress of the distillation was observed by placing a direct reading radiation meter under the receiving vessel and observing the increase in intensity of irradiation.

Aliquots of the solution (A) were taken for the preparation of the inorganic iodide reagent in the various solvents used in the investigation. The general procedure is outlined in Figure I.

The oxidation of the iodide ion in acid solution by dichromate in the first step of the procedure resulted in a 97% recovery of the activity in the benzene phase. The remaining 3% was accounted for in the aqueous acid layer which was separated and counted. This may be considered a

1

Figure I. Procedure for the Preparation of Potassium Iodide Containing I131 in Specified Solvent



reasonably rapidly [illegible] it [illegible] not take place [illegible]^{18} and [illegible] in the [illegible] com- plete oxidation. The [illegible] of the [illegible] solution is [illegible] by [illegible] portions of distilled water [illegible] activity.

The [illegible] from the [illegible] in the [illegible] tend later to [illegible] the [illegible] accomplished by [illegible] and iodine.^{20} The [illegible] with [illegible] exchange reaction [illegible] on the respective con- centrations of [illegible]. [illegible] iodine solution [illegible] from 0.5 - 5 millilitres, [illegible] of [illegible] active iodine [illegible]. In most of [illegible] atoms are [illegible] and [illegible] the iodine fraction [illegible].

[illegible] solution was [illegible] lead.

[illegible]

In [illegible]

all the activity in solution (A) was iodine activity and in the form of iodide ion. This assumption was based upon the observation that in all experiments involving solution (A), the activity followed the known chemistry of iodine and, therefore, was considered to be iodine activity. For example, oxidation of solution (A) with potassium dichromate in an acid medium followed by an extraction of the oxidized material with benzene resulted in a complete recovery of the activity in the benzene phase. Benzene extractions of the unoxidized solution resulted in less than 2% recovery of the activity in the benzene phase. These results are consistent with the known behavior of iodide ion in aqueous solution. Also, the activity in solution (A) was exchangeable with I_2 according to the exchange reaction

$$I^{*-} + I_2 = I_2^{*} + I^{-}$$

and the exchange was found to be instantaneous.[30]

Two additional experiments were performed in order to establish further the purity of the radioactive material; the distribution of the oxidized material between benzene and an acid sulfate solution, (0.05M H_2SO_4 ; 0.03M Na_2SO_4) was determined using tracer techniques, and the half-life of the active material was determined by observing its decay.

The general procedure for the determination of the

all the activity in [illegible] [illegible] [illegible] had [illegible] [illegible] in the
the form of [illegible] [illegible] [illegible] [illegible]
observation that [illegible] [illegible] [illegible] [illegible]
the activity [illegible] [illegible] [illegible] [illegible]
therefore, [illegible] [illegible] [illegible] [illegible]
oxidation of [illegible] [illegible] [illegible] [illegible]
acid medium followed by [illegible] [illegible] [illegible]
tel with [illegible] [illegible] [illegible] [illegible]
ivity in the [illegible] phase. [illegible] [illegible]
oxidized [illegible] [illegible] [illegible] [illegible]
activity in the [illegible] phase. [illegible] [illegible]
with the [illegible] [illegible] [illegible] [illegible]
Also, [illegible] [illegible] [illegible] [illegible]
according to the [illegible] [illegible]

and the [illegible] [illegible] [illegible].

The [illegible] [illegible] [illegible] [illegible]
establish whether the [illegible] [illegible] [illegible]
distribution of [illegible] [illegible] [illegible]
acid [illegible] [illegible] [illegible] [illegible]
determined using [illegible] [illegible] [illegible]
active [illegible] [illegible] [illegible] [illegible].

The general [illegible] [illegible] [illegible] [illegible] distribution of the active iodine between benzene and the acid sulfate buffer is outlined in Figure II. The distribution coefficient obtained by this method ranged from 360 to 400. These values are in satisfactory agreement with those obtained by actual titration of the iodine in each phase with sodium thiosulfate.[31]

The decay of a representative radioactive iodine solution was followed over a period of five half-lives. The half-life of the iodine isotope was determined as 8.0 days which agrees with the value of 8.0 days reported in the literature.[32]

Detection of Radioactivity

The decay scheme of I^{131} proposed by Metzger and Deutsch is given below[33]

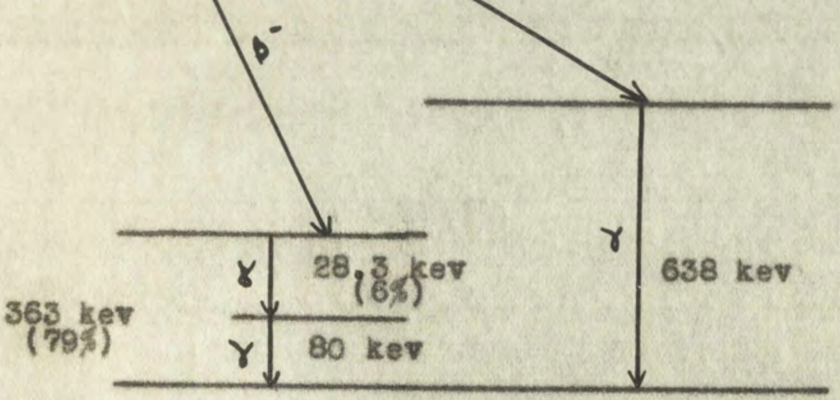
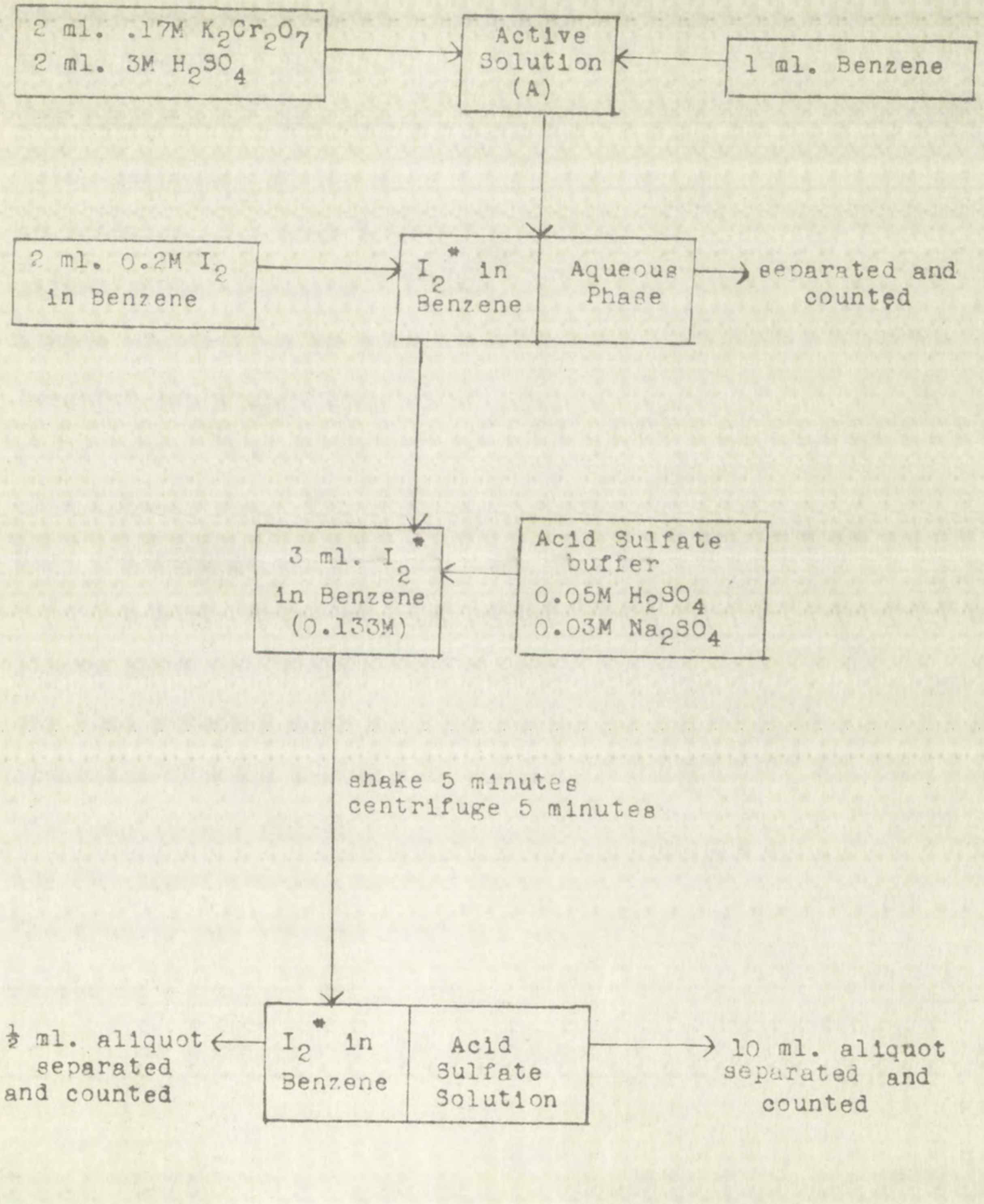


Figure 2. Determination of Distribution of Iodine Between Benzene and Acid Sulfate Buffer

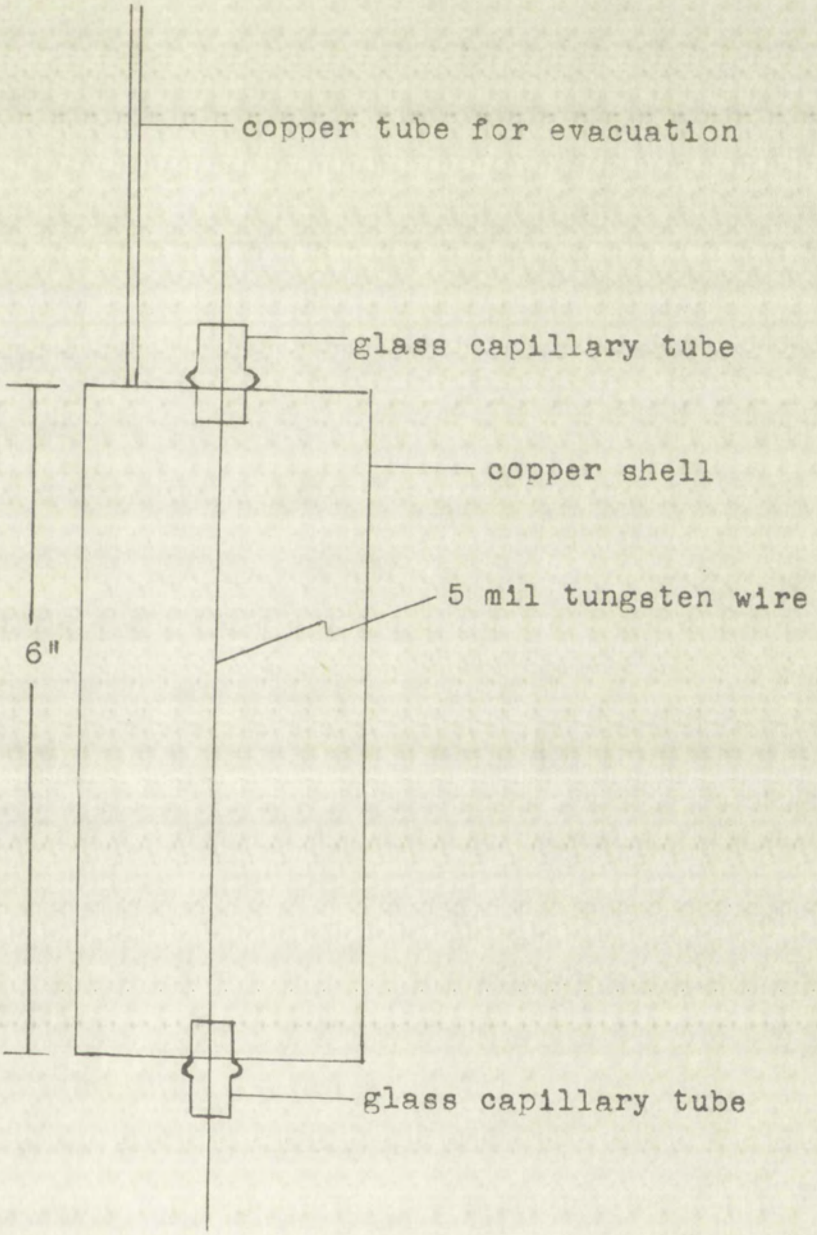


The [illegible]
measurement [illegible]
counter. The [illegible]
ter cylinder was [illegible]
a 1/32 inch [illegible]
1/4 inch [illegible]
into the [illegible]
In addition, [illegible] 1/8 inch [illegible]
silver soldered [illegible]
A hole was drilled in [illegible]
inserted and [illegible]
glass tubing was [illegible]
with [illegible] wax. The counter [illegible]
base and [illegible]

[illegible] all [illegible]
illary tubes and sealed with [illegible]
was then [illegible]
apparatus through [illegible]
The counter [illegible]
ing 90% argon and 10% alcohol [illegible]
The counter was [illegible]
nected to a [illegible]

The stability of [illegible]

Figure 3. Counting tube for gamma radiation detection



a cobalt standard before each run. The standard consisted of a sample tube which was filled to a given height with a solution of cobalt chloride containing the five-year Co^{60}. The tube was sealed to prevent evaporation of the standard solution.

The plateau of the counting tube was obtained by plotting the counting rate of the standard cobalt solution vs. the applied voltage. This plateau was 25- to 50-volts long with a slope of approximately 4%.

Coincidence corrections were less than 1% for most of the samples used and these corrections were not applied. The largest counting rate observed was 2400 counts per minute and the coincidence correction for this sample amounted to 24 counts, or 1%.

Ordinary six-inch Pyrex test tubes were used as sample holders. These tubes were calibrated by placing identical volumes of an active solution into each test tube and diluting each solution to a standard height. The tubes were then placed in a fixed slot at the side of the counter tube and the counting rate of each solution determined. Selecting one tube as a standard, the other tubes were then calibrated by the ratio of their counting rates to that of the standard. The tubes were etched for identification and correction

factors corresponding to their calibrated values were applied whenever used.

CHAPTER IV

CHEMICAL MATERIALS

Benzyl Iodide

Benzyl iodide was prepared by the reaction of Eastman Kodak chlorine-free benzyl alcohol and concentrated aqueous hydriodic acid.[34] A twenty per cent excess (327 grams) of Bakers Analyzed C.P. 47% hydriodic acid, specific gravity 1.50, was added to 108 grams of benzyl alcohol and the mixture refluxed for one hour. The refluxed mixture was cooled to 0°C and the supernatant aqueous layer was decanted from the impure benzyl iodide. The product was dried for 24 hours with drierite and twice distilled at reduced pressure. The distillate was collected at 91°C under 9.5 mm. pressure. In each distillation the first and last few milliliters were discarded and a middle portion of approximately 70 milliliters retained.

The final distillate was colored yellowish-brown due to the decomposition of benzyl iodide at the elevated temperature of the distillation. This product was washed with a two per cent solution of sodium bisulfite and then twice more with distilled water. The washed product was dried with anhydrous magnesium sulfate and decanted at 25°C into

a glass stoppered flask and stored at 10°C. The final material was composed of needle-like crystals and analyzed 99.9 per cent benzyl iodide on the basis of the iodine content. The product was analyzed by a modified Volhard method.[35]

Due to the observable decomposition of benzyl iodide during its preparation, it was necessary to determine the extent of this decomposition as a function of time at operating temperatures. Fifteen solutions of varying concentrations of benzyl iodide in absolute alcohol were prepared in a darkened room and placed in 125 milliliter Erlenmeyer flasks. The cork stoppers were covered with aluminum foil and the flasks placed in covered containers. These samples were then placed in locations which varied with the amount of light and heat to which it was anticipated the samples would be subjected. The containers were then opened at successive intervals and the extents of decomposition determined. One solution was examined immediately after preparation to determine the zero-time decomposition.

The method used for the above determination consisted of adding a benzene-water mixture to the benzyl iodide solution. The presence of free iodine produced by the decomposition of the organic iodide is indicated by the coloring of the benzene layer in the mixture. It is possible to

a glass stoppered [illegible] at 100° [illegible]. The final [illegible]-
tal was [illegible]
per cent [illegible]
The product was [illegible].

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during [illegible]
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a darkened room [illegible].
The cork [illegible]
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heat to which [illegible]
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vals and the [illegible]
ation was [illegible]
the zero-time [illegible].

In order [illegible]
of adding a [illegible]
ation. The [illegible]
position of the [illegible] is indicated by [illegible]
of the [illegible]

detect, visually, the color of a solution of iodine in benzene at concentrations as low as 10^{-5} molar.

The control experiment at zero-time showed no evidence of decomposition. Samples which had been placed in darkened locations also showed no coloration of the benzene layer at the end of three days. However, solutions which were exposed to light showed a noticeable discoloration in thirty minutes at room temperature. After four days, samples which were not exposed to light showed signs of slight decomposition. This was observed in samples examined in the fifth through seventh day with increasing intensity.

The possibility that dissolved oxygen in the absolute alcohol was causing the oxidation of the benzyl iodide was then investigated by bubbling nitrogen gas through the solvent for one-half hour before use. It was found that this procedure decreased the amount of decomposition in each of the time intervals investigated.

The results of the above control experiments showed that it would be necessary to keep the reaction solutions in darkened containers during the course of the experiments. An attempt was made to remove the oxygen by passing nitrogen gas through the solution for one-half hour. Since the longest experiment was concluded in less than twenty-six hours, it detect, visually, the [illegible] in [illegible] zone at concentrations [illegible].

The control [illegible] of decomposition. [illegible] in dry [illegible] locations also showed [illegible] before [illegible] the end of three days. [illegible] to light showed a noticeable [illegible] at room temperature. [illegible] exposed to light [illegible]. [illegible] was observed to [illegible] day with increasing intensity.

The possibility that [illegible] on the [illegible] alcohol was [illegible] of the [illegible] then investigated by [illegible] nitrogen [illegible] vent for one-half hour before [illegible] procedure [illegible] the time intervals [illegible].

The results of the above [illegible] showed that it would be necessary to [illegible] ened containers during [illegible]. [illegible] attempt was [illegible] through the [illegible] experiment [illegible] may be assumed that no appreciable decomposition occurred during any experiment.

The purified benzyl iodide was maintained in the solid state at a temperature of 10°C and stored in a darkened container. It was found that under these conditions the rate of decomposition was very slow and the reagent could be maintained for a period of 60 to 90 days. Aliquots of this material were taken to prepare the benzyl iodide reagent used in the investigation.

Absolute Alcohol

Absolute ethyl alcohol was prepared by the action of U. S. Industrial Chemicals, Inc. absolute alcohol on magnesium methoxide.[36] This method consisted of treating five grams of magnesium turnings with sixty milliliters of absolute alcohol to form the methoxide. Solid iodine, 0.5 gram, was used as a catalyst in this reaction. One liter of absolute alcohol was added and the mixture refluxed for one hour with a drying tube attached to the open end of the condenser. The alcohol was then distilled from the mixture at 74°C and 645 mm. pressure. Nitrogen gas was bubbled through the solvent for a half-hour prior to use in each experiment.

A Henle test,[37] capable of detecting 0.05 per cent of water in organic solvents, was run on the alcohol reagent may be assumed that it is practically [illegible] occurred during any experiment [illegible].

The purified [illegible] [illegible] [illegible] at a temperature of $25°$ [illegible] [illegible]. It was found that [illegible] of decomposition [illegible] [illegible] tained for [illegible] [illegible]. The material [illegible] not used in this investigation.

Absolute Alcohol

Absolute ethyl alcohol [illegible] of the U. S. Industrial Chemicals, Inc. [illegible] magnesium methylate.[25] [illegible] grams of magnesium [illegible] alcohol [illegible] [illegible] used as a catalyst [illegible] alcohol was added [illegible] a drying tube [illegible]. The alcohol was [illegible] 340 mm. pressure. [illegible] solvent for a half-hour [illegible].

A [illegible] test,[26] [illegible] of water in [illegible] alcohol [illegible] after it had been treated with nitrogen. The test consisted of adding solid calcium carbide to the reagent and observing the evolution of acetylene. No gas evolution was observed.

Acetone

Bakers Analyzed C. P. acetone was stored over drierite for twenty-four hours and then distilled at 51°C and 645 mm. pressure prior to use. Nitrogen gas was bubbled through the acetone for a half hour before use. The Henle test[37] described above was negative.

Methyl Alcohol

Mallinckrodt absolute methyl alcohol was treated as described above for the absolute ethyl alcohol reagent.[38] The distillate was collected at 60°C and 644 mm. pressure. Nitrogen gas was bubbled through the reagent for one-half hour before use. The Henle test[37] described above was negative.

Potassium Thiocyanate

A standard solution of potassium thiocyanate was prepared by the method described by Kolthoff and Furman.[39] The solution was standardized against a standard silver nitrate solution.

after it has been [illegible]

of adding acid [illegible]

the solution [illegible].

[illegible]

[illegible] for twenty-four hours and [illegible]

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cribed above [illegible].

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The [illegible].

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hour before [illegible]

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[illegible]

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prepared by [illegible].

The solution [illegible]

nitrate solution.

Silver Nitrate

Standard solutions of silver nitrate were prepared by the method described by Kolthoff and Furman.[40]

CHAPTER V

EXPERIMENTAL

Procedure

The general procedure used in all experiments consisted of mixing benzyl iodide and active potassium iodide solutions of known concentrations, allowing them to stand at a given temperature for varying intervals of time, separating the two reactants, and determining the amount of activity present in each reactant.

The reaction vessel used is shown in Figure IV. The body of the vessel consisted of 16 mm. pyrex tubing onto which was sealed a 12/18 standard taper joint. The vessel had a total capacity of 20 milliliters and was designed to fit into the 50 ml. cup of a clinical centrifuge. The bottom of the reaction tube was drawn out to a point to facilitate the separation of an aqueous phase from an immiscible organic phase.

The benzyl iodide solution was prepared by dissolving a weighed amount of benzyl iodide in the specified nitrogen-treated solvent and diluting to the mark in a 25 ml. volumetric flask. The active potassium iodide solution was prepared as described in Chapter III. Both solutions were then analyzed on the basis of iodine content. Then the two solutions

Figure 4. Reaction Vessel

of 8 mm. soft glass tubing to a fine point, was lowered into the tip of the reaction vessel and the liquid sucked into the pipette by means of a small rubber bulb attached to the upper end. The two layers were then separated with the extraction pipette and the two solutions placed into separate calibrated sample holders. Each solution was then diluted with the appropriate solvent to a predetermined, reproducible height. The samples were then stirred by bubbling a stream of air through the solution to insure uniform distribution of the activity throughout the sample. The sample holders were then placed in reproducible positions at the side of the counter tube and the total activity of each solution determined.

Control experiments, using inactive potassium iodide, were conducted in order to establish the separation as a quantitative procedure. A known weight of potassium iodide was dissolved in absolute alcohol and a 1 ml. aliquot of this solution was placed in the reaction vessel. To this was added a 1 ml. aliquot of a benzyl iodide solution of known concentration. The solution was then shaken and treated with the benzene-water mixture. The two phases were separated and each analyzed for total iodine content. The total amount of iodine (calculated as potassium iodide) recovered in the aqueous phase agreed to within 1% with the total amount of

potassium iodide initially placed in the reaction vessel. Similar results were obtained with the benzene phase of the separation mixture.

Constant temperature was maintained by a thermostat utilizing an Aminco thermal regulator. Two such regulators were employed to reproduce the temperatures of 27.3°C and 44.0°C for each solvent. For all runs at 0°C, the thermostat was packed with ice. The temperature was maintained to within ± 0.1°C for all experiments.

Operating Blank

It was found that potassium iodide could be extracted from aqueous solutions with benzene, the percentage of potassium iodide extracted with the benzene being independent of the concentration of potassium iodide. This was determined by shaking solutions of active potassium iodide with several portions of benzene, separating each benzene phase, and determining the total activity of each benzene solution. Due to the constancy of these results, the activity extracted by the benzene was considered an operating blank and, as such, was deducted from the total amount of the activity found in the benzene phase at the conclusion of each run. This blank was determined for each solvent at each of the three temperatures reported and ranged from 0.7-1.0% at 0°C to 3% at

44.0°C.

Experiments were also carried out to determine the amount of benzyl iodide remaining in the aqueous phase after separation. This was done by treating 1 ml. of an alcoholic solution of benzyl iodide with the separation mixture. The two phases were separated, and the aqueous phase treated with 5 ml. of a 0.1N silver nitrate solution. There was no noticeable precipitation of silver iodide. Because of the low solubility of silver iodide (3×10^{-7} g. per 100 g. of water), this observation was sufficient to indicate that there need be no correction applied to this part of the separation procedure.

Method of Analysis

The Volhard method for the determination of aqueous iodide solutions is a standardized analytical procedure.[35] It was necessary to prove that this procedure could be used for the determination of iodide in methyl alcohol, ethyl alcohol, and acetone. This was done by dissolving a known amount of potassium iodide in each solvent and analyzing each solution for its iodine content using the Volhard method. The total amount of iodide found in each of the above analytical determinations was the same as that known to be present within a probable error of 0.2%.

Error

The principle sources of experimental error were the statistical fluctuations in the counting rate (± 1%), accuracy of the analytical determination (± 0.5%), the uncertainty of the operating blank (± 1%), and the correction for the time of separation of the reactants (± 0.5%).

CHAPTER VI

RESULTS

The data obtained for the exchange reaction in methyl alcohol, ethyl alcohol, and acetone-ethyl alcohol mixtures are summarized in Tables III through XXXXII. They cover a temperature range of 0° to 44°C and a concentration range of 0.00147 to 0.01485M benzyl iodide and 0.00135 to 0.01595M potassium iodide. For each temperature and concentration ln (1-F) is plotted against the time. These curves are shown in Figures 5 through 20. The values of the half-times obtained from these plots are recorded in Tables III, XV, and XXIV.

The fraction exchanged, F, was calculated as the ratio of activity present in the benzyl iodide at time t (after correcting this value for the operating blank) to the activity that would be present at infinite time. The latter value was obtained by multiplying the total activity initially present by the fraction of the total iodide ion present in the benzyl iodide reactant. This fraction will determine the ultimate distribution of the radioactive iodide atoms.

The zero-time exchange was determined for each concentration and temperature used in the investigation.

The [illegible] alcohol, [illegible] are [illegible] in [illegible] temperature range of [illegible] and a concentration range of 0.00147 to [illegible] potassium iodide. For each temperature and concentration [illegible] in (1-F) is plotted against [illegible] in Figures 8 through [illegible]. The values of the [illegible] tained from these [illegible] XXIV.

The fraction of exchange, F, [illegible] of activity present in the [illegible] correcting this value for [illegible] ivity that would be [illegible] value was obtained by [illegible] istically present [illegible] present in the [illegible] determine the [illegible] atoms.

The zero-time [illegible] centration and temperature [illegible].

This was done by mixing the two reactants and immediately separating the mixture. The values obtained for the exchange, F, at zero-time were all within 2% of the operating blank.

Duplicate determinations were made of all points with a maximum time of 30 seconds separating the two samples. Values obtained for the fraction exchanged, F, for all duplicate runs checked to within 2.5%.

For the exchange reaction in acetone-ethyl alcohol mixtures, solvent concentrations were calculated by assuming that the total volume of the mixture was the sum of the volumes of each solvent added.

The rate of exchange, R, was calculated for each temperature and concentration as shown in equation (3). These values are recorded in Tables III, XV, and XXIX and are expressed in the units of moles per liter per minute.

If the rate law for the exchange reaction in a given solvent at a given temperature can be expressed as

$$R = k_1 [C_6H_5CH_2I] [KI] + k_2 [C_6H_5CH_2I]$$

then a plot of $\frac{R}{[C_6H_5CH_2I]}$ against $[KI]$ should yield a straight line with a slope equal to k_1 and intercept equal to k_2. According to the plots shown in Figures 8, 13, and 21, the exchange reaction is first order with respect to the concentration of $C_6H_5CH_2I$ and the concentration of KI in methyl

This was done by mixing the two solutions and [illegible] separating the [illegible] F, at zero-time [illegible] the [illegible].

Sulfuric [illegible] a certain [illegible]. Values obtained [illegible] exchange, [illegible] licate runs plotted as shown in [illegible].

For the exchange reaction [illegible] mixtures, solvent and [illegible], [illegible] that the total volume of the mixture [illegible] uses of each [illegible].

The rate of exchange, [illegible] temperature and concentration as shown in [illegible]. These values are reported in [illegible] are expressed in the [illegible].

If the rate law for the exchange reaction is [illegible] solvent at a given concentration [illegible]

$$R = k_1 [\;] [\;] + k_2 [\;]$$

then a plot of [illegible] versus [illegible] should [illegible] a straight line with a slope [illegible]. According to the plots shown in Figures [illegible], the exchange reaction is first order [illegible] centration of [illegible] and [illegible] the concentration of [illegible].

alcohol, ethyl alcohol, and mixtures of ethyl alcohol and acetone.

The values for the specific rate constant, k, for the exchange reaction in the various solvents at different temperatures are recorded in Tables III, XV, and XXIX, and it is seen that they are constant for any given temperature. In order to determine the activation energy for the exchange reaction in methyl alcohol and ethyl alcohol, ln k was plotted against the reciprocal of the absolute temperature as shown in Figures 9 and 14. These plots are linear in agreement with equation (7). The rate laws for the exchange reaction in the methyl alcohol and ethyl alcohol solvents are given below:

$$R = 2 \times 10^{11} e^{\frac{-15,650}{RT}} [C_6H_5CH_2I][KI] \text{ (in methyl alcohol)}$$

$$R = 5 \times 10^{12} e^{\frac{-17,150}{RT}} [C_6H_5CH_2I][KI] \text{ (in ethyl alcohol)}$$

where the units of R are moles per liter per minute.

Exchange runs were attempted in pure acetone and it was found that the rate of exchange in this medium was immeasurably fast. The half-time of the exchange reaction was estimated at 30 seconds to 1 minute at 0°C and at the lowest available concentrations.

In order to determine the role of acetone in this

alcohol, dotted lines in [illegible] [illegible] [illegible]
acetone.

The values [illegible] [illegible] [illegible] [illegible] the exchange reaction in the [illegible] [illegible] at different temperatures [illegible] [illegible] [illegible] it is [illegible] [illegible] [illegible] [illegible] [illegible]. In order to [illegible] the [illegible] [illegible] [illegible] exchange reaction in methyl alcohol [illegible] [illegible] plotted against the reciprocal of the absolute temperature, as shown in Figures [illegible] and [illegible]. [illegible] [illegible] agreement with equation [illegible]. The [illegible] [illegible] [illegible] reaction in the [illegible] alcohol [illegible] [illegible] are given below:

[illegible]

[illegible]

where the units of [illegible] are [illegible].

Although [illegible] [illegible] [illegible] [illegible] it was found that [illegible] [illegible] [illegible] [illegible] [illegible]. The half-life of the [illegible] was [illegible] seconds [illegible] [illegible] [illegible].

In order to [illegible] [illegible] [illegible] reaction, the rate of exchange, R, was determined for various concentrations of benzyl iodide and potassium iodide in mixtures of ethyl alcohol and acetone. If the rate law for the exchange reaction in ethyl alcohol-acetone mixture is

$$R = k_1 [C_6H_5CH_2I][KI] + k_3 [C_6H_5CH_2I][KI][CH_3COCH_3]^X$$

then a plot of $\frac{R}{[C_6H_5CH_2I]}$ against $[KI]$ should yield a straight line for each mixture, passing through the origin. The curves in Figure 21 suggest that the exchange reaction is first order with respect to both the benzyl iodide and potassium iodide.

In order to determine the value of the exponent, X, of the acetone concentration, the quantity $\frac{R}{[C_6H_5CH_2I][KI]}$ was plotted against $[\text{Acetone}]^X$ where X was assigned the value 1/2, 1, 2, and 3. For the proper value of X a straight line should be obtained with a slope equal to k_3 and intercept equal to k_1, where k_1 is the specific reaction rate in pure ethyl alcohol at the particular temperature. The curves obtained are shown in Figures 22 through 25. The plot against the square of the acetone concentration ($X = 2$) yields the best straight line and the intercept agrees with the value of k_1 obtained from experiments using pure ethyl alcohol.

It may be pointed out that, in the evaluation of the exponent X in the rate law shown above for the exchange reaction in acetone-ethyl alcohol mixtures, it has been assumed that the specific rate constants k_1 and k_3 are independent of small changes in the dielectric constant of the medium. In order to show that this variable does not effect the determination of X as shown above, it is necessary to make the following reasonable assumptions:

1. The dielectric constant of a solvent mixture may be expressed as a linear function of the concentration of the respective solvents. For example, the dielectric constant of the acetone-ethyl alcohol mixtures may be shown as

$$D_{mixt} = D_{Ac} + (D_{Al} - D_{Ac})\ N_{Al}$$

where the subscripts Ac and Al represent acetone and alcohol respectively and N_{Al} represents the mole fraction of alcohol in the solvent mixture.

2. A linear relationship exists between ln k and the reciprocal of the dielectric constant of the medium as shown by the Laidler and Eyring[13] theory of ion-molecule reactions. This plot is shown in Figure 25 for 0°C.

The equation of the line obtained by plotting ln k vs. 1/D for each specific rate constant, k_1 and k_3, may be expressed mathematically by [illegible] (10) [illegible]

exponent n is [illegible] is [illegible]

action in [illegible] [illegible]

that the [illegible]

of small changes in [illegible]

In order to show that this [illegible] the

determination of [illegible] is [illegible]

the following [illegible]

1. The [illegible] of [illegible] is

expressed as a linear function of the concentrations of the

respective [illegible] and [illegible], the [illegible]

of the [illegible]

$$[illegible]$$

where the subscripts [illegible] and [illegible] respectively and [illegible] in the [illegible] mixture.

2. A linear relationship exists between [illegible] and the

reciprocal of the dielectric constant of the [illegible], as [illegible]

by the [illegible] and [illegible] of [illegible].

This plot is shown in Figure [illegible].

The equation of the [illegible]

vs. 1/D for [illegible] dielectric constants, [illegible] can be

expressed mathematically by

$$1).\quad \ln k_1 = S/D + Q$$

$$2).\quad \ln k_3 = P/D + B$$

where S and P represent the slopes of the straight lines and Q and B represent the respective intercepts. These values of k_1 and k_3 may be substituted in the rate expression

$$R = e^{Q} e^{S/D} \left[C_6H_5CH_2I\right] \left[KI\right] + e^{P/D} e^{B} \left[C_6H_5CH_2I\right] \left[KI\right] \left[A\right]^{X}.$$

A plot of $\dfrac{R}{\left[C_6H_5CH_2I\right] \left[KI\right] e^{1/D}}$ vs. $\left[A\right]^{X}$ should again produce a straight line from which the X may be evaluated as before. This plot is shown for $X = 2$ in Figure 26 and is found to be identical with the plot shown in Figure 23 in which the effect of the dielectric constant was assumed to be negligible.

In order to determine the activation energy and frequency factor for the reaction path associated with acetone, the rate of exchange, R, was determined for an ethyl alcohol-acetone mixture (2.27 molar acetone) at 27.3°C (see runs 34 and 35, Table XXIX). The overall rate law in this particular alcohol-acetone mixture may be written as

$$R = 5 \times 10^{12}\, e^{-\frac{17,150}{RT}} \left[C_6H_5CH_2I\right] \left[KI\right] + 2.5 \times 10^{10}\, e^{-\frac{13,900}{RT}} \left[C_6H_5CH_2I\right] \left[KI\right] \left[A\right]^{2*}$$

where R is expressed as moles per liter per minute. The rate law will be essentially the same for other acetone-alcohol mixtures, the rate constants varying with change in dielectric constant of solvent mixture.

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* See Appendix A for the calculation of the activation energy and frequency factor for the second path in the rate law.

[illegible]

[illegible]

where [illegible] and [illegible] represent the [illegible]

4 and 5 represent the [illegible]

of k_1 and k_2 [illegible] in equation [illegible]

R = [illegible]

A plot of [illegible] vs. [illegible] should [illegible]

a straight line [illegible]

This plot [illegible] Figure [illegible]

identical with [illegible]

of the [illegible]

In order to [illegible] the [illegible]

[illegible] the [illegible]

the rate of [illegible]

acetone [illegible]

and 25, Table [illegible] the [illegible]

alcohol-acetone mixture may be written as:

$$R = [illegible]$$

$$[illegible]$$

where R is expressed as moles per liter per minute. [illegible]

[illegible]

mixtures, the rate constants [illegible]

tric constant of [illegible]

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* See Appendix [illegible]
[illegible]

TABLE III

Experimental Data for the Exchange Reaction Between Benzyl Iodide and Iodide Ion in Methyl Alcohol

Run Number	Temp. ^{o}C	$C_6H_5CH_2I$ Conc., Molar	KI Conc., Molar	Half-time, Minutes	R moles liter^{-1} min^{-1} x 10^{-5}	k liters mole^{-1} min^{-1}
1	0.0	0.01150	0.01150	453	0.88	0.066
2	0.0	0.004225	0.004275	1368	0.108	0.060
3	0.0	0.01485	0.01570	366	1.447	0.062
4	0.0	0.00885	0.0089	637	0.482	0.061
5	27.3	0.00453	0.003615	95.5	1.46	0.89
6	27.3	0.00615	0.006625	60	3.65	0.90
7	27.3	0.002875	0.00225	144	0.606	0.94
8	27.3	0.01048	0.0073	44.5	6.70	0.88
9	44.0	0.00283	0.00271	38.25	2.51	3.27
10	44.0	0.00385	0.00405	23.25	5.87	3.77
11	44.0	0.00147	0.00135	66.5	0.733	3.69

TABLE IV

Experimental Data for Run 1*

$[C_6H_5CH_2I]$ = 0.0115 M; $[KI]$ = 0.0115 M

$t_{\frac{1}{2}}$ = 453 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
120	127	1186	0.192	0.213
120	113	1192	0.172	0.188
240	194	1104	0.297	0.352
240	198	1110	0.301	0.358
420	313	968	0.486	0.665
420	331	950	0.515	0.728
510	384	1019	0.545	0.788
510	356	950	0.557	0.814

* Experimental procedure II used.

** Corrected for operating blank, 0.6%.

TABLE V

Experimental Data for Run 2*

$[C_6H_5CH_2I]$ = 0.004225 M; $[KI]$ = 0.004275 M

$t_{\frac{1}{2}}$ = 1368 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
240	79	1349	0.111	0.118
240	80	1311	0.115	0.122
600	182	1216	0.261	0.302
600	187	1212	0.268	0.312
1095	280	1049	0.423	0.55
1440	349	1046	0.500	0.693
1440	343	976	0.521	0.736

* Experimental Procedure II used.

** Corrected for operating blank, 0.6%.

TABLE VI

Experimental Data for Run 3*

$[C_6H_5CH_2I] = 0.01485$ M; $[KI] = 0.0157$ M

$t_{\frac{1}{2}} = 366$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
150	217	1533	0.255	0.294
150	212	1551	0.247	0.284
300	368	1366	0.435	0.571
420	473	1308	0.545	0.788
420	451	1272	0.539	0.775

* Experimental procedure II used.

** Corrected for operating blank, 0.6%.

TABLE VII

Experimental Data for Run 4*

$[C_6H_5CH_2I]$ = 0.00885 M; $[KI]$ = 0.0089 M

$t_{\frac{1}{2}}$ = 637 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
45	67	2029	0.064	0.066
45	69	2043	0.065	0.067
300	310	1843	0.287	0.338
300	304	1836	0.284	0.334
480	426	1695	0.400	0.511
480	399	1547	0.410	0.528
660	488	1438	0.505	0.703

* Experimental procedure II used.
** Corrected for operating blank, 0.6%.

TABLE VIII

Experimental Data for Run 5*

$[C_6H_5CH_2I] = 0.00453$ M; $[KI] = 0.003615$ M

$t_{\frac{1}{2}} = 95.5$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
21	130	1385	0.153	0.166
21	140	1476	0.154	0.167
47	270	1446	0.28	0.329
74	411	1203	0.455	0.607
74	385	1253	0.419	0.544
100	414	1081	0.49	0.673
100	404	1054	0.496	0.685

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE IX

Experimental Data for Run 6*

$[C_6H_5CH_2I]$ = 0.00615 M; $[KI]$ = 0.006625 M

$t_{\frac{1}{2}}$ = 60 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
20	174	1536	0.21	0.236
20	183	1483	0.226	0.256
45	339	1338	0.416	0.538
70	415	1150	0.547	0.792
70	415	1137	0.550	0.799
95	485	1009	0.67	1.109
95	480	1000	0.67	1.109

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE X

Experimental Data for Run 7[*]

$[C_6H_5CH_2I]$ = 0.002875 M; $[KI]$ = 0.00225 M

$t_{\frac{1}{2}}$ = 144 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
40	189	1282	0.227	0.257
40	155	1376	0.181	0.199
80	273	1250	0.317	0.381
80	272	1226	0.309	0.370
120	322	972	0.44	0.58
160	427	943	0.552	0.804
160	366	892	0.516	0.726

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XI

Experimental Data for Run 8*

$[C_6H_5CH_2I]$ = 0.01048 M; $[KI]$ = 0.0073 M

$t_{\frac{1}{2}}$ = 44.5 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
60	486	837	0.62	0.968
60	495	789	0.648	1.044
90	572	728	0.743	1.359
90	572	731	0.742	1.355
120	631	637	0.84	1.833

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XII

Experimental Data for Run 9*

$[C_6H_5CH_2I]$ = 0.00283 M; $[KI]$ = 0.00271 M

$t_{\frac{1}{2}}$ = 38.25 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
10	96	1133	0.13	0.364
10	93	1139	0.125	0.365
20	198	1052	0.305	0.536
20	195	1032	0.306	0.540
30	279	1016	0.415	0.139
30	309	1119	0.417	0.133
40	318	918	0.495	0.683
40	309	866	0.506	0.705

* Experimental procedure I used.
** Corrected for operating blank, 2%.

TABLE XIII

Experimental Data for Run 10*

$[C_6H_5CH_2I]$ = 0.00385 M; $[KI]$ = 0.00405 M

$t_{\frac{1}{2}}$ = 23.25 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
10	230	1785	.23	0.261
10	199	1585	.225	0.255
15	320	1431	.369	0.460
15	352	1576	.373	0.467
20	415	1380	.467	0.629
25	447	1290	.52	0.734
25	442	1304	.512	0.717

* Experimental procedure I used.
** Corrected for operating blank, 2%.

TABLE XIV

Experimental Data for Run 11*

$[C_6H_5CH_2I] = 0.00147$ M; $[KI] = 0.00135$ M

$t_{\frac{1}{2}} = 66.5$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
11	67	1191	0.10	0.105
11	64	1278	0.09	0.094
25	151	1086	0.23	0.261
25	160	1217	0.219	0.247
47	266	995	0.398	0.508
47	279	1034	0.400	0.511
64	334	932	0.497	0.687
64	350	1049	0.473	0.641

* Experimental procedure II used.
** Corrected for operating blank, 2%.

Figure 5. Exchange Runs in Methyl Alcohol at 0°C

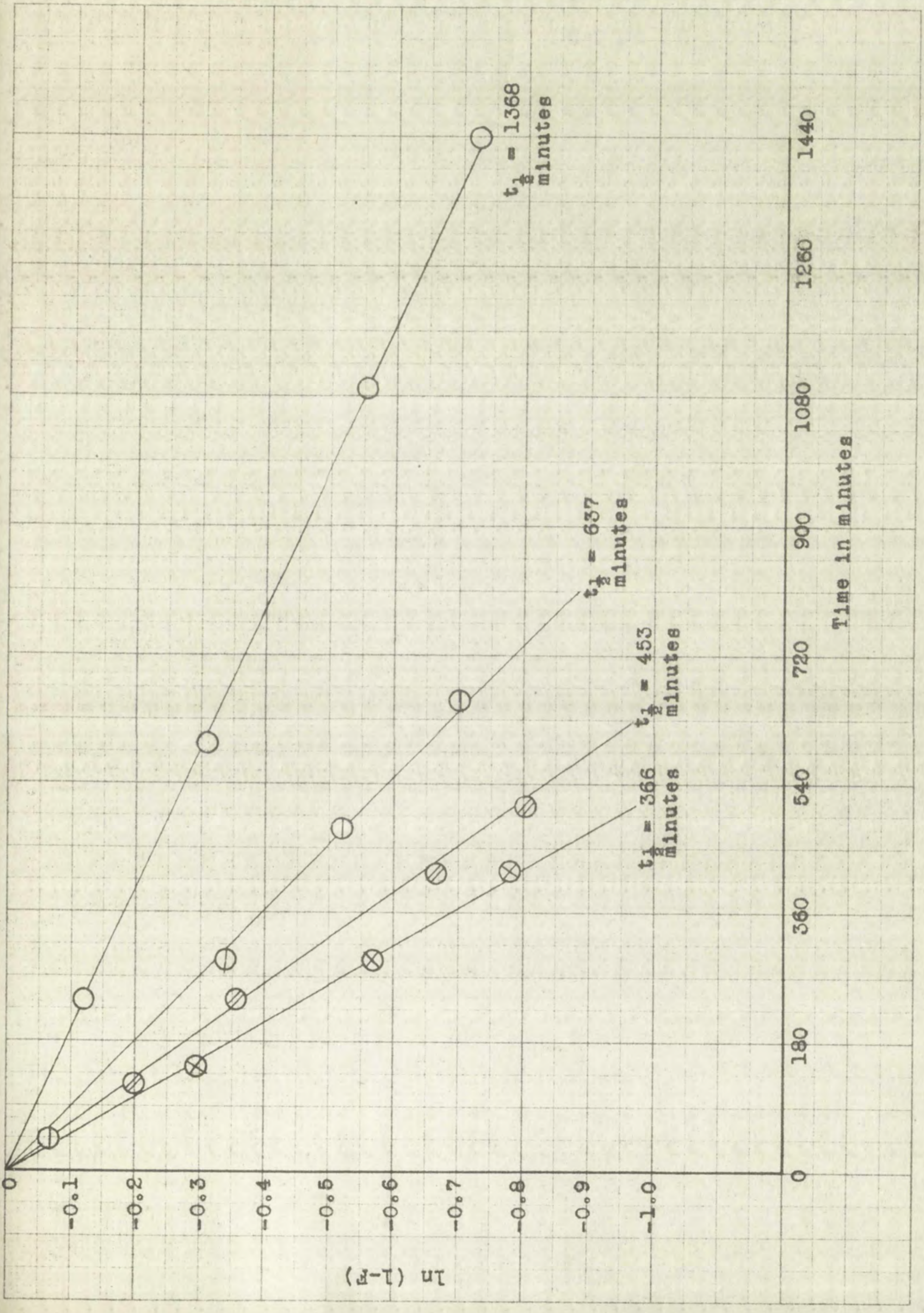


Figure 6. Exchange Runs in Methyl Alcohol at 27.3°C

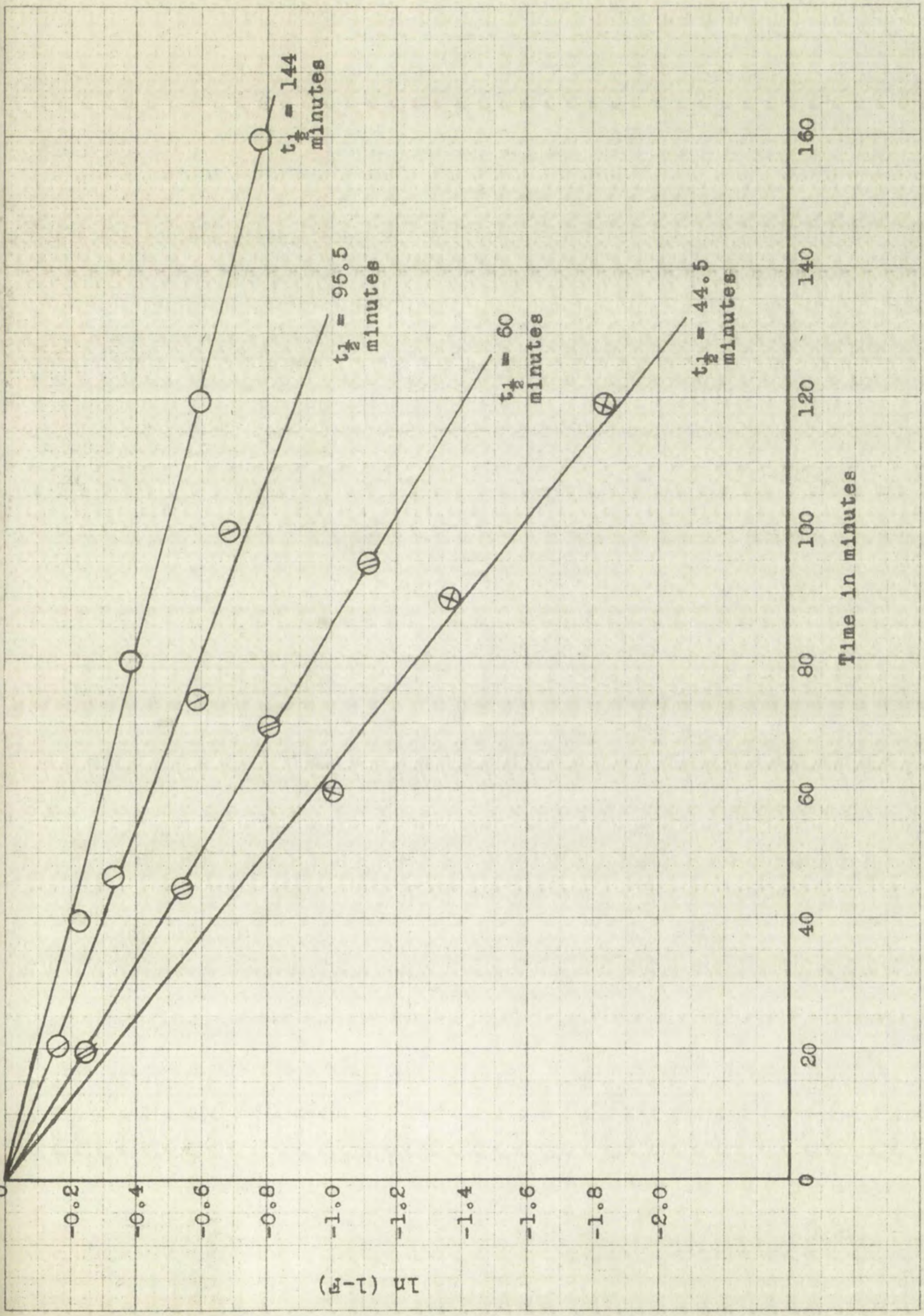


Figure 7. Exchange Runs in Methyl Alcohol at 44.0°C

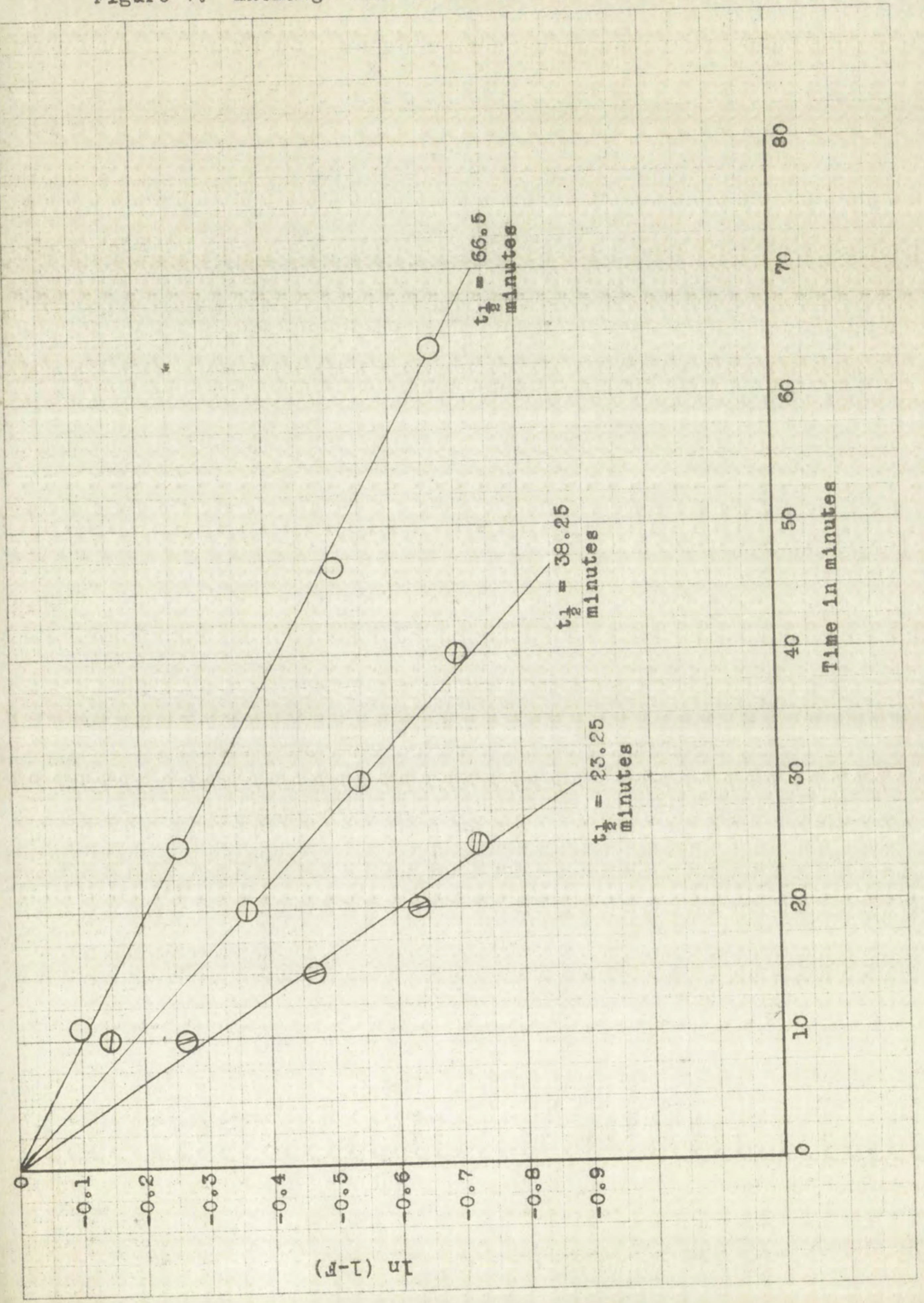


Figure 8. Plot of $\frac{R}{[C_6H_5CH_2I]}$ vs. [KI] in Methyl Alcohol

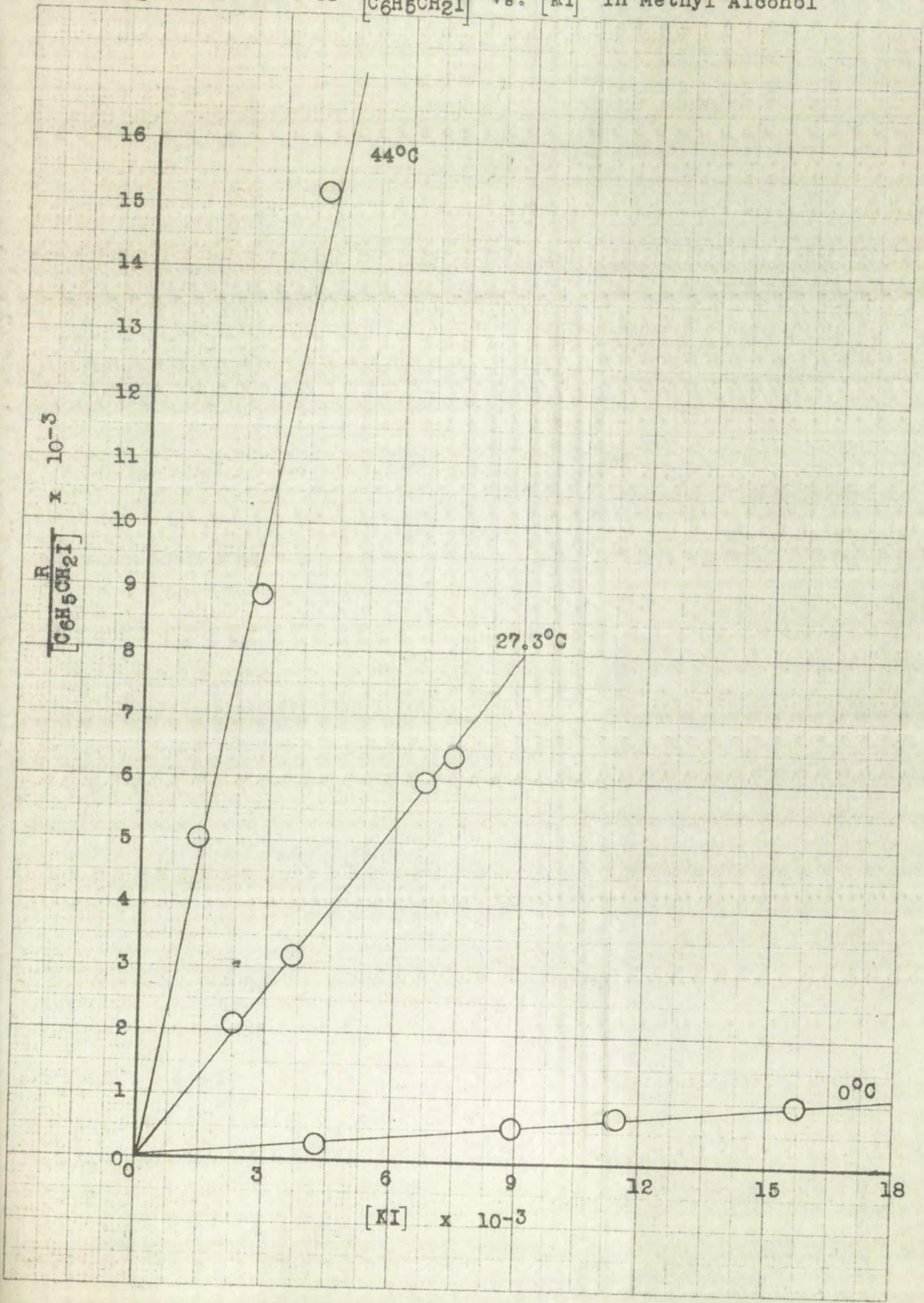


Figure 9. Temperature Dependence of the Velocity Constant in Methyl Alcohol

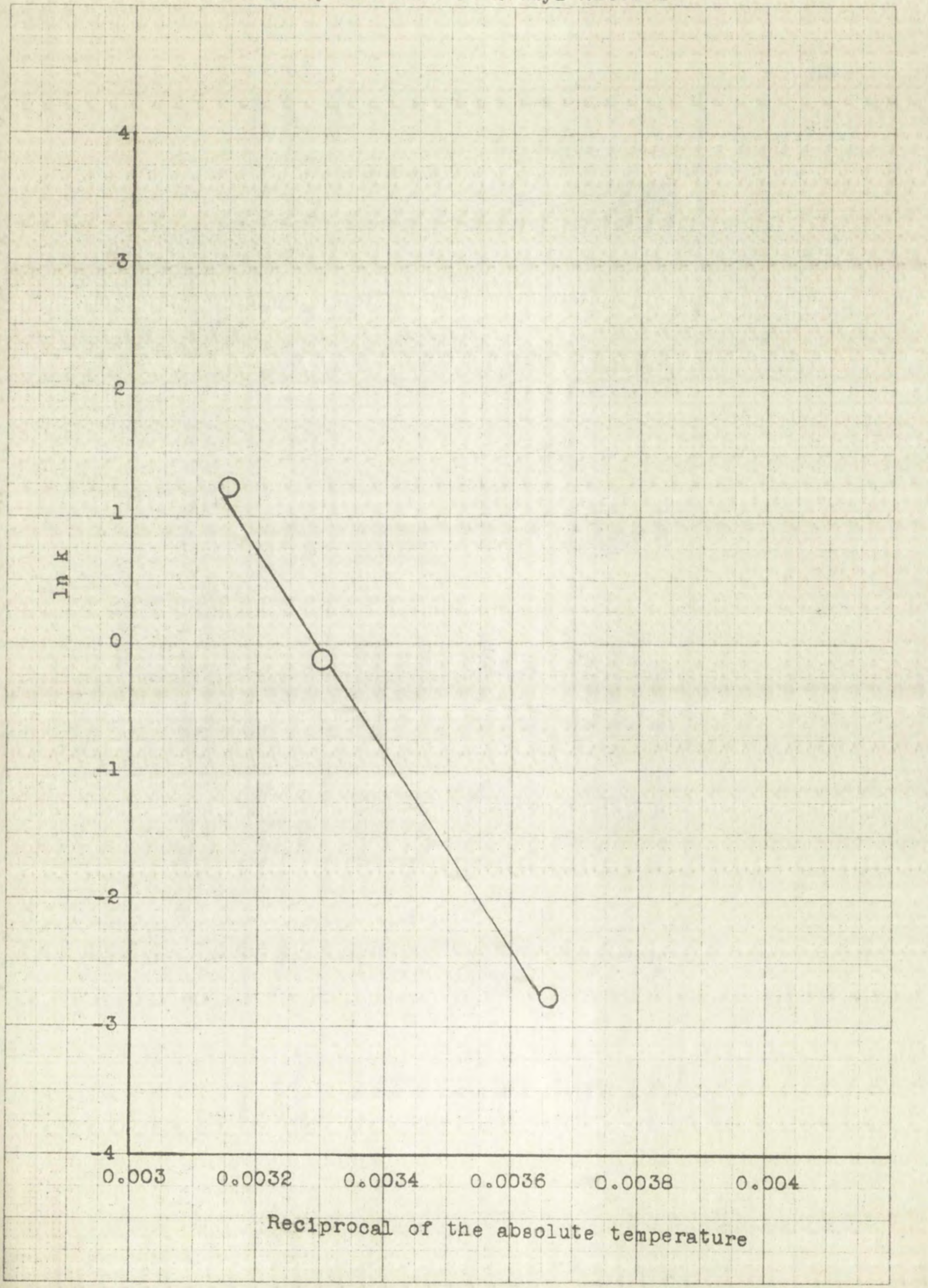


TABLE XV

Experimental Data for the Exchange Reaction Between Benzyl Iodide and Iodide Ion in Ethyl Alcohol

Run Number	Temp. °C	$C_6H_5CH_2I$ Conc., Molar	KI Conc., Molar	Half-time, Minutes	R moles liter^{-1} min^{-1} x 10-5	k liters mole^{-1} min^{-1}
12	0.0	0.0128	0.01035	306	1.30	0.098
13	0.0	0.0138	0.01245	270	1.68	0.098
14	0.0	0.0112	0.0080	358	0.902	0.101
15	0.0	0.0088	0.00247	574	0.233	0.107
16	27.3	0.00312	0.00251	72.5	1.33	1.70
17	27.3	0.00675	0.003725	39.25	4.25	1.69
18	27.3	0.01025	0.0074	23.5	12.68	1.67
19	27.3	0.00372	0.0022	66.0	1.45	1.77
20	44.0	0.0013	0.000815	39	0.891	8.41
21	44.0	0.003125	0.0027	14.5	6.93	8.20
22	44.0	0.0024	0.00185	19.5	3.71	8.35
23	44.0	0.0023	0.001525	22	2.89	8.24
24	44.0	0.002532	0.0021	18.5	4.30	8.10

TABLE XVI

Experimental Data for Run 12*

$[C_6H_5CH_2I]$ = 0.0128 M; $[KI]$ = 0.01035 M

$t_{\frac{1}{2}}$ = 306 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
60	65	791	0.133	0.143
60	65	789	0.133	0.143
120	105	819	0.200	0.223
120	114	740	0.236	0.269
180	151	732	0.301	0.358
180	171	701	0.347	0.426
240	218	666	0.436	0.573
240	212	680	0.420	0.545

* Experimental procedure I used.
** Corrected for operating blank, 3%.

TABLE XVII

Experimental Data for Run 13*

$[C_6H_5CH_2I]$ = 0.0138 M; $[KI]$ = 0.01245 M

$t_{\frac{1}{2}}$ = 270 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
60	78	995	0.137	0.147
60	82	1013	0.14	0.151
120	152	910	0.269	0.314
120	146	909	0.26	0.301
180	214	895	0.362	0.449
180	213	845	0.378	0.475
240	263	808	0.461	0.618

* Experimental procedure I used.
** Corrected for operating blank, 1.5%.

TABLE XVIII

Experimental Data for Run 14*

$[C_6H_5CH_2I] = 0.0112\ M; \quad [KI] = 0.0080\ M$

$t_{\frac{1}{2}} = 358$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
60	60	974	0.098	0.102
60	77	974	0.123	0.131
120	146	902	0.235	0.267
120	121	953	0.189	0.21
180	173	859	0.281	0.33
180	192	820	0.32	0.386
240	238	819	0.379	0.476
240	219	780	0.37	0.462

* Experimental procedure I used.

** Corrected for operating blank, 2.3%.

TABLE XIX

Experimental Data for Run 15*

$[C_6H_5CH_2I]$ = 0.0088 M; $[KI]$ = 0.00247 M

$t_{\frac{1}{2}}$ = 574 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
120	93	907	0.117	0.125
120	97	881	0.125	0.133
180	173	791	0.226	0.256
180	153	745	0.215	0.242
240	185	769	0.245	0.281
240	202	786	0.258	0.298
285	227	720	0.303	0.361
285	214	755	0.279	0.328

* Experimental procedure I used.

** Corrected for operating blank, 1.8%.

TABLE XX

Experimental Data for Run 16*

$[C_6H_5CH_2I] = 0.00312$ M; $[KI] = 0.00251$ M

$t_{\frac{1}{2}} = 72.5$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
20	89	857	0.169	0.185
20	94	821	0.184	0.203
40	161	742	0.32	0.386
40	153	710	0.317	0.382
60	220	696	0.43	0.562
60	218	670	0.44	0.580

* Experimental procedure I used.
** Corrected for operating blank, 1%.

TABLE XXI

Experimental Data for Run 17*

$[C_6H_5CH_2I]$ = 0.00675 M; $[KI]$ = 0.003725 M

$t_{\frac{1}{2}}$ = 39.25 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	120	661	0.236	0.269
15	120	654	0.238	0.271
30	199	575	0.397	0.506
30	218	569	0.426	0.555
49	298	462	0.604	0.932
49	270	484	0.553	0.806

* Experimental Procedure I used.

** Corrected for operating blank, 1%.

TABLE XXII

Experimental Data for Run 18*

$[C_6H_5CH_2I]$ = 0.01025 M; $[KI]$ = 0.0074 M

$t_{\frac{1}{2}}$ = 23.5 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	269	977	0.358	0.443
15	264	983	0.351	0.432
25	360	858	0.506	0.705
25	384	863	0.527	0.748
36	476	761	0.66	1.079
36	480	790	0.65	1.05

* Experimental procedure I used.

** Corrected for operating blank, 1%.

TABLE XXIII

Experimental Data for Run 19*

$[C_6H_5CH_2I] = 0.00372$ M; $[KI] = 0.0022$ M

$t_{\frac{1}{2}} = 66.0$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	54	560	0.138	0.149
15	55	539	0.145	0.157
30	112	562	0.262	0.305
30	111	554	0.264	0.307
45	145	453	0.383	0.483
45	155	475	0.387	0.489
62	193	482	0.45	0.598
62	205	451	0.492	0.677

* Experimental procedure I used

** Corrected for operating blank, 1.3%.

TABLE XXIV

Experimental Data for Run 20*

$[C_6H_5CH_2I] = 0.0013\ M; \quad [KI] = 0.000815\ M$

$t_{\frac{1}{2}} = 39$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
13	369	2506	0.203	0.227
13	376	2504	0.207	0.232
22	622	2238	0.346	0.425
22	576	2389	0.309	0.37
35	899	2046	0.487	0.667
35	867	2300	0.436	0.573
43	998	2143	0.506	0.705
43	1025	1780	0.584	0.878

* Experimental procedure I used.

** Corrected for operating blank, 2.85%.

TABLE XXV

Experimental Data for Run 21*

$[C_6H_5CH_2I]$ = 0.003125 M; $[KI]$ = 0.0027 M

$t_{\frac{1}{2}}$ = 14.5 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
5	93	652	0.222	0.25
10	187	639	0.404	0.518
10	174	615	0.393	0.499
17	261	589	0.55	0.799
17	260	629	0.521	0.736
30	371	487	0.774	1.488
30	375	463	0.806	1.64
45	473	434	0.945	2.904
45	452	409	0.941	2.83

* Experimental procedure I used.

** Corrected for operating blank, 3.75%.

TABLE XXVI

Experimental Data for Run 22*

$[C_6H_5CH_2I] = 0.0024$ M; $[KI] = 0.00185$ M

$t_{\frac{1}{2}} = 19.5$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
10	190	912	0.295	0.349
10	186	918	0.292	0.345
20	328	781	0.514	0.721
30	421	652	0.685	1.155
30	425	628	0.705	1.221
40	477	627	0.755	1.406
40	467	621	0.75	1.386

* Experimental procedure I used.

** Corrected for operating blank, 2.65%.

TABLE XXVII

Experimental Data for Run 23*

$[C_6H_5CH_2I] = 0.0023$ M; $[KI] = 0.001525$ M

$t_{\frac{1}{2}} = 22$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
11	259	1165	0.297	0.352
11	256	1169	0.294	0.348
20	407	1053	0.455	0.607
20	402	1015	0.464	0.624
30	525	922	0.594	0.902
30	539	913	0.608	0.937
40	644	804	0.73	1.309
40	650	826	0.724	1.287

* Experimental procedure I used.

** Corrected for operating blank, 2.15%.

TABLE XXVIII

Experimental Data for Run 24*

$[C_6H_5CH_2I]$ = 0.002532 M; $[KI]$ = 0.0021 M

$t_{\frac{1}{2}}$ = 18.5 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
6	200	1878	0.172	0.188
6	202	1856	0.175	0.192
12	452	1684	0.379	0.476
12	433	1628	0.377	0.473
18	592	1561	0.491	0.675
24	751	1375	0.635	1.008
24	722	1330	0.632	1.000

* Experimental procedure I used.

** Corrected for operating blank, 2.89%.

Figure 10. Exchange Run in Ethyl Alcohol at 0°C

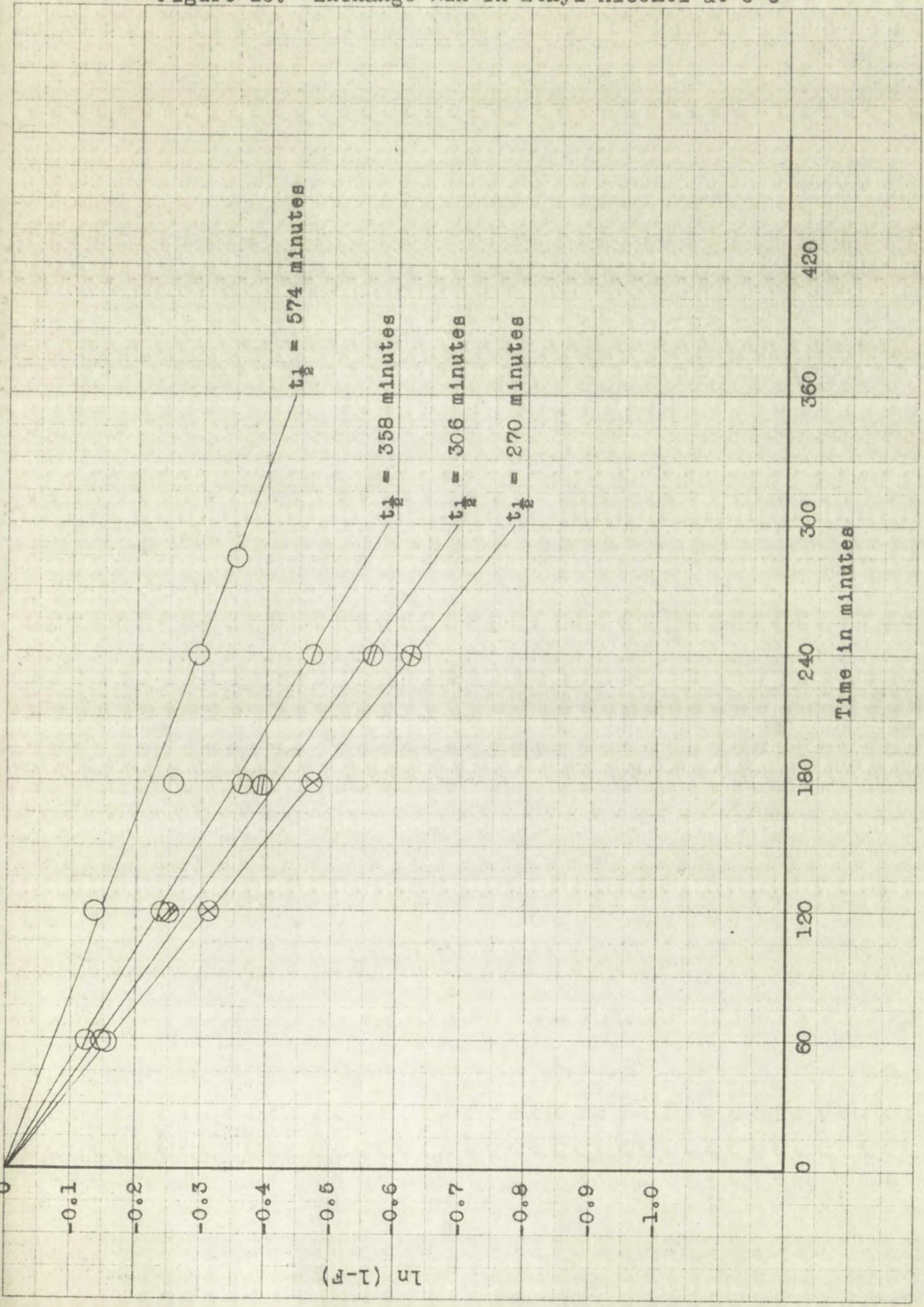


Figure 11. Exchange Run in Ethyl Alcohol at 27.3°C

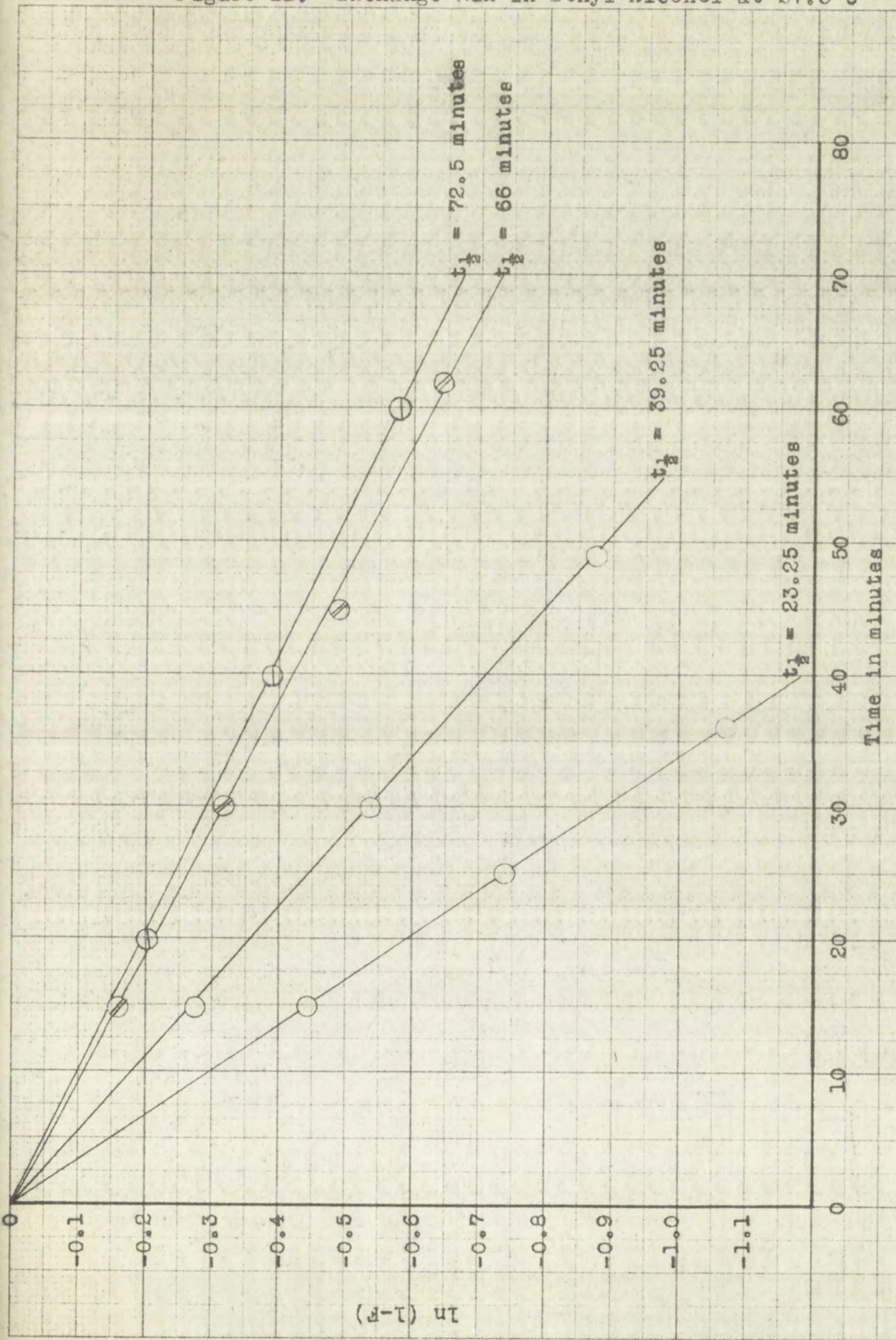


Figure 12. Exchange Run in Ethyl Alcohol at 44.0°C

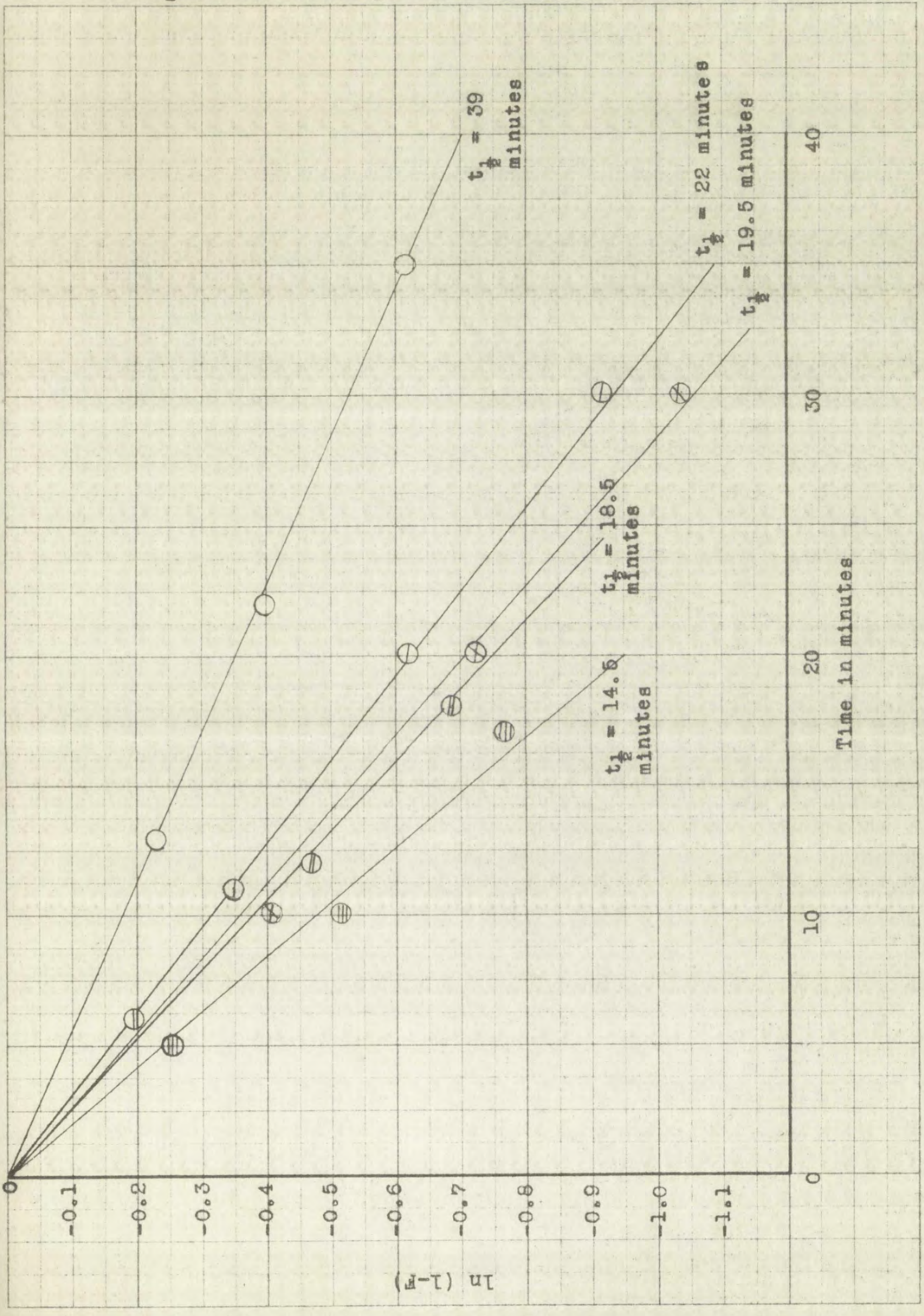


Figure 13. Plot of $\frac{R}{[C_6H_5CH_2I]}$ vs. [KI] in Ethyl Alcohol

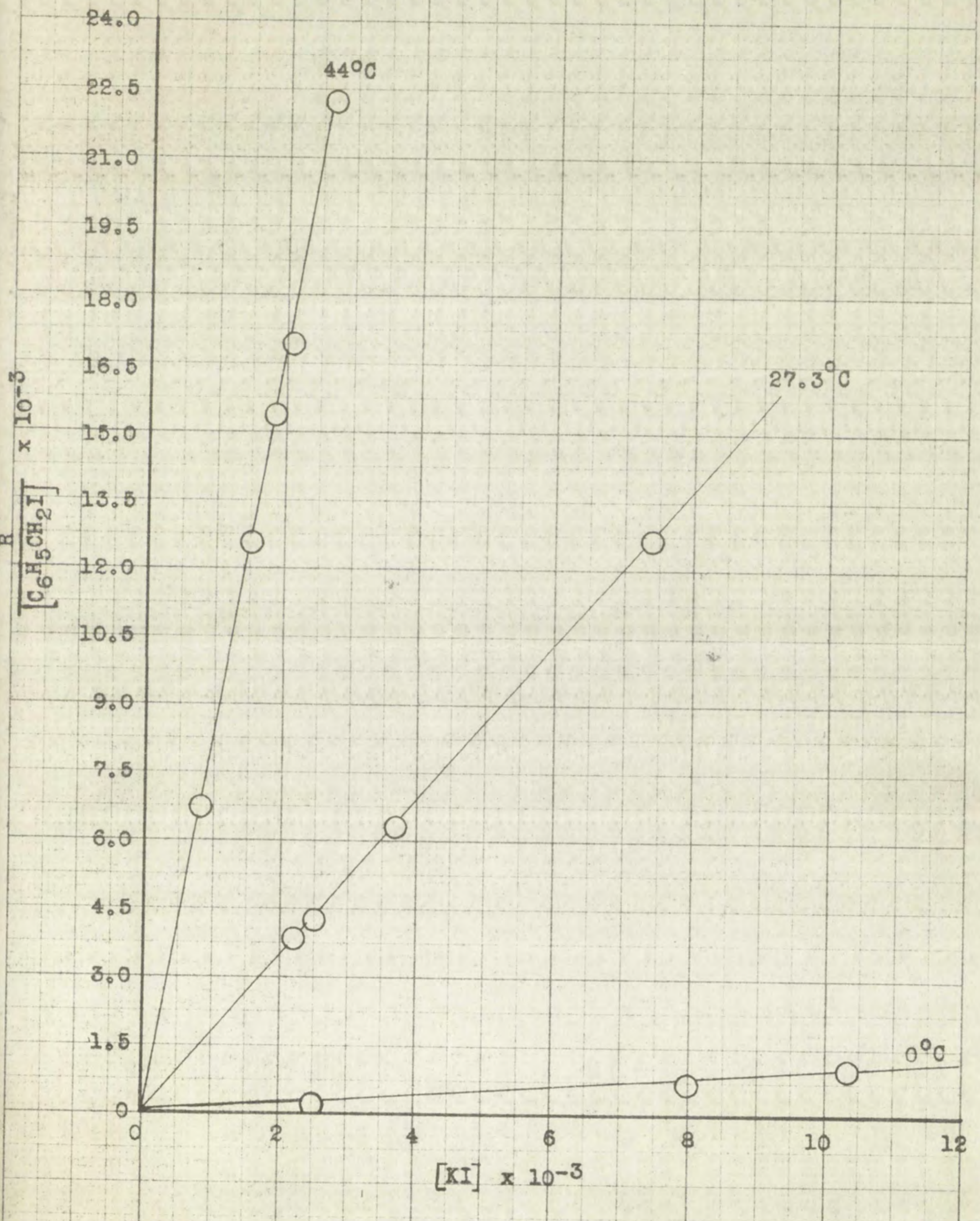


Figure 14. Temperature Dependence of the Velocity Constant in Ethyl Alcohol

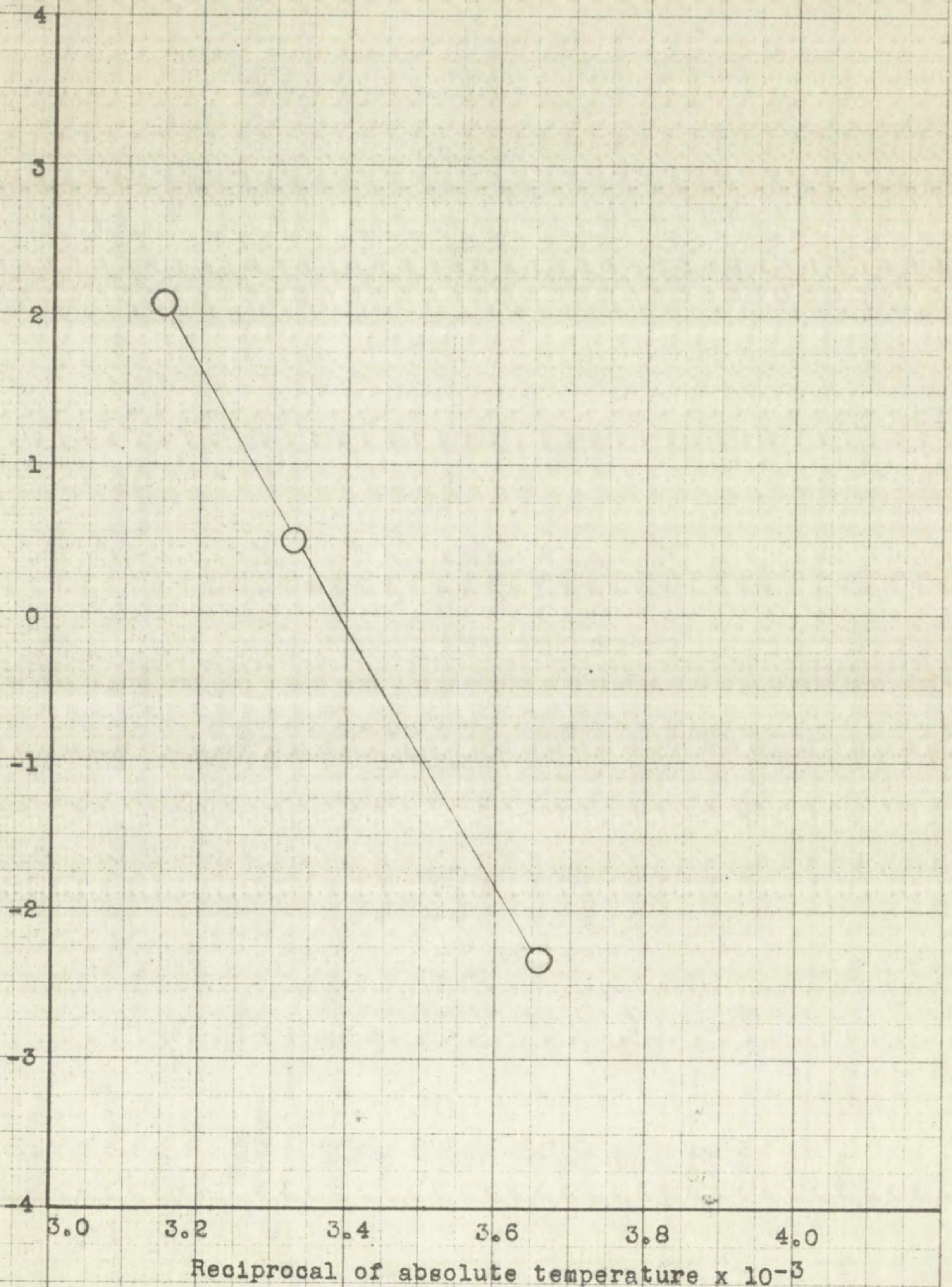


TABLE XXX

Experimental Data for Run 25*

$[C_6H_5CH_2I]$ = 0.00522 M; $[KI]$ = 0.0045 M

$t_{\frac{1}{2}}$ = 73 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
20	185	1697	0.182	0.201
20	218	1646	0.216	0.243
40	277	1395	0.306	0.365
40	305	1346	0.341	0.417
60	429	1462	0.419	0.543
60	380	1273	0.425	0.553

* Experimental procedure II used.
** Corrected for operating blank, 1%.

TABLE XXXI

Experimental Data for Run 26*

$[C_6H_5CH_2I] = 0.0074$ M; $[KI] = 0.00585$ M

$t_{\frac{1}{2}} = 50$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged F	ln (1-F)
10	192	2200	0.142	0.153
10	249	2152	0.183	0.202
20	306	1849	0.251	0.289
20	326	1761	0.278	0.326
30	447	1931	0.332	0.403
30	436	1836	0.34	0.416

* Experimental procedure I used.

** Corrected for operating blank, 1%.

TABLE XXXII

Experimental Data for Run 27*

$[C_6H_5CH_2I]$ = 0.005295 M; $[KI]$ = 0.003375 M

$t_{\frac{1}{2}}$ = 80 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
22	185	1523	0.176	0.193
22	215	1508	0.202	0.226
40	283	1252	0.299	0.355
40	294	1247	0.309	0.37
60	382	1199	0.392	0.497
60	394	1189	0.403	0.516

* Experimental procedure II used.
** Corrected for operating blank, 1.5%.

TABLE XXXIII

Experimental Data for Run 28*

$[C_6H_5CH_2I]$ = 0.003585 M; $[KI]$ = 0.0045 M

$t_{\frac{1}{2}}$ = 145 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	19	695	0.059	0.061
15	23	693	0.071	0.074
46	61	642	0.194	0.216
46	56	645	0.178	0.196
78	82	606	0.266	0.309
78	112	566	0.37	0.462

* Experimental procedure II used.
** Corrected for operating blank, 1%.

TABLE XXXIV

Experimental Data for Run 29*

$[C_6H_5CH_2I]$ = 0.0103 M; $[KI]$ = 0.00922

$t_{\frac{1}{2}}$ = 59 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	107	997	0.182	0.201
15	107	1081	0.17	0.186
40	216	876	0.371	0.464
40	230	946	0.368	0.459
50	281	827	0.443	0.586
50	281	918	0.477	0.648

* Experimental procedure I used.

** Corrected for operating blank, 1%.

TABLE XXXV

Experimental Data for Run 30*

$[C_6H_5CH_2I] = 0.01415\ M$; $[KI] = 0.0145\ M$

$t_{\frac{1}{2}} = 40$ minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
15	101	801	0.224	0.253
15	102	827	0.219	0.247
30	164	688	0.384	0.434
30	181	684	0.418	0.542
45	257	664	0.557	0.814
45	232	637	0.534	0.764

* Experimental procedure I used.

** Corrected for operating blank, 1.5%.

TABLE XXXVI

Experimental Data for Run 31*

$[C_6H_5CH_2I] = 0.01385\ M; \quad [KI] = 0.01505\ M$

$t_{\frac{1}{2}} = 117$ minutes

Time , Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
35	168	1674	0.189	0.21
35	167	1650	0.190	0.21
65	271	1496	0.317	0.381
65	278	1477	0.328	0.397
88	330	1403	0.395	0.503
88	322	1369	0.395	0.503

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XXXVII

Experimental Data for Run 32*

$[C_6H_5CH_2I] = 0.0088$ M; $[KI] = 0.0090$ M

$t_{\frac{1}{2}} = 186$ **minutes**

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
45	138	1468	0.172	0.188
45	117	1313	0.164	0.179
90	226	1343	0.288	0.339
90	218	1235	0.301	0.358
135	313	1285	0.392	0.497
135	280	1156	0.391	0.496

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XXXVIII

Experimental Data for Run 33*

$[C_6H_5CH_2I]$ = 0.005385 M; $[KI]$ = 0.00473 M

$t_{\frac{1}{2}}$ = 293 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
75	120	1200	0.169	0.185
75	125	1214	0.174	0.191
160	215	1083	0.309	0.37
160	216	1108	0.302	0.36
235	305	1011	0.432	0.566

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XXXIX

Experimental Data for Run 34*

$[C_6H_5CH_2I]$ = 0.004865 M; $[KI]$ = 0.004525 M

$t_{\frac{1}{2}}$ = 28 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
10	100	838	0.204	0.228
10	106	822	0.219	0.247
20	206	745	0.415	0.536
20	194	743	0.397	0.506
35	278	640	0.580	0.868
35	263	608	0.578	0.865

---

* Experimental procedure I used.

** Corrected for operating blank, 1.1%.

TABLE XXXX

Experimental Data for Run 35*

$[C_6H_5CH_2I]$ = 0.004865 M; $[KI]$ = 0.00317 M

$t_{\frac{1}{2}}$ = 32 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
10	134	1023	0.199	0.222
10	140	1100	0.193	0.215
20	222	893	0.342	0.419
20	254	1000	0.347	0.426
35	357	779	0.54	0.777
35	390	832	0.548	0.795

* Experimental procedure I used.
** Corrected for operating blank, 1%.

TABLE XXXXI

Experimental Data for Run 36*

$[C_6H_5CH_2I]$ = 0.0135 M; $[KI]$ = 0.01595 M

$t_{\frac{1}{2}}$ = 166 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
66	191	1483	0.246	0.282
66	196	1546	0.244	0.280
110	297	1407	0.378	0.475
110	301	1448	0.373	0.467
166	373	1285	0.486	0.665
166	421	1399	0.500	0.693

* Experimental procedure II used.

** Corrected for operating blank, 1%.

TABLE XXXXII

Experimental Data for Run 37*

$[C_6H_5CH_2I]$ = 0.0136 M; $[KI]$ = 0.0135 M

$t_{\frac{1}{2}}$ = 210 minutes

Time, Minutes	Activity, Benzyl Iodide fraction,** counts per minute	Activity, Iodide Ion fraction, counts per minute	fraction exchanged, F	ln (1-F)
60	142	1358	0.187	0.207
60	153	1452	0.188	0.208
120	247	1269	0.321	0.387
180	331	1178	0.432	0.566
180	364	1238	0.448	0.594
220	396	1130	0.513	0.719
220	428	1191	0.522	0.738

* Experimental procedure II used.

** Corrected for operating blank, 1%.

Figure 15. Exchange Run in Acetone-Ethyl Alcohol at 0°C
(6.82 moles per liter Acetone)

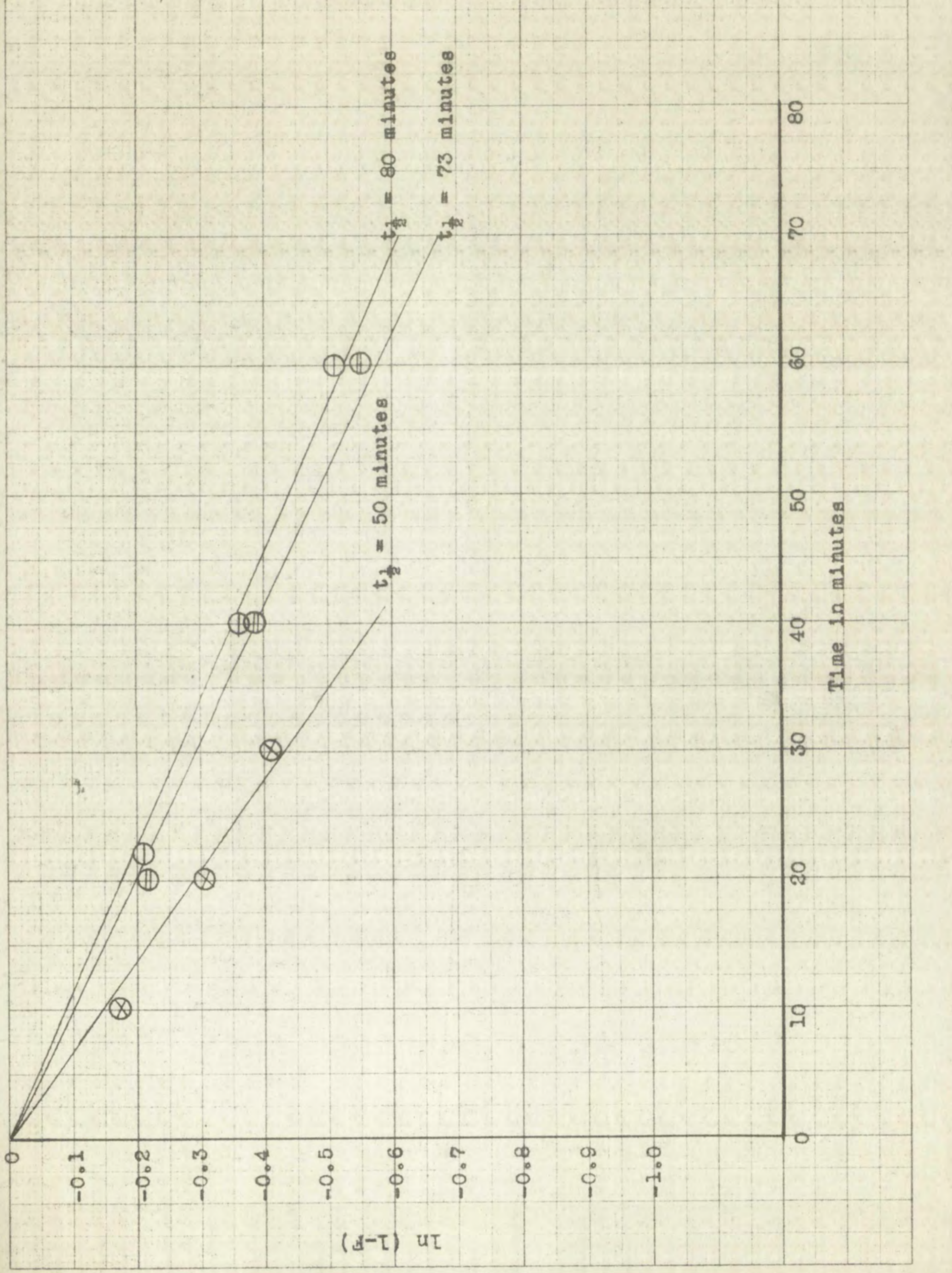


Figure 16. Exchange Run in Acetone-Ethyl Alcohol at 0°C
(4.55 moles per liter Acetone)

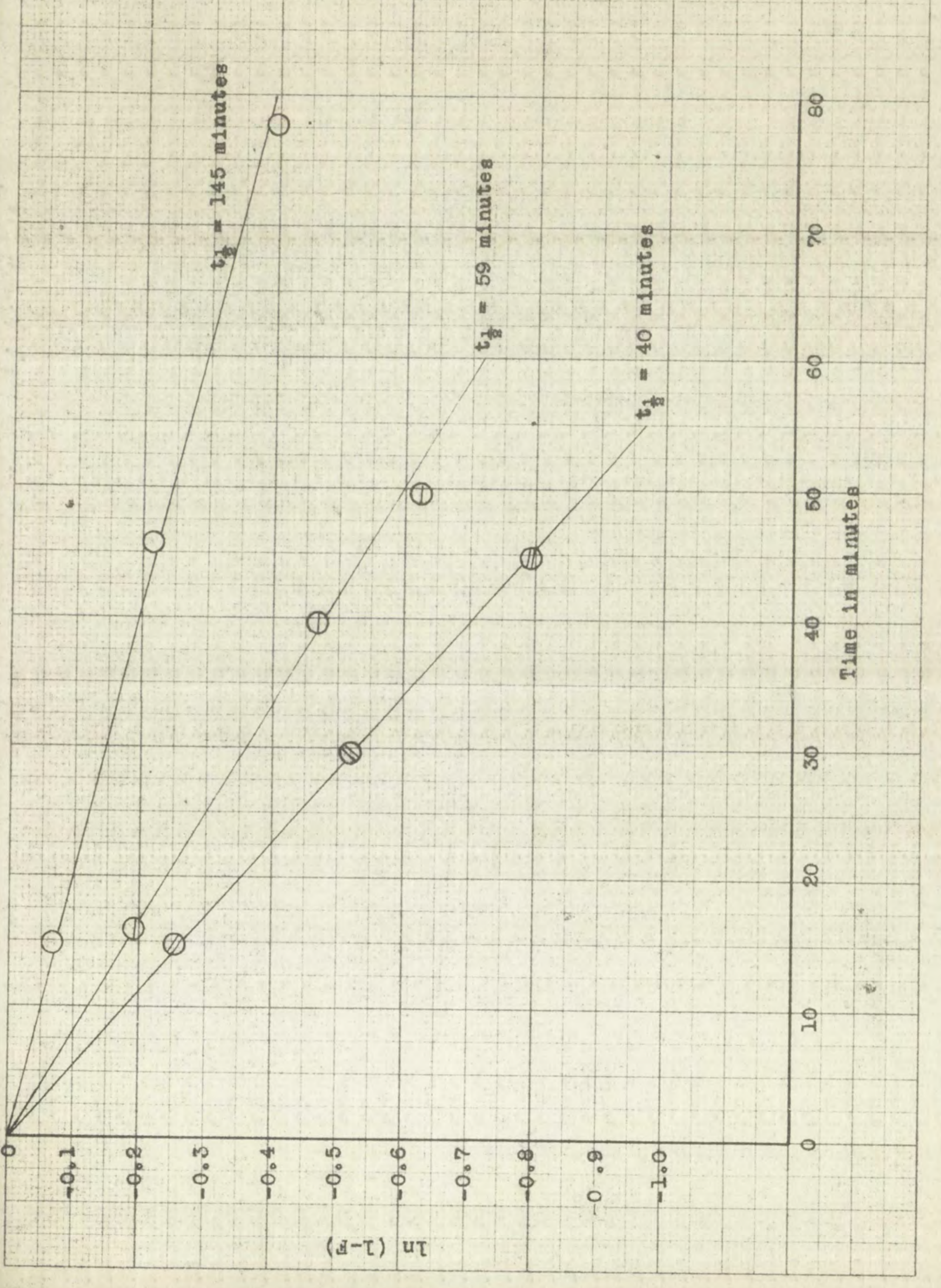


Figure 17. Exchange Run in Acetone-Ethyl Alcohol at 0°C (2.27 moles per liter Acetone)

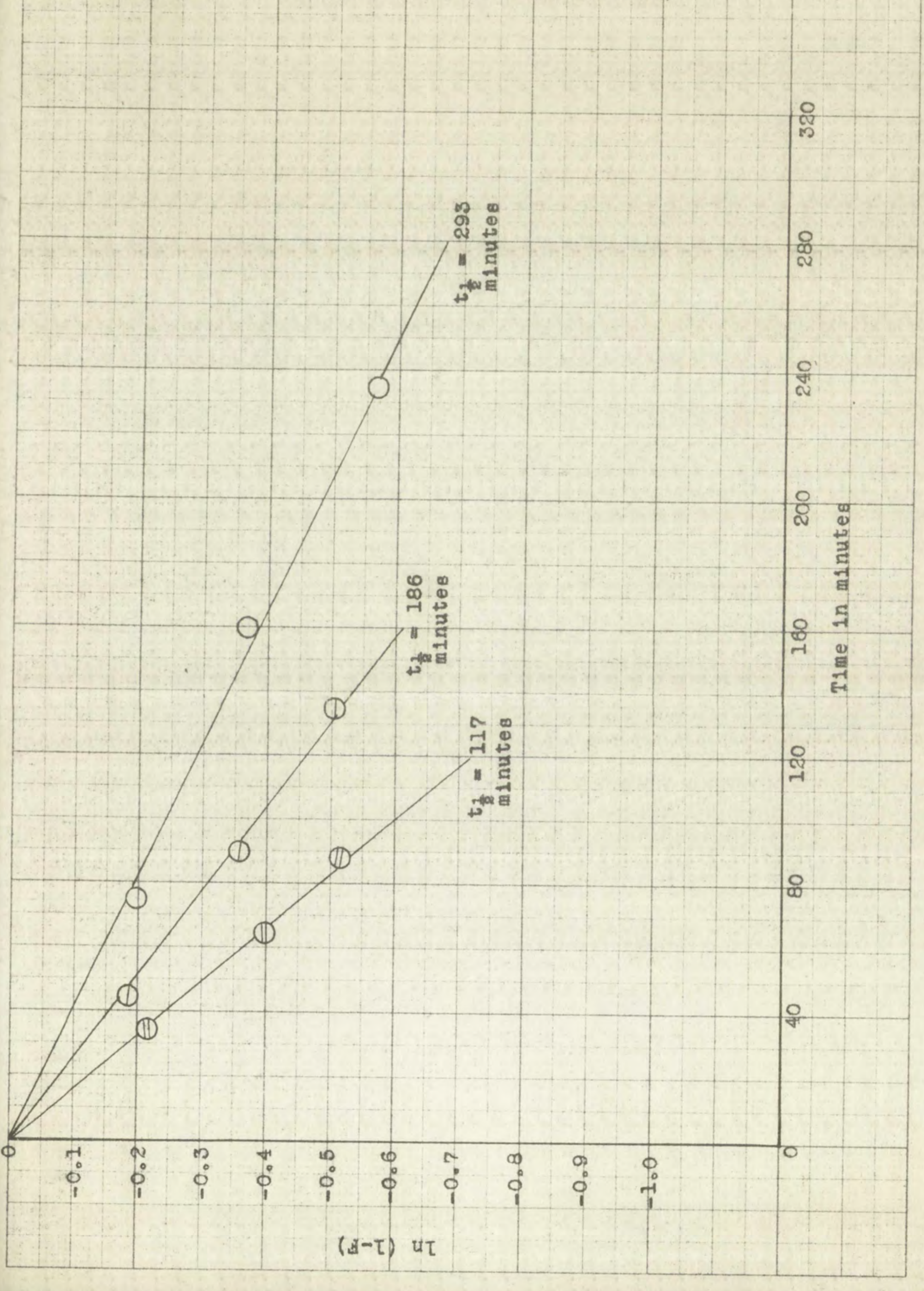


Figure 18. Exchange Run in Acetone-Ethyl Alcohol at 27.3°C
(2.27 moles per liter Acetone)

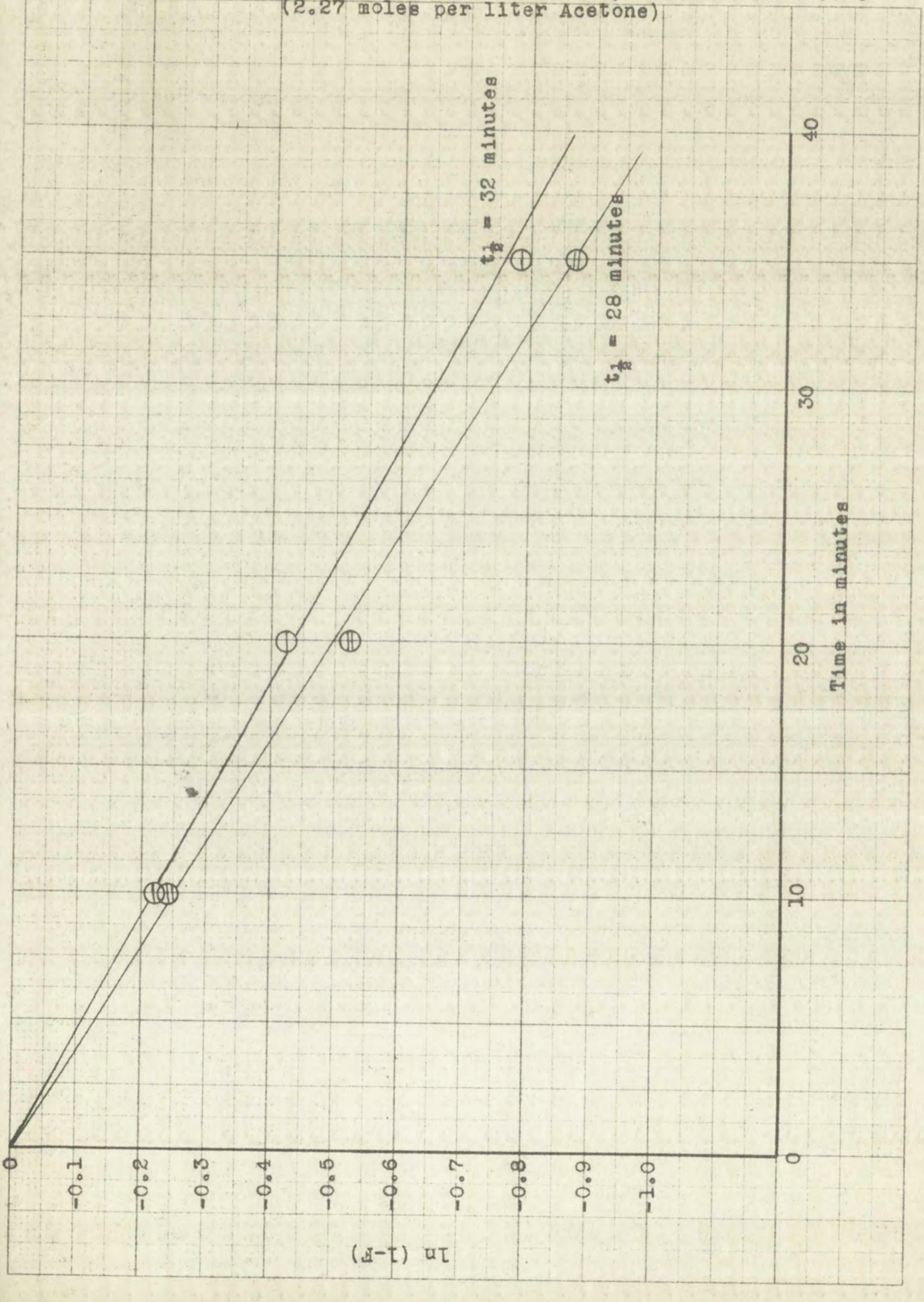


Figure 19. Exchange Run in Acetone-Ethyl Alcohol at 0°C
(1.24 moles per liter Acetone)

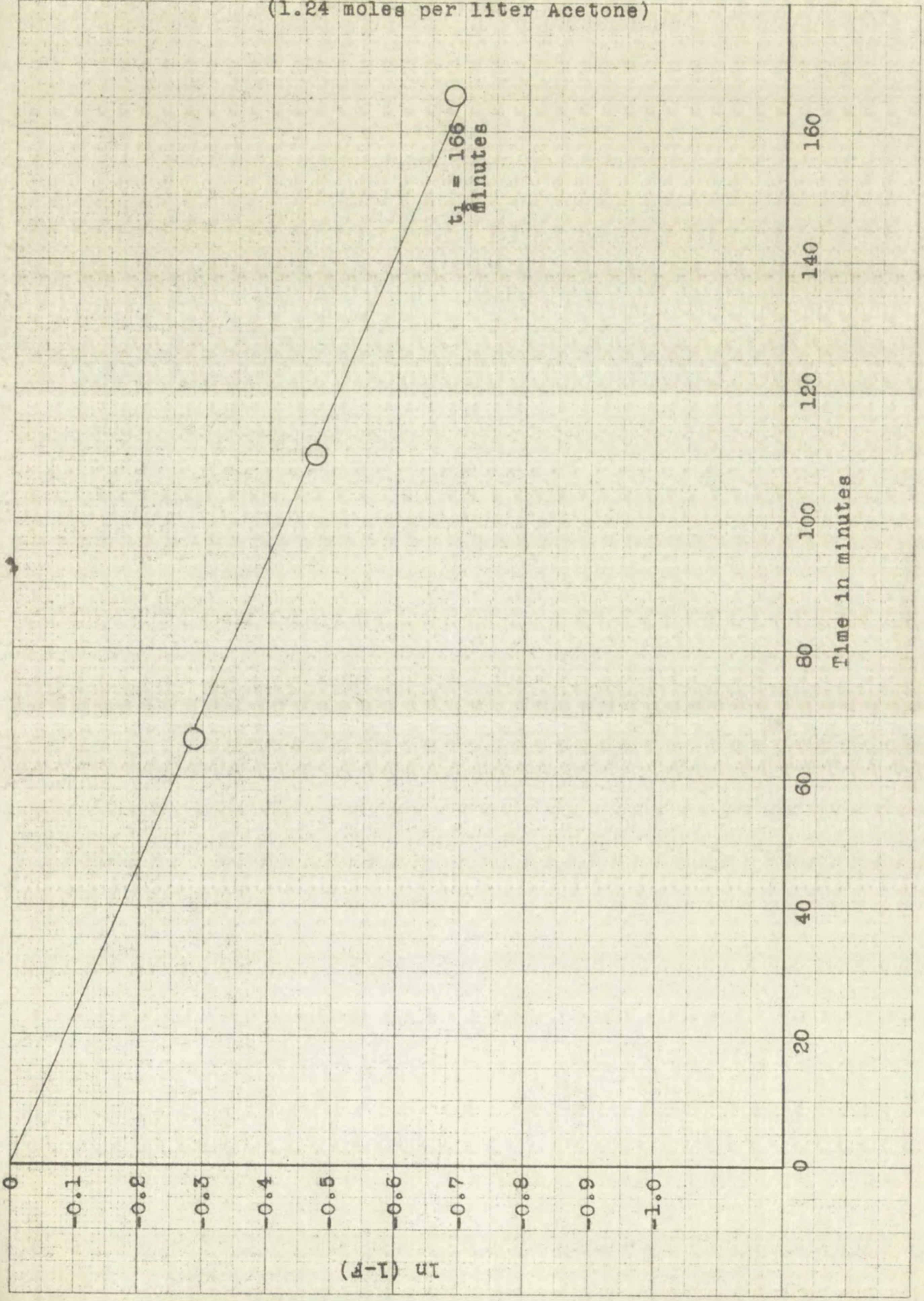


Figure 20. Exchange Run in Acetone-Ethyl Alcohol at 0°C
(0.525 moles per liter Acetone)

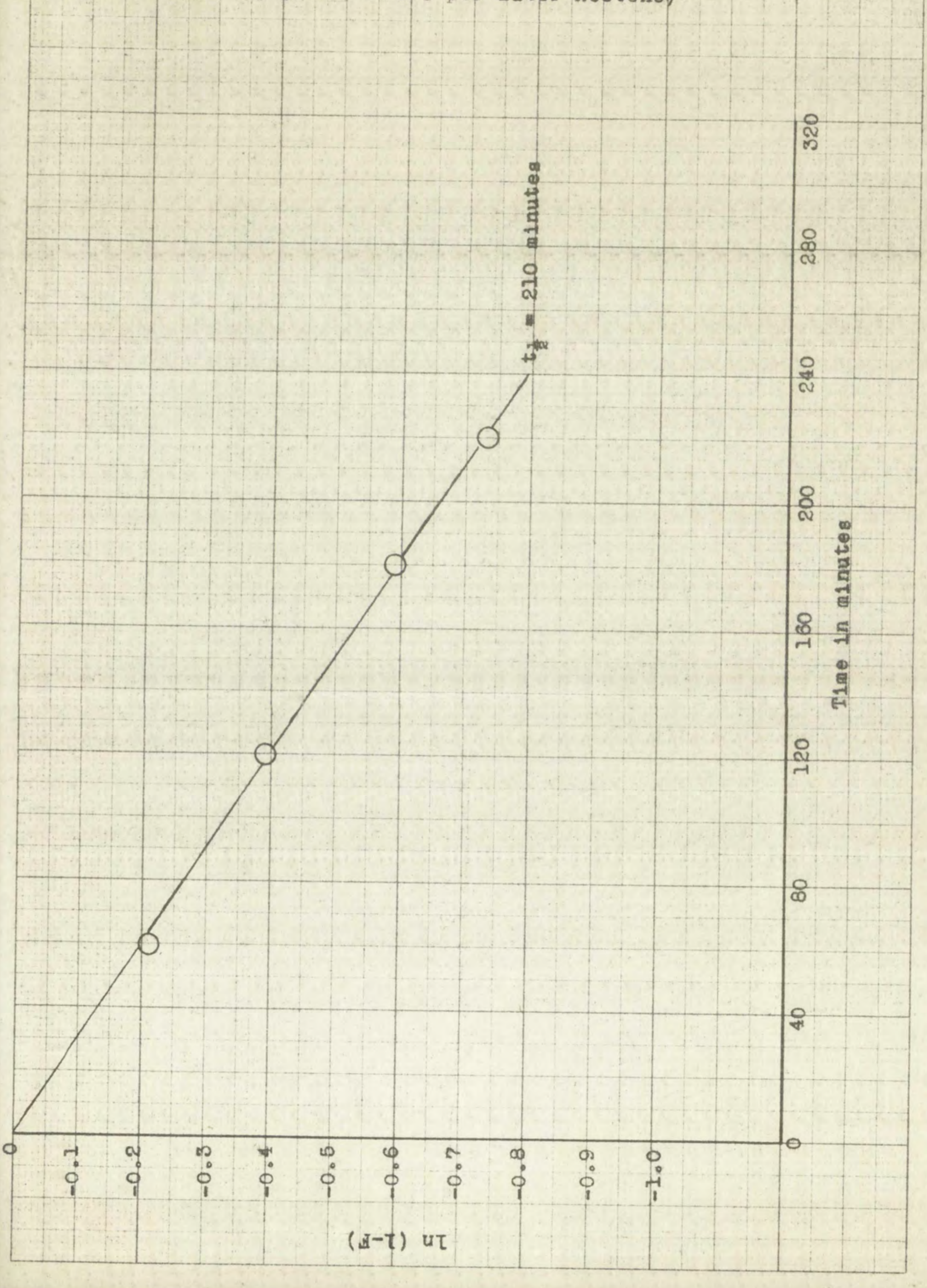


Figure 21. Plot of $\frac{R}{[C_6H_5CH_2I]}$ vs. [KI] in Acetone-Ethyl Alcohol at 0°C

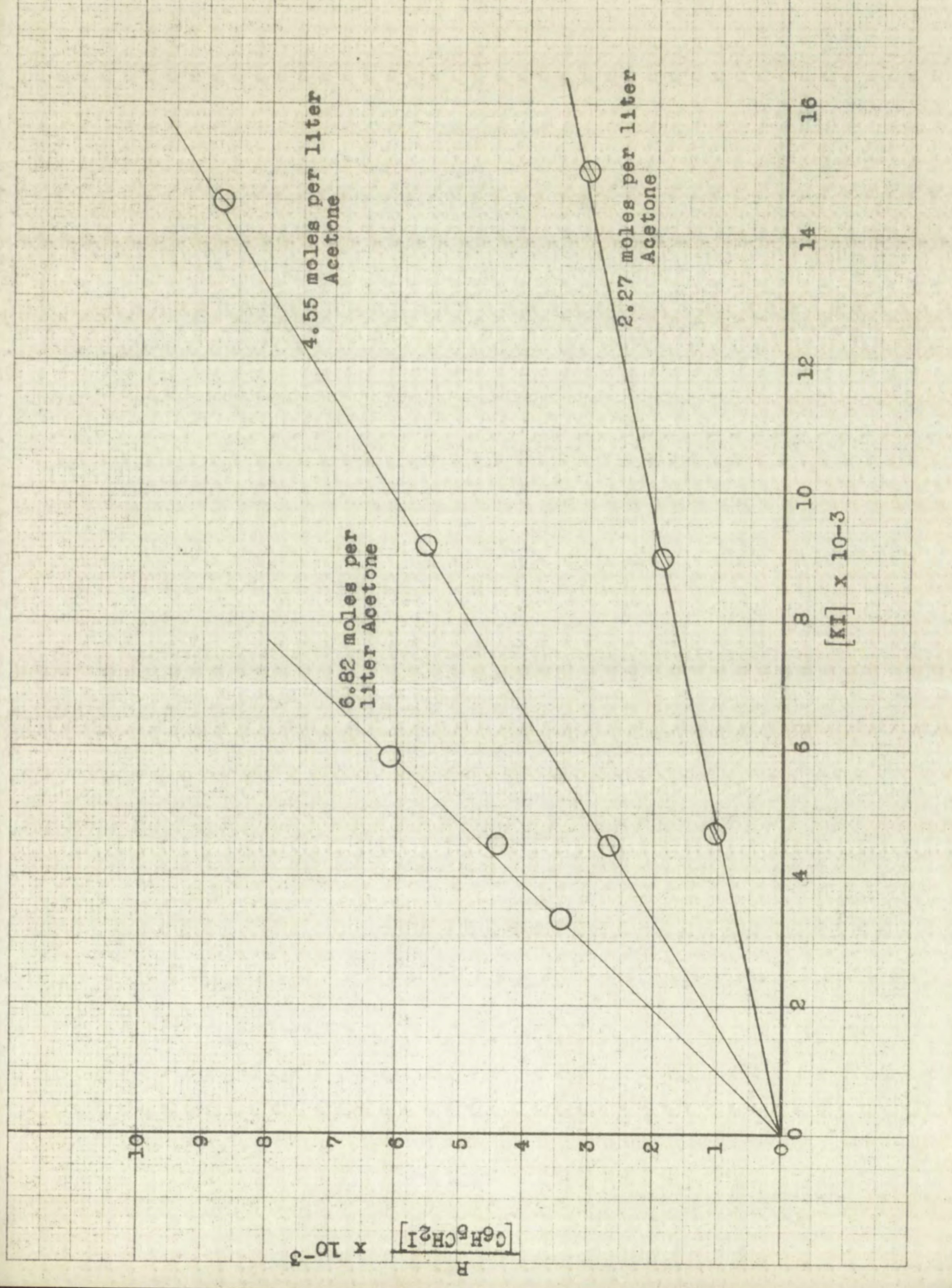


Figure 22. Plot of $\frac{R}{[C_6H_5CH_2I]\,[KI]}$ against $[\text{Acetone}]^x$ where $x = \frac{1}{2}$

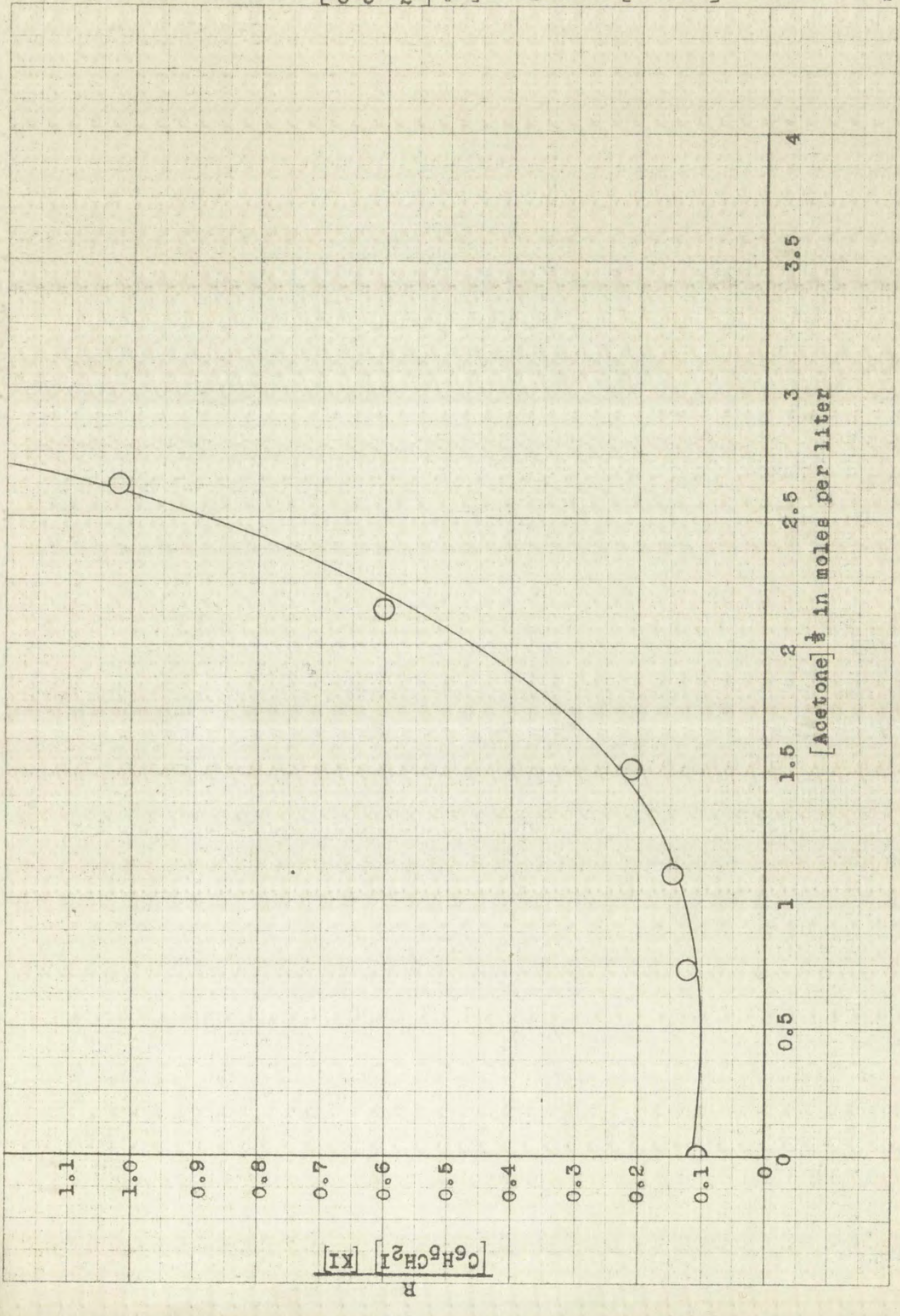


Figure 23. Plot of $\frac{R}{[C_6H_5CH_2I]\,[KI]}$ vs. $[\text{Acetone}]^x$ where x = 1

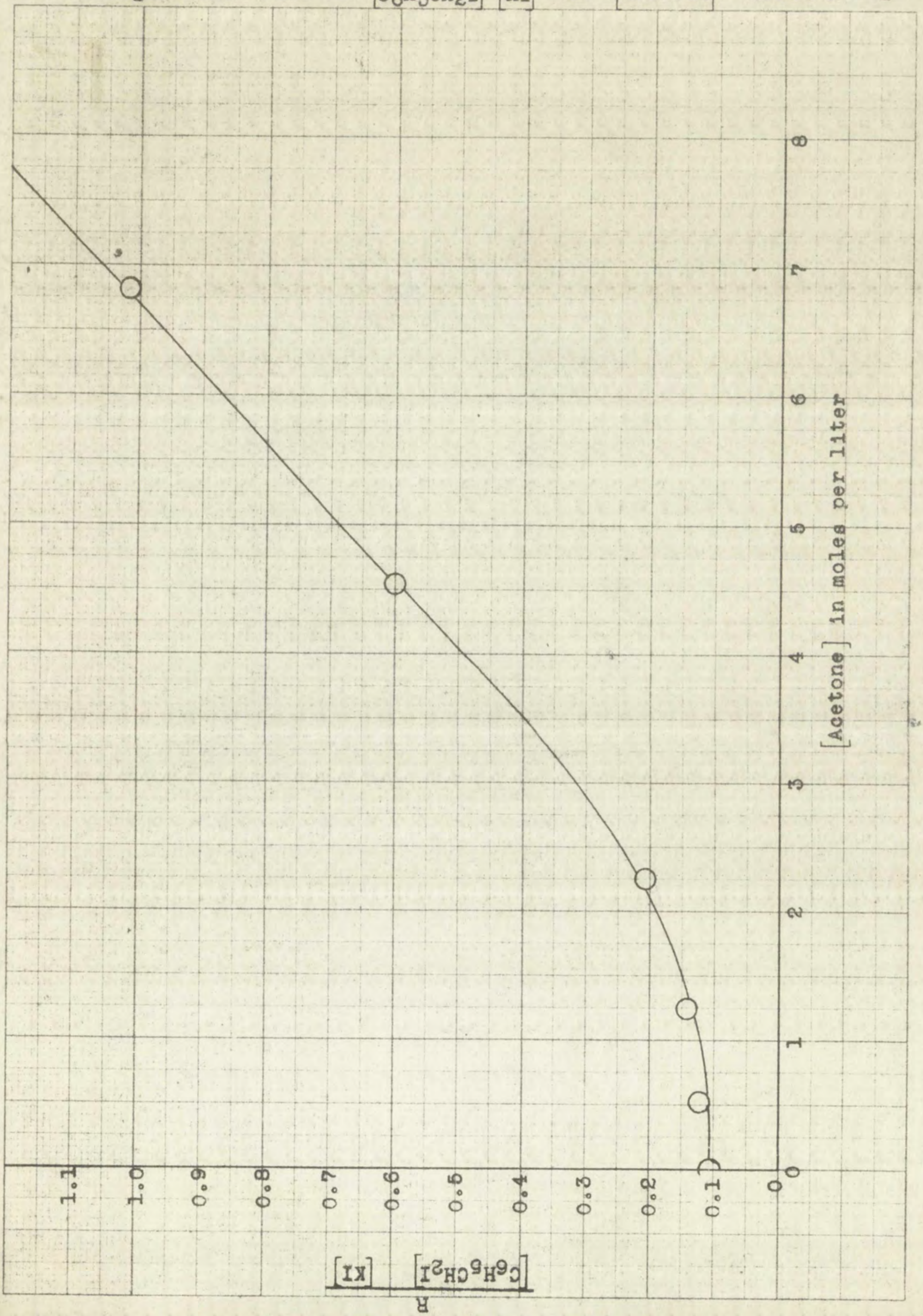


Figure 24. Plot of $\frac{R}{[C_6H_5CH_2I]\,[KI]}$ against $[\text{Acetone}]^x$ where x = 2

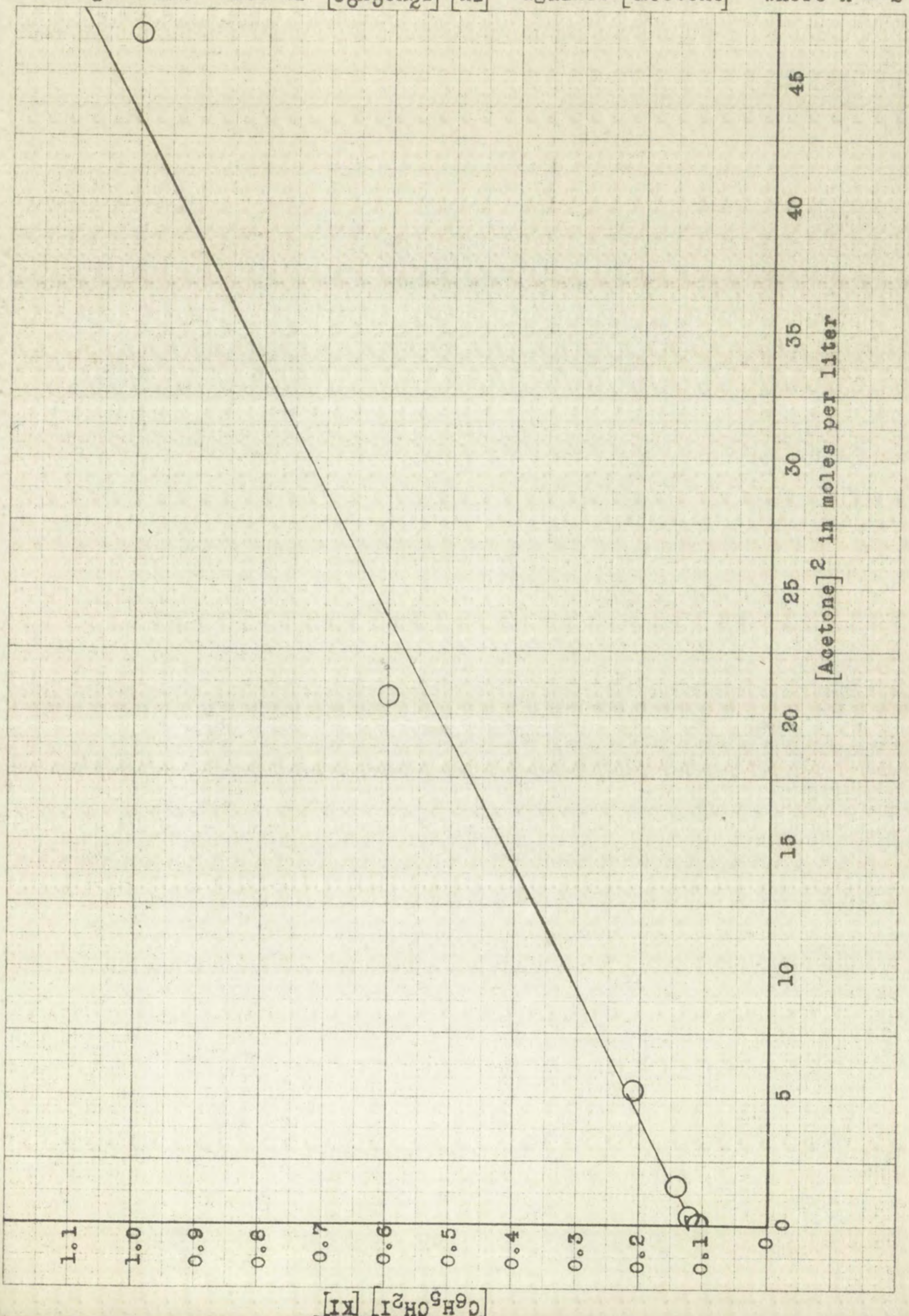


Figure 25. Plot of $\frac{R}{[C_6H_5CH_2I][KI]}$ vs. $[\text{Acetone}]^x$

where x = 3

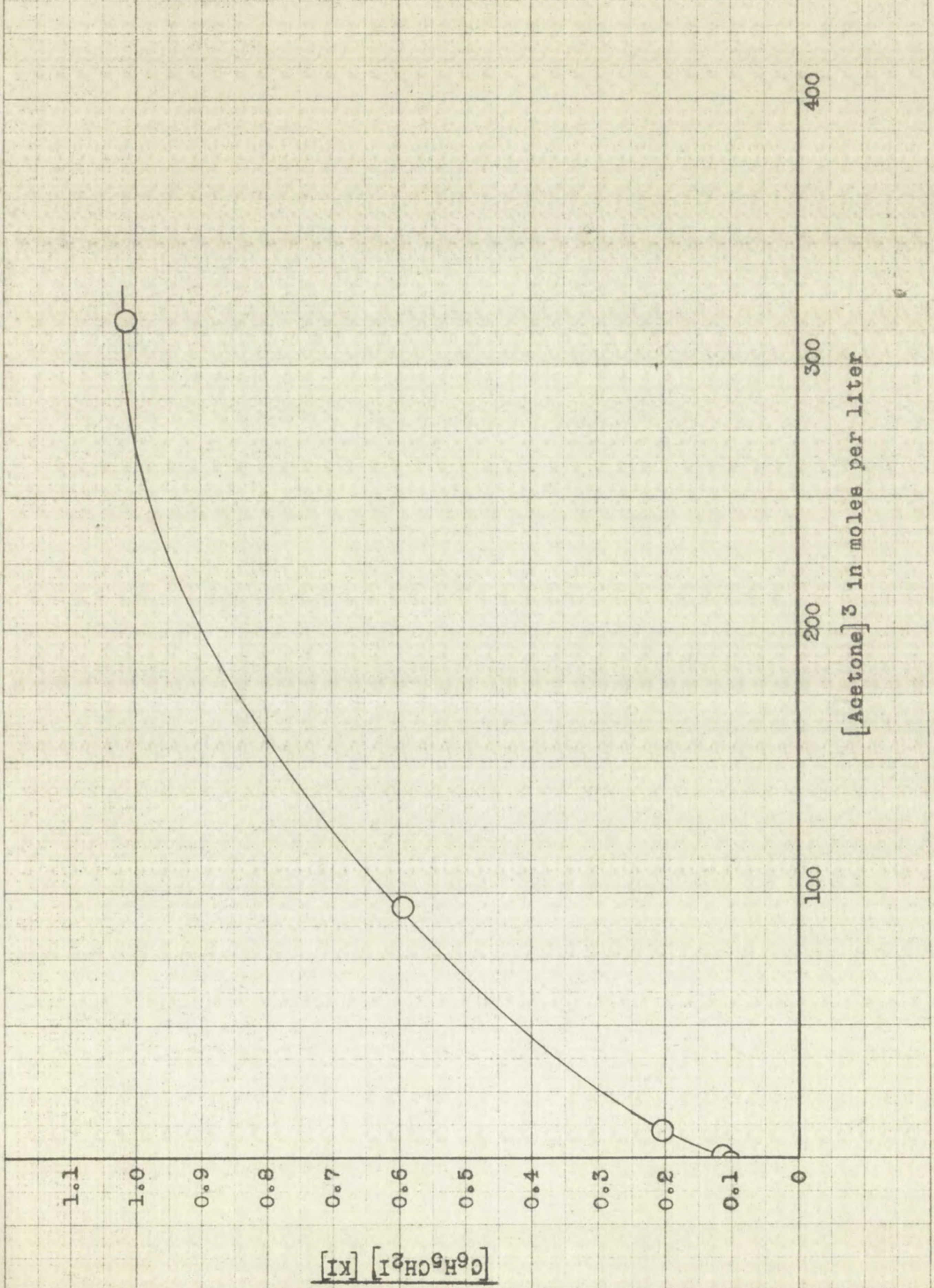


Figure 26. Plot of ln k vs. $^1/_D$ for 0°C where

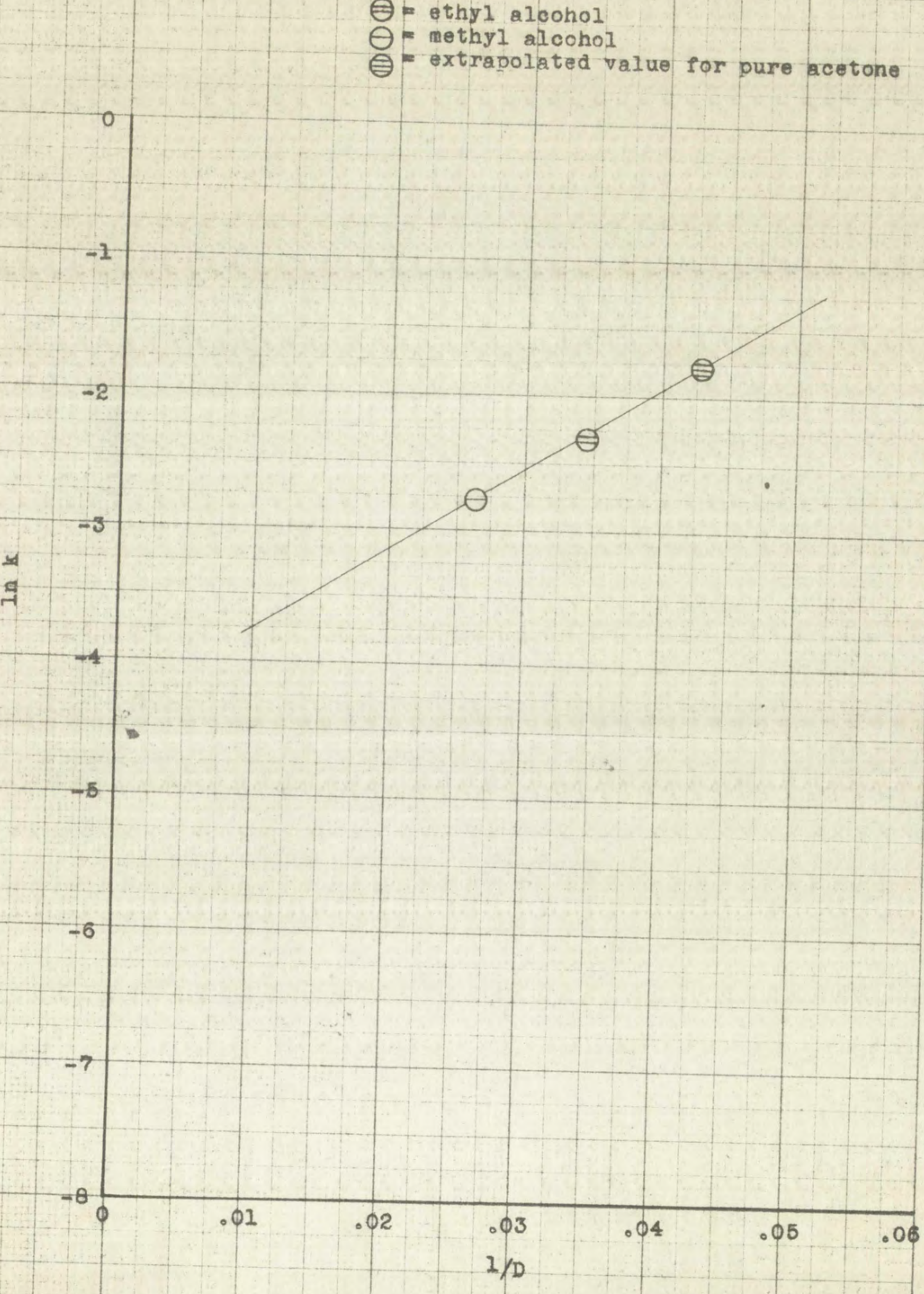
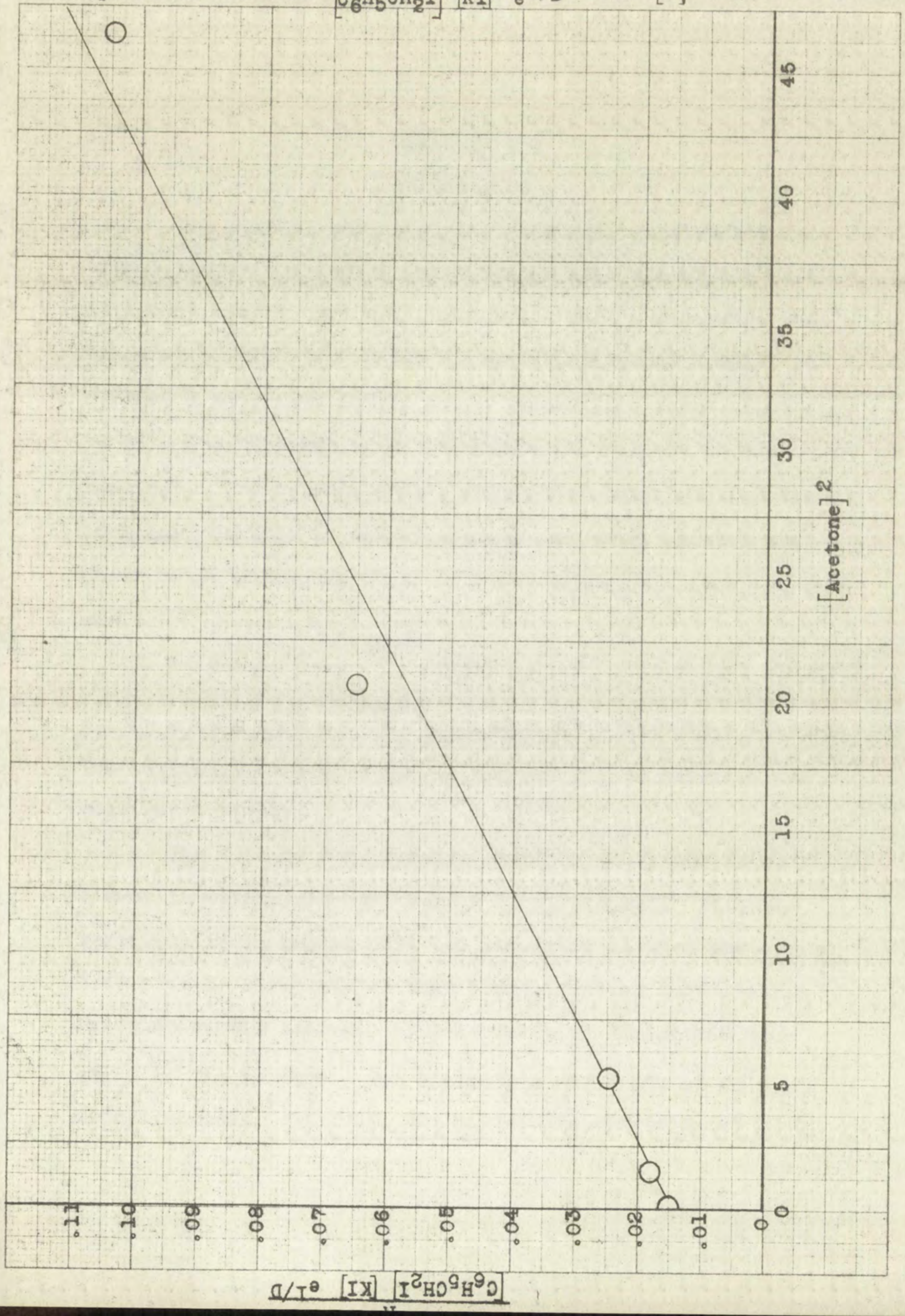


Figure 27. Plot of $\frac{R}{[C_6H_5CH_2I]\,[KI]\,e^{1/D}}$ vs. $[A]^x$ where $x = 2$



The results [illegible] the exchange [illegible]
benzyl iodide [illegible]
in methyl alcohol [illegible]
range of [illegible]
0.01595 [illegible]
to 45°C the reaction [illegible]
reaction. The experimental [illegible]
exchange reaction is [illegible]
shown below where the [illegible]
ute.

$$k = [illegible]$$

$$k = [illegible]$$

The activation energies [illegible] 17,880 [illegible]
mole respectively.

The rate of the exchange reaction [illegible]
alcohol [illegible]
correlation [illegible]
(see page [illegible]) which [illegible]
reaction would [illegible]
stant of the solvent. [illegible]
methyl alcohol [illegible]

of ethyl alcohol[41] is 28.9.

It is interesting to note that, although the rate of the exchange reaction is decreased in methyl alcohol, the energy of activation, E, is 1500 calories per mole less than that for the reaction in ethyl alcohol. This decrease in activation energy is compensated for by a twenty-five fold decrease in the frequency factor.

The increase in the rate of the exchange reaction in acetone over that in ethyl alcohol, was too large to be attributed solely to the small difference between the dielectric constants of the two solvents. For example, according to equation (1) and Figure 25, it is possible to obtain the value of the specific rate constant, k, in pure acetone by plotting ln k vs. 1/D for any given temperature. This value, based solely upon the dependence of k on the dielectric constant of the medium, is found to be 0.17 liters per mole per minute at 0°C. The half-time for the exchange reaction between 0.004 M benzyl iodide and 0.004 M potassium iodide in pure acetone should then be 510 minutes. The observed half-time was 30 seconds - 1 minute.

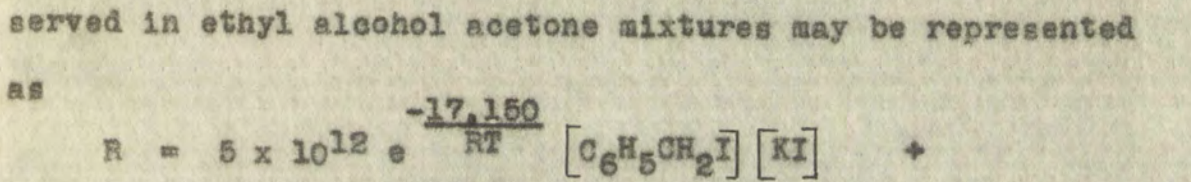
It was mentioned previously (see page 6) that the rate of the reaction may vary with the solvent because of the possibility of solvation of the reactants and the activated complex. It is conceivable because of solvation of the

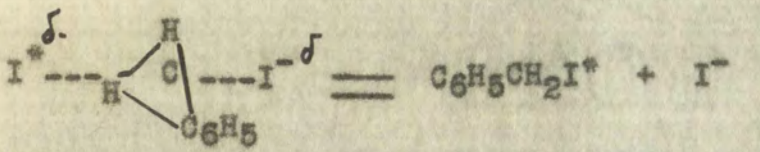
activated complex, that the exchange reaction could have changed from a bimolecular one in alcohol to a unimolecular one in acetone wherein the rate of the reaction is dependent only on the benzyl iodide. This type of mechanistic change is usually accompanied by an increase in reaction rate. This possibility was ruled out on the basis of experiments carried out in ethyl alcohol-acetone mixtures (see Figure 21, page 105). The experimental results showed conclusively that the rate of the exchange reaction was dependent on the concentrations of both $C_6H_5CH_2I$ and KI . The rate law observed in ethyl alcohol acetone mixtures may be represented as

$$R = 5 \times 10^{12} e^{-\frac{17,150}{RT}} \left[C_6H_5CH_2I\right]\left[KI\right] + $$
$$2.5 \times 10^{10} e^{-\frac{13,900}{RT}} \left[C_6H_5CH_2I\right]\left[KI\right]\left[A\right]^2$$

where the value of k_1 is equal to that obtained for the specific reaction rate in ethyl alcohol. The units of R are moles per liter per minute.

A plausible mechanism for the exchange reaction in methyl alcohol and ethyl alcohol may be represented as follows:





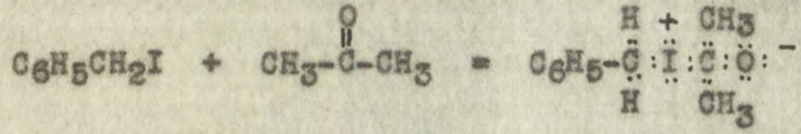
rate-determining step

carbonium ion
(planar configuration)

The activated complex, $C_6H_5CH_2II^*$, may decompose with equal probability to yield a benzyl iodide molecule with or without a radioactive iodine atom. This mechanism is commonly referred to in the literature as the S_N2 mechanism.[1,2,3]

One mechanism for exchange through the acetone-dependent path is represented by the following equations:

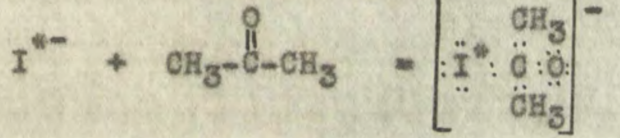
1).



$$C_6H_5CH_2I + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 = C_6H_5-\underset{H}{\overset{H}{\ddot{C}}}:\ddot{I}:\underset{CH_3}{\overset{+\ CH_3}{\ddot{C}}}:\ddot{O}:^{-}$$

Rapid and reversible reaction (solvation of benzyl iodide).

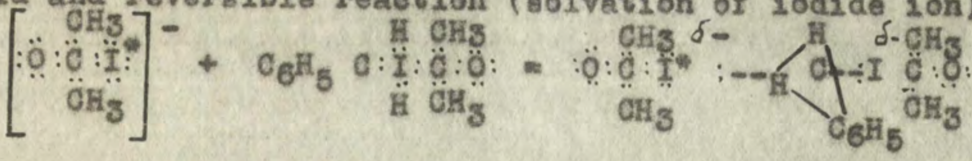
2).



$$I^{*-} + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 = \left[:\ddot{I}^*:\underset{CH_3}{\overset{CH_3}{C}}:\ddot{O}:\right]^-$$

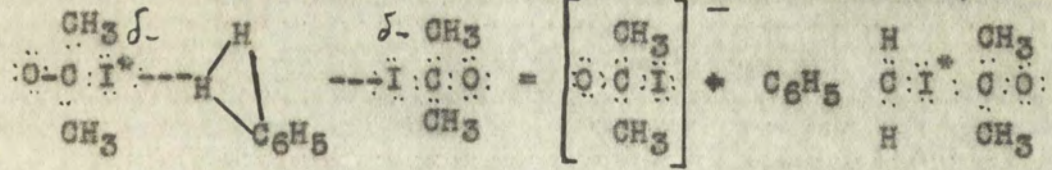
Rapid and reversible reaction (solvation of iodide ion).

3).



Rapid and reversible reaction (activated complex in equilibrium with reactants)

4).



Rate-Determining Step.

The interaction between the benzyl iodide and acetone as pictured above would tend to weaken the carbon-iodine bond in benzyl iodide and decrease the negative charge on the carbon atom which is being attached. These two factors should cause the energy of activation for the exchange reaction to be lower in acetone than in ethyl alcohol where the type of interaction postulated between acetone and $C_6H_5CH_2I$ could not take place. The energy of activation for the exchange reaction via the path involving acetone is determined to be 3,250 calories per mole less than that in ethyl alcohol, which is in accord with the foregoing hypothesis.

According to the mechanism postulated above, the iodide-acetone complex ion would have to be oriented in its approach to a benzyl iodide-acetone complex molecule, that is, the "iodide end" of the iodide-acetone complex should approach the benzyl iodide-acetone complex in order that a reaction between the two take place. It follows that the frequency factor for the acetone-dependent path (also the entropy of activation) should be smaller than that for the exchange path in pure ethyl alcohol. The frequency factor for the acetone-dependent path is 2.5×10^{10} liters per mole per minute, or $\frac{1}{200}$ for the exchange path in ethyl alcohol, which is 5×10^{12}.

The interaction between the normal [illegible] and [illegible] as pictured above would tend to weaken the carbon-[illegible] bond in benzyl iodide and [illegible] the [illegible] on the carbon atom which is being attacked. [illegible] would cause the energy of activation for the [illegible] to be lower in [illegible] than in [illegible] where the [illegible] of interaction [illegible] between [illegible] and [illegible] would not take place. The energy of activation for the [illegible] reaction via the [illegible] mechanism [illegible] 3,250 calories per mole less than that in [illegible], which is in accord with the foregoing hypothesis.

According to the mechanism [illegible] here, the [illegible]-acetone [illegible] [illegible] approach to a [illegible] that is, the "iodide end" of the [illegible] should approach the [illegible] reaction between the [illegible]. [illegible] that the frequency factor for [illegible] and the entropy of activation would be smaller than that for the exchange with [illegible]. The frequency factor for the [illegible]-dependent [illegible] per minute, or [illegible] for the [illegible], which is 5×10^{11}.

APPENDIX A

Activation Energy and Frequency Factor for the Acetone-Dependent Exchange Path

The rate law established for the exchange reaction in acetone-ethyl alcohol mixtures is shown as

$$R = k_1 \left[C_6H_5CH_2I\right]\left[KI\right] + k_3 \left[C_6H_5CH_2I\right]\left[KI\right]\left[A\right]^2$$

where k_1 and k_3, are the velocity constants for the respective paths, and $[A]$ is the concentration of acetone in moles per liter. Through the use of equation (7) it is possible to rewrite this rate expression as

$$R = A_1 e^{-E_1/RT} \left[C_6H_5CH_2I\right]\left[KI\right] + A_3 e^{-E_3/RT} \left[C_6H_5CH_2I\right]\left[KI\right]\left[A\right]^2$$

where E_1, A_1, and E_3, A_3 refer to the activation energies and the frequency factors for the respective paths. A similar rate expression may be written for each temperature at which R is determined. This may be illustrated by the following equations:

$$1).\quad R_o = A_1 e^{-E_1/RT_o} \left[C_6H_5CH_2I\right]\left[KI\right] + A_3 e^{-E_3/RT_o} \left[C_6H_5CH_2I\right]\left[KI\right]\left[A\right]^2$$

$$2).\quad R_{27.3} = A_1 e^{-E_1/RT_{27.3}} \left[C_6H_5CH_2I\right]\left[KI\right] + A_3 e^{-E_3/RT_{27.3}} \left[C_6H_5CH_2I\right]\left[KI\right]\left[A\right]^2$$

where the subscripts o, and 27.3, refer to the temperature

of the reaction. From equations (1) and (2) it is possible to eliminate A_3 and $[A]^2$ and solve the resulting equation for E_3 and A_3 since A_1 and E_1 are known from the results obtained in pure ethyl alcohol. The values for A_1 and E_1 in ethyl alcohol were corrected for the small difference between the dielectric constants of pure ethyl alcohol and 2.27M acetone in alcohol.

BIBLIOGRAPHY

1. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 244 (1935).
2. E. D. Hughes, Trans. Faraday Soc., 37, 603 (1941).
3. E. D. Hughes, J. Chem. Soc., 968 (1946).
4. L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 925 (1940).
5. E. D. Hughes, C. K. Ingold, and C. S. Patel, J. Chem. Soc., 526 (1933).
6. L. C. Bateman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1017 (1940).
7. A. M. Ward, J. Chem. Soc., 2285 (1927).
8. M. M. Sprung, J. Am. Chem. Soc., 52, 1640 (1930).
9. J. W. Baker, J. Chem. Soc., 987 (1934).
10. J. W. Baker and W. S. Nathan, J. Chem. Soc., 519 (1935).
11. W. Koskoski, H. Thomas, and R. D. Fowler, J. Am. Chem. Soc., 63, 2451 (1941).
12. R. P. Bell, J. Chem. Soc., 629 (1943).
13. K. J. Laidler, "Chemical Kinetics" 1st ed., McGraw-Hill Book Company, Inc., New York City, 1950, p. 130.
14. E. D. Hughes, C. K. Ingold, and U. G. Shapiro, J. Chem. Soc., 225 (1936).
15. J. L. Gleave, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 236 (1935).

16. L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, J. Chem. Soc., 979 (1940).

17. E. D. Hughes, J. Chem. Soc., 976 (1946).

18. L. C. Bateman and E. D. Hughes, J. Chem. Soc., 945 (1940).

19. S. C. J. Olivier and A. P. Weber, Rec. trav. chim., 53, 869 (1934) (C.A. 28:6117).

20. S. C. J. Olivier and A. P. Weber, Rec. trav. chim., 53, 891 (1934) (C.A. 28:6122^3).

21. E. T. Butler and M. Polanyi, Trans. Faraday Soc., 39, 19 (1943).

22. J. L. Tuck, Trans. Faraday Soc., 34, 222 (1938).

23. H. C. Urey, J. Chem. Soc., 562 (1947).

24. H. A. C. McKay, Nature, 142, 997 (1938).

25. R. B. Duffield and M. Calvin, J. Am. Chem. Soc., 68, 557 (1946).

26. G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York City, 1949, pp. 346 and 391.

27. D. S. Ballantine and W. E. Cohn, MDDC-1600 (1947).

28. A. W. Kenny and W. T. Spragg, J. Chem. Soc., Supplements and Index, p. 323 (1949).

29. I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York City, 1929, p. 369.

30. D. E. Hull, C. H. Schiflett, and S. C. Lind, J. Am. Chem. Soc., 58, 535 (1936).

31. M. Kahn, Thesis, "The Chemical Behavior of Iodine at Tracer Concentrations," Wash. Univ., St. Louis (1950).

32. J. J. Livingood and G. T. Seaborg, Phys. Rev., 54, 1015 (1938).

33. F. Metzger and M. Deutsch, Phys. Rev., 74, 1640 (1948).

34. J. F.Norris, Am. Chem. Journal, 38, 639.

35. I. M. Kolthoff, and N. H. Furman, Ibid, p. 218.

36. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York City, 1941, p. 359.

37. L. F. Fieser, Ibid, p. 359.

38. L. F. Fieser, Ibid, p. 360.

39. I. M. Kolthoff and N. H. Furman, Ibid, p. 221.

40. I. M. Kolthoff and N. H. Furman, Ibid, p. 222.

41. International Critical Tables, Vol. 6, (1927).